

Accelerated Design and Testing of New Nickel-Based Superalloys



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To Crystal, Mara, and Wolfgang.

I favour the philosophy of René Dubos that “trend is not destiny”. When faced with need and sufficient freedom, people are marvellously efficient in their capacity to shatter trends, to cut the Gordian knot. On freedom, I follow Norman Cousins, who stated, “The only safe assumption for human beings is that the world will be what we make it [...] our dreams and not our predictions are the great energizers”. It is that faith that animates superalloy people.

— R.F. Decker, “Superalloys – Does Life Renew at 50?”

Abstract

Nickel-based superalloys have emerged as the materials of choice for high-temperature jet propulsion and industrial gas turbine applications due to their unique combination of resistance to loading under static, fatigue, and creep conditions, as well as to environmental degradation. The specific fuel consumption and CO₂ emissions of turbines can be significantly reduced by increasing the operating temperature, thus providing a continued drive within the materials research community to develop new alloy grades with improved properties. However, design and qualification activities are difficult and costly, which explains why the time needed to insert novel materials into industrial applications can be notoriously long. The research of the present work was carried out with the aim of accelerating the overall design–make–test–analyse development cycle for new superalloys, with a focus on the design and testing of single-crystal compositions with improved creep properties. First, a novel mechanical testing system using miniaturised testpieces is introduced. Rapid testing methods involving temperature ramping and stress relaxation are employed to extract key high-temperature strength parameters, with the quantitative data measured then compared to conventional tests. Second, operating creep damage mechanisms during such tests are investigated with cutting-edge electron microscopy characterisation techniques and dislocation dynamics modelling. This combination of experiments and simulations yields an improved understanding of damage evolution and of the roles played by alloy composition and microstructure in imparting creep strength. Third, these new insights into damage mechanisms inform a novel physically based model for the creep resistance of single-crystal superalloys. A comprehensive critical assessment of previous modelling methods is carried out in an effort to approach best practice. Predictions are tested against a large experimental data set and it emerges that the present model is more accurate for alloy design purposes than existing merit indices from the literature. Last, a set of trial alloys with carefully controlled chemistries is extensively analysed to reveal the complex influence of composition on physical properties. Experimental results provide an important benchmark for thermodynamic calculations and help derive a set of guidelines for alloy design within this particular compositional space.

Preface

Research in this thesis has been prepared for publication as follows:

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Superalloy metallurgists have invented and developed alloys more complex and used at a higher fraction of their melting point than any other comparable group! These accomplishments appear to have far surpassed that in any other equivalent metallurgical field in the last 50 years. However, the advance would not have been so total without the driving force emanating from the fortuitously parallel invention of the gas turbine jet engine. All together, this synergy has generated one of the great advances in engineering.

— C.T. Sims, “A History of Superalloy Metallurgy for Superalloy Metallurgists”

1

Design of New Superalloys for Industrial Gas Turbines

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1.1 Superalloys for Industrial Gas Turbine Applications

In December 2015, representatives of 195 countries met in Paris and set the ambitious long-term goal of holding the global average temperature increase to below 2 °C and of attempting to limit it to 1.5 °C [1]. Reviews of existing climate modelling studies show that to achieve this goal, greenhouse gas emissions must remain by 2030 below 55 billion metric tonnes of annual CO₂ equivalent emissions (GtCO₂eq yr⁻¹) and should ideally fall well below 45 GtCO₂eq yr⁻¹ [2–5]. In the context of increasing worldwide energy consumption, this will undoubtedly require a strong shift from fossil fuels towards renewable energy sources, which are projected to

account for 40% of total power generation by 2040 [6]. Nonetheless, fluctuations in the power output from key renewable sources including solar photovoltaics and wind must be compensated and balanced. Barring any unexpected, major developments in large-scale energy storage, gas-fired plants powered by industrial gas turbines (IGT) provide the best combination of a flexible, relatively clean, cost-effective, and process efficient power source [6–8]. In this context, the consumption of natural gas is projected to rise by nearly 20% by 2030 and to remain at a similar level towards 2040 [6]. Simulation results of integrated energy–economy–carbon-cycle–climate models, illustrated in Figure 1.1, confirm that, regardless of model assumptions, gas-fired plants will play a key role for future power generation and for supporting the transition towards low-carbon technology [9–11].

With the above in mind, it is imperative to improve both the flexibility and the efficiency of IGT during service. A key factor determining the achievable efficiency is the turbine inlet temperature, which has almost doubled over the last 40 years due to advances in high-temperature materials and in processing and cooling of turbine parts [7, 12–14]. Within this scope, certain components such as blades and vanes are exposed to extreme operating conditions and must withstand high temperatures and loads in oxidising and corrosive environments for prolonged periods of time, with common lifetime requirements of 25,000 to 50,000 hours [15].

The performance of such structural elements, denoted here as P , can be linked to three key factors — functional requirements, F , geometry, G , and material properties, M — through a function $P = f(F, G, M)$ [16]. For many engineering applications, it is reasonable to assume that the functions for F , G , and M are separable and can be multiplied together, and that a certain structural index involving F and G is already fixed for given components [16]. For example, the functionality and the dimensions of turbine blades and vanes are normally set by engine manufacturers during their design processes [17], which leads to the revised relation $P = f_1(F) \times f_2(G) \times f_3(M) \approx f(M)$. This means that performance can be markedly improved by using new materials with superior properties.

Nickel-based superalloys (NBSA) have emerged as the materials of choice for high-temperature IGT applications due to their unique combination of resistance to loading under static, fatigue, and creep conditions, as well as to environmental degradation [12, 18–21]. Despite ongoing research in other alloy systems which might possess better high-temperature properties, including cobalt- [22–25], molybdenum- [26–29], and niobium-based alloys [27, 30, 31], the position of nickel-based materials remains unchallenged.

Historically, the focus of the superalloy industry had been on the aeroengine market and IGT materials have been commonly derived from aerospace counterparts. While IGT technology had long been trailing behind by 10 to 20 years, as shown in Figure 1.2, recent developments have minimised this gap. This is not surprising in the context of the IGT industry projected to become the largest consumer of superalloys by 2025 [12]. Materials tailored to particular gas turbine specifications are needed, as a simple material adaptation or modification cannot yield optimal results due to distinct design factors including weight restriction, operating time, fuel quality, and cyclic duty [7].

In Figure 1.3, a proposed design space for new, improved IGT alloys [32] is compared to existing commercial compositions. The latter tend to either possess (1) a high Al/Cr ratio and exhibit good creep properties, but weak corrosion resistance, having been developed for aerospace applications, or (2) a low Al/Cr ratio, resulting in IGT environment suitability, but at the cost of lower strength. Only relatively few compositions satisfy both requirements and populate the envisioned area above 12 wt.% chromium and 4 wt.% aluminium. In order to optimise the performance of an IGT superalloy, the particular design requirements must be first understood and related to necessary material properties.

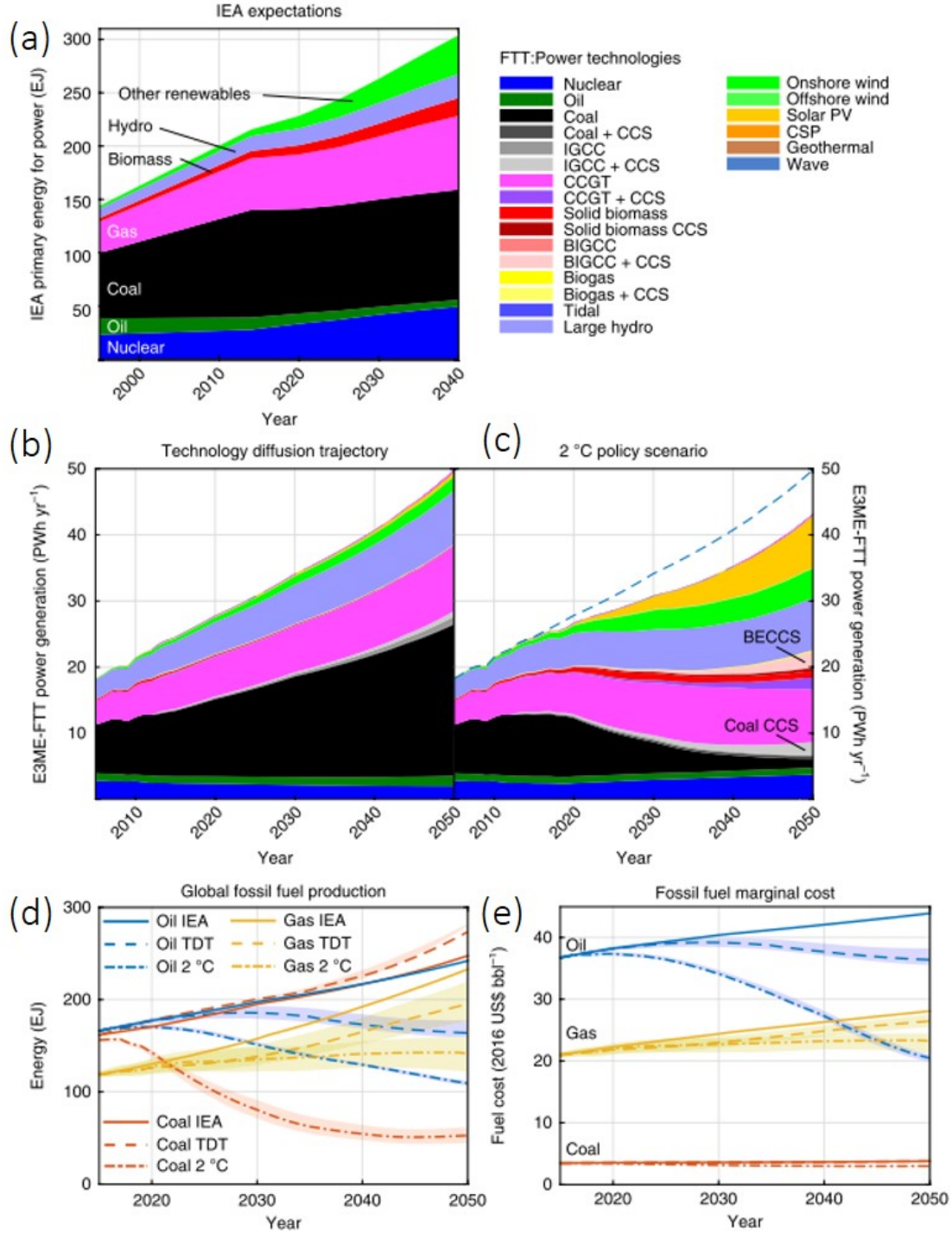
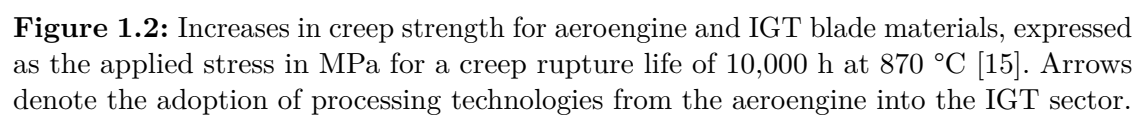


Figure 1.1: Simulation results of the future macroeconomic impact of fossil fuel assets, adapted from reference [10]. Projections of future energy use for power generation are made based on (a) the ‘New Policies Scenario’ of the International Energy Agency (IEA) [6], (b) the ‘Technology Diffusion Trajectory’ (TDT) model by Mercure et al. [10] which accounts for ongoing technological trends, and (c) an amended version of the TDT model which accounts for an optimal ‘2 °C Policy Scenario’ following the 2015 Paris Agreement. The same three models are also used to forecast (d) global production of fossil fuels and (e) marginal costs of fossil fuels.



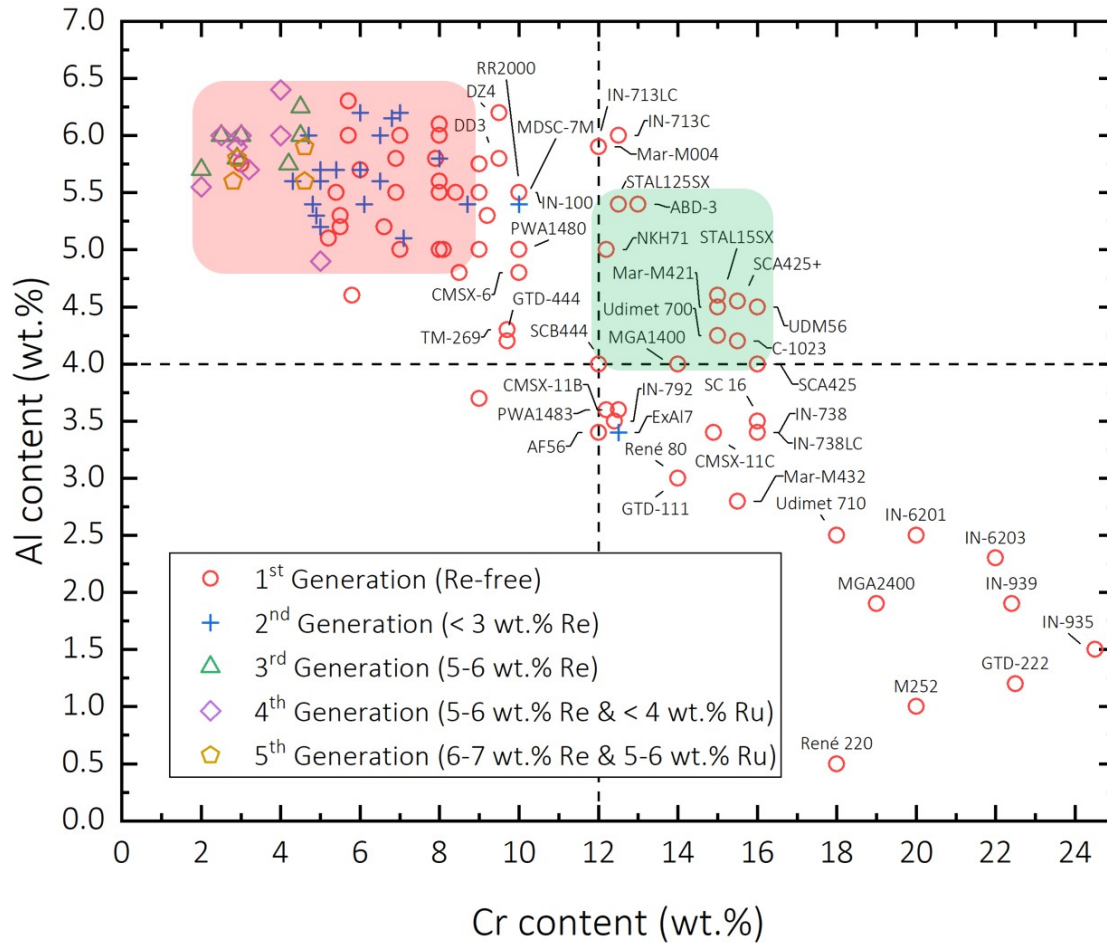


Figure 1.3: Comparison of the proposed design space for new IGT superalloys (green rounded rectangle) and the general compositional space occupied by rhenium-containing aerospace alloys (red rounded rectangle). Alloys with higher chromium contents above 9.5 wt.% are labelled accordingly. This dataset of around 125 alloys was compiled from literature published as journal articles or patents, as such, slight differences to versions sold commercially may exist.

1.2 Design Requirements for IGT Blades

An IGT can be modelled as a gas-only heat engine system, in which the power output scales proportionally with the temperature increment through which the working fluid is raised [13, 14]. A simple analysis of a Carnot cycle for an ideal gas yields the following expression for engine efficiency, η :

$$\eta = 1 - \frac{T_1}{T_2} \quad (1.1)$$

where T_1 is the temperature at which the ideal gas undergoes isothermal compression in thermal contact with a cold reservoir and T_2 is conversely the temperature at which the gas undergoes an infinitely slow expansion in contact with a hot reservoir. Although practical turbine theory involving the Brayton cycle is less idealised [33, 34], the key conclusion that efficiency can be raised by increasing T_2 holds true. As shown in Figure 1.4, a steady increase of about 10 °C per year in blade metal temperature has been achieved over the last six decades, resulting in significant gains in both power output and cycle efficiency [13].

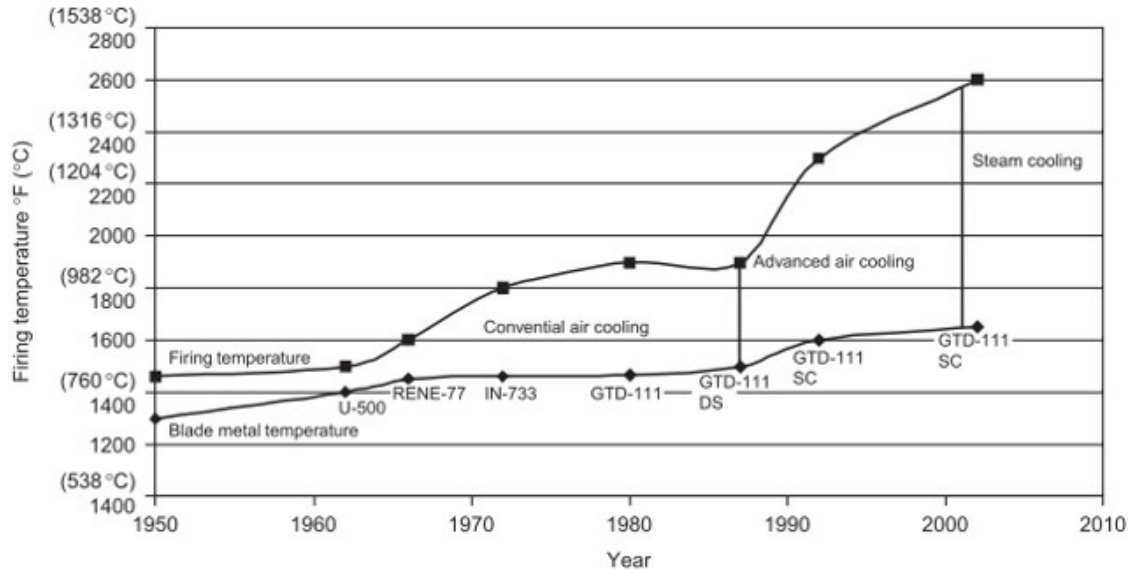


Figure 1.4: Increases in gas turbine firing temperature and blade metal temperature due to the development of advanced materials and of new cooling schemes [13].

Schulenberg [35] identifies a number of physical boundary conditions acting on a first stage IGT blade. These include a steady state gas temperature of 1200 to

1400 °C, a gas temperature after load rejection of 500 °C, a steady state pressure loading of 2 to 3 bar, a vibratory acceleration of 500 to 1000 m/s², and finally, a centrifugal acceleration of 85,000 m/s². Since these are estimates made in 1990, it can be asserted that current operating conditions will be even more demanding. Owing to advanced cooling technologies, the overall surface temperature of the blade can be estimated at around 850 °C, although areas towards the tip can experience temperatures as high as 1100 °C [36]. Based on typical superalloy densities and wall thicknesses of 2 to 3 mm for first stage blades, IGT service conditions result in an applied stress due to centrifugal forces of 150 MPa and a vibrational stress of 5 MPa, in agreement with estimates by Glenny et al. [18]. Reed [12] used the following simplified relation to determine the centrifugal stress at the root of a blade with an assumed uniform cross section:

$$\sigma = \int_{r_{\text{root}}}^{r_{\text{tip}}} \rho \omega^2 r dr = \frac{\rho \omega^2}{2} (r_{\text{tip}}^2 - r_{\text{root}}^2) \quad (1.2)$$

Inserting typical values in Equation (1.2) — an alloy density of 9000 kg/m³, a mean blade radius of 50 cm, a blade length of 10 cm, and a rotational frequency of 100 Hz — yields a rough estimate of 180 MPa for the stress at the blade root. Equation (1.2) clearly shows that materials must be compared in terms of their specific tensile and creep strengths, taken in relation to their density [37]. Furthermore, the challenge of maintaining a low alloy density is exacerbated by a potential additional weight penalty associated with a heavier turbine disc that must support the blades [18].

Numerical modelling methods reveal significant differences in temperature and stress distribution throughout the blade cross section, as illustrated in Figure 1.5. For single-crystal components, any deviations from the ideal [001] crystal orientation along the loading axis will lead to significantly higher loads and deformation rates. Adding to these complex imposed stresses is the requirement to resist potential impacts with foreign objects and exhibit sufficient ductility and fracture toughness.

Of the different types of material strength used to qualify IGT blade materials — low-cycle fatigue (LCF), high-cycle fatigue (HCF), thermal-mechanical fatigue

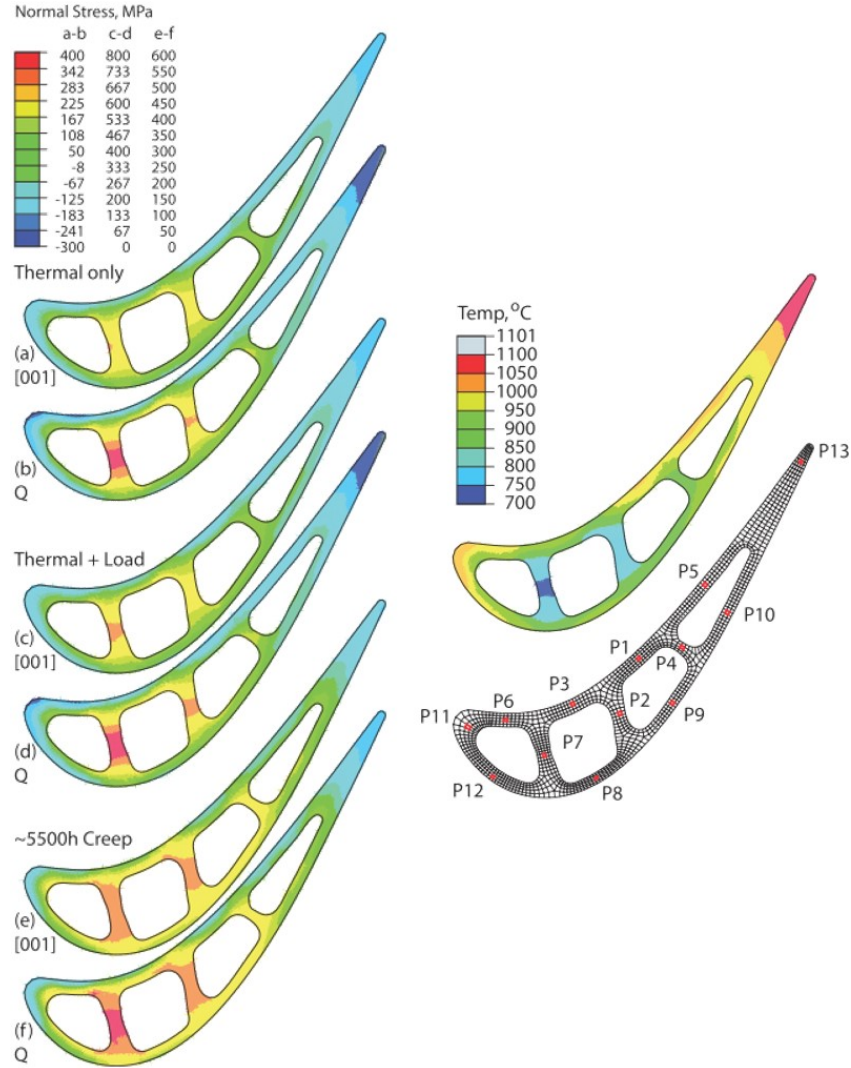


Figure 1.5: Normal stress distribution in a turbine blade section made of the single-crystal superalloy CMSX-4 [36]. The images on the left show stresses due to thermal load only (a&b), due to thermal and centrifugal loads (c&d), and predicted stresses after 5500 h exposure to creep (e&f). Images in (a,c,e) correspond to an ideal [001] crystal orientation (Euler angles $\phi_1 = 0$, $\Phi = 0$, $\phi_2 = 0$) along the loading axis; those in (b,d,f) to an off-axis misorientation (Euler angles $\phi_1 = -166.4$, $\Phi = 23$, $\phi_2 = 180$). Thermal inputs and the mesh used for the numerical analysis are shown on the right.

(TMF), and creep — the last two are seen as most restrictive [13]. Following the considerations of Ashby & Abel [37], IGT blades are a case of deflection-limited design since relatively small total creep strains of 1% lead to component failure, owing to the tight tolerances needed to ensure a good seal. However, IGT operating cycles are becoming more flexible to cope with daily fluctuations in energy consumption and in the availability of renewable energy sources [38]. The resulting higher number

of successive start-ups and cool-downs raises the importance of TMF damage [39–41].

Finally, IGT materials operate under oxidising, corrosive, and erosive conditions due to hot gases containing different salt contaminants such as Na_2SO_4 , NaCl , and V_2O_5 [42–44]. Although service conditions are normally oxidising, reducing conditions can also occur during ignition and can lead to damage to protective surface oxide layers [44].

While design requirements are often considered separately, it has been shown that damage mechanisms influence one another in complex ways, warranting an integrated approach [45–49]. Furthermore, material behaviour must be represented and considered statistically, as the failure of the weakest blade will invariantly result in a shut-down of the entire turbine [50, 51]. This makes it difficult to design an alloy possessing a chemical composition and a resulting microstructure capable of satisfying all the conditions stated above at the same time. In order to deal with implicit trade-offs, a new paradigm for alloy design is required.

1.3 Alloys-By-Design Concept

Traditionally, new alloys have been developed on a trial-and-error basis and incremental improvements have been achieved empirically [52]. In principle, it would thus be possible to manufacture a number of trial compositions within the design space in Figure 1.3, carry out appropriate tests, and finally screen and rank the alloys. What might still seem a viable option when varying only chromium and aluminium compositions, quickly becomes an impossible undertaking when considering that NBSA contain ten or even more elements. Assuming relatively coarse increments of 1 wt.% for each element and looking at typical compositional ranges yields over 10^8 possible combinations [53]. When further considering that different heat treatments also strongly influence material properties, it becomes obvious that an empirical procedure cannot generate optimal results.

One approach to tackling this issue has involved the use of regression analysis, neural networks, and genetic algorithms, based on already existing experimental data [54–62]. While these methods have proven useful and have yielded materials with

somewhat improved mechanical properties, they lack a fundamental, physically based reasoning for the predictions made. A comprehensive review on the performance of neural networks in materials science revealed that in the vast majority of studies, predictions made are not investigated experimentally, modelling uncertainties find little consideration, and neither the models nor the underlying data are disseminated [63]. A further review of regression modelling has pointed out this approach is not a panacea, nor should it be seen as a long-term solution, thus raising the challenge for materials scientists and engineers to develop better quantitative treatments of complex problems [55].

The earliest use of a computer-assisted, theoretically-based design approach for superalloys can be traced back to the PHACOMP (PHase COMPutation) method in the 1960s [64, 65]. This involved extending the concept of an electron vacancy number, N_v , first defined by Pauling [66] for transition metals, to include all alloying elements in NBSA [67]. It was found that once a critical value for N_v is exceeded, deleterious topologically close-packed (TCP) phases are likely to precipitate. PHACOMP was later revised, leading to the New PHACOMP methodology [68–70], with two new alloying parameters — the d-orbital energy level of alloying transition elements, M_d , and the bond order, Bo . While New PHACOMP and similar approaches proved useful in predicting volume fractions and compositions of phases in NBSA ([71–74], they have since been supplanted by thermodynamic CALPHAD (CALculation of PHase Diagrams) techniques [75–77]. CALPHAD, which should be regarded as neither purely empirical nor theoretical in nature, makes use of mathematical models to describe thermodynamic properties of different alloy phases and to predict which phases will coexist under given equilibrium conditions. These calculations involve numerous coefficients stored in databases, commonly obtained by fitting to experimental data. Therefore, the quality of CALPHAD predictions mainly depends on the accuracy of databases and on the range of element interactions they include [76].

Given the complexity of superalloys, alloy design continued to be largely based on empirical relations [78] and it was not until the end of the 1990s that development of

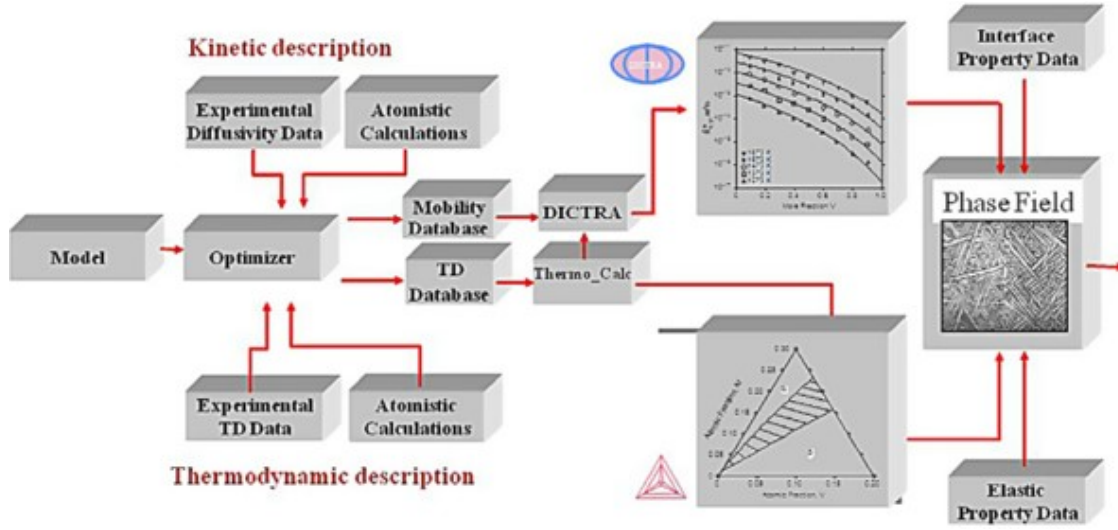


Figure 1.6: Suggestion of a future framework for CALPHAD as a tool for quantitative microstructure engineering. The initial thermodynamic descriptions have been complemented by kinetic descriptions; both are envisioned to be extended to include first-principles atomistic calculations [77].

improved databases enabled CALPHAD to be applied successfully [79–81]. Several commercial software packages exist today, the most commonly used for superalloys being Thermo-Calc [82–84] and JMatPro [85]. In the context of recent developments as part of the Materials Genome Initiative (MGI) and of the broader field of Integrated Computational Materials Engineering (ICME), CALPHAD is envisioned to become part of a multi-scale, hierarchical framework for designing new materials [86–88], as illustrated in Figure 1.6. The goal behind MGI and ICME is to decrease the development cycle of new materials from currently 10 to 20 years to below 5 years [88], a challenge that has long been posed for high-temperature applications [17, 89]. Figure 1.7 presents a timeline of the evolution of ICME technology, which expanded from CALPHAD to encompass a range of more fundamental calculations of thermochemical and physical properties [87].

Within this scope, Olson et al. [88, 90, 91] proposed a new design paradigm, named Materials by Design, which views materials as systems and provides a hierarchical infrastructure linking processing, structure, properties, and performance, as shown schematically in Figure 1.8. It involves predictive computational modelling, reinforced by experimental calibration, in order to relate changes in alloy composition

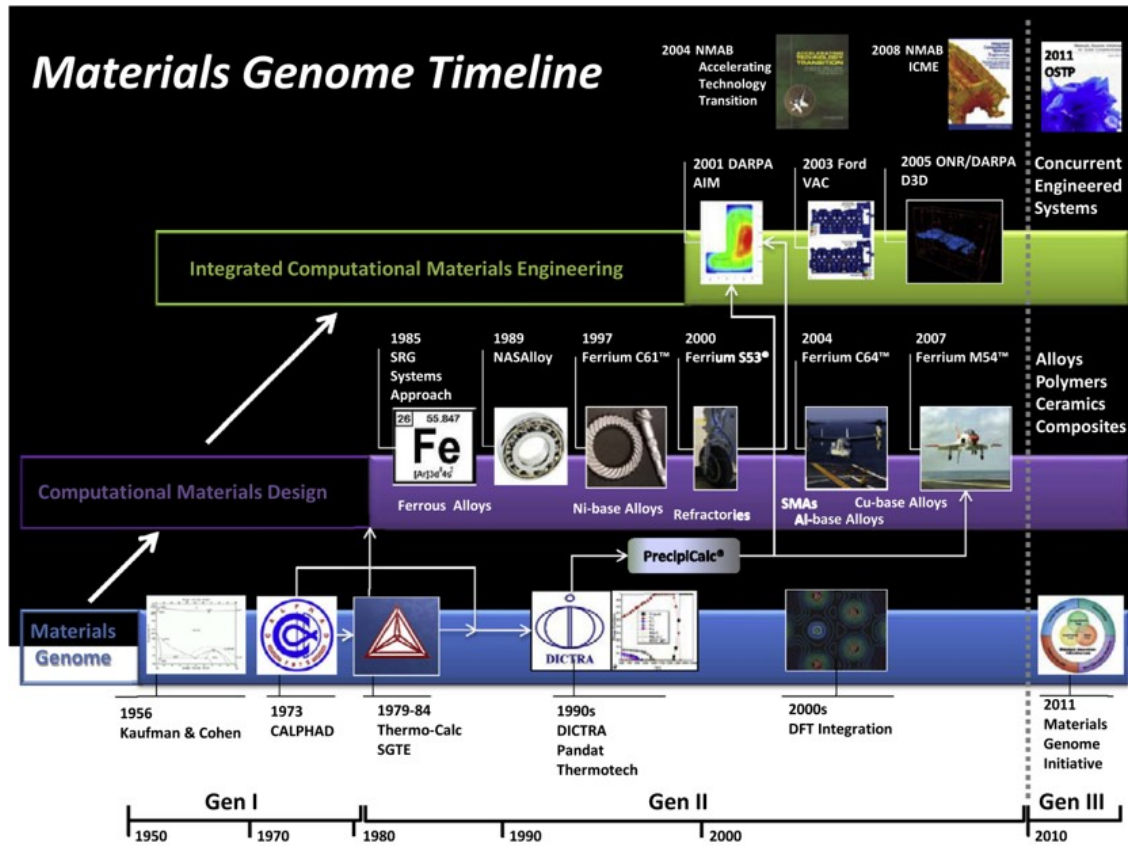


Figure 1.7: Timeline of Materials Genome technology including examples of its use for computational materials design and of its application within larger-scale ICME projects [87].

and processing parameters to changes in microstructural evolution and phase stability, and then in turn to important physical, chemical, and mechanical properties [88]. Although this approach might appear straightforward and while tools such as CALPHAD can indeed provide a wealth of information to alloy designers, the fundamental and most challenging step remains relating thermodynamic predictions to key material properties such as creep and oxidation resistance, while taking into account potential shortcomings of the models involved. In short, it is simple to discuss the concept of Materials by Design, but it is difficult to apply it successfully to the development of improved engineering materials.

Materials by Design approaches have been applied to modelling precipitation in turbine disc superalloys [92–94] and to developing a new single-crystal NBSA [95]. Significant advances in applying CALPHAD and ICME to superalloy design came

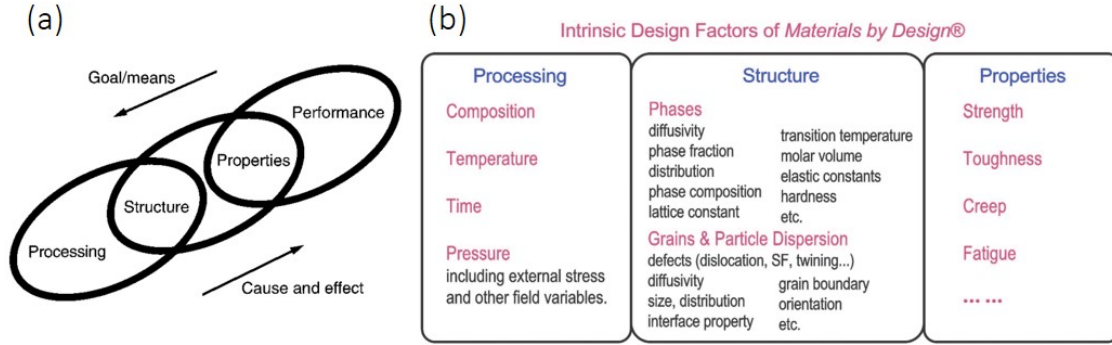


Figure 1.8: (a) Three-link chain model relating processing, structure, properties, and performance as the foundation of ICME [90] and (b) main design factors for the Materials by Design approach [88].

from Saunders et al. [85, 96–101], who modelled several processing-structure relations in superalloys including solidification, phase precipitation, and particle coarsening, as well as structure-property relations like flow stress, LCF, and creep strength. These efforts were, however, mostly directed towards the optimisation of already existing materials and not towards a systematic development of new, improved ones.

The Alloys-By-Design (ABD) multi-scale modelling project [52, 53] was established with this particular purpose in mind. Analogue to Materials by Design, ABD involves developing an integrated array of models, which in combination with computational thermodynamic calculations can be used for rapid development of NBSA. While the general paradigm remains the same, the novelty of ABD is represented by the systematic reduction of large compositional spaces to ideal compositions, following the flow block diagram shown in Figure 1.9. Such a relatively brute-force approach would have been impractical in the past, however, it has become a viable option as costs associated with high-performance computational resources have steadily decreased [102].

In a first step, unsuitable alloys which do not meet design constraints for microstructural architecture are eliminated. For IGT superalloys, key parameters include γ' volume fraction [104], chromium content [105], and the volume fraction of deleterious TCP phases such as σ [106]. Remaining compositions are sorted and ranked in a second step based on previously developed merit indices for cost, density, oxidation, and creep resistance among others [52]. In principle, remaining

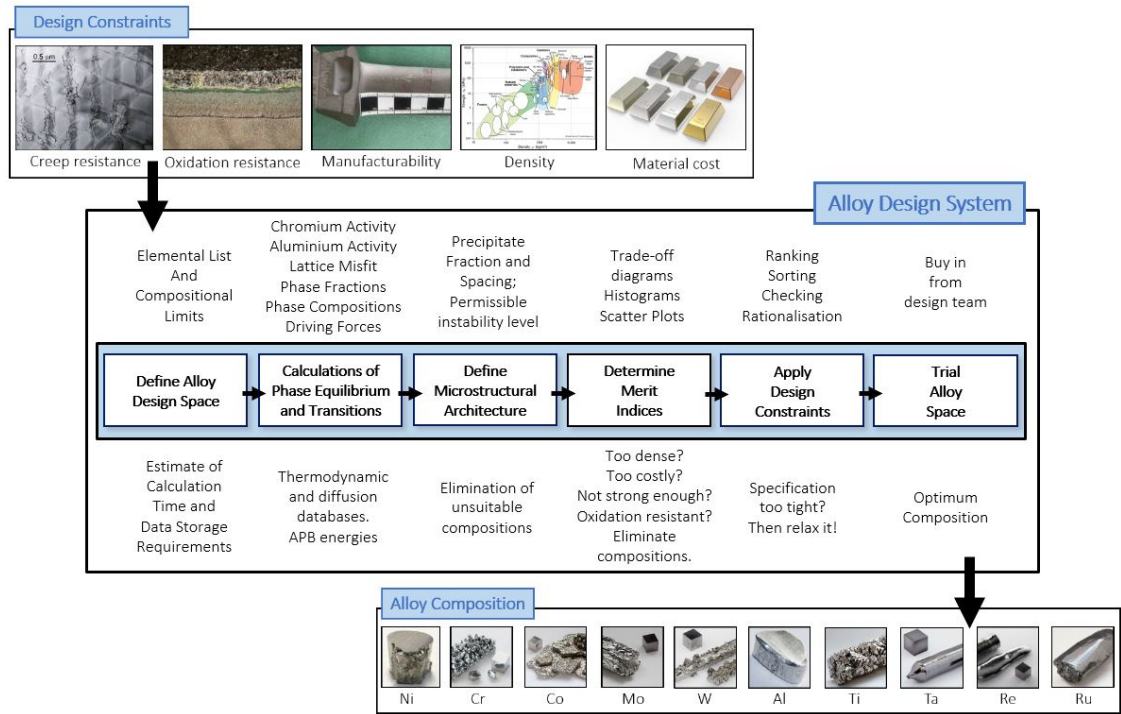


Figure 1.9: Flow block diagram of the ABD approach, adapted from reference [103]. The main steps leading from pre-defined design constraints to an optimal alloy composition are connected by arrows; additional explanations concerning the design tools and actions involved within each step are shown above and below the main sequence.

alloys should be close to an optimal result, within the centre of the Venn diagram in Figure 1.10. At this stage, it is useful to compare the performance of trial compositions to that of known commercial alloys, as targets to be reached or surpassed.

The importance of an ABD-type approach for the development of new NBSA becomes clear when considering the trade-offs between alloy density, raw material cost, and creep performance, illustrated in Figure 1.11. These results show that improved creep resistance can be primarily achieved by adding heavy and expensive solid solution strengtheners like tungsten and rhenium [12]. Besides the prohibitive raw material cost for certain applications, this also brings to mind the concerns regarding density-corrected strength [18, 37], as discussed in Section 1.2. Similar trade-off plots including constraints for microstructure, mechanical strength, environmental resistance, manufacturability, etc. can be found in references [69, 70, 78, 107, 108].

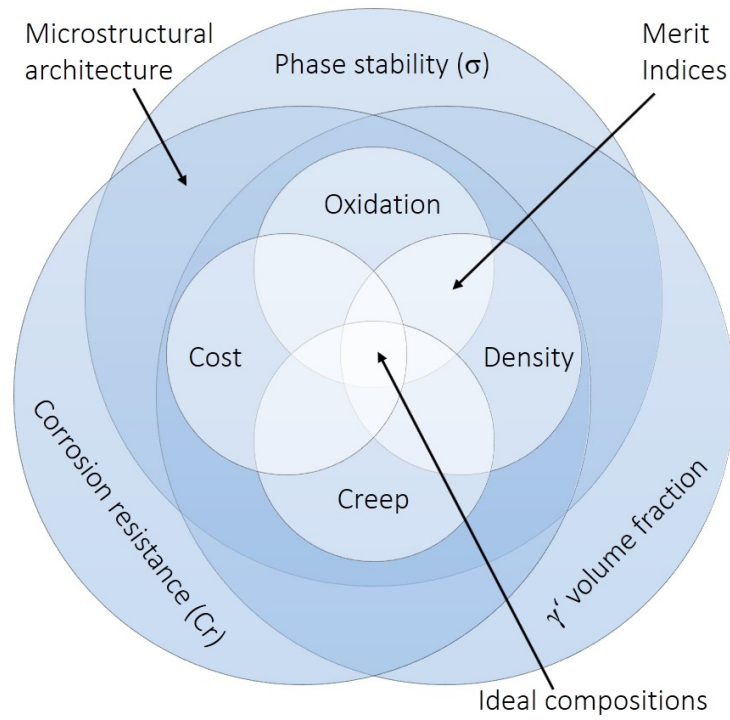


Figure 1.10: Key microstructure parameters and merit indices for IGT superalloys used for screening and ranking possible compositions. Ideal compositions meet all screening criteria and are ranked highest.

While ABD calculations have been successfully applied in the past to the design of new alloys for turbine blades [102, 103, 109] and turbine discs [102, 110, 111], there is still much room for improvement, especially with regard to the selection of suitable merit indices and design constraints.

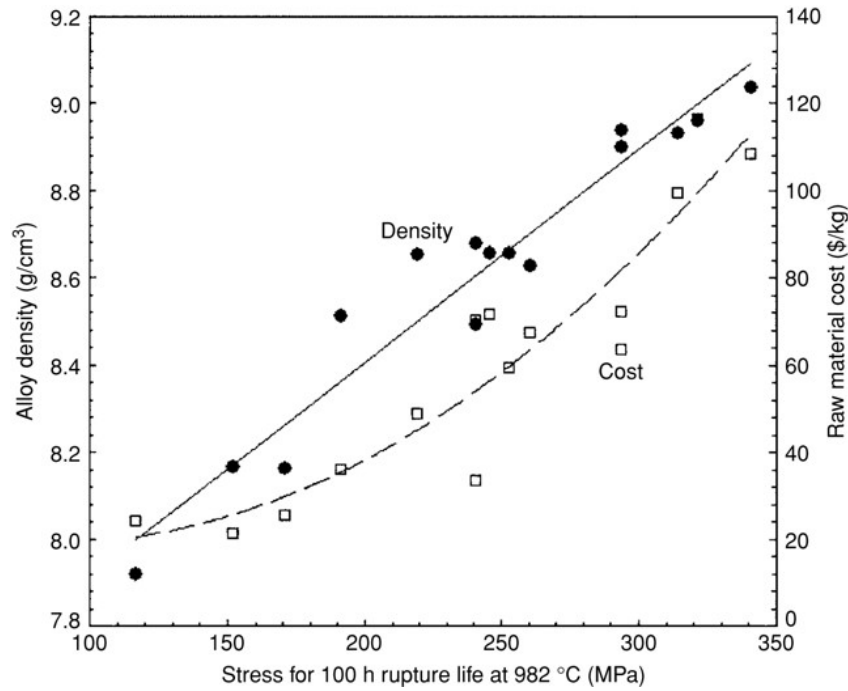


Figure 1.11: Trade-offs between density, raw material cost, and creep performance expressed as applied stress for 100 h rupture life at 982 °C for a set of third- and fourth-generation single-crystal superalloys [12].

1.4 Towards an Accelerated Design–Make–Test–Analyse Cycle for Superalloys

Previous sections have outlined the importance of an accelerated design–make–test–analyse development cycle for new NBSA. The present work provides a contribution towards this goal, with a focus on the design and testing of new single-crystal superalloys with improved creep properties. Key research activities carried out within this scope and their interdependences are illustrated in the project flow diagram of Figure 1.12.

While substantial advances have been recently made in the rapid design [52, 60, 61, 102, 103] and manufacturing [112–114] of superalloys, rapid testing techniques are sorely lacking. Qualification activities based on conventional mechanical tests are difficult and costly, which explains why the time needed to insert new alloys into service can be notoriously long [17, 89]. This provides the motivation for Chapter 3, in which the mechanical behaviour of a prototype single-crystal superalloy suitable for IGT applications is assessed using a novel Electro-Thermal Mechanical Testing

(ETMT) system. Miniaturised testpieces of a few mm^2 cross section are used, allowing relatively small volumes to be tested. Rapid testing methods involving temperature ramping and stress relaxation are employed to extract key high-temperature strength parameters, with the quantitative data measured then compared to conventional tests. Advantages and limitations of the ETMT system are identified. Particularly for the rapid assessment of prototype alloys prior to scale-up to pilot-scale quantities, it is concluded that some significant benefits emerge.

Advantages associated with the ETMT system are of paramount importance in the context of Chapter 4. This work investigates the evolution of creep damage in single-crystal NBSA under deformation conditions of applied stress and temperature similar to those encountered in service. Interrupted creep tests are carried out using the ETMT system on miniaturised specimens. High-resolution electron backscatter diffraction (HR-EBSD), electron channelling contrast imaging under controlled diffraction conditions (cECCI), and discrete dislocation dynamics (DDD) modelling are employed to obtain comprehensive qualitative and quantitative information regarding dislocation densities and dislocation structures up to 1% plastic creep strain. It is shown that isolated, individual dislocation sources within the otherwise undeformed crystal become active at macroscopic strain levels on the order of 0.1% and result in a sudden increase in dislocation density by several orders of magnitude. Subsequently, dislocations percolating through γ matrix channels mutually impede their movement, leading to an exponential decrease in the dislocation multiplication rate. Three trial superalloys with distinct chemistries and microstructures are compared in order to assess which factors have the largest influence on creep resistance.

Insights gained from the extensive HR-EBSD, cECCI, and DDD analyses are used to inform a numerical model for creep damage in single-crystal NBSA in Chapter 5. While a range of similar approaches have been presented in the literature, it is unclear whether any particular one is superior and many open questions remain, in particular because models are commonly validated using limited experimental data sets. This situation motivates a comprehensive critical assessment of existing

modelling methods. Advantages and disadvantages are identified in an effort to approach best practice and to obtain a physically faithful model. Predictions are tested against a large experimental data set built from publications in the open literature. It is demonstrated that the creep resistance can be estimated to within approximately one-half of a Larson-Miller parameter, from an input of alloy composition, deformation conditions, and estimates of microstructural parameters, rate laws (and parameters therein), and physical constants. Furthermore, it emerges that the present model is more accurate and more appropriate for alloy design purposes when compared to a range of different merit indices from the literature.

Nonetheless, an important caveat regarding the new creep damage model and ABD methods in general is that key input parameters are derived from thermodynamic CALPHAD calculations, which in turn depend on commercial databases. This makes it imperative to improve and expand the performance of CALPHAD tools and to gain a better understanding of the influence of chemistry on thermochemical and physical alloy properties and on microstructure. The study presented in Appendix A is carried out with the above in mind. A set of six IGT alloys are manufactured using a novel lab-scale casting facility and their carefully controlled chemistries make it possible to isolate the effects of individual elements. Results from an extensive characterisation campaign including SEM, electron probe microanalysis (EPMA), energy dispersive X-ray spectroscopy (EDX), atom probe tomography (APT), and differential scanning calorimetry (DSC) are compared to predictions from the commercial thermodynamic software package Thermo-Calc and the associated nickel alloy databases TCNi8 and TTNi8.

Finally, the findings of the present work are summarised in Chapter 6. Special attention is given to the integration of experimental and numerical modelling activities illustrated in Figure 1.12, which has led to new methods, tools, and guidelines for the rapid design and testing of NBSA. Future research work is also identified to complement and refine the present investigation.

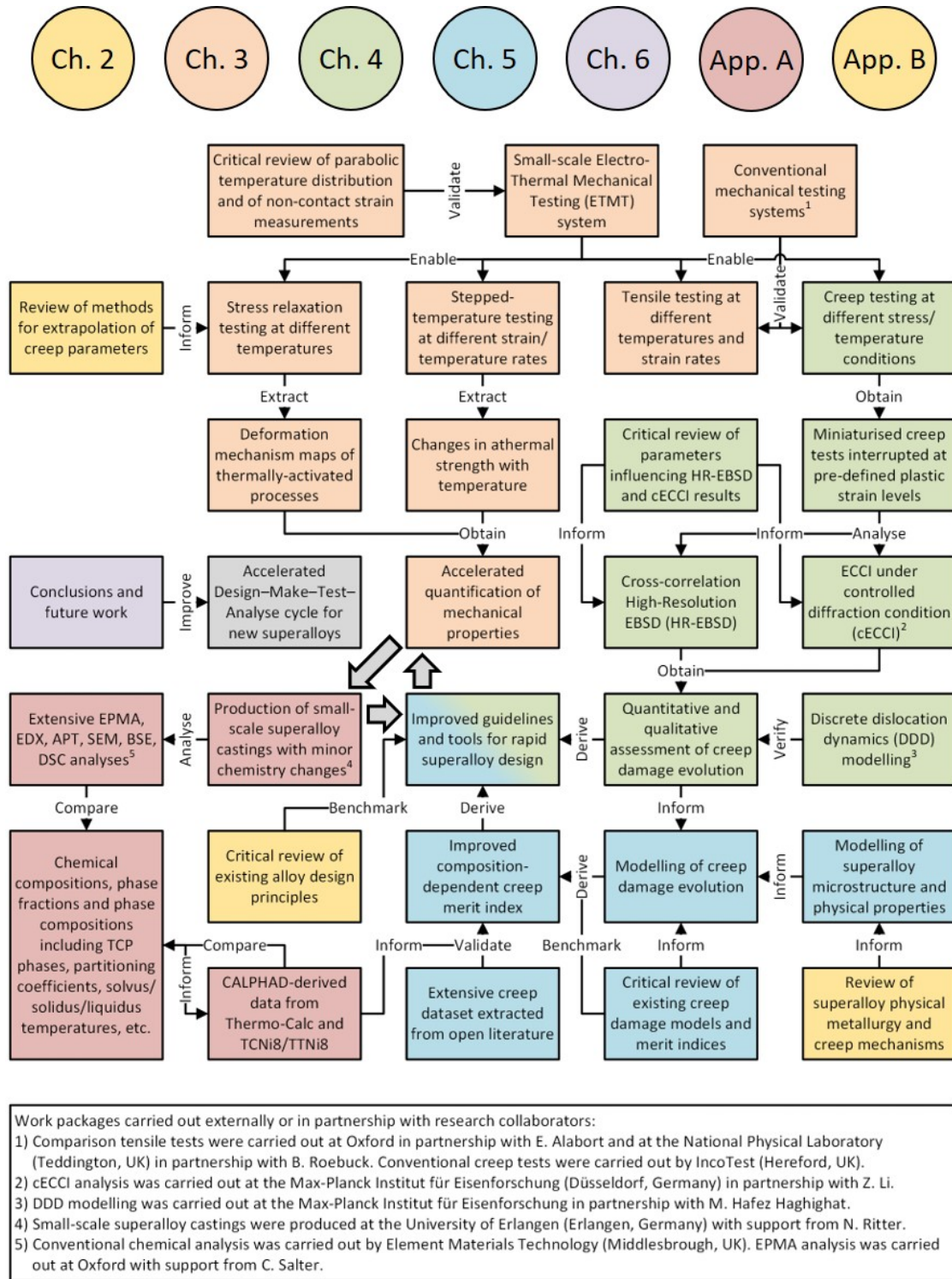


Figure 1.12: Project integration of key research activities divided by thesis sections. Work packages carried out externally or in partnership with research collaborators are indicated by superscript numbers and their extent is described in the legend box.

The origin of the term “Superalloy” is rather obscure. Early works refer only to “Heat Resisting Alloys” or “High Temperature Alloys”. The nomenclature “Superalloy” did not surface until the late ’40s when the very popular fictional character, Superman, became a television hero. From that day forward, the word “Super” became a popular descriptor in the vocabulary.

— W. Boesch, “Introduction–Superalloys” in
“Superalloys, Supercomposites, and Superceramics”

2

Background of Superalloys as High-Temperature Structural Materials

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2.1 Nickel-Based Superalloys

2.1.1 Introduction

Until today, the chemical composition of an alloy has remained the principal specification for awarding patents. In his seminal work on the historical development of superalloys, Sims [115] illustrated the main qualitative trends in chemistry, along with problems encountered over time as key drivers for change, as shown in Figure 2.1(a) and Figure 2.2. These are, however, largely simplified overviews. A more thorough, quantitative analysis of cast alloy compositions over six decades in Figure 2.3 reveals that metallurgists have focused on distinct design aspects and have weighted the value of chemical additions in different ways.

A comprehensive analysis of Figure 2.3 goes beyond the scope of this work, however, several key trends can be identified for modern superalloys, in agreement with Figure 2.1(b). On the one hand, tantalum and tungsten have been added in increasing amounts as solid solution strengtheners, but have been supplanted by the more potent strengthener rhenium in the newest generations. Chromium levels have dropped markedly to accommodate higher γ' volume fractions, while titanium has lost favour over time as it has been related to higher oxidation rates and poor retention of thermal barrier coatings. Lastly, ruthenium has been added to modern alloys with high rhenium contents to reduce their susceptibility to TCP phase formation. Besides chemistry, Sims [115] also highlights important inventions in the field of processing, which ultimately led to a transition from alloying- to processing-based improvements, as depicted in Figures 2.4 and 2.5. To understand the current state of alloy design efforts, a more in-depth review of advances in both alloying and processing is warranted.

2.1.2 Historical Development

Since their initial development, the evolution of NBSA has been linked to their use as high-temperature structural materials and has been driven by increasingly demanding operating conditions [50, 117]. Their origins can be traced back to

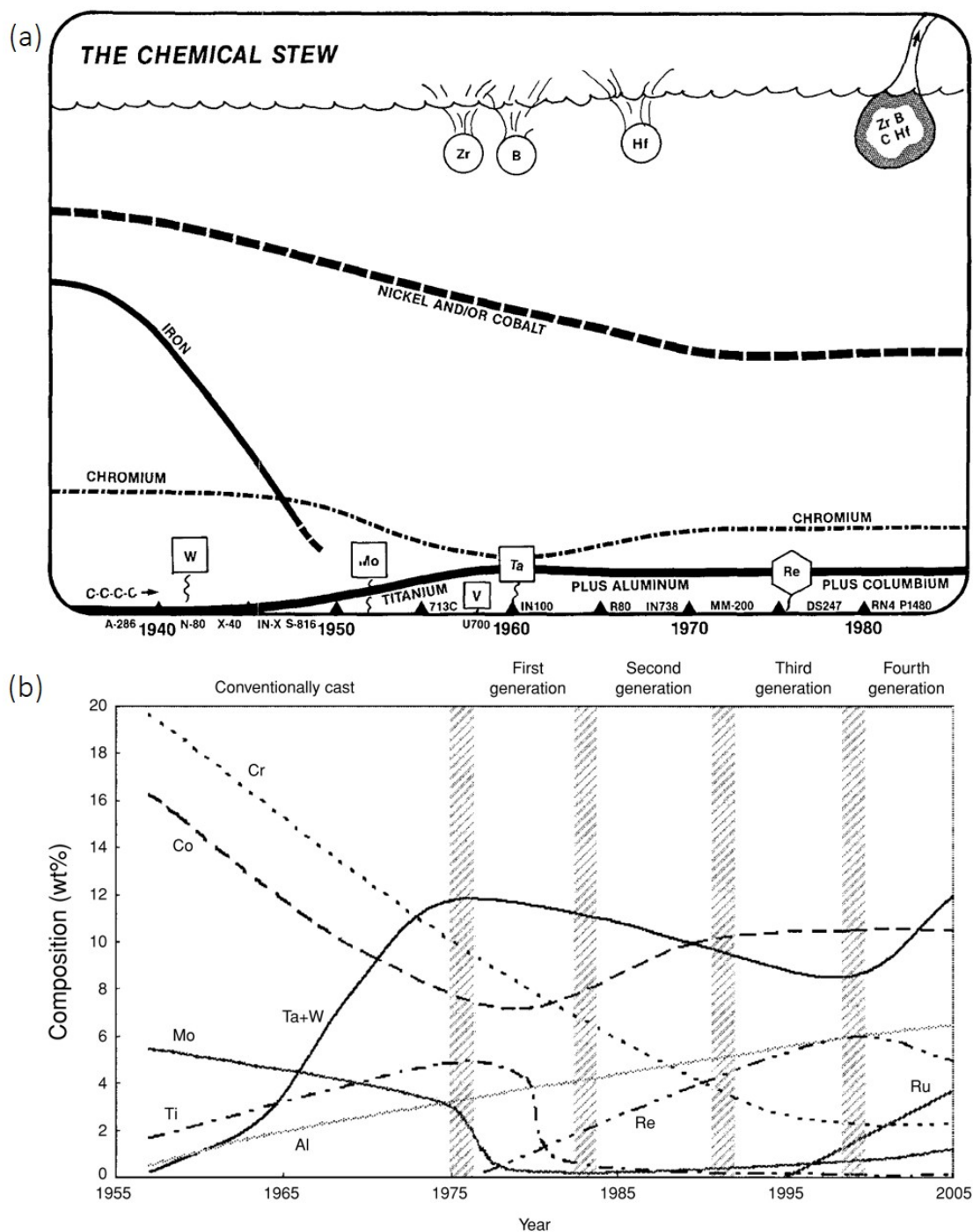


Figure 2.1: Estimated qualitative trends in the development of superalloy chemical compositions from (a) 1935 to 1985 [115] and (b) 1955 to 2005 [12]. Significant milestone alloys are displayed along the time axis in (a).

advancements in austenitic stainless steels at the beginning of the 20th century, which possessed the face-centred cubic (FCC) gamma (γ) phase that was to become crucial for the later success of superalloys [115]. At that time, austenitic steels were

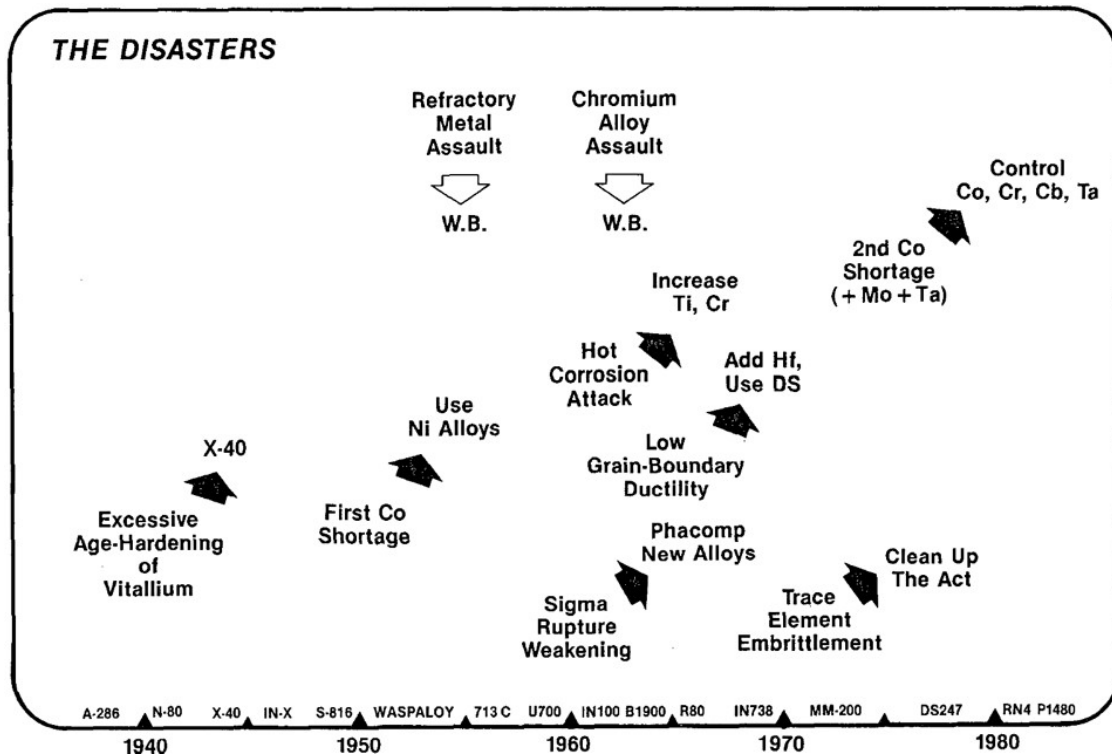


Figure 2.2: Chronology of the main problematic issues encountered during the development of superalloys, along with their solutions [116].

the materials of choice for newly developed gas turbines and turbosuperchargers [51, 115, 117].

Early nickel-iron- and cobalt-based alloys were strengthened with carbide dispersions and contained significant levels of chromium for oxidation resistance [117]. Problems of uncontrolled age-hardening from carbides led to a stricter control of carbon and carbide-forming element contents and to improved heat treatments. Iron gradually disappeared as an alloy base in favour of nickel and cobalt, which are better FCC stabilisers, and has only resurfaced in lower-cost alloys. The iron-free Ni-20Cr Nichrome alloy, patented in 1918, was used as a basis by Bedford and Pilling, as well as by Merica, who in 1929 patented alloys with small additions of titanium and aluminium to Nichrome [115]. These exhibited significant creep strengthening through the precipitation of the coherent FCC gamma prime (γ') phase, although this was only realised later, after the invention of the electron microscope [115, 118].

Parallel advancements in jet turbine engines during the 1930s and 1940s spawned the need for increasingly strong and temperature-resistant materials, initially for

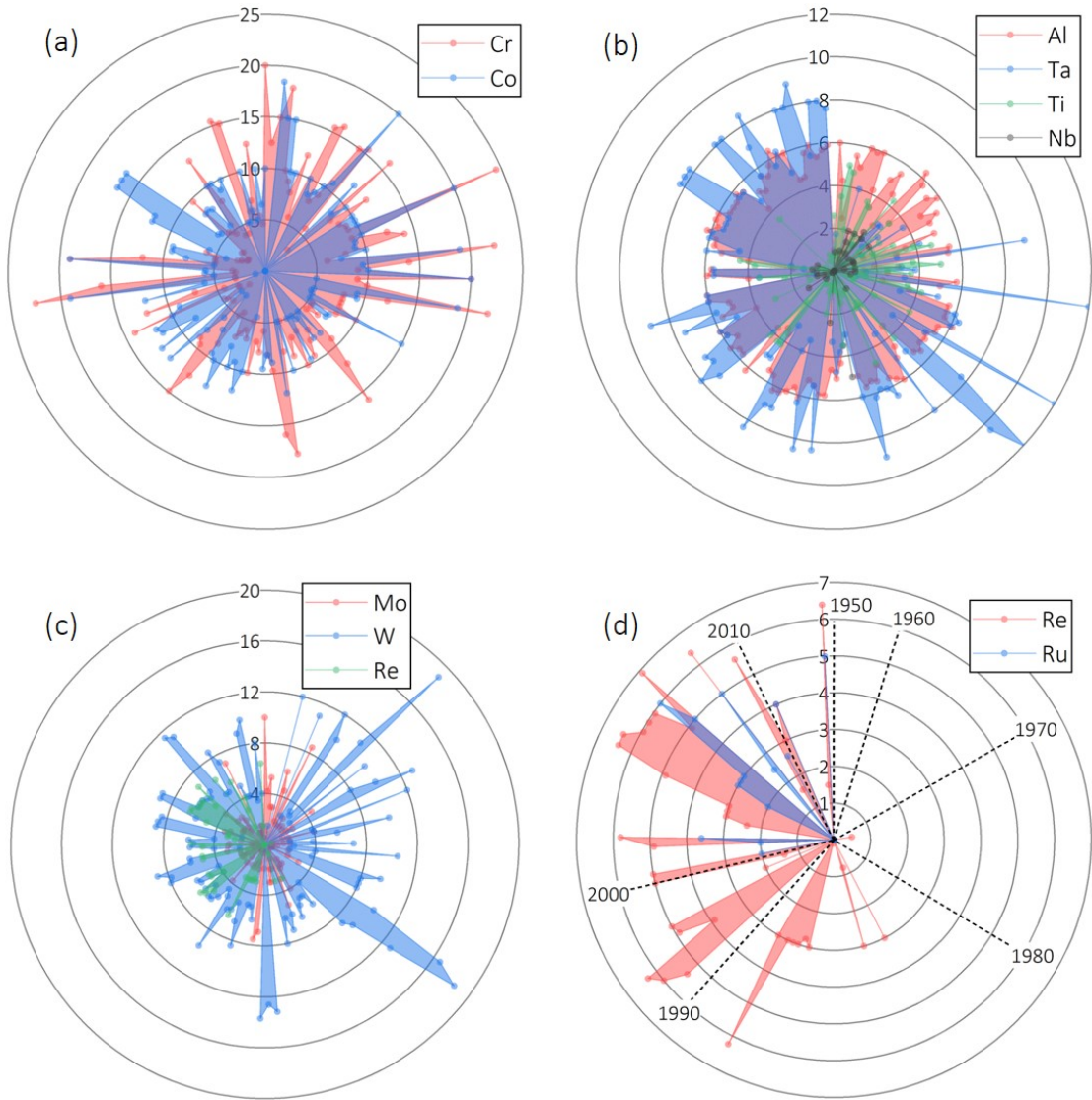


Figure 2.3: Radar diagrams of variations in the compositions of cast NBSA over six decades. Values are shown in wt.% for the list of alloys compiled from literature and plotted in the chromium/aluminium diagram of Figure 1.3. The diagrams show changes in (a) alloying for corrosion and sulphidation resistance, (b) γ' -formers, (c) main γ solid solution strengtheners, and (d) rhenium and ruthenium contents determining the limits of later superalloy generations. All radar graphs have the same time scale, with time running clockwise. In (d), additional dashed lines delimiting individual decades have been added. Each alloy has been assigned the year in which it is first known to have been mentioned in a journal article or in a patent, however, discrepancies from actual initial use in industry can be expected. It should also be noted that many of the newer alloys — as a rule of thumb those developed after the year 2000 — have not yet found an industrial application.

military jet engines and later on for IGT [51, 115]. It should be pointed out that many early discoveries, such as the development of cobalt-based alloy Haynes Stellite

21 as an initial turbine blade material, or the observation that post-casting heat treatments had a significant impact on material properties were pure cases of serendipity [119]. In like manner, most alloy development programmes during the 1940s and 1950s were based on the extensive manufacturing and screening of large numbers of alloys for creep rupture strength, in an attempt to relate minor changes in chemistry to mechanical properties [119]. Development efforts focused on both wrought and cast alloys, driven by a continuous contest between these processing routes. However, the latter were eventually preferred for blade and vane components due to their higher intrinsic strength at high temperatures [12, 120]. Furthermore, investment casting techniques enabled more complex component shapes and, most importantly, the addition of internally-cast cooling passageways [121].

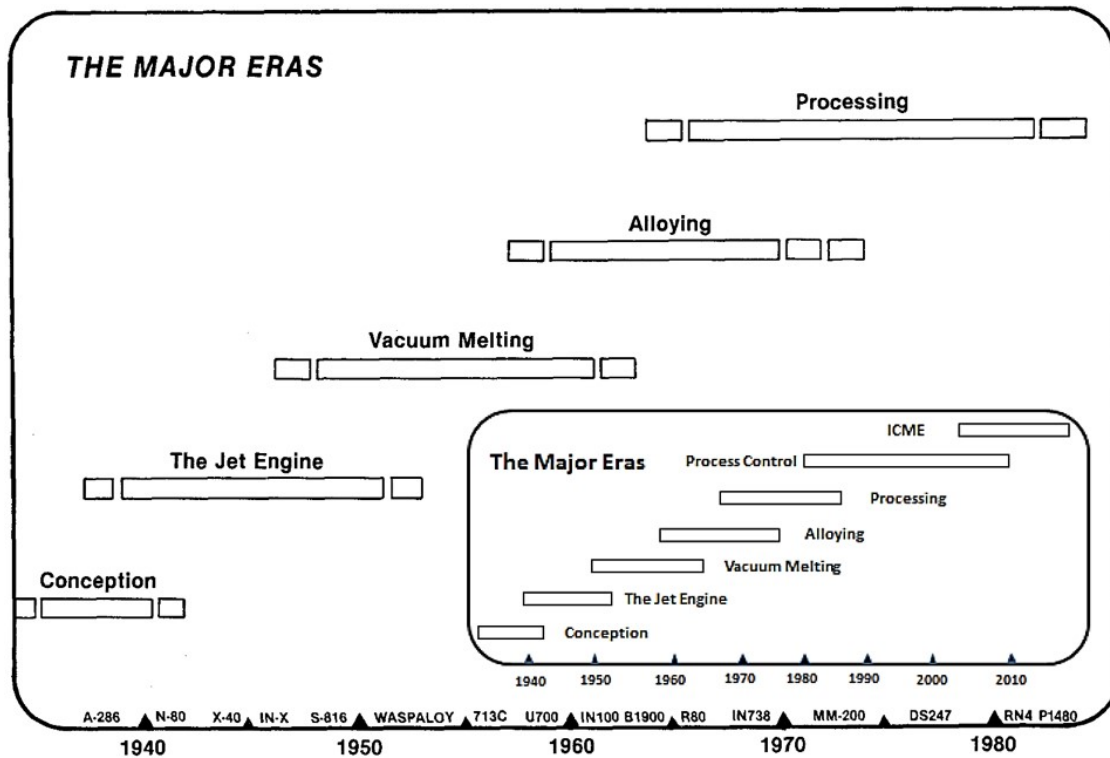


Figure 2.4: Qualitative overview of the defining technological developments in superalloys over time, each marking a different ‘era’ [115]. The inset shows an updated version, proposed to include process control and ICME as subsequent defining eras [122].

A crucial invention was the advent of vacuum induction melting (VIM), introduced commercially in the 1950s. As the charge could remain molten for longer time, VIM improved degasification and the removal of detrimental volatile

impurities and enabled a more precise compositional control of the melt [51, 117–119]. Furthermore, VIM paved the way for other innovations, resulting in a processing ‘horn of plenty’, as shown in Figure 2.5. With regard to novel processing routes, the introduction of directional solidification should be emphasised, as this enabled at first a partial removal of transverse grain boundaries (GB) in columnar microstructures and ultimately a complete removal of GB in monocrystalline structures [123, 124]. GB strengtheners were no longer required and were removed from single-crystals, enabling super-solvus heat treatments which could provide a complete solutioning of γ' precipitates and the re-precipitation of a controlled, homogeneous microstructure during cooling [12, 125].

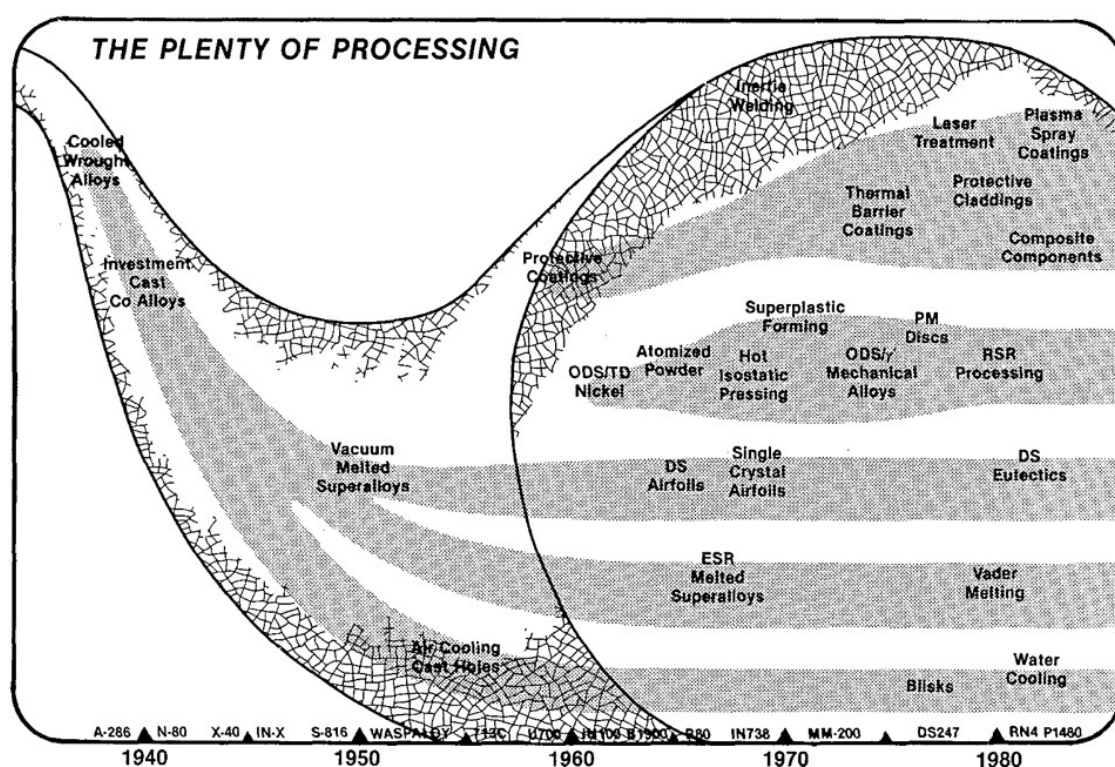


Figure 2.5: Chronology of the diversification of superalloy processing methods, leading to different approaches towards the improvement of alloy performance [115].

Three specific influences on chemistry through VIM must be highlighted [115]. First, higher levels of aluminium and titanium could be added for precipitation strengthening, as these elements would no longer suffer from rapid oxidation. Second, GB strengtheners including hafnium, boron, and zirconium could be dosed more

precisely, leading to increased ductility. Third, VIM enabled higher levels of refractory metals for solid solution strengthening. Molybdenum had been introduced as a solid solution strengthener in the late 1940s and was added in increasing amounts along with tungsten, tantalum, and eventually rhenium [115].

Unfortunately, this design trend led to a pronounced precipitation of deleterious plate-like phases, which induced premature cracking and reduced material performance [64]. As a response, alloy chemistry was controlled more closely through computerised calculation techniques based on solid-state electron theory such as PHACOMP [65]. It should be noted that in 1968, the first International Symposium on Superalloys, which reached its 13th instalment in 2016, was held specifically to discuss issues of phase stability [126].

In an attempt to conserve relatively high levels of refractory metals while averting TCP phase formation, chromium contents were reduced in the 1960s. This in turn led to several catastrophic engine failures from oxidation and hot corrosion. The response was a more careful consideration of chromium and aluminium levels as key additions against environmental damage, as well as increased research into diffusion and MCrAlY coatings [51, 117].

Lastly, geopolitical considerations and strategic resource management have been of significant importance for superalloy manufacturing, considering the complex nature of raw material supply chains and mineral import dependences [115, 127]. This challenge was clearly evidenced by cobalt crises in the 1950s, late 1970s, and early 1980s and by a chromium shortage in the 1970s [128]. Concerns for the availability of certain strategic metals — most critically cobalt, niobium, tantalum, and chromium — were heightened by their increased use in superalloys, as shown in Figure 2.6. This led to research programmes on conserving available resources and on reducing the dependence on strategic metals through element substitution, advanced processing, and the development of alternative materials [128, 129]. In parallel, techniques for recycling scrap material were improved [130–133]. Until today, strategic resource management remains a critical issue within the superalloy

industry, especially considering increasing additions of platinum group and rare earth metals and emerging oligopolies of certain mining regions [134–136].

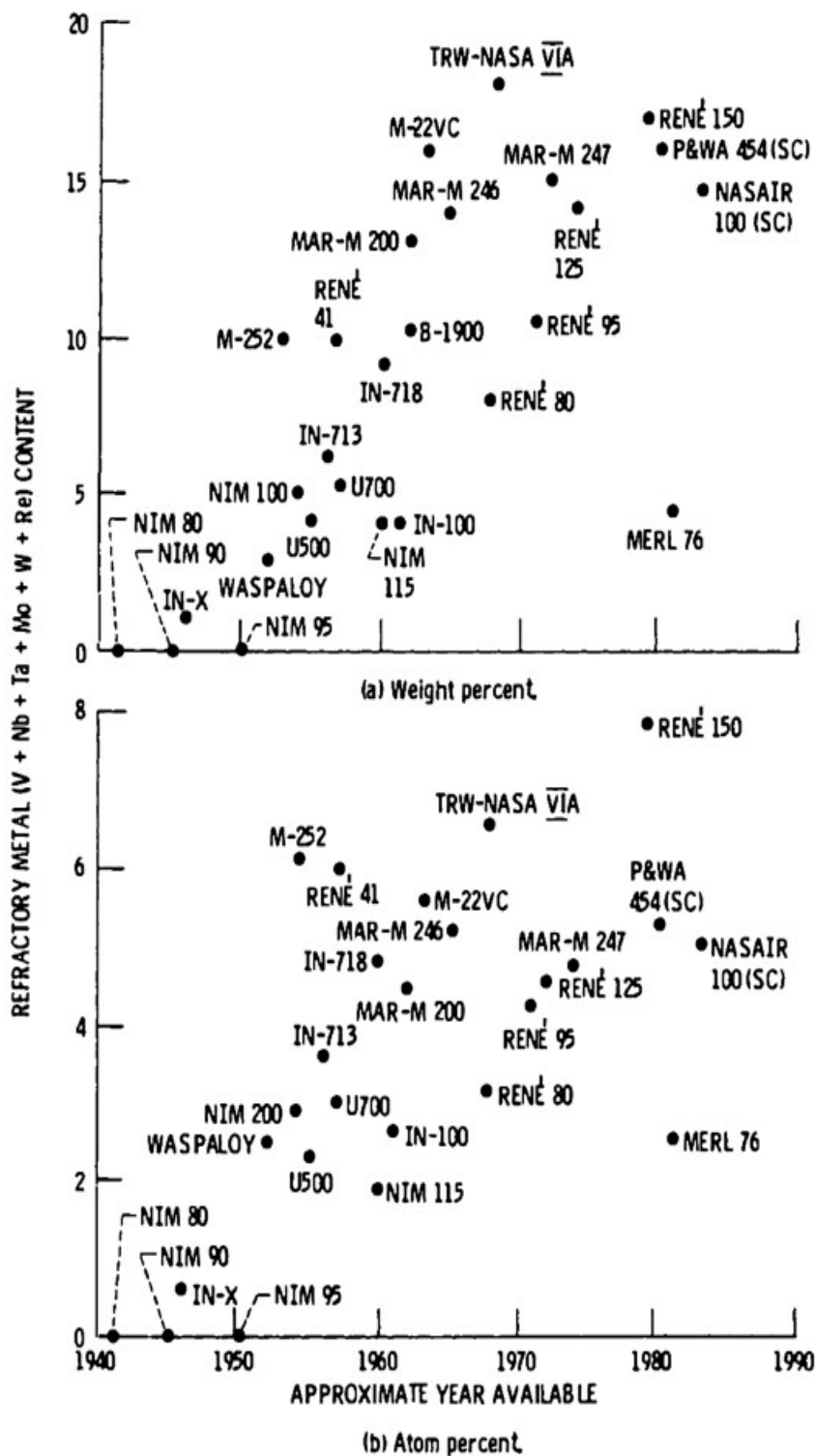


Figure 2.6: Increased use of refractory metals in NBSA demonstrated by plots of total refractory content in (a) weight percent and (b) atomic percent over time [128].

Table 2.1 presents a compilation of commercial NBSA compositions, most of which are also suitable for single-crystal casting. First-generation single-crystal alloys were derived from previously existing cast compositions, such as Mar-M247, through the removal of GB strengtheners and an increase in refractory elements and γ' -formers. These alloys benefited greatly from the possibility of fine-tuning microstructure through simplified heat treatments [125]. Development was driven by both alloy and engine manufacturers, each patenting their compositions under specific brand names. Among the most famous are “René” and “GTD” from General Electric Comp., “PWA” from Pratt & Whitney (now part of United Technologies Corp.), and “SRR” from Rolls-Royce on the consumer side; and “CM” and “CMSX” from Cannon-Muskegon Corp., “Inconel (IN)” from International Nickel Comp. (now Special Metals Corp.), and “Mar-M” from Martin Marietta Corp. (now Lockheed Martin) on the supplier side. Differentiation occurred mostly through tweaking of refractory metal additions. It was within this context that rhenium was first added to superalloys as a substitute for tungsten and molybdenum and was found to result in significant creep strengthening [125]. This led to second-generation alloys with around 3 wt.% rhenium and later to a third generation with 5 to 6 wt.%, as also shown schematically in Figure 2.1(b).

The so-called ‘rhenium effect’ was initially associated with the presence of rhenium atom clusters providing increased solid solution strengthening within the matrix phase [137, 138]. However, this hypothesis was later disproved through advanced microscopy studies [139–142]. Besides its confirmed effect of decreasing the interfacial energy at γ/γ' interfaces [143–146], it appears that the slow diffusion rate of rhenium is responsible for retarding high-temperature deformation mechanisms such as climb-assisted glide of dislocations near precipitates [147, 148].

Similar to the problematic issues encountered in the 1960s, these later generations of single-crystal superalloys exhibited pronounced deleterious phase precipitation at high temperatures [149–151], decreased corrosion resistance due to lower chromium levels, more casting errors [152–154], as well as higher densities and cost. Ruthenium and in some cases other rare metals like iridium or platinum have been added

to fourth- and fifth-generation alloys, as they have been shown to improve phase stability [155–158]. Other shortcomings have been dealt with by adopting new manufacturing methods [159–161] and further innovations in processing are expected to have a significant positive impact [162]. Alloying, on the other hand, will likely only play a minor role, as superalloys have been approaching an asymptote in terms of their high-temperature capabilities [19]. Instead, the key potential of current superalloy design lies in the tailored optimisation of materials for specific operating conditions with the help of novel computer-assisted methods [162].

Alloy	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Re	Ru	Hf	Other
ABD-3 [52]	13	10	0	5	5.4	0	7	0	0	0	0	0
AF56 [163]	12	8	2	4	3.4	4.2	5	0	0	0	0	0
AM1 [164]	7	8	2	5	5	1.8	8	1	0	0	0	0
AM3 [165]	8	5.5	2.25	5	6	2	3.5	0	0	0	0	0
CM247LC [166]	8	9.3	0.5	9.5	5.6	0.7	3.2	0	0	0	1.4	0.07 C, 0.015 B, 0.01 Zr
CMSX-11B [167, 168]	12.5	7	0.5	5	3.6	4.2	5	0.1	0	0	0.04	0
CMSX-11C [167, 169]	14.9	3	0.4	4.5	3.4	4.2	5	0.1	0	0	0.04	0
CMSX-2 [166, 170]	8	5	0.6	8	5.6	1	6	0	0	0	0	0
CMSX-3 [166, 170]	8	4.8	0.6	8	5.6	1	6.3	0	0	0	0.1	0
CMSX-6 [171]	10	5	3	0	4.8	4.7	6	0	0	0	0.1	0
CMSX-7 [172-174]	6	10	0.6	9	5.7	0.8	9	0	0	0	0.2	0
GTD-111 [175]	14	9.5	1.5	3.8	3	5	3.15	0.07	0	0	0	0.1 C, 0.014 B, 0.007 Zr
GTD-222 [175]	22.5	19.1	0	2	1.2	2.3	0.94	0.8	0	0	0	0.08 C, 0.004 B, 0.02 Zr
IN-100 [176]	10	15	3	0	5.5	4.7	0	0	0	0	0	0.18 C, 0.014 B, 0.06 Zr, 1 V
IN-591 [177]	3	12	0	19	5.75	0	3	0	0	0	0	0.1 C, 0.8 B, 0.05 Zr
IN-6203 [178]	22	19	0	2	2.3	3.5	1.1	0.8	0	0	0.75	0.15 C, 0.01 B, 0.1 Zr
IN-713LC [179]	12	0	4.5	0	5.9	0.6	0	2	0	0	0	0.05 C, 0.01 B, 0.1 Zr
IN-738LC [180]	16	8.5	1.75	2.6	3.4	3.4	1.75	0.9	0	0	0	0.11 C, 0.01 B, 0.04 Zr
IN-792 [181]	12.4	9.2	1.9	3.9	3.5	3.9	4.2	0	0	0	0	0.07 C, 0.016 B, 0.018 Zr
IN-939 [182]	22.4	19	0	2	1.9	3.7	0	1	0	0	0	0.15 C, 0.009 B, 0.1 Zr
Mar-M002 [183]	8	10	0	10	5.5	1.5	2.6	0	0	0	1.5	0.15 C, 0.015 B, 0.03 Zr
Mar-M200Hf [184]	8	9	0	12	5	1.9	0	1	0	0	2	0.13 C, 0.015 B, 0.03 Zr
Mar-M246 [184]	9	10	2.5	10	5.5	1.5	1.5	0	0	0	1.5	0.15 C, 0.015 B, 0.05 Zr
Mar-M247 [185]	8	10	0.6	10	5.5	1	3	0	0	0	1.5	0.15 C, 0.015 B, 0.03 Zr
Mar-M421 [184]	15	10.8	1.8	3.3	4.5	1.6	0	2.3	0	0	0	0.18 C, 0.019 B, 0.04 Zr
MC2 [186]	8	5	2	8	5	1.5	6	0	0	0	0.1	0
Nasair 100 [187]	9	0	1	10.5	5.75	1.2	3.3	0	0	0	0	0

Alloy	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Re	Ru	Hf	Other
PWA1422 [188]	9	10	0	12	5	2	0	1	0	0	1.5	0.14 C
PWA1480 [189]	10	5	0	4	5	1.5	12	0	0	0	0	0
PWA1483 [190]	12.2	9.2	1.9	3.8	3.6	4.2	5	0	0	0	0	0.07 C
René 125 [191]	9	10	2	7	1.4	2.5	3.8	0	0	0	0.05	0.11 C, 0.017 B, 0.05 Zr
René 220 [192]	18	12	3	0	0.5	1	3	5	0	0	0	0.02 C, 0.01 B
René 80 [193]	14	9	4	4	3	4.7	0	0	0	0	0.8	0.16 C, 0.015 B, 0.01 Zr
René N4 [194]	9	8	2	6	3.7	4.2	4	0.5	0	0	0	0
RR2000 [195, 196]	10	15	3	0	5.5	4	0	0	0	0	0	0
SC 16 [197]	16	0	3	0	3.5	3.5	3.5	0	0	0	0	0
SCA425 [198]	16	5	1	4	4	3.5	3.5	0	0	0	0.1	0
SCA425+ [199]	15.5	5	1	4	4.55	0	8	0	0	0	0.1	0
SCB444 [200]	12	5	1	4	4	4.4	2	0	0	0	0.1	0
SRR99 [195, 196]	8	5	0	10	5.5	2.2	12	0	0	0	0	0
STAL125SX1 [201]	12.5	5	1.5	3.5	5.4	0	8	0	0	0	0.1	0.05 C
STAL15SX [32]	15	5	1	4	4.6	0	8	0	0	0	0.1	0.25 C, 0.015 B
TMS-12 [202]	6.6	0	0	12.8	5.2	0	7.7	0	0	0	0	0
TMS-26 [203]	5.2	8.2	1.9	11.5	5.1	0	8.1	0	0	0	0	0
TMS-6 [202]	9.2	0	0	8.7	5.3	0	10.4	0	0	0	0	0
CMSX-8 [172, 174, 204]	5.4	10	0.6	8	5.7	0.7	8	0	1.5	0	0.2	0
ABD-1 [52]	8	10	0	8.5	5.8	0	8.5	0	1.6	0	0	0
TMS-82+ [205]	4.9	7.8	1.9	8.7	5.3	0.5	6	0	2.4	0	0.1	0
René 142 [206]	6.8	12	1.5	4.9	6.15	0	6.35	0	2.8	0	1.5	0.12 C, 0.015 B, 0.02 Zr
CM186LC [207]	6	9.3	0.5	8.4	5.7	0.7	3.4	0	3	0	1.4	0.07 C, 0.015 B, 0.005 Zr
CMSX-4 [207, 208]	6.5	9.6	0.6	6.4	5.6	1	6.5	0	3	0	0.1	0
CMSX-486 [209]	5	9.3	0.7	8.6	5.7	0.7	4.5	0	3	0	1.2	0.07 C, 0.015 B, 0.005 Zr
CMSX-681 [209]	5	9.3	0.5	8.4	5.7	0.1	6	0	3	0	1.4	0.09 C, 0.015 B, 0.005 Zr
PWA1426 [210]	6.5	10	1.7	6.5	6	0	4	0	3	0	1.5	0.1 C, 0.015 B, 0.1 Zr

Alloy	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Re	Ru	Hf	Other
PWA1484 [211]	5	10	2	6	5.6	0	9	0	3	0	0.1	0
PWA1487 [212]	5	10	1.9	5.9	5.6	0	8.4	0	3	0	0.25	0
René N5 ([213])	7	8	2	5	6.2	0	7	0	3	0	0.2	0
RR2072 [214]	6	4	3.3	1.9	6.2	0.4	5.95	0.8	3	0	0.1	0
SC 180 [215]	5	10	2	5	5.2	1	8.5	0	3	0	0.1	0
SMP14 [216]	4.8	8.1	1	3.9	5.4	0	7.2	1.4	3.9	0	0	0
TMS-139 [217]	2.9	5.8	2.9	5.8	5.8	0	5.5	0	4.9	0	0.1	3 Ir
TMS-80 [218]	2.9	11.6	1.9	5.8	5.8	0	5.8	0	4.9	0	0.1	3 Ir
TMS-75 [205, 218]	3	12	2	6	6	0	6	0	5	0	0.1	0
René N6 [219]	4.2	12.5	1.4	6	5.75	0	7.2	0	5.4	0	0.15	0.05 C, 0.004 B
CMSX-10 [220, 221]	2	3	0.4	5	5.7	0.2	8	0	6	0	0.03	0
Alloy 5A [222]	4.5	12.5	0	5.75	6.25	0	7	0	6.25	0	0.15	0.05 C
TMS-138 [223]	2.9	5.9	2.9	5.9	5.9	0	5.6	0	4.9	2	0.1	0
TMS-174 [203]	5	7.9	2.8	11.1	4.9	0	8.1	0	0	2.5	0	0
ABD-2 [52]	4	9	0	7.4	6.4	0	5.6	0	5.6	2.6	0	0
EPM-102/PWA 1497 [224]	2	16.5	2	6	5.55	0	8.25	0	5.95	3	0.15	0.03 C
TMS-138A [223]	3.2	5.8	2.8	5.6	5.7	0	5.6	0	5.8	3.6	0	0
MC-NG [225]	4	0	1	5	6	0.5	5	0	4	4	0.1	0
TMS-162 [217, 226]	2.9	5.8	3.9	5.8	5.8	0	5.6	0	4.9	6	0.09	0
TMS-173 [217, 226]	2.8	5.6	2.8	5.6	5.6	0	5.6	0	6.9	5	0.1	0
TMS-196 [227, 228]	4.6	5.6	2.4	5	5.6	0	5.6	0	6.4	5	0.1	0
TMS-238 [229, 230]	4.6	6.5	1.1	4	5.9	0	7.6	0	6.4	5	0.1	0

Table 2.1: Chemical compositions of cast NBSA in wt.% with nickel as balance. The list includes the most common commercial products [12, 117, 118, 125], several compositions determined *via* ABD calculations [52], and some alloys of particular interest for IGT applications [231]. Next to each alloy name are references to journal articles or patents in which it was first described. Horizontal lines denote transitions between superalloy generations. First-generation alloys are arranged alphabetically, while later-generation alloys are ordered according to increasing rhenium and ruthenium contents.

2.1.3 Physical Metallurgy

To understand the origin of the unique combination of high-temperature properties that has made superalloys the materials of choice for advanced turbine engine applications, it is necessary to relate these properties to alloy microstructure and this in turn to composition and processing. Aspects of the physical metallurgy of NBSA have been amply reviewed in the literature [12, 232–237], as such, only key relations are presented here.

2.1.3.1 Structure and Constitution

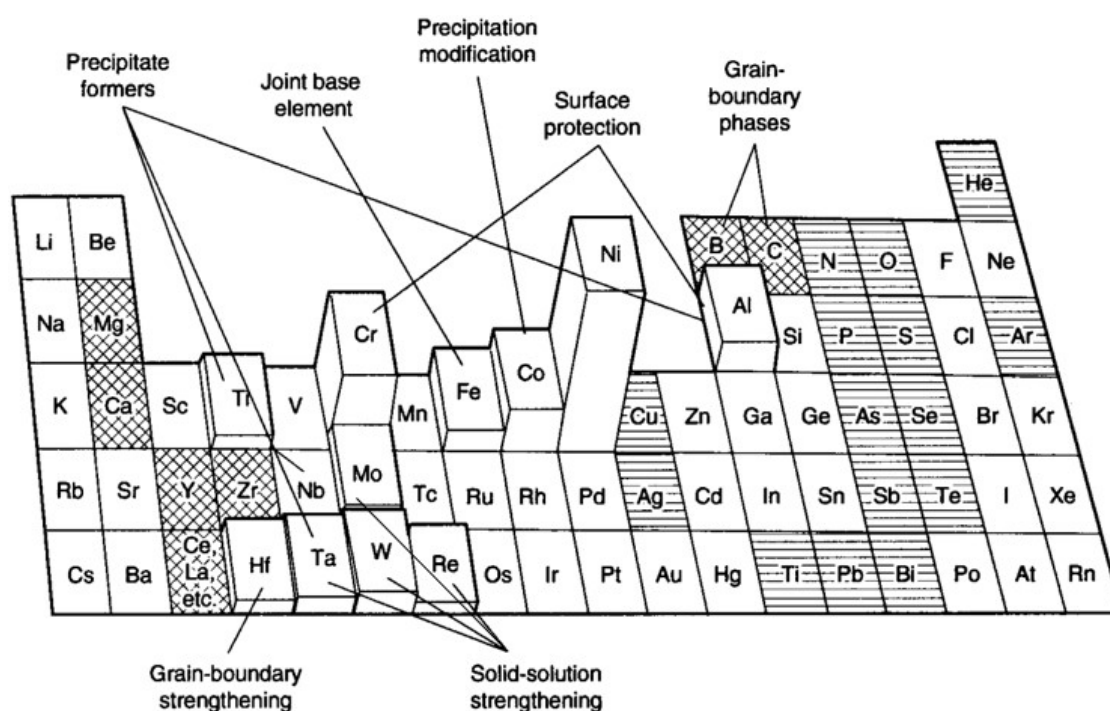


Figure 2.7: Main alloying elements in NBSA, with the height of each column qualitatively representing the common weight fraction of each element [120]. Beneficial roles played by individual elements are identified. Desired trace additions are marked by cross-hatching, while detrimental tramp elements are indicated with horizontal lines. Note that platinum group metals are not considered here.

When discussing a justification for nickel as a basis for high-temperature materials, reviewers [12, 238, 239] point out three main characteristic traits: (1) nickel exhibits a stable FCC crystal structure from room temperature to its melting point, resulting in it being both tough and ductile and possessing low diffusion

Effect	Elements
Solid solution strengtheners	Co, Cr, Fe, Mo, W, Ta, Re, Al, Ti
Carbide formers:	
MC	W, Ta, Ti, Mo, Nb, Hf
M ₇ C ₃	Cr
M ₂₃ C ₆	Cr, Mo, W
M ₆ C	Mo, W, Nb, Ta
Carbonitride M(CN) precipitation	C, N
γ' precipitation	Al, Ti
Raises γ' solvus temperature	Co
Hardening precipitates and/or intermetallics	Al, Ti, Nb, Ta
Oxidation resistance	Al, Cr, Y, La, Ce
Hot corrosion resistance	Cr, La, Th
Sulphidation resistance	Cr, Co, Si
Improves creep properties	B, Ta, Re
Increases rupture strength	B
Grain boundary refiners	B, C, Zr, Hf
Facilitates working	Fe, B, C
Retards γ' coarsening	Re

Table 2.2: Overview of beneficial alloying effects in superalloys, adapted from references [117, 120].

rates of alloying elements; (2) it is possible to apply various coatings which enhance the resistance to environmental damage; and (3) many elements possess a high solubility within the nickel matrix, enabling overall additions of up to 50 wt.% and the precipitation of intermetallic compounds.

A graphical summary of the roles played by alloying elements in NBSA is illustrated in Figure 2.7; these are again compiled in Table 2.2. In-depth reviews on the positive and negative effects associated with each element, including major and minor additions as well as impurities can be found in references [117, 239, 240]. Due to the complex interactions between elements, a given alloy may not automatically benefit from a particular addition and/or may only do so under certain circumstances [239]. This reinforces the need for a physically based alloy design approach, which accounts for reciprocal influences.

Chemical composition establishes the occurring phases, which in turn give rise to alloy microstructure, as illustrated in Figure 2.8. In this overview image, the top part shows desirable phases, which have been engineered over time through

appropriate changes in chemistry and heat treatments, while the lower part contains deleterious phases found to increase brittleness [116]. While materials are exposed at high temperatures, their microstructures do not remain constant, but rather evolve towards thermodynamic equilibrium. This has a critical impact on material properties, as such, a large body of work has been dedicated to understanding phase stability.

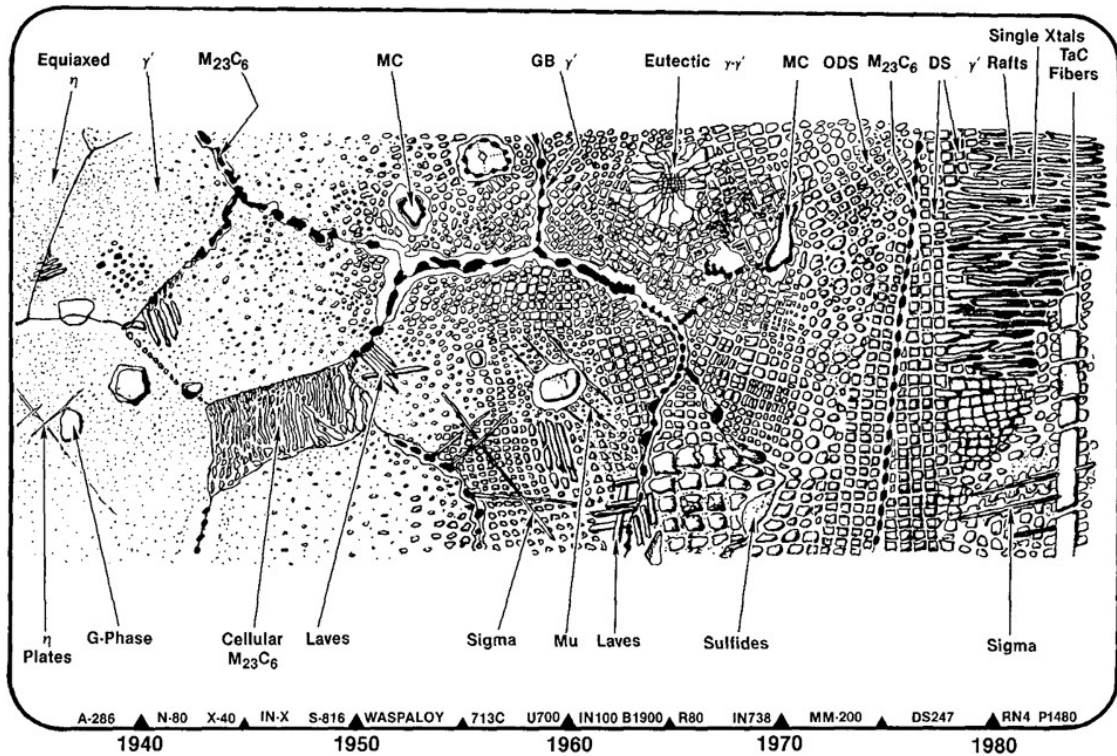


Figure 2.8: Overview of the historical development of common phases in NBSA, containing both useful (upper part of the image) and deleterious phases (lower part) [116]. Some phases will only be stable under certain thermodynamic conditions and/or will only form after certain specific processing steps.

Typical superalloy microstructure is represented by a continuous FCC γ matrix containing a number of secondary phases, including geometrically close-packed (GCP) intermetallic phases like the coherent γ' precipitates, carbides, and borides and detrimental TCP phases. Comprehensive listings of common NBSA phases along with their crystal structures, lattice parameters, chemical compositions, and basic physical properties can be found in references [117, 120].

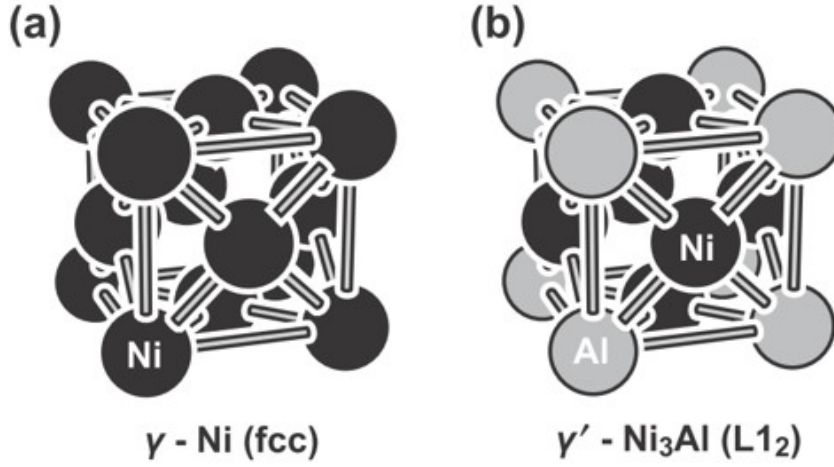


Figure 2.9: Illustration of the crystal structures of (a) the disordered γ matrix phase and (b) the ordered γ' precipitate phase.

The gamma (γ) matrix: The austenitic γ matrix mainly contains elements with a similar radius to that of nickel, including cobalt, iron, chromium, ruthenium, molybdenum, rhenium, and tungsten. As shown in Figure 2.10, high levels of solubility are only reached for similar atomic sizes. This in turn leads to significant differences in the partitioning of elements within superalloys [241], which directly affects the coherency between matrix and precipitates, quantified through the value of lattice misfit:

$$\delta = 2 \times \frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}} \quad (2.1)$$

Estimates of partitioning coefficients and of the effects of alloying additions on the lattice parameters a_{γ} and $a_{\gamma'}$ are shown in Figures 2.11 and 2.12. Lattice parameters can be calculated based on Vegard's law using values reported in the literature [242, 243]. The sign and magnitude of lattice misfit has profound effects on the microstructural evolution and the mechanical properties of superalloys, making it one of the key parameters considered by alloy designers. It should be noted that a_{γ} is affected more strongly by alloying additions compared to $a_{\gamma'}$ [239]. It also increases more rapidly with rising temperature, thus decreasing the value of misfit at high temperatures [244].

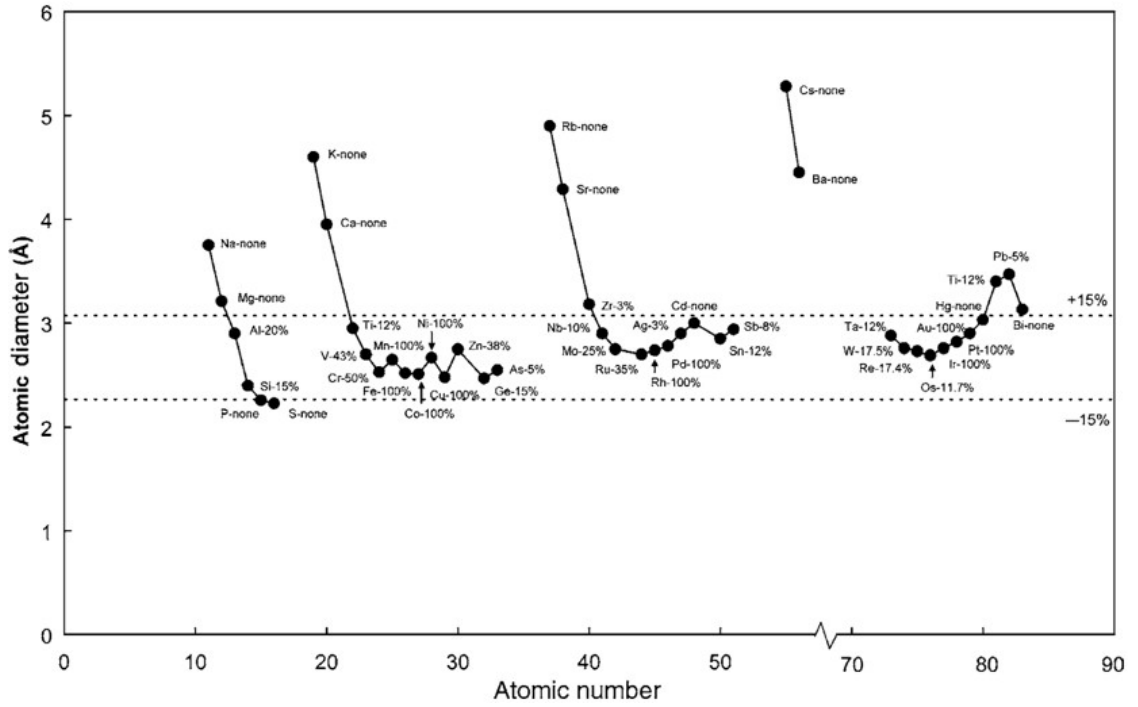


Figure 2.10: Variation of the atomic diameter of different elements, with the dashed lines delimiting a deviation of $\pm 15\%$ from the diameter of nickel. Percentage indications represent the maximum solubility within the γ matrix [12].

Solution elements are not homogeneously distributed in cast materials, but rather exhibit heterogeneous segregation due to the dendritic character of solidification processes and their different solubilities in the melt and in the solidified matrix [20, 239]. The degree to which these effects can be ameliorated through subsequent heat treatments depends largely on the interdiffusion coefficients of individual elements. As illustrated in Figure 2.13, it proves difficult to achieve a uniform distribution of slow-diffusing elements such as rhenium, tungsten, or molybdenum across the entire microstructure [245, 246].

The gamma prime (γ') phase: As discussed in Section 2.1.2, the existence of intermetallic γ' precipitates contributed to the success of superalloys as high-temperature materials right from their very beginnings. Reviewers [12, 238, 239] have pointed out several very fortunate properties of γ' , best summarised in the work of Maier et al. [239] as follows. First, misfit values are generally small, meaning that precipitation occurs readily and leads to a homogeneous particle distribution.

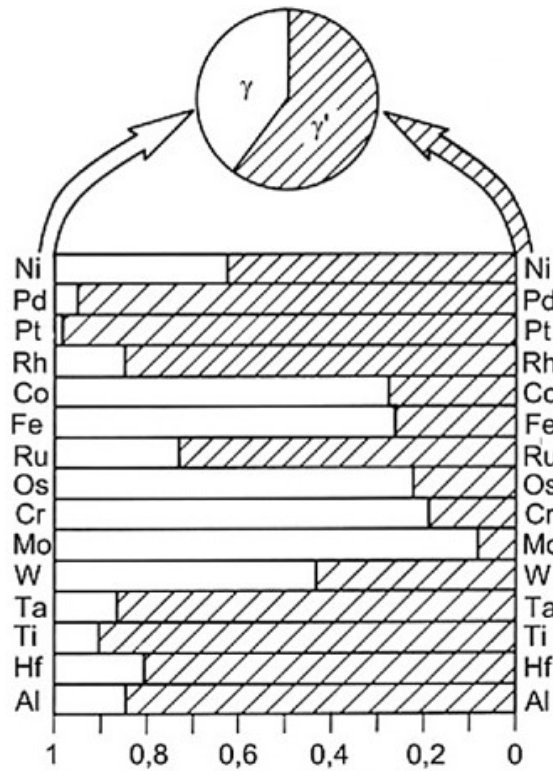


Figure 2.11: Partitioning coefficients of different alloying elements between γ' (hatched bars) and γ (white bars) [241], adapted from reference [239]. Elements have been ordered from top to bottom based on an increasing N_v number of electron vacancies.

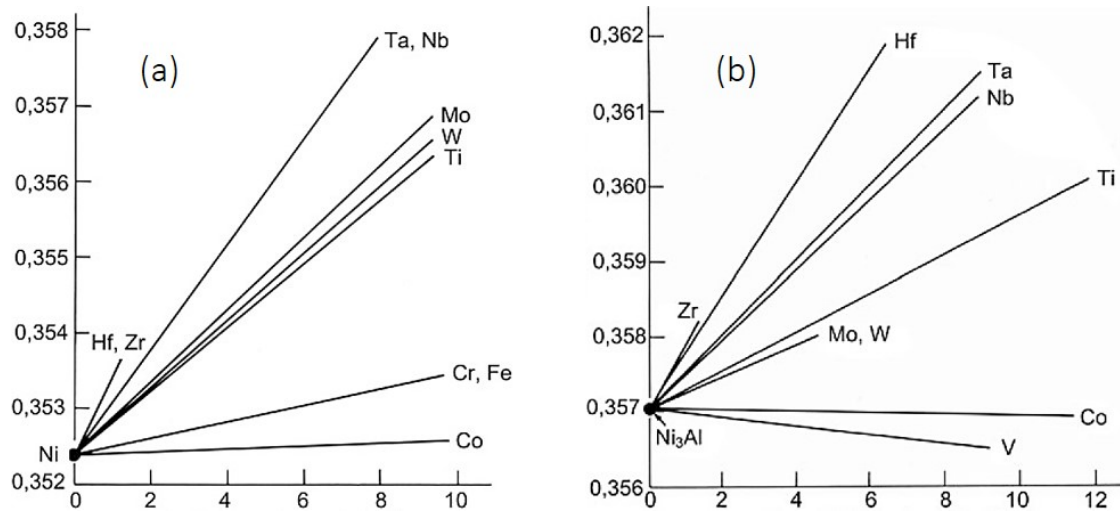


Figure 2.12: Change in lattice parameters for (a) pure nickel and (b) Ni_3Al due to different elemental additions [242], adapted from reference [239]. y -axis values are in nm, x -axis values are in at.%. Misfit can be controlled primarily through a_γ , as such, tantalum, niobium, molybdenum, tungsten, and titanium are of particular interest.

Second, the L_{12} crystal structure, illustrated in Figure 2.9(b), remains ordered virtually until the melting point is reached [248]. Third, different substitutions with

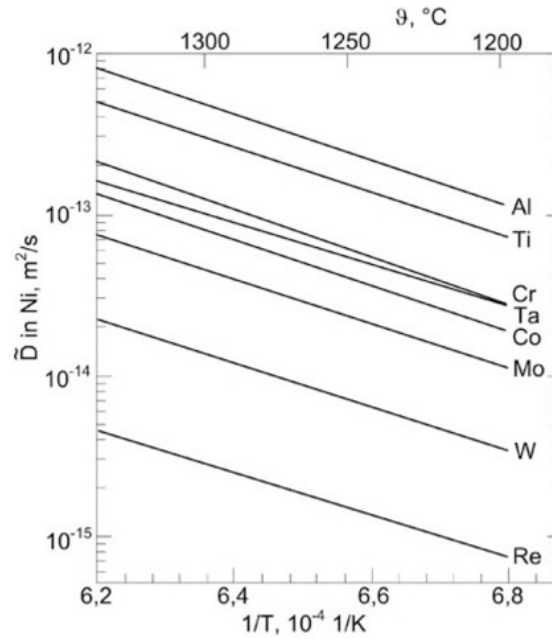


Figure 2.13: Interdiffusion coefficients in pure nickel for various alloying elements as an inverse function of temperature [247]. Potent solid solution strengtheners like rhenium, tungsten, or molybdenum exhibit the lowest values.

other atoms are possible, leading to an increased potential for controlled phase design of the $(\text{Ni},\text{Co})_3(\text{Al},\text{Ti},\text{Ta})$ structure [249]. Fourth, owing to low values of lattice misfit, the precipitates exhibit good long-term thermal stability. Fifth, it is possible to achieve high γ' volume fractions, which contribute to remarkable strengthening, while retaining sufficient ductility to avoid material embrittlement and premature fracture. Last, strengthening exhibits a unique, anomalous temperature-dependency effect, wherein the strength increases with temperature up to about 800 °C. The ordered nature of γ' and the potential for chemical substitutions are illustrated in Figure 2.14. These substitutions occur preferentially based on atomic size. Larger elements such as tantalum or titanium tend to replace aluminium, smaller ones like cobalt tend to replace nickel, and a mixed behaviour is only observed in a few cases including chromium and iron.

The initial size distribution of precipitates can be adjusted through controlled heat treatments, specifically through controlled cooling rates after solutioning and through subsequent ageing steps [250–253]. It has been shown that cooling rates significantly influence chemical composition [254, 255] and particle morphology [256,

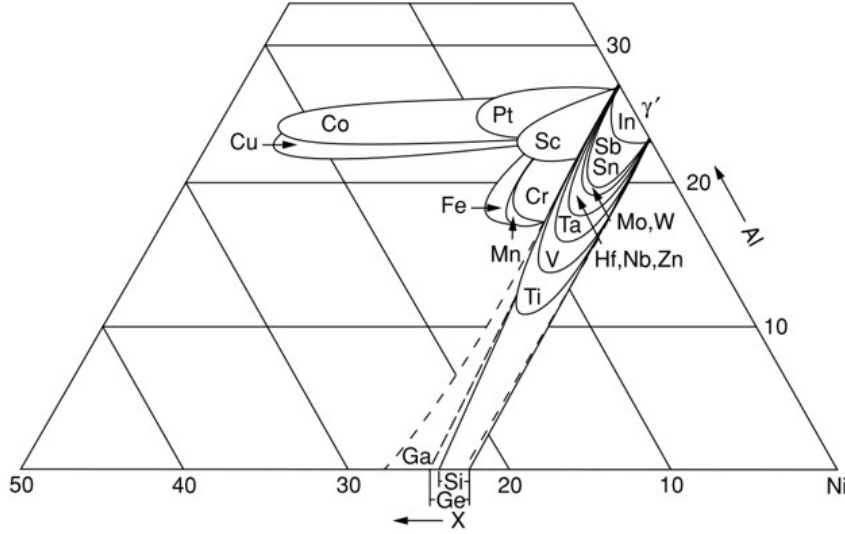


Figure 2.14: Superimposed Ni–Al–X ternary phase diagrams, illustrating how various additions of X can extend the γ' phase field by either replacing nickel on the first sublattice (e.g. cobalt) or aluminium (e.g. tantalum, titanium) on the second sublattice [249].

257] and through these characteristics in turn mechanical properties. Morphology also depends strongly on lattice misfit [233, 258], however, for usual misfit values in superalloys the microstructural evolution always follows the same path [259]. γ' first precipitates as small spheroids to minimise surface energy, which eventually turn cuboidal during ageing to reduce elastic energy. If significant coarsening occurs, precipitate shapes can take the form of arrays of cubes and then of solid-state dendrites.

Unfortunately, complex models for γ' precipitation, which would enable the optimisation of cooling steps after solutioning, are lacking. Several authors have attempted to tackle this issue and have reported good agreement with experimental results [260–262]. Nonetheless, it remains questionable to what extent these models can be generally applied to other alloy compositions and heat treatment conditions. The most accurate tools for general purposes appear to be CALPHAD-based software packages such as PrecipiCalc or TC-PRISMA [263], however, these are still restricted to simple ternary systems like Ni–Al–Cr.

As such, the main potential for controlling the precipitate size lies with controlled ageing, as the coarsening kinetics of γ' have been amply researched. The classical

Lifshitz-Slyozov-Wagner (LSW) theory [264, 265] is commonly used as a basis to describe the increase in mean precipitate radius, $\bar{R}$, after an exposure time, t , as:

$$\begin{aligned}\bar{R}(t)^3 &= \bar{R}(0)^3 + kt \\ k &= \frac{A(\phi_p)D_{\text{eff}}C_e\sigma_{\text{int}}\Omega^2}{RT}\end{aligned}\quad (2.2)$$

The rate of coarsening is described by the parameter k , which depends on the effective diffusion coefficient, D_{eff} , the matrix concentration of the constitutive particle element, C_e , the interfacial energy between matrix and particles, σ_{int} , and the molar volume of the precipitate, Ω . $A(\phi_p)$ is a dimensionless proportionality factor and takes a constant value of 64/9 for cuboidal particles in the classical LSW theory.

However, as the LSW theory makes several assumptions which do not readily apply to NBSA, such as spherical particles with a small volume fraction, constant interface mobility, and negligible processes of nucleation and/or aggregation, some authors have proposed different values for $A(\phi_p)$, which take into account the γ' volume fraction, ϕ_p , and particle size distributions. The work of Ardell et al. [266–268] on a modified LSW theory, denoted simply as MLSW, paved the way for many other approaches [269–274]. Proposed $A(\phi_p)$ values range between about 1.5 and 20 for modern NBSA exposed at standard operating temperatures, thus showing strong discrepancies between different theories. Two comprehensive review papers by Baldan [275, 276], which include in-depth analyses of the influences of different parameters in Equation (2.2), reveal that any given theory is more or less applicable depending on the considered alloy system and on the exposure conditions, and that no general solution is in sight. This has provided an incentive for the development of CALPHAD-based approaches for coarsening predictions [96]. Unfortunately, like the CALPHAD tools for precipitation kinetics, these remain in an early development stage.

In the context of long-term IGT applications, it must be highlighted that the importance of a carefully designed microstructure after heat treatment decreases with exposure time during service [239]. As illustrated in Figure 2.15 for the polycrystalline superalloy IN-738LC, curves for the mean particle diameter, denoted

here as d_T , converge after long exposure times regardless of the initial γ' size, d_{T_0} . The speed at which this occurs is controlled by the coarsening rate and by the temperature. The slope of the linear asymptote, denoted here as k_1 , is obtained as $k_1 = 2k^{1/3}$. The coarsening rate parameter k can be determined experimentally through microscopy studies of d_T in relation to the exposure time, t [239].

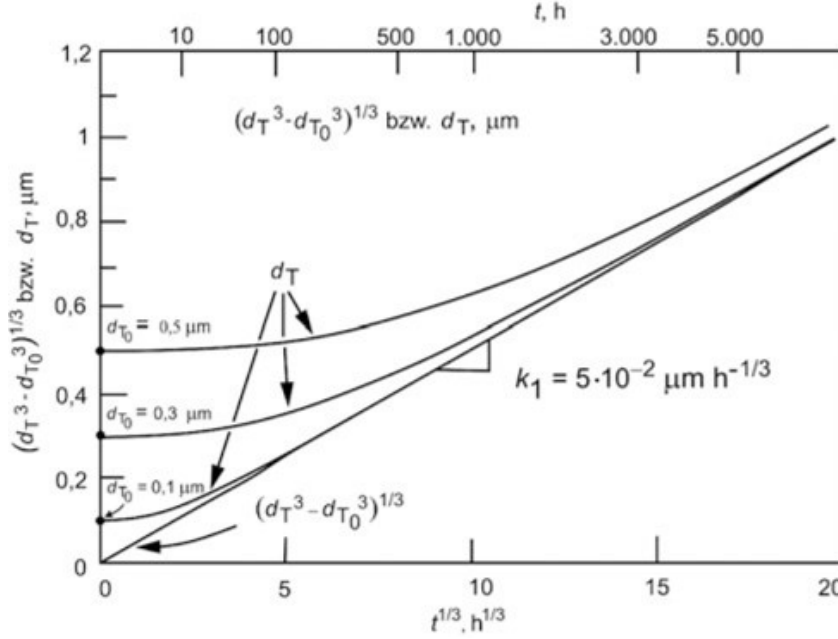


Figure 2.15: Changes in mean particle diameter for the polycrystalline superalloy IN-738LC, based on the LSW theory and starting from different initial diameters [239].

Carbide and boride phases: These GB phases play a particularly important role in polycrystalline superalloys due to their capability of improving high-temperature rupture strength and ductility, if present in the right type and morphology and with the right distribution [277–279]. Alloy design approaches to achieve this goal and general aspects of GB strengthening in conventional superalloys are discussed in detail in references [238] and [239].

By adjusting alloying additions and processing conditions, GB can be purposely engineered, as illustrated in Figure 2.16 for the case of changes in carbide morphology. Primary MC carbides, where M usually denotes tantalum, titanium, hafnium, or tungsten, form during cooling as discrete blocky or script-like particles and are distributed throughout the alloy [117]. Their benefit is indirect, by providing a

source of carbon for the precipitation of secondary carbides. These secondary $M_{23}C_6$ or M_6C phases form mainly at GB as irregular, discontinuous particles due to the breakdown of MC carbides through reactions such as:



$M_{23}C_6$ carbides are mostly chromium-, tungsten-, and molybdenum-rich. Due to their location, they play a key role in increasing GB strength along with the large, blocky γ' particles formed in the reaction above [280–283]. If carbon contents are not properly controlled, continuous carbide films can form and provide easy paths for crack propagation, as illustrated on the left side of Figure 2.16.

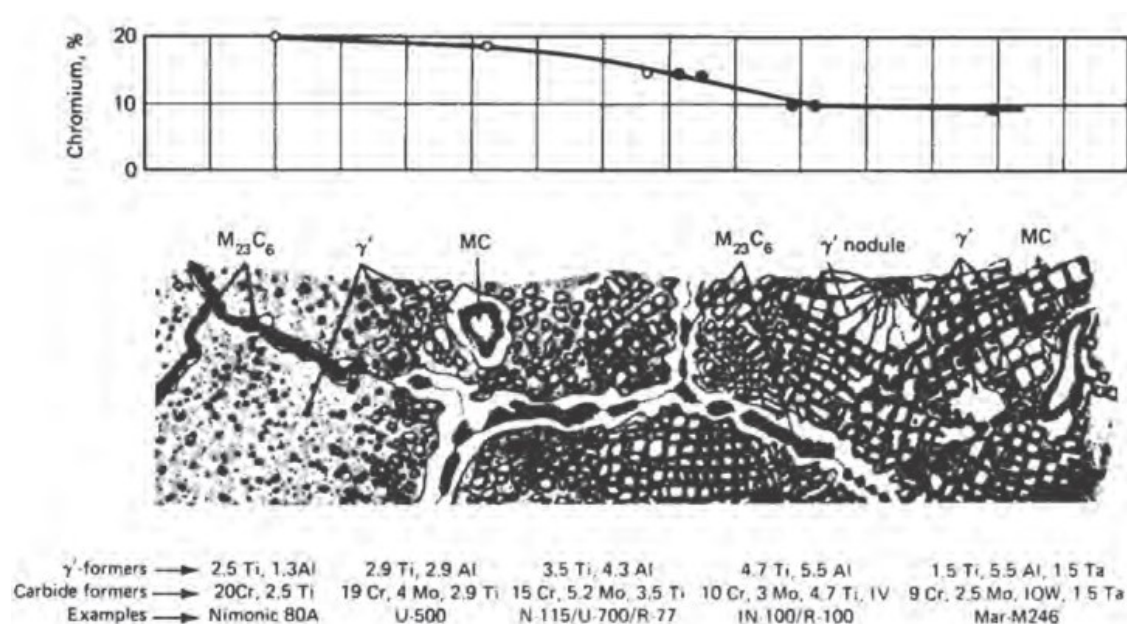


Figure 2.16: Dependence of γ' and GB carbide morphology on the levels of γ' -formers and chromium [117]. The microstructure sketch is an excerpt from Figure 2.8, while the graph above it and the composition examples below were supplemented in reference [120].

Borides, with typical formulas M_3B_2 or M_5B_3 , where M is commonly molybdenum, chromium, titanium, or nickel, can act as a supply of boron at GB and inhibit GB sliding by improving cohesion [284, 285]. Recent studies have also associated borides with increased GB serrations and a retarded formation of voids and cavities [286, 287].

Although GBs are in theory absent in single-crystal superalloys, this is not fully the case in practice. As such, doping single-crystals with small amounts of carbon and boron has been shown to render the material more tolerant to problems related to low-angle sub-grain boundaries which form during casting [214, 288–290].

TCP phases: Deleterious intermetallic TCP phases may precipitate during long-term high-temperature exposures of superalloys containing excessive quantities of chromium, molybdenum, tungsten, and rhenium [151, 291, 292]. Their general structure has been characterised as layers of close-packed atoms forming interwoven nets [238]. Common TCP phases in superalloys include σ , μ , P, and R, with general chemical formulas of the type $(\text{Cr},\text{Mo})_x(\text{Ni},\text{Co})_y$, where x and y can vary between 1 and 7 [238]. The general appearance of selected TCP phases can be observed in the schematic drawing of Figure 2.8 and more clearly in the SEM micrographs of Figure 2.17.

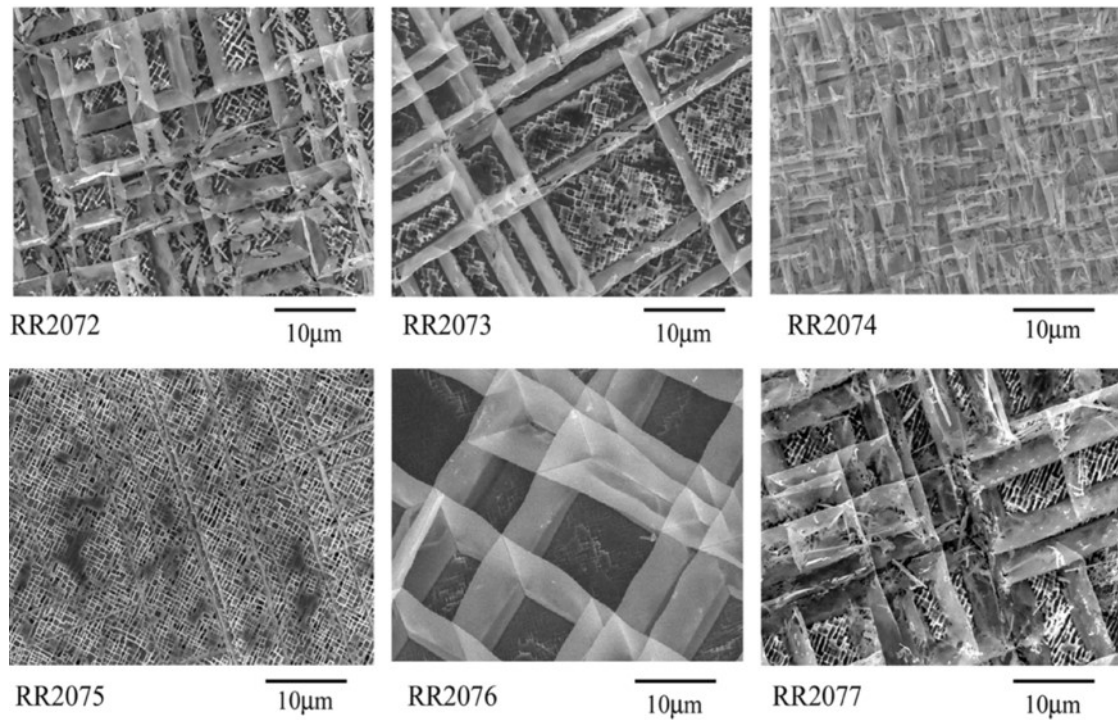


Figure 2.17: SEM micrographs revealing a range of TCP phases which precipitated in second-generation single-crystal superalloys after annealing at 950 °C for 2000 h [151]. The γ matrix and γ' precipitates were electrolytically etched to show the deleterious phases more clearly.

Their presence affects superalloy performance in two ways. First, their hard and brittle nature and their plate-like morphology make them excellent sources for crack initiation and propagation [214, 293–295]. This effect is found to be strongest for the σ phase [117]. Second, and of more concern for high-temperature properties, the formation of TCP plates leads to a depletion of solid solution strengthening elements from the γ matrix, thus indirectly decreasing the resistance to creep deformation mechanisms [280, 296–300]. Although this depletion has been shown to critically decrease creep strength, no attempts have been made to examine and quantify the rate at which this occurs in superalloys [292], although this effect has been studied in highly-alloyed bearing steels [301]. Alloy design tools which predict the formation of TCP phases are mainly based on electron band theory methods like PHACOMP and New PHACOMP, as discussed in Chapter 1. Recent work [106, 302–304] has proven that these techniques have many shortcomings and reiterated the aforementioned viewpoint that accurate CALPHAD-based calculations are required.

2.1.3.2 Strengthening Mechanisms in Single-Crystal NBSA

Strengthening in single-crystal NBSA is primarily a combination of solid solution strengthening imparted by solute alloying elements and of precipitation hardening from γ' particles [305]. The presence of forest hardening due to dislocation interactions is acknowledged, but not further considered due to its negligible impact [236]. In general, strengthening contributions are regarded as independent and additive for the sake of simplicity [306]. However, some concerns and alternative ways of summation have been put forward [307, 308]. Furthermore, each strengthening mechanism arises from an interaction of different, more fundamental physical effects, thus increasing the complexity of a general description. Main contributions are reviewed in the following, while maintaining an independent treatment.

Solute elements have been reported to influence creep strength by affecting a range of alloy properties including lattice mismatch, elastic modulus, stacking fault energy (SFE), and effective diffusivity [234, 309]. Figure 2.18 presents a comparison of potent solid solution strengthening elements — tantalum, tungsten, and rhenium —

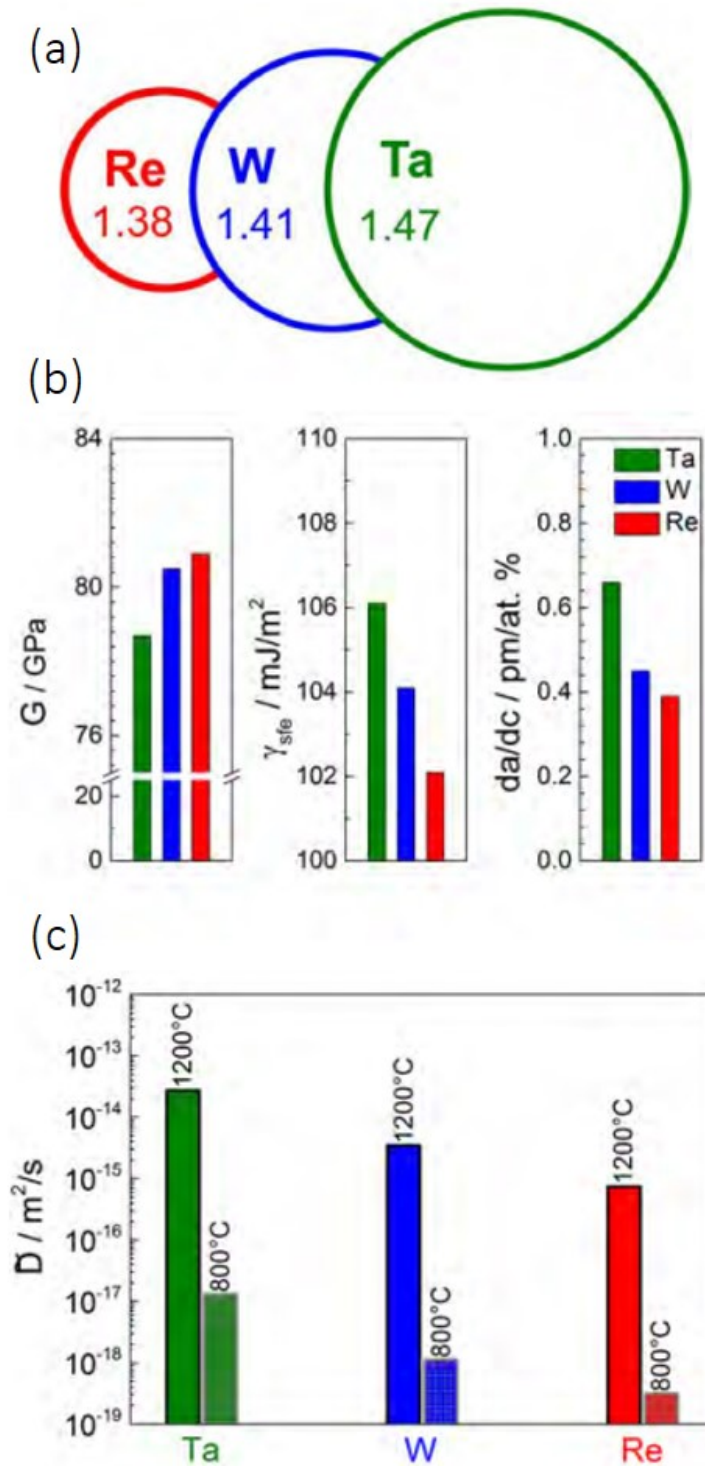


Figure 2.18: Comparison of potent solid solution strengthening elements in NBSA with regard to (a) their Goldschmidt atomic radii in Å, (b) their effects on shear modulus, stacking fault energy, and the change in γ phase lattice parameter at room temperature, and (c) their effects on interdiffusion coefficients at 800 and 1200 °C [309]. Results have been compiled from references [242, 310–314].

with regard to their atomic radii and their impact on shear modulus, SFE, γ lattice parameter at room temperature, and interdiffusion coefficients at high temperatures [309]. Values were obtained for Ni-2at.%X solid solutions (X=Ta,W,Re) and reveal that strengthening potency increases in this order. In general, increased creep strength can be expected for lower values of SFE and of effective diffusivity [12]. Fundamental model equations for single-phase solid solutions combining these effects have been reviewed in reference [234] and are commonly expressed in terms of a steady-state creep rate as:

$$\dot{\epsilon}_s = AD_{\text{eff}} \left(\frac{\gamma_{\text{SFE}}}{Gb} \right)^m \left(\frac{\sigma}{E} \right)^n \exp \left(-\frac{Q}{RT} \right) \quad (2.4)$$

Here, A is a constant, γ_{SFE} is the SFE of the γ matrix, and Q represents the activation energy for self-diffusion. Values cited for m and for n vary within the literature [12, 234, 236, 315] and usually lie in the range of 3 to 5 for m and of 3 to 7 for n . Divergence from these values is observed in particle-strengthened engineering materials. In the context of creep modelling, this is usually accounted for through the introduction of additional terms in Equation (2.4), such as an internal back-stress [316, 317]. The effective diffusion coefficient, D_{eff} , can be expressed for binary Ni-X alloys in relation to the diffusion coefficients and atomic fractions of Ni and X as:

$$D_{\text{eff}} = \frac{D_{\text{Ni}}D_{\text{X}}}{x_{\text{Ni}}D_{\text{X}} + x_{\text{X}}D_{\text{Ni}}} \quad (2.5)$$

A number of studies on the potency of individual additions have been reviewed in references [12, 234, 236] and have been found to make qualitatively sound, but quantitatively somewhat different predictions. Recent work by Fleischmann et al. on molybdenum, tungsten, and rhenium [315, 318] concluded that taking into account usual partitioning coefficients, it would be necessary to add 2.2 wt.% molybdenum or 4.3 wt.% tungsten in order to replace 1 wt.% rhenium. Previous experiments by Wöllmer et al. [319] found that the optimal ratio of tungsten and rhenium additions depends on creep deformation conditions and highlighted the importance of also considering the detrimental increases in density caused by these heavy solutes. Figure 2.19(a&b) illustrates how creep strengthening scales with solute

concentration and how this can be related to changes in SFE, effective diffusivity, and elastic modulus. The effects of varying lattice parameters cannot be readily extended from model solid solutions to two-phase alloys. Furthermore, the influence of misfit values on effective stresses within the γ matrix during creep has proven difficult to express [306, 320–323]. This issue is further discussed in the context of creep deformation modelling in Chapter 5.

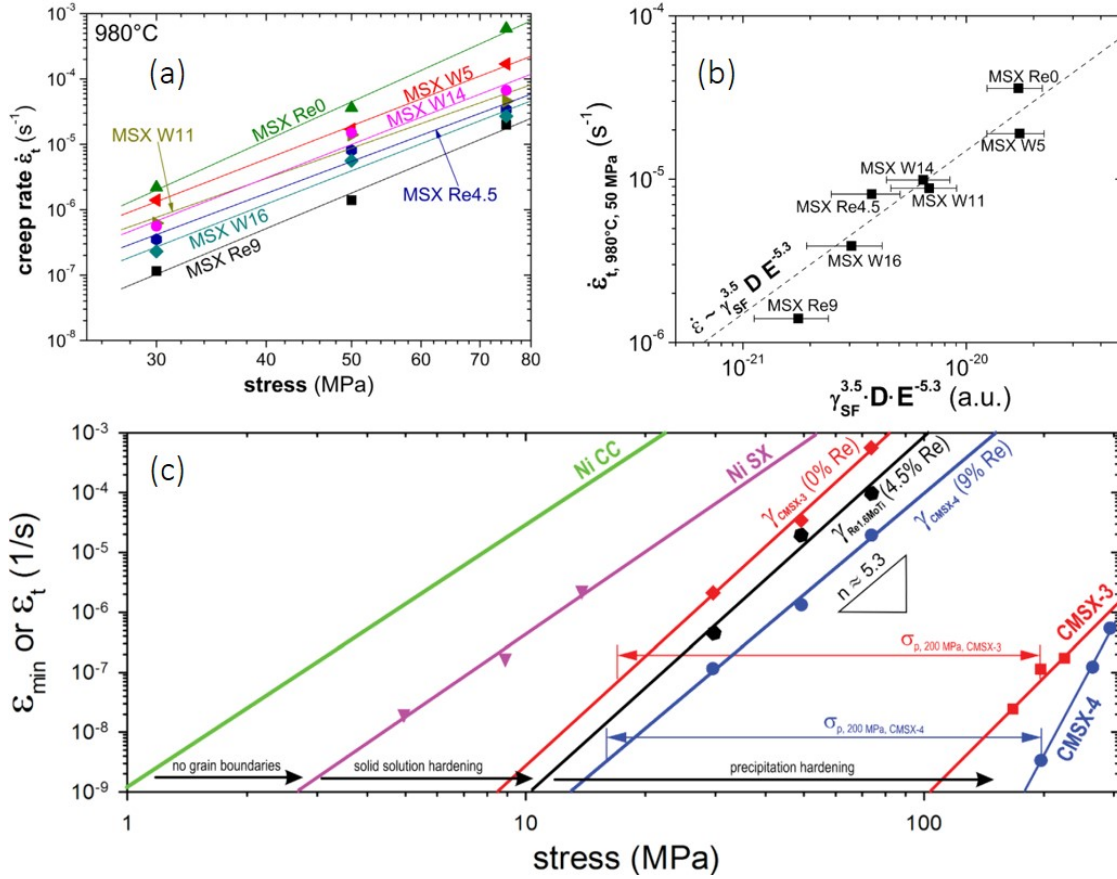


Figure 2.19: (a) Norton plot for a number of tungsten- and rhenium-containing solid solution single-crystal alloys, showing measured transition creep rates between primary and secondary creep, $\dot{\epsilon}_t$, as a measure of creep strength [315]. Solute concentrations are given in at.% behind the particular element, e.g. Re9 for a Ni–9at.%Re alloy [315]. (b) Measured transition creep rates at 980 °C and 50 MPa as a function of $\gamma_{SFE}^{3.5} D_{eff} E^{-5.3}$ [315]. (c) Norton plot of minimum creep rates or transition creep rates for conventionally cast polycrystalline pure Ni (Ni CC), single-crystal pure Ni (Ni SX), single-crystal matrix alloys, and commercial single-crystal superalloys [112].

Precipitation hardening due to γ' has an even more pronounced effect on the creep resistance of superalloys [237], as seen in Figure 2.19(c). The main influencing factors are the precipitate volume fraction and the size distribution, as well as

the magnitude of solid solution strengthening the particles themselves observe. An overview of the main precipitate strengthening mechanisms [324] is shown in Figure 2.20. Theoretical and modelling aspects of these three contributions are reviewed in references [232, 234, 237].

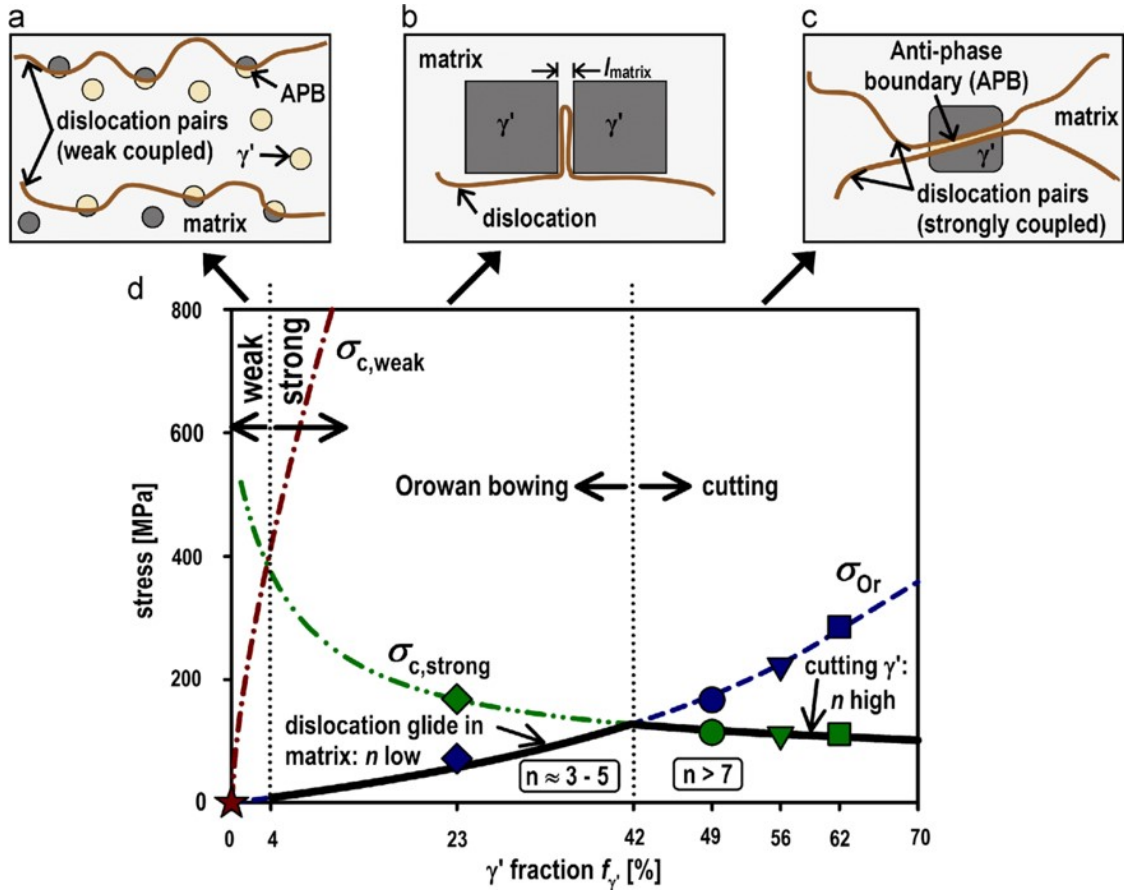


Figure 2.20: Overview of the main strengthening effects arising from precipitates: (a) weakly coupled (brown) and (c) strongly coupled (green) dislocation pairs shearing γ' particles and (b) dislocation loops bowing around particles *via* the Orowan mechanism (blue), adapted from reference [324]. The linear strengthening addition of these effects is shown in (d) as a function of γ' volume fraction, with dotted lines denoting individual regimes. Quantitative values were obtained for a particular alloy studied in reference [324], however, the qualitative trends hold true for NBSA in general.

The regimes in which individual mechanisms dominate depend on the γ' volume fraction, as seen in Figure 2.20, but in a similar manner also on γ' size. For small volume fractions and when the spacing of two paired dislocations is large in comparison to particle size, the case of weakly coupled dislocation shearing is observed. Conversely, when particles are larger and comparable in size to the

spacing of a dislocation pair, strongly coupled shearing occurs. A derivation of the critical resolved shear stresses for both cases, as carried out in reference [237], leads to the expressions:

$$\begin{aligned}\tau_{c,weak} &= \frac{\gamma_{APB}}{2b} \left(\left(\frac{12\gamma_{APB}\phi_p r}{\pi G b^2} \right)^{1/2} - \phi_p \right) \\ \tau_{c,strong} &= \sqrt{\frac{3}{2}} \frac{Gb}{r} \phi_p^{1/2} \frac{\lambda_p}{\pi^{3/2}} \left(\frac{2\pi\gamma_{APB}r}{\lambda_p G b^2} - 1 \right)^{1/2}\end{aligned}\tag{2.6}$$

Here, γ_{APB} is the energy required to form an anti-phase boundary (APB), b is the length of the Burgers vector, and G is the shear modulus. ϕ_p , λ_p , and r represent the γ' volume fraction, particle spacing, and particle radius. Studies have confirmed that maximum strengthening occurs for a certain critical particle size, which delimits the transition between mechanisms [325, 326]. However, in an intermediate range, bypass of precipitates is expected. The necessary stress for this is commonly expressed following the Orowan bowing model as:

$$\tau_{Or} = \sqrt{\frac{2}{3}} \frac{Gb}{\lambda_p}\tag{2.7}$$

It should be again mentioned that NBSA exhibit an anomalous yielding effect, with alloy strength increasing up to about 800 °C before falling steeply, the details of which are discussed in reference [237]. Besides compositional effects leading to differences between individual alloys, the magnitude of this anomaly depends on the γ' volume fraction, as shown by Beardmore et al. [327] and illustrated in Figure 2.21.

Early experiments on conventionally cast alloys situated along γ - γ' tie lines further revealed that both the minimum creep rate and the creep rupture life increase for higher γ' volume fractions, as shown in Figure 2.22. This effect was found to be more pronounced for large grain sizes, as the overall effects of creep cavitation at GB are reduced [328, 329]. For the case of single-crystal superalloys this is further exploited, as GB are completely removed. This then gives rise to unique creep deformation mechanisms in different operating conditions, as discussed in the following.

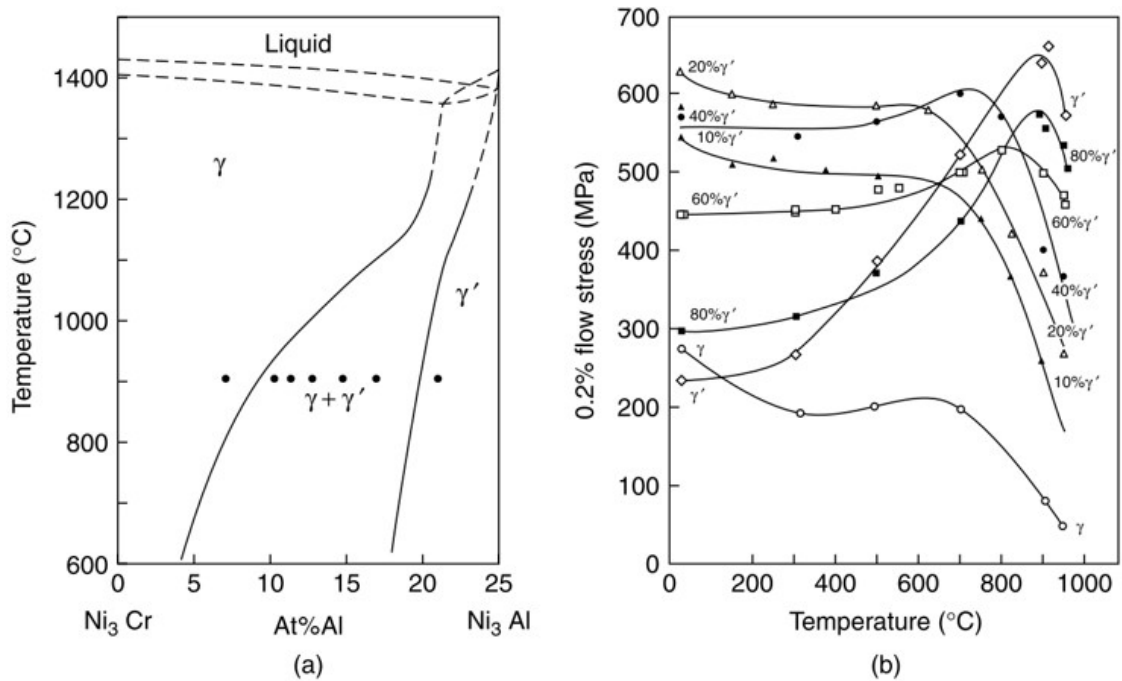


Figure 2.21: (a) Section through the ternary Ni–Al–Cr phase diagram showing examined alloy compositions along the same tie line possessing identical γ and γ' phase compositions. (b) Variation of flow stress with temperature for the alloys in (a) as a function of the γ' volume fraction and temperature [327].

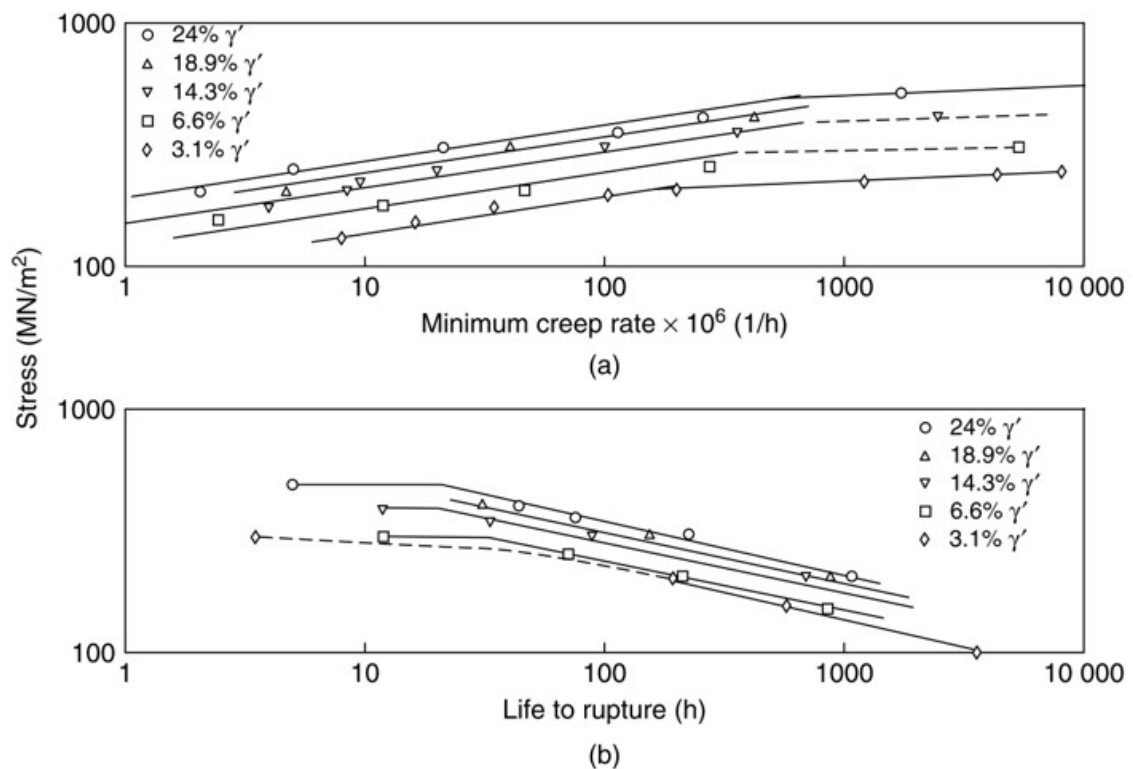


Figure 2.22: Changes in the (a) minimum creep rate and (b) life to rupture for coarse grained alloys containing different γ' volume fractions at 800 °C [328].

2.2 Creep Deformation of Single-Crystal Superalloys

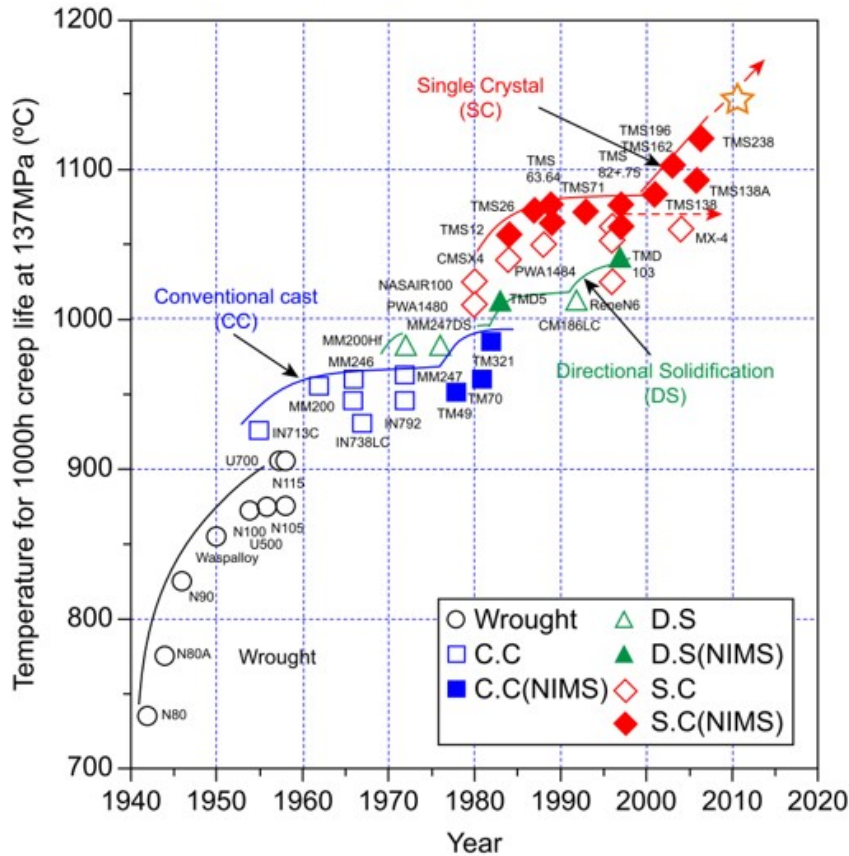


Figure 2.23: Evolution of superalloy creep resistance, expressed as the maximum operating temperature under an applied stress of 137 MPa for a creep rupture life of 1000 h [330]. The current goal of 1150 °C [331] is marked by a star. Different symbol shapes denote major changes in processing techniques; within each group it can be observed that effects of alloying diminish over time and that innovations in processing are required for further major advances. Image courtesy of the National Institute for Materials Science (NIMS) (Tsukuba, Japan).

Time-dependent inelastic deformation occurring at levels of stress far below those required for yielding, commonly known as creep, is one of the main limiting factors for the service life of IGT blades. In order to assess how developments in alloying and processing enabled the advances shown in Figure 2.23, it is first necessary to discuss common deformation mechanisms for single-crystal superalloys, as well as empirical and theoretical descriptions of these phenomena. An extension to conventionally cast polycrystalline alloys is difficult considering the key role

played by GB deformation mechanisms and by GB engineering [332–334] and is not within the scope of this work.

2.2.1 Creep Deformation Mechanisms

Dominating mechanisms for creep have been observed to be very sensitive to operating conditions in terms of temperature and applied stress. Figure 2.24 shows the three commonly identified regimes of primary, tertiary, and rafting creep deformation for the case of alloy CMSX-4 [335–338]. Other single-crystal superalloys exhibit similar behaviour, albeit at slightly different absolute values of temperature and stress. ‘Primary’ and ‘tertiary’ creep owe their names to the fact that creep strain rate vs. creep strain curves resemble those obtained for pure metals in these regimes. The term ‘rafting’ is associated with the characteristic precipitate shape after directional coarsening [12]. An alternative notation, also used within the present work, is based on the general temperature ranges, yielding low-, intermediate-, and high-temperature regimes [236]. Exemplary plots of data obtained from creep tests in each of the three regions are presented in Figure 2.25. Since IGT turbine blades are largely operating under conditions associated with intermediate-temperature creep, this regime will be discussed in more detail, whilst the other two are only briefly reviewed.

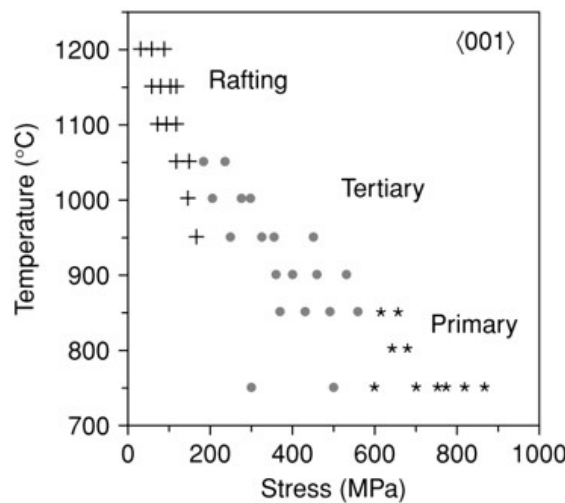


Figure 2.24: Influence of temperature and applied stress on the creep deformation regimes observed for single-crystal CMSX-4 specimens loaded along their $\langle 001 \rangle$ crystal orientation [12].

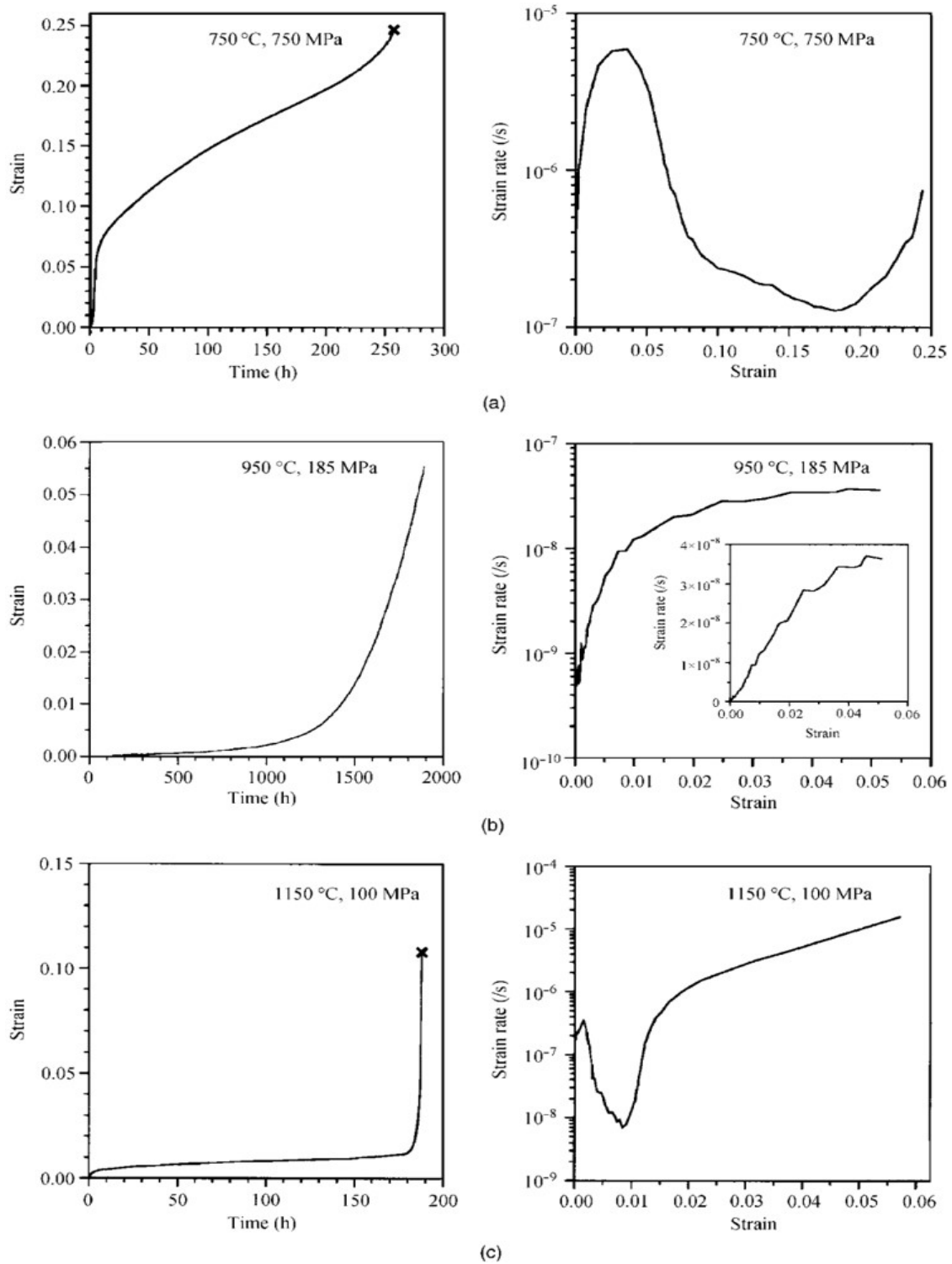


Figure 2.25: Strain vs. time and strain rate vs. strain plots for creep tests on CMSX-4 specimens in $\langle 001 \rangle$ orientation. Tests were carried out to demonstrate the characteristics of (a) low-temperature creep at 750 °C and 750 MPa, (b) intermediate-temperature creep at 950 °C and 185 MPa, and (c) high-temperature creep at 1150 °C and 100 MPa [335, 337]. The inset in (b) shows strain rate vs. strain plotted on double-linear axes.

2.2.1.1 Low-Temperature Creep

At low temperatures, in the range of $T/T_m \leq 0.6$, and under high applied stresses, shearing of the γ' precipitates can occur by dislocation ribbons of overall Burgers vector $a\langle 112 \rangle$ [339], as shown in Figures 2.26 and 2.27. This leads to significant levels of primary creep, followed by a period of secondary creep at a much slower rate, which however depends directly on the primary creep rate [340]. Further deformation occurs linearly in the secondary stage until failure, as seen in Figure 2.25(a). The key characteristic of low-temperature creep is the heterogeneity of slip, which in cylindrical specimens results in an elliptical shape after testing [341]. This realisation of severe non-uniform deformation led Kear and co-workers [342–345] to suggest a new model for $\langle 11\bar{2} \rangle \{111\}$ slip, which was also supported by TEM studies.

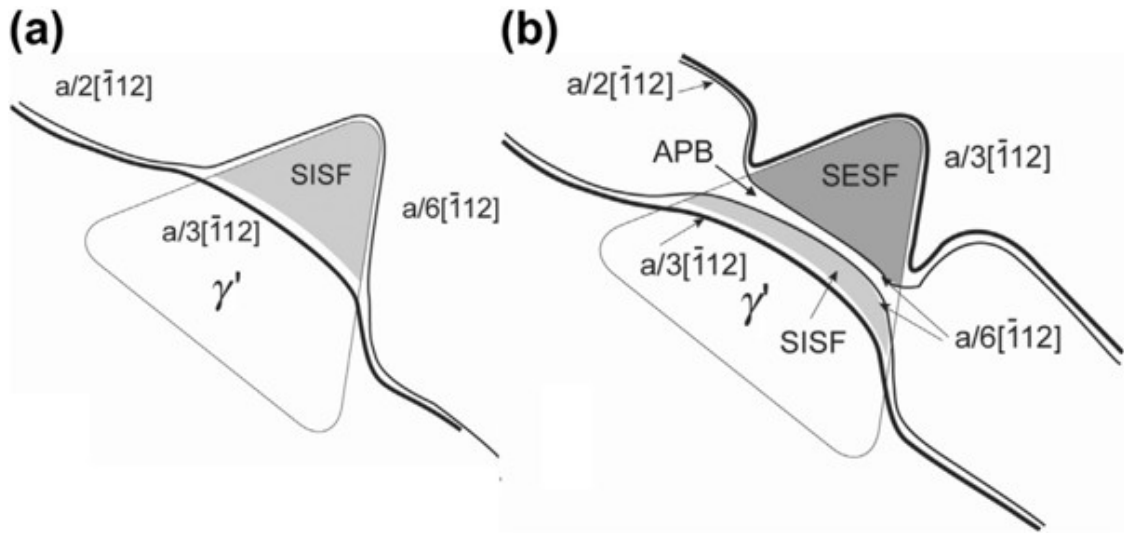


Figure 2.26: Schematic showing a $a\langle 112 \rangle$ dislocation ribbon shearing a γ' particle during primary creep [339]. The ribbons are composed of four distinct dislocations separated by faults in the following order: superlattice intrinsic stacking fault (SISF), anti-phase boundary (APB), superlattice extrinsic stacking fault (SESF). The complex dislocation mechanisms involved are discussed in detail in references [12] and [237].

The complex mechanisms involved in primary creep have been reviewed recently by Rae et al. [339, 340] and have been shown to depend greatly on single-crystal orientation [296, 346]. Due to changes in microstructure and in the SFE that needs to be overcome by dislocations shearing into precipitates, alloying elements also have a profound effect, with cobalt, rhenium, and molybdenum reported to

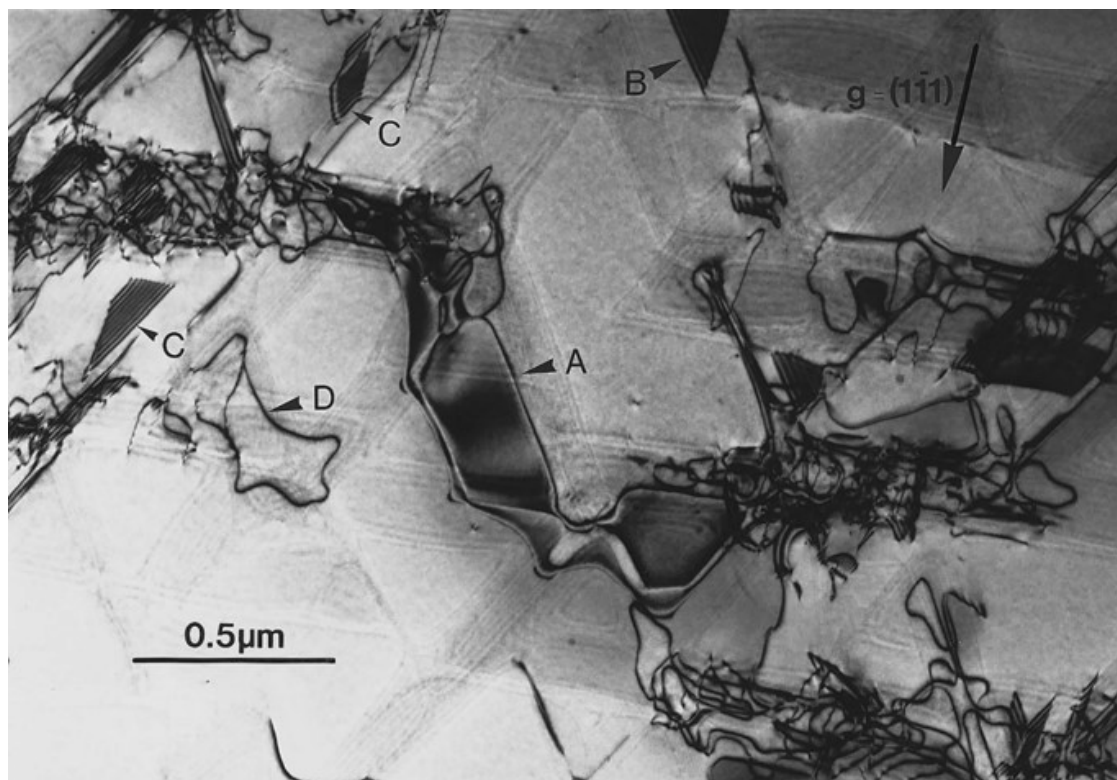


Figure 2.27: TEM micrograph of CMSX-4 crept in the primary regime at 750 °C and 750 MPa to 1.4% strain in 2 hours [335]. Foil normal is $\{111\}$.

promote primary creep, while tantalum inhibits it [347–351]. Some authors have also associated changes in primary creep resistance with γ' precipitate size and volume fraction and these relations have in turn been shown to also depend on crystal orientation [346, 352, 353]. However, the effects of alloying on microstructure and on primary creep deformation prove difficult to uncouple [340].

Interesting recent results concern a ‘double minimum creep’ behaviour, wherein plots of strain rate vs. strain analogue to that of Figure 2.25(a) exhibit two minima separated by an intermediate maximum [354–356]. The initial minimum has been associated with an exhaustion mechanism, in which the high applied stresses pull misfit dislocations away from the γ/γ' interfaces, and with a run-and-stop mechanism, in which favourably oriented dislocation segments are rapidly immobilised by precipitates [355]. Following an increase of the overall dislocation density in the matrix, stacking fault shearing will become operational, as discussed above. Finally, the second minimum in creep rate is governed by strain hardening effects within

both the γ channels and the γ' precipitates, along with atomic re-ordering processes which stabilise the interfacial dislocation networks [355].

2.2.1.2 Intermediate-Temperature Creep

The creep regime in the range of $T/T_m \approx 0.6$ – 0.7 and at intermediate stress levels is characterised by deformation confined to the γ matrix to a large degree and by a creep strain rate which increases steadily with creep strain [12, 236, 357], as observed in Figure 2.25(b). As such, a steady-state creep regime often observed in engineering alloys is absent. Since intermediate levels of applied stress and temperature are most similar to actual IGT service, this regime is of most interest and concern for IGT alloy development.

Prior to the onset of creep deformation, a short incubation period is normally observed, during which dislocations of $a/2\langle 1\bar{1}0 \rangle \{111\}$ type are generated. These dislocations then migrate further into the γ channels, which had initially been dislocation-free [358, 359]. This phenomenon was shown clearly in early TEM studies by Pollock and Argon [306, 360] and has been confirmed by recent ECCI observations [361].

Modern commercial superalloys possess a negative lattice misfit at high temperatures. The superposition of the resulting misfit stress with an applied tensile creep load gives rise to a higher resolved shear stress perpendicular to loading and leads to a preferential expansion of dislocation loops in ‘horizontal’ matrix channels [362, 363]. As illustrated in Figure 2.28, leading segments become arrested at γ/γ' interfaces and have to overcome these obstacles *via* coupled climb/glide processes [364]. Within this scope, a combination of adequate solid solution and precipitation strengthening is imperative for increased creep resistance [364–367].

The next stage of intermediate-temperature creep occurs when propagating dislocation loops begin to interact with one another, giving rise to three-dimensional dislocation networks at γ/γ' interfaces, as shown schematically in Figure 2.30 [368]. Aspects concerning the formation, evolution, and general role of these networks remain an important topic of research and debate [368–373]. However, it is generally

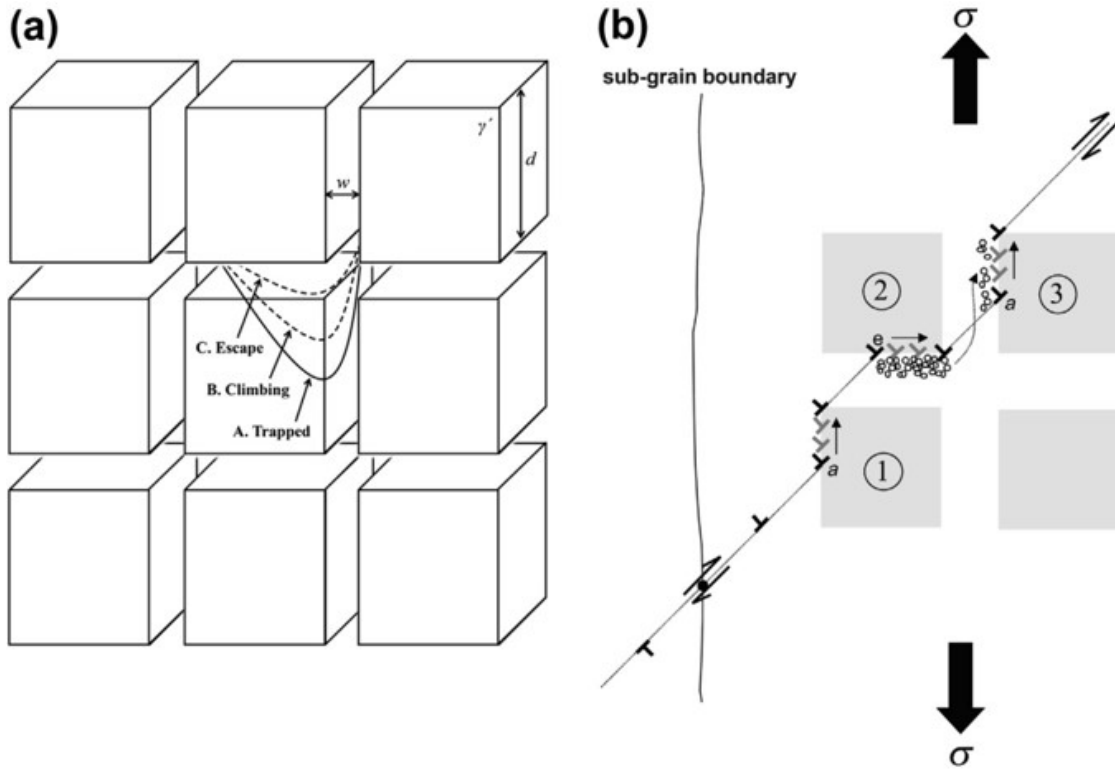


Figure 2.28: (a) Dislocation configurations during climb-assisted glide of dislocations [364]. Dislocations are first held up at γ' precipitates in A, begin climbing along the γ/γ' interfaces in B, and can eventually escape and glide through γ matrix channels in C before the cycle starts again. (b) Schematic illustration of tertiary creep deformation, with dislocations generated at sub-grain boundaries overcoming precipitates *via* a series of combined climb/glide events associated with the abSORption and eMISSION of vacancies.

accepted that they have an important function in determining high-temperature properties [373] and that this is associated with strain hardening and recovery softening processes as creep damage amasses [236, 374]. This continuous, monotonic accumulation of strain at an increasing rate is facilitated by the presence of large fractions of γ' particles, which cannot be easily circumvented through Orowan looping and which are resistant to dislocation shearing at intermediate levels of applied stress. Particle shearing will eventually occur given enough time and the complex mechanisms and interactions between dislocation networks and precipitates that lead to it have been discussed in the literature [306, 323, 360, 363, 368].

Link and Epishin [375, 376] developed a novel procedure for observing the grooves and ledges left on γ' particles by impinging dislocations. Subsequent studies applied this method to show conclusively that the intricate interactions between

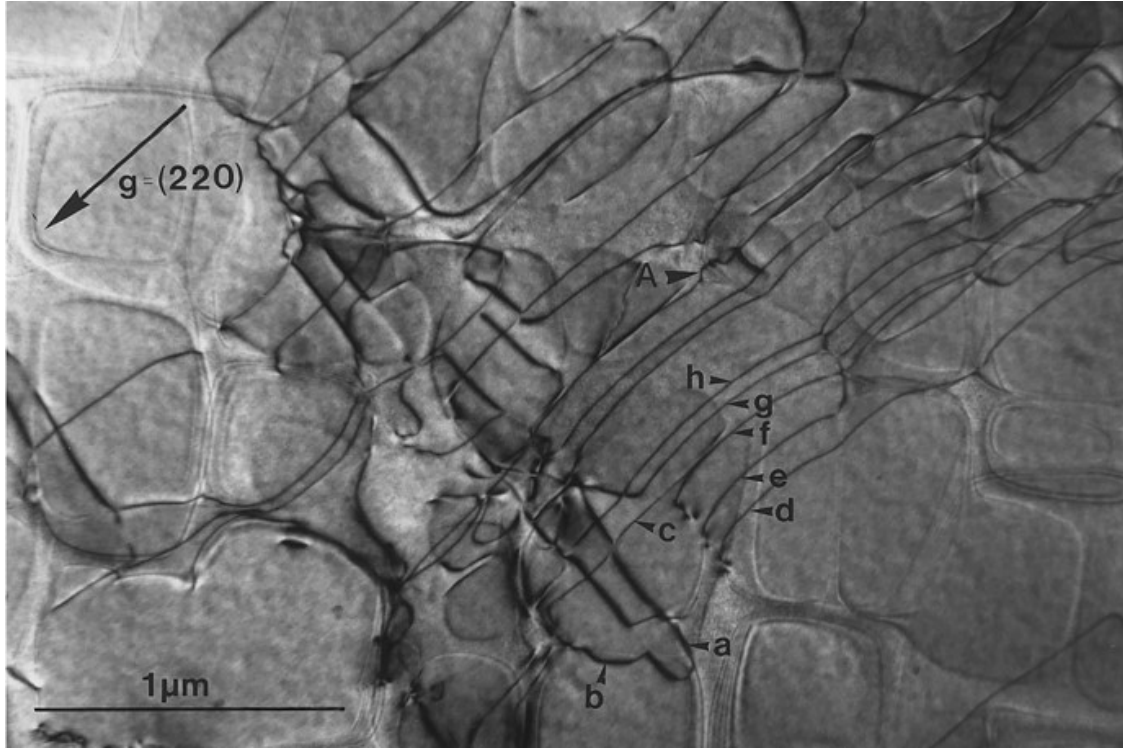


Figure 2.29: TEM micrograph of CMSX-4 crept in the tertiary regime at 950 °C and 185 MPa to 0.07% strain in 280 hours [335]. Foil normal is {100}.

network dislocations and precipitates — involving pinning, cutting, or knitting out of misfit dislocations — cannot be fully captured by idealised deformation models [355, 377, 378]. As such, these recent results shed some doubt on previous attempts to describe strengthening during intermediate-temperature creep. These generally assumed that creep resistance arises from a simple summation of Orowan, solid solution, and dislocation interaction strengthening, in further combination with constraints set by the nearly coherent γ/γ' interfaces which lead to a build-up of pressure gradients [236, 379].

2.2.1.3 High-Temperature Creep

The final, high-temperature regime at $T/T_m \geq 0.7$ can be regarded as a special form of intermediate-temperature creep, in which deformation is accompanied by significant changes in precipitate morphology dictated by the effective stresses within the matrix channels [363, 380]. Inhomogeneous creep again dominates at an early stage due to limited dislocation sources, however, microstructural degradation

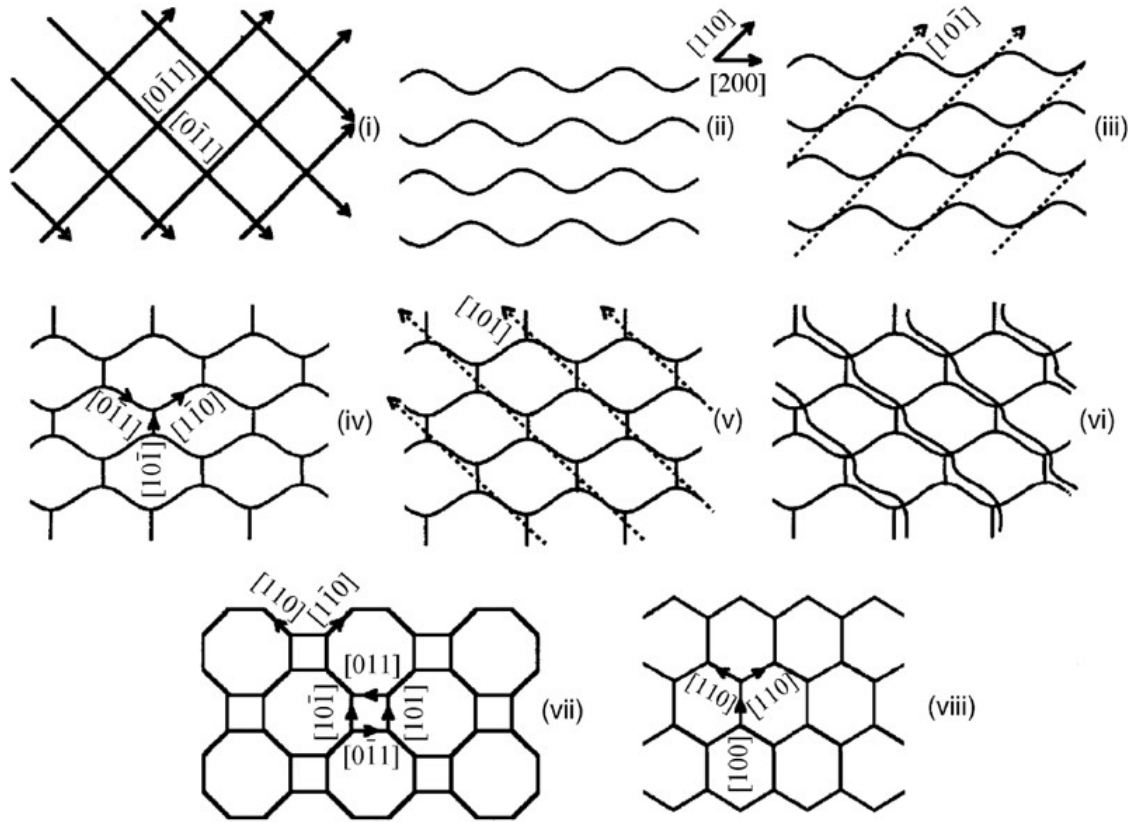


Figure 2.30: Schematic representation of possible dislocation reactions during high-temperature creep which lead to the formation of nets accommodating misfit on (001) γ/γ' interfaces [368].

occurs much faster than during tertiary creep owing to increased diffusion [12, 236]. The two prominent effects influencing microstructure are the rapid formation of aforementioned interfacial dislocation networks, which in this case reach an equilibrium state [371, 381–383], and the coalescence of γ' particles by a process of directional coarsening, commonly denoted as rafting [384–387]. Kinematic details of network formation, general deformation mechanisms within this regime, and their influence on material properties have been reviewed extensively in reference [236].

Equilibrium configurations are reached after dislocations have rearranged themselves through climb processes, which occur much faster at high temperatures. Based on information obtained from ample TEM studies, Field et al. [368] proposed a range of successive mechanisms giving rise to such configurations, as shown in Figure 2.30. Their main characteristic is that they lead to a loss of the perfect elastic coherency between phases and thus gradually relieve misfit stresses. This is

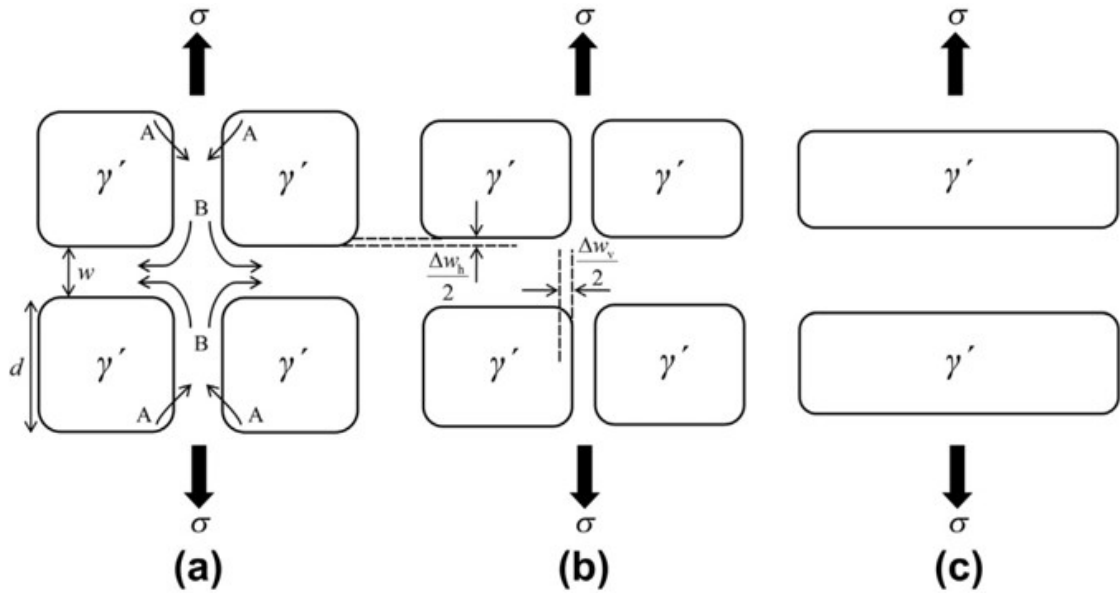


Figure 2.31: Modelling approach which explains directional coarsening based on the concept of a preferential flow of γ - and γ' -forming elements into horizontal and vertical matrix channels, respectively [364]. The initial microstructure in (a) becomes partially-rafted in (b) and finally fully-rafted in (c). The flow of γ' -formers is indicated by arrows labelled A, the flow of γ -formers with B.

significant, since directional coarsening will only take place after misfit relaxation [336, 363, 388, 389]. For the usual case of negative misfit values in NBSA, rafting occurs perpendicular to an applied tensile load or parallel to a compressive load [390, 391]. Analogue to the preferred expansion of dislocation loops in horizontal channels during tertiary tensile creep, the direction of rafting is dictated by the superposition of uniaxial, applied stress and biaxial, misfit stress to a net, effective stress within γ channels [362, 392]. An alternative explanation proposed in reference [12] is shown schematically in Figure 2.31 and invokes vacancy fluxes and opposed atom fluxes between vertical and horizontal channels [364].

It should be noted that after misfit relaxation, rafting will occur even if the external stress has been removed [393]. The effects of rafting on creep resistance and the optimal sign and magnitude of lattice mismatch remain an ongoing subject of debate. Some authors consider rafting to be beneficial, as γ' floats and the dislocation networks around them may both act as barriers to dislocation motion [358, 370, 394–396]. Other studies see it as detrimental, since dislocation networks can act as potent dislocation sources [387, 397].

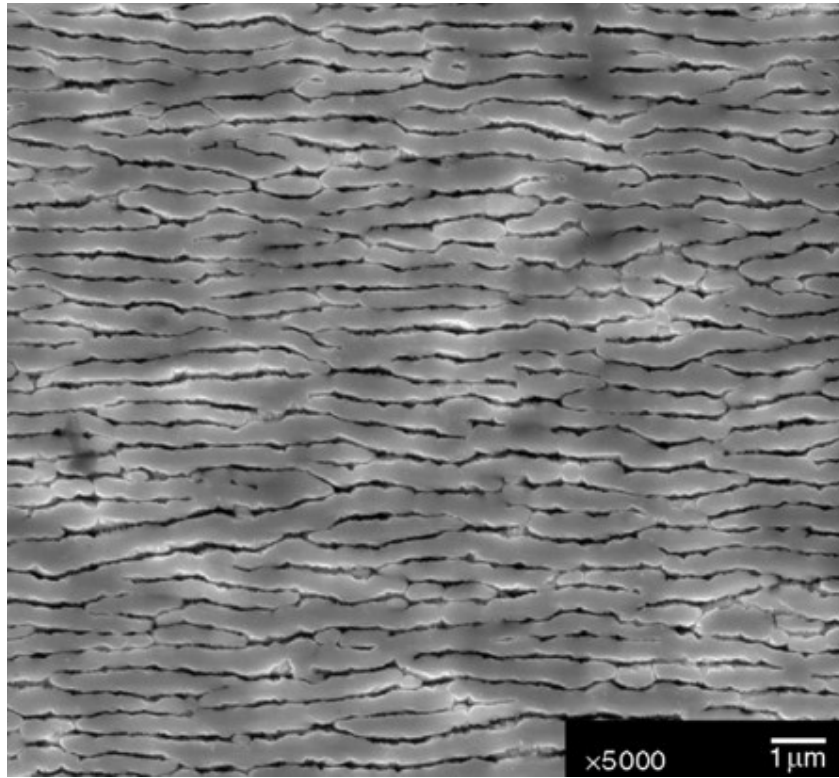


Figure 2.32: SEM micrograph of CMSX-4 crept in the rafting regime at 1150 °C and 100 MPa to 0.39% strain in 10 hours [337]. Tensile loading occurred along the vertical image direction.

Based on several comparative studies [217, 226, 236], it can be ascertained that in a low-stress, high-temperature environment, rafting will remain beneficial as long as the γ' phase is strong enough to resist cutting for prolonged periods of time and as long as TCP phase precipitation is inhibited. These conditions will give rise to the typical creep strain plateau observed in Figure Figure 2.25(c). The kinetics of γ' cutting for the technically important [001] tensile creep condition have been associated with $\langle 200 \rangle$ superdislocations which result from $\langle 110 \rangle$ network dislocations with different Burgers vectors and which move inside the particles by a combined process of glide and climb [398–402]. However, the rate-controlling step for γ' cutting remains unclear and may depend on the formation of an appropriate dislocation pair at the interface, on the transfer of these segments into the precipitate, or on the mobility of the superdislocation inside the γ' phase [401]. Within this scope, the addition of elements such as tantalum, niobium, and molybdenum, which decrease

the magnitude of the lattice misfit and promote the formation of closely spaced interfacial networks is assumed to be beneficial [331, 380, 403].

2.2.2 Extrapolation of Creep Parameters

During the development process of new alloys, it is essential to rapidly assess their feasibility for use in actual components and, therefore, to predict key material properties after service exposures of up to 100,000 hours, or in other terms 11.4 years [239, 404]. Such data is already scarce for existing commercial materials and obtaining values for newly developed ones is impractical. As such, various theoretical and empirical methods have been devised to extrapolate creep design parameters from short-term tests, as illustrated in Figure 2.33. Creep performance is known to depend critically on applied stress and temperature; small changes of these quantities can have a drastic impact on material life. Therefore, the critical attribute of extrapolation methods is to account for the severity of increases in stress and/or temperature during shorter tests from which the raw data is gathered.

Penny and Marriott [404] provide a comprehensive review of the historical development of extrapolation techniques and divide these into three categories: parametric methods, graphical methods, and algebraic methods. Within industry, parametric methods [405–411] are the ones most often used due to their simplicity and widespread application. However, it is precisely because of these associated simplifications that such methods warrant a critical review.

Common to all parametric descriptions is the assumption of a function involving three main variables — rupture time, temperature, and applied stress — which remains constant for any particular material. Most creep parameters express stress as a function of time and temperature, including the Larson-Miller [405], Manson-Haferd [409], Manson-Succop [408], and Orr-Sherby-Dorn [407] parameters. These allow the estimation of a certain critical design stress which can be withstood at a certain temperature up to a certain time without rupture. To relate the three variables, empirical descriptions of the creep curve are used, such as the Monkman-Grant relation [412], the Dobeš-Milička relation [413], the θ -projection model [414,

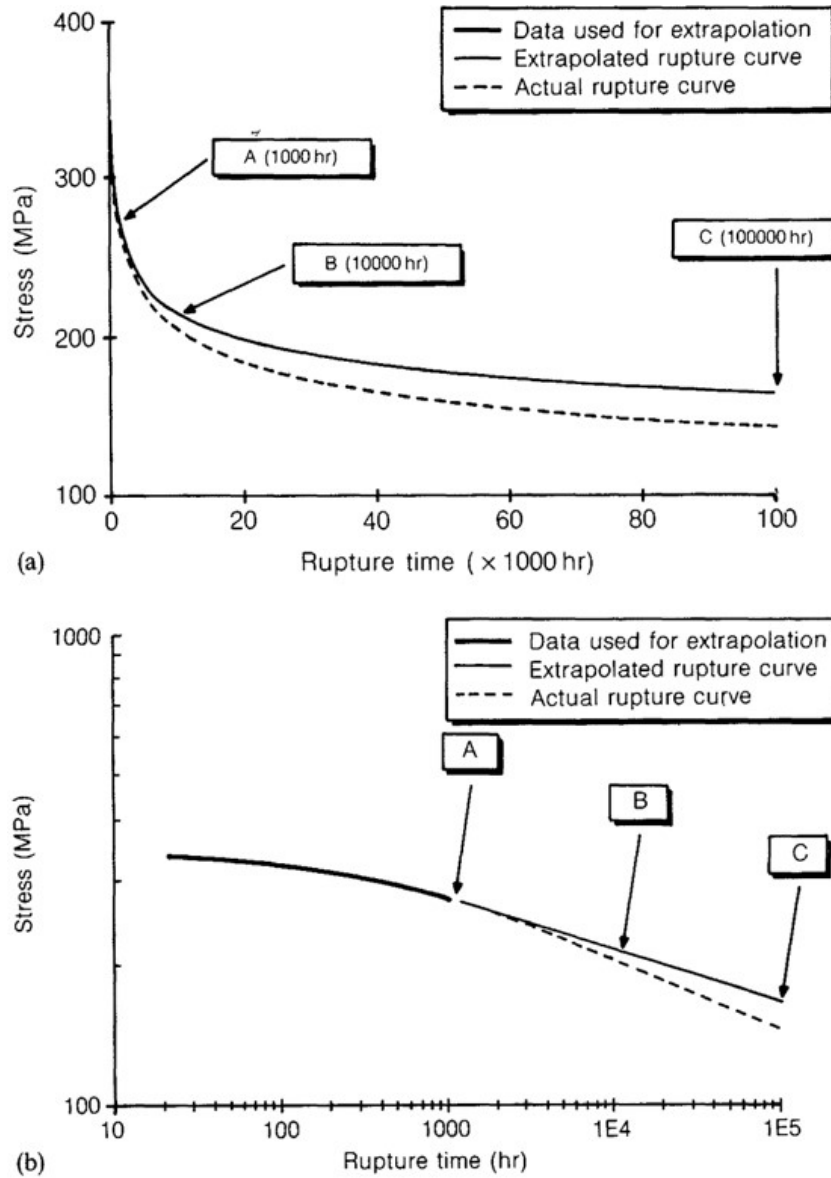


Figure 2.33: Extrapolation of creep rupture data plotted on a (a) double-linear plot and (b) double-logarithmic plot. Discrepancies to actual rupture time values are shown by the dashed line.

415], or the Ω -method [416]. All of these relations use fitting parameters to describe experimental data, which in turn results in certain constant terms within the time-temperature parameters. This can be exemplified for the case of the most widespread approach, proposed by Larson and Miller [405]. These authors first assumed that the time until rupture can be described by the Monkman-Grant relation as:

$$t_r \dot{\epsilon}_s = B \quad (2.8)$$

where B is a constant and t_r is the creep rupture time. The steady-state creep rate, $\dot{\epsilon}_s$, is obtained using the Arrhenius-function:

$$\dot{\epsilon}_s = A\sigma^n \exp\left(-\frac{Q}{RT}\right) \quad (2.9)$$

with all parameters as previously defined for Equation (2.4). Equations (2.8) and (2.9) are then combined to yield the Larson-Miller relation of the form:

$$P_{LM} = T(C + \log(t_r)) \quad (2.10)$$

where the Larson-Miller parameter, P_{LM} , and the constant, C , correspond to:

$$P_{LM} = \frac{0.4343Q}{R}; \quad C = \log A - \log B \quad (2.11)$$

A visual representation of the derivation of a Larson-Miller master curve for superalloy IN-718 is shown in Figure 2.34. When calculating values from experimental data, the magnitude of P_{LM} lies in the range of 23,000 to 33,000 for single-crystal NBSA, while C is traditionally taken as a constant value of 20. A compilation of Larson-Miller plots for several single-crystal superalloys is shown in Figure 2.35. Curves are mostly straight and possess a similar slope regardless of alloy composition, while a clear shift towards larger P_{LM} values can be noted for newer, rhenium-containing alloys.

Several authors [418–424] have criticised the validity and the physical basis of parametric extrapolation methods in the case of NBSA. Main points of contention are the fact that these approaches do not account for shape changes of the creep curve due to service-induced degradation and the inherent assumption that just one expression can describe the creep rate across a wide range of testing conditions. Careful analysis of creep data reveals that a general value of 20 for C is in some cases too conservative [425], while in others it is too optimistic and would lead to critical overestimations of creep life [426]. An extensive study using long-term rupture data for nickel- and cobalt-based alloys reported an average C value of 18.3, but also an overall spread from around 13 to 23 [427]. Suggestions for a

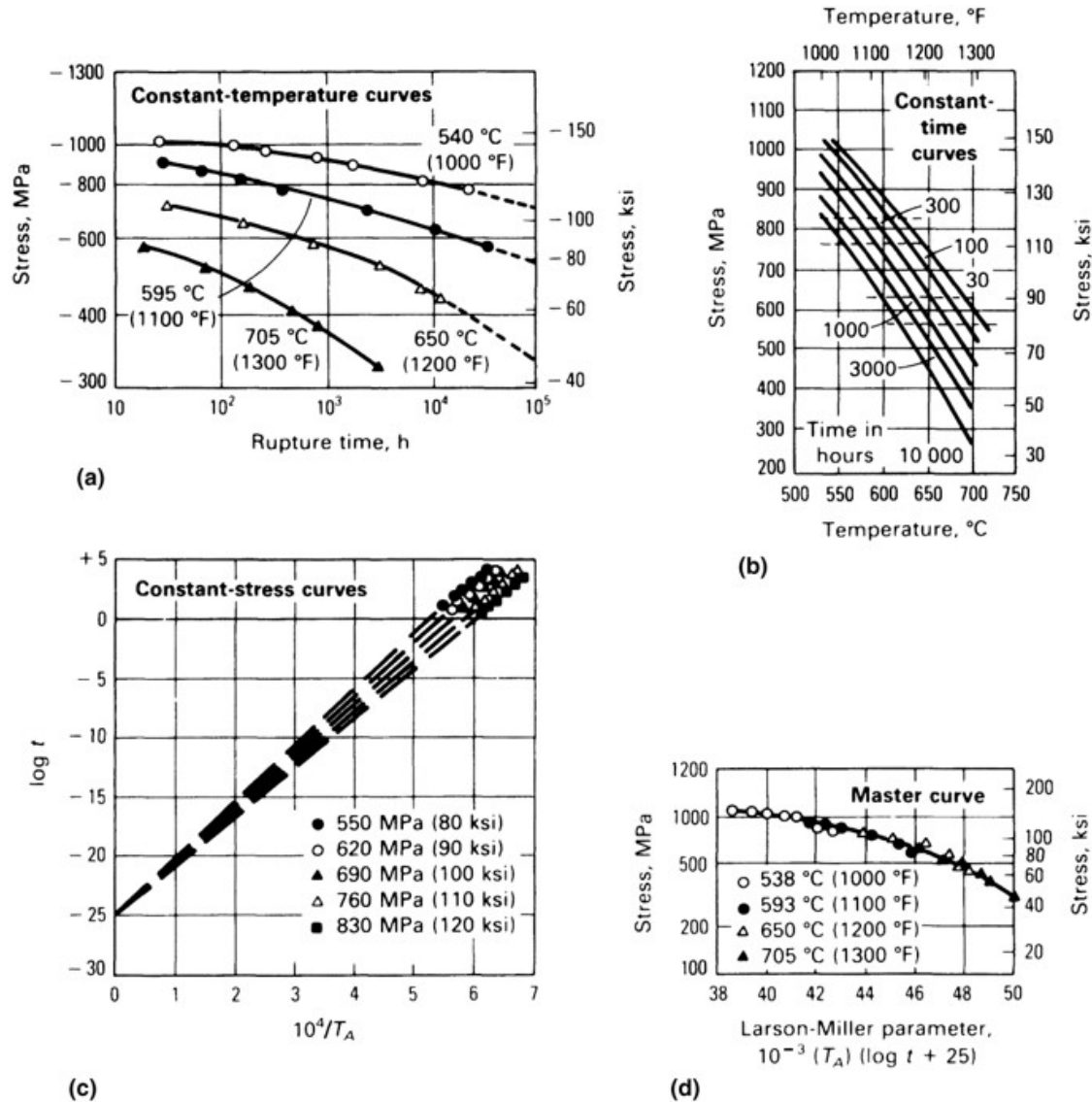


Figure 2.34: Method of creating a Larson-Miller master curve for the polycrystalline superalloy IN-718 [417]. A data set from experimental isothermal stress-rupture tests in (a) is replotted as constant-time curves on coordinates of stress vs. temperature in (b). Values of temperature obtained from the dashed line intercepts in (b) are then plotted in (c) as constant-stress curves. By extending these lines, the optimal convergence value for the Larson-Miller constant, C , is found to be equal to 25. Finally, it is then possible to plot all the creep data on a master curve in (d) using the Larson-Miller expression.

dependency of C on applied stress have been put forward [419, 420, 427], but have been criticised as ultimately defeating the point of a simple approach towards interpreting creep data [428].

Penny and Marriott [404] and Monma [426] carried out extensive error estimation calculations for different extrapolation parameters and came to the same conclusion

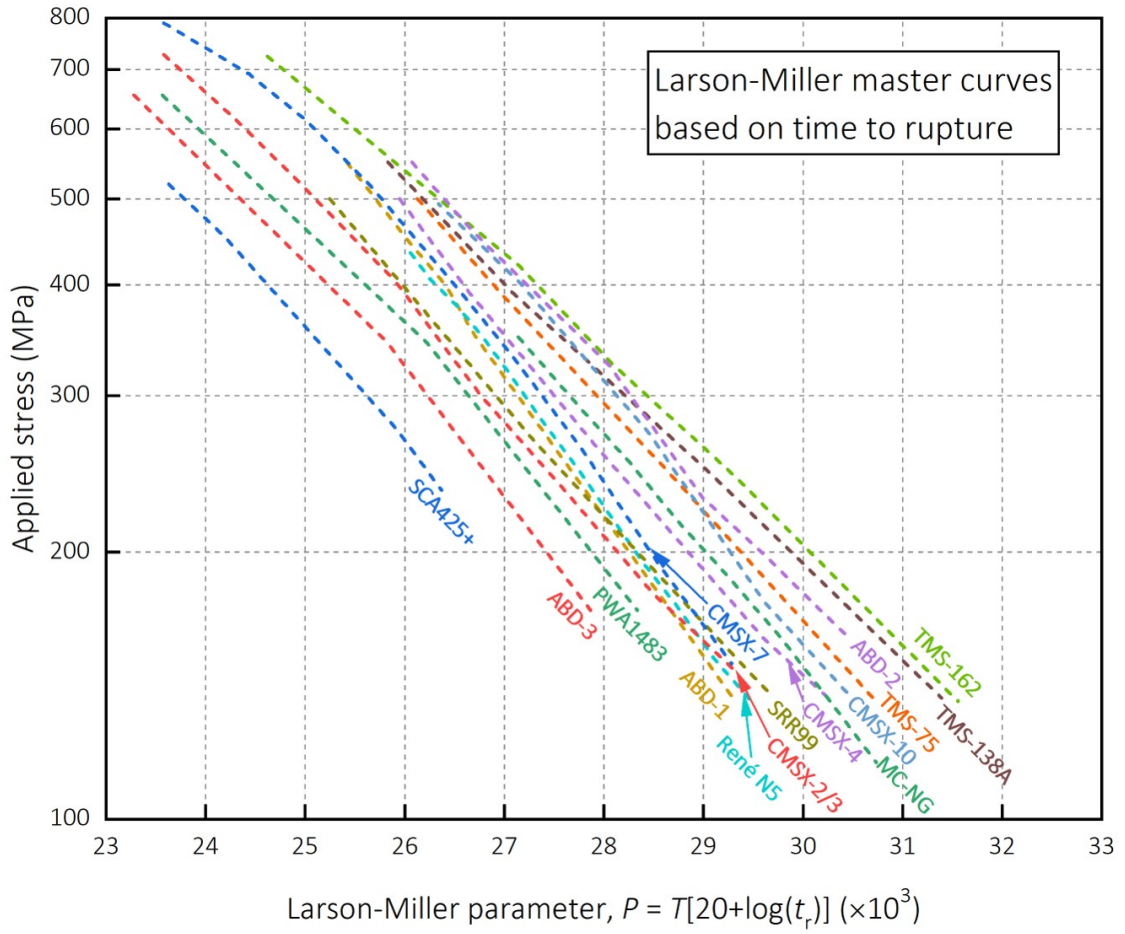


Figure 2.35: Larson-Miller master curves for several first- to fourth-generation single-crystal superalloys based on time to rupture. Alloy compositions can be found in Table 2.1 and it can be noted that the creep performance expressed by the Larson-Miller parameter increases over successive generations.

that it is not possible to single out an ideal approach. Moreover, it has been shown that the optimal extrapolation method will depend on the accuracy of available data, on desired simplicity, and on the physical feasibility of assumptions made [404, 423, 429, 430]. As such, using the Larson-Miller parameter or similar methods to describe creep strength must be done with caution.

A novel solution proposed by Woodford [431, 432] involves a paradigm shift away from attempting to re-create microstructural evolution and damage development, as is done in a regular creep test, and towards assessing the consequences of changes occurring under actual operating conditions. Instead of defining a certain critical design strength for a certain exposure period, this new approach assesses

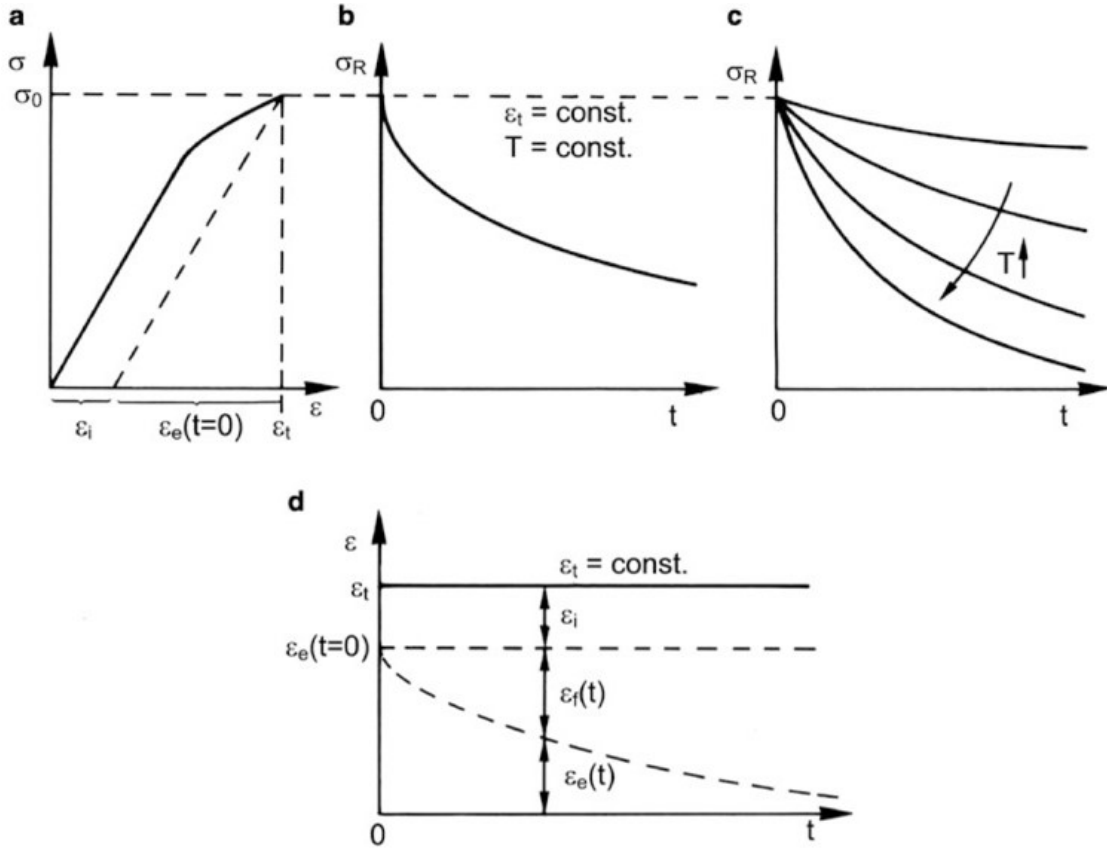


Figure 2.36: Development of test parameters during SRT [239]. (a) Load is initially increased at a constant strain rate until a pre-defined level of total strain is reached, at which point the crosshead is held in place. (b) Load relaxes over time at a constant temperature and a constant total strain. (c) Analogue to standard creep experiments, relaxation occurs at a faster rate at higher temperatures. (d) Simplified variation of strain components over time showing that elastic strain is gradually replaced by plastic strain, while the initial plastic deformation remains unchanged.

changes in material strength after service exposures. Based on previous work by Hart and Solomon [433], Woodford et al. applied stress relaxation testing (SRT) to determine the high-temperature creep strength of superalloys after exposure, without changing the material state significantly [434–438]. The common procedure for SRT is illustrated in Figure 2.36. By assuming that total strain after loading remains constant and ignoring possible influences of machine and fixture compliance, the evolution of plastic creep strain rate, $\dot{\epsilon}_p$, can be obtained by differentiating the stress vs. time curve from SRT:

$$\dot{\epsilon}_p = -\dot{\epsilon}_e = -\dot{\sigma}/E \quad (2.12)$$

Derived stress vs. creep strain rate data can be parametrised by an exponential temperature function, as shown in Figure 2.37, ultimately allowing the selection of design points. As such, the final result is of similar nature to design based on time-temperature parameters, however, the overall rationale is radically different. Although several other authors have made use of SRT to determine superalloy properties [439–443], it can be asserted that this method has not yet found widespread use within industry.

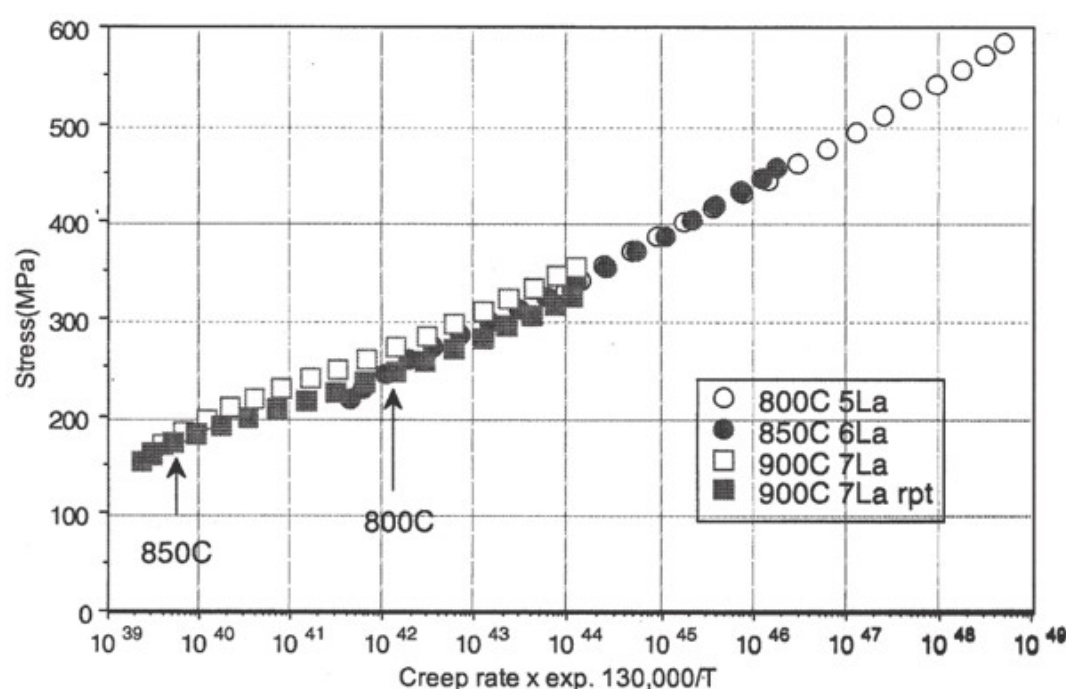


Figure 2.37: Plot of stress vs. creep strain rate/temperature for superalloy IN-738 [432]. Log stress vs. log strain rate data obtained from SRT at 800, 850 and 900 °C was parametrised by an exponential temperature function to create a master curve. This curve can be used as a basis for creep life design, with the two identified design points at 800 and 850 °C corresponding to a 1% creep strain after 100,000 h service exposure.

2.2.3 Design for Creep

It can be ascertained that the increases in creep strength observed in Figure 2.35 for successive generations of single-crystal superalloys stem from incremental improvements enabled by the continuous development of guidelines for alloy design [12]. A compilation of such design principles found in the literature is presented in Table 2.3 and reveals good general agreement between different studies. While this

Alloy design principle	Reference					
	[234]	[78]	[12]	[444]	[445]	[60]
Maximise solid solution strengthening	X	X	X			X
Control solute additions to avoid TCP phases		X	X		X	X
Precipitate an optimal γ' volume fraction	X	X	X	X	X	X
Precipitate γ' particles of optimal size	X			X	X	X
Adjust γ/γ' lattice misfit through composition	X	X	X	X	X	X
Control chromium levels for corrosion resistance		X	X			X

Table 2.3: Alloy design principles for increasing overall creep strength taken from lists of guidelines found in the literature, arranged chronologically from left to right. Agreement between different studies is good overall, however, the emphasis placed on individual aspects varies.

list is not exhaustive, it does contain the main six design parameters for increased creep resistance, which are discussed individually in the following.

2.2.3.1 Maximise Solid Solution Strengthening

The importance of solid solution strengthening for increasing creep resistance has been emphasised in several studies [112, 315, 318, 446, 447]. Considering the improvements in creep strength over subsequent superalloy generations and observing the compositions in Table 2.1, it is clear that this design approach has been successful. To a large degree, this can be associated with the beneficial effects of rhenium and to a lesser degree with tungsten, tantalum, and molybdenum additions [12]. Such considerations led Rettig et al. [60, 61] to propose a solid solution strengthening index, I_{SS} , which yields a weighted value based on the experimentally observed strengthening levels imparted by individual solute additions [315]. As deformation is assumed to remain confined within γ matrix channels during tertiary creep, I_{SS} is defined using molar fractions within γ obtained from CALPHAD as:

$$I_{SS} = 2.44 \cdot x_{Re}^{\gamma} + 1.22 \cdot x_{W}^{\gamma} + x_{Mo}^{\gamma} \quad (2.13)$$

The rationale for I_{SSS} as a design parameter is that slow-diffusing solutes impede dislocation climb at γ/γ' interfaces and that their effectiveness scales linearly with atomic fraction. This approach has recently been applied to the development of new and somewhat improved single-crystal superalloys [60, 61]. Nonetheless, this method could not offer satisfactory predictions of creep strength when compared to a large selection of creep data from the literature, as discussed in Chapter 5. Furthermore, as illustrated in Figure 2.38, levels of slow-diffusing elements must be carefully considered against necessary additions of chromium for corrosion resistance, the probability of precipitating TCP phases, and total alloy density.

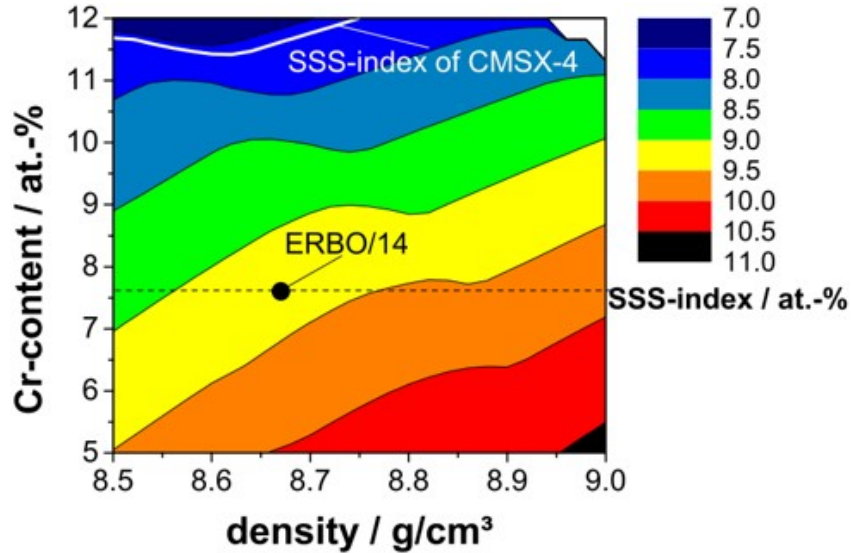


Figure 2.38: Pareto front diagram showing the maximum possible level of solid solution strengthening within a pre-defined design space in relation to density and chromium content [60]. The designed alloy ERBO/14 is predicted to exhibit improved properties compared to CMSX-4, while still satisfying density and corrosion resistance constraints.

2.2.3.2 Control Solute Additions to Avoid TCP Phases

Creep tests on alloy ERBO/14 from Figure 2.38 revealed that it fails to reach the CMSX-4 benchmark due to microstructural instability and failure associated with TCP phases [60]. As discussed in Section 2.1.3.1, these brittle phases decrease high-temperature properties by acting as crack initiation and propagation sites [214, 293–295] and by depleting the material of beneficial solutes [280, 296–300].

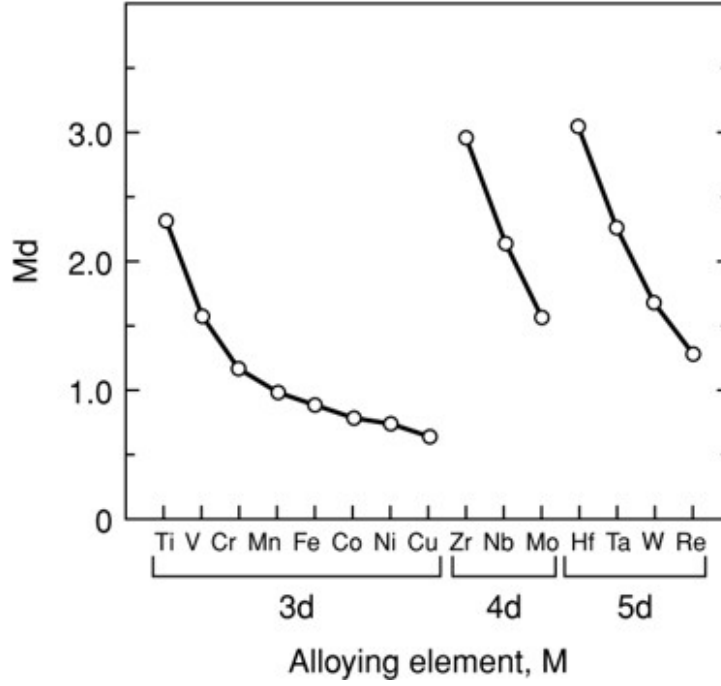


Figure 2.39: Values of Md parameters for typical superalloy additions [448]. Within each series, Md correlates strongly with the atomic number, with lighter elements in a series having the most negative impact on stability.

Accurate predictions of TCP phase precipitation would be a milestone in superalloy design and would lead to significant cost and time savings associated with long-term exposures of trial compositions. Unfortunately, as yet, no satisfactory method has been found [106, 292, 449]. Among simpler approaches based on electron band theory, the one regarded as most reliable and accurate is the New PHACOMP method, which takes into account both electronic structure and atomic size factors [68]. Using molecular orbital simulations of the d-electron state, the d-orbital energy level Md was derived as a new alloying parameter and was found to correlate with the electronegativity and the atomic radii of elements [68]. Figure 2.39 shows the Md values of typical superalloy additions.

For alloy design purposes, it is assumed that TCP phase precipitation will initiate in the γ matrix, which contains higher solute levels [69, 70, 107, 448, 450], and an average value $\overline{\text{Md}}_\gamma$ is derived as:

$$\overline{\text{Md}}_\gamma = \sum_i x_i^\gamma \text{Md}_i \leq \text{Md}_{\text{crit}} \quad (2.14)$$

Here, x_i^γ and Md_i are the mole fraction and the Md number of element i within the γ matrix. Higher $\overline{Md}_\gamma$ values imply a higher probability of TCP phase formation and a critical value that should not be exceeded, Md_{crit} , has been proposed at around 0.93 eV [107].

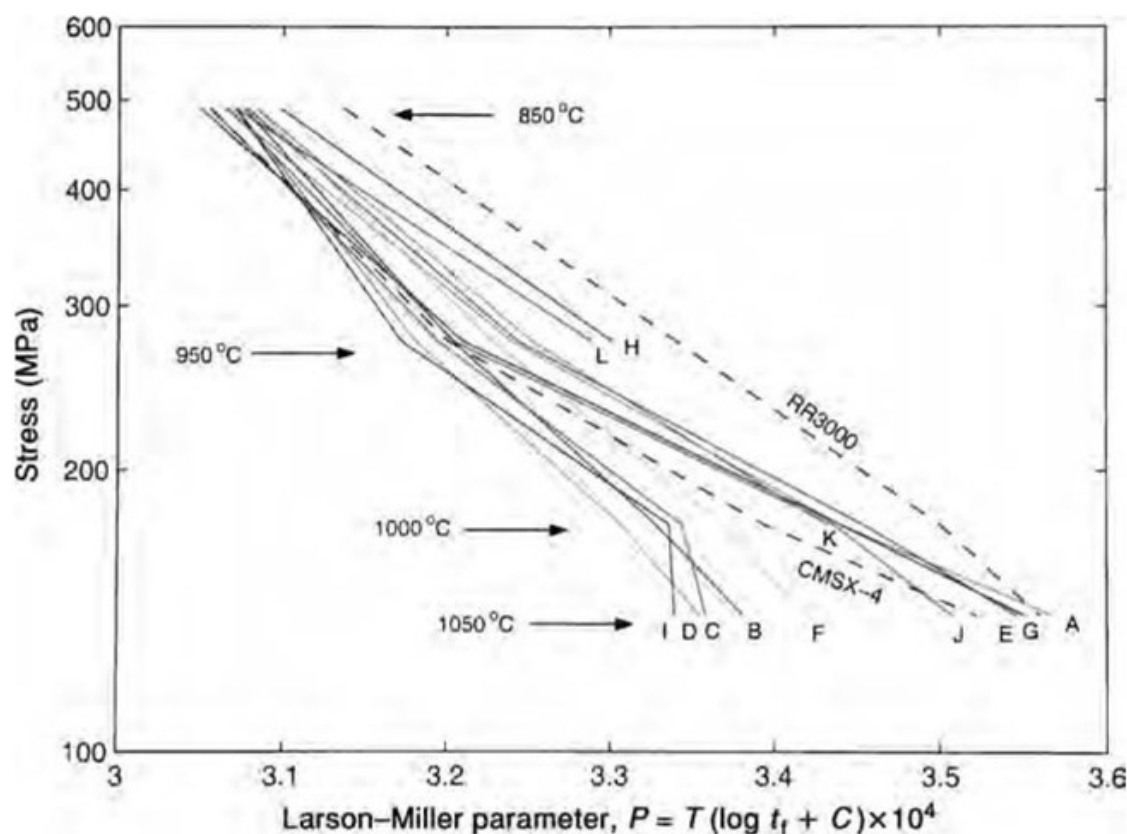


Figure 2.40: Larson-Miller plots for several model second-generation single-crystal superalloys containing 3 wt.% rhenium [12]. Alloys marked as B, C, D, F, and I were found to form TCP phases, which led to markedly lower creep rupture strength at high temperatures compared to stable alloys like A, E, G, J, and K.

Ultimately, the only way of being certain of TCP phase precipitation are microstructural studies after long-term exposures. A large-scale study on second-generation NBSA confirmed that the impact of deleterious phases on creep properties becomes stronger at higher temperatures when thermodynamic processes are accelerated [12], as illustrated in Figure 2.40. Much of the recent work on preventing TCP phases in later-generation superalloys has involved the addition of platinum group metals, primarily ruthenium [158, 451–454], but in some cases also iridium and platinum [230, 455–457]. While several mechanisms for their beneficial effects

have been proposed and debated, recent studies concluded that ruthenium additions lead to a reduction in the thermodynamic driving force for TCP phase precipitation [158, 453, 458, 459] and further impede TCP phase nucleation by influencing microstructural parameters [155, 454].

2.2.3.3 Precipitate an Optimal γ' Volume Fraction

Considering the importance of precipitate strengthening, it is of little surprise that a guideline mentioned by all studies in Table 2.3 is to design alloys with a certain optimal volume fraction of γ' . Results of elegant creep studies on model single-crystal alloys situated along the same tie line — thus containing different γ' fractions, but possessing identical phase compositions — reveal that ideal values are in the range of 55 to 70% [104, 205]. These confirm previous results obtained for conventionally cast polycrystalline NBSA [232, 327, 359].

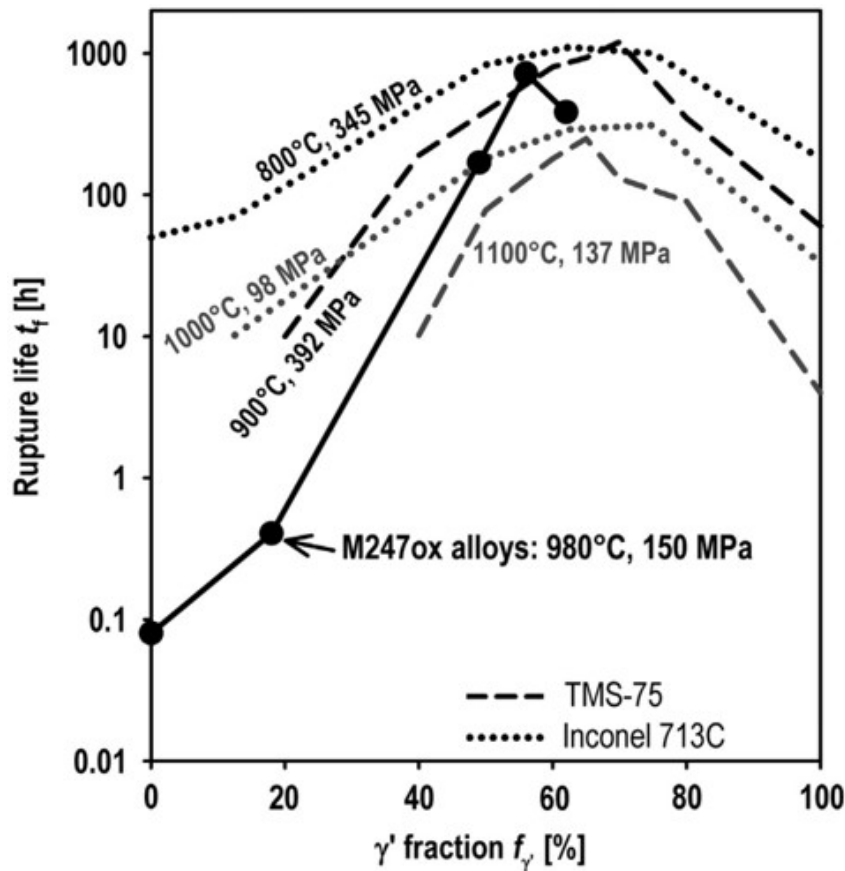


Figure 2.41: Influence of the γ' volume fraction on the creep rupture lives of single-crystal tie-line alloys IN-713C [108], TMS-75 [104, 205], and M247ox [324].

Optimal values can be rationalised by considering the dominating creep deformation mechanisms discussed in Section 2.2.1. During intermediate-temperature creep, it is favourable to decrease the fraction of γ channels, thus confining dislocations to small regions which must be overcome by diffusion-controlled climb processes [12, 445]. The ideal γ' fraction of around 70% can be explained by a superposition of strengthening mechanisms [324], as illustrated in Figure 2.20. During high-temperature creep, the total area of γ/γ' interfaces after rafting reaches a maximum at 50% γ' , thus offering the highest creep resistance as long as the rafts are not sheared [445]. At larger γ' fraction values, a topological inversion can occur, with γ' effectively becoming the matrix phase, which leads to a strong decrease of high-temperature mechanical properties [460–462].

2.2.3.4 Precipitate γ' Particles of Optimal Size

Besides a dependency on γ' volume fraction, some authors also note that creep properties are influenced by the size distribution of precipitates [358, 387, 463, 464]. Optimal values are cited to lie in the range of 300 to 700 nm [463], 300 to 400 nm [239], or around 450 nm [315], thus showing fair agreement. Traditional explanations invoke transitions between strengthening mechanisms based on precipitate size, as illustrated in Figure 2.42.

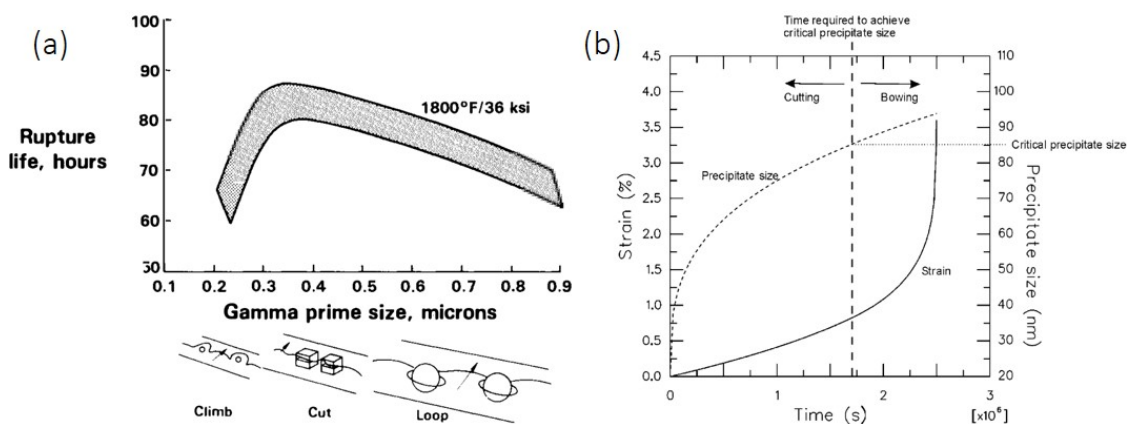


Figure 2.42: (a) Effect of γ' size on the creep rupture life of a single-crystal superalloy [465]. (b) Predictions for γ' precipitate size and creep strain evolution based on the model developed by Manonukul et al. [466]. Both images invoke the concept of a critical size, which marks the transition from (a) climbing to shearing and (b) shearing to bowing.

However, taking into account the asymptotic convergence of particle size after long exposure times regardless of initial values, as illustrated in Figure 2.15, it is unlikely that the mean precipitate size after heat treatment will be of critical concern for IGT applications. Indeed, several studies which compared the creep response of pre-aged and virgin materials reported little or no difference in creep strength during long-term tests [467–469]. Instead, a more pertinent design guideline is to ensure a homogeneous microstructure, with evenly distributed γ' particles orientated along the $\langle 001 \rangle$ crystal direction, which will give rise to improved creep strength [358]. The optimal particle size of such a homogeneous distribution has been reported to depend on the value of lattice misfit [463]. Finally, an interesting study by van Sluytman and Pollock [470, 471] proved that γ' morphology should also be considered and that ideal shape parameter ratios are obtained for low absolute values of lattice mismatch.

2.2.3.5 Adjust γ/γ' Lattice Misfit Through Composition

As observed in Table 2.3, lattice misfit is widely regarded as a key design parameter for creep resistance. Unfortunately, extensive literature reviews reveal a lack of agreement between studies regarding both its optimal magnitude and its sign [392, 472]. These points are discussed critically in the following.

Two schools of thought exist concerning the magnitude of misfit. The first suggests keeping the value close to zero, in order to obtain a low coarsening rate coefficient and homogeneous, cuboidal precipitates [12, 60, 234, 239, 363, 390, 473]. The second advocates a high, usually negative, mismatch, which promotes dense dislocation networks at γ/γ' interfaces. These networks have been associated with the formation of stable lamellar structures [272, 474] and with an increased protection of γ' rafts against shearing [217, 370, 396, 445, 475–479], as discussed in Section 2.2.1.3. This beneficial effect of a reduced lattice misfit on creep resistance is illustrated in Figure 2.43(a) for a range of commercial NBSA. However, several studies have conversely reported that interfacial dislocation networks are detrimental to creep properties by acting as dislocation sources and by reducing coherency strains [236,

397, 480–482]. Finally, some studies were inconclusive with regard to the effects of lattice misfit [450, 483, 484]. Mughrabi [392] points out that many of these uncertainties could be removed if publications differentiated more strictly between creep regimes in terms of applied stress and temperature. This idea is supported by regression analysis studies carried out by Harada et al. [78, 331, 403, 485], which reveal strong variations in the relative significance of different alloy design parameters, including misfit, as shown in Figure 2.43(b).

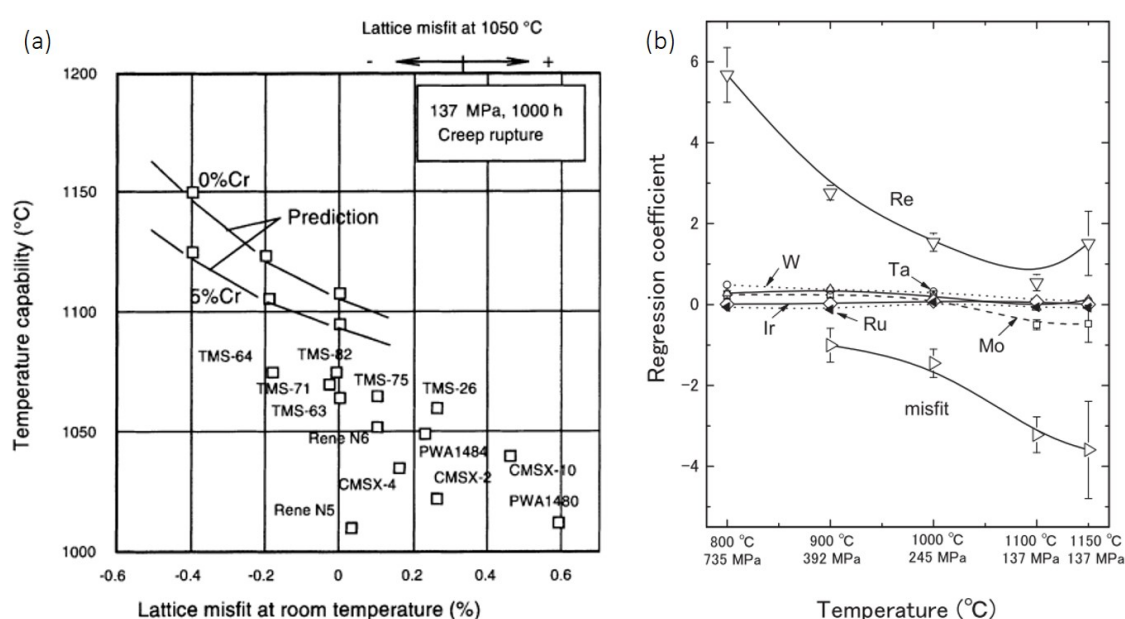


Figure 2.43: (a) Variation of creep strength, expressed in terms of temperature capability for a rupture life of 1000 h under 137 MPa applied stress, with lattice misfit at room temperature [78]. Note that the transition from positive to negative misfit at 1050 °C is estimated separately on the top x -axis, as misfit commonly decreases with temperature for NBSA. (b) Regression coefficients relating additions of molybdenum, tungsten, tantalum, rhenium, ruthenium, and iridium, as well as lattice misfit, to creep rupture life under various test conditions [331]. The importance of individual parameters varies strongly between creep deformation regimes.

Furthermore, as noted by several authors [234, 392, 445], it is impossible to change the value of misfit without significantly affecting other key alloy properties, such as the amount of solute strengthening. As such, many of the factors in Figure 2.43(b) cannot be considered to be fully independent. This dilemma led Svoboda and Lukáš [486, 487] to inspect variations in the sign and magnitude of misfit within their creep deformation model, without changing any other inputs.

Results interestingly showed maximum resistance for a large, positive mismatch. This was rationalised by Mughrabi [390, 392, 472] with an improved resistance to dislocation climb and glide for γ' rafts parallel to the tensile axis. However, a positive misfit cannot be obtained for usual NBSA compositions at elevated temperatures and is therefore of limited concern.

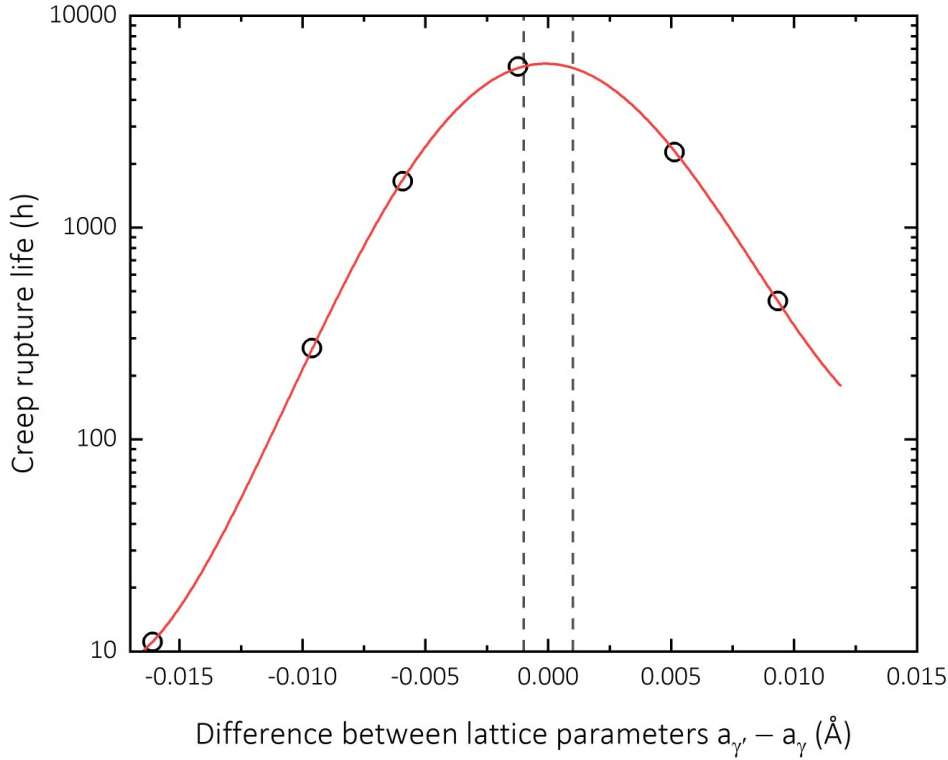


Figure 2.44: Effects of lattice misfit on creep rupture life at 700 °C under 150 MPa applied stress, adapted from reference [488]. Note that the x -axis shows the difference in lattice parameters between γ' and γ instead of actual misfit values. A polynomial fit predicts maximum creep strength for vanishing levels of misfit. The two dashed lines at ± 0.001 Å difference between the lattice parameters correspond to a misfit of about $\pm 0.03\%$.

To conclude, this design rule must be considered critically in the context of IGT operating conditions. As most literature studies focus on materials for aerospace applications, they tend to involve shorter-term experiments and attribute less importance to microstructural stability. Conversely, for IGT materials, coarsening and potential TCP phase formation are expected to play a much more important role. As such, a low, ideally vanishing level of misfit should provide optimal results for IGT components [12, 234]. This point is illustrated in Figure 2.44 for the case of

model Ni–Cr–Al alloys designed to possess identical γ' volume fractions, but varying levels of mismatch [488]. Tests were carried out at 700 °C and 150 MPa applied stress, therefore in similar conditions to those experienced by IGT blades during service.

2.2.3.6 Control Chromium Levels for Corrosion Resistance

This final guideline is sometimes mentioned as an addendum and it emphasises the importance of taking design trade-offs into account. Adding more chromium is usually detrimental to creep properties, as this element leads to lower γ' fractions and increases the susceptibility to TCP phase formation, while only providing a minor benefit to solution strengthening [12, 117]. However, chromium can be regarded as the key element imparting hot corrosion resistance, as well as contributing to the formation of protective oxide scales. Early work by Mrowec et al. [105] on sulphidation showed that chromium levels of at least 15 wt.% are necessary in an aggressive, sulphur-containing environment. This value is in good agreement with results obtained by McLean [489] for conventionally cast alloys, illustrated in Figure 2.45.

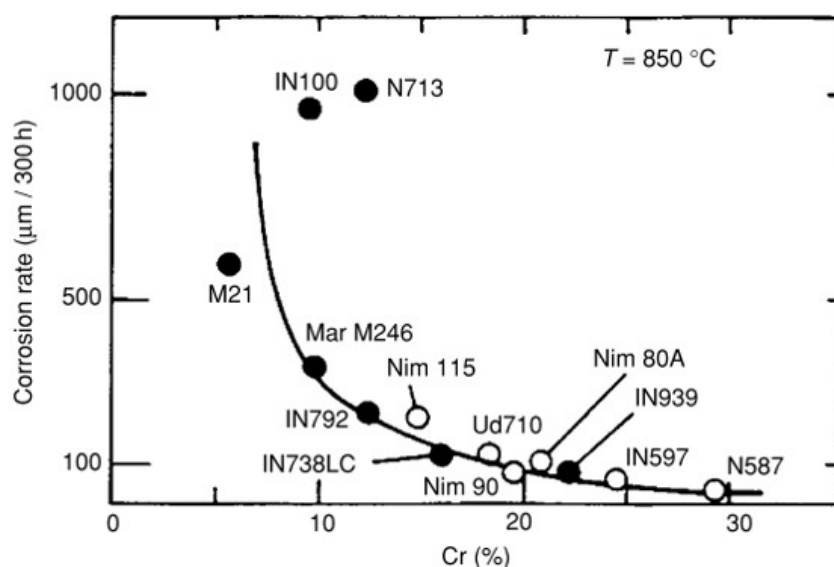


Figure 2.45: Changes in resistance to hot corrosion, expressed as depth of attack after 300 h exposure, with chromium content [489]. A strong increase in corrosion resistance is observed above around 15 wt.% chromium.

These considerations are confirmed by elegant plots from an early systematic alloy design study [69], which focused on the compositional space shown in Figure 2.46.

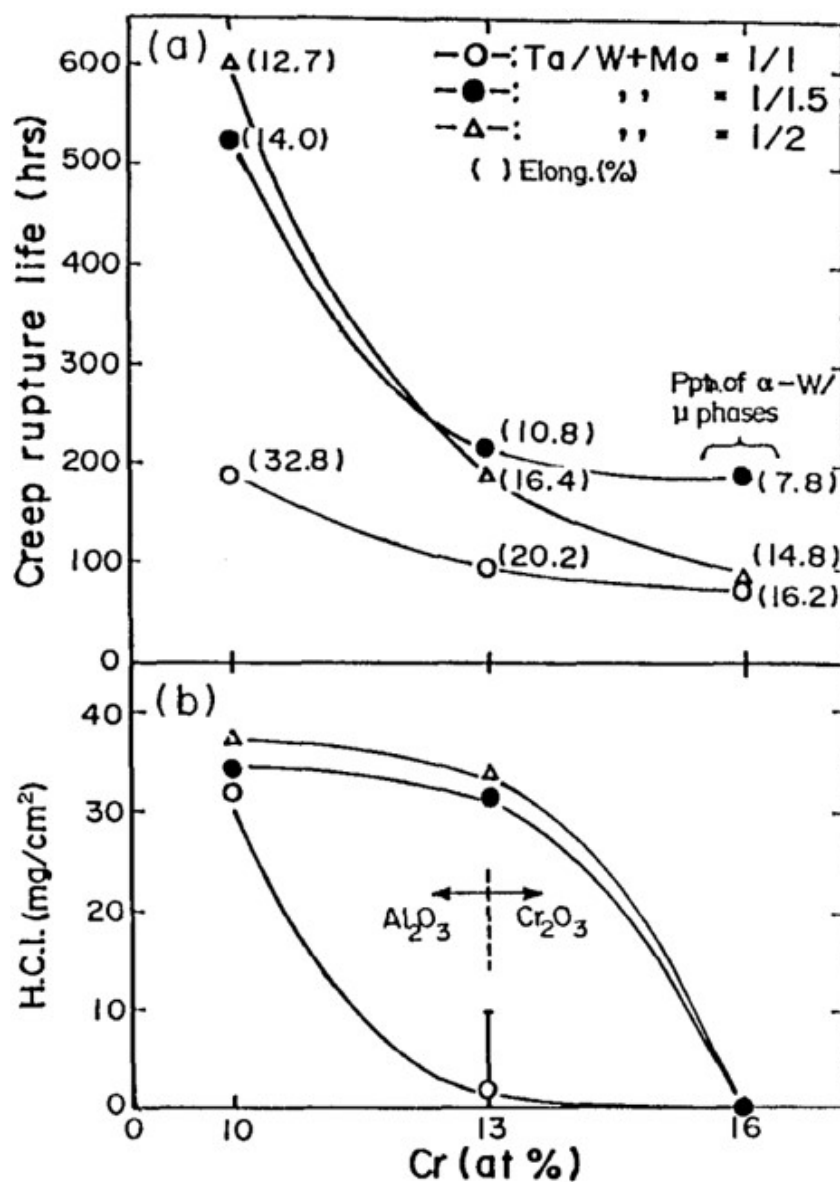


Figure 2.47: Effects of chromium content on (a) creep rupture life and (b) hot corrosion resistance for alloys from the previously determined design space in Figure 2.46. The influence of varying ratios of tantalum to tungsten and molybdenum is also considered [69].

The advances in both test methods and in the understanding of material behaviour at the microscale have been remarkable over the past 10–15 years, and one can expect similar, if not accelerated, progress in the future. New experimental methods and advanced models will address a broad range of mechanical properties and service conditions.

— K.J. Hemker & W.N. Sharpe, Jr., “Microscale Characterization of Mechanical Properties”

3

Rapid Assessment of Mechanical Behaviour using Small-Scale Testing

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3.1 Introduction

As discussed throughout Chapter 2, new alloy grades are never deployed without careful testing of their properties and performance under conditions close to those experienced in service. Such qualification activities are difficult and costly, which explains why the time needed to insert novel materials into industrial applications can be notoriously long [17, 88, 162]. Furthermore, processing costs for the production of pilot-scale material quantities can be excessively large, thus leading to conservatism and undue emphasis on maintaining the status quo. Without a doubt, such challenges lead to a slackening in the pace of technological change.

Consider, for example, the assessment of the mechanical response of a material destined for high-temperature applications. The yield stress depends upon temperature, but also on the strain rate. The creep resistance depends upon temperature once again, but also on the stress level. Even before the cyclic loading needed to assess fatigue behaviour or the effects of a biaxial or triaxial stress state are considered, the number of conditions for which mechanical tests are needed can quickly become very significant. The difficulties identified above are then exacerbated. Moreover, there is a traditional emphasis, even today, on the use of standardised testpieces, which means that substantial volumes of material are needed. Might there be better ways of approaching this problem?

The research reported in this chapter was carried out with these ideas in mind. Miniaturised testpieces are used within a novel ETMT system [494] to assess relatively small volumes of material, with nonetheless representative mechanical behaviour being shown to arise. First, a novel temperature ramping test is devised to allow the rapid assessment of the athermal yielding behaviour of a new material, from just a single non-isothermal test. Second, a stress relaxation test is used to quickly deduce the time-dependent response at high temperature. To garner confidence in these approaches, comparisons are made with more traditional techniques.

3.2 Experimental Method

3.2.1 Material

A single-crystal superalloy recently developed in partnership with Siemens Industrial Turbomachinery (SIT) was chosen for the present study [495]. Its nominal composition in wt.% is Ni–5.2Co–15Cr–1Mo–4W–4.6Al–8Ta–0.1Hf–0.25Si–0.015C, with further minor additions of B and Ce. This alloy is a candidate for future IGT applications and lies within the new design space presented in Figure 1.3. Its chemistry and processing parameters have been optimised to yield good resistance to oxidation, hot corrosion, creep, and TMF damage [32, 495, 496]. Single-crystal test bars of 16 mm diameter and 165 mm length were cast with near $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ crystal growth directions. Chemistry measurements using X-ray fluorescence (XRF), glow discharge mass spectrometry (GDMS), optical emission spectroscopy (OES), and LECO combustion analysis showed a very good agreement between measured and nominal values. Impurity levels were confirmed to be far lower than the maximum values allowed by the specification.

All the bars were macro-etched to check for the absence of GB and were then subjected to X-ray analysis using the Laue back-reflection technique to ensure their orientation differed by less than 15° from the specified direction. Heat treatment consisted of solutioning at 1280°C for 5 h, followed by primary ageing at 1100°C for 4 h and secondary ageing at 850°C for 20 h, in each case concluding with gas fan cooling in argon. SEM images of test bar cross sections were obtained using a JEOL JSM-6500F SEM operating at 20 keV and are shown in Figure 3.1.

The microstructure is characteristic of IGT superalloys and is composed of cuboidal, secondary γ' precipitates with side lengths of ≈ 400 nm (coloured teal in Figure 3.2(a)-(c)) and spherical, tertiary γ' particles with diameters on the order of 10 nm (coloured golden), embedded in the γ matrix (coloured grey). Secondary particle size distributions were analysed using the image processing software package MIPAR [497]. Results are presented qualitatively as size heat maps in Figure 3.2(d)-(f) and quantitatively as distribution plots of equivalent diameter with a bin width of

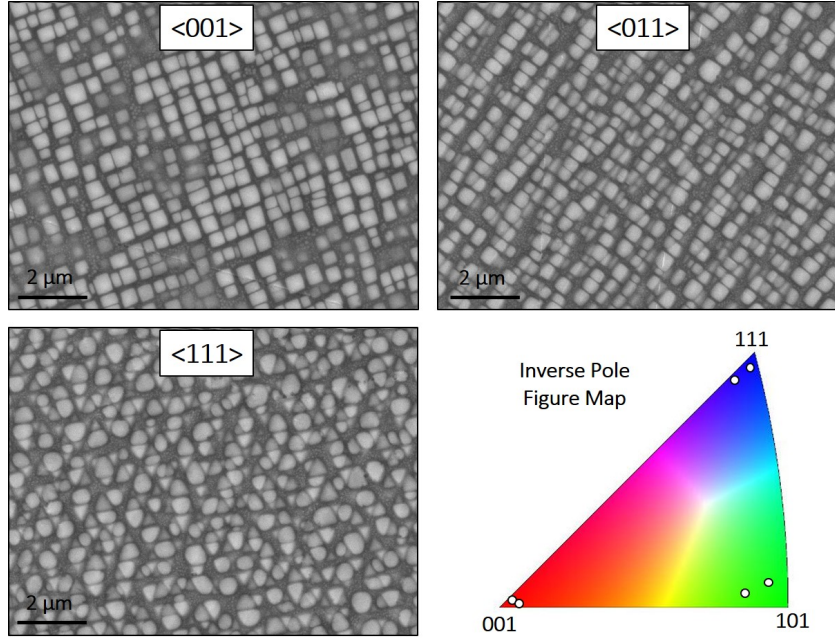


Figure 3.1: SEM images of alloy microstructures and IPF map of test bar orientations.

Test bar	Average misorientation (°)	Standard deviation (°)
$\langle 001 \rangle$ #1	2.39	0.56
$\langle 001 \rangle$ #2	4.59	0.45
$\langle 011 \rangle$ #1	2.86	2.40
$\langle 011 \rangle$ #2	11.82	3.44
$\langle 111 \rangle$ #1	0.90	0.92
$\langle 111 \rangle$ #2	1.99	1.88

Table 3.1: Results of crystal orientation measurements with EBSD.

50 nm in Figure 3.2(g)-(i). The secondary γ' volume fraction in Figure 3.2(a) was estimated following the method proposed by Maier & Bürgel [239] for single-crystal superalloys with a $\langle 001 \rangle$ orientation. The determined value of 47.6% is equal to that predicted by Thermo-Calc and the TTNi8 thermodynamic database for equilibrium conditions during the final ageing step at 850 °C.

The orientations of the six bars used to manufacture the test specimens for the present study were checked again using a Zeiss EVO MA10 SEM fitted with a high-speed Bruker Quantax e-Flash¹⁰⁰⁰ EBSD detector. Areas of $3 \times 2.5 \text{ mm}^2$ were scanned at 20 keV with a 5- μm step size. Average misorientations calculated using the EBSD results and standard deviations for each data set are given in Table 3.1. EBSD orientations are also shown in the simplified inverse pole figure map of Figure 3.1.

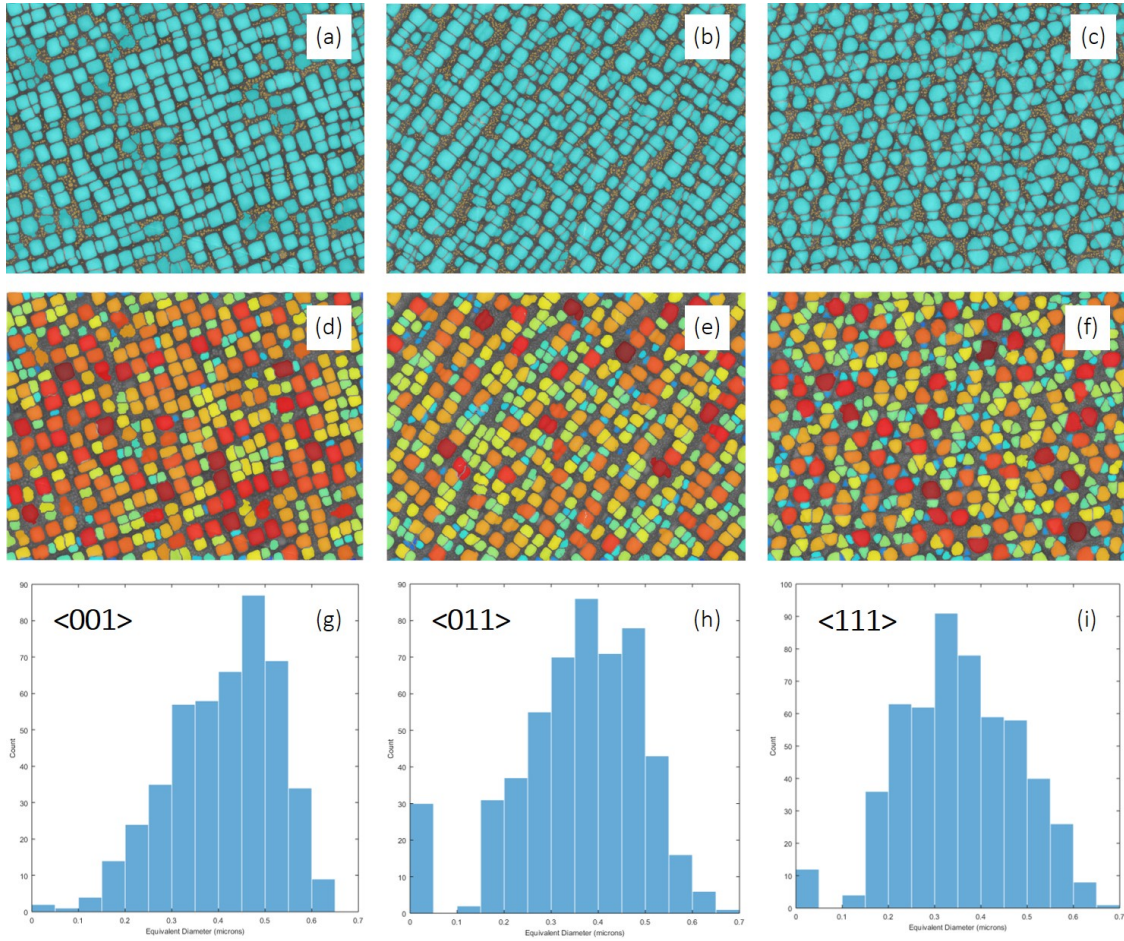


Figure 3.2: Processed SEM images with extracted secondary (teal) and tertiary (golden) precipitate features for the (a) $\langle 001 \rangle$ direction, (b) $\langle 011 \rangle$ direction, and (c) $\langle 111 \rangle$ direction. (d)-(f) Qualitative and (g)-(i) quantitative analyses of the secondary particle size distributions for the three crystal orientations.

Miniaturised ETMT blanks with a nominal size of either $40 \times 3 \times 1$ or $40 \times 4 \times 2 \text{ mm}^3$ were manufactured along longitudinal bar directions by wire-guided electro-discharge machining (EDM). These blanks were further waisted *via* EDM to give nominal widths in the centre of the testpiece of 1.1 and 2 mm, respectively, as shown in Figure 3.3. The main advantage of the waisted geometry is that it enables using customised grips, which precisely fit the waist radius and which ensure a correct alignment during testing.

A further benefit is that this geometry gives rise to a concentration of stress and temperature within the central region. This limits the influence of the anomalous yielding effect in NBSA, mentioned in Section 2.1.3.2, which could otherwise lead

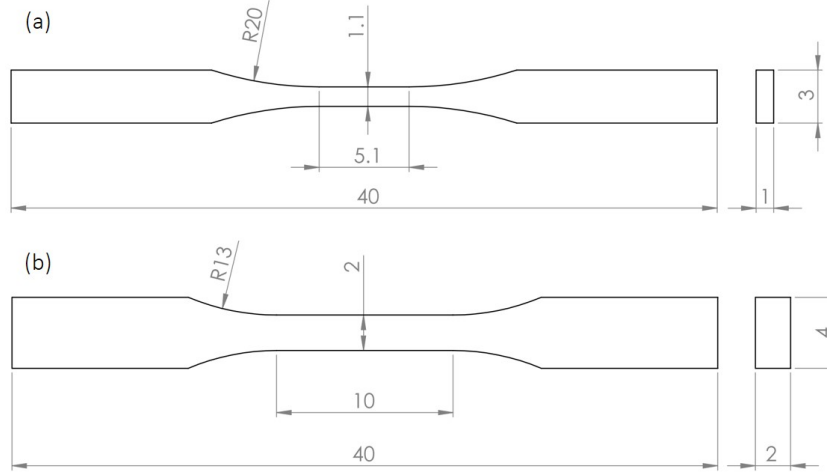


Figure 3.3: ETMT specimen geometries used in the present study for (a) verification tensile and stepped-temperature tests and (b) stress relaxation tests (all measurements in mm).

to higher levels of plastic deformation in cooler regions closer to the grips. This point is of particular importance in the context of the present work and is discussed in further detail in Section 3.4.1. Nonetheless, a parallel-sided section is maintained in the centre of the specimen to ensure a constant stress level and a uniform temperature distribution.

Surfaces were ground to a 4000-grit mirror finish using silicon carbide grinding paper. Besides ensuring a constant, repeatable finish, this step is crucial for removing the recast layer caused by EDM and for minimising residual stresses in the sample prior to testing [498]. The actual cross section dimensions were measured with a micrometer gauge for each specimen and were used to compute engineering stress. Lastly, each specimen was cleaned in an ultrasonic bath with ethanol, after which a high-temperature paint pattern for direct image correlation (DIC) was applied.

3.2.2 The ETMT System

Interest in high-temperature miniaturised testing has grown over time and has led to a multitude of approaches [499–502]. However, ensuring accurate and reproducible results remains challenging, especially for the case of NBSA, which must be qualified at very high temperatures, often close to their melting point. This makes the design and implementation of the load string and of small-scale specimens, grips, and

extensometers, difficult. The ETMT system was developed at the National Physical Laboratory (NPL) with these concerns in mind and has been successfully used for the characterisation of γ' precipitate volume fraction [503], recrystallisation kinetics [504], TMF [505, 506], flow stress [494, 507–509], and creep strain evolution [510, 511] in NBSA.

The Instron ETMT system used in the present work is illustrated in Figure 3.4. It uses a mechanical loading assembly capable of testing in both tension and compression up to a maximum load of 5 kN. Load cell readings are based on a strain gauge element with integrated automatic calibration. A versatile gripping system allows the use of customised grips for each specimen geometry, in order to ensure correct alignment. Displacement of the top, moving grip can be readily measured with a LVDT and strain at room temperature can be calculated after considering the initial grip separation.

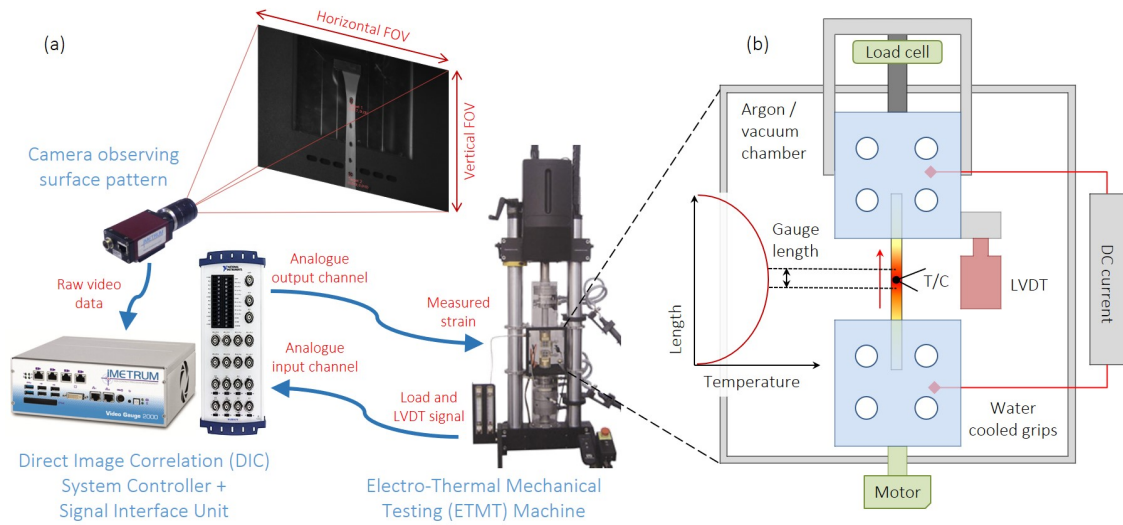


Figure 3.4: (a) Overview of the testing system used for miniaturised testing of superalloys; images courtesy of Instron and Imetrum Ltd. (b) Schematic illustration of ETMT components.

Specimens are heated using a 400-A DC power supply *via* the Joule effect. An advantage — for example over furnace-based apparatus — is that a wide range of heating and cooling rates can be achieved and accurately controlled. The testing temperature is measured and controlled with a type K thermocouple composed

of thin, 0.1-mm-diameter wires of chromel and alumel, fusion-welded under argon gas to form a small bead. This bead is carefully positioned and spot-welded under argon at the centre of the specimen.

As the grips are water-cooled, a parabolic temperature distribution will develop along the specimen. Previous studies [506, 508] have shown that the peak temperature remains reasonably uniform ($T = \pm 5$ °C) in the central 2–3 mm of the sample at high temperatures between 500 and 1000 °C, with the size of this region decreasing with increasing temperature. A consequence is that the majority of plastic deformation is localised in this central region.

Two different strain measurement techniques were used to account for this effect. The first is the method proposed by Roebuck [494], in which resistance is measured over the central 2–3 mm using two thin, spot-welded Pt–13%Rh wires. Changes in cross-sectional area during testing lead to changes in resistance and in the voltage drop measured over the two wires. Roebuck showed that, assuming the test volume remains constant and neglecting elastic changes, plastic strain can be calculated as:

$$\varepsilon_p = \ln \sqrt{(R_t/R_s)} \quad (3.1)$$

where R_s and R_t are the resistances measured before and during deformation, respectively.

The second approach measures strain by DIC. A fine speckle pattern is produced on one of the sample surfaces using high-temperature paint. The resulting pattern with many light, dark, and grey areas offers an ideal target for tracking. During testing, the specimen is illuminated by a bright, diffuse LED light source positioned behind an Allied Vision Technologies Manta G-146 camera which records the test. The camera has a resolution of 1.4 megapixels and offers a nominal frame rate of 17.8 fps when the full field of view (FOV) of 1388×1038 pixels is monitored. Higher frame rates of up to around 50 fps can be achieved when the full FOV is reduced to a smaller region of interest (ROI), which for the case of present tests measures around 250×1000 pixels. However, such high frame rates produce unnecessarily

large amounts of data and offer little additional information at typical strain rates; hence, frame rates between 1 and 10 fps were chosen.

The Imetrum Ltd Video Gauge software tool analyses the images captured by the camera and applies proprietary sub-pixel pattern recognition algorithms to detect any changes occurring during testing in comparison to a reference state. Displacement and strain are measured and calculated in real time between user-defined target areas, in this case set 3 mm apart around the centre of the specimen, with a strain resolution of around 20 microstrain. The target areas were chosen to be quadratic, with the side length corresponding to the width of the specimen. This choice was made as a compromise between improved strain accuracy provided by larger windows and increased spacial resolution provided by smaller ones [512]. Finally, analogue signals for the load, LVDT, and temperature channels are transmitted from the ETMT to the Video Gauge software through a Signal Interface Unit, thus allowing all relevant data to be collected and saved in one location and averting potential issues of synchronising data.

3.2.3 Stepped-Temperature Testing (STT)

Non-isothermal tensile tests — with the temperature being ramped at a constant rate after reaching the plastic regime — were carried out to deduce information regarding the variation of flow stress with temperature.

A schematic illustration of the method is given in Figure 3.5(a). Samples are first deformed isothermally at a constant initial temperature T_i of 500 or 750 °C and constant initial strain rates $\dot{\varepsilon}_i$ close to 2×10^{-5} , 10^{-4} , and 5×10^{-4} /s. After reaching an initial plastic strain value $\varepsilon_{p,i}$ of 0.2%, 0.5%, or 1%, the temperature is ramped, at a constant rate $\dot{T}$ of 0.4, 2, or 10 °C/s up to 1150 °C. The values of these temperature ramps were chosen in accordance with the three different strain rates to yield similar total levels of plastic deformation. In the case of tests between 500 and 1150 °C, the durations of the temperature ramps were 1625 s, 325 s, and 65 s, respectively. In each case, this corresponds to a total strain of around 3.25% during ramping. This value was selected to be significantly lower than the total elongation observed

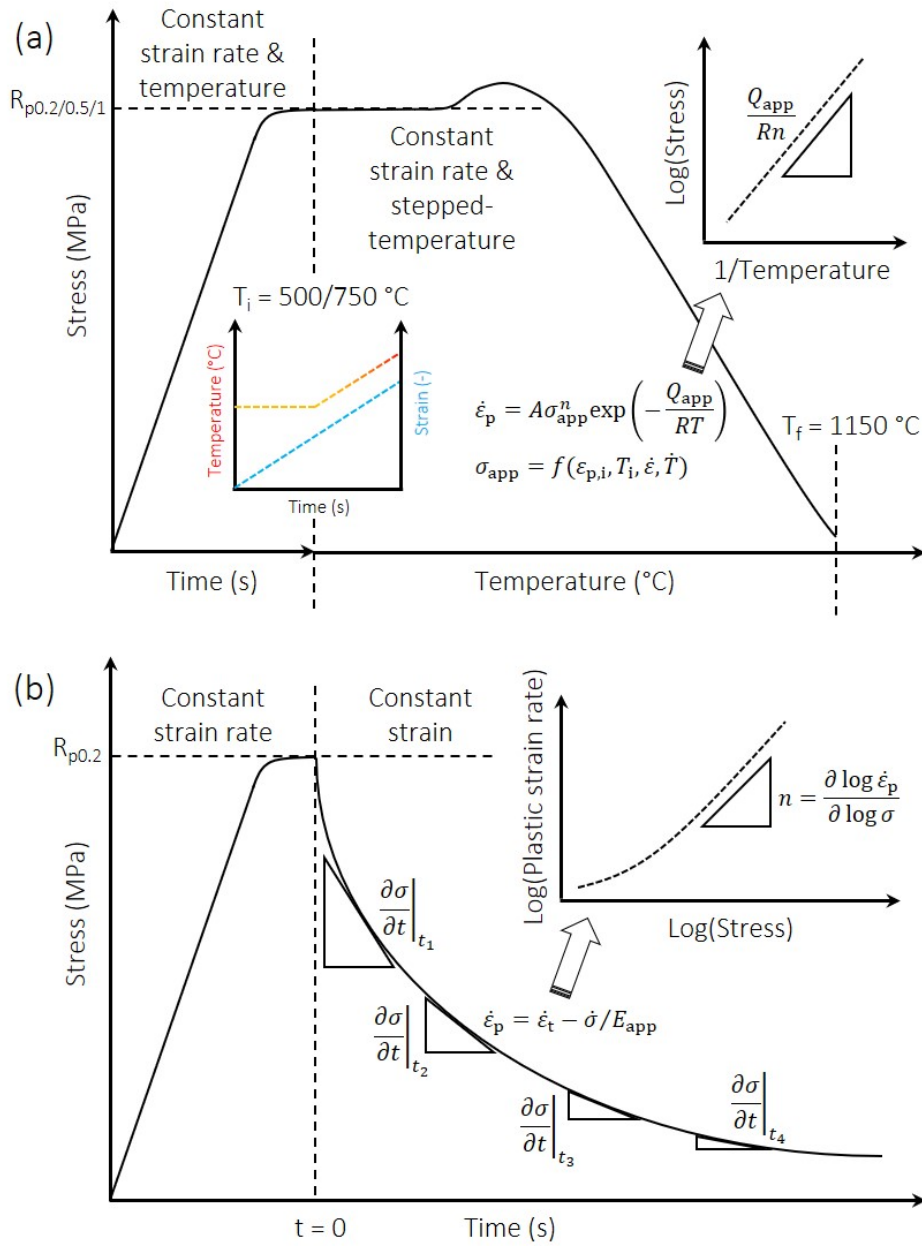


Figure 3.5: Schematic ETMT test methodology for (a) stepped-temperature testing and (b) stress relaxation testing.

in standard tensile tests. This implies that specimen necking can be disregarded and that the apparent flow stress can be calculated as engineering stress. The reason for repeating tests over two different temperature ranges, of 650 °C and 400 °C, was to check whether the level of initial plastic hardening will affect the

deformation behaviour at higher temperatures.

As it is intended that the specimen continues to deform plastically at the prescribed strain rate during temperature ramping, the crosshead speed must be compensated to also account for thermal expansion effects in accordance with:

$$\dot{\epsilon}_t = \dot{\epsilon}_{\text{mechanical}} + \dot{\epsilon}_{\text{thermal}} \quad (3.2)$$

Here, $\dot{\epsilon}_t$ is the total strain rate measured for the specimen, $\dot{\epsilon}_{\text{mechanical}}$ is the strain rate component resulting from the constant crosshead displacement, and $\dot{\epsilon}_{\text{thermal}}$ is the additional strain rate due to thermal expansion and changes in γ' volume fraction. $\dot{\epsilon}_{\text{thermal}}$ was measured for each testing condition in a separate stepped-temperature test at zero load and $\dot{\epsilon}_{\text{mechanical}}$ was adjusted accordingly to yield the desired total strain rate.

All testing conditions for STT are summarised in Table 3.2.

3.2.4 Stress Relaxation Testing (SRT)

Isothermal stress relaxation tests were performed between 650 and 1050 °C at intervals of 100 °C to extract information on creep performance. As illustrated in Figure 3.5(b), specimens are deformed at a constant initial strain rate of approximately 10^{-4} /s until a predefined plastic strain level of 0.2% is reached. This value was chosen following reference [432] in order to achieve a steady-state stress behaviour and to provide a measure of the current creep strength of the alloy. Crosshead displacement is then stopped and held in that exact position under LVDT control. Load relaxation is measured over a period t_R of 20 h, again following reference [432]. Considering the much longer test durations compared to tensile tests or stepped-temperature tests, a larger specimen cross section of $2 \times 2 \text{ mm}^2$ was chosen to ensure that oxidation would not affect mechanical properties. The values for specimen width and thickness were chosen based on extensive experimental and modelling work on creep and oxidation damage in thin-walled specimens [324, 513, 514].

Test system	Specimen cross section	Heating method	Strain measurement method	ΔT (°C)		$\dot{T}$ (°C/s)			$\dot{\varepsilon}$ (s ⁻¹)			$\varepsilon_{p,i}$ (%)		
				500 – 1150	750 – 1150	0.4	2	10	2×10 ⁻⁵	10 ⁻⁴	5×10 ⁻⁴	0.2	0.5	1
Instron ETMT	1×1.1 mm ²	Joule heating	DIC	✗		✗			✗			✗		
				✗			✗			✗		✗		
				✗				✗			✗		✗	
					✗	✗			✗			✗		
					✗							✗		
													✗	
				✗			✗							
				✗			✗						✗	
				✗			✗							✗

Table 3.2: Summary of stepped-temperature tests carried out on the ETMT system.

Comparison tests were carried out for the $\langle 001 \rangle$ direction on cylindrical specimens of 6 mm gauge length and 3 mm diameter using an Instron Electropuls E10000 linear-torsion all-electric system. This testing rig is equipped with a split furnace controlled using a type K thermocouple positioned close to the specimen gauge. For both systems, the DIC method was used to measure strain.

Testing conditions employed for SRT are summarised in Table 3.3.

3.2.5 Verification Testing

A limited number of tensile tests was carried out on each crystallographic orientation for verification purposes and to prove the reliability of the new testing system, as summarised in Table 3.4. Benchmark tests on the Instron ETMT were performed on samples of $1 \times 1.1 \text{ mm}^2$ cross section at 500 °C and an initial strain rate close to $10^{-5}/\text{s}$, and at 750 °C and initial strain rates of 10^{-5} , 10^{-4} , and $10^{-3}/\text{s}$.

Comparison tests were performed under similar conditions at NPL using an in-house ETMT system. As this setup lacks an LVDT sensor for displacement control, tests were carried out at constant loading rates of 0.4, 2, and 10 N/s, which came close to replicating the constant displacement rate conditions for the Instron ETMT. Further validation tests at 750 °C were carried out on regular, cylindrical testpieces of 6 mm gauge length and 3 mm diameter using an Instron 8862 servo-electric system. In this case, the high temperature was achieved with a split furnace arrangement and was controlled with a type K thermocouple positioned close to the specimen gauge.

With regard to strain measurements, the DIC method was used for all tests on the Instron ETMT and the 8862 servo-electric systems. For tests on the NPL ETMT, plastic strain was calculated from resistance measurements, as described in Equation (3.1). The elastic strain component was added separately using temperature-dependent values for the elastic moduli, $E(T)$, calculated from high-temperature dynamic resonance measurements carried out for each individual orientation at NPL. For further details regarding this procedure, the interested reader is directed to references [515–517].

Test system	Specimen cross section	Heating method	Strain measurement method	T (°C)						$\dot{\epsilon}$ (s ⁻¹)	$\epsilon_{p,i}$ (%)	t_R (h)
				650	750	850	950	1050	10 ⁻⁴	0.2	20	
Instron ETMT	2×2 mm ²	Joule heating	DIC	✗	✗	✗	✗	✗	✗	✗	✗	✗
Instron E10000	7.1 mm ²	Furnace	DIC		✗	✗				✗	✗	✗

Table 3.3: Summary of stress relaxation tests carried out on the ETMT and the E10000 systems.

Test system	Specimen cross section	Heating method	Strain measurement method	T (°C)					$\dot{\epsilon}$ (s ⁻¹)		
				500	750	10 ⁻⁵	10 ⁻⁴	10 ⁻³			
Instron ETMT	1 × 1.1 mm ²	Joule heating	DIC	✗		✗					
					✗	✗	✗	✗			✗
NPL ETMT	1 × 1 mm ²	Joule heating	Resistance	✗			✗				
					✗	✗	✗	✗			✗
Instron 8862	7.1 mm ²	Furnace	DIC		✗	✗	✗	✗			✗

Table 3.4: Summary of tensile tests carried out on the Instron and NPL ETMT systems, as well as on the Instron 8862 servo-electric system.

3.3 Results

3.3.1 Verification Tests

Tensile curves at 500 °C are shown in Figure 3.6; comparison is made to duplicate tests on the NPL ETMT system. The results show good agreement for all orientations, however, values of engineering stress in the plastic regime for the $\langle 011 \rangle$ and $\langle 111 \rangle$ directions are slightly higher in the NPL tests. This could be related to the higher strain rate of around 10^{-4} /s corresponding to the chosen constant loading rate of 2 N/s, as opposed to a strain rate of 10^{-5} /s in Instron ETMT tests. Nonetheless, a similar study on alloy CMSX-4 showed that the influence of strain rate only becomes significant above 700 °C and justified differences in flow stress with changes in the off-axis deviation of the test specimens [518]. Considering that specimens tested on the Instron and NPL systems were manufactured from distinct bars and that cross section measurements were carried out independently, some discrepancies caused by crystal orientation and/or sample dimensions cannot be ruled out.

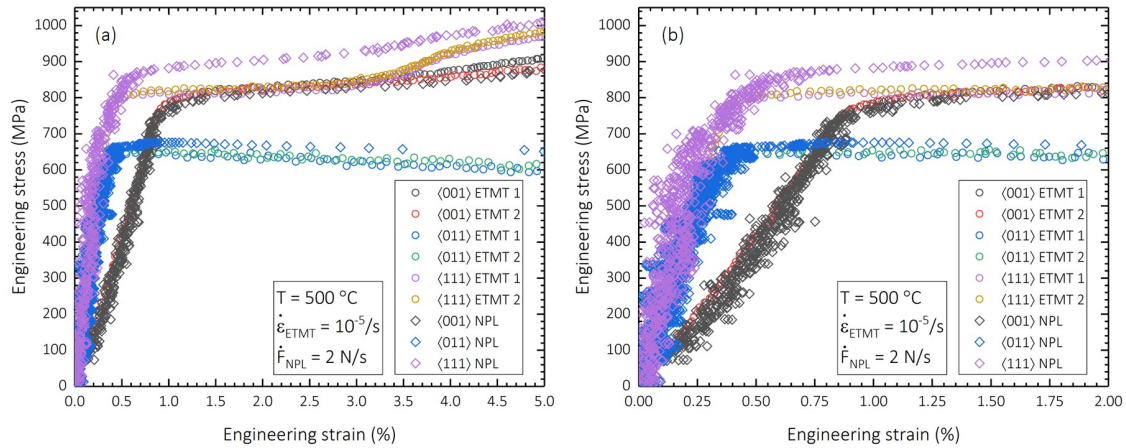


Figure 3.6: Tensile test results at 500 °C from the Instron and NPL ETMT systems. Results are plotted up to (a) 5% engineering strain to provide an overview of the tests and (b) 2% engineering strain to provide a more detailed view of the elastic regime and initial yielding.

Likewise, good agreement is found for tests at 750 °C across all testing conditions, as illustrated in Figure 3.7(a)-(f). Agreement is best at intermediate strain rates of 10^{-4} /s, regardless of crystal orientation. At 10^{-5} /s, tests on the Instron ETMT exhibit lower engineering stress values, most likely due to effects of oxidation over longer

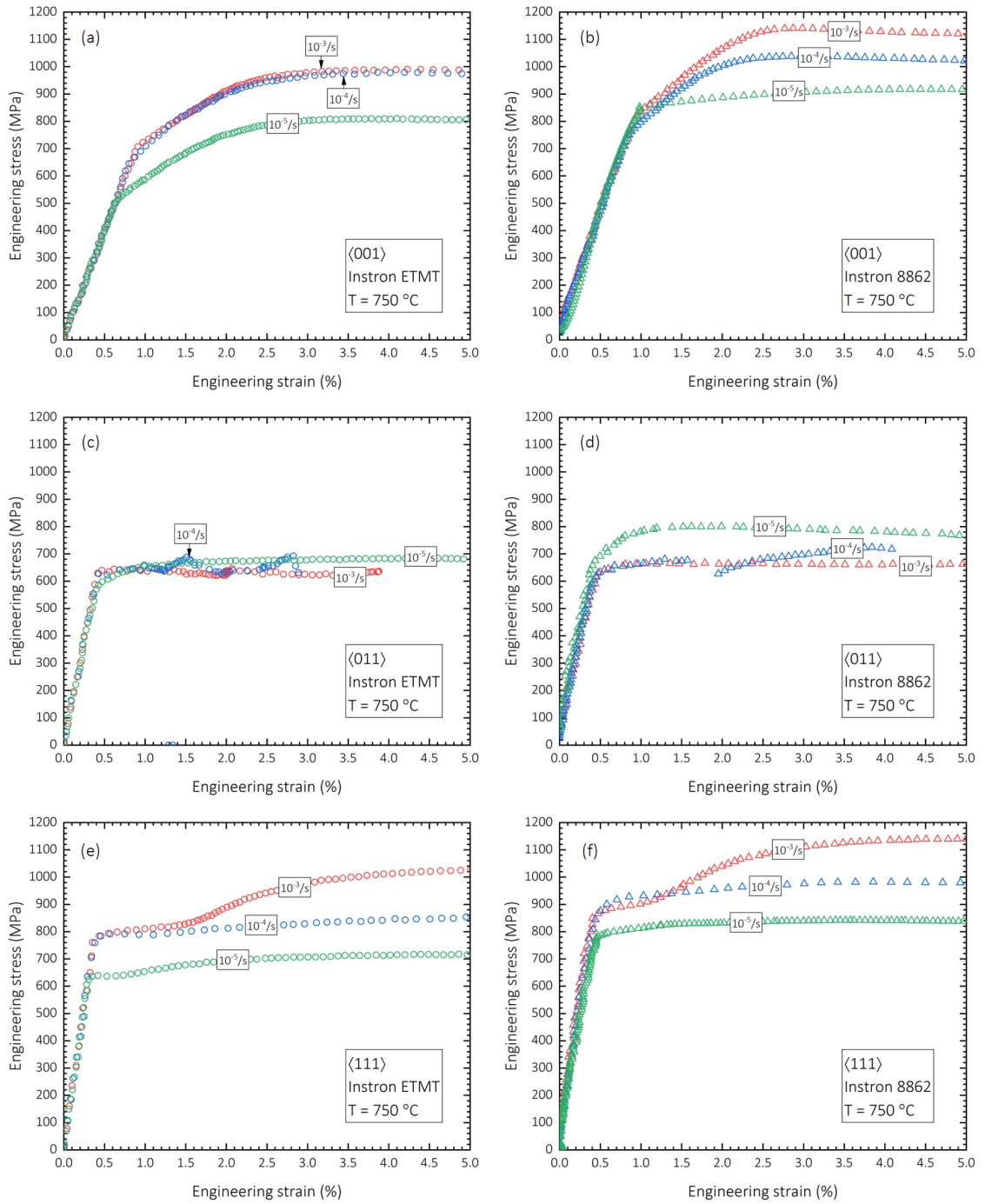


Figure 3.7: Tensile test results at 750 °C from the Instron ETMT and 8862 servo-electric systems presented for the (a&b) <001> direction, (c&d) <011> direction, and (e&f) <111> direction.

testing periods. Oxidation damage in thin-walled specimens is characterised by both (1) a reduction in load-bearing cross section through the formation of a continuous oxide scale and a γ' -denuded zone near the surface and (2) changes in γ' volume

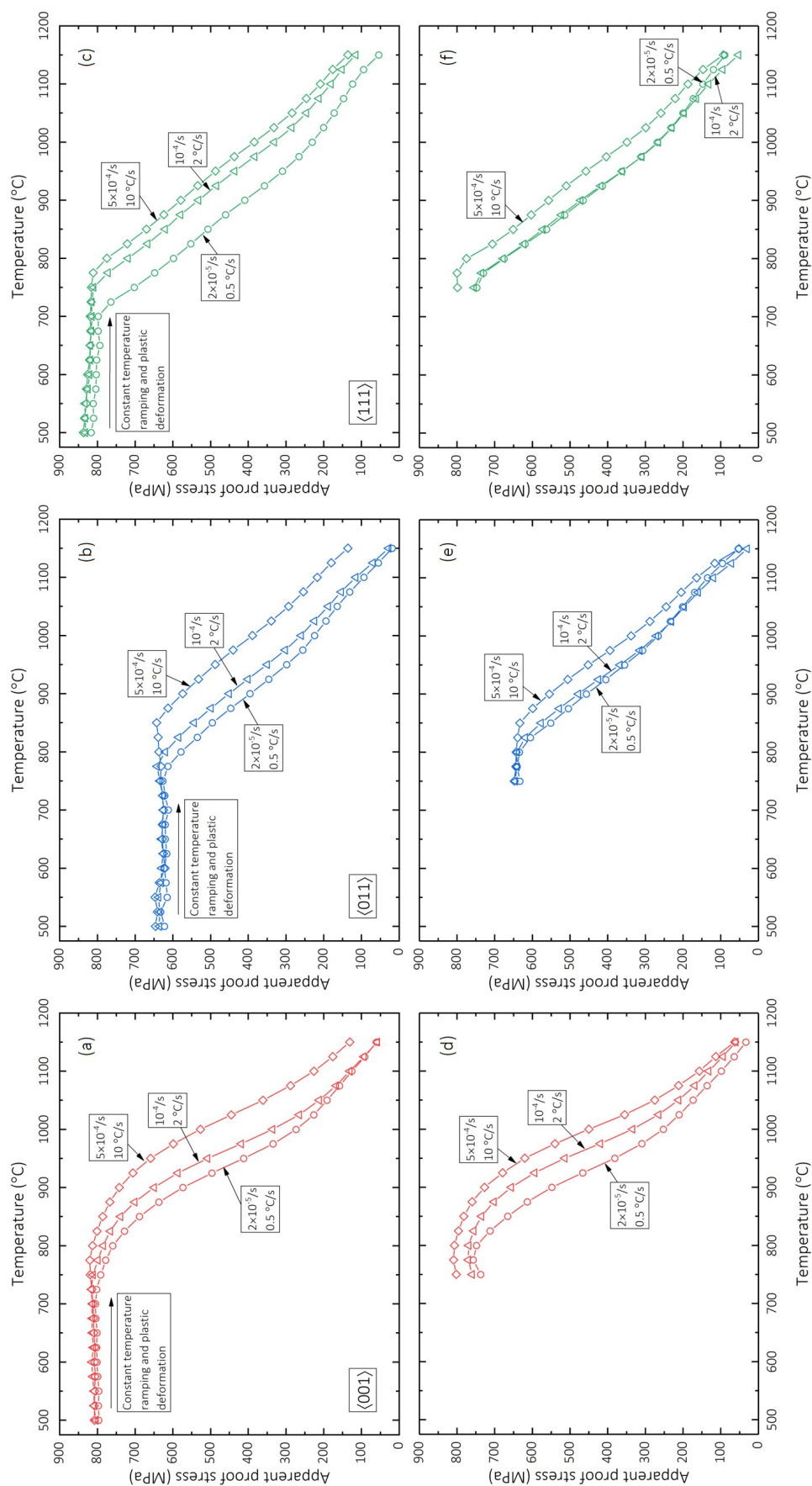
fraction and chemical concentration profiles within the substrate [239, 514]. On the one hand, this highlights the importance of taking into account environmental damage and of carrying out small-scale tests at low strain rates in a protective argon atmosphere if they are to be compared directly to standard tests [508]. On the other hand, this also proves the usefulness of miniaturised ETMT testing for replicating service conditions experienced by thin-walled turbine blade sections. For rapid tests at 10^{-3} /s, verification tests on the 8862 servo-electric system yield higher stress values than ETMT tests in the $\langle 001 \rangle$ and $\langle 111 \rangle$ directions.

3.3.2 Stepped-Temperature Tests

The variation of proof stress with temperature is illustrated as a function of orientation in Figure 3.8(a)-(f) and as a function of deformation rate in Figure 3.9(a)-(f). The ramping step was started after reaching an initial plastic strain of 0.2% at (a)-(c) 500 °C and (d)-(f) 750 °C, in order to compare the effects of prior deformation at lower temperatures on the anomalous yielding effect. One can see that, for all orientations, a peak in the apparent proof stress occurs in the range of 750 to 800 °C. This is in accordance with the results of Shah & Duhl [519] for PWA1480, of Miner et al. [520, 521] for René N4, and of Allan [522] and Bullough et al. [518] for CMSX-4.

Several points emerge from the results presented in Figures 3.8 and 3.9. First, the proof stress is not influenced by strain rate and/or temperature ramping rate until a peak stress has been reached, in agreement with previous experimental and modelling work [518, 523–525]. In this anomalous yielding regime, cross-slip of short dislocation segments from $\{111\}$ to $\{001\}$ glide planes — leading to either small Paidar-Pope-Vitek (PPV) locks or large Kear-Wilsdorf (K-W) locks [237, 526] — is operative. Such cross-slip events are promoted by the anisotropy of both the APB energy and the elastic properties along the $\{111\}$ and $\{001\}$ planes [237].

Second, once the material strength decreases above 750 °C, a higher strength at larger strain rates is observed consistently, in accordance with time-dependent plasticity. The initial decline in proof stress has been commonly related to slip activation on the cube plane by $a/2\langle 110 \rangle$ pairs and, at higher temperatures, by



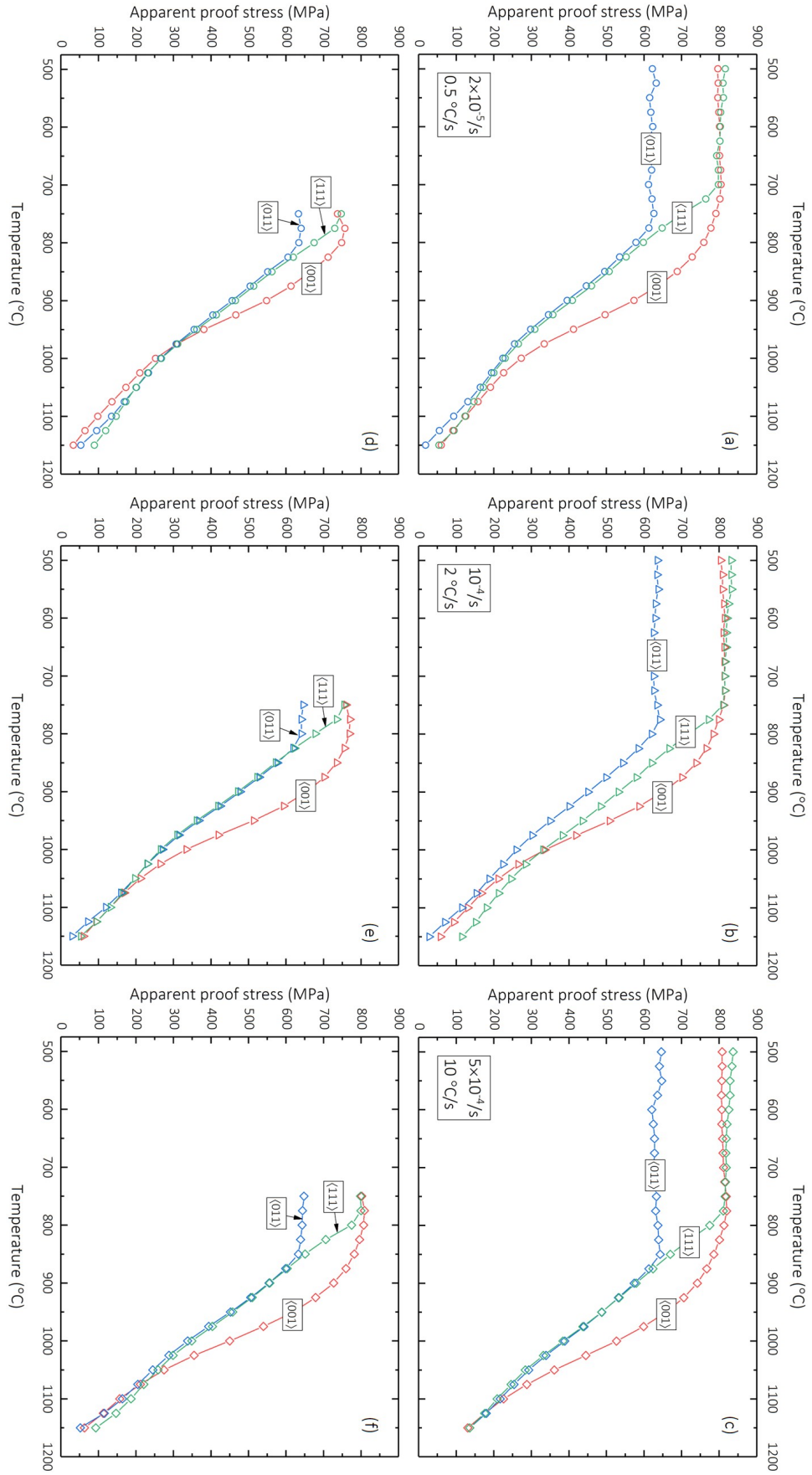


Figure 3.9: STT results for tests carried out at initial strain rates of (a&d) $2 \times 10^{-5}/s$, (b&e) $10^{-4}/s$, and (c&f) $5 \times 10^{-4}/s$.

perfect $a[100]$ single dislocations [237]. Recent studies have identified diffusion-activated plasticity as an additional operating mechanism which could explain the decreasing strength in this temperature regime [527, 528]. A further significant weakening effect at higher temperatures is a decrease in γ' volume fraction, ϕ_p . Calculations using Thermo-Calc and the TTNi8 database predict a decrease from 58% at 600 °C to nearly 0% at 1150 °C, see Figure 3.14(d). The maximum precipitate strength has been estimated to scale with the square root of ϕ_p [111], thus explaining this pronounced drop.

For all tests — and regardless of strain rate — the strength of the $\langle 011 \rangle$ direction is much lower until temperatures of 1000 °C and above are reached, at which point all orientations exhibit similar values of apparent proof stress. This observation is of particular interest, as previous studies [518, 519, 522] reported that yield strength above 750 °C consistently increases from the $\langle 111 \rangle$ to the $\langle 011 \rangle$, and finally to the $\langle 001 \rangle$ orientation. While $\langle 001 \rangle$ remains the direction with the highest strength for the SIT superalloy, there is now a discrepancy between the $\langle 011 \rangle$ and $\langle 111 \rangle$ directions. Proof stress values converge above 800 °C, but, at lower temperatures, the $\langle 111 \rangle$ direction is much stronger than $\langle 011 \rangle$ and even surpasses $\langle 001 \rangle$ below 600 °C. The lower strength of $\langle 011 \rangle$ specimens can be rationalised by the relatively large misorientations observed in Figure 3.1. Recent work on precisely oriented $\langle 011 \rangle$ single-crystal NBSA showed that even small deviations will result in a substantial decrease of high-temperature mechanical properties due to the activation of additional slip systems [529].

Third, the results are nearly identical regardless of whether temperature ramping was initiated at 500 or at 750 °C, thus suggesting that the degree of strain hardening imposed at lower temperatures does not substantially alter the estimated flow stress. Nonetheless, to study the influence of pre-straining on measured stress values in greater detail, tests at an initial constant temperature of 500 °C were repeated while varying the plastic strain level before ramping from 0.2% to 0.5% and 1%. As shown in Figure 3.10(a)-(c), this has little effect on the proof stress in the plateau region, in agreement with previous reports [518, 523–525]. In the high-temperature

regime, the influence of initial plastic strain and of the accumulated total strain level is unclear and there are differences in the responses of the three orientations. While for $\langle 001 \rangle$ and $\langle 111 \rangle$ the strength decreases with increasing initial strain, for $\langle 011 \rangle$ the results are almost identical for initial plastic strain levels of 0.2% and 0.5% and the strength is higher above 800 °C in the specimen pre-strained up to 1%. It can be concluded that, if a fair comparison is to be made, the level of pre-straining should be carefully controlled and maintained constant across all tests.

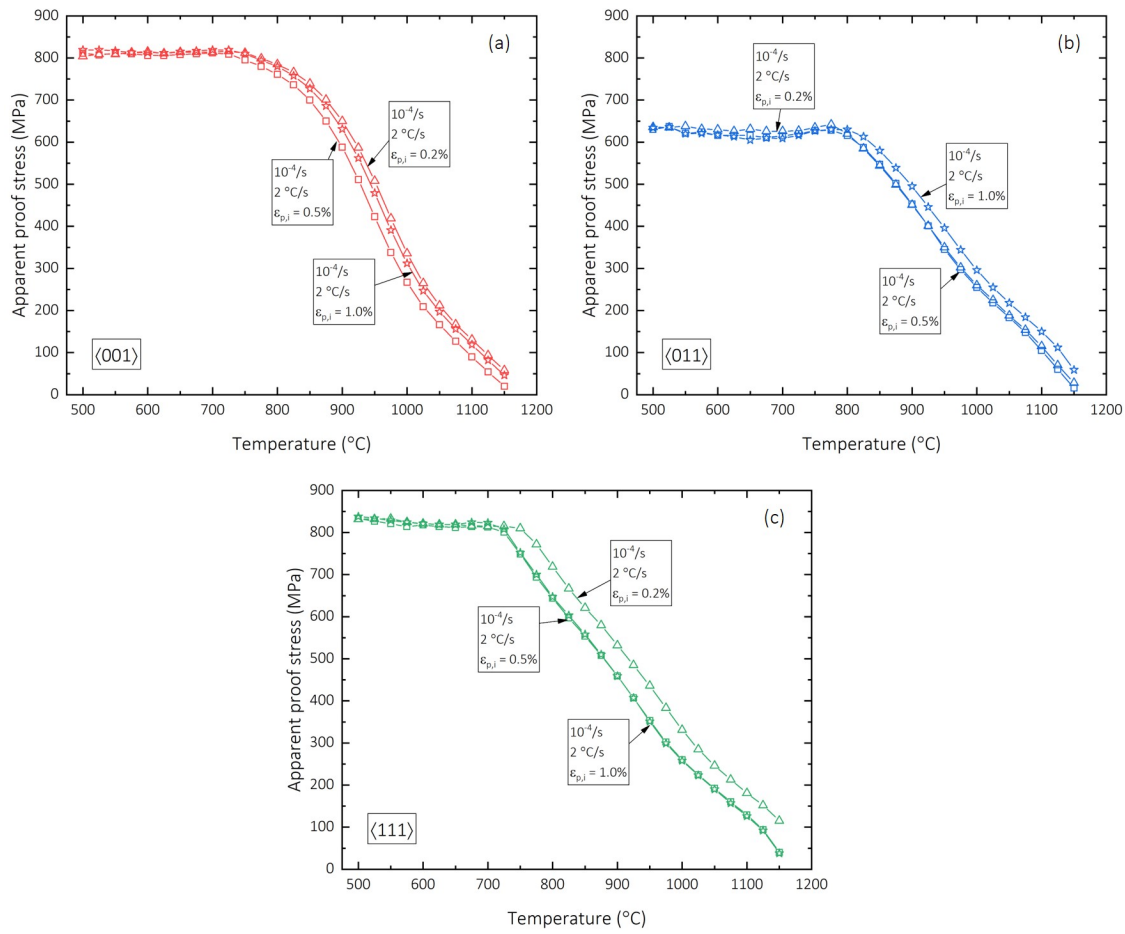


Figure 3.10: STT results from tests in which the temperature ramping step was started at different initial plastic strain levels of 0.2%, 0.5%, and 1%. Results are shown separately for the (a) $\langle 001 \rangle$ direction, (b) $\langle 011 \rangle$ direction, and (c) $\langle 111 \rangle$ direction.

Finally, it has been found that STT curves can be analysed at temperatures beyond those associated with a maximum in the apparent flow stress to extract an estimate of the apparent activation energy, as shown schematically in Figure 3.5(a). For this, it is assumed that deformation rates of 2×10^{-5} and 10^{-4} /s are slow enough

for a steady-state condition to be approached at each temperature level during the ramping segment. Estimates of the steady-state creep rate, $\dot{\epsilon}_s$, can then be expressed as:

$$\dot{\epsilon}_s = A\sigma_{\text{app}}^n \exp\left(-\frac{Q_{\text{app}}}{RT}\right) \quad (3.3)$$

where A is a material-specific constant, n is the stress exponent, R is the gas constant, σ_{app} is the measured apparent proof stress, and Q_{app} is the apparent activation energy. Equation (3.3) can be rearranged to yield a plot of $\ln(\sigma_{\text{app}})$ vs. $1/T$, in which the slope will be equal to Q_{app}/Rn . Results of this analysis are shown for the three crystal directions in Figure 3.11(a)-(c). The dashed lines used to extract estimates for Q_{app} were fitted to experimental data from lower strain rate tests.

Qualitative results confirm that resistance to high-temperature creep deformation increases from the $\langle 011 \rangle$ to the $\langle 111 \rangle$, and finally to the $\langle 001 \rangle$ direction. Quantitative values are obtained assuming a constant stress exponent of 8 for this range of strain rates and temperatures, chosen based on the SRT results presented in Figure 3.13. This leads to apparent activation energies of 1028, 620, and 631 kJ/mol, respectively. In normalised terms, these figures correspond to $75.9RT_m$, $45.8RT_m$, and $46.5RT_m$, with the melting temperature T_m of 1630 K predicted by Thermo-Calc. Activation energies must be considered carefully, as they are directly influenced by the chosen stress exponent, which in turn corresponds to an apparent, extrapolated value rather than an effective, physically based one [320, 530]. Nonetheless, these figures are in fair agreement with the value of $41RT_m$ reported by Carey & Sargent [531] for IN-738LC and that of $53.3RT_m$ obtained by Sajjadi & Nategh [532] for GTD-111 in this regime.

3.3.3 Stress Relaxation Tests

SRT has been used to rapidly assess material performance in different creep regimes with regard to levels of applied stress and temperature, building on efforts made elsewhere [434–436, 438]. As discussed in Section 2.2.2, this method represents a paradigm shift away from attempting to re-create microstructural damage evolution, as done in a regular creep test [432]. Several recent studies have made use of SRT

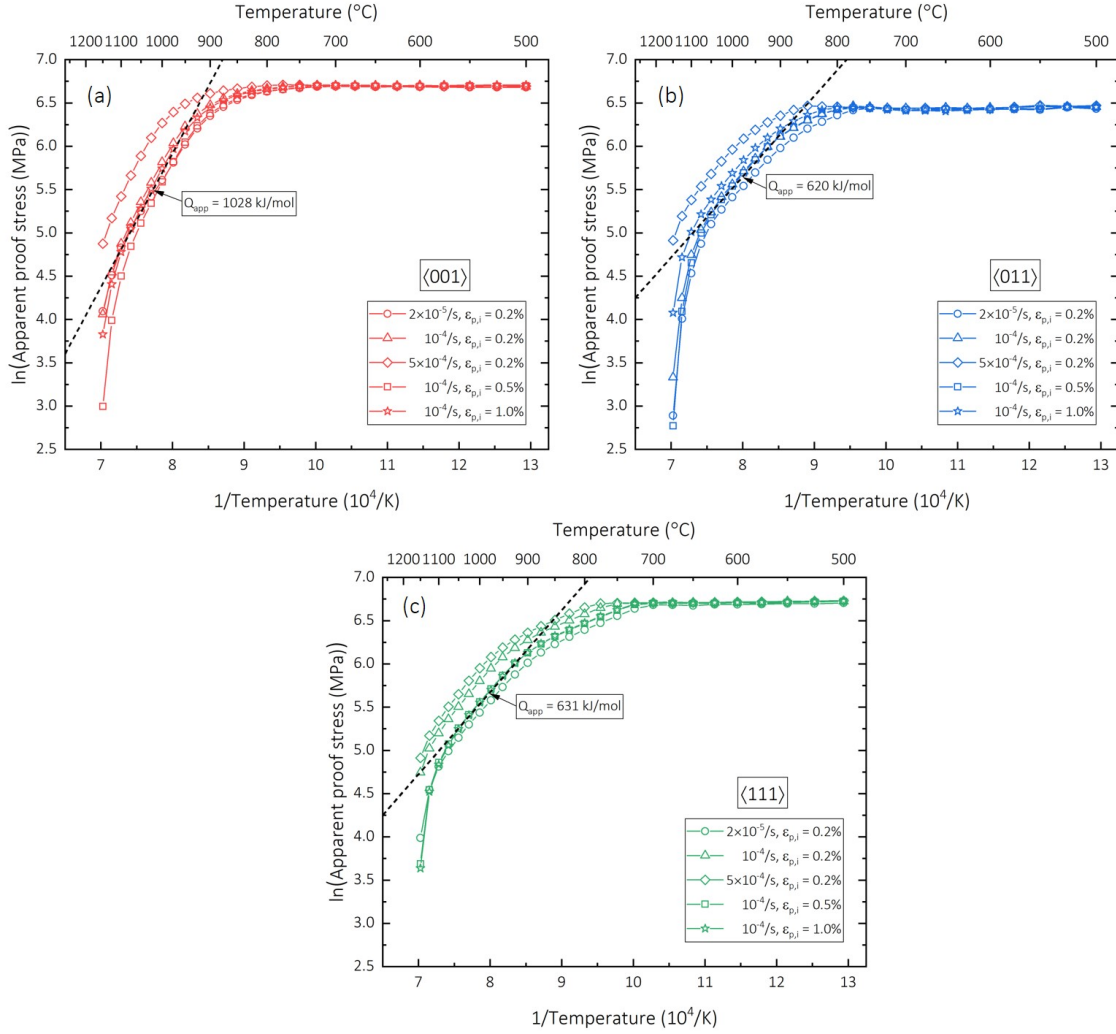


Figure 3.11: Apparent activation energies extracted from STT between 850 and 1150 °C for the (a) $\langle 001 \rangle$ direction, (b) $\langle 011 \rangle$ direction, and (c) $\langle 111 \rangle$ direction. Estimates were obtained by fitting the dashed lines to experimental data from lower strain rate tests.

for the mechanical characterisation of superalloys and have shown results consistent with conventional creep data from the literature, thus enabling accelerated testing campaigns of new alloys [439, 441, 442].

Here, in common with such approaches, it is assumed that the total strain rate of the system remains in equilibrium while the crosshead displacement is fixed, consistent with:

$$\dot{\epsilon}_t = \dot{\epsilon}_p + \dot{\epsilon}_e + \dot{\epsilon}_m = 0 \quad (3.4)$$

where $\dot{\epsilon}_t$, $\dot{\epsilon}_p$, and $\dot{\epsilon}_e$ are the total, the plastic, and the elastic strain rates of the

specimen and $\dot{\epsilon}_m$ is the elastic strain rate of the testing apparatus. Plastic strain rate can then be expressed following reference [533] as:

$$\dot{\epsilon}_p = -\frac{\dot{\sigma}}{E} - \frac{A\dot{\sigma}}{Lk_m} = -\frac{\dot{\sigma}}{E_{app}} \quad (3.5)$$

where $\dot{\sigma}$ is the change in stress with time during load relaxation and E_{app} is the apparent modulus of the material. The latter can be calculated using E as the elastic modulus, A as the sample cross section, k_m as the stiffness of the machine, and L as the specimen gauge length. Although k_m is initially unknown, it can be estimated by analysing elastic data obtained during loading and/or unloading [432, 533].

As load relaxation occurs across the entire ETMT specimen and not only in the central high-temperature region, slight changes in total strain cannot be avoided. Here, these have been measured with DIC in the central 3 mm of the specimen to provide a correction for Equation (3.5), yielding $\dot{\epsilon}_p = \dot{\epsilon}_t - \dot{\sigma}/E_{app}$. Applying this correction has been found to be especially important for the first minutes of relaxation, during which the ETMT apparatus contracts elastically as the applied load decreases. Longer-term SRT results are not affected by the finite stiffness of the load frame and corrections to Equation (3.5) are minimal [533].

Curves of applied stress over plastic strain rate are presented on double-logarithmic plots in Figure 3.12(a)-(d). Noticeable changes in gradient occur at intermediate strain rates, giving the curves a characteristically sigmoidal shape.

By using the approach illustrated in Figure 3.5(a), the apparent stress exponent, n , can be obtained as a function of the logarithmic values of stress, σ , and plastic strain rate, $\dot{\epsilon}_p$:

$$n = \left. \frac{\partial \log \dot{\epsilon}_p}{\partial \log \sigma} \right|_{\epsilon, T} \quad (3.6)$$

for given values of total strain and temperature. Applying this equation locally to segments of the stress vs. strain rate curves allows contour maps to be derived for the apparent stress exponent at strain rates between 10^{-5} and 10^{-9} /s and temperatures between 650 and 1050 °C, as shown in Figure 3.13(a)-(c). These can be regarded

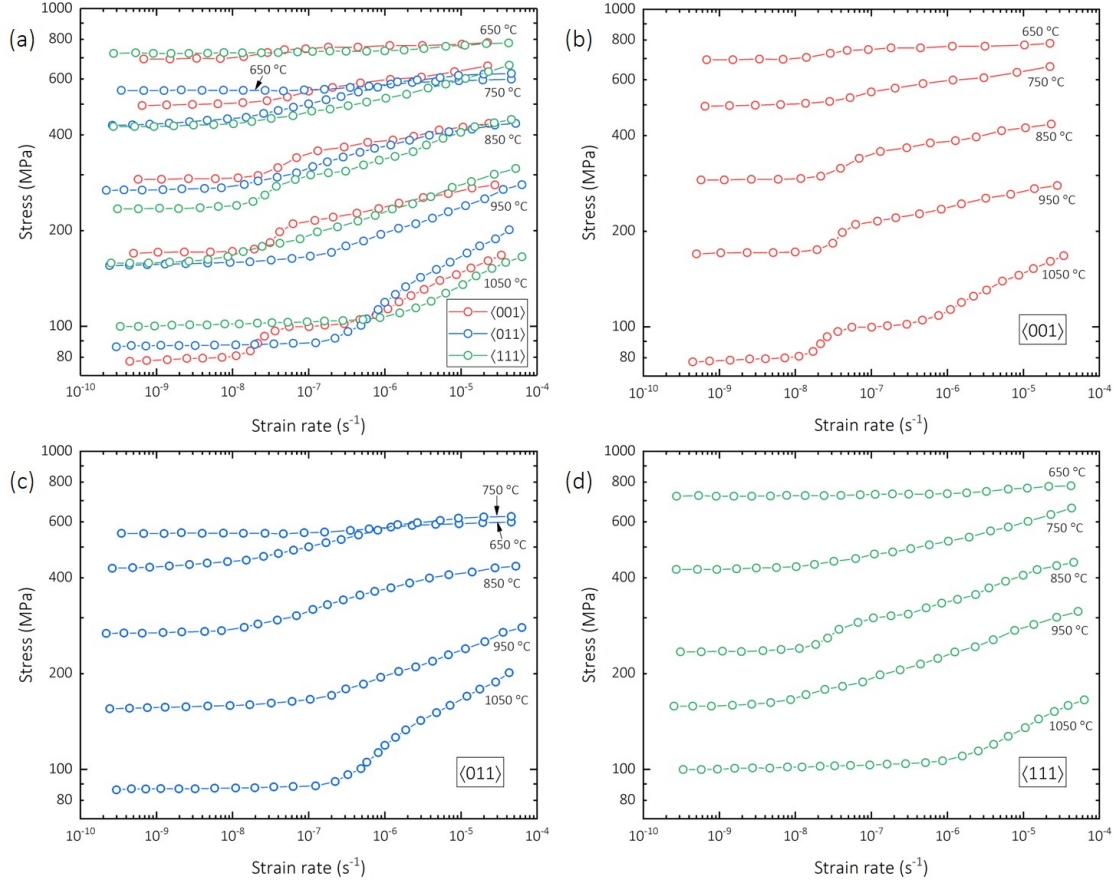


Figure 3.12: Double-logarithmic plots of strain rate over applied stress extracted from SRT between 650 and 1050 °C. A comparison of all results is shown in (a). SRT data are then presented separately for the (b) $\langle 001 \rangle$ direction, (c) $\langle 011 \rangle$ direction, and (d) $\langle 111 \rangle$ direction. Arrows identify testing temperatures when lines are overlapping.

as Ashby-type high-temperature deformation mechanism maps and can be rapidly constructed using the present ETMT-based approach.

An initial decrease in the apparent stress exponent has been observed for tests performed above 750 °C at strain rates between 10^{-6} and 10^{-8} /s. This occurs earlier in the test, i.e. at higher strain rates, as the temperature increases. Similar behaviour has been reported by Nathal et al. [442] for the first-, second-, and fourth-generation single-crystal superalloys, NASAIR 100, CMSX-4, and EPM-102. These authors showed that the effect disappears if specimens are crept prior to stress relaxation, as the pre-rafterd microstructure offers higher resistance to primary creep. As such, this transition can be related to a shift from primary creep deformation, dominated by APB shearing of γ' precipitates, to tertiary creep, dominated by dislocation climb

bypass. Transition stress values at different temperatures are in accordance with the deformation mechanism maps for NBSA proposed by Smith et al. [534] and Barba et al. [511]. No transition is clear at 650 °C, probably because this temperature is too low to enable diffusional climb around the precipitates.

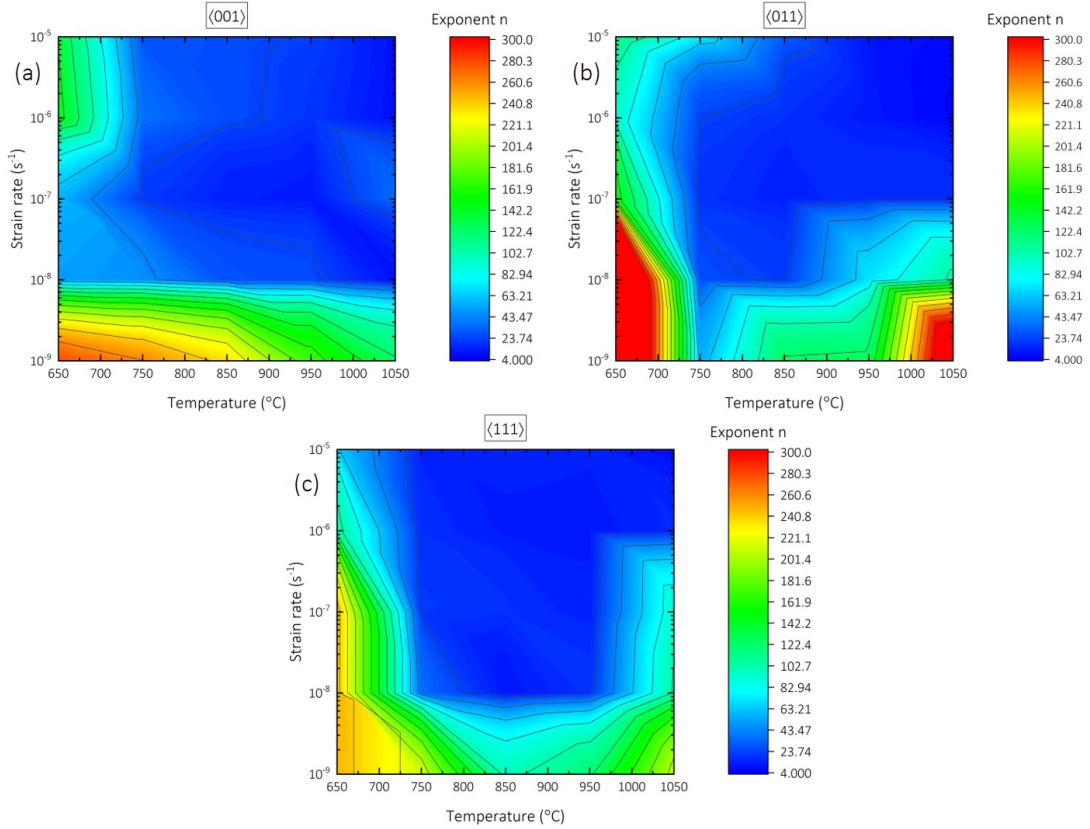


Figure 3.13: Contour maps of the apparent stress exponent as a function of temperature and strain rate for the (a) $\langle 001 \rangle$ direction, (b) $\langle 011 \rangle$ direction, and (c) $\langle 111 \rangle$ direction. Quantitative values are shown next to the colour bars. Minimum and maximum values were manually set to 4 and 300 and 16 linearly distributed major levels were generated in between. Dark grey lines mark the limits of individual major levels.

Values of apparent stress exponents associated with primary and tertiary creep decrease with increasing temperature. This reduction has been shown to be related to the directional coarsening of precipitates at higher temperatures [442]. It should be noted that these figures cannot be readily compared to effective stress exponents used in creep models, as explained by Carry & Strudel for both primary [530] and tertiary creep [320]. Discrepancies between apparent and effective exponents were also confirmed by the experimental results of Dupeux et al. from stress relaxation

[533] and conventional creep tests [535] on alloy CMSX-2. At strain rates below 10^{-8} /s, apparent stress exponents show a significant rise, with values that can no longer be rationalised by any type of high-temperature deformation mechanism. As opposed to a standard creep test, the driving force for directional coarsening and creep strain accumulation decreases with time during SRT and exceedingly tends towards zero. Nathal et al. [442] observed no further microstructural changes when comparing specimens relaxed at 982 °C for 100 and 370 h. As such, once a steady-state stress value has been reached, the results from SRT are increasingly affected by mechanical noise and provide little further insight into high-temperature damage accumulation mechanisms.

SRT data can also be presented in the form of stress/temperature deformation mechanism maps, following Frost & Ashby [311]. The resulting maps shown in Figure 3.14(a)-(c) provide a means of visualising material performance in different deformation regimes and of comparing normalised results to data from the literature [531, 532].

As discussed by Frost & Ashby [311], any deformation mechanism can be described by a rate equation of the form:

$$\dot{\gamma} = f(\tau, T, S_i, P_j) \quad (3.7)$$

This relates the shear strain rate, $\dot{\gamma}$, to shear stress, τ , temperature, T , a set of i state variables, S_i , which describe the current microstructural state of the material, and a set of j material properties, P_j , which are inherent to the material. Key simplifying assumptions are that steady-state conditions are reached during deformation and that material properties and state variables either remain constant or are directly determined by τ and/or T . This leads to a reduction of Equation (3.7) to $\dot{\gamma} = f(\tau, T)$.

In order to construct maps following the approach of Frost & Ashby, the tensile stress/strain data from Figure 3.12 are first converted to shear stress/strain. Geometrical transformation factors are chosen based on the work of Ghosh et al. [536],

who modelled the crystallographic anisotropy of tensile creep deformation in single-crystal superalloys. These authors assumed that macroscopic creep deformation results from glide on both the $\{111\}\langle\bar{1}01\rangle$ and $\{001\}\langle110\rangle$ systems, while neglecting macroscopic contributions from $\{111\}\langle\bar{1}\bar{1}2\rangle$ slip vectors. Their work contains an in-depth discussion on the predicted number of active slip systems and their respective Schmid factors, leading to geometrical conversions for each orientation [536].

In a second step, shear stress and temperature values are normalised with respect to the shear modulus and the melting temperature. The aforementioned value of 1630 K predicted by Thermo-Calc and the TTNi8 database for T_m is used to calculate the homologous temperature, see Figure 3.14(d). Values for temperature-dependent shear moduli, $G(T)$, were obtained for each individual orientation from high-temperature dynamic resonance measurements at NPL. These are the same assessments mentioned in Section 3.2.5 in the context of measuring temperature-dependent elastic moduli, $E(T)$, for each orientation.

As suggested by Frost & Ashby, data points in Figure 3.14 are labelled with the value of the third macroscopic variable, in this case $\log(\dot{\gamma})$. The red dashed lines represent contours of constant shear strain rate based on data between 750 and 1050 °C. The solid green lines divide fields dominated by power law creep, diffusion creep, and low-temperature plasticity controlled by dislocation glide. These boundaries were reported by Frost & Ashby for Mar-M200 material with a large grain size of around 1 cm, meaning they can be used as estimates for the behaviour of directionally solidified or single-crystal material [311] and can offer a benchmark for the SIT superalloy. A further power law breakdown regime, dominated by APB shearing of γ' precipitates, can be inferred in the upper left corner of the maps and would include data at 650 °C. The lower limit of this area is estimated at around $10^{-3}G$ [311].

A direct comparison of constant strain rate lines suggests that the SIT superalloy does not match the creep resistance of Mar-M200. This can be explained by considering chemical compositions and the phase diagrams in Figure 3.14(d). First, the level of precipitation strengthening is higher in Mar-M200, as the γ' phase

fraction remains approximately 10% above that of the SIT alloy across the entire temperature range. Second, the level of solid solution strengthening is higher in Mar-M200, as it contains 12.5 wt.% tungsten as opposed to 1 wt.% molybdenum and 4 wt.% tungsten in the SIT alloy. Furthermore, the slow-diffusing tungsten and molybdenum atoms are predicted to partition preferentially to the γ matrix, meaning their relative contribution will be even stronger in Mar-M200 due to its lower γ fraction.

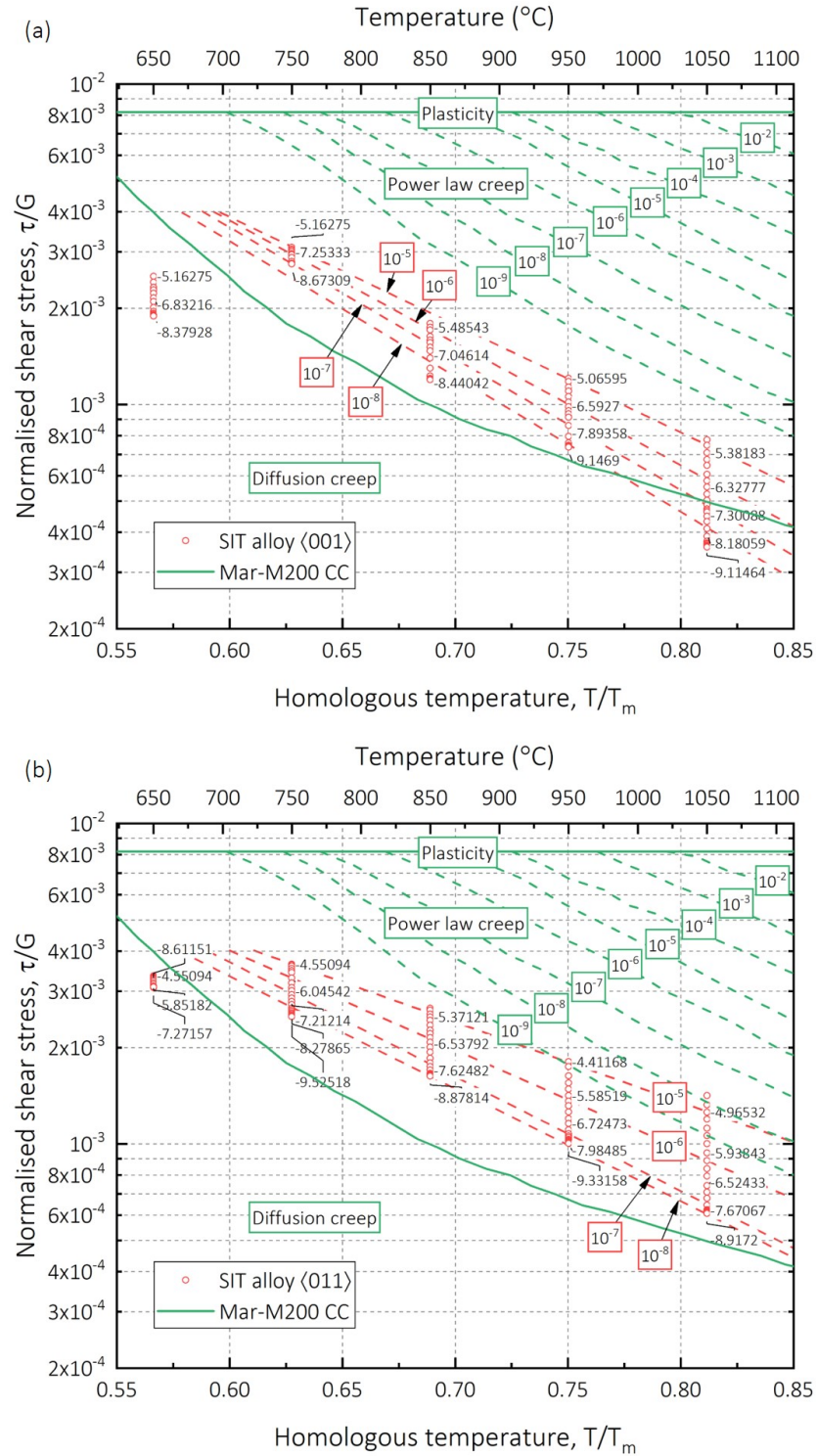


Figure 3.14: Stress/temperature deformation mechanism maps for material deformed along the (a) $\langle 001 \rangle$ direction, (b) $\langle 011 \rangle$ direction, and (c) $\langle 111 \rangle$ direction. Contours of shear strain rate are given in s $^{-1}$. Field boundaries reported by Frost & Ashby [311] for conventionally cast Mar-M200 material are added for comparison. The plot in (d) shows changes in γ , γ' , and liquid phase fractions for the SIT superalloy and Mar-M200, as predicted by Thermo-Calc and the TTNi8 database.

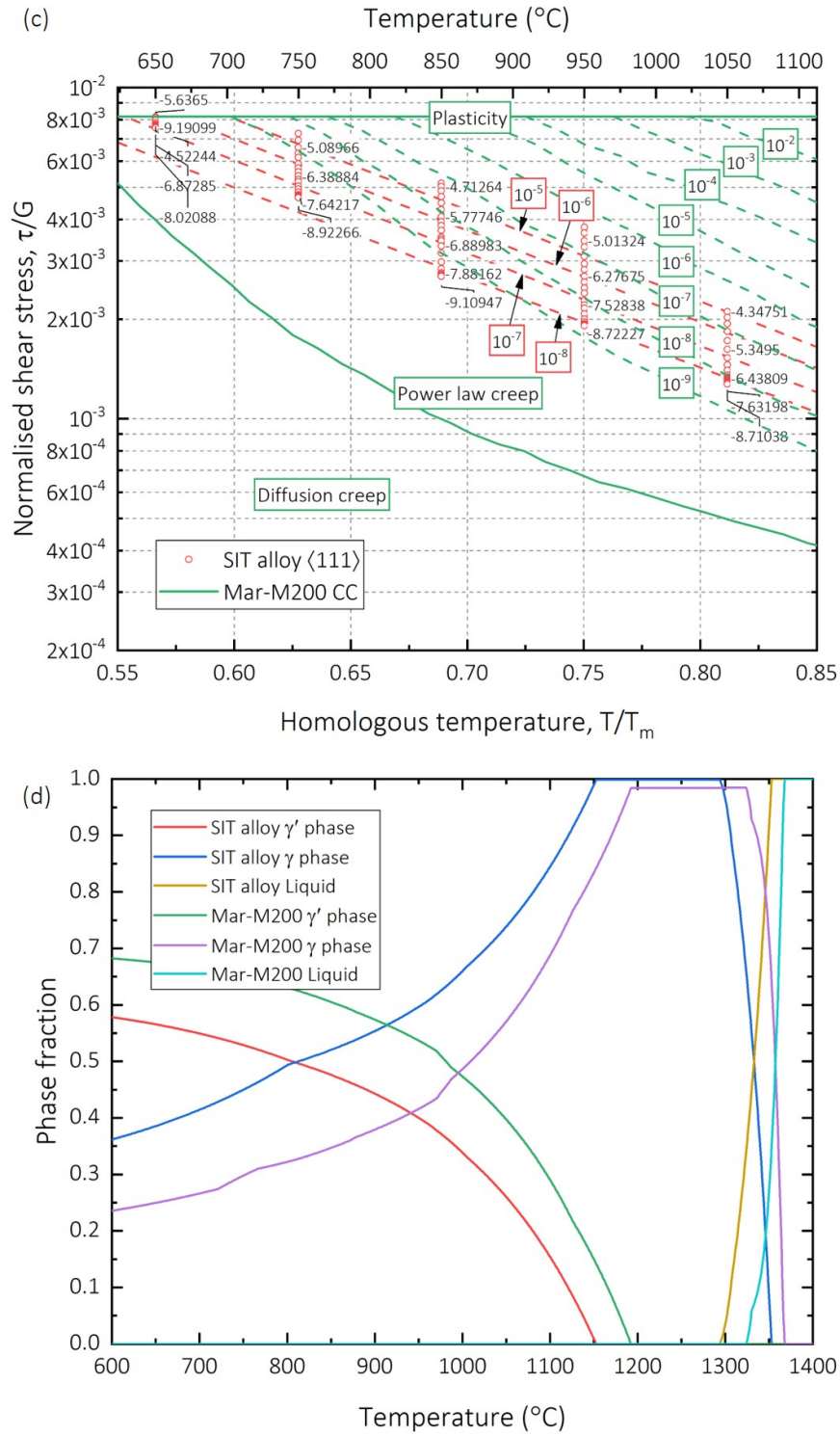


Figure 3.14: (continued)

3.4 Discussion

3.4.1 Validity and Limitations of the ETMT System

In this work, it has been demonstrated that the ETMT offers substantial practical advantages associated with testpiece miniaturisation. Nevertheless, a critical issue concerns whether results are comparable to those obtained from established techniques which are regarded as more standardised. In particular, one should be concerned with (1) real size effects — such as the effect of oxidation damage at low strain rates — and (2) potential errors and increased data scatter arising from sub-scale testing.

In this context, several generic issues have been identified [500, 501]. First, a minimum representative material volume must be sampled. This is less of an issue for the case of single-crystal specimens; however, it poses a significant challenge for testing polycrystalline materials with grain sizes on the order of the testpiece dimensions. Second, there is an increased probability that small defects or heterogeneities will affect bulk material response. Considering the good quality of the castings, which exhibit low levels of porosity and reduced segregation after heat treatment, this point is not deemed to be critical. Third, test specimens must be carefully manufactured and mechanically finished to reduce the possibility of surface residual stresses or re-cast layers influencing the results. Preparation steps taken to avoid this are described in Section 3.2.1. Last, uncertainties associated with measurements of load (stress), temperature, and strain must be critically assessed. The effect of temperature heterogeneity along the sample and the accuracy of DIC strain measurements are discussed in the following. Potential errors in load are not considered, as the 5 kN load cell was calibrated against a reference before the testing campaign.

3.4.1.1 Modelling of the Temperature Distribution in ETMT Specimens

Previous ETMT studies [494, 508, 512] have reported a uniform temperature distribution in the central 2–4 mm of the specimen. However, these observations

are based on limited experimental results and lack validation by modelling. This issue is considered in more detail here.

For a given material volume containing a heat source, the temperature distribution $T(x, y, z, t)$ — depending on three spatial variables (x, y, z) and the time variable t — can be expressed by the heat equation:

$$C_p \rho \frac{\partial T}{\partial t} - k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) = \dot{q}_v \quad (3.8)$$

Here, C_p is the specific heat capacity, ρ is the mass density of the material, k is the thermal conductivity, and $\dot{q}_v$ represents the volumetric heat source. Two assumptions are made at this point to simplify the integration of Equation (3.8).

First, a steady state case is considered in which the heat equation is time-independent, so that $\partial T / \partial t = 0$. For temperature or current control, the Instron ETMT system uses a high bandwidth 8800 servo-hydraulic controller with a maximum internal acquisition and control loop sampling rate of 10 kHz. This high bandwidth enables fast and accurate control even when large heating or cooling rates are required [512]. With well-tuned PID control parameters, the system shows an immediate response to changes in the command channel, as well as very good long-term stability. As such, steady state conditions are a reasonable assumption, even in the case of stepped-temperature tests.

Second, the heat equation is treated as a one-dimensional problem, in which the temperature only varies along the tensile axis of the specimen, chosen here as the x spatial coordinate, as shown in Figure 3.15. While the temperature will also vary across the width and thickness of the testpiece, relative differences are much smaller than along the tensile axis. Equation (3.8) can now be simplified to:

$$-k \left(\frac{\partial^2 T}{\partial x^2} \right) = \dot{q}_v \quad (3.9)$$

An additional negative term of the form $-\mu T$ could be added to Equation (3.9) to account for radiative heat loss to the immediate environment. However, it is assumed here that cooling rates are primarily determined by the thermal diffusivity of the specimen and by heat loss to the water-cooled grips and that radiation can

be neglected. While this final assumption is incorrect at very high temperatures, it should not have a significant impact on modelling results for temperatures below 1100 °C [512].

The volumetric heat source $\dot{q}_V$ for a certain portion of the testpiece volume can be described using Joule's first law and Ohm's law as:

$$\dot{q}_V = \frac{P_{el}}{\Delta V} = \frac{I^2 R}{\Delta x A} = \frac{I^2 \rho}{A^2} \quad (3.10)$$

where P_{el} is the power converted from electrical to thermal energy in a volume element ΔV , I is the current travelling through the testpiece, R is the electrical resistance, ρ is the electrical resistivity, and A is the specimen cross section.

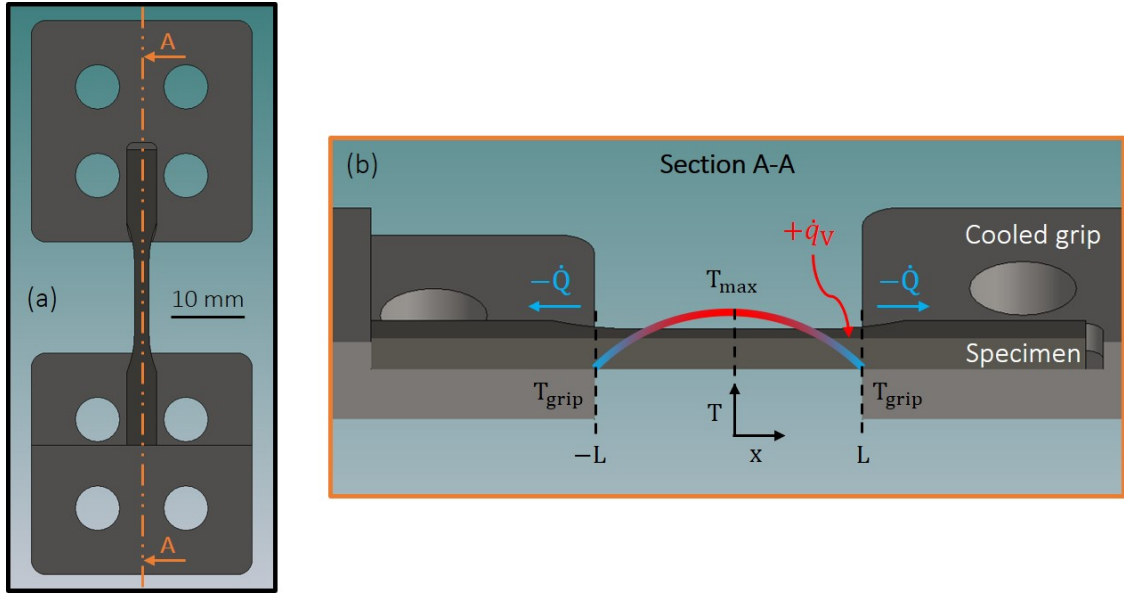


Figure 3.15: (a) CAD-derived drawing of a gripped ETMT specimen. (b) Schematic representation of heat conduction in an ETMT specimen with heat generation from Joule heating.

The boundary condition necessary to solve Equation (3.9) uniquely is that the temperature at both gripped ends, $T(\pm L) = T_{grip}$, remains constant during testing. This yields the one-dimensional temperature distribution:

$$T(x) = \dot{q}_V \frac{L^2}{2k} \left(1 - \frac{x^2}{L^2} \right) + T_{grip} = \left(\frac{I}{A} \right)^2 \frac{L^2}{2} \left(1 - \frac{x^2}{L^2} \right) \frac{\rho}{k} + T_{grip} \quad (3.11)$$

It can be seen that the temperature scales with the square of the applied current over the specimen cross section. The term T_{grip} has been measured during testing at high temperatures and remains constant at around 80 °C. For the case of the larger ETMT testpiece geometry chosen for stress relaxation tests, A is equal to 4 mm² and L to 7.5 mm.

The two remaining material parameters — electrical resistivity, ρ , and thermal conductivity, k — both depend on chemical composition and on temperature, thus requiring a discrete solution of Equation (3.11). Considering that the same master heat was used to cast all the bars, it is anticipated that the temperature distribution will not depend on the crystal orientation. Several extensive studies have discussed the measurement and calculation of thermophysical properties of superalloys [537–540]. In the present work, results obtained for the second-generation single-crystal superalloy CMSX-4 at temperatures between 298 and 1550 K are used as estimates for the SIT superalloy [538]. Data for $\rho(T)$ and $k(T)$ are fitted using a cubic and a linear equation, respectively, as shown in Figure 3.16(a):

$$\begin{aligned}\rho(T) &= 9.06032 \times 10^{-7} + 1.88864 \times 10^{-9}T - 1.55977 \times 10^{-12}T^2 \\ &\quad + 3.53139 \times 10^{-16}T^3 \quad [\Omega\text{m}] \\ k(T) &= 3.50617 + 0.01909T \quad \left[\frac{\text{W}}{\text{mK}} \right]\end{aligned}\tag{3.12}$$

The applied current, I_{app} , is registered during testing. However, due to previous imprecise assumptions and estimates, the temperature calculated for the centre of the specimen using I_{app} in Equation (3.11) does not exactly match T_{max} . As such, a current correction parameter, I_{corr} , is introduced to ensure that $T(0) = T_{\text{max}}$.

Modelling results for the distribution of temperature, electrical resistivity, and thermal conductivity in ETMT specimens between 500 and 1200 °C are shown in Figure 3.16(b)-(d). Qualitative and quantitative results are in good agreement with previous findings [494, 508]. The section of the testpiece at $T_{\text{max}} \pm 5$ °C decreases with increasing temperature. It is predicted to have a length of 1.7 mm at 700 °C and of 1.56 mm at 900 °C, close to the experimentally determined values of 2.4 mm

and 2.2 mm, respectively, for the disc superalloy RR1000 [508]. Modelling predicts that the central 3-mm region observed for DIC strain measurements remains at a reasonably uniform temperature of $\pm 15^\circ\text{C}$. These results represent an important validation of the temperature distribution in ETMT specimens and they furthermore highlight the significance of precise, localised strain measurements in the hot zone.

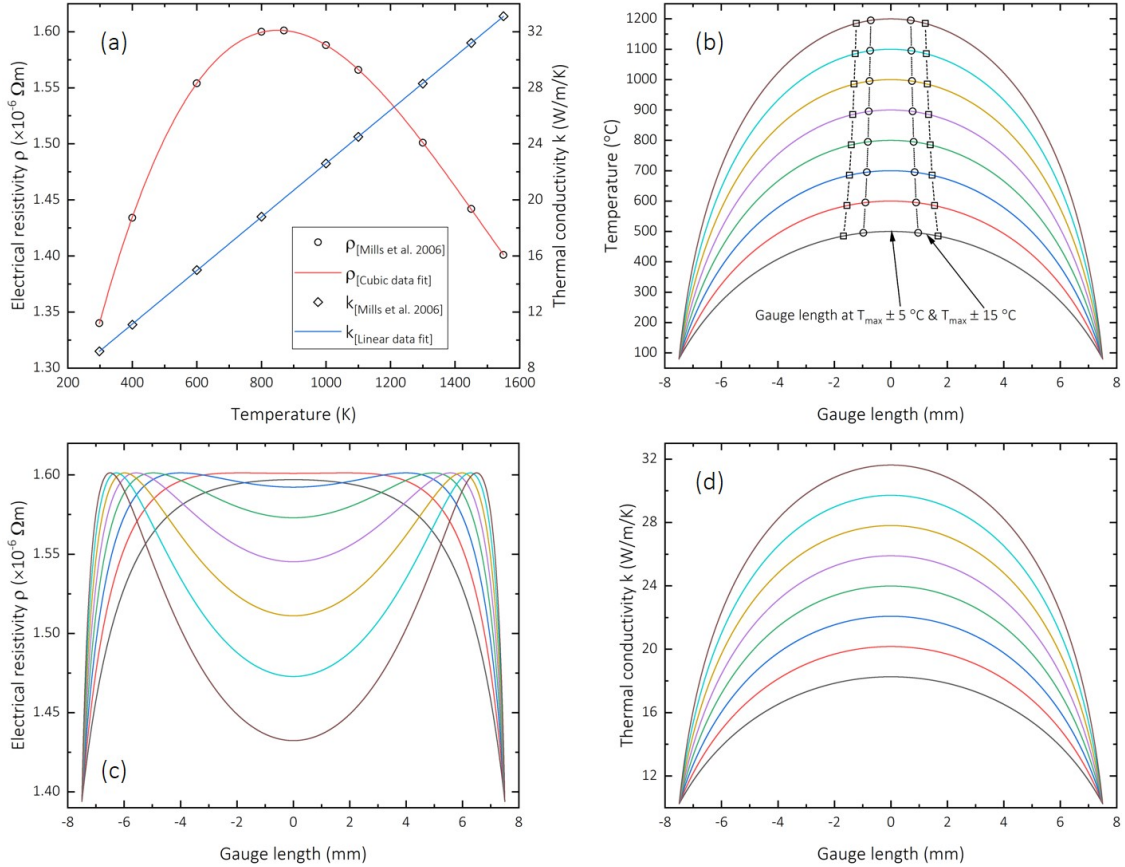


Figure 3.16: (a) Cubic and linear fits for electrical resistivity and thermal conductivity data obtained by Mills et al. [538] for alloy CMSX-4. Modelling results for the distribution of (b) temperature, (c) electrical resistivity, and (d) thermal conductivity along a heated ETMT specimen. The dotted and dashed lines in the temperature distribution graph mark regions predicted to remain, respectively, at $T_{\max} \pm 5^\circ\text{C}$ and $T_{\max} \pm 15^\circ\text{C}$.

3.4.1.2 Non-Contact Strain Measurements *via* DIC

A recent review on miniaturised testing compared several strain measurement techniques including LVDT, line scan cameras, capacitance gauges, electrical resistance measurements, interferometry techniques, and DIC [501]. It was concluded that, despite the modest strain resolution obtained for usual camera/lens/FOV

combinations, DIC provides substantial advantages as a full field non-contact method, especially considering ongoing developments in higher-resolution cameras and increased computing power.

A convenient feature is that, once a test video has been recorded and stored, it can be readily post-processed using different window sizes, gauge lengths, and image correlation parameters. An analysis of this type, which explores the effects of different gauge lengths between virtual target windows, is shown in Figure 3.17. An ETMT tensile test on the $\langle 001 \rangle$ direction at 750 °C and an initial strain rate of $10^{-4}/\text{s}$ was chosen as an example. The importance of selecting a correct reduced gauge length is evident. As this value increases, it encompasses more of the cooler regions of the specimen, in which less plastic deformation takes place. This leads to large discrepancies between analysis results at higher plastic strain values. While the impact on the 0.2% proof stress — and therefore on the initial conditions for stepped-temperature testing — is limited, choosing an incorrect gauge length will have a strong impact on stress relaxation results through Equation (3.5). The analysis below confirms the validity of DIC strain measurements in the central 3 mm of the specimen.

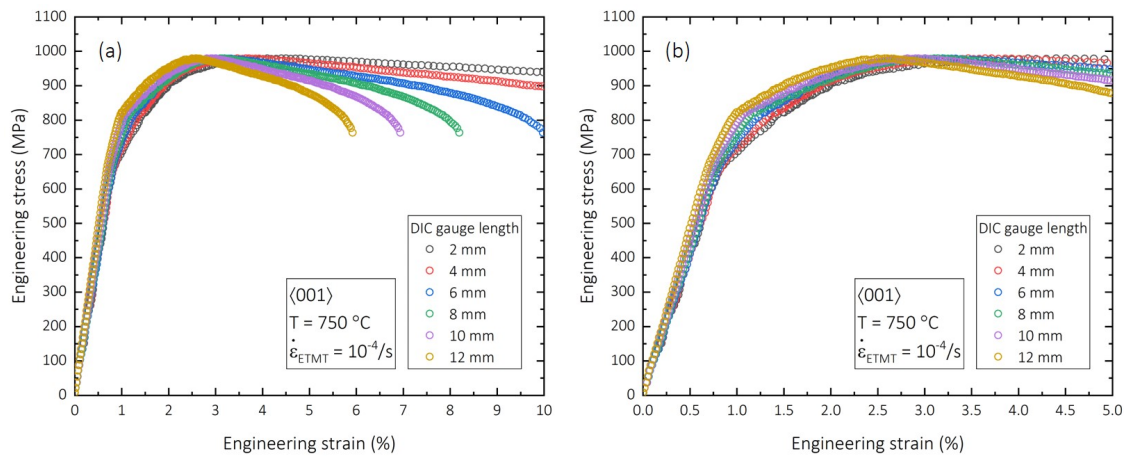


Figure 3.17: Effects of the selected virtual gauge length for DIC strain measurements on experimental results. A test on the $\langle 001 \rangle$ direction at 750 °C and $10^{-4}/\text{s}$ was chosen for this analysis. Results are plotted up to (a) 10% engineering strain to provide an overview of the test and (b) 5% engineering strain to provide a more detailed view of the elastic regime and initial yielding.

Another useful feature of DIC — and in particular of the Video Gauge software package — is the ability to output 2D strain maps. These provide a simple means of locating strain concentrations and of investigating potential effects of anomalous yielding. In order to generate a strain map, the ROI is first divided into a grid of targets. Displacements between these targets are then continuously analysed and used to calculate the Lagrangian strain tensor at each node of the grid. For the present calculations, the side length of the quadratic targets and their grid spacing were both chosen to be 15 pixels, as a compromise between spacial resolution and computing time. A filter size of 30 pixels was used to smoothen displacements around each node and to reduce image noise. Finally, changes in 2D strain distribution over time are exported as a .avi video file.

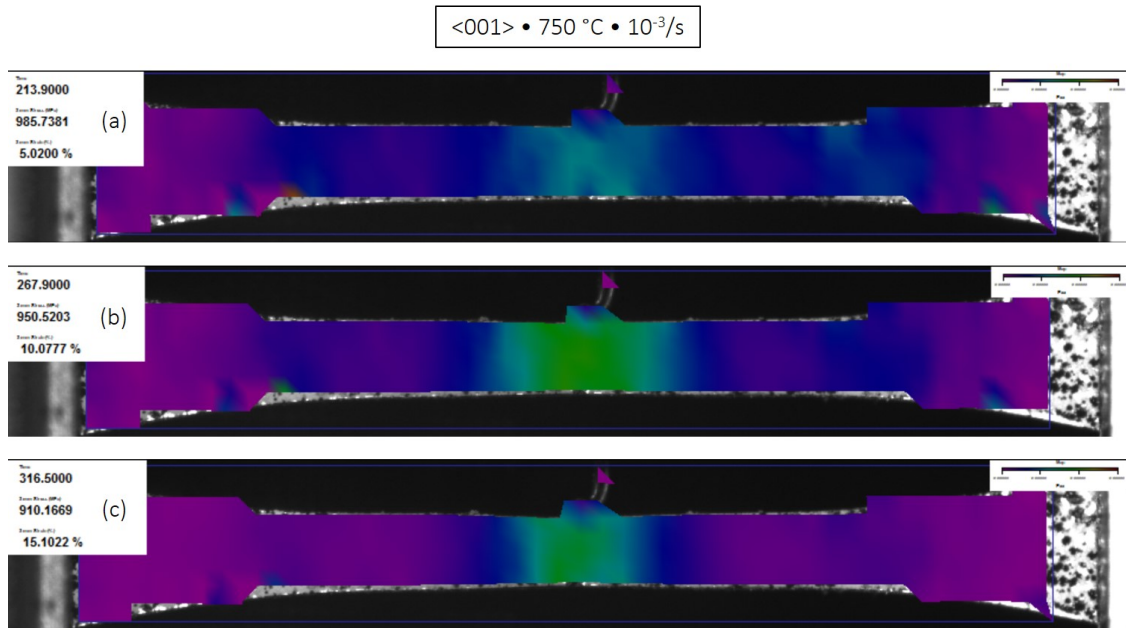


Figure 3.18: 2D colour maps of strain distribution in a $\langle 001 \rangle$ specimen tested at 750 °C and $10^{-3}/s$. Results are shown for total strain levels of (a) 5%, (b) 10%, and (c) 15%.

Figures 3.18 and 3.19 show the development of strain distribution within ETMT specimens with $\langle 001 \rangle$ orientation tested at 750 °C and initial strain rates of 10^{-3} and $10^{-4}/s$, respectively. Individual video frames were selected for comparison at total strain levels of 5%, 10%, and 15%. The colour maps show the calculated strain in tensile direction and the colour range is scaled between the minimum and maximum strain values detected up to that point during the test. Some artefacts appear

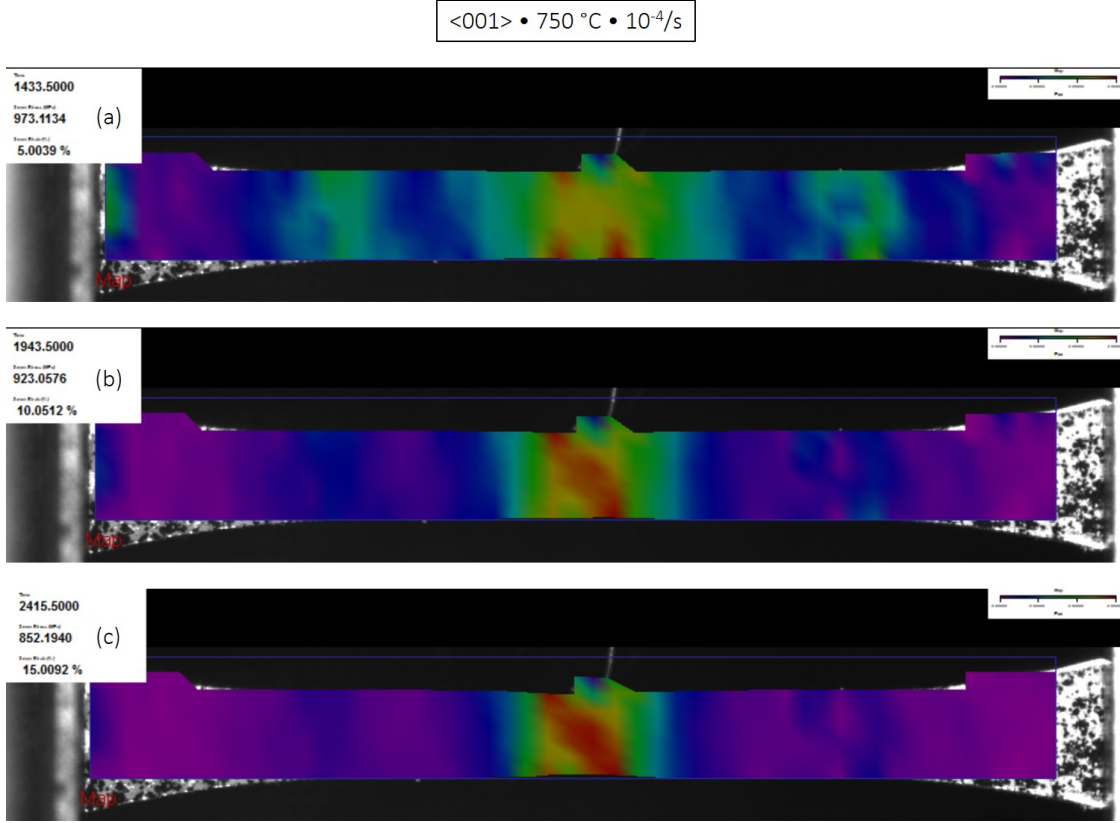


Figure 3.19: 2D colour maps of strain distribution in a $\langle 001 \rangle$ specimen tested at 750 °C and $10^{-4}/\text{s}$. Results are shown for total strain levels of (a) 5%, (b) 10%, and (c) 15%.

due to discontinuities in the ROI, commonly at specimen edges or in areas where the high-temperature paint layer was damaged. The 2D strain maps confirm that deformation is localised in the centre of the specimen. Furthermore, they show that anomalous yielding does not impact test results. Particularly in the test at $10^{-4}/\text{s}$, it is also clear that macroscopic deformation is concentrated along $\{111\}$ slip planes at a 45° angle to tensile loading, in agreement with known deformation mechanisms.

3.4.2 On the Potential of the ETMT for Rapid Alloy Development

As discussed in Section 1.3, the importance of accelerated material development cycles has led to large-scale enterprises like the Materials Genome Initiative, part of the broader field of ICME [87, 88]. Several promising approaches towards alloy design have been proposed and applied to the development of new grades of superalloys [52, 60, 61, 102, 103]. Furthermore, laboratory-scale process chains for rapid production

of single-crystal superalloy trial castings have been successfully established [112–114]. However, testing methods continue to be dominated by standard approaches. It can be concluded that, within the design–make–test–analyse cycle, the ‘test’ segment currently offers the most potential for improvement in the context of ICME goals.

The ETMT testing methods presented here offer a viable and convenient contribution to this overarching goal of more efficient and rapid materials development. Acquired data can be used to extract estimates of key material properties and to make critical decisions regarding screening and/or ranking of trial alloys during the development stage. Based on the reported dimensions of small-scale single-crystal rods [114] and using the testpiece dimensions shown in Figure 3.3, a sufficient number of ETMT samples for STT and SRT can be produced from each trial casting.

Stepped-temperature testing enables a rapid assessment of changes in athermal material strength with temperature at a certain deformation rate. Data obtained from STT is valuable for informing TMF and cyclic fatigue lifing models [541, 542]. In our experience, several trial alloys can be compared in only a few hours and optimal compositions can be identified. Furthermore, it should be noted that STT can be readily applied to other classes of high-temperature materials. For example, tests on titanium alloys for aerospace applications have shown that STT results capture the microstructural changes introduced by different heat treatments and indicate a composition-dependent transition in the operating deformation mechanisms between low and high temperatures [543].

Stress relaxation tests over a temperature range of interest can rapidly yield Ashby-type deformation mechanism maps. Plotting data in this fashion offers a direct comparison to other materials under different operating conditions. For any given application, a target region can be added using the range of temperatures and stresses encountered in service. Contours of constant strain rate provide a first estimate for screening alloys that surpass the maximum acceptable strain rate and for ranking the remaining ones. SRT results can be readily exported as inputs for commercial FEM software packages like ABAQUS. This ensures that FEM

simulations — increasingly applied to modelling high-temperature deformation in superalloy components [544–546] — will provide reliable quantitative results.

3.5 Summary and Conclusions

Miniaturised testing using an Electro-Thermal Mechanical Testing system has been carried out on a prototype single-crystal superalloy along the $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ loading axes. Compared to full-scale testing methods on testpieces of more standard geometry, the approach is advantageous owing to its increased speed, degree of simplicity, and the use of smaller quantities of material. The following specific conclusions can be drawn from the present study:

1. The ETMT has been shown to be a viable tool for assessing the material properties of single-crystal NBSA. Mechanical properties derived from miniaturised testing are found to be comparable to those obtained from conventional tensile tests over a range of temperatures and strain rates.
2. Stress relaxation tests and stepped-temperature tests have been used as rapid means of extracting creep and tensile strength estimates and parameters.
3. It has been demonstrated that changes in athermal plastic deformation with temperature can be determined with a single test by ramping up the temperature during deformation at a constant strain rate. This has allowed for an estimate of the variation of flow stress with temperature.
4. Stress relaxation tests with the ETMT enable a rapid assessment of time-dependent deformation at high temperatures. Changes in operating mechanisms are revealed through deformation mechanism maps, generated using data measured at different temperatures. The results show a transition from precipitate shearing to dislocation climb bypass at higher temperatures and lower plastic strain rates.

5. Such rapid testing methodologies can be applied in studies of small-scale superalloy castings to determine both athermal and time-dependent plastic responses. This accelerated design–make–test–analyse cycle has the potential to significantly reduce the time for qualification and insertion of new grades of superalloys.

In reflecting on where we are and what has been accomplished, the author is reminded of the remark by a famous scientist, “I have never encountered a problem, however complex, that after careful study did not turn out to be even more complex”. In this sense metallurgists and physicists will find interesting employment with dislocations in superalloys for some time to come.

— J.H. Westbrook, “Superalloys (Ni-base) and Dislocations — An Introduction”

4

Experimental Assessment of Creep Damage Evolution in Single-Crystal Superalloys

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4.1 Introduction

Dislocations are agents of plastic deformation. But nonetheless, it remains a major challenge to relate dislocation activity on the microscale to the plastic strain induced macroscopically by external loading. This is particularly the case for viscoplastic deformation — such as creep deformation in NBSA — because it is difficult to distinguish between a situation in which relatively few dislocations are propagating quickly and one in which a greater number of dislocations are moving sluggishly. Traditionally, the major difficulty has been that accurate and reliable estimates of the dislocation density and its spatial distribution have not been available due to a lack of suitable experimental techniques of sufficient accuracy and necessary spatial resolution.

The present chapter addresses this topic for the case of single-crystal NBSA. An advantage of their use is that other contributions to viscoplastic deformation — such as GB sliding — are not present to complicate matters. To facilitate the precisely controlled experimentation needed, interrupted creep tests are carried out using the ETMT system introduced in Chapter 3 at 900 °C and 450 MPa to various levels of accumulated strain. In this regime, denoted as ‘tertiary’ creep, the applied stress is too low to enable shearing of γ' particles, whereas the temperature is too low to give rise to pronounced precipitate rafting. Deformation is confined to a large degree to the γ matrix, resulting in a steady increase of the creep strain rate with creep strain, as shown schematically in Figure 4.1. A steady-state creep rate, as commonly observed in other engineering alloys, is absent. The main operational source of damage is considered to be the accumulation of mobile dislocations in the γ matrix channels [364, 365, 468]. Dislocation structures are characterised using two distinct methods, each with its advantages and limitations: (1) ECCI, which allows direct imaging of dislocation structures and (2) HR-EBSD analysis, which allows estimates of the geometrically necessary dislocation (GND) content from local misorientations of the crystal lattice.

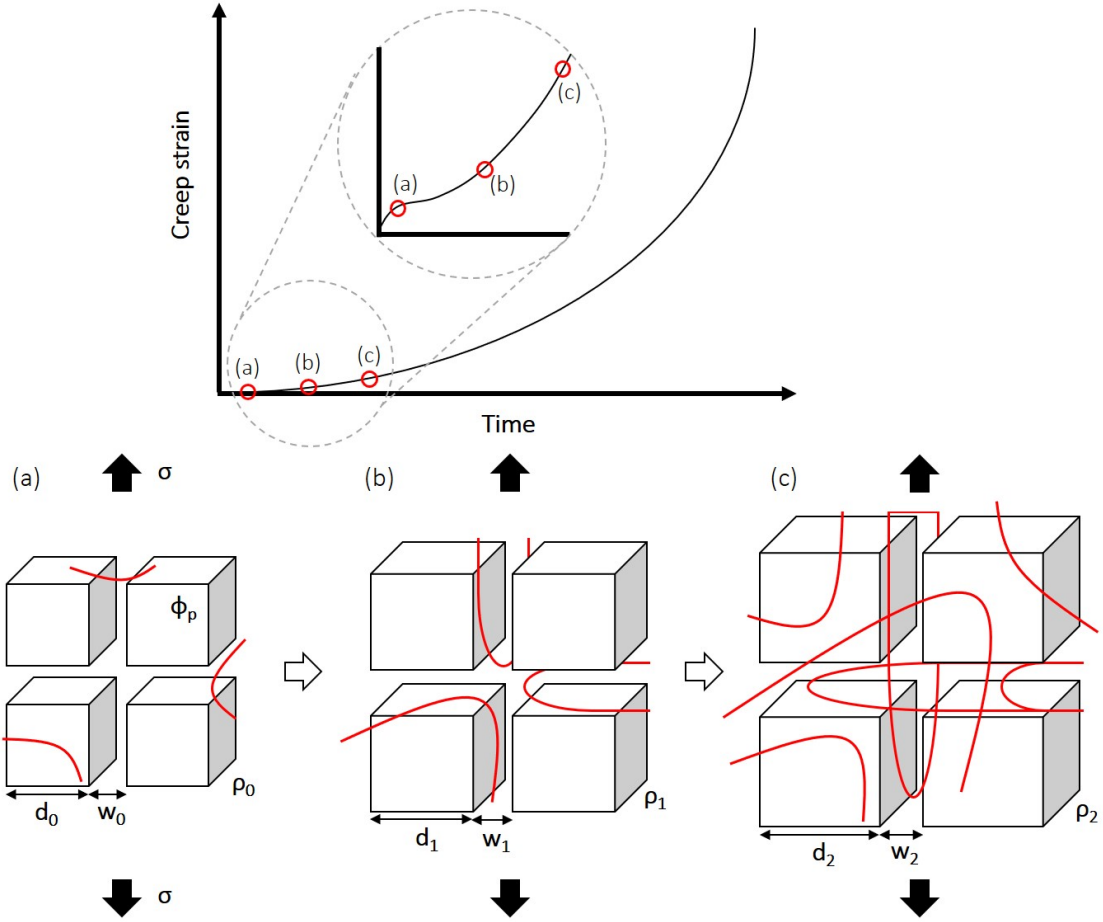


Figure 4.1: Schematic evolution of dislocation structures during early stages of tertiary creep. The main operating mechanisms are (1) an increase in mobile dislocation density in γ matrix channels, ρ , and (2) coarsening of γ' precipitates, i.e. an increase of the average cube side length, d , and of the interparticle spacing, w .

Experimental approaches are repeated on single-crystal superalloys of significantly different composition, in order to identify any effects of alloying; these are representative of the more- and less-heavily alloyed superalloys which have found industrial application. These results are compared with predictions obtained using DDD modelling. This combined experimental and simulation approach leads to key insights into the mechanism of dislocation multiplication in these materials, accurate measurements of dislocation content, but also a dislocation evolution law which will be useful for modelling and alloy design efforts.

4.2 Experimental Method

4.2.1 Material

The three single-crystal superalloys considered in the present work were designed using the theory-based ABD modelling method [52]. Nominal chemical compositions and mass densities measured using a DahoMeter DE-120T electronic densimeter are shown in Table 4.1. ABD-1 is designed for general jet propulsion applications, with the goal of balancing creep and oxidation resistance. The level of costly rhenium is reduced to 1.6 wt.% compared to commercial benchmark alloys which normally contain 3 wt.%. ABD-2 is aimed at high-performance jet engine parts which require maximum creep strength, while still maintaining sufficient oxidation resistance. Additions of 5.6 wt.% rhenium and 1.6 wt.% ruthenium restrict diffusion-controlled deformation at high temperatures, but they also significantly increase raw material cost. ABD-3 is intended for IGT components and exhibits a high resistance to hot corrosion and oxidation damage. The larger size of IGT blades increases the importance of cost and castability constraints and prohibits rhenium and ruthenium additions. Details regarding the modelling procedures, the design criteria, and the characterisation of the ABD alloys can be found in reference [103].

Bars of 10 mm diameter and 160 mm length were cast in single-crystal form with near $\langle 001 \rangle$ growth directions in an industrial-scale investment casting facility. Casting was carried out under a vacuum better than 10^{-4} Pa at a withdrawal speed of 229 mm/h and a mould temperature of 1540 °C. The bars were then sand blasted and macro-etched using a solution of HCl + 5–10 vol.% H₂O₂ to check for the absence of GB. X-ray analysis using the Laue back-reflection technique was carried out to ensure that the crystal orientation differed by less than 15° from the specified $\langle 001 \rangle$ direction. Heat treatment steps were chosen based on differential thermal analysis studies to reduce microsegregation and to precipitate homogeneously distributed, cuboidal γ' particles. Temperatures and holding times are shown in Table 4.2; each step was completed by air cooling.

Alloy	Cr	Co	W	Al	Ta	Re	Ru	Ni	Mass density
ABD-1	8	10	8.5	5.8	8.5	1.6	–	Bal	8.83
ABD-2	4	9	7.4	6.4	5.6	5.6	2.6	Bal	8.90
ABD-3	13	10	5	5.4	7	–	–	Bal	8.51

Table 4.1: Nominal chemical compositions of ABD alloys in wt.% and measured mass densities in g/cm³.

Alloy	Solutioning	Primary ageing	Secondary ageing
ABD-1	1305°C/6h	1120°C/3h	870°C/16h
ABD-2	1325°C/6h	1120°C/2h	870°C/16h
ABD-3	1300°C/4h	1125°C/1h	870°C/16h

Table 4.2: Temperature/time combinations for solutioning and ageing steps of the ABD alloys.

Backscatter electron (BSE) images of fully heat treated microstructures, illustrated in Figure 4.2(a)-(c), were obtained using a Zeiss Merlin Field Emission Gun (FEG) SEM operating at an accelerating voltage of 10 keV and a probe current of 500 pA. ABD-1 and ABD-2 exhibit unimodal distributions of cuboidal particles with edge lengths on the order of 350 nm and 200 nm, respectively. ABD-3 shows a bimodal distribution with secondary, cuboidal precipitates similar in size to the ones in ABD-1 and tertiary, spheroidal particles with diameters in the range of tens of nm. The working distance was set at 8.5 mm to yield optimal EDX results using an Oxford Instruments X-Max^N silicon drift detector with a size of 150 mm². EDX data was processed using the TruMap function of the Oxford Instruments AZtec 3.3 software package to eliminate artefacts, correct background and peak overlaps, and enhance compositional variations. EDX element maps in Figure 4.2 reveal an expected preferential partitioning of tantalum to γ' precipitates and of rhenium and ruthenium to the γ matrix [12, 117]. Tungsten shows a preference for γ in ABD-1 and to a lesser extent in ABD-3 and a homogeneous distribution in ABD-2. This can be related to the decreasing tantalum content from ABD-1 to ABD-3 to ABD-2, as it has been shown that tantalum and tungsten share the same aluminium sublattice sites in γ' and that tantalum atoms have a greater affinity for these sites, thus displacing tungsten atoms into the γ phase [114, 547, 548].

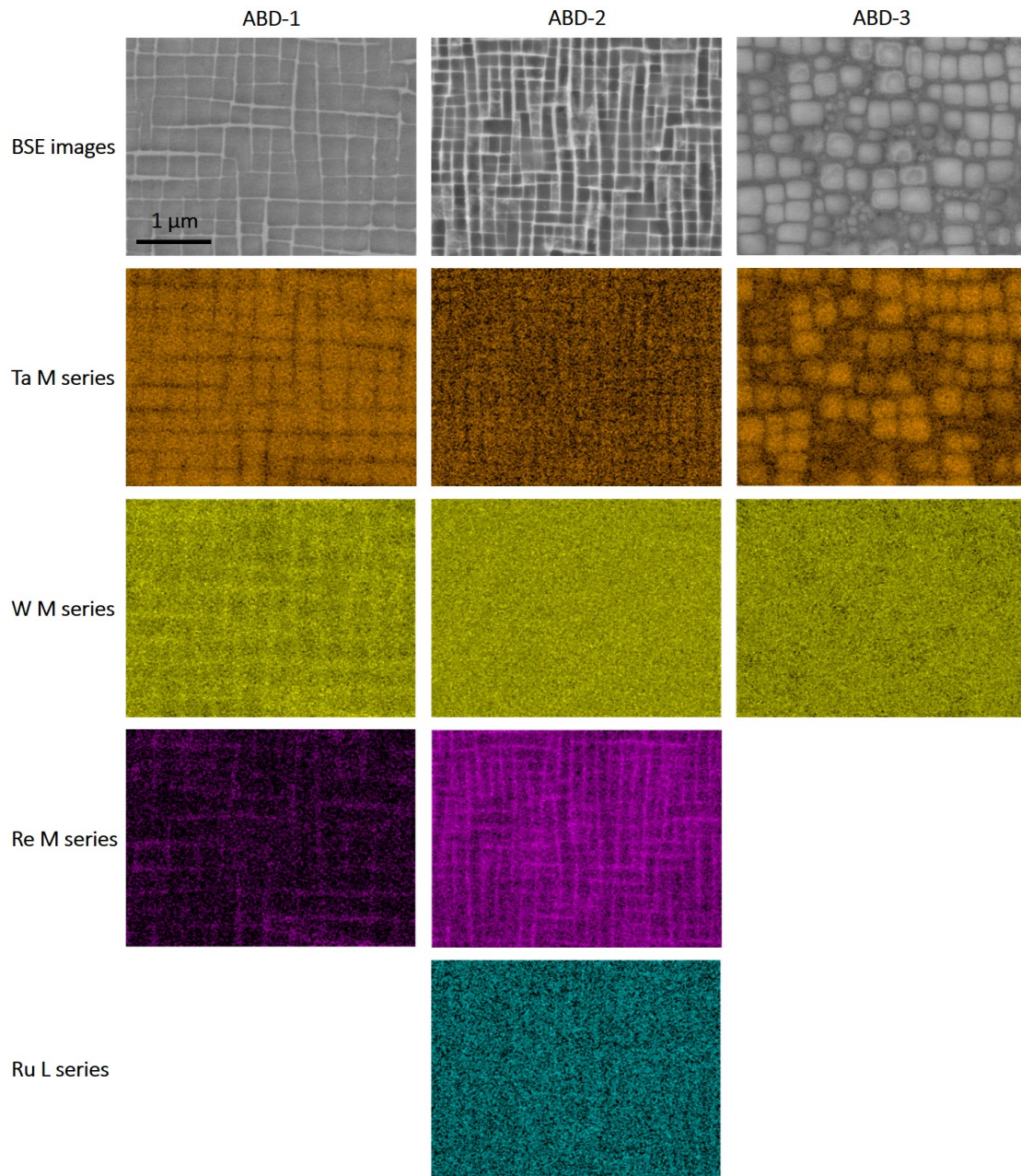


Figure 4.2: BSE micrographs of fully heat treated microstructures and EDX element maps showing the preferential partitioning of tantalum, tungsten, rhenium, and ruthenium. The illustrated scale bar applies to all images.

4.2.2 Miniaturised Creep Tests

Creep testing was carried out using the ETMT system presented in detail in Chapter 3. Three main advantages over conventional testing systems can be identified in the context of the present work. First, the miniaturised specimen geometry allows a full testing campaign to be carried out using limited volumes of material. This is

of particular importance for small-scale trial alloy castings. Second, DIC methods enable a full field non-contact measurement of accumulated creep strain. Unlike conventional strain gauges or transducers attached to the specimen, DIC does not affect the compliance of the system or the sample surface and it provides high degrees of precision and repeatability [501]. Third, once a certain level of creep strain has been reached, tests can be readily interrupted and specimens can be removed without inducing further damage. This allows an accurate post-mortem assessment of creep damage evolution with HR-EBSD and ECCL.

Miniaturised ETMT blanks with a nominal size of $40 \times 4 \times 2 \text{ mm}^3$ were manufactured along longitudinal bar directions by wire-guided EDM. These blanks were further waisted *via* EDM to give a nominal width in the centre of the testpiece of 2 mm. The main advantage of the waisted geometry is that it enables using customised grips, which precisely fit the waist radius and which ensure correct alignment during testing, as shown in Figure 4.3(a). A parallel-sided section is maintained in the centre of the specimen to assure a constant stress level and a uniform temperature distribution.

Surfaces were ground to a 4000 grit mirror finish using silicon carbide grinding paper. Besides ensuring a constant, repeatable finish, this step is crucial for removing the recast layer caused by EDM and for minimising residual stresses in the sample prior to testing [498]. The actual cross section dimensions were measured with a micrometer gauge and were used to compute creep load. Finally, each specimen was cleaned in an ultrasonic bath with ethanol, after which a high-temperature paint pattern for DIC was applied.

Temperature and applied stress were chosen as 900 °C and 450 MPa following the experimental work of Matan and Reed [12, 335, 337] on CMSX-4 to ensure that neither precipitate rafting, nor precipitate shearing will be active deformation mechanisms. In CMSX-4, rafting was observed at 950 °C and became pronounced at 1000 °C, while significant levels of shearing were found at applied stresses of 600 MPa and above [12]. Creep tests were carried out following ASTM standards [549], albeit with a non-standard setup. The load of around 1800 N was applied

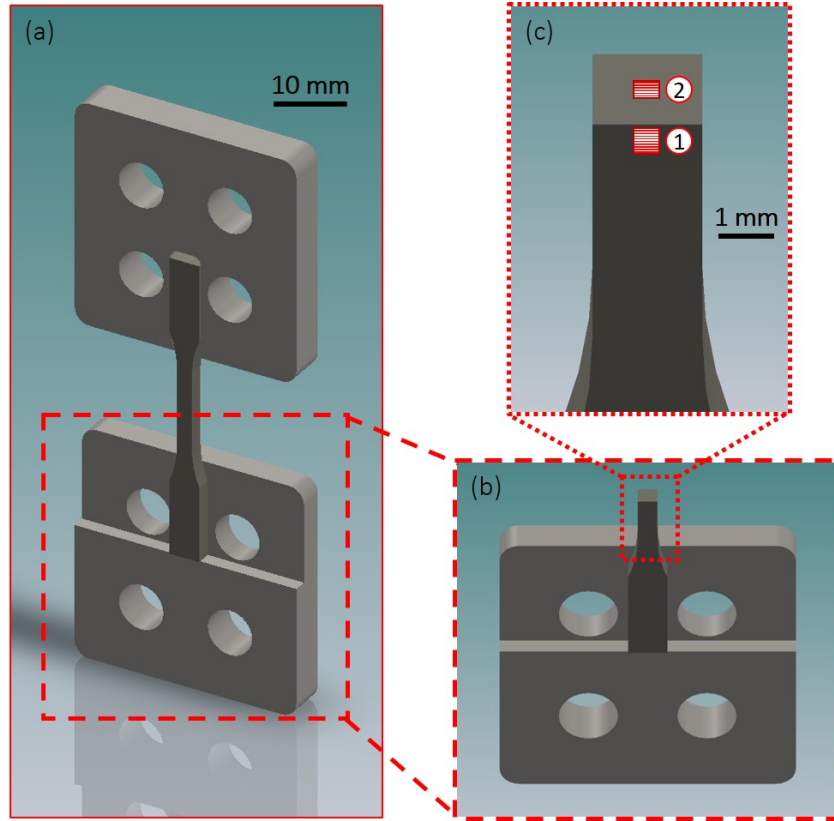


Figure 4.3: (a) ETMT sample and grip assembly during testing. (b) Cross-sectional view at the centre of the specimen. (c) Enlarged view showing the approximate locations in which HR-EBSD and cECCI analyses were carried out parallel to and perpendicular to the loading direction, respectively. Sizes of the marked areas are not to scale.

starting from a preload of 200 N at a rate of 100 N/s and was then held constant. Specimens were heated using a 400-A DC power supply *via* the Joule effect. The testing temperature was measured and controlled with a type K thermocouple spot-welded under argon at the centre of the specimen.

Changes in creep strain are measured through DIC by tracking a fine speckle pattern produced on one of the sample surfaces using high-temperature paint. The specimen is illuminated by a bright, diffuse LED light source positioned behind an Allied Vision Technologies Manta G-146 camera which records the test. A reduced field of view of 250×1000 pixels was tracked at a frame rate of 1 fps. The Imetrum Ltd Video Gauge software tool analyses captured images and applies proprietary sub-pixel pattern recognition algorithms to detect any changes occurring during testing in comparison to a reference state. Displacement and strain are measured and

calculated in real time between user-defined target areas, in this case set 2 mm apart around the centre of the specimen, with a strain resolution of around 20 microstrain. Despite the parabolic temperature distribution along the specimen, this region was shown to remain at a reasonably uniform temperature of 900 ± 5 °C [508, 550]. Finally, analogue signals for load and temperature are transmitted from the ETMT to the Video Gauge software through a Signal Interface Unit, allowing all relevant data to be collected and saved in one location.

4.2.3 Cross-Correlation HR-EBSD

For each interrupted creep specimen, two regions were metallographically prepared as shown in Figure 4.3(c). Surface normals are (1) perpendicular to and (2) parallel to the loading direction. Grinding and polishing steps were carried out on a Struers Tegramin-25 preparation system down to 1 μm diamond suspension. An optimal finish was achieved by polishing for 15–30 min with a 1 to 1 mixture of Struers OP-S 0.04 μm colloidal silica suspension and water on a Struers MD-Chem polishing cloth. Specimens were cleaned in an ultrasonic bath with acetone and then with ethanol. After analysis of region (1) was completed, specimens were sectioned with a Struers Accutom-50 cutting machine and the central region (2) was prepared as above.

Electron backscatter patterns (EBSPs) were obtained using a Zeiss Merlin FEG SEM equipped with a Bruker Quantax e⁻Flash^{HR} detector run with Esprit 2.1 software. The microscope was operated at 20 keV and 15 nA. Samples were positioned on a pre-tilted holder at 70° towards the detector and at a distance of 18 mm. For each specimen, a minimum of three rectangular maps of 11.5×8.6 μm^2 were scanned with a step size of 50 nm. Their positions in relation to other microstructural features were recorded on SEM images taken at lower magnification, to ensure that ECCI analysis will be carried out in the same regions. For each map, around 40,000 EBSPs were captured and recorded with a 12-bit 1600×1200 pixels CCD camera with minimum gain and contrast stretching while applying a dynamic background correction. Patterns were obtained either without binning and a dwell time of 200 ms or with 2×2 binning and a dwell time of 50 ms, thus maintaining a ratio of 1 to

4. Choices of binning level and step size significantly impact GND estimates from HR-EBSD and are discussed in more detail in Section 4.4.1.

Cross-correlation HR-EBSD [551, 552] is an offline image processing method which analyses the obtained EBSPs to determine strain gradients and to extract related GND densities. First, shifts between 40 square sub-regions of interest on related patterns are measured using cross-correlation techniques. These calculations are performed in the Fourier domain, in which a band pass filter is applied to remove high frequency noise and low frequency background intensity variations [553].

Second, these measurements are related to the shape change and rotation of the crystal lattice using a set of simultaneous linear equations, which yield eight of the nine possible degrees of freedom in a general strain and rotation [551]. Robust iterative fitting methods are used to attain statistically reliable measurements and to reduce noise [554]. To obtain the final degree of freedom represented by pure hydrostatic strain, equilibrium conditions for a free surface which must remain traction-free are assumed and the stress normal to the free surface is set to zero. This is a reasonable assumption, as EBSPs originate from the topmost few nanometres of the sample [553]. The elastic stiffness constants at room temperature were assumed to be equal to those determined by Siebörger et al. [555] for CMSX-4, namely $C_{11} = 262$ GPa, $C_{12} = 161$ GPa, and $C_{44} = 144$ GPa. Actual values for the ABD alloys will be very similar, as it has been shown that alloy chemistry has only a minor influence on compliance [517].

Third, the GND density can be estimated using the geometrical constructions first developed by Nye [556] and later extended by Kröner [557], who showed that stored GNDs within a Burgers circuit are intimately linked to elastic strain gradients and rotation gradients. It is assumed here that elastic strain contributions can be neglected for deformed metallic samples, following references [558–560]. Two issues must be considered when estimating GNDs on various slip systems *via* the Nye tensor. First, only six of the nine curvature tensor components can be calculated in two dimensions parallel to the sample surface [558, 559]. These can be linked to five components of the Nye dislocation density tensor and to one difference

between two other components [561]. Second, for the case of a FCC crystal, it can be assumed that the slip systems storing GNDs are comprised of 6 types of pure screw dislocations with Burgers vectors and line directions along $\langle 110 \rangle$ and 12 types of pure edge dislocations with Burgers vectors along $\langle 110 \rangle$ and line directions along $\langle 112 \rangle$ [558, 559]. The combination of 18 unique slip systems and only 6 known components of the Nye tensor makes this a highly underconstrained problem. To find a reasonable estimate of GND density, additional constraints are incorporated into an L^1 optimisation method, which minimises the total dislocation line energy [562].

For more in-depth reviews of the theoretical background of HR-EBSD, of recent advances, and of remaining challenges, the reader is referred to references [553, 563–567].

4.2.4 ECCI under Controlled Diffraction Conditions

Besides the EBSD data required for cross-correlation HR-EBSD, EBSD scans also yield basic crystal orientation maps for each scanned area. The classical two-dimensional Hough transform algorithm is first used to convert Kikuchi bands to points which can be more easily located and indexed. The Bruker Esprit 2.1 software then converts peak locations to a table of interplanar angles which are compared to look-up tables for expected phases within the sample, in the present case pure nickel. By choosing the most consistent indexing solutions, phase and crystal orientation maps are obtained. For each scanned area, the average Euler angles are inputted into the TOCA (Tools for Orientation Determination and Crystallographic Analysis) software programme [568], which simulates Kikuchi patterns for this particular crystal orientation. TOCA is then used to estimate the necessary SEM stage settings required to bring the region of interest into two-beam conditions for ECCI. While some discrepancies between simulated and observed patterns are unavoidable due to errors in EBSD measurements [569] or slight differences in how the specimen is mounted in the SEM, this controlled ECCI (cECCI) method makes it much easier to accurately locate suitable diffraction conditions.

ECC images were obtained using a Zeiss Merlin FEG SEM operating at 30 keV and 3 nA. Samples were positioned at a working distance of 6 mm and were tilted following TOCA predictions to angles in the range of -4° to 6° for areas corresponding to region (2) in Figure 4.3(c) and of up to 16° for some surfaces corresponding to region (1). This low-tilt ECCI configuration was introduced by Crimp et al. [570, 571] and offers a convenient imaging position, higher spatial resolution, and enhanced contrast compared to a high-tilt geometry [572]. In short, rotation and/or tilt angles are chosen so that a plane or several planes diffract electrons incident on the sample. Dislocations are revealed as spots or lines with black-white contrast, as they cause local changes of the lattice constant and thus also changes in the intensity of backscattered electrons.

Images were captured at the same magnification, resulting in a nearly constant imaging area of $4.75 \times 3.55 \mu\text{m}^2$. A significant advantage of ECCI over TEM methods is its ability to probe a much larger material volume and to easily identify and characterise regions of interest. For each superalloy and deformation level, at least five images were captured both within a dendrite core and at an interdendritic low-angle grain boundary (LAGB). Total dislocation density — in this case containing both GNDs and statistically stored dislocations (SSDs) — was determined in a similar fashion to reference [573]. ECCI images were first processed with the MIPAR software package [497] to isolate all dislocation lines within the scanned region and eliminate noise. After applying a Frangi filter [574] to highlight linear-type features, and manually removing precipitate edges or matrix channels erroneously detected as dislocations, the total length of dislocation lines, L , is estimated.

The dislocation density is calculated as $\rho = L/(A \times t)$, where A is the imaged area and t is the probing depth. The term t is difficult to estimate accurately given the complexity of modelling the backscattering of electrons from a thick crystalline material [573]. Here, we follow the considerations of Wilkinson et al. [575], who estimated the limiting probing depth for imaging dislocations with ECCI to about $5 \times \xi_g$, where ξ_g is the extinction distance. The value of ξ_g for a certain material depends on the chosen reflectors for two-beam conditions and on

the acceleration voltage. For this, we consider the theoretical reviews of Reimer [576, 577] and the earlier experimental work of Hirsch et al. [578] and Thomas et al. [579] on pure nickel and estimate ξ_g at 18 nm for the accelerating voltage of 30 keV and the chosen reflectors. This then yields a probing depth of 90 nm and a total probing volume of around $1.52 \mu\text{m}^3$.

For more information on cECCI, the reader is referred to the recent in-depth review by Zaefferer and Elhami [572], which covers the theoretical background, practical considerations, optimal experimental procedures, and several application case studies. Earlier reviews of electron backscattering and ECCI can be found in references [580–582].

4.2.5 Discrete Dislocation Dynamics Modelling

Three-dimensional DDD models provide a robust means of studying how dislocations move and interact under given deformation conditions and have been applied in several studies to simulate the mechanical response of single-crystal NBSA [583–591]. An important advantage in the context of the present study is the ability of DDD to compare the effects of microstructural constraints (i.e. different γ' volume fractions), of dislocation mobility (i.e. different levels of solid solution strengthening), and of dislocation sources (i.e. LAGB or isolated dislocation (ID) sources) on damage accumulation [586]. DDD predictions help identify the rate-limiting relationships between microstructure, loading conditions, and macroscopic creep rate and lead to a more general understanding of tertiary creep damage in conjunction with the HR-EBSD and cECCI analyses.

DDD simulations were carried out using the ParaDiS code [592]. A more in-depth discussion of the simulation methodology and of the employed coupled glide-climb mobility law can be found in reference [586]. The simulation cell is taken to be a cube of $1.5 \mu\text{m}$ edge length orientated along crystallographic $\langle 001 \rangle$ directions. It contains $3 \times 3 \times 3$ cuboidal γ' precipitates, also orientated in $\langle 001 \rangle$ directions. Differences in γ' volume fraction at 900 °C have been estimated by Thermo-Calc and the TCNi8 database and are accounted for by adjusting the precipitate edge

Alloy	Predicted γ' fraction (%)	γ' edge length (nm)	M_g/M_c ratio
ABD-1	61.1	424	10
ABD-2	71.1	446	13.7
ABD-3	47.5	390	3

Table 4.3: DDD parameters used to account for γ' precipitate strengthening and γ matrix solid solution strengthening.

length as summarised in Table 4.3. Particles are considered to remain impenetrable. Isotropic elastic properties with a shear modulus $G = 37$ GPa and a Poisson ratio $\nu = 0.37$ are assumed for the γ phase. Its lattice parameter is taken as $a_\gamma = 0.36$ nm, which leads to a $\langle 110 \rangle$ Burgers vector length $b = 0.25$ nm. The γ/γ' interface is modelled as a fixed rigid boundary and misfit stresses are not accounted for.

Dislocation motion in the γ matrix is described by a hybrid glide and climb mobility law which mimics the climb-assisted motion of typical mixed $a/2\langle 110 \rangle\{111\}$ dislocations. The glide mobility values, M_g , of both edge and screw dislocation segments are set to $1 \text{ (Pa}\cdot\text{s)}^{-1}$. Differences in the levels of solid solution strengthening in the γ matrix imparted by slow-diffusing elements such as molybdenum, tungsten, and rhenium are accounted for by adjusting the climb mobility, M_c , of edge components in accordance with the glide/climb mobility ratios M_g/M_c shown in Table 4.3. Here, ABD-1 is assigned a M_g/M_c ratio of 10 based on previous DDD studies of creep deformation in single-crystal superalloys [586, 587]. The values for ABD-2 and ABD-3 result from analytical estimates of drag coefficients for pure edge glide and pure edge climb, B_g and B_c , from the work of Takeuchi and Argon [593, 594]. Segment mobility is then obtained as the inverse of the drag coefficient via $M_x = 1/B_x$. It is important to note that the absolute mobility values for both glide and climb are unreasonably high compared to analytical estimates or to experimentally-derived values at 900 °C. However, this alteration is necessary to run simulations at reasonable computation times. Nonetheless, as discussed by Hafez Haghighat [586], the relatively high strain rates and low creep times obtained in DDD studies, as opposed to real creep tests, do not influence the predicted material response or the increase in mobile dislocation density with accumulated creep strain, as these depend on the relative M_g/M_c ratio rather than on absolute values.

Consistent with the ETMT tests, a tensile stress of 450 MPa was assumed along the $[001]$ direction. Periodic boundary conditions are applied along $\langle 001 \rangle$ directions to account for bulk microstructure. Following reference [361], five Frank-Read sources of $1/2\langle 110 \rangle$ mixed character with an individual line length of $0.35 \mu\text{m}$ are introduced into the simulation cell. This corresponds to an initial dislocation density of $5.2 \times 10^{11} \text{ m}^{-2}$, in agreement with experimentally determined values [361].

4.3 Results

4.3.1 Interrupted Creep Tests

Results of interrupted ETMT creep tests are illustrated in Figure 4.4(a)-(c). The Larson-Miller plot in Figure 4.5 shows good agreement with conventional creep tests.

ABD-1 exhibits a ‘typical’ single-crystal superalloy behaviour in the tertiary creep regime. After a transient primary stage, the creep strain rate gradually increases with creep strain, yielding the type of curve illustrated in Figure 4.1. Good agreement is found with the conventional test carried out under identical conditions of applied stress and temperature.

Tests on ABD-2 consistently show a strong initial increase in creep strain after loading, followed by a period of negative creep. While in the conventional creep test this period ended after around 35 h, in the ETMT tests normal deformation behaviour resumed after less than 2 h. Negative creep was initially reported in single-crystal superalloys tested at high temperatures and low uniaxial stresses along $\langle 001 \rangle$ directions [535, 595]. This paradoxical contraction was rationalised by a minimisation of the free internal energy of the material during tensile loading [596, 597]. However, it was improperly attributed to directional coarsening [596], when in fact these effects are simply concomitant [598]. Instead, recent DDD results have shown that negative creep emerges from the initial dislocation activity at γ/γ' interfaces during creep, where dislocations relax most of the misfit stresses [598]. The decrease in creep strain over time arises as the sum of positive plastic strain computed from the area swept by dislocation lines and negative elastic relaxation induced by the local rearrangement of dislocations. While the stress levels

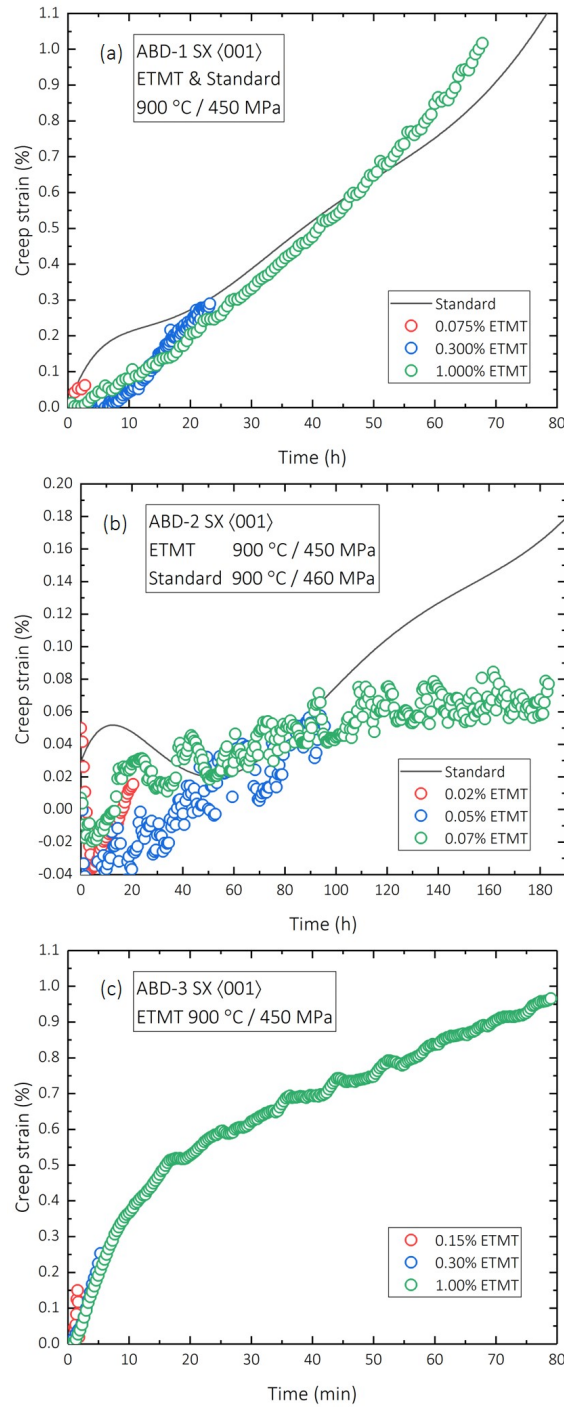


Figure 4.4: Results of miniaturised ETMT creep tests for (a) ABD-1, (b) ABD-2, and (c) ABD-3. For ABD-1 and ABD-2, comparisons are made to conventional creep tests.

in the present tests may appear too high to give rise to negative creep, studies on polycrystalline powder metallurgy superalloys tested under 700 °C and 650 MPa showed clear negative creep regimes after load application, with the magnitude of

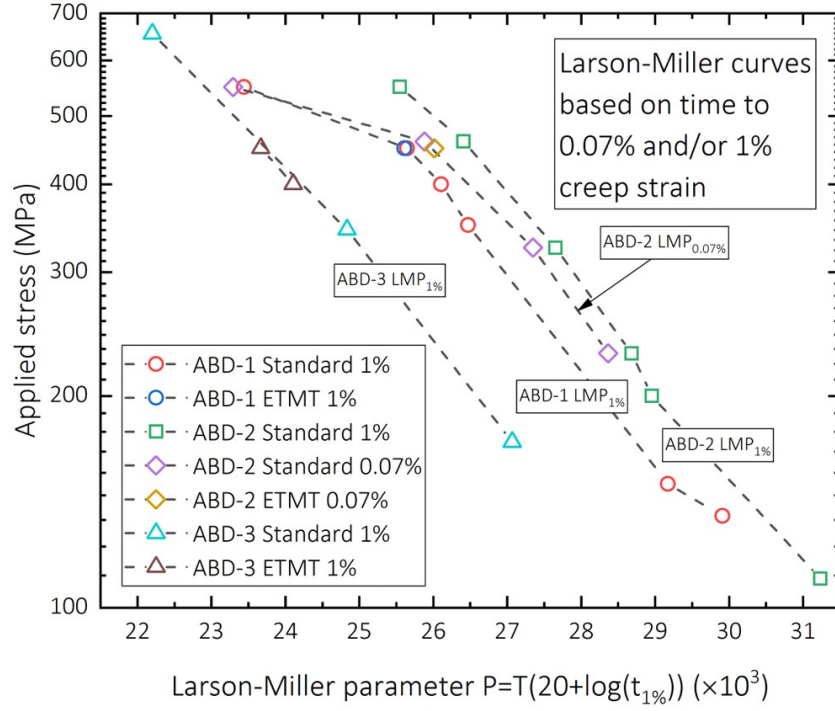


Figure 4.5: Larson-Miller plot expressing the relative creep strength of ABD alloys; comparisons are again made to conventional tests.

this effect scaling with the creep strength of the alloy [598–600]. The same situation is encountered in the present work, where the much more rapid creep deformation in ABD-1 and ABD-3 effectively masks any negative creep effects.

Since ABD-3 has been designed for IGT components, it is not meant to withstand the creep deformation conditions chosen here during service. The applied stress of 450 MPa represents an estimated 75% of the yield stress of similar IGT alloys at 900 °C [550]. As such, the material undergoes rapid deformation, comparable to primary creep conditions in which particle shearing cannot be fully excluded.

4.3.2 GND Density Analysis with HR-EBSD

Figure 4.6 shows lattice strain and rotation maps obtained from cross-correlation analysis relative to a reference point of high pattern quality. The x_3 direction corresponds here to a $\langle 001 \rangle$ crystal orientation. The largest strain variations are found for the in-plane normal strains, ε_{11} and ε_{22} , and to a lesser degree for the out-of-plane normal strain, ε_{33} . The relative strain distribution clearly shows that

damage is localised within γ matrix channels. Furthermore, the higher strain values for ε_{11} and ε_{22} indicate that ‘horizontal’ matrix channels perpendicular to loading are deformed preferentially. This is a result of the higher operating stresses arising from a superposition of applied stress and misfit stresses associated with a negative lattice misfit at high temperatures [306, 362].

The strain and rotation data in Figure 4.6 is used within the Nye-Kröner framework to produce an estimate of the GND density distribution, illustrated in Figure 4.7(a). The GND density map confirms that deformation is localised in γ channels, exhibiting densities on the order of 10^{14} m^{-2} for the case of this ABD-1 sample deformed up to 1% creep strain. Precipitates appear as cold spots with values of around 10^{13} m^{-2} , which are on the order of the HR-EBSD resolution limit for the chosen step size of 50 nm [601, 602]. The average GND density is not homogeneous across the image and hot spots emerge either in areas with locally wider matrix channels or in areas in which the top specimen layer being probed happens to be a γ channel as opposed to the bulk of a γ' precipitate.

The weighted mean angular error (MAE) and the geometric mean of normalised peak heights of the cross-correlation functions (PH) shown in Figure 4.7(b&c) are used as quality metrics for the HR-EBSD method. The MAE represents the angular difference between measured pattern shifts and those expected from a best-fit solution for the displacement gradient tensor [553]. For high MAE values, measured strains and rotations may fall below the noise limit and lead to erroneous results. The normalisation of PH is such that a value of 1 is obtained for the reference pattern with the highest quality in the imaged region [553]. Low PH values indicate poor correlation and suggest doubtful measurements. Analysis of simulated EBSPs showed that thresholds of 0.004 rad for MAE and 0.3 for PH are reasonable cut-offs [554]. Across all experiments, results showed high quality HR-EBSD data, similar to Figure 4.7(b&c).

Quantitative changes in GND density distributions are illustrated for ABD-1 using histograms in Figure 4.8(a,c,e). For each deformation level, data from three maps like the one in Figure 4.7(a) are considered. Results are consistent across these

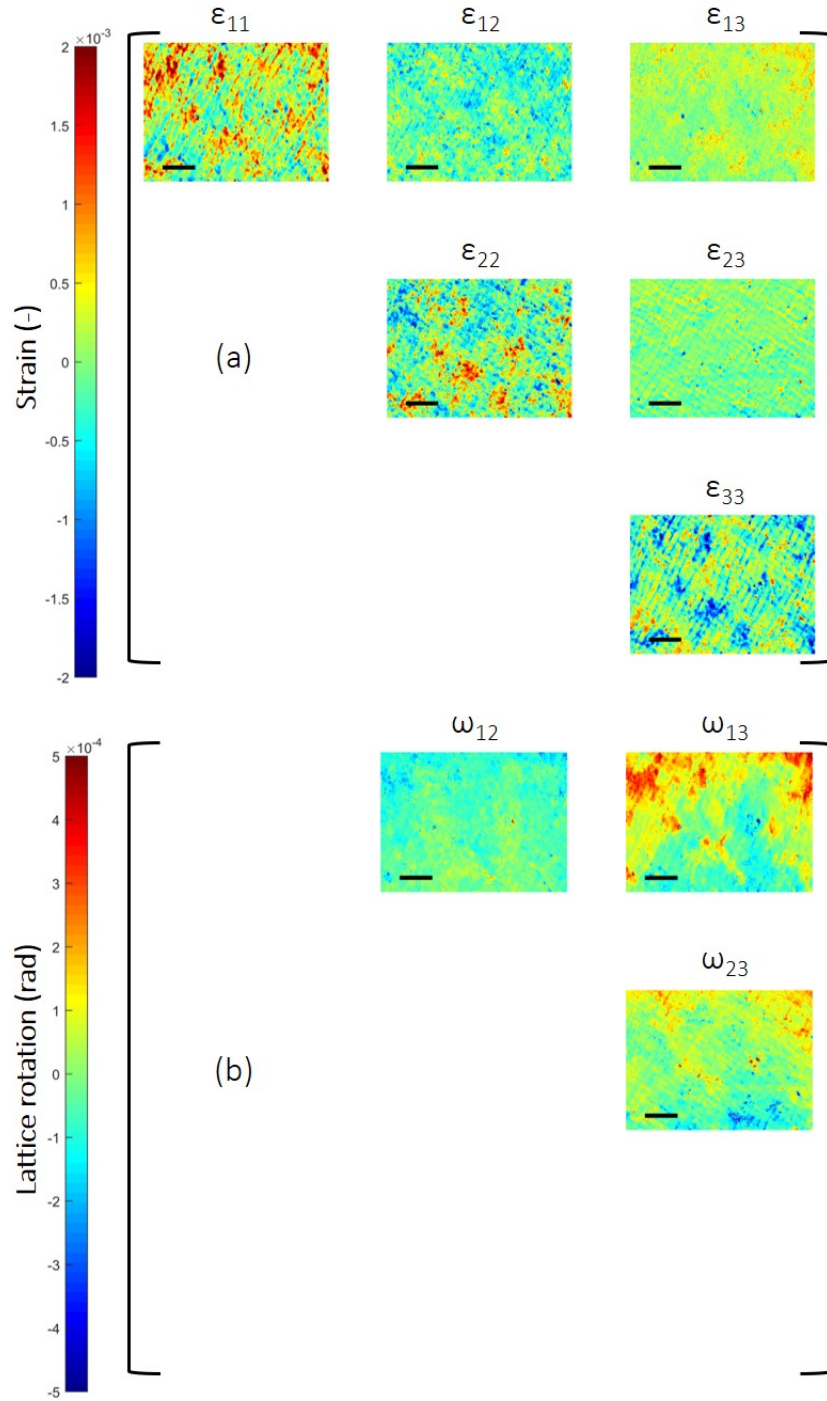


Figure 4.6: Variations in (a) lattice strains and (b) lattice rotations determined by cross-correlation HR-EBSD in an ABD-1 sample deformed to 1% creep strain. The colour scales shown on the left in (a) and (b) are used for each map. The scale bars are 2 μm long.

regions, although larger discrepancies are observed as the deformation level rises. A strong increase in mean distribution is observed between 0.1% and 0.3%, with

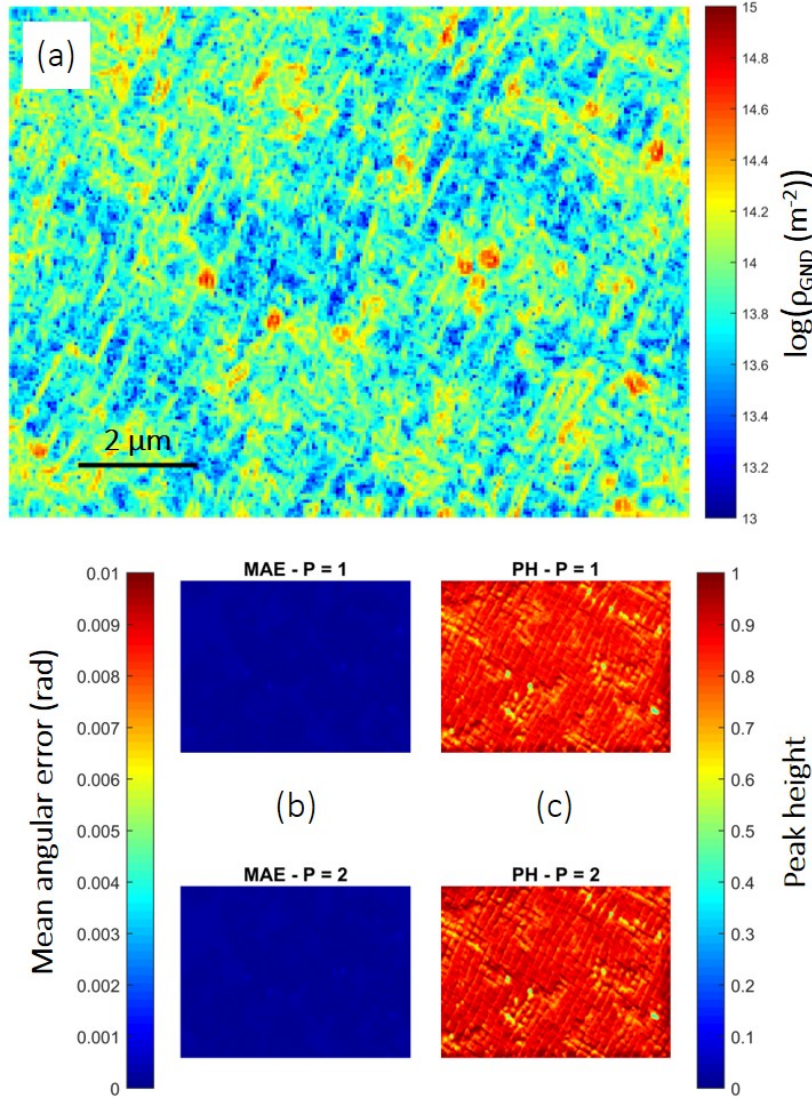


Figure 4.7: (a) Lower bound estimate of stored GNDs obtained by applying an L^1 optimisation method to relate the strains and rotations from Figure 4.6 to combinations of stored dislocations on different slip systems. (b&c) Quality parameter maps of MAE and PH across the scanned region showing good data quality.

only a slight further rise at 1% creep strain. To assess the functional form of the probability distributions, results for each map were first normalised with respect to the geometric mean. The data was then fitted to a log-normal distribution, showing good agreement in Figure 4.8(b,d,f). Fits to normal and Rayleigh distributions were also attempted, but found to be less accurate than the log-normal function, in agreement with the work of Jiang et al. [559] on pure copper and of Kamaya et al. [603] on stainless steel after tensile loading. The gradients of the log-normal

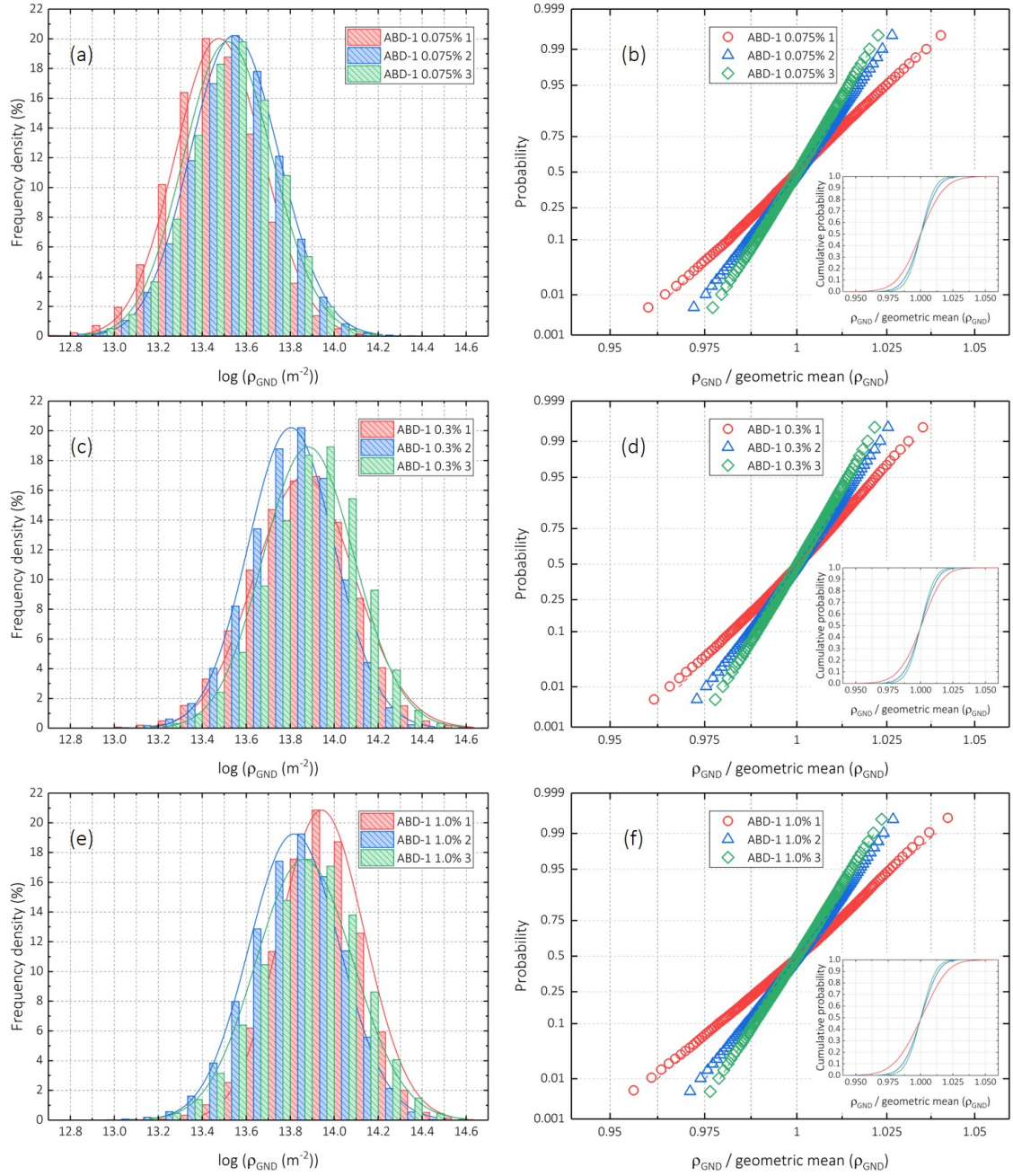


Figure 4.8: Evolution of measured GND density distributions in ABD-1 samples deformed to (a&b) 0.075%, (c&d) 0.3%, and (e&f) 1% creep strain. Data from three scanned areas has been plotted for each deformation level. The histograms in (a,c,e) show GND frequency densities using a bin width of 0.1 on a logarithmic scale. The probability plots in (b,d,f) compare normalised GND density distributions to the log-normal distribution. Each distribution was normalised with respect to its geometric mean. The inset plots show the cumulative probability of normalised GND density distributions using a bin width of 0.1.

probability plots remain similar for all strain levels, indicating constant widths of the GND density distributions.

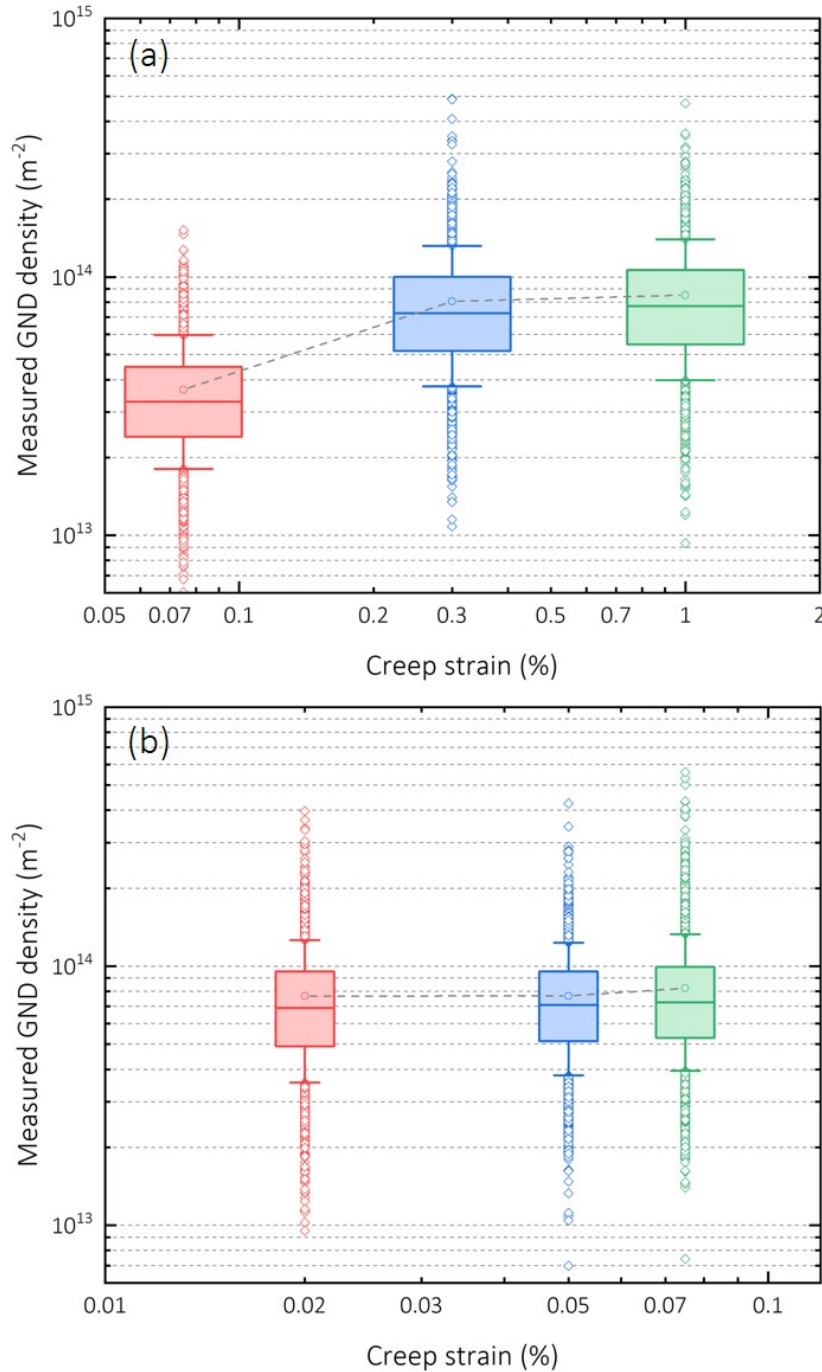
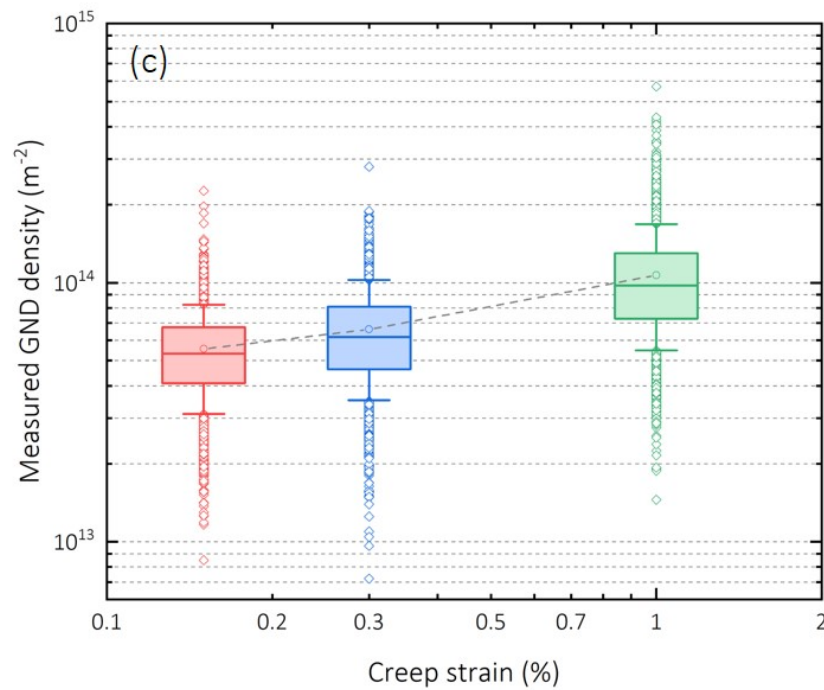


Figure 4.9: Evolution of measured GND density with creep strain for (a) ABD-1, (b) ABD-2, and (c) ABD-3. Boxes range from the 25th to the 75th percentile, whiskers from the 10th to the 90th percentile, and all other data points are plotted separately. Mean values are indicated by circles and are connected by dashed lines.

**Figure 4.9:** *(continued)*

The evolution of the measured GND density with creep strain for all three alloys is shown in the box and whisker plots of Figure 4.9. Data from at least five GND maps was considered in each case. The alloys show distinct deformation behaviours, which are discussed in more detail in Sections 4.3.4 and 4.4.2. However, relative GND distributions are comparable with regard to the difference between percentiles and the median and also with a similar spread in outliers beyond the 10th and 90th percentiles.

4.3.3 GND and SSD Density Analysis with cECCI

The low-magnification BSE micrographs in Figure 4.10(a,c,e) show characteristic mosaicity in all three alloys. This is associated with the LAGB created by the competitive growth of dendrites during solidification and with differences in contrast arising from the segregation of heavier solutes to the dendrite cores [246, 604]. Furthermore, contrast also changes on a larger scale across each sample due to the controlled imaging conditions for cECCI. Dark ‘triangles’ can be discerned, corresponding to the dark areas between simulated Kikuchi bands from the TOCA

software package in Figure 4.10(b,d,f). As illustrated in these images, the crystal orientation is rotated such that the primary beam direction overlaps with simulated Kikuchi lines. The Kikuchi band of interest is aligned parallel to the tilt axis of the stage to achieve the sharpest possible diffraction profile [572]. Two-beam diffraction conditions with $\mathbf{g} = (220)$ and $\mathbf{g} = (2-20)$ are chosen such that all types of dislocations are visible [361].

Figure 4.11 shows six cECCI micrographs processed with MIPAR to extract dislocation line features. Some γ matrix channels and/or γ' precipitate edges are also detected as lines and are shown here for clarity, however, they are removed from the total dislocation line length. Analogue to GND maps from HR-EBSD, the dislocation networks are not homogeneously distributed across the imaged areas, warranting a statistical analysis, as discussed in Section 4.4.2. Nonetheless, the dislocation densities extracted from Figure 4.11 range from $8.33 \times 10^{13} \text{ m}^{-2}$ to $1.05 \times 10^{14} \text{ m}^{-2}$ and therefore vary by only a factor of 1.26. Consistent results were found for all alloys and all deformation levels.

4.3.4 Correlative HR-EBSD/cECCI Assessments

Figures 4.12 and 4.13 illustrate damage accumulation in longitudinal sections of ABD-1 specimens. As shown previously in Figure 4.9(a), the lower bound of the GND density determined using HR-EBSD increases strongly from 0.075% to 0.3% creep strain and by a much lower factor to 1%. GND maps reveal higher dislocation densities in ‘horizontal’ matrix channels perpendicular to the loading axis. For the case of tensile creep and a negative lattice misfit at high temperatures, as designed for the three ABD alloys [103], a higher net stress will arise in these channels from the superposition of applied and misfit stresses [392, 525]. As such, dislocations glide preferentially in ‘horizontal’ channels where they gradually relieve interfacial coherency stresses [236, 237]. This misfit relaxation provides the driving force for directional precipitate coarsening [363, 388, 389, 393, 473]. As shown in the cECCI micrographs, γ' particles retain their cuboidal shape after 0.075% strain, whereas at

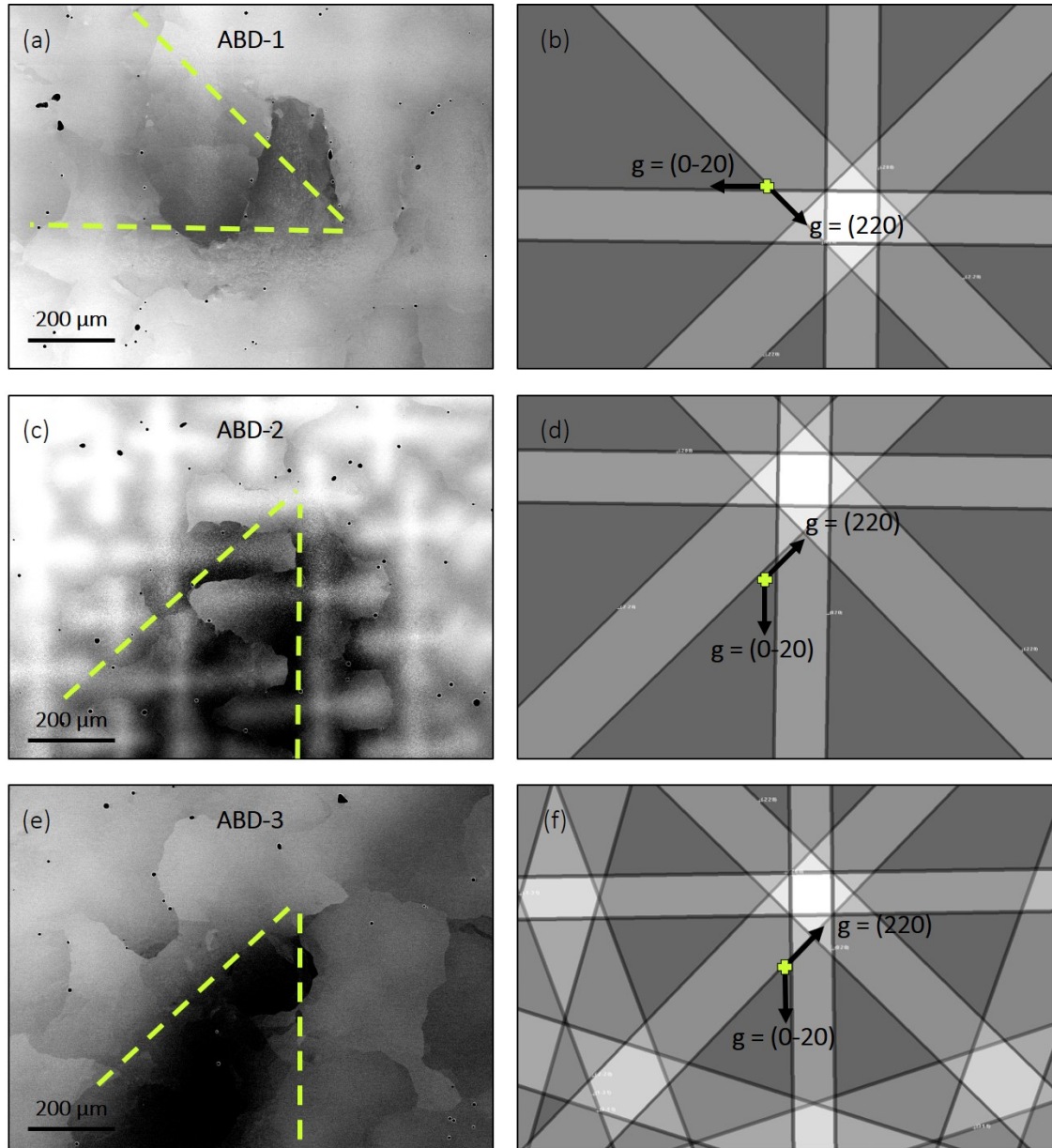


Figure 4.10: BSE micrographs of transverse sections through (a) ABD-1, (c) ABD-2, and (e) ABD-3, showing characteristic mosaicity. The crosses in (b), (d), and (e) illustrate approximate crystal orientations on simulated ECPs from the TOCA software. Active reflectors are labelled in each case. Good qualitative agreement is observed between simulated patterns and experimental BSE contrast, for which the dark ‘triangles’ are highlighted by dashed lines.

0.3% incipient precipitate coalescence can be observed, leading to the formation of more prominent rafted structures at 1% strain.

These observations are in agreement with reported levels of plastic strain necessary to relax misfit and to induce rafting. Pollock and Argon [363] estimated

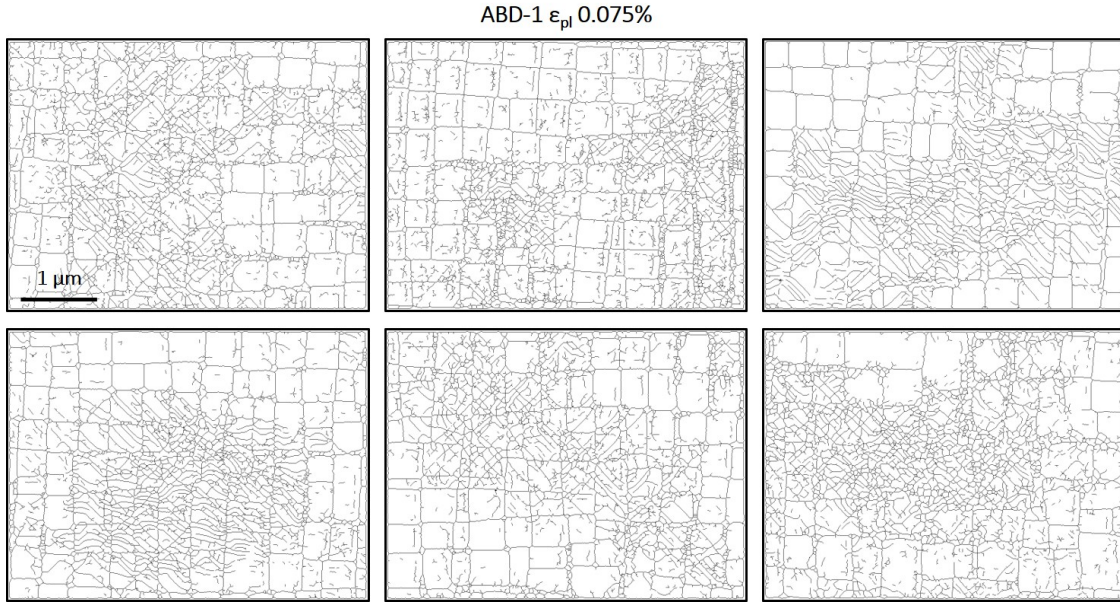


Figure 4.11: Dislocation line features extracted from six cECCI images of the transverse section in an ABD-1 sample deformed to 0.075% creep strain.

this to be 0.07% for CMSX-3, while Matan et al. [336] reported 0.1% for CMSX-4. Similarly, Socrate and Parks [605] analysed experimental creep transients of Ni–15at.%Al [606], Udimet 700 [607], and CMSX-3 [306] single-crystal specimens and concluded that misfit stresses are relieved in the range of $0.5 \leq \varepsilon_p/|\delta| \leq 2.0$, where ε_p is the accumulated plastic creep strain and δ is the lattice misfit. Lastly, Link et al. [321] assessed the loss of coherency during creep of SRR99 and CMSX-4 single-crystals in intermediate- and high-temperature regimes. These authors developed a microstructural model of equilibrium misfit, relating it to microscopic plastic strains in the γ and γ' phases and further to macroscopic strains. It was shown that the plastic primary strains resulting from misfit relaxation can be estimated as $\varepsilon_p \approx 2V|\delta|$ when precipitates retain their cuboidal shape and as $\varepsilon_p \approx 2V^N|\delta|$ when rafting occurs, with V and V^N representing the total matrix volume fraction and the volume fraction of ‘horizontal’ channels, respectively. Considering common misfit levels of $|\delta| = 0.3\%–1.5\%$ at 900 °C [608], these estimates are in good agreement with the observed behaviour of ABD-1 in the present work.

A shortcoming of analysing longitudinal sections is that the relative size of ‘horizontal’ and ‘vertical’ channels can be skewed by the direction the samples were

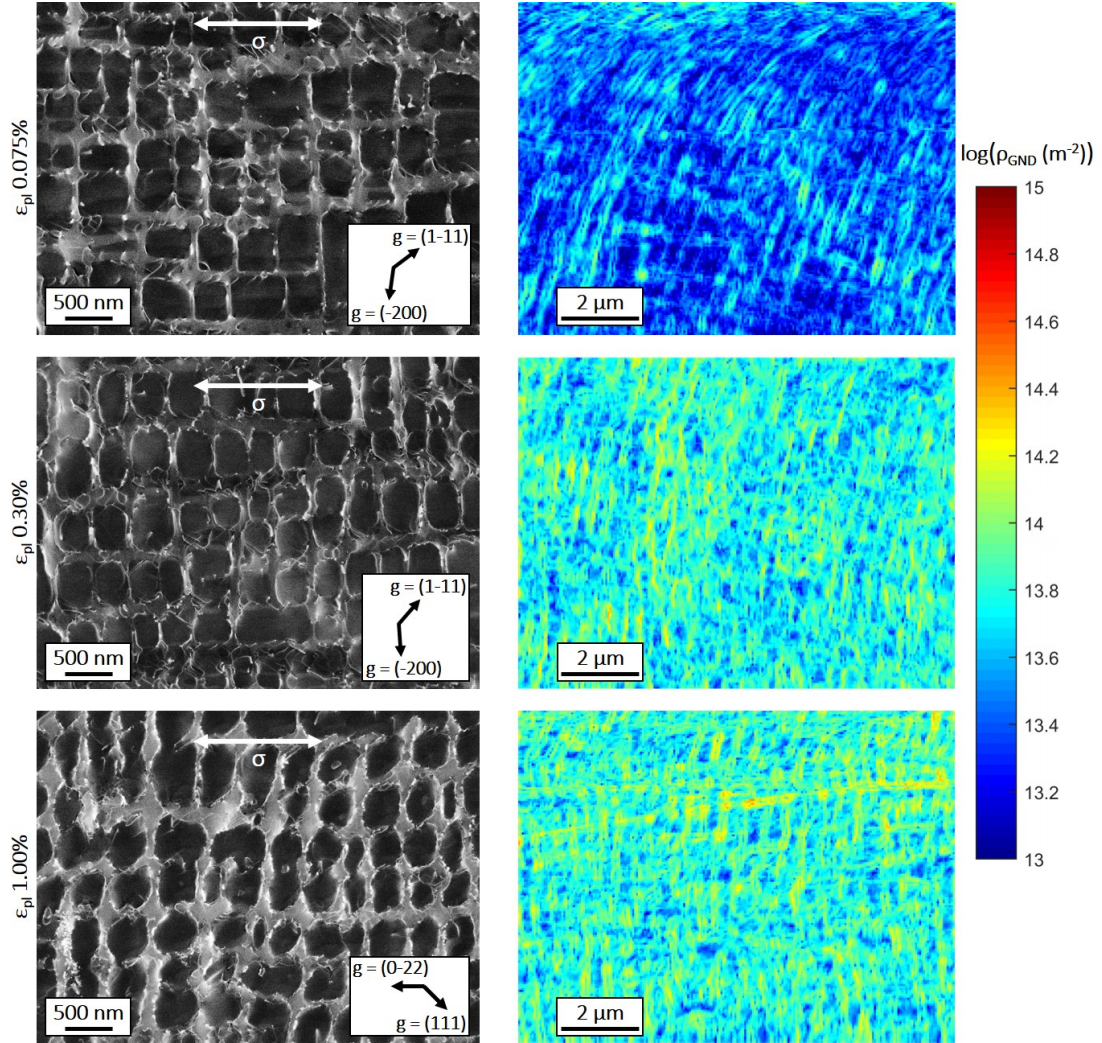


Figure 4.12: cECCI micrographs and HR-EBSD GND maps showing damage accumulation in longitudinal sections of ABD-1. The reflectors used for cECCI imaging are marked at the bottom right of each micrograph. The logarithmic colour scale corresponds to GND densities between 10^{13} and 10^{15} m^{-2} in the HR-EBSD maps. The same labelling is maintained for all further cECCI/HR-EBSD comparisons.

cut in, as the surface normal for these images was not controlled to correspond to a $\langle 001 \rangle$ direction. As such, a more accurate view of damage accumulation in ABD-1 can be gained from the transverse sections in Figures 4.14 and 4.15. Dislocations accumulate primarily in γ matrix channels, as seen clearly in the GND maps of Figure 4.14. No signs of stacking fault shear [339] could be detected in any of the cECCI micrographs, thus confirming the assumption that γ' precipitates remain impenetrable during early stages of tertiary creep. The GND density rises rapidly from an order of $3 \times 10^{13} \text{ m}^{-2}$ at 0.075% strain to $7 \times 10^{13} \text{ m}^{-2}$ at 0.3% and then at a

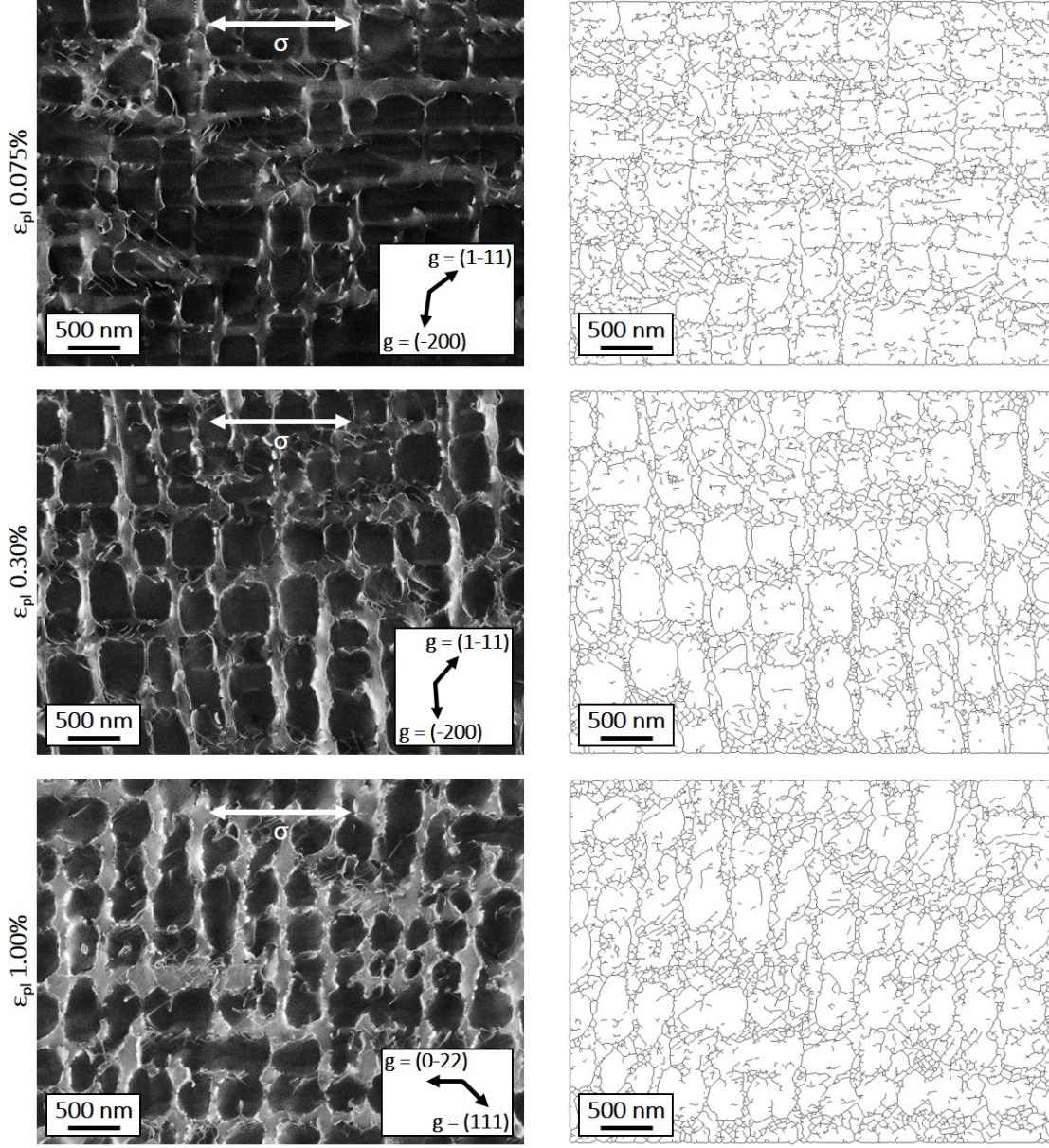


Figure 4.13: cECCI micrographs and corresponding extracted dislocation line features showing damage accumulation in longitudinal sections of ABD-1.

reduced rate up to 10^{14} m^{-2} at 1%. It should be noted that for the lowest deformation level, GND density estimates are close to the resolution limit of HR-EBSD [601, 602] and this aspect is discussed in more detail in Section 4.4.1. Deformation hot spots again appear in regions with locally wider matrix channels or in areas where the transverse section was made through a channel.

The development of dislocation networks with plastic creep deformation in Figure 4.15 follows the general trends identified previously in TEM [236], SEM

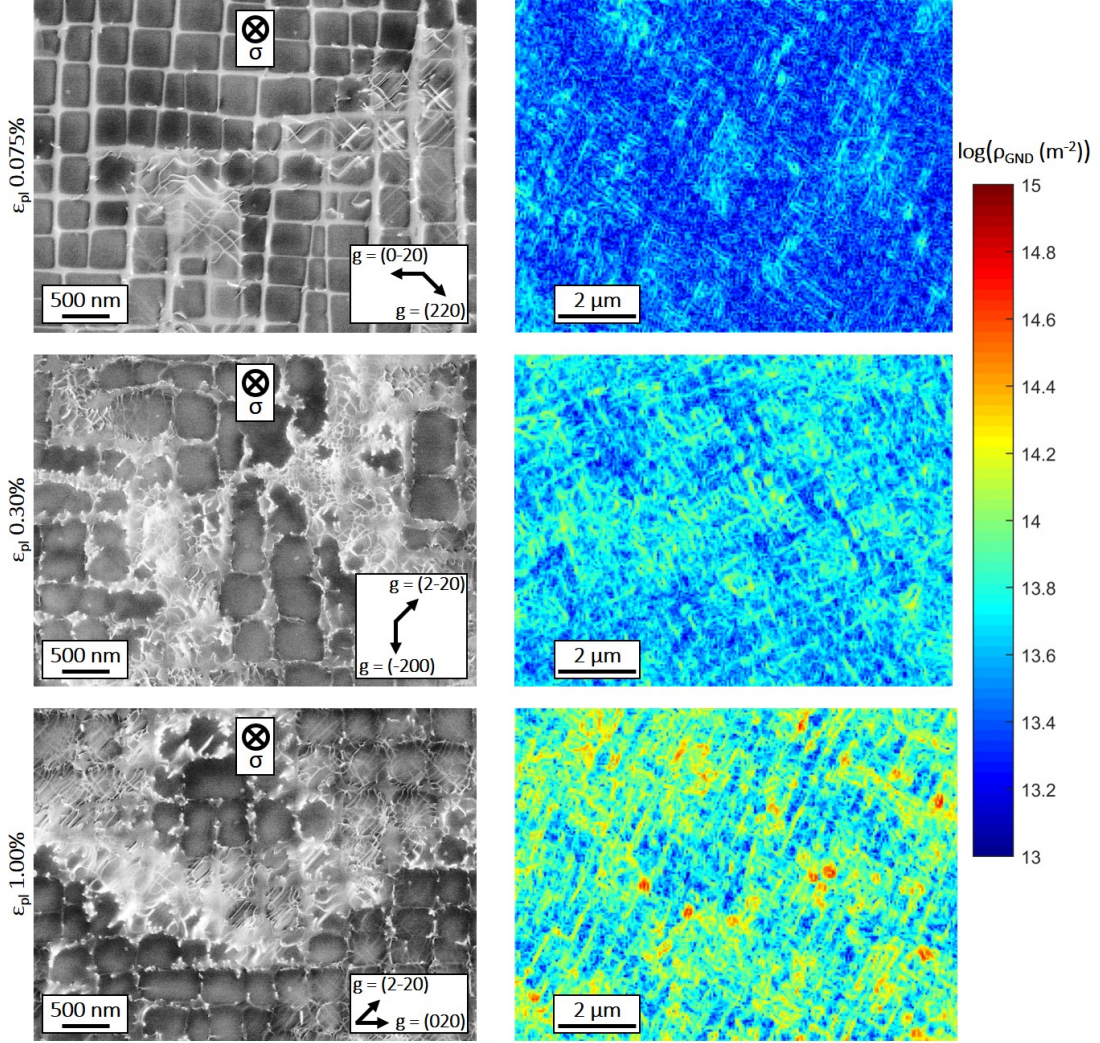


Figure 4.14: cECCI micrographs and HR-EBSD GND maps showing damage accumulation in transverse sections of ABD-1.

[375], and ECCI [361] micrographs. In uncrept regions, far from the specimen gauge section, only a few isolated dislocations are observed, amounting to average densities on the order of 10^{11} m^{-2} . A recent cECCI study has identified these ID sources as the main active dislocation emitters during later stages of creep [361]. They were shown to induce dislocation ‘avalanches’ *via* Frank-Read [609] or double cross-slip [610] mechanisms once a critical plastic strain level has been reached. The ‘avalanche’ events gives rise to a rapid increase in dislocation density and to the formation of dislocation networks with some degree of mechanical stability. This observation contradicts earlier TEM studies which suggested that LAGB, formed as crystal defects during casting [611], are the primary sources of new

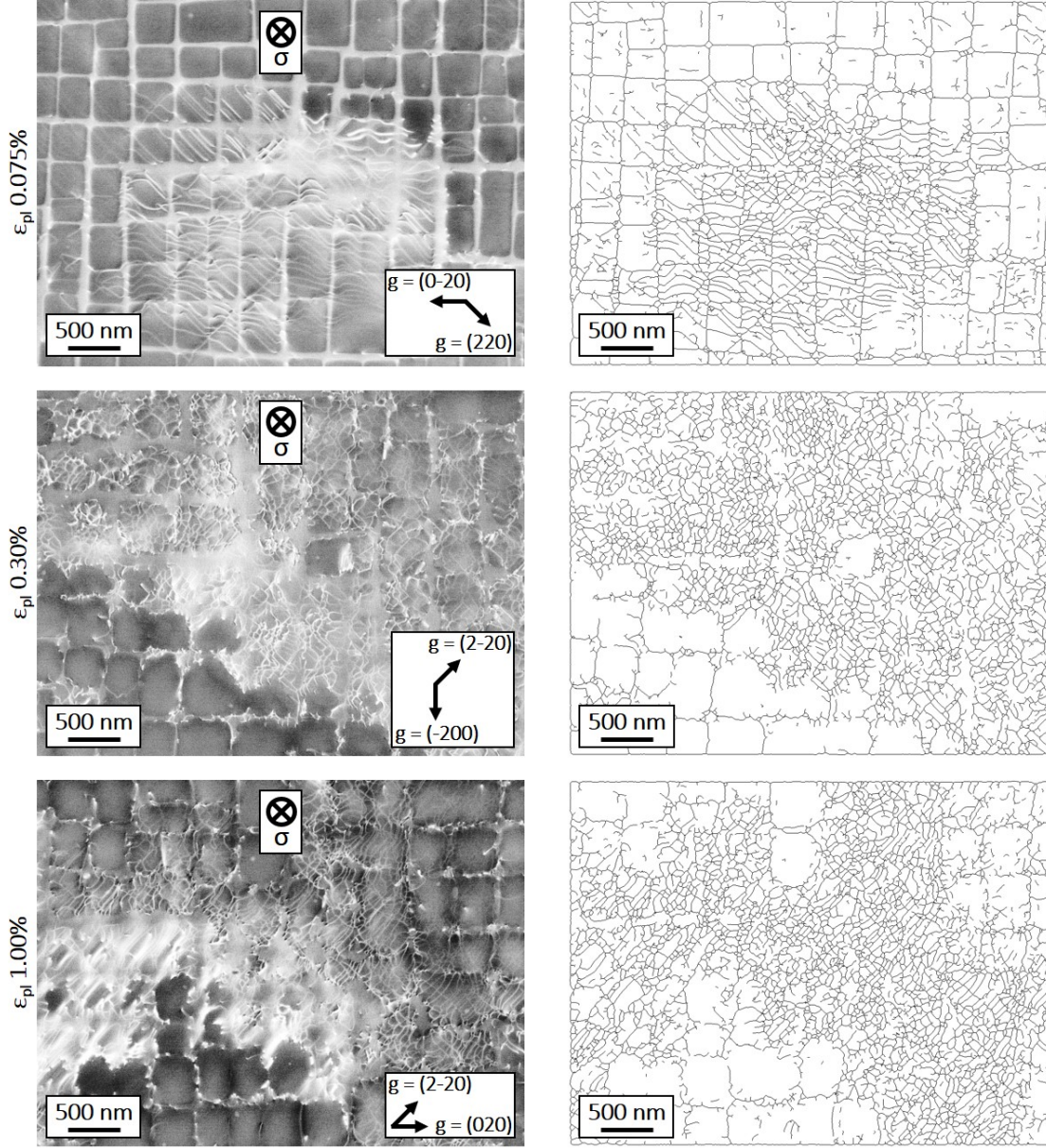


Figure 4.15: cECCI micrographs and corresponding extracted dislocation line features in transverse sections of ABD-1.

mobile dislocations [236, 306, 322, 323, 363].

Given the limited number of sources, dislocations predominantly of a single Burgers vector are observed at the early stage of 0.075% strain in ABD-1. As interfacial coherency strains are relieved and the end of the primary creep transient is approached, dislocations with different Burgers vectors react to form three-dimensional nodal networks [236]. During this process, they create new, non-slip dislocations, possessing Burgers vectors with zero resolved shear stress for the

given $\langle 001 \rangle$ tensile stress. The reactions by which dislocations move from ‘slip’ to ‘mismatch’ orientations and reduce misfit have been discussed in detail in references [236, 237, 368]. For the case of ABD-1, most dislocations remain in $\langle 011 \rangle$ ‘slip’ orientations at 0.075% and go on to form distorted ‘mismatch’ networks at 0.3% and 1% strain. In agreement with previous work [236, 368], these last two networks exhibit square- and hexagon-shaped dislocation configurations with Burgers vectors of type $a/2\langle 110 \rangle$, which form through local dislocation rearrangements. It is worth noting that the alloy microstructure appears uniformly avalanched with dislocations, regardless of whether the imaged areas were far away from grown-in LAGB or directly surrounding a LAGB, in agreement with the work of Ram et al. [361]. This aspect is discussed in further detail in Section 4.4.2.

Results for ABD-2 in Figures 4.16 and 4.17 show that the deformation levels reached in ETMT tests are too low to give rise to dislocation ‘avalanches’. GND maps reveal a fairly homogeneous distribution of dislocations in matrix channels. The estimated average GND densities are higher than in the ABD-1 sample deformed to 0.075% creep strain, despite lower deformation levels of up to 0.07%. As such, it appears that deformation largely occurs immediately after load application during the observed initial creep transient in Figure 4.5(b) and prior to the onset of negative creep. After 0.02% and 0.05% strain, most regions exhibit very little dislocation activity in cECCI micrographs. Interestingly, areas surrounding LAGB show even lower dislocation densities than those in dendrite cores, as discussed in Section 4.4.2. Dislocation segments emitted from LAGB are observed to only percolate a few matrix channels away into the undeformed crystal. At 0.07% strain, dislocations appear more evenly distributed in both LAGB and dendrite core regions. Similar signs of network formation to relieve misfit stresses can be observed as for ABD-1.

The rapid damage evolution observed in ETMT tests of ABD-3 is confirmed by the results in Figures 4.18 and 4.19. GND density rises rapidly to levels on the order of 10^{14} m^{-2} . Furthermore, while GNDs are observed to accumulate in γ matrix channels after 0.15% strain, their distribution becomes much more uniform at 0.3% and 1% strain. This is supported by cECCI micrographs, which show

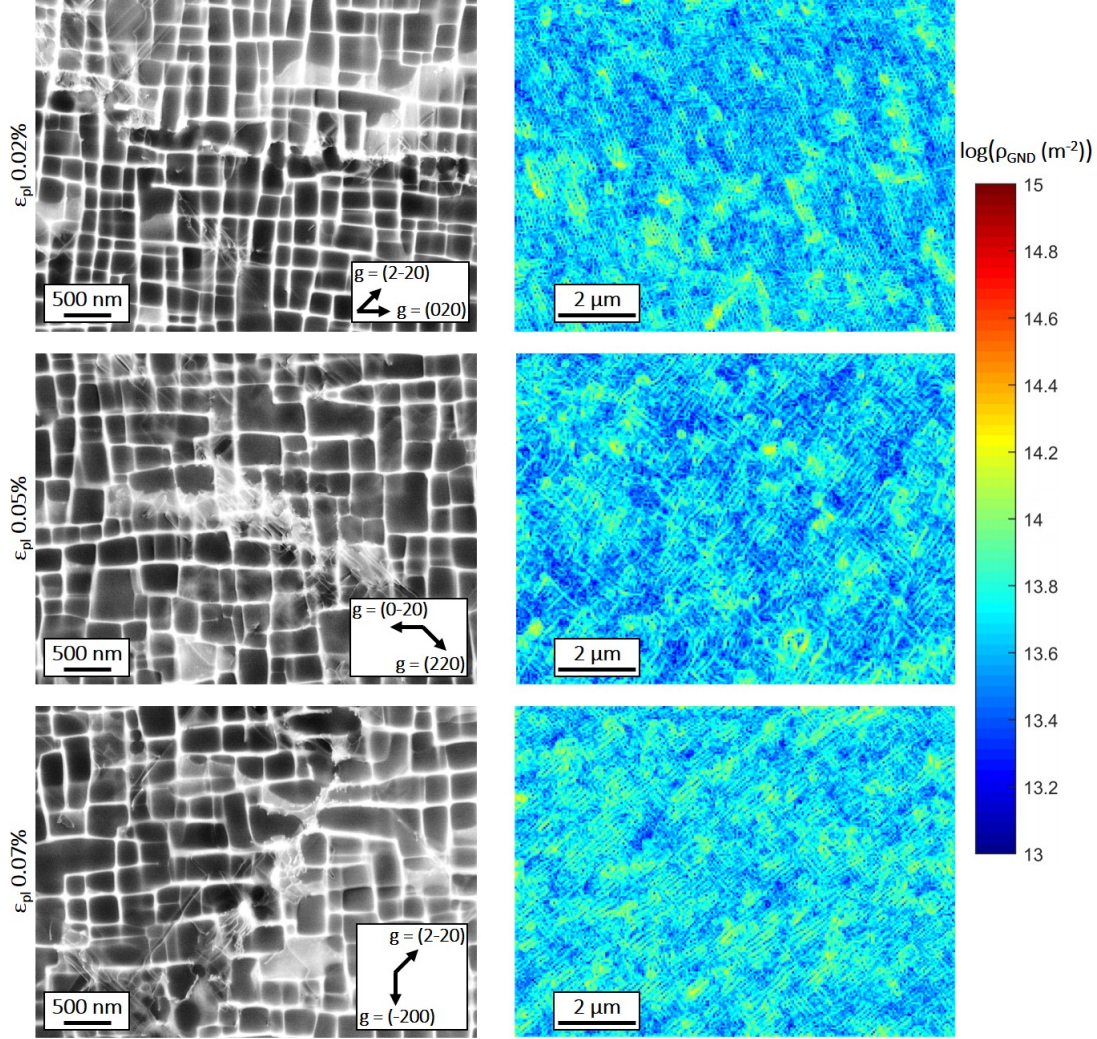


Figure 4.16: cECCI micrographs and HR-EBSD GND maps showing damage accumulation in transverse sections of ABD-2.

that dislocation networks form immediately after load application, with the entire microstructure being ‘avalanched’ after 1% strain. Furthermore, unlike the previous two alloys, ABD-3 exhibits some signs of stacking fault shearing, as dislocations are seen emerging from several γ' precipitates. Previous work [338–340, 612] showed that primary creep is mainly a result of the propagation of $a\langle 112 \rangle$ dislocation ribbons through both γ and γ' and that each ribbon nucleates from two pairs of $a/2\langle 110 \rangle$ dislocations. Therefore, the rapid formation of $a/2\langle 110 \rangle$, as observed in the specimen deformed to 0.015% strain, is a requirement for the subsequent activation of $\langle 112 \rangle\{111\}$ systems. Additional $a/2\langle 110 \rangle$ dislocations accumulating in the γ channels at 0.3% and 1% plastic strain provide effective pinning for the $a\langle 112 \rangle$ ribbons and

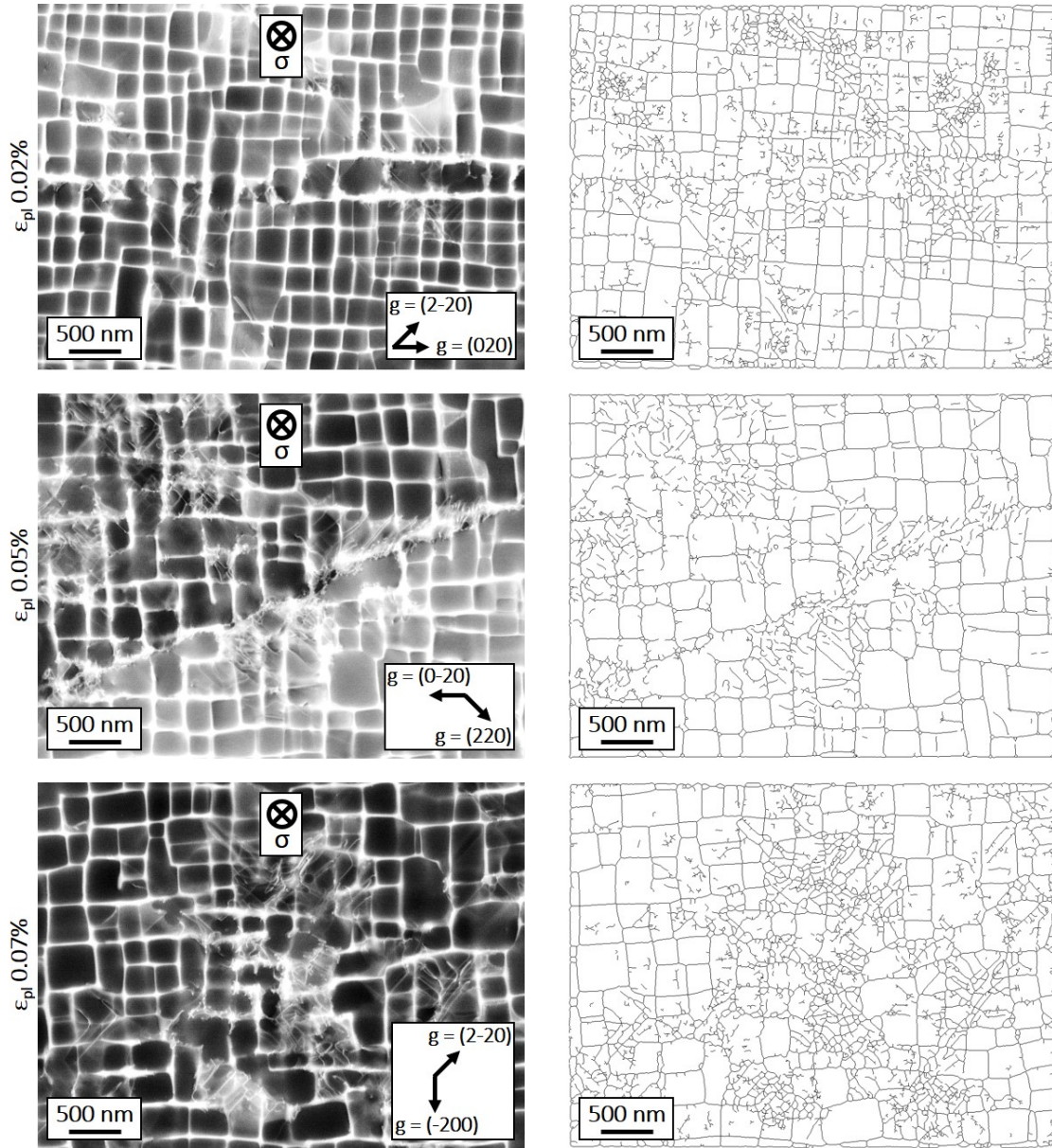


Figure 4.17: cECCI micrographs and corresponding extracted dislocation line features in transverse sections of ABD-2.

terminate the primary creep stage, as observed in Figure 4.4(c). No attempt has been made to accurately identify the SISF, SESF, or APB faults known to separate the four partial dislocations of each ribbon. Nonetheless, several precipitates in the cECCI micrographs show characteristic signs of ribbon propagation, as observed conventionally with TEM [338–340, 612].

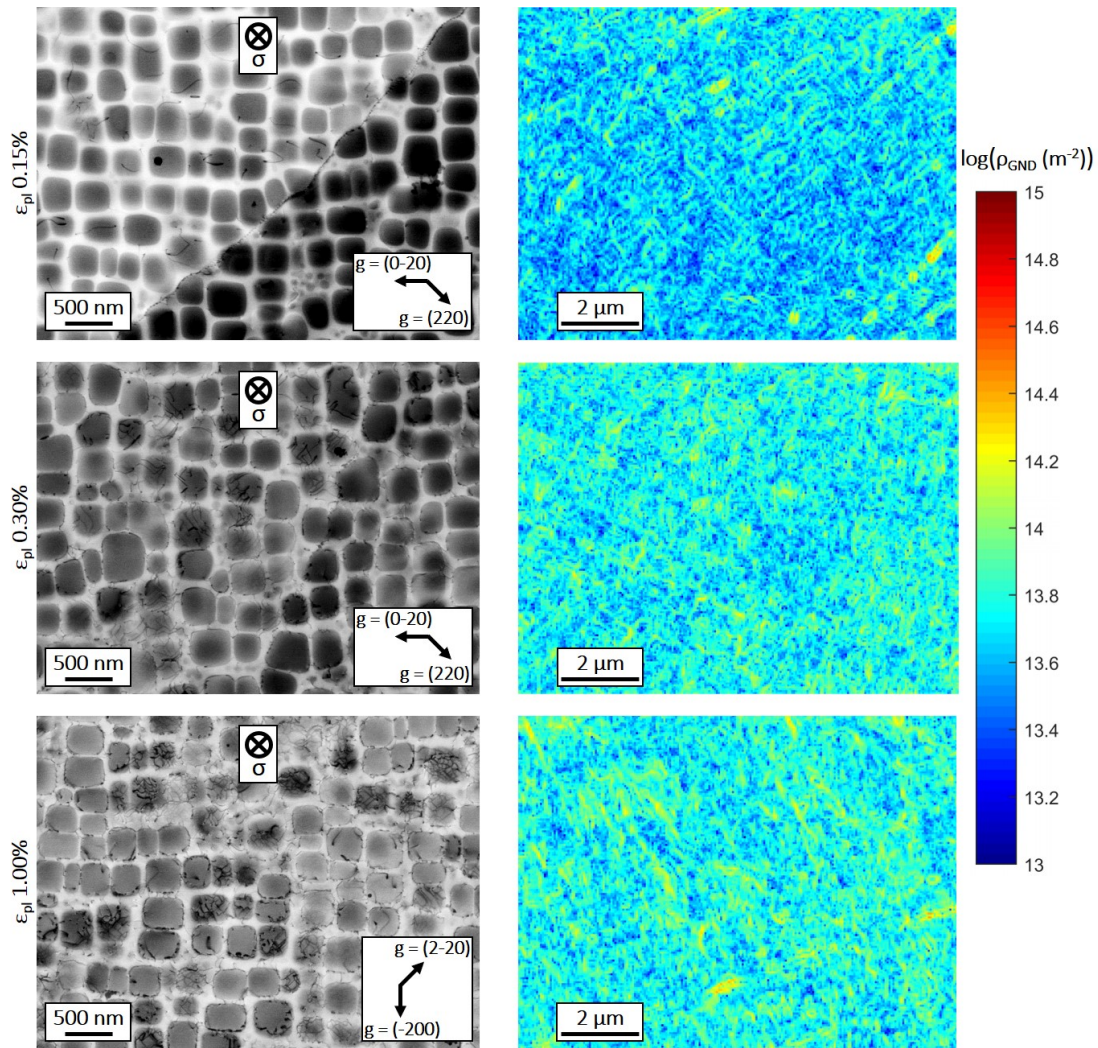


Figure 4.18: cECCI micrographs and HR-EBSD GND maps showing damage accumulation in transverse sections of ABD-3.

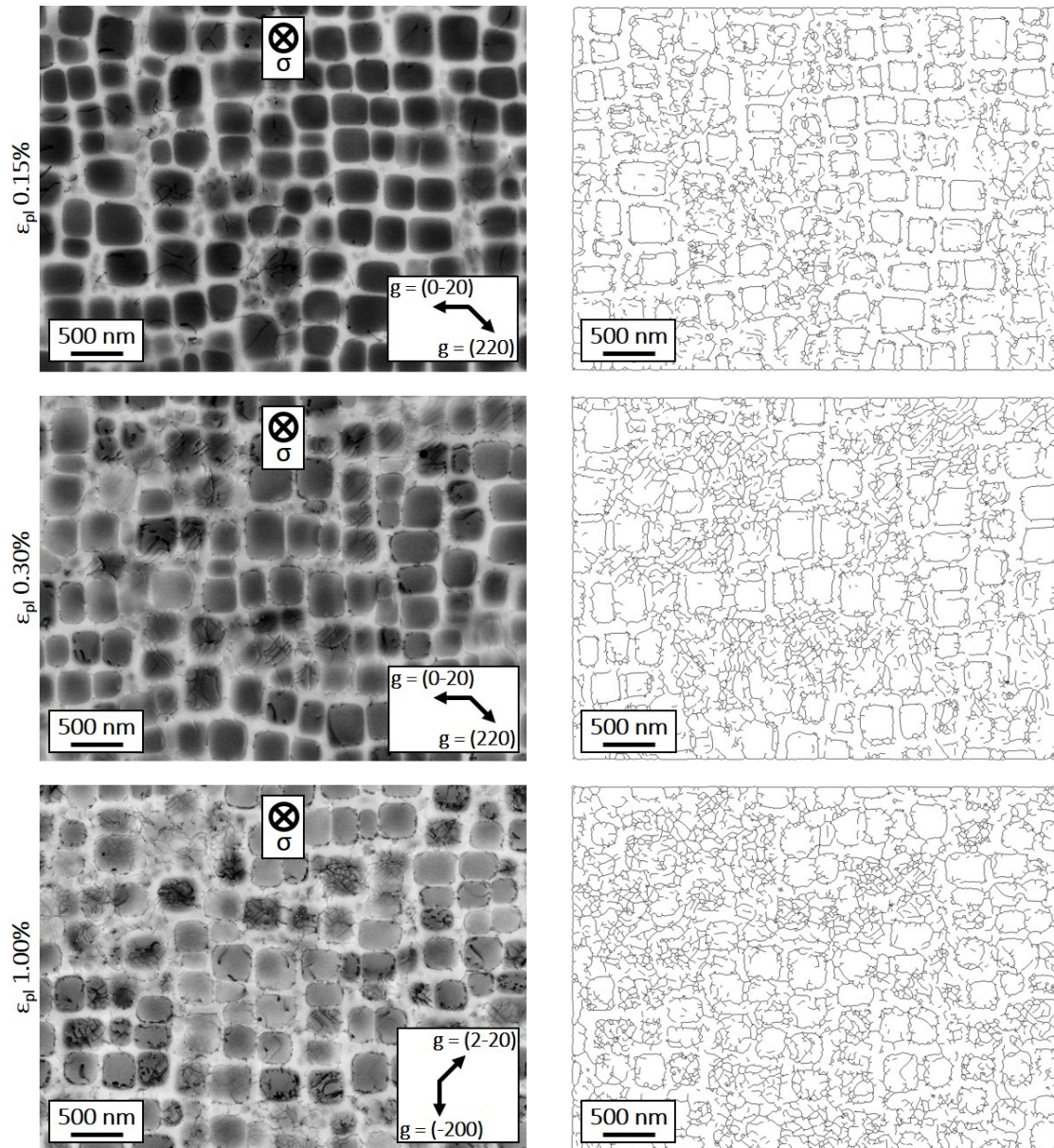


Figure 4.19: cECI micrographs and corresponding extracted dislocation line features in transverse sections of ABD-3.

4.4 Discussion

4.4.1 Accuracy of Dislocation Density Estimates from HR-EBSD and cECCI

Before discussing and comparing dislocation density values obtained from HR-EBSD and cECCI, it is instructive to briefly consider the key factors influencing these results.

Following the considerations of Ashby [613], NBSA deformed in tertiary creep conditions are a good example of a plastically non-homogeneous material, as the hard γ' particles impose gradients of plastic deformation. These local gradients require an increasingly dense array of GNDs, which allow for a compatible deformation of the matrix and of the particles. GNDs correspond to the excess dislocations accounting for a closure failure of the Burgers circuit around a given measurement area with HR-EBSD [614]. In contrast, SSDs accumulate by random mutual trapping events associated with general, uniform deformation [613]. They consist of the dipoles, multipoles, and loops within the considered Burgers circuit and do not result in curvatures at the length scale of the circuit [614]. Therefore, the fraction of the total dislocation density determined as GNDs by HR-EBSD will decrease as the size of the Burgers circuit increases, and the overall distinction between SSDs and GNDs will be dependent on length scale [614].

This raises important questions regarding the choice of step size for HR-EBSD [559, 615, 616], denoted in the following as L . On the one hand, if L is chosen to be too small, the measured GND density will be dominated by noise and the map size will be constrained by the time required for pattern capture and cross-correlation processing [559]. Furthermore, it has been shown for a wide range of materials that the calculated GND density scales roughly inversely with L and this relationship has been associated with a transition of SSDs to GNDs as the size of the Burgers circuit is reduced [615]. On the other hand, if L is too large, important deformation features will no longer be resolved. As such, an appropriate choice for L can only be made by estimating characteristic deformation length scales for the studied material. Ashby [613] derived the simple relation $\lambda^G = d/\phi_p$ for the geometric slip distance, λ^G ,

in a material with non-deforming, equiaxed, cuboidal particles of volume fraction ϕ_p and side length d . For the ABD alloys, inserting measured values for ϕ_p and d yields geometric slip distances of between 280 nm for ABD-2 and 760 nm for ABD-3. However, considering HR-EBSD results, these estimates appear too high and a more reasonable value is the matrix channel width, w [306]. This value ranges between around 60 nm for ABD-2 and 110 nm for ABD-3. Another constraint that must be considered at this point is the physical spatial resolution of EBSD in a FEG SEM due to the limit of electron interaction volumes. For the case of EBSD scans on copper at 20 keV and 10 nA, Chen et al. [617] reported a lateral resolution of 39.2 ± 4.5 nm and a longitudinal resolution of 120.8 ± 5.0 nm.

Two further scan parameters that must be chosen alongside the step size are the binning size, which controls how many charges of adjacent pixels are combined into a single super-pixel during the readout process, and the exposure time, which represents the time spent collecting sufficient charge to form an EBSP [559, 602]. Following the work of Jiang et al. [559], the overall signal-to-noise ratio should not change significantly despite the binning process. These authors carried out HR-EBSD analyses of undeformed, single-crystal silicon and of deformed, polycrystalline copper at a constant ratio of binning size to exposure time. For the case of low dislocation densities in the silicon specimen, the GND sensitivity increased by around a factor of 2 after 2×2 binning to about $2.8 \times 10^{13} \text{ m}^{-2}$. However, for higher deformation levels on the order of $2 \times 10^{14} \text{ m}^{-2}$ in copper, no critical changes were observed even at 8×8 binning. Hansen et al. [602] found that 2×2 binning did not impact GND estimates from simulated EBSPs, however, reported in contrast to Jiang et al. that GND density decreases with further binning. Similarly, in the present work, no significant differences could be noted between unbinned and 2×2 binned results.

All things considered, a relatively low step size of 50 nm, 2×2 binning, and a dwell time of 50 ms were chosen, in an attempt to capture damage accumulation in the matrix channels as accurately as possible. Nonetheless, it must be acknowledged that the noise floor for HR-EBSD under these conditions will be at around $2 \times 10^{13} \text{ m}^{-2}$ [601, 602]. This presents a challenging lower limit to overcome in the context

of analysing earlier stages of tertiary creep and the activation of ID sources in single-crystal superalloys.

Finally, it must be acknowledged that other factors may further degrade pattern quality and decrease accuracy. These include sample preparation, possible oxide layers and hydrocarbon deposition, illumination conditions, detector and camera properties, and post-processing parameters [559, 602, 615, 618, 619].

A discussion on the accuracy of dislocation estimates from cECCI is more straightforward, but also more basic compared to the considerations on HR-EBSD. Several factors listed above again come into play, including sample preparation, illumination conditions, and detector properties [572]. Based on their theoretical review of ECC, Zaefferer and Elhami [572] pointed out that in order to obtain a strong contrast, the crystal has to be orientated such that the primary beam enters the crystal close to the Bragg angle of only one low-index lattice plane. These authors further explained the importance of measuring and calibrating errors in the axes of the SEM stage and of making final position adjustments to attain minimum brightness conditions for the observed area. For the present work, stage axes were previously calibrated using a silicon single-crystal and optimal channelling conditions were found following TOCA predictions.

In addition to accurate positioning, Zaefferer and Elhami [572] noted that only the newest generation of FEG SEMs — including the Zeiss Merlin with Gemini 2 optics used in the present study — combine the necessary attributes of a high beam current and a good signal-to-noise ratio on the one hand and a small beam convergence on the other. Using data provided by Carl Zeiss Microscopy GmbH for the Gemini 2 column, a primary beam resolution of 2.9 nm was estimated when the instrument is running in similar conditions to those of the present study — high beam current mode, beam energy of 30 keV, beam current of 11.6 nA, aperture of 120 μm , and working distance of 7 mm [572].

An unavoidable error source for ECCI is associated with changes in sample orientation across LAGB. These have been shown to be on the order of several degrees [611], meaning they give rise to a noticeable change in contrast, as observed

in Figures 4.16 to 4.18. As such, dislocation densities obtained from regions around LAGB may be artificially low, as some dislocations are not properly captured with cECCI.

The assumption that the probing depth is five times larger than the extinction distance and the estimates for the extinction distance given a certain accelerating voltage and certain reflectors are unlikely to have a major impact on relative dislocation density values. As all micrographs were obtained in nearly identical conditions, errors in the probing depth will likely be uniform and will only affect absolute values [573]. Errors will also arise from the image processing steps used to extract dislocation line features. This procedure involves several steps: first, line features are detected using a Frangi filter [574]; second, brightness and contrast are equalized across the image; third, a basic threshold is used to select only pixels above a certain value (for the case of bright dislocation lines); fourth, a clean-up filter is applied to reject erroneous features; and fifth, incorrectly detected precipitate edges or matrix channels are manually removed. It is difficult to estimate the magnitude of these errors, but it can be presumed these will increase with plastic strain level.

4.4.2 **Assessment of Damage Accumulation during Tertiary Creep**

Although combining HR-EBSD and ECCI analyses shows great potential, only few studies have applied this approach to the study of deformation in engineering materials. Seal et al. [620] analysed stress fields ahead of dislocation pile-ups at GB in pure titanium, but made no attempt to quantitatively determine GND and/or total dislocation densities. Vilalta-Clemente et al. [614] assessed threading dislocation densities in InAlN thin films grown on SiC and Al₂O₃ substrates and found a good agreement between HR-EBSD and ECCI, with the former giving slightly higher values for edge dislocations and the latter for screw and mixed dislocation types. Dunlap et al. [616] analysed nanoindentation damage in high purity tantalum and intriguingly obtained higher density values from HR-EBSD. Most recently, Breitbarth et al. [621] investigated plastic zones ahead of crack tips introduced by

fatigue loading in the aluminium alloy AA2024 and found that GND density values from Hough-based EBSD were around 10% of the total density obtained with ECCI.

Discrepancies regarding higher density values from HR-EBSD have been associated with noise caused by the selected EBSD step size and detector binning conditions [614, 616], which highlights the importance of carefully controlling these parameters, as discussed in Section 4.4.1. Furthermore, ECCI may miss dislocations under invisibility conditions and may also fail to resolve individual dislocations in highly-deformed regions [616, 621]. Finally, an important point raised by Vilalta-Clemente et al. [614] is that the original Nye-Kröner formulation was aimed at deformed metals with relatively high dislocation densities, whereas at lower values, dislocations should be viewed as discrete entities rather than a continuous field.

Despite some of these shortcomings and the possible error sources discussed in Section 4.4.1, it remains instructive to compare dislocation density estimates from HR-EBSD and cECCI. Figure 4.20 shows the total dislocation density measured in cECCI micrographs of dendrite cores (DC) and interdendritic regions (IR). The error bars correspond to one standard deviation based on individual density estimates of at least five micrographs. For ABD-1 and ABD-3, differences between DC and IR are minute. This is in agreement with the results of Ram et al. [361], who showed that ID rather than LAGB are the main sources of mobile dislocations and that deformation is distributed homogeneously across all regions.

Interestingly, dislocation densities in ABD-2 are lower near LAGB. This appears counterintuitive at first, as the segregation of heavy solutes to the DC, also observed for ABD-2 in Figure 4.10(c), is expected to slow down diffusion-controlled processes like dislocation climb at γ/γ' interfaces. However, this observation can be linked to a lower γ' volume fraction in DC due to the microsegregation of γ' -formers aluminium, tantalum, and titanium to IR [246, 604, 622–626] and to a less homogeneous size distribution [463, 627, 628]. These same effects have been reported in several studies on the fourth-generation single-crystal superalloy MC-NG [629–631], with a comparable chemical composition to ABD-2 [225]. Accelerated incipient plasticity and rafting were also observed in the DC of single-crystal superalloys CMSX-2 [632],

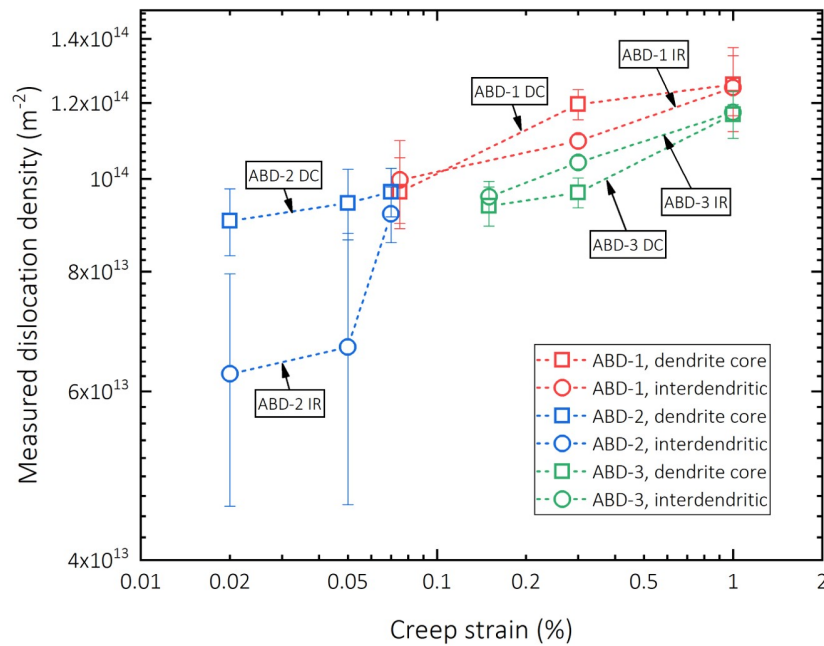


Figure 4.20: Changes in total dislocation density observed in cECCI micrographs with creep strain. Each point corresponds to the average value from at least five images taken in dendrite core regions or around LAGB. The error bars correspond to one standard deviation.

CMSX-4 [633], and ERBO-1 [529] and of directionally solidified IN-792 [628]. As such, the accelerated plasticity in DC can be associated with higher effective stresses arising from the chemical heterogeneity. These can overcome the opposite effects of retarded diffusion kinetics and will promote dislocation activity in DC [529, 628, 630].

The previous cECCI results from DC are compared to GND density estimates from HR-EBSD in Figure 4.21. A first reassuring point is that total GND+SSD values lie above those for GNDs alone for all alloys and deformation levels. Results are in good agreement with previous reports of GNDs representing between 10% and 50% of the total dislocation density [621, 634, 635]. Significant overlap of the error bars can be noted, with scatter appearing to be much larger for HR-EBSD. However, this scatter is a result of HR-EBSD capturing the quantitative damage distribution across the scanned area, whereas the error bars for cECCI encompass one standard deviation for individual data sets and do not account for actual dislocation distributions. Changes of dislocation density with plastic creep strain are challenging to rationalise due to possible inaccuracies in data

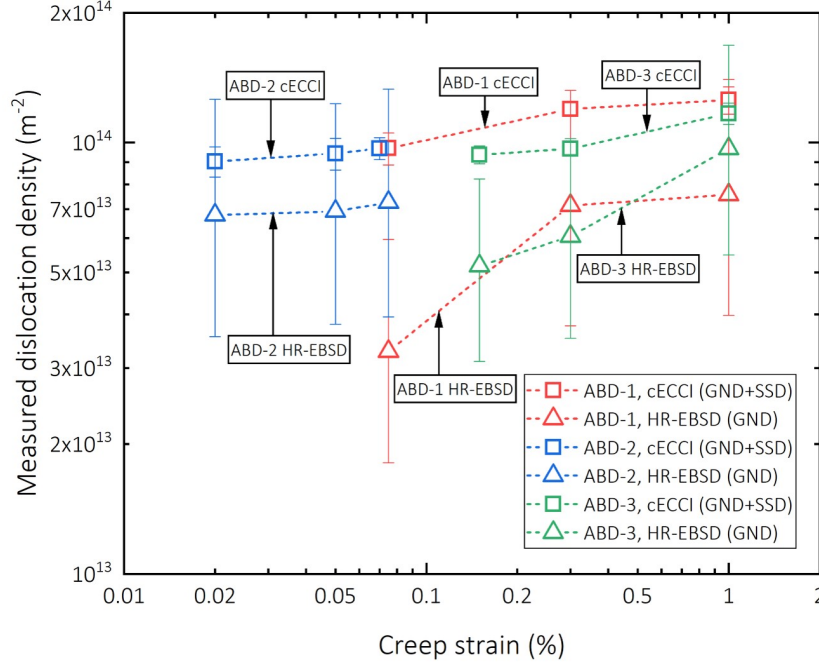


Figure 4.21: Comparison of GND+SSD densities observed in cECCI micrographs and GND densities estimated with HR-EBSD. Both cECCI images and HR-EBSD scans were carried out in dendrite core regions. Each point corresponds to the average value from at least five cECCI images or HR-EBSD GND maps, respectively. The error bars for cECCI correspond to one standard deviation; those for HR-EBSD to the span between the 10th and the 90th percentile, considering GND data from all maps at a certain strain level.

acquisition and analysis. As such, in order to more carefully examine creep damage accumulation in the ABD alloys and to obtain a benchmark for HR-EBSD and cECCI results, DDD modelling is employed.

4.4.3 Implications of Creep Damage Accumulation on Alloy Design

The simulation environments for DDD generated using the parameters described in Section 4.2.5 are illustrated in Figures 4.22 and 4.23. In each case, the five Frank-Read sources of $1/2\langle 110 \rangle$ mixed character are positioned at the same locations within the simulation cell, as shown in Figure 4.22(a)-(c). The percolation of dislocations through γ channels as creep deformation proceeds is presented in Figure 4.22(d)-(o) and Figure 4.23(a)-(l) at 0.01%, 0.03%, 0.1%, and 0.3% plastic strain. Simulation cells are viewed along the $[001]$ tensile axis in Figure 4.22, analogue to the transverse

sections imaged with HR-EBSD and cECCI, and perpendicular to the tensile axis in Figure 4.23, analogue to the longitudinal sections. To maintain a clear view, only the central 3×3 precipitates are illustrated.

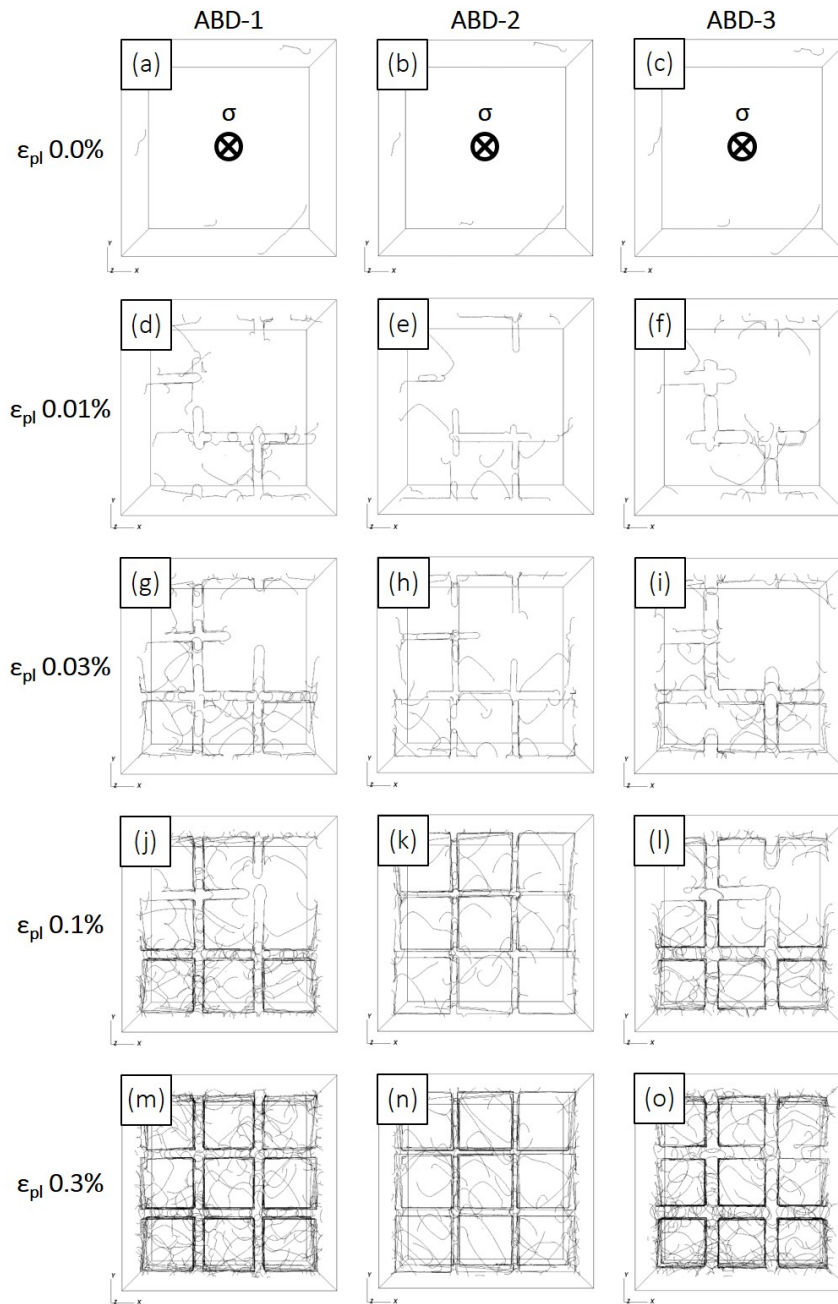


Figure 4.22: (a)-(c) Initial simulation states for ABD-1, ABD-2, and ABD-3, consisting of five Frank-Read sources of $1/2\langle 110 \rangle$ mixed character with an individual line length of $0.35 \mu\text{m}$. (d)-(o) Simulation states after creep deformation between 0.01% and 0.3% plastic strain. All cells are viewed along the $[001]$ tensile direction, corresponding to the z -axis. Likewise, the x - and y -axes correspond to the $[100]$ and the $[010]$ directions, respectively.

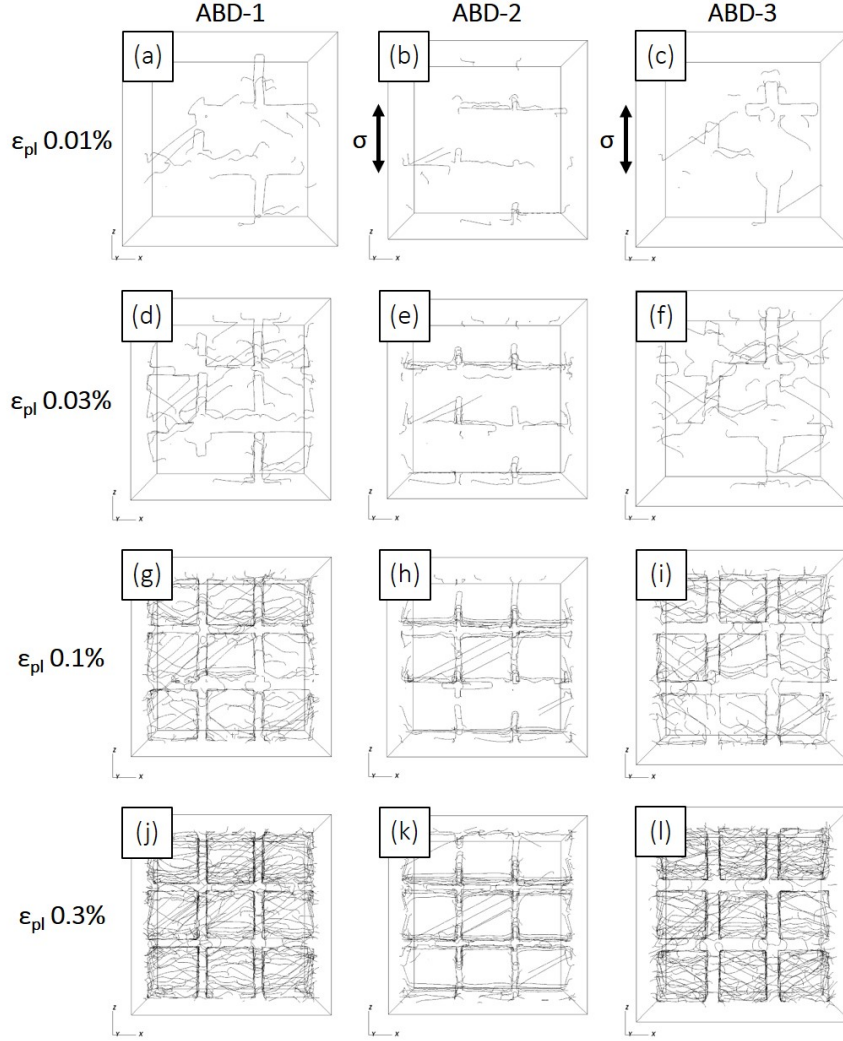


Figure 4.23: (a)-(l) Simulation states after creep deformation between 0.01% and 0.3% plastic strain. All cells are viewed along the $[010]$ direction, corresponding to the y -axis. Likewise, the x - and z -axes correspond to the $[100]$ and the $[001]$ directions, respectively.

After the onset of plastic deformation, the Frank-Read sources bow out and propagate dislocation loops along different $\{111\}$ glide planes. Given their low initial density, dislocations can at first move freely through the matrix channels, with little mutual interaction. Ram et al. [361] surmise that this unconstrained glide is what gives rise to the strong initial increase in total dislocation density, as observed in Figure 4.24. For all three alloys, the rate of dislocation multiplication, $\partial\rho/\partial\varepsilon$, exhibits an initial peak at levels up to $1.5 \times 10^{15} \text{ m}^{-2}$. Furthermore, as the ID sources can be assumed to be homogeneously distributed throughout the material, they can give rise

to equally homogeneous dislocation ‘avalanches’, as seen in the cECCI micrographs.

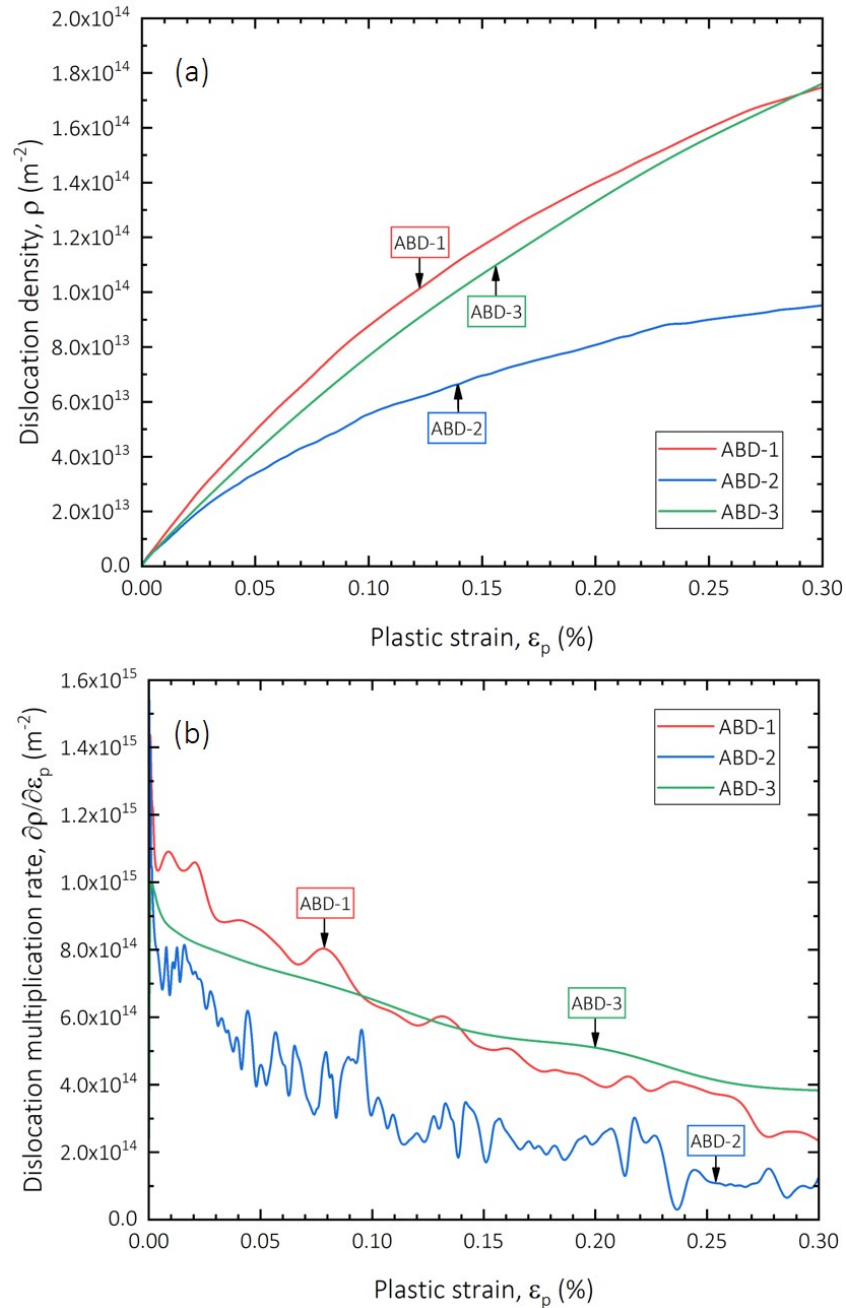


Figure 4.24: Changes in (a) total dislocation density, ρ , and (b) rate of dislocation multiplication, $\partial\rho/\partial\varepsilon$, with plastic creep strain, obtained from DDD simulations.

As creep deformation continues, dislocation lines are gradually deposited at γ/γ' interfaces. The segments located between precipitates bow out into matrix channels, where they move sluggishly to overcome the solid solution resistance. Short-range interactions between dislocations with different Burgers vectors occur

at an increasing rate in the channels and lead to an exponential reduction in the dislocation multiplication rate and to the formation of three-dimensional nodal networks, as also observed in cECCI. Finally, an equilibrium state is reached, in which the glide/climb mobility plays a decisive role in controlling further damage accumulation. The general trend for the evolution of dislocation density with creep strain can be described using the fundamental equation proposed by Gilman [636] for the dependence of mobile dislocation density on plastic strain in crystalline solids: $\rho_m = (\rho_0 + M\varepsilon) \exp(-\phi\varepsilon)$. Here, ρ_0 is the initial dislocation density, M is a multiplication parameter leading to an initial rise in mobile dislocation density, and ϕ is an attrition parameter which expresses the exponential decay over time. This equation has been used successfully to describe the creep response of single-crystal CMSX-4 specimens in the tertiary and rafting regimes [335, 337].

While the general trends for the dependence of the total dislocation density and the dislocation multiplication rate on creep strain in Figure 4.24 are the same for all three alloys, some important differences must be noted, with particular relevance for alloy design. The rate and the ‘smoothness’ of the exponential decay regime both depend on the width of the matrix channels and therefore on the γ' volume fraction. In alloy ABD-2, with a predicted precipitate volume fraction of 71.1% at 900 °C, the multiplication rate drops rapidly and in a ‘jerky’ fashion. The serrations in Figure 4.24(b) can be related to the generation and annihilation of dislocation segments through interactions in the thin matrix channels. Figure 4.23 illustrates how dislocation loops must navigate through horizontal channels with a combined glide-climb motion. This promotes the role of climb mobility in plastic strain accumulation when compared to the other two alloys, as shown in Figure 4.24(a). Conversely, in alloy ABD-3, with a predicted γ' fraction of 47.5%, dislocations have much more space to propagate, leading their multiplication rate to decay more slowly and more smoothly.

The observed changes in dislocation density compare well with cECCI micrographs. At low plastic strain levels, some regions of the microstructure remain free of dislocations until loops generated by nearby sources have propagated enough, as seen

in Figures 4.14 to 4.19. The longitudinal sections of Figure 4.23 show dislocations with largely the same Burgers vector, as observed in Figures 4.14 and 4.15 for ABD-1.

ABD-1 and ABD-3 exhibit a similar evolution of the dislocation density with creep strain in Figure 4.24 and comparable microstructures at 0.3% plastic strain, with vertical channels appearing filled with dislocation segments in Figure 4.23(j&l). This can be rationalised by considering the critical Orowan shear stress $\tau_{Or} = \sqrt{2/3}Gb/w$, where w is the γ channel width. For ABD-1 and ABD-3, τ_{Or} is estimated at 116 MPa and 84 MPa, respectively, lower than the resolved shear stress of 183 MPa arising from the applied tensile stress of 450 MPa. This allows dislocations to bow out into γ channels and to gradually form dense dislocation networks, mainly through the glide mechanism. Contrarily, the Orowan critical stress for ABD-2 is just above the resolved shear stress at 185 MPa, thus limiting the ability of dislocations to bow around γ' particles.

The insights into damage accumulation from DDD are in agreement with the design rules suggested by Pollock and Field [236] for resisting tertiary creep in single-crystal superalloys, namely precipitating a high γ' volume fraction of 60 to 70% [104, 205] and controlling misfit and heat treatments to obtain small, evenly distributed, cuboidal particles with edge lengths of 350 to 500 nm [358, 463]. Once an equilibrium state has been reached after around 0.3% plastic strain, dislocation movement is largely controlled by diffusion processes and the importance of solid solution strengthening increases. With regard to alloy design, it is then desirable to carefully control the alloy chemistry such that high levels of slow-diffusing elements like molybdenum, tungsten, and rhenium partition to the γ phase [112, 315, 318], however, not at the expense of precipitating deleterious brittle phases [106, 151, 292].

4.5 Summary and Conclusions

1. Interrupted creep tests are carried out on small-scale specimens using a novel ETMT system combined with DIC strain measurements. This setup offers significant benefits over conventional testing methods when assessing the mechanical behaviour of prototype single-crystal superalloys.

2. The evolution of dislocation density with creep strain is analysed for three single-crystal superalloys with distinct γ' volume fractions and levels of solid solution strengthening using a combination of HR-EBSD and cECCI. Experimental analyses are rationalised by DDD simulations.
3. The current best estimate is that the total dislocation content in these materials is approximately $1 \times 10^{14} \text{ m}^{-2}$ after 1% plastic strain has been introduced; at 0.02% strain, the dislocation content is about 70% of this value. The uncertainties are about $3 \times 10^{13} \text{ m}^{-2}$ for our HR-EBSD measurements and $1 \times 10^{13} \text{ m}^{-2}$ for the cECCI ones.
4. Differences between HR-EBSD and cECCI are in good agreement with previous reports of GNDs representing between 10% and 50% of the total dislocation density.
5. Both methods yield the same trend of a strong initial rise in mobile dislocation density, followed by an exponential decay over time. A simple evolution law of the form $\rho_m = (\rho_0 + M\varepsilon) \exp(-\phi\varepsilon)$ can accurately describe the experimental data and DDD simulation results. This law holds true for all investigated alloys and appears to be independent of chemistry.
6. The present observations suggest that LAGB are not the main sources of mobile dislocations. Instead, individual dislocation sources become active emitters once a critical local shear stress is reached. Dislocations can at first move with little constraints through the matrix channels, resulting in the high initial multiplication rate.
7. DDD reveals that after several sources have become operative, dislocation ‘avalanches’ result in the formation of equilibrium dislocation networks at macroscopic creep strains of $\approx 0.1\%$. Further dislocation movement through matrix channels is then impeded and the dislocation multiplication rate decreases exponentially. The dynamics of this decay depend strongly on the γ' volume fraction.

8. Quantitative descriptions of the change in dislocation density with creep strain represent a critical input for creep damage modelling and can inform improved alloys design models.
9. Future work will focus on extending this initial test matrix to include other stress/temperature/strain conditions in the tertiary regime, as well as in the primary and rafting regimes. Furthermore, mechanisms by which individual dislocations become active sources are being investigated.

Significant challenges remain for present and future superalloy metallurgists. Most importantly, the physical metallurgy of the superalloys needs to be placed on a much firmer quantitative basis. Quantitative modelling will help in this regard, with important roles being played by modern electron theory, treatments of the kinetics of dislocation motion and process modelling tools which are sensitive to alloy chemistry. Since superalloy metallurgy is now in a highly developed state, the design of next-generation alloys will demand this.

— R.C. Reed, “The Superalloys: Fundamentals and Applications”

5

Modelling of Tertiary Creep Damage in Single-Crystal Superalloys

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5.1 Introduction

As discussed in Chapter 2, the NBSA, especially when cast in single-crystal form, display outstanding resistance to creep behaviour even at temperatures beyond 1000 °C. This justifies their use for critical components needed for jet propulsion and power generation [12, 20, 162]. Nevertheless, when one examines typical compositions employed in practice, one finds that only relatively few alloys have entered service. Over time, there has been a trend to improve creep performance *via* alloying with refractory elements such as tantalum, molybdenum, tungsten, and particularly rhenium, at the expense of reduced corrosion resistance impaired by the lower chromium contents needed to maintain alloy stability, e.g. with respect to the precipitation of TCP phases [637, 638].

Why are relatively few alloy compositions available? The main reason is the traditional, overarching emphasis on empirical means of alloy development, which involves many make/test iterations for the purpose of screening, ranking, and subsequent down-selection, as discussed in Chapter 3. This leads to considerable cost but also significant lag in the insertion of new grades into practice [52]. There is no doubt also that the theory and models developed so far have been insufficiently accurate to make a difference to the prevailing situation. Consider the available models for the creep deformation behaviour of this class of alloy, for example, those based on damage mechanics approaches. The earliest contain many fitting parameters and are rather empirical [329, 639–642]. The latest are more microstructurally explicit and depend upon estimates of microstructural-scale and rate-dependent evolution laws for the dislocation content [364–367, 466]. Most can be applied well once a given alloy composition has been fixed, for example, to predict the effects of altering the temperature or the stress state. So they are useful for component lifing. But it is very rare for such models to be sensitive to changes in material chemistry; it is only with this capability that optimisation of alloy composition can be achieved [53].

The research in the present chapter was carried out with the above in mind. Modelling of the creep phenomenon in single-crystal NBSA is discussed, with an emphasis on the influence of alloy composition, microstructural architecture, and dislocation evolution. Analogue to the experimental work of Chapter 4, the focus is on the tertiary creep deformation mode, operative at intermediate levels of applied stress and temperature, as illustrated in Figure 5.1. Its main characteristics are that neither precipitate shearing nor rafting is prevalent and that deformation is largely confined to the γ matrix, thus giving rise to a steady increase in creep strain rate with creep strain [12, 236, 237]. Existing analysis procedures available in the literature are reviewed first. Then, a new merit index which relates alloy composition to creep performance is introduced. By testing against a significant set of experimental data mined from the literature, it is demonstrated that the new approach has advantages over those currently available.

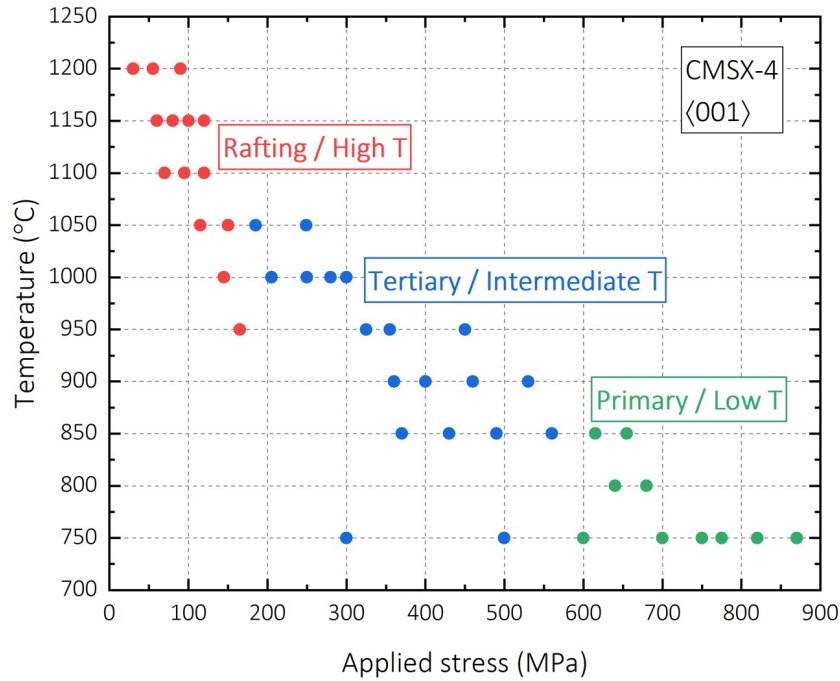


Figure 5.1: Plot illustrating the regimes of temperature and applied stress under which primary, tertiary, and rafting modes of creep deformation are dominant for the single-crystal superalloy CMSX-4, adapted from reference [12].

5.2 Background and Literature Review

Early attempts to describe the evolution of creep damage in engineering materials by da Andrade [643], Dorn [414], Garofalo [644], or Webster [645] were based largely upon empiricism and sought to offer optimal mathematical representations of observed experimental creep curves. Later advances including the 6- θ -projection technique [415] or the Ω -method [416] added more fitting parameters to their formulations. While this facilitated reasonable mathematical descriptions of large creep data sets, only limited further insight into operative creep damage mechanisms was gleaned.

Such shortcomings led to the development of creep continuum damage mechanics (CDM) models [404, 646]. These relate the creep strain rate to measurable, external parameters — stress, strain, temperature, and time — and to a number of internal state variables, ω_i , which provide a measure for accumulated damage [404]. A constitutive model is then proposed by an equation for the evolution of creep strain rate and by i equations for the evolution of ω_i :

$$\begin{aligned}
 \dot{\varepsilon} &= f(\sigma, \varepsilon, T, t, \omega_1, \omega_2, \dots, \omega_i) \\
 \dot{\omega}_1 &= f_1(\sigma, \varepsilon, T, t, \omega_1, \omega_2, \dots, \omega_i) \\
 \dot{\omega}_2 &= f_2(\sigma, \varepsilon, T, t, \omega_1, \omega_2, \dots, \omega_i) \\
 &\vdots \\
 \dot{\omega}_i &= f_i(\sigma, \varepsilon, T, t, \omega_1, \omega_2, \dots, \omega_i)
 \end{aligned} \tag{5.1}$$

The origins of creep CDM lie in the attempts of Kachanov [647] and Rabotnov [648] to quantify damage evolution during tertiary creep using a single internal damage parameter. This method was later expanded by Leckie & Hayhurst [649] to also include the effects of multiaxial stress states. Despite these approaches being similar to previous empirical relations, they laid the foundations for physically based CDM, in which damage parameters and damage rates are associated with distinct physical mechanisms and are directly related to microstructural evolution. Dyson [468] identified three broad categories of operating mechanisms based on the kinetics of damage evolution: (1) strain-induced damage, where the damage rate depends on

stress, temperature, the level of internal back-stress, H , and the current level of accumulated damage, D ; (2) thermally induced damage, depending on temperature and accumulated damage alone; and (3) environmentally induced damage, in which the mean radius of the specimen, R , also plays a role in controlling the damage rate:

$$\begin{aligned}\dot{D}_{\text{strain}} &= \dot{D}(\sigma, T, H, D) \\ \dot{D}_{\text{thermal}} &= \dot{D}(T, D) \\ \dot{D}_{\text{environmental}} &= \dot{D}(\sigma, T, H, D, R)\end{aligned}\tag{5.2}$$

A comparison of Equations (5.1) and (5.2) reveals that H and D represent two physically rationalised state variables, ω_1 and ω_2 , for which the evolution functions f_1 and f_2 are derived from theory. Suitable damage parameters and damage rates have been compiled by McLean & Dyson [646] for the most common examples of creep damage: multiplication of mobile dislocations and creep-constrained cavity growth (strain-induced), particle coarsening and depletion of solid solution elements (thermally induced), and internal oxidation or corrosion (environmentally induced). The present work focuses on the first two categories and assumes that environmental effects can be neglected for bulk specimens, as do virtually all other creep CDM models for NBSA.

A selection of constitutive equation sets describing tertiary creep in superalloys is presented chronologically in Table 5.1. A general comparison reveals a persisting lack of agreement on the impact of certain factors on creep resistance. However, the overall approach has remained the same and can be discussed in the context of physically based CDM [650]. For example, an early creep model proposed by Dyson & McLean [639] can be re-written as a CDM formulation involving multiplication of mobile dislocations and particle coarsening. Furthermore, Dyson [468] showed that empirical lifing methods including the Larson-Miller parameter can be readily derived from CDM after making suitable physical assumptions.

Early creep models [329, 640–642] provide few or no explanations for the values of fitting parameters involved. Although this issue was acknowledged later on [468], most parameters were still obtained by fitting numerical calculations to experiments.

5.2. Background and Literature Review

Study	Year	Constitutive model equations	Fitting parameters
Dyson & McLean [639]	1983	$\dot{\epsilon} = \alpha \left(\sigma - \sigma_0 - \beta \left(\sigma_0^3 + k(\phi) t \right)^{-p/3} \right)^4$; $\dot{\epsilon} = \rho_m \nu u$; $\dot{\rho}_m = C_d \dot{\epsilon}$	$\alpha, \sigma_0, \beta, p, C_d$
Ion et al. [640]	1986	$\dot{\epsilon} = \dot{\epsilon}_0 (1 - S) (1 + \omega)$; $\dot{S} = H \dot{\epsilon}_0 (1 - S) - \alpha \dot{S}$; $\dot{\omega} = \Omega \dot{\epsilon}$	$\dot{\epsilon}_0, H, \alpha, \Omega$
Dyson & Osgetby [642]	1993	$\dot{\epsilon} = \dot{\epsilon}_0 \sinh \left(\frac{\sigma(1-H)}{\sigma_0(1-S)(1-\omega)} \right)$; $\dot{H} = \frac{h\dot{\epsilon}}{\sigma} (1 - \frac{H}{H^*})$; $\dot{S} = \frac{k_s}{3} (1 - S)^4$; $\dot{\omega} = \Omega \dot{\epsilon}$	$\dot{\epsilon}_0, \sigma_0, h, H^*, k_s, \Omega$
McLean & Dyson [646]	2000	$\dot{\epsilon} = \dot{\epsilon}_0 \frac{1+D_d}{1-D_s} \sinh \left(\frac{\sigma(1-H)}{\sigma_0(1-D_c)} \right)$; $\dot{H} = \frac{h\dot{\epsilon}}{\sigma} (1 - \frac{H}{H^*})$; $\dot{D}_d = k_d \dot{\epsilon}$; $\dot{D}_c = \frac{k_c}{3} (1 - D_c)^4$; $\dot{D}_s = k_s D_s^{1/3} (1 - D_s)$	$\dot{\epsilon}_0, \sigma_0, h, H^*, k_d, k_c, k_s$
Manonukul et al. [466]	2002	$\dot{\epsilon} = \frac{\rho_m \nu_1 \left(\left(\frac{4\pi}{3\phi_p} \right)^{1/3} - 2 \right)}{\left(\frac{4\pi}{3\phi_p} \right)^{1/3} M} \rho^{-2} \nu \exp \left(\frac{-\Delta F_p}{k_B T} \right) \sinh \left(\frac{\sigma \lambda_p \beta^2}{k_B T M (1 - \omega)} \right)$; $\lambda_p = r \left(\left(\frac{4\pi}{3\phi_p} \right)^{1/3} - 2 \right)$; $2r = 2\tau \left(\frac{4}{3600} \right)^{1/3} + 2\tau_0$; $2\tau_0 = \frac{2.96 \exp(0.012T)}{10^5}$; $\rho_1 = \alpha \rho_m^2 v - \beta D_{\text{eff}} \rho_1^{3/2}$; $\dot{\rho}_m = C_d \dot{\epsilon}$; $\dot{\omega} = \Omega \dot{\epsilon}$; $\phi_p = f(T)$	$\alpha, \beta, k_d, \Omega$
Miodownik et al. [97]	2003	$\dot{\epsilon} = A D_{\text{eff}} \left(\frac{2SFE}{GB} \right)^m \left(\frac{\sigma - \sigma_0}{E} \right)^n$; $A = \frac{10^{19} \tau}{\phi_p + 0.005}$; $m = 3$; $n = 4$; $\sigma_0 = \frac{3}{4} \sigma$ if $\sigma < \frac{4}{3} \sigma_p$; $\sigma_0 = \sigma_p$ if $\sigma > \frac{4}{3} \sigma_p$; $\sigma_p = f(\sigma, \phi_p)$; $D_{\text{eff}} = D_0 \exp \left(-\frac{Q_{\text{eff}}}{RT} \right)$; $D_{\text{eff}} = \sum_m x_m D_0^m$; $Q_{\text{eff}} = \sum_m x_m Q_{m, \text{Ni}}$	σ_p
Basoalto et al. [366]	2004	$\dot{\epsilon} = \dot{\epsilon}_0 (1 + D_d) \exp \left(\frac{-Q_d}{RT} \right) \sinh \left(\frac{\sigma(1-H)}{\sigma_0} (1 - D_c) \right)$; $H = \frac{h\dot{\epsilon}}{\sigma} \left(1 - \frac{H}{H^*} \right)$; $\dot{D}_d = k_d \dot{\epsilon}$; $\dot{D}_c = \frac{k_c}{3} (1 - D_c)^4$; $H^* = \frac{2\phi_p}{1+2\phi_p}$; $h = E\phi_p$; $\sigma_0 = \frac{K_{\text{CF}} M k_B T}{b^2 \lambda_p}$; $K_{\text{CF}} = 1 + \frac{2\phi_p^{1/3}}{3\sqrt{3}\pi(1-\phi_p)} \left(\frac{1}{1-\phi_p} \right)^{1/3}$ if $\phi_p \geq 0.3$, else $K_{\text{CF}} = 1$	$\dot{\epsilon}_0, k_d, k_c$
Reed [12]	2006	$\dot{\epsilon} = \dot{\Gamma}_i + \Omega \dot{\epsilon}$; $\Omega = \alpha \exp \left(\beta \sigma - \frac{Q_A}{RT} \right)$; $\dot{\Gamma}_i = \chi \exp \left(\psi \sigma - \frac{Q_2}{RT} \right)$	$\alpha, \beta, \chi, \psi, Q_1, Q_2$
Dyson [365]	2009	$\dot{\epsilon} = \frac{1.6}{M} \rho_m \phi_p (1 - \phi_p) \left(\left(\frac{\pi}{4\phi_p} \right)^{1/2} - 1 \right) c_1 D_{\text{eff}} \sinh \left(\frac{(\sigma - \sigma_0 - \hat{\sigma}_{\text{nct}}) \beta^2 \lambda_p}{M k_B T} \right)$; $\lambda_p = 1.6r \left(\left(\frac{\pi}{4\phi_p} \right)^{1/2} - 1 \right)$; $r^3 = r^3 + \exp \left(-\frac{3 \times 10^5}{RT} \right)$; $\phi_p = f(C_0, T)$; $\dot{\sigma}_0 = \frac{\phi_p E}{1 - \phi_p} \left(1 - \frac{\sigma_0}{\sigma} \right) \dot{\epsilon}$; $\sigma_0^* = \frac{2\phi_p}{1+2\phi_p} \sigma$; $\dot{\rho}_m = C_d \dot{\epsilon}$; $C_d = f(\rho_0)$	C_d
Oruganti [424]	2012	$\dot{\epsilon} = \alpha \exp \left(-\frac{Q_C}{RT} \right) \sinh(\beta(\sigma - \sigma_0)^n)$; $\dot{\sigma}_0 = E \dot{\epsilon} \left(\phi_p D_f - \frac{\sigma_0}{\sigma} \right)$; $D_f = 1 - k_f \exp \left(-\frac{Q_f}{RT} \right) \epsilon$	α, β, k_f, Q_f
Zhu et al. [364]	2012	$\dot{\epsilon} = \frac{1.6}{6} \rho_m D_{\text{eff}} \phi_p (1 - \phi_p) \left(\frac{1}{\phi_p^{1/3} - 1} \right) \sinh \left(\frac{\sigma b^2 \lambda_p}{\sqrt{6} K_{\text{CF}} k_B T} \right)$; $\lambda_p = d \left(\frac{1}{\phi_p^{1/3} - 1} \right)$; $K_{\text{CF}} = 1 + \frac{2\phi_p^{1/3}}{3\sqrt{3}\pi(1-\phi_p)} \left(\frac{1}{1-\phi_p} \right)^{1/3}$; $\dot{\rho}_m = C_d \dot{\epsilon}$; $C_d = f(\rho_0)$; $D_{\text{eff}} = D_0^{\text{eff}} \exp \left(-\frac{Q_{\text{eff}}}{RT} \right)$; $D_0^{\text{eff}} = \sum_m \frac{1}{x_m \text{Ni}} \frac{x_m}{D_0^{\text{eff}} \text{Ni}}$; $Q_{\text{eff}} = Q_{\text{Ni}} + \sum_m x_m Q_{m, \text{Ni}}$	C_d
Kim et al. [367]	2016	$\epsilon = \frac{\dot{\epsilon}_m}{K} \ln \left(1 + \left(\frac{\dot{\epsilon}_1 - \dot{\epsilon}_m}{\dot{\epsilon}_m} \right) (1 - \exp(-Kt)) \right) + \frac{1}{C} (\exp(C \dot{\epsilon}_m t) - 1)$; $\dot{\epsilon}_m = A_1 \phi_p (1 - \phi_p) \left(\frac{1}{\phi_p^{1/3} - 1} \right) \frac{D_{\text{eff}} C^b}{k_B T} \left(\frac{\lambda_p}{b} \right)^2 \left(\frac{\sigma - \sigma_0}{C} \right)^5 + A_2 \frac{D_{\text{eff}} C^b}{k_B T} \left(\frac{b}{d_C} \right)^2 \left(\frac{\sigma}{C} \right)^2$; $K = \phi_p E \dot{\epsilon}_1 / \sigma_0^m$; $C = 4/t_r \dot{\epsilon}_m$; $t_r = 0.0134 \dot{\epsilon}_m - 0.5309$; $A_1 = 7.5 \times 10^6$, $A_2 = 15$; $\sigma_0 = \sigma_{\text{Orowan}}$ if $0.75\sigma > \sigma_{\text{Orowan}}$ else $\sigma_0 = 0.75\sigma$	A_1, A_2

Table 5.1: Models of tertiary creep in superalloys compiled from open literature. Each model is represented by a set of constitutive CDM equations describing creep damage evolution. The column on the right lists parameters determined by fitting models to experimental results and which are not given a clear physical derivation in the respective studies. A general trend towards less fitting parameters over time can be observed.

The first truly physically based model, relating damage rates directly to alloy composition and microstructure, was that of Manonukul et al. [466]. It was followed by other similar formulations with certain adjustments [364–366, 651]. For example, Coakley et al. [652, 653] expanded a previous model by Dyson [365] to account for multimodal particle distributions. A notable recent entry is the work of Kim et al. [367], who followed a similar approach to the present study and used thermodynamic calculations to inform their creep model with regard to microstructure. It should be pointed out that the list in Table 5.1 is only exemplary and that many other models have been proposed, some of which include mechanistic expressions too complex to be reproduced above in short [379, 486, 487, 651, 654–658].

When comparing physically based models for intermediate-temperature creep, several common traits within the expressions for creep strain rate become clear. First, creep resistance increases with higher γ' volume fraction, ϕ_p , and lower effective diffusivity, D_{eff} . Second, the internal back-stress, usually depending on the particle spacing, λ_p , has a profound significance on creep rate evolution. Third, particle coarsening plays an important role in affecting particle spacing and in turn internal stresses. Fourth, the choice of values defining the initial microstructure, including the initial dislocation density, ρ_0 , and the initial precipitate radius, r_0 , influence model predictions significantly. Finally, the same is also the case for functions derived to describe parameters like effective diffusivity, γ' volume fraction, or an invoked constant damage multiplication parameter, k_d or C_d , used to quantify the increase in mobile dislocation density over time. The last two points have been clearly illustrated in the work of Zhu et al. [364], who observed significant changes in simulated creep curves with varying values of γ' volume fraction, γ' particle size, initial dislocation density, and dislocation multiplication parameters. It can be expected that other models will behave similarly. This is problematic in the context of developing a model suitable for a wide range of alloys, as constant values rationalised for one particular case may not apply to others.

A critique on the usefulness of the different models is challenging for a number of reasons. Oruganti [424, 469] pointed out that cases of poor correspondence between

experiments and model predictions are often attributed to gaps in understanding damage mechanisms rather than to the basic constitutive creep laws used. As such, the critical assessment of these laws is of importance. For example, efforts to describe creep over a wide range of conditions led in the 1940s to the use of exponential or hyperbolic sine laws [659]. These were later rationalised theoretically by Friedel [660] and Hirth & Lothe [661] in their seminal works on dislocation theory. An advantage of $\sinh(\sigma)$ expressions is their ability to capture the strong influence of applied stress on creep life. However, when used in some of the models of Table 5.1, they give rise to an overestimation of the role of particle spacing, which is not backed up by experiments [424, 646]. Furthermore, the use of constant stress exponents within power-law descriptions has been recently criticised as too simplistic and not supported by microstructural and physical observations [662]. The same can also be stated in the case of constant internal back-stresses associated with certain strengthening mechanisms [663, 664]. Attempts at addressing such issues with the introduction of effective — as opposed to directly measured — creep parameters do not shed more light on intrinsic damage accumulation [320, 530]. Lastly, damage multiplication parameters, which relate the increase in mobile dislocations to the respective strain rate, have been assumed to depend linearly on the initial dislocation density and to remain constant [365, 366]. No clear explanation for this choice exists and recent DDD modelling efforts revealed that severe fluctuations in the value of C_d can be expected during creep [586]. Such shortcomings provide an incentive for the development of a new modelling approach, complex enough to capture key influences of chemistry and microstructure on alloy properties, but simple enough to be applied in alloy design studies.

5.3 Modelling of Tertiary Creep Phenomenon

5.3.1 General Modelling Approach

The main procedural steps and computational aspects used in this paper build on those of the ABD method [52] and are illustrated in the process flow diagram of Figure 5.2. Necessary inputs include alloy chemistry and creep conditions —

applied stress along the technically relevant $\langle 001 \rangle$ crystal direction and temperature. These inputs can be precisely specified for known commercial alloys or standard testing conditions. Alternatively, a large design space can be generated by setting ranges and increments for each chemical element and can then be investigated to isolate compositions predicted to possess optimal property trade-offs, following references [102, 103].

Alloy composition and temperature serve as inputs for CALPHAD thermodynamic modelling which estimates key microstructural parameters. In the present work, version 2016b of the Thermo-Calc software package was used along with the TCNi8 thermodynamic database and the MOBNI3 mobility database. Computed values include the interfacial energy between γ and γ' , σ_{int} , the partitioning coefficients of different elements, and phase volume fractions. Of particular interest are the γ' fraction, ϕ_p , and — for less stable alloys — the fractions of deleterious TCP phases. In combination with further models and data from the literature, Thermo-Calc predictions are used to estimate other important parameters such as the lattice misfit, δ , and the coarsening rate coefficient, k . As noted by the use of dashed arrows in Figure 5.2, the current approach can be extended with other simulation packages. This includes using TC-PRISMA to analyse the effects of chemistry and heat treatments on nucleation and growth of γ' precipitates, or using DICTRA to estimate effective diffusivity parameters.

In the final steps, sets of constitutive model equations are integrated for each alloy from time zero using standard finite difference methods. The results are predictions regarding (1) the coarsening of precipitates during high-temperature exposure and (2) the evolution of creep strain. Further user-defined merit indices — such as density-corrected creep strength — can be applied within ABD studies.

A novel addition is incorporating data from the correlative HR-EBSD and cECCI studies presented in Chapter 4. These provide both a quantitative and a qualitative evaluation of dislocation structure evolution during creep and lead to a more experimentally grounded description of damage through dislocation accumulation.

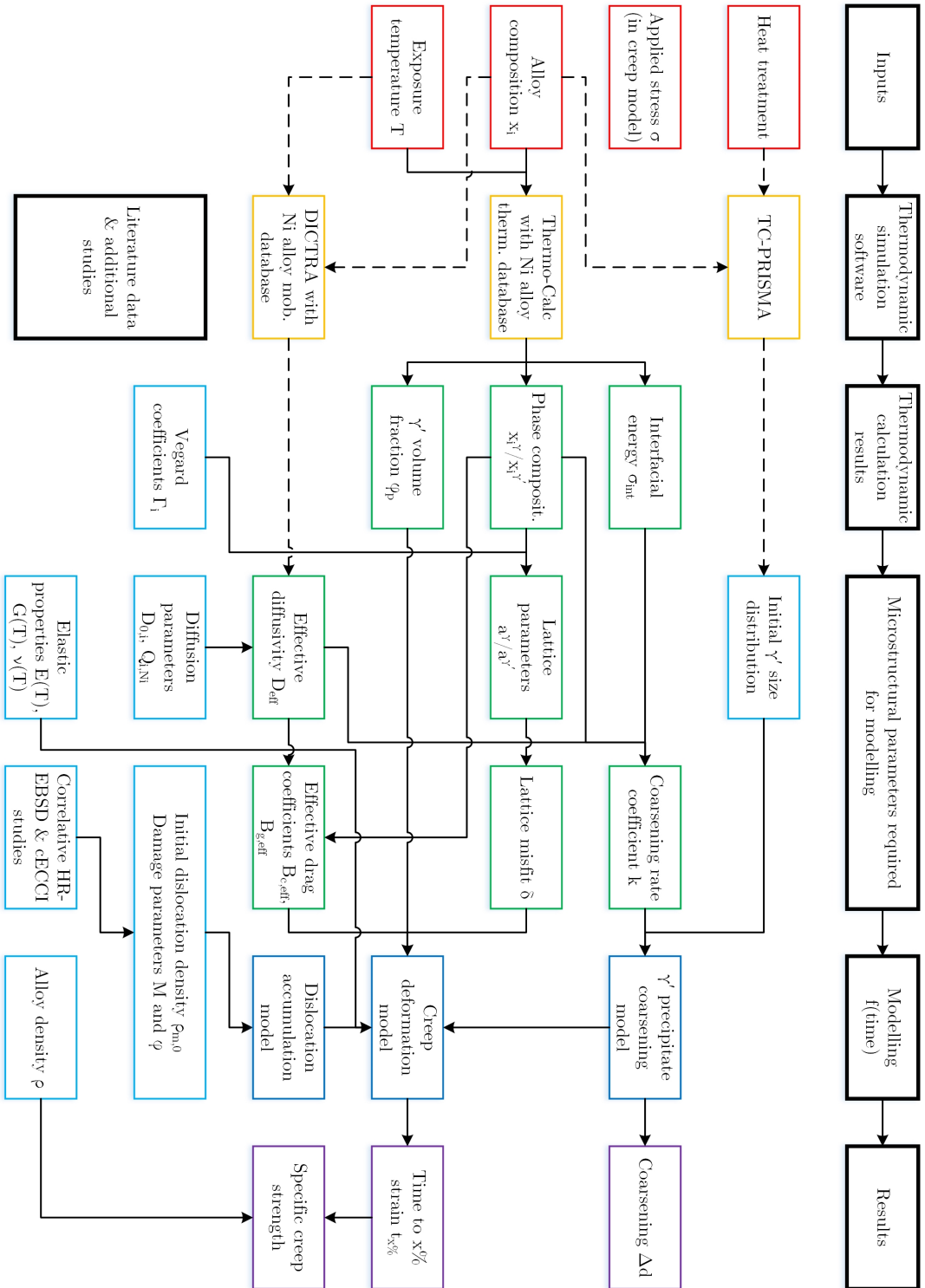


Figure 5.2: Process flow diagram representing the main steps taken to model precipitate coarsening and creep strain accumulation.

5.3.2 Modelling of Superalloy Microstructure and Physical Properties

Most creep models in the literature focus on reproducing experimental results for a few commercial alloys and so they apply known values of γ' precipitate size, elastic modulus, or lattice misfit. However, for alloy design purposes, changes of these properties with chemistry must be considered in further detail. In certain cases, this cannot be achieved accurately with current CALPHAD methods and pragmatic estimates are needed.

5.3.2.1 γ' Particle Distribution

Essential features of the microstructure being modelled are shown in Figure 5.3. For modern single-crystal superalloys, it consists of a high volume fraction of the ordered γ' precipitate phase residing within the FCC γ matrix. Precipitates are modelled as cubes with side length d and interparticle spacing w . A simple, unimodal distribution is shown in Figure 5.3; however, the model accounts for variations in size by assuming a normal size distribution for d , with a mean value of 450 nm and a standard deviation of 150 nm. As the constitutive creep equations require discrete values, this distribution is approximated by a histogram containing 5 bins with an equal bin width of 100 nm.

The mean value of 450 nm has been noted to lead to optimal creep properties in typical modern superalloys with a low, negative lattice misfit at high temperatures [315, 463]. It is assumed here that it can be attained for any particular composition through appropriate heat treatments. However, it would be insufficient to only consider the mean particle size — as done in most creep models — since it has been shown that a homogeneous microstructure, with evenly distributed particles orientated along the $\langle 001 \rangle$ crystal direction, significantly improves creep strength [358]. The standard deviation of 150 nm was chosen based on particle size measurements carried out on recently developed ABD alloys [103] and is also assumed to remain constant for all investigated compositions. For regions with

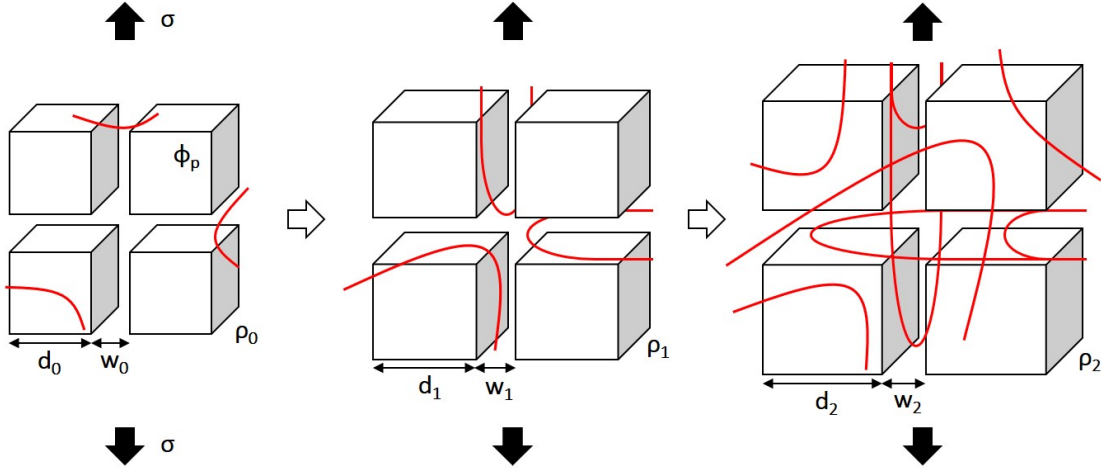


Figure 5.3: Assumed evolution of damage during tertiary creep in single-crystal superalloys. The main operating mechanisms are (1) an increase in mobile dislocation density in γ matrix channels, ρ , and (2) coarsening of γ' precipitates, i.e. an increase of the average cube side length, d , and of the interparticle spacing, w .

constant γ' volume fraction and size, it follows from geometry that $\phi_p = d^3 / (w + d)^3$ and that $w = d \left(1/\phi_p^{1/3} - 1 \right)$.

5.3.2.2 Elastic Properties

Influences of chemistry on elastic properties have been commonly estimated separately for each phase using ‘rule-of-mixtures’ approaches, with the moduli of individual elements being scaled for temperature [309, 367]. For example, Kim et al. [367] calculated the temperature dependence of the shear modulus, G , as:

$$\begin{aligned}
 G(T) &= (1 - \phi_p) G^\gamma + \phi_p G^{\gamma'} \\
 G^\gamma(T, x) &= G_{\text{Ni}}(T) \left(1 + \sum_i x_i \delta G_i \right); \quad \delta G_i = \frac{1}{\Delta x_i} \left(\frac{\Delta G_i}{103.2} \right) \\
 G^{\gamma'}(T, x) &= G_{\text{Ni}_3\text{Al}}(T) \left(1 + \sum_i \left(0.75 \times y_i^{\text{Ni site}} \delta G_i^{\text{Ni site}} + 0.25 \times y_i^{\text{Al site}} \delta G_i^{\text{Al site}} \right) \right); \\
 \delta G_i^{\text{Ni site}} &= \frac{1}{\Delta y_i^{\text{Ni site}}} \left(\frac{\Delta G_i^{\text{Ni site}}}{78} \right); \quad \delta G_i^{\text{Al site}} = \frac{1}{\Delta y_i^{\text{Al site}}} \left(\frac{\Delta G_i^{\text{Al site}}}{78} \right)
 \end{aligned} \tag{5.3}$$

Here, factors δG_i represent changes in the shear moduli of pure nickel and of pure Ni_3Al caused by an amount Δx_i of alloying element i . For the γ' phase, different changes in modulus depending on the location of alloying elements on Ni

or on Al sites are taken into account. Partitioning coefficients x_i and site fractions y_i can be obtained from CALPHAD calculations. Ultimately, Kim et al. derived optimal values for δG_i , $\delta G_i^{\text{Ni site}}$, and $\delta G_i^{\text{Al site}}$ for a range of elements by calibrating Equation (5.3) to match experimental data.

While this approach shows promise for general alloy design purposes, it assumes isotropic elastic properties and can only be applied to polycrystalline materials. In contrast, early studies of elastic properties in directionally solidified superalloys showed a strong dependence on crystal direction [665, 666]. As discussed in more detail by Reed [12], this stems from the anisotropic elasticity of pure nickel in single-crystal form and must be considered when modelling the mechanical properties of new single-crystal superalloys.

Siebert et al. [555] carried out extensive measurements of the temperature dependence of the Young's modulus, the shear modulus, and Poisson's ratio for superalloy CMSX-4 and its isolated γ and γ' phases. Based on tests in near [001] and [111] directions, these authors derived linear temperature dependences for $E_{\langle 001 \rangle}^{\gamma/\gamma'}$, $G_{\langle 001 \rangle}^{\gamma/\gamma'}$, and $\nu_{\langle 001 \rangle}^{\gamma/\gamma'}$ between room temperature and 1000 °C. This data can be used to calculate the stiffness matrix components $c_{11}^{\gamma/\gamma'}$, $c_{12}^{\gamma/\gamma'}$, and $c_{44}^{\gamma/\gamma'}$ at a certain temperature. Lastly, elastic properties along the active {111} slip planes during loading along the $\langle 001 \rangle$ tensile axis can be obtained.

Morrell et al. [517] compared the relative effects of temperature, crystal orientation, and chemical composition on the elastic moduli of several commercial single-crystal superalloys. These authors concluded that the effect of composition on stiffness tensor values is a minor one. This is in agreement with the observations of Dye et al. [667], who compiled experimental data on stiffness matrix components for a range of superalloys and compared these results to the levels of solid solution strengtheners (Cr+Mo+Re+W) and of γ' -formers (Al+Ta+Ti) in each alloy. No clear trends could be distinguished for solid solution strengtheners, while titanium in particular was noted to increase the stiffness of γ' . Considering the results of Morrell et al. and Dye et al. pragmatically, it can be expected that deviations from the ideal $\langle 001 \rangle$ orientation during casting will have a much more significant effect

than chemistry. As such, in the present work, the temperature-dependent results obtained by Siebörger et al. for CMSX-4 are applied generally to all compositions.

5.3.2.3 γ/γ' Lattice Misfit

Interfaces between the matrix and precipitates are assumed to remain coherent in the present study and misfit stresses are not taken into account. As lattice misfit is often cited as a key parameter for alloy design and improved creep strength, reasons for this omission are discussed in the following.

First, as discussed in Section 2.2.3.5, there is no clear consensus regarding either the optimal magnitude, or the optimal sign of lattice misfit for increased creep resistance [392]. On the one hand, it seems beneficial to keep the value close to zero, in order to obtain a low coarsening rate coefficient and homogeneous, cuboidal precipitates [12, 60, 234, 488]. On the other hand, it has been suggested that a high, usually negative, mismatch will promote dense dislocation networks at γ/γ' interfaces, ultimately leading to increased protection against precipitate shearing [217, 244, 272, 370, 395, 476–479].

Second, regression analysis studies carried out by Harada et al. [78, 331, 403, 485] revealed a decreasing influence of misfit and an increasing influence of solid solution strengthening on creep properties as testing temperature is reduced. While dense interfacial dislocation networks appear important in the rafting regime, they do not play a main role for tertiary creep.

Third, and of most importance from a practical perspective, influences of chemistry and temperature on the lattice misfit cannot be accurately predicted by current methods, as seen in Figure 5.4. With respect to misfit calculations for alloy design, most authors including Caron [450], Reed [12, 52], and Rettig [60] follow the approach proposed by Watanabe & Kuno [669] to calculate lattice misfit, δ , and lattice constants for γ and γ' at room temperature as:

$$\delta = 2 \frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}}; \quad a_{\gamma} = a_0^{\gamma} + \sum_i \Gamma_i^{\gamma} \cdot x_i^{\gamma}; \quad a_{\gamma'} = a_0^{\gamma'} + \sum_i \Gamma_i^{\gamma'} \cdot x_i^{\gamma'} \quad (5.4)$$

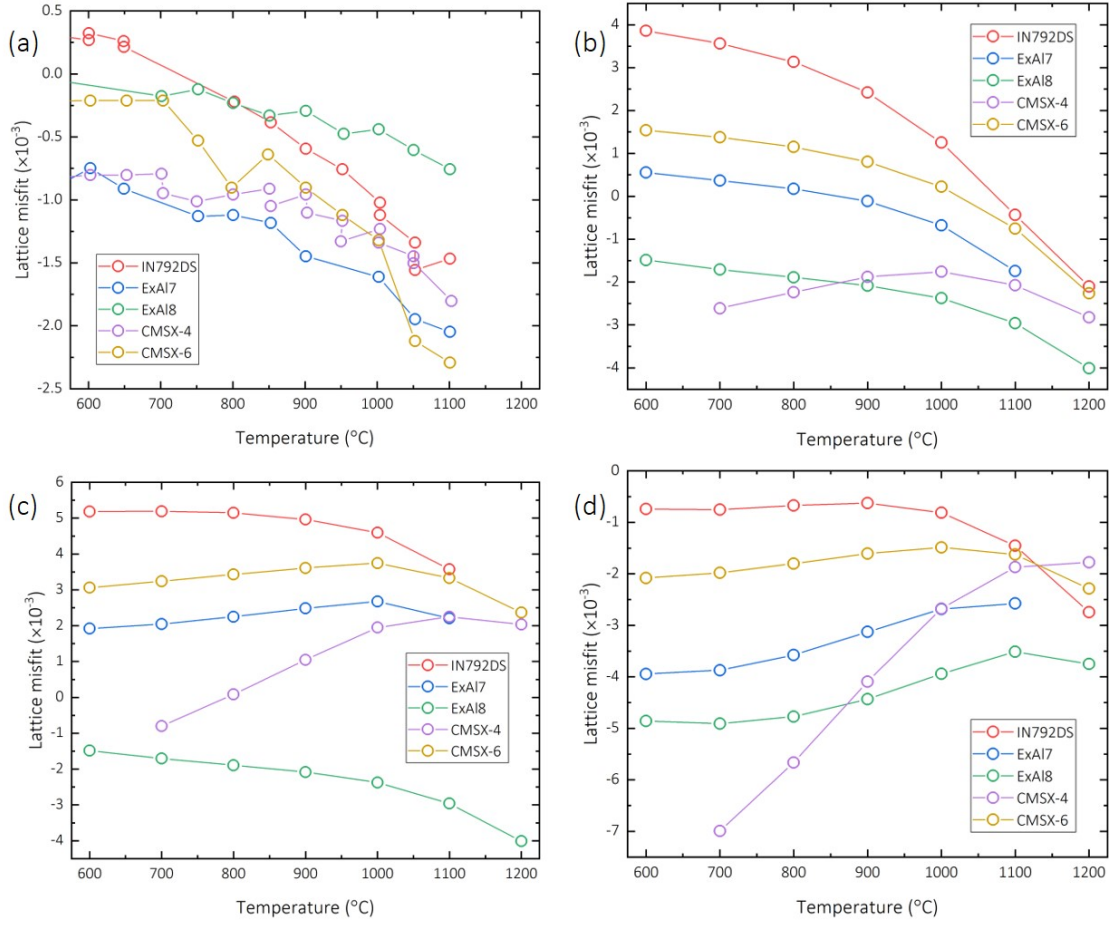


Figure 5.4: Comparison of changes in lattice misfit with temperature from (a) experimental XRD measurements [608], (b) empirical calculations of lattice constants [60], (c) empirical calculations of lattice constants and thermal expansions coefficients [668], and (d) CALPHAD calculations of molar volumes.

where a_0^j is the lattice constant of pure nickel or pure Ni_3Al and Γ_i^j and x_i^j are the Vegard coefficient and the atomic fraction of chemical element i in phase j . Following Caron [450], a_0^γ and $a_0^{\gamma'}$ are taken as 3.524 Å and 3.57 Å, respectively. Values for the Vegard coefficients of different elements can be found in the works of Mishima et al. [242], Nash [243], Kablov et al. [670], or Reed [12]. Phase compositions can be estimated using CALPHAD methods. While reported values for Vegard coefficients are in reasonable agreement, there are significant differences for certain elements, leading to discrepancies between misfit results based on different data sets.

The influence of temperature on the lattice constants of pure nickel and Ni_3Al has been reported in the work of Kamara et al. [671] and Reed et al. [52] and is also

taken into consideration in the alloy design studies cited above. However, chemical additions will influence not only the lattice constants at room temperature, but also the thermal expansion coefficients. The most comprehensive studies covering this topic are the empirical model of Sung & Poirier [668], based on experimental data for a range of superalloys, and the phase mixture model of Karunaratne et al. [672]. Both approaches show good agreement with selected literature data, however, prove difficult to be applied more broadly.

A promising and straightforward approach is to obtain lattice constants for the γ and γ' phases from molar volumes calculated by CALPHAD, which accounts for both chemical composition and temperature [673, 674]. As these phases contain four atoms in each unit cell, lattice constants a_j can be obtained as $a_j = (4V_m^j/N_A)^{1/3}$, where V_m^j is the calculated molar volume of phase j and N_A is the Avogadro constant.

Unfortunately, when compared to the experimental work of Pyczak et al. [608], none of the approaches discussed above can accurately predict changes in lattice misfit with temperature, as shown in Figure 5.4. Pyczak et al. carried out X-ray diffraction (XRD) measurements on a range of rhenium-containing and rhenium-free superalloys and noted an increasingly negative mismatch at higher temperatures for all compositions (Figure 5.4(a)). This qualitative trend is reproduced correctly by the misfit formula used by Rettig et al. [60] for alloy design, although quantitative values differ markedly (Figure 5.4(b)). Misfit values obtained based on the empirical model of Sung & Poirier [668] (Figure 5.4(c)) or based on CALPHAD calculations of molar volumes (Figure 5.4(d)) deviate even more from experiments. Finally, it is interesting to note that all three modelling approaches in Figure 5.4(b)-(d) largely predict the same ‘descending order’ of lattice misfit from IN792DS to ExAl8, although this is not in good agreement with XRD results.

5.3.3 Modelling of Damage Evolution during Tertiary Creep

5.3.3.1 Kinetic Creep Equation

The derivation of the kinetic creep equation follows the considerations of Dyson [365] and Zhu et al. [364], who identify dislocation accumulation in γ matrix channels and coarsening of γ' precipitates as the main sources of damage. It is acknowledged that strain-induced nucleation and growth of cavities and microcracks will occur in the later stages of creep [236, 237]; however, these additional damage mechanisms are omitted in the present model, which focuses on the initial deformation regime up to several percent plastic strain.

In the undeformed state, only a few dislocations are located within the γ channels, as represented schematically in Figure 5.3. Recent cECCI work by Ram et al. [361] showed conclusively that such isolated dislocations are the main dislocation sources during tertiary creep. Under an applied uniaxial stress, some of them will become active *via* Frank-Read [609] or double cross-slip mechanisms [610] once a critical shear stress has been reached locally. LAGB formed as crystal defects during casting [611] also give rise to dislocations; however, these were observed to only percolate a few micrometers away, meaning that LAGBs are not major sources as previously assumed [361].

Newly generated dislocations glide until reaching the nearest particle, where they become arrested at γ/γ' interfaces. Depending on the local geometry and on the sign of uniaxial stress, a series of climb events through vacancy absorption or vacancy emission are required to overcome precipitates [365]. For the usual case of an applied tensile load, vacancy absorption will take place in ‘vertical’ channels and emission in ‘horizontal’ ones, leading to progressing creep deformation through combined climb/glide events. This situation has been theoretically assessed by Friedel [660] and Hirth & Lothe [661], who derived expressions for the jump frequencies of vacancy-absorbing and vacancy-emitting jogs. These can in turn be combined to yield a net escape frequency under the premise of an equal number of absorption and emission events. The particular rate at which trapped dislocations

are released constitutes the core of previous creep models by Dyson [365] and Zhu et al. [364]. However, a linear dependency between the creep strain rate and $\sinh(\sigma)$ is debatable, as discussed in Section 5.2.

In the present work, a different approach is taken by considering relations between (1) effective forces acting on dislocations under the influence of solute drag and (2) average dislocation velocities, for both the climb and the glide step. This approach builds on insights gained from recent DDD studies [586, 587, 675] and also considers novel experimental work by ur Rehman et al. [309] on quantifying climb and glide drag coefficients in the γ matrix. It is acknowledged that not all theoretical contributions towards the forces acting on dislocation segments are considered [587]. Some sources such as the line tension which minimises the dislocation core energy, the elastic force due to the stress field of the dislocation network, or the osmotic force due to vacancy depletion or supersaturation are too complex in nature to be included in the present model. Furthermore, following the simplified approach proposed by Takeuchi & Argon [593], the same ‘effective stress’ acting on dislocations is assumed for both the climb and the glide step.

The average dislocation velocity can be expressed as $\bar{v} = \tau b / B$, where τ is the effective shear stress, b is the length of the Burgers vector, and B is the drag or friction coefficient [676]. It can be further related to the microscopic shear strain rate, $\dot{\gamma}_m$, via the Orowan equation, $\dot{\gamma}_m = b \rho_m \bar{v}$, where ρ_m is the total density of mobile dislocations. A few points must be taken into consideration. First, the total density ρ_m is composed of the density of climbing dislocations at particle/matrix interfaces, ρ_c , and the density of gliding dislocations within matrix channels, ρ_g . Second, a distinction must also be made between the average velocities of climbing and gliding dislocations, $\bar{v}_c$ and $\bar{v}_g$, owing to different drag coefficients, B_c and B_g . Third, the standard Orowan equation cannot be readily applied to precipitate-strengthened materials like superalloys, since to a large extent, deformation is localised within the matrix and precipitates only deform elastically during tertiary creep. This point is addressed by Dyson [365] by considering the necessary load transfer from matrix to particles as plastic creep strain accumulates. Assuming

that the elastic moduli of the matrix and of the precipitates are equal, a simple relation between the measured global shear strain rate, $\dot{\gamma}$, and the microscopic shear strain rate within the matrix, $\dot{\gamma}_m$, is given by $\dot{\gamma} = (1 - \phi_p) \dot{\gamma}_m$. The premise that no precipitate shearing occurs is not entirely true, however, TEM and ECCI studies confirm that it is not significant during tertiary creep [236, 361]. Finally, following the considerations of Ghosh et al. [536], eight $a/2\{111\}\langle\bar{1}01\rangle$ slip systems will be active during symmetrical loading along the $\langle 001 \rangle$ tensile axis and will have equal Schmid factors of $1/\sqrt{6}$. Thus, the macroscopically measured creep strain rate, $\dot{\epsilon}$, can be expressed as $\dot{\epsilon} = 8/\sqrt{6} \times \dot{\gamma}$. Overall, we obtain:

$$\dot{\epsilon} = \frac{8}{\sqrt{6}} (1 - \phi_p) b \rho_m \bar{v} = \frac{8}{\sqrt{6}} (1 - \phi_p) b^2 \tau \left(\frac{\rho_c}{B_c} + \frac{\rho_g}{B_g} \right) \quad (5.5)$$

Attention should now be given to the effective operating shear stress, τ , resulting from the externally applied stress on the one hand and strengthening mechanisms on the other. Following the considerations of Pollock & Field [236], the creep strain rate in the tertiary regime is obtained as:

$$\dot{\epsilon} = \dot{\epsilon}_0 \left(\sigma_{\text{app}} - \left(\zeta \left\{ \frac{d}{w} \right\} (\sigma_{\text{Or}} + \sigma_{\text{SSS}} + \sigma_{\text{Dis}}) \right) \right)^n \quad (5.6)$$

where $\dot{\epsilon}_0$ is a material constant, σ_{app} is the applied stress, and σ_{Or} , σ_{SSS} , and σ_{Dis} are the respective contributions from Orowan strengthening, solid solution strengthening, and dislocation resistance.

Some models also include an additional stress component arising due to the lattice misfit, σ_{Mis} , which is added to the applied stress. As most commercial alloys exhibit negative misfit at high temperatures, this superposition leads to significantly increased deformation in ‘horizontal’ γ matrix channels, perpendicular to the loading direction, and only limited creep in ‘vertical’ channels, parallel to loading [362]. Considering the aforementioned issues regarding ABD calculations of misfit, it is both difficult and open to doubt to incorporate misfit stresses in a model used for alloy design, as incorrect predictions of misfit — and therefore of misfit-induced stress — could lead to faulty conclusions and design rules.

In Equation (5.6), the main source of strengthening is the local Orowan resistance of matrix channels, which must be overcome in order to bow dislocations between precipitates. The resolved shear stress required can be expressed as:

$$\tau_{\text{Or}} = \frac{Gb}{l} = \sqrt{\frac{2}{3}} \frac{Gb}{w} \quad (5.7)$$

where G is the shear modulus, l is the distance between precipitates in $\langle 110 \rangle$ direction, and w is the γ channel width. A small contribution is also provided by dislocation passing stresses and can be approximated for the case of random interactions between dislocations as:

$$\tau_{\text{Dis}} = \alpha Gb \sqrt{\rho_{\text{m}}} \quad (5.8)$$

A value of 0.1 is chosen for α , in accordance with references [236, 306].

A creep stress exponent, n , is not included in the present model, as such exponents have been shown to only remain constant over a restricted stress and temperature range [468]. As a correction, Dyson [468] derived a more advanced expression for n , in relation to empirical hyperbolic sine functions, as $n = \sigma/\sigma_0 \times \coth(\sigma/\sigma_0)$, with σ_0 being a function of temperature, γ' volume fraction, and the Orowan resistance stress. Such calculated values for n would range between 1 and 2 for NBSA, in agreement with the expected dominating mechanism of diffusional climb. Nonetheless, such an expression ultimately does little towards improving the basic understanding of creep deformation [662].

The constraint factor $\zeta \left\{ \frac{d}{w} \right\}$ in Equation (5.6) accounts for the additional frictional resistance imposed by non-deforming particles on the matrix, which results in large pressure gradients in the γ channels. This factor is discussed in detail by Pollock & Argon [306], who offer an analytical approximation as a function of the precipitate side length, d , and the channel width, w .

Assuming an ideal, unimodal particle distribution like in Figure 5.3, the constraint factor can be expressed as depending only on the γ' volume fraction:

$$\zeta \left\{ \frac{d}{w} \right\} = 1 + \frac{2\phi_p^{1/3}}{3\sqrt{3}\pi (1 - \phi_p^{1/3})} \quad (5.9)$$

This expression is incorporated readily into the models of Basoalto et al. [366] and Zhu et al. [364]. However, Pollock & Argon [306] debated its general validity, as it leads to values of tensile creep resistance far in excess of experimental estimates. Instead, it appears that as γ channels become populated by a knitted network of dislocations, many of which are lying along γ/γ' interfaces, some additional sliding will become possible [306]. As such, Pollock & Field put forward a value between 1 and 2 for ζ , depending on the size and shape of γ' precipitates [236].

Van Sluytman & Pollock [471] discussed how such a factor might vary with γ' morphology and in turn with lattice misfit. They predict optimal values can be reached in the range of $|\delta| \approx 0.4\%$. However, since accurate misfit predictions are again required, it is difficult to incorporate a shape- and misfit-dependent factor into the present model.

Furthermore, this resistance from the build-up of pressure gradients due to frictional drag will evolve during the creep test. Dyson [365, 468] took ζ to increase from unity to a maximum value of $\zeta^* = 1 + 2\phi_p$ due to stress redistribution around particles and proposed a stochastic approach to describe the evolution of the internal stress, σ_i , as:

$$\dot{\sigma}_i = \frac{\phi_p E}{1 - \phi_p} \left(1 - \frac{\sigma_i}{\sigma_i^*} \right) \dot{\epsilon} \quad (5.10)$$

where σ_i^* is the upper bound collapse value. An analogue relation to Equation (5.10) is constructed to describe the evolution of ζ with creep strain rate and the upper bound value of ζ^* is chosen as 1.75. This is slightly lower than the initial, ideal estimate of Pollock & Argon from Equation (5.9) and the simple expression of $1 + 2\phi_p$ proposed by Dyson [468], in order to account for imperfect particle shapes and reduced resistance to sliding at particle interfaces.

Equation (5.5) for the creep strain rate can now be expressed as:

$$\begin{aligned}\dot{\epsilon} &= \frac{8}{\sqrt{6}} (1 - \phi_p) b^2 (\tau_{\text{app}} - \zeta (\tau_{\text{Or}} + \tau_{\text{Dis}})) \left(\frac{\rho_c}{B_c} + \frac{\rho_g}{B_g} \right) \\ \dot{\zeta} &= \frac{\phi_p E}{1 - \phi_p} \frac{1}{\sqrt{6}(\tau_{\text{Or}} + \tau_{\text{Dis}})} \left(1 - \frac{\zeta}{\zeta^*} \right) \dot{\epsilon}\end{aligned}\quad (5.11)$$

5.3.3.2 Effective Climb and Glide Drag Coefficients

As a consequence of the substantial levels of solid solution strengthening in modern superalloys — normally maximised up to the limit of TCP phase precipitation [60] — dislocations experience significant drag forces and move through γ channels in a viscous manner [306]. Therefore, the values of the effective climb and glide drag coefficients in Equation (5.11), B_c and B_g , play a key role in determining the creep strain rate.

Early estimates come from the theoretical studies of Cottrell & Jawson [677] and Hirth & Lothe [661], who considered gliding dislocations surrounded by atmospheres of solute atoms at high temperatures. Takeuchi & Argon [593, 594] expanded on these results and derived expressions for modelling the effects of viscous drag on climbing and on gliding edge dislocations. In more recent studies, ur Rehman et al. [309] applied the model of Takeuchi & Argon to assess climb and glide resistances in single-crystal binary Ni-X (X=Re,Ta,W) solid solution alloys, while Hafez Haghighat et al. [586] and Liu et al. [587] used similar descriptions as part of DDD simulations of tertiary creep in single-crystal superalloys. The authors of the latter study expressed the drag coefficient for climb as:

$$B_c = \frac{b^2 k_B T \log(r_2/r_1)}{2\pi\Omega D_{\text{sol}} c_{\text{sol}}}\quad (5.12)$$

where k_B is the Boltzmann constant, D_{sol} is the diffusion coefficient of the solute, c_{sol} is the solute concentration at a theoretically infinite distance from the dislocation, and Ω is the atomic volume of the solvent. Due to the inverse relation between B_c and D_{sol} , additions of slow-diffusing elements — particularly molybdenum, rhenium,

tantalum, and tungsten for superalloys — will have a profound effect on generating increased drag. Similarly, the drag coefficient for glide was evaluated as [309]:

$$B_g = \frac{c_{\text{sol}} \beta^2 \log(r_2/r_1)}{k_B T D_{\text{sol}} \Omega} \quad (5.13)$$

with factors as defined above. While solute diffusivity again plays an important role, it is supplemented by misfit effects due to differences between the atomic radii of the solutes and the solvent. These are expressed by the size interaction parameter, β , which can be obtained as [593]:

$$\beta = \frac{Gb}{3\pi} \frac{1+\nu}{1-\nu} (\Omega_{\text{solute}} - \Omega_{\text{solvent}}) \approx \frac{Gb^4}{3} \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \quad (5.14)$$

The term $\log(r_2/r_1)$, present in both expressions, is used to define the interaction between dislocations and the solute environment, with r_1 and r_2 being the inner and the outer cut-off radii. Following the considerations of Hirth & Lothe [661], r_1 is equal to the length of the Burgers vector, b , while r_2 depends on the velocity and the diffusivity of the solute as $r_2 = D_{\text{sol}}/v_{\text{sol}}$. However, when this ratio becomes larger than the average distance between dislocations in the crystal — which is the case for densely packed dislocations in matrix channels — it no longer represents a meaningful estimate and must be replaced by an appropriate distance, R [661]. Pollock & Argon [306] used the value of γ channel width, w , as an estimate for R . Considering microstructural coarsening during creep, the term $\log(r_2/r_1) = \log(w/b)$ will increase gradually towards a constant value. As a simplification, we assume this value to be effective throughout the duration of creep tests. Taking w equal to 70 nm as a representative value for the coarsened state [678] yields $\log(r_2/r_1) \approx 5.6$, similar to the constant factor of 4.3 first derived by Cottrell & Jawson [677].

So far, only the influence of an individual solute species has been considered. In order to estimate total, effective drag coefficients, we follow the considerations of Reed et al. [52] with regard to dislocation pinning by different types of solute atoms.

These authors defined an effective time to circumvent a unit length of pinning atoms as:

$$t_{\text{eff}} = n_{\text{Mo}}t_{\text{Mo}} + n_{\text{Re}}t_{\text{Re}} + n_{\text{W}}t_{\text{W}} + \cdots + n_i t_i \quad (5.15)$$

Terms n_i denote the site densities of pinning solute atoms met by the leading segment of the dislocation, while t_i are the characteristic times of escape, depending on the relative pinning strength of the solutes. The time of escape will scale inversely with the average dislocation velocity and, therefore, linearly with the drag coefficient, as $t_i \propto 1/v_i \propto B_i$. As such, total, effective drag coefficients for climb and for glide can be estimated as:

$$B_{\text{c,eff}} = \frac{5.6b^2k_{\text{B}}T}{2\pi\Omega} \sum_i \frac{x_i^\gamma}{D_i c_i} \quad (5.16)$$

and

$$B_{\text{g,eff}} = \frac{5.6}{k_{\text{B}}T\Omega} \sum_i \frac{x_i^\gamma c_i \beta_i^2}{D_i} \quad (5.17)$$

The factor $\sum_i x_i/D_i$, with x_i and D_i being the mole fraction and the interdiffusion coefficient of solute i , respectively, is identical to the merit index for creep resistance proposed by Reed et al. [52]. For single-crystal superalloys with a similar microstructural architecture — in terms of lattice misfit and γ' volume fraction — a clear correlation between the Larson-Miller parameter and this merit index has been established [52, 102, 103]. This correlation was strengthened when the calculated solute mole fraction in the γ matrix, x_i^γ , was used instead of the mean composition, x_i . The same is done in the present study, as it seems reasonable to calculate drag coefficients based on the composition of the γ phase, where most of the creep damage is accumulated.

Interdiffusion coefficients, D_i , are calculated as $D_i = D_{0,i} \exp(-Q_{i,\text{Ni}}/RT)$. Pre-exponential factors, $D_{0,i}$, and activation energies pertaining to the interdiffusion process, $Q_{i,\text{Ni}}$, have normally been obtained experimentally using Ni–X diffusion couples. The ample work of Karunaratne et al. [314, 679–681] covered all relevant

Element	Experiment			CALPHAD		
	$D_{0,i}$ [m ² /s]	$Q_{i,Ni}$ [kJ/mol]	Refer- ence	$D_{0,i}$ [m ² /s]	$Q_{i,Ni}$ [kJ/mol]	Refer- ence
Cr	5.20×10^{-4}	289	[683]	4.33×10^{-4}	287	[684]
Co	1.80×10^{-4}	282	[683]	2.94×10^{-4}	284.2	[684]
Mo	1.15×10^{-4}	281.3	[681]	1.19×10^{-4}	281.8	[685]
Re	8.20×10^{-7}	255	[314]	3.28×10^{-6}	278.8	[684]
Ru	2.48×10^{-4}	304.4	[680]	2.52×10^{-4}	304.5	[686]
W	8.00×10^{-6}	264	[314]	2.79×10^{-5}	282.1	[684]
Al	2.30×10^{-4}	265	[679]	7.52×10^{-4}	284	[684]
Ti	2.30×10^{-4}	269	[679]	9.06×10^{-5}	256.9	[684]
Ta	2.19×10^{-5}	251	[314]	6.71×10^{-5}	267.7	[684]

Table 5.2: Pre-exponential factors and activation energies for solute diffusion in nickel based on diffusion couple experiments and CALPHAD predictions.

chemical additions in superalloys with the exception of chromium and cobalt, which had been assessed previously [682, 683]. A critical review reveals significant discrepancies between experimental results in different reports and makes it difficult to choose ‘optimal’ values for estimating effective diffusivity [683]. For alloy design purposes, a CALPHAD-based approach using a multicomponent diffusion mobility database, as proposed by Campbell et al. [684], appears more promising. A comparison between experimental and CALPHAD-based results, along with their respective sources, are shown in Table 5.2. While most values are in good agreement, it is clear that using experimental rather than CALPHAD-based data will give more weight to tungsten and rhenium additions. It can be argued that CALPHAD-based data will help minimise experimental scatter by considering several sources, as such, values in the ‘CALPHAD’ column are used in the present study.

Finally, it is instructive to estimate the ratio B_c/B_g at operating temperatures for successive generations of superalloys. This serves both as a sanity check, by comparing these results to usual assumptions in DDD studies, and as a critical assessment of the effects of solid solution strengthening in the present model. Following Zhu et al. [364], the alloys SRR99, CMSX-4, TMS-75, and EPM-102 are taken as representative of first- to fourth-generation superalloys. Their nominal chemical compositions are shown in Table 5.3.

Gen.	Alloy	Cr	Co	Mo	Re	Ru	W	Al	Ti	Ta	Hf	Ni	Reference
First	SRR99	8.0	5.0	—	—	—	10.0	5.5	2.2	3.0	—	Bal	[195]
Second	CMSX-4	6.5	9.0	0.6	3.0	—	6.0	5.6	1.0	6.5	0.1	Bal	[207]
Third	TMS-75	3.0	12.0	2.0	5.0	—	6.0	6.0	—	6.0	0.1	Bal	[476]
Fourth	EPM-102	2.0	16.5	2.0	6.0	3.0	6.0	5.55	—	8.25	0.15	Bal	[224]

Table 5.3: Nominal chemical compositions of exemplary first- to fourth-generation single-crystal superalloys in wt.%.

Results in Figure 5.5(a) show an increase in the resistance to dislocation motion in higher-generation superalloys. This trend is related to the rising amounts of slow-diffusing elements, particularly molybdenum, tungsten, and rhenium. However, it is important to consider that although these elements partition preferentially to the γ phase, actual values of the partitioning coefficients $K_i = x_i^{\gamma'}/x_i^{\gamma}$, and consequently effective levels of solution strengthening, may differ. Absolute values for B_c and B_g are in good agreement with the recent modelling estimates of ur Rehman et al. [309] and Zhao et al. [687].

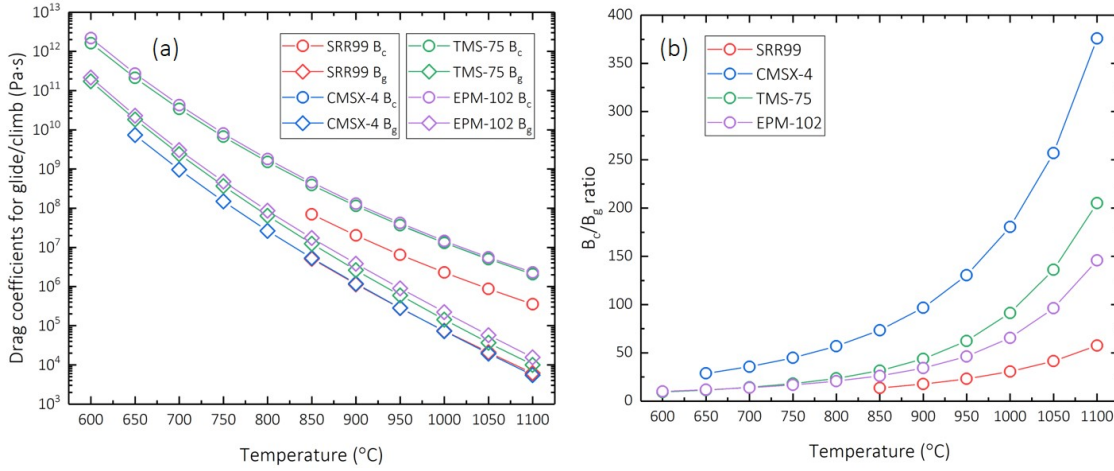


Figure 5.5: (a) Estimated drag coefficients for dislocation climb and glide in matrix channels. (b) Estimated ratio of B_c/B_g .

Since the climbing step controls the rate of creep strain accumulation, it is of particular importance to increase B_c rather than B_g . The plot in Figure 5.5(b) reveals to what extent this is achieved for different superalloys. CMSX-4 provides the highest relative level of solution strengthening, benefiting from a favourable partitioning of rhenium to γ . In the case of EPM-102, ruthenium has been added specifically to increase k_{Re} and limit TCP phase precipitation [224]. This obvious

trade-off brings to mind the difficulty of developing new superalloys with improved specific creep strength, as discussed in the introduction. The range of observed B_c/B_g ratios is in good agreement with the commonly assumed constant value of 100 from recent DDD studies [586, 587].

5.3.3.3 Mobile Dislocation Density

The first type of damage accumulation considered within Equation (5.11) is the strain-induced multiplication of mobile dislocations. As discussed in Section 5.2, most phenomenological models for tertiary creep assume a linear relation for the evolution of mobile dislocation density with increasing creep strain:

$$\dot{\rho}_m = C_d \dot{\epsilon} \quad (5.18)$$

where the constant dislocation multiplication parameter, C_d , is expressed as a multiple of the initial dislocation density, ρ_0 , as $C_d = K \times \rho_0$. Depending on the study, the assumed value for K is 50 [329], 300 [365], 67 [366], or 100 [364, 468].

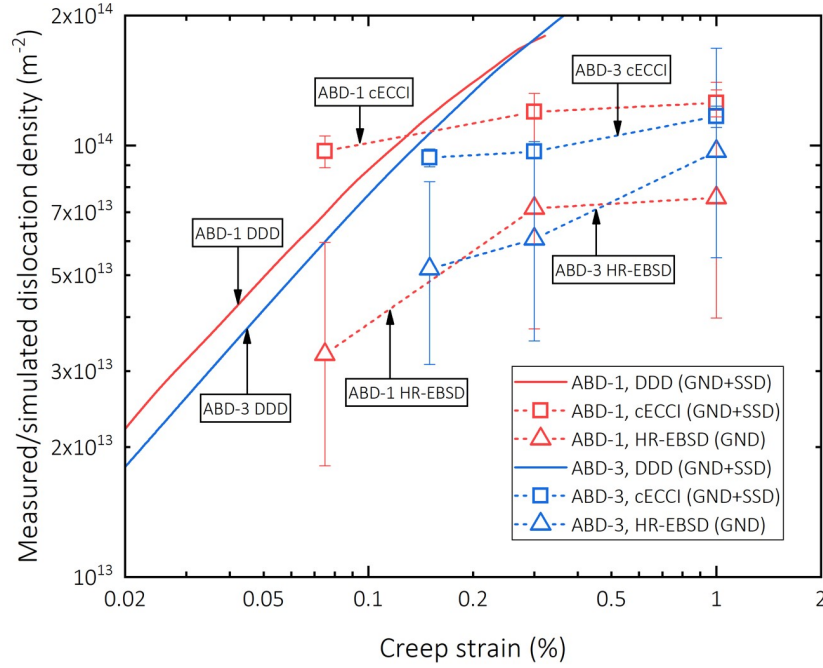


Figure 5.6: Evolution of dislocation density with plastic creep strain for the single-crystal superalloys ABD-1 and ABD-3 deformed at 900 °C and 450 MPa. DDD simulation results are compared to experimental values from HR-EBSD and cECCI analyses and show good overall agreement.

A first matter of contention is that such differences in the value of K , albeit apparently small, result in significant changes in the predicted time to 1% creep strain [364]. Furthermore, recent DDD studies of tertiary creep deformation in superalloys suggest a non-constant value for C_d [361, 586], as illustrated in Figure 5.6. In this graph, HR-EBSD and cECCI measurements as well as DDD predictions are reproduced from Chapter 4 for the second-generation, rhenium-containing superalloy ABD-1 and the first-generation, rhenium-free superalloy ABD-3 under deformation conditions of 900 °C and 450 MPa. Results consistently show a strong initial increase in C_d at low plastic strain values, followed by an exponential decrease as more creep strain accumulates [361, 586]. Furthermore, despite the differences in γ' volume fraction and level of solid solution strengthening, similar trends are observed for both alloys.

The evolution of the dislocation density with creep strain observed in Figure 5.6 can be described using the fundamental equation proposed by Gilman [636] for the dependence of the mobile dislocation density on plastic strain in crystalline solids:

$$\rho_m = (\rho_0 + M\varepsilon) \exp(-\phi\varepsilon) \quad (5.19)$$

Here, M is a multiplication parameter which leads to an initial rise in the mobile dislocation density and ϕ is an attrition parameter which expresses an exponential decay over time. Equation (5.19) has been used successfully to describe the creep response of single-crystal CMSX-4 specimens in the tertiary and rafting regimes [335, 337]. Based on values obtained from fitting to experimental results, it was concluded that M increases exponentially with applied stress and that ϕ depends on the crystal orientation and appears to scale inversely with applied stress. Approaches for estimating M and ϕ are discussed in more detail in Sections 5.4.1 and 5.4.2.

For small strain values — as is the case for common design targets of NBSA — Equation (5.19) can be simplified to:

$$\dot{\rho}_m = (M - \phi\rho_m) \dot{\varepsilon} \quad (5.20)$$

As the present model differentiates between climbing and gliding dislocations, their mobile densities must be treated separately. Following the considerations of Dyson [365], slightly modified by Zhu et al. [364] for cuboidal rather than spherical precipitates, the change in the net rate of climbing dislocations can be expressed as:

$$\dot{\rho}_c = \rho_g v_g \frac{1}{w} - \rho_c v_c \frac{2}{d} \phi_p \quad (5.21)$$

with all terms as defined previously. This change is obtained as the sum of the rate at which trapped climbing dislocations are released from γ' precipitate interfaces and of the rate at which gliding dislocations become temporarily arrested at the next particle. The half of the cuboid side length, $d/2$, and the channel width, w , are assumed to be the average distances that dislocations must overcome in each step [364]. Furthermore, the likelihood of climbing dislocations escaping depends on their probability of encountering a particle in the first place, which is taken to be equal to ϕ_p [365]. As climbing and gliding dislocation densities are codependent, the change in the net rate of gliding dislocations can be obtained as:

$$\dot{\rho}_g = \dot{\rho}_m - \dot{\rho}_c = (M - \phi \rho_m) \dot{\epsilon} + \rho_c v_c \frac{2}{d} \phi_p - \rho_g v_g \frac{1}{w} \quad (5.22)$$

Manonukul et al. [466] discussed the inclusion of two further terms in Equation (5.22) to account for changes in the net rate of pinned dislocations, $\dot{\rho}_i$, arising from individual dislocations being immobilised by the dislocation network and from thermally activated network recovery. However, as argued by these authors, the rate of climbing dislocations can be assumed to dominate the rate of pinning, $\dot{\rho}_c \gg \dot{\rho}_i$, therefore $\dot{\rho}_i$ can be neglected.

Finally, initial values must be chosen for $\rho_{c,0}$ and $\rho_{g,0}$. Considering ECCI and TEM results, it can be assumed that all mobile dislocations will begin by gliding through γ channels once an external load has been applied. As such, we take $\rho_{c,0} = 0$ and $\rho_{g,0} = \rho_{m,0} = \rho_0$. An often cited value for ρ_0 in the literature has been 10^{10} m^{-2} [364–366, 466], though none of these studies provide a clear source for this estimate. Similarly, Preußner et al. [688] chose an initial value of $5 \times 10^{10} \text{ m}^{-2}$. An early TEM study of dislocation densities in cast superalloys does indeed mention

densities as low as 10^{10} m^{-2} for the undeformed state [689] and this value is also in accordance with the estimate of Hull & Bacon [676] for as-cast crystals. Nonetheless, as the choice of this parameter may severely impact model results [364] and as the material undergoes further processing and machining steps prior to testing, a careful consideration is essential. Recent HR-EBSD and cECCI studies [361] yielded a dislocation density of $5 \times 10^{11} \text{ m}^{-2}$ in the undeformed regions of machined creep specimens. As such, in the present work, a figure of 10^{11} m^{-2} is considered more representative of the initial microstructure prior to creep testing.

5.3.3.4 γ' Precipitate Coarsening

The second type of damage considered is the thermally induced coarsening of precipitates. The fundamental equation for competitive particle growth can be expressed as:

$$\bar{R}(t)^n - \bar{R}(0)^n = kt \quad (5.23)$$

Here, $\bar{R}(t)$ and $\bar{R}(0)$ represent the average particle sizes at times t and 0. The exponent n is characteristic for the dominating coarsening mechanism and takes a value of 2 for interface-controlled reactions and of 3 for diffusion-controlled reactions. The latter case corresponds to the widely applied LSW theory [264, 265] for diffusion-controlled Ostwald ripening. Coarsening in modern NBSA can be accurately described by Equation (5.23), with $n = 3$ and $\bar{R} = d/2$, where d is the average side length of γ' cuboids [276]. As discussed in Section 2.1.3.1, the key parameter defining the coarsening rate is k , and the way in which it is estimated remains a matter of contention between different theories. An ample discussion of this point can be found in the reviews by Baldan [275, 276] on the progress in Ostwald ripening theories and on their application to γ' precipitates in NBSA. A similar analysis is beyond the scope of the present work, nonetheless, it is important to carefully choose the method of calculating k , as particle coarsening and the corresponding increase in particle spacing will have a significant effect on creep resistance.

ϕ_p (%)	$A(\phi_p)$			
	LSW [264, 265]	MLSW [267]	LSEM [270]	BW [269]
2	0.89	2.37	1.02	1.16
5	0.89	3.49	1.09	1.44
10	0.89	5.06	1.17	1.75
20	0.89	7.90	1.30	2.19
40	0.89	13.25	1.54	2.98
60	0.89	18.44	1.84	3.69

Table 5.4: Comparison of proportionality factors $A(\phi_p)$ estimated by different coarsening theories.

All coarsening theories developed for NBSA express k as having the form:

$$k = \frac{A(\phi_p) D_{\text{eff}} C_e \sigma_{\text{int}} \Omega^2}{RT} \quad (5.24)$$

Here, $A(\phi_p)$ is a dimensionless proportionality factor, D_{eff} is the effective diffusion coefficient, C_e is the matrix concentration of the constitutive particle element, σ_{int} is the interfacial energy between matrix and particles, and Ω is the molar volume of the precipitate phase. Different methods of estimating D_{eff} , C_e , σ_{int} , and Ω have been proposed in the literature.

The LSW theory assumes a negligible precipitate volume fraction and obtains from theoretical considerations $A(\phi_p) = 8/9 \approx 0.89$. Later studies argued that k should scale with ϕ_p and provided different analytical or numerical approaches to estimate $A(\phi_p)$. McLean [690] compared the LSW theory with the modified LSW (MLSW) theory of Ardell et al. [266–268], the Lifshitz-Slyozov encounter modified (LSEM) theory of Davies et al. [270], and the Brailsford-Wynblatt (BW) theory [269] and compiled a table of $A(\phi_p)$ values for different γ' volume fractions, reproduced in Table 5.4. Six additional theories, each yielding somewhat different results, have been reviewed and discussed by Baldan [275]. Considering all these discrepancies, it can be concluded that no single theory is optimal and that each will be more or less effective depending on the alloy system and the coarsening conditions involved. Furthermore, while numerical approaches provide certain improvements, for example, by reproducing realistic particle size distributions, they also require extensive computational resources, which remain prohibitive for alloy design purposes.

In the present work, four analytical methods of calculating the coarsening rate coefficient k are compared to experimental results. These are the standard LSW theory, the MLSW theory, the LSW-type theory of Li et al. [96], and the MLSW-type theory of Ai et al. [691]. The last two methods have been developed specifically to guide the development and design of new NBSA and include estimates of $A(\phi_p)$, D_{eff} , C_e , σ_{int} , and Ω depending on alloy composition and temperature. For the LSW and the MLSW theories, these factors must still be evaluated. Following Ai et al. [691], $A(\phi_p)$ for the MLSW theory is estimated with a polynomial function as $A(\phi_p) = 2.22 + 25.55\phi_p - 1.60\phi_p^2 + 0.65\phi_p^3$. For both theories, D_{eff} is obtained following Reed et al. [52] as $D_{\text{eff}} = \sum_i x_i^\gamma / D_i$; $D_i = D_{0,i} \exp(-Q_{i,\text{Ni}}/RT)$, analogue to the calculations described in the section on effective drag coefficients. C_e represents the matrix concentration of the rate-controlling element. According to McLean [690], aluminium is likely to be rate-controlling for both Ni_3Al and $\text{Ni}_3(\text{Al,Ti})$. The increasing amounts of slower-diffusing tantalum in modern alloys may, however, affect C_e for $\text{Ni}_3(\text{Al,Ti,Ta})$. As such, C_e is taken as the sum of the matrix concentrations of aluminium, titanium, and tantalum, following Li et al. [96]. Lastly, σ_{int} and Ω are estimated from CALPHAD calculations using Thermo-Calc and the associated databases TCNi8 and MOBNi3.

Experimental data for testing the models were selected to cover the first three superalloy generations and include results on first-generation CMSX-2 exposed between 800 and 1050 °C [692], on second-generation CMSX-4 exposed between 850 and 1000 °C [678], and on third-generation CMSX-10 exposed at 950 and 1050 °C [693]. This data set allows to check whether theories correctly reproduce the beneficial effects of increased rhenium additions, as this slow-diffusing element has been shown to play a key role in reducing D_{eff} and in turn k [144, 145]. Results in Figure 5.7 show that the MLSW theory and the approaches of Ai et al. and Li et al. increasingly overestimate k . This observation is in accordance with the critical review by McLean [690], who concluded that neither the particle shape, nor the volume fraction appear to have an obvious effect on k , thus implying that the factor $A(\phi_p)$ can be largely neglected. The standard LSW theory slightly underestimates

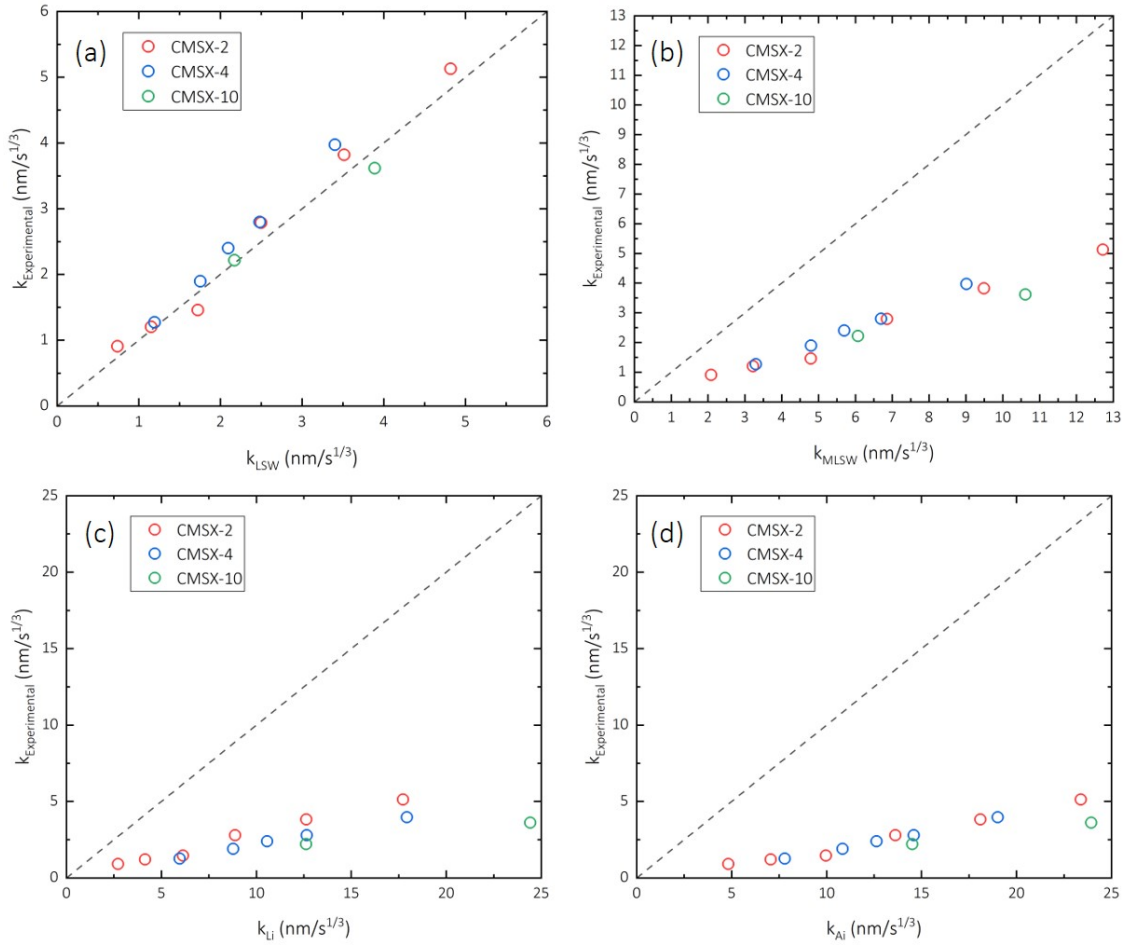


Figure 5.7: Comparison of experimental coarsening rate coefficients with model predictions from (a) the LSW theory [264, 265], (b) the MLSW theory [267], (c) the model of Ai et al. [691], and (d) the model of Li et al [96].

k . As such, a slight correction as provided by the LSEM theory would be beneficial but remains challenging to implement due to the associated computational cost.

Equations (5.11), (5.21), (5.22) and (5.24) now represent a set of physically based constitutive equations describing the evolution of the creep strain rate based on strain-induced mobile dislocation multiplication and thermally induced precipitate coarsening. An amended version of the process flow diagram from Figure 5.2 which includes these relations is presented in Figure 5.8. Assumed microstructural parameters are summarised in the inset table. This set of differential equations can be integrated using standard finite difference methods to yield the full shape of the creep curve. Modelling predictions are compared to experimental results to validate the present approach.

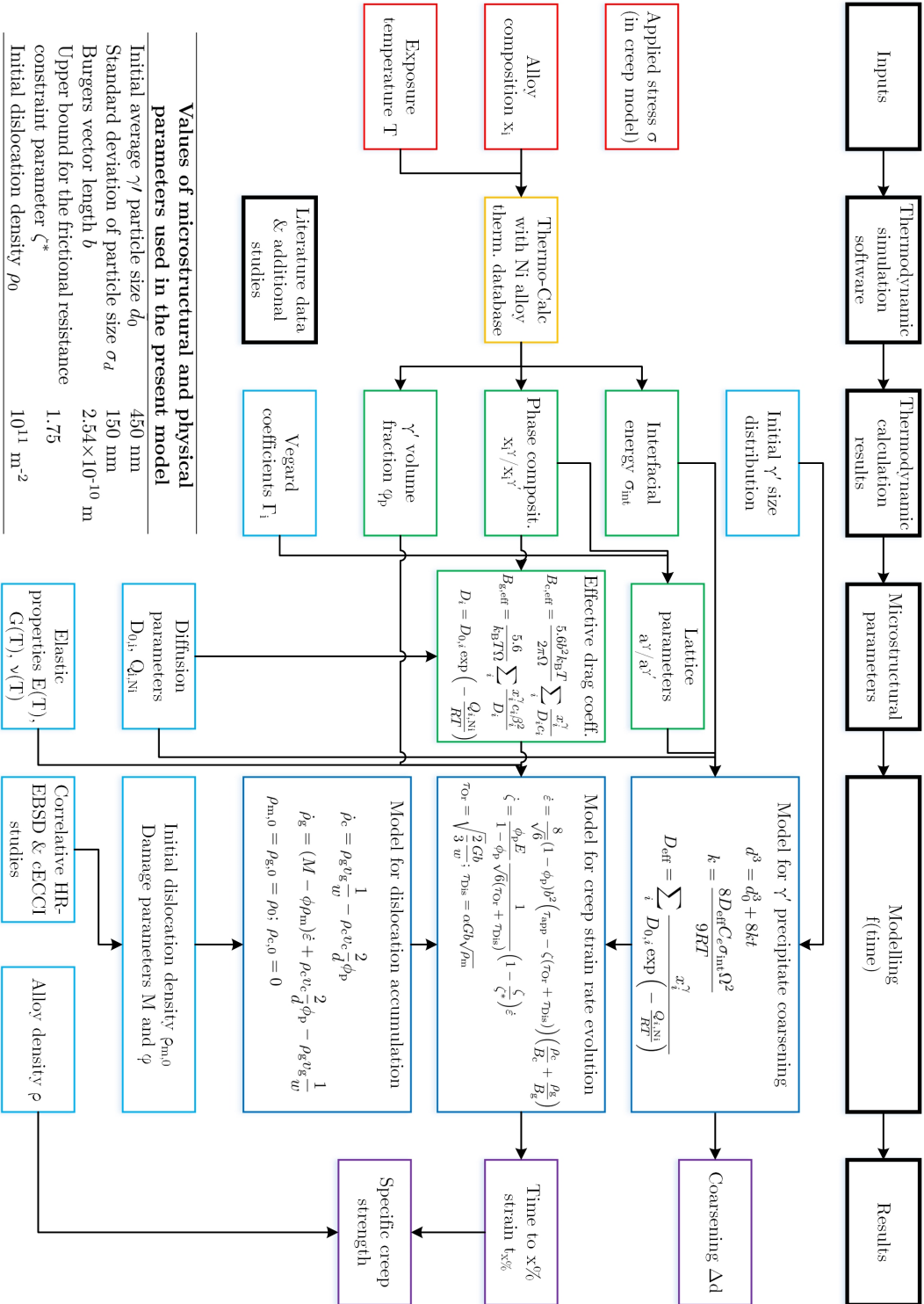


Figure 5.8: Process flow diagram including explicit constitutive equations and microstructural parameters used in the present model.

5.4 Critical Appraisal of Model Predictions

5.4.1 Predictions of Tertiary Creep in CMSX-4

Model predictions are first compared to an experimental creep data set for CMSX-4 [335, 336], which includes a wide range of testing conditions over which the model can be assessed. As shown in Figure 5.9, experimental results are closely reproduced by the present model. Predictions for the time to 1% strain — often used as a design parameter for turbine blade applications [37] — are close to measured values. Only two parameters were varied in order to achieve a good agreement — the coefficients for dislocation multiplication and attrition, M and ϕ , in Equation (5.20).

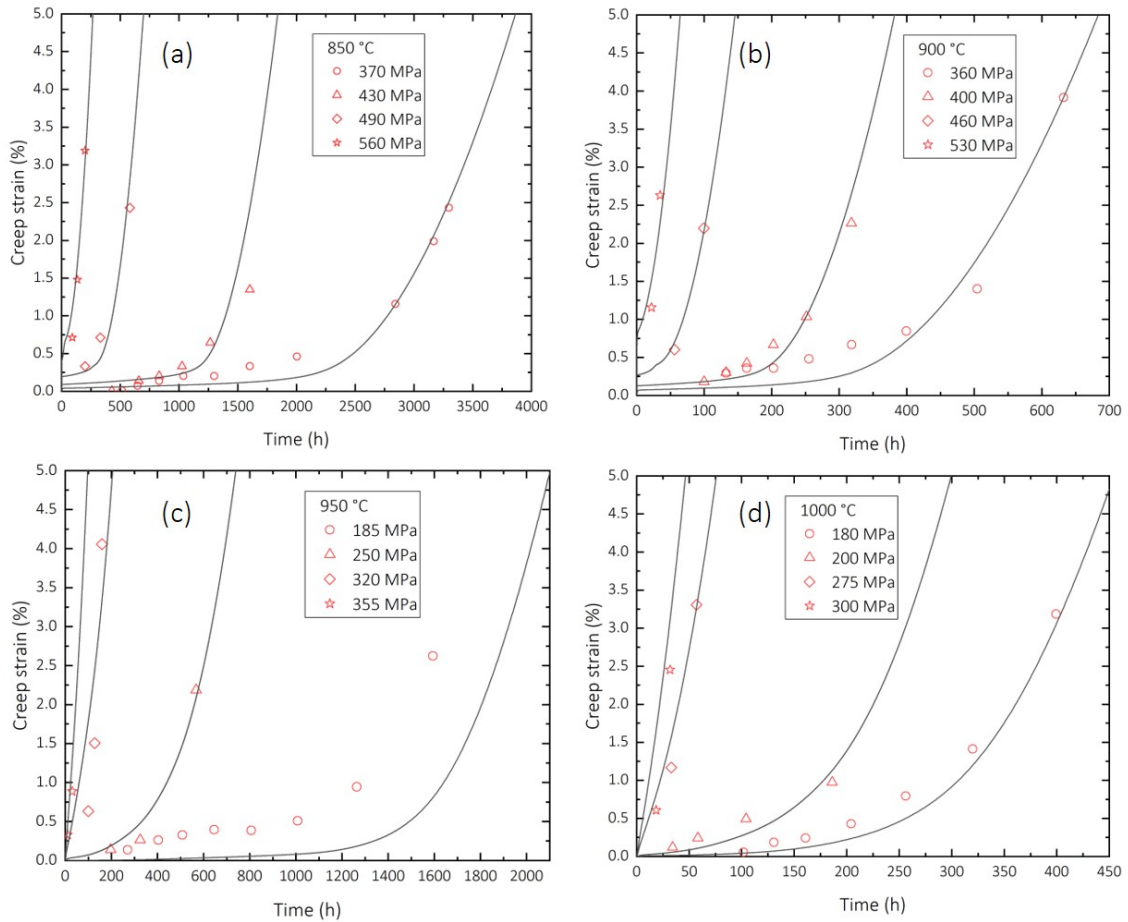


Figure 5.9: Comparison of simulated creep curves with experimental data for CMSX-4 at (a) 850 °C, (b) 900 °C, (c) 950 °C, and (d) 1000 °C.

As discussed by Reed et al. [337], the exponential decrease of the mobile dislocation density will be more pronounced in the high-temperature rafting regime.

This higher value of ϕ has been related to additional hardening provided by the rafted microstructure, which traps dislocations in the γ matrix channels. In the case of CMSX-4, rafting can be expected to begin playing a role at 950 °C and to become dominant at 1000 °C [12]. In the present model, ϕ was taken to be equal to 225 at 850 and 900 °C and equal to 1500 at 950 and 1000 °C. The former value of 225 corresponds to the attrition parameter obtained by Ram et al. [361] from DDD simulations of tertiary creep in single-crystal superalloy ABD-1 deformed at 900 °C and 450 MPa. The latter value of 1500 was chosen based on the attrition parameters derived by Reed et al. [337] from creep tests on CMSX-4 at 1050 °C. These figures are assumed to remain constant for the duration of the creep tests for the sake of simplicity. However, the magnitude of operating dislocation attrition mechanisms is expected to fluctuate with changes in alloy microstructure, which will result in varying levels of resistance to dislocation movement [337].

5.4.2 On the Increase in Mobile Dislocation Density

Values of the dislocation multiplication parameter, M , obtained from fitting to experimental data for CMSX-4 are illustrated in Figure 5.10. Furthermore, a data point obtained from DDD simulation results for ABD-1 deformed at 900 °C and 450 MPa has been added [361]. As ABD-1 and CMSX-4 possess similar chemistries and microstructures, comparable rates of dislocation multiplication can be expected. Although the M value from DDD will be strongly influenced by assumptions and restrictions pertaining to this modelling technique, it is nonetheless interesting to note that it is in good agreement with the inferred values for CMSX-4, which gives further confidence in the present approach.

Results also confirm the trend reported by Matan et al. [336, 337] that the rate of dislocation multiplication increases exponentially with the applied stress. Furthermore, the stress exponent in a relation of the form $M = M_0 \times \sigma^n$ appears to depend on the dominating damage mechanism — in this case, intermediate-temperature dislocation climb at particle interfaces or high-temperature precipitate rafting. In the tertiary regime, a pronounced dependence on applied stress is found

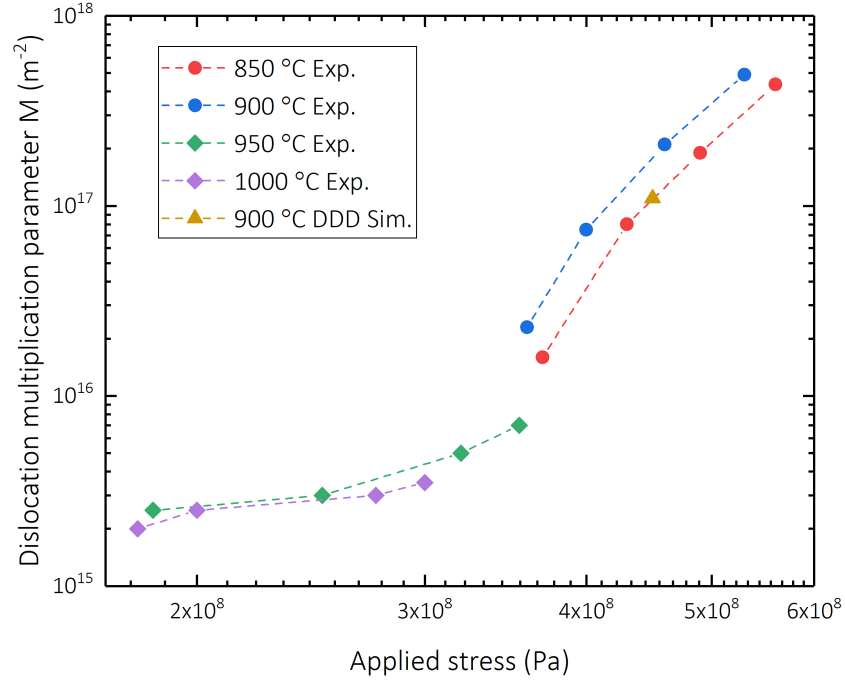


Figure 5.10: Dislocation multiplication parameters obtained from fitting to experimental data for CMSX-4 plotted against applied stress. A value obtained from DDD simulations of ABD-1 deformed at 900 °C and 450 MPa has also been added [361].

at both 850 and 900 °C, whereas in the rafting regime at 950 and 1000 °C, applied stress plays a lesser role. This is in line with the expectation that the coarsening rate, dictated primarily by temperature, will control deformation rates for rafting.

Quantitative values for M_0 and n lack a clear physical meaning, as it has not yet been determined when isolated dislocation sources become active dislocation emitters, nor by which mechanism this occurs. Moreover, previous studies on the influence of stress and temperature on M and in turn on ρ_m have only reported the observed trends, but have not discussed these in a physical sense [336, 337, 586]. For the case of low-temperature plasticity governed by continuous dislocation glide, Kocks et al. [694, 695] derived a function of the form:

$$\rho_m = \alpha \left(\frac{\sigma}{Gb} \right)^2 \quad (5.25)$$

where α is a constant on the order of unity. It is acknowledged that this simplified relation cannot be readily extended to the present case of a complex engineering material deformed at high temperatures. Nonetheless, it suggests a clear dependence

of ρ_m and M on applied stress, as shown in Figure 5.10. The influence of temperature can be related to a lower shear modulus, G , at higher temperatures.

5.4.3 Model Sensitivity Analysis

While model predictions appear reasonable, it is essential to assess their sensitivity to individual parameters. Figure 5.11 shows simulated creep curves for CMSX-4 at the common design point of 900 °C and 400 MPa. In each case, a different parameter is varied while keeping the others constant: (a) γ' volume fraction, ϕ_p , (b) initial mean particle size, $\bar{d}_0$, (c) dislocation multiplication parameter, M , and (d) dislocation attrition parameter, ϕ .

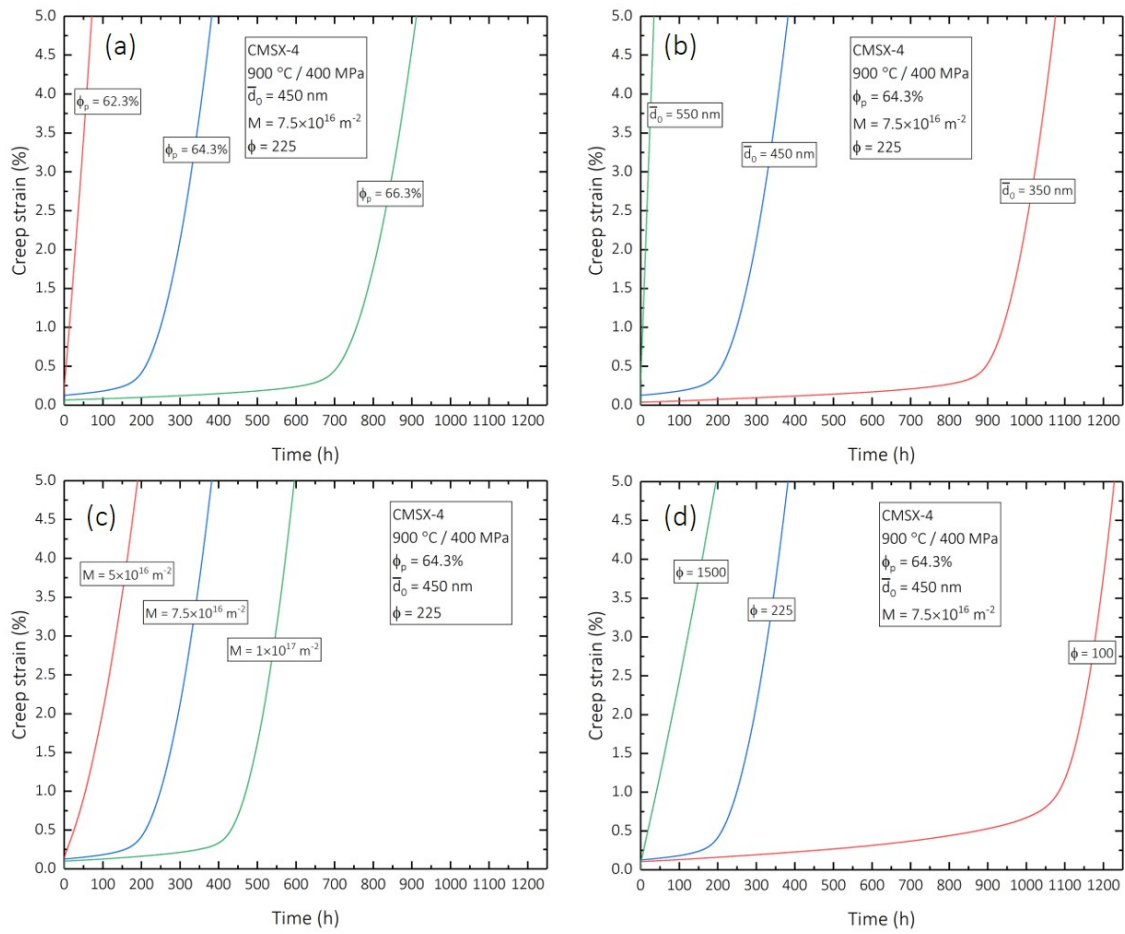


Figure 5.11: Assessment of the influence of microstructural parameters on the creep performance of CMSX-4 at 900 °C and 400 MPa: (a) γ' volume fraction, (b) initial γ' mean particle size, (c) dislocation multiplication parameter, and (d) dislocation attrition parameter.

In Figure 5.11(a), results for the volume fraction predicted by Thermo-Calc and TCNi8 for CMSX-4 at 900 °C, 64.3%, are compared to volume fractions 2% lower and higher. Creep performance is very sensitive to slight changes in γ' fraction. This is in good agreement with the design guidelines of Section 2.2.3 and with the work of Murakumo et al. [104, 205] on tie-line single-crystal superalloys. These authors obtained the longest creep lives at 900 °C and 392 MPa for 70% γ' alloys and associated this with an increasing Orowan resistance provided by narrower matrix channels, in line with Equation (5.7).

The same qualitative trend can be observed in Figure 5.11(b) for different initial particle size distributions. In this case, the standard deviation of 150 nm was kept constant and only the mean particle size was varied from 450 to 350 and to 550 nm. These distributions were again estimated through histograms containing 5 bins with an equal bin width of 100 nm. As expected based on the guidelines of Section 2.2.3, the Orowan resistance and the creep strength are increased by smaller particles. However, three caveats must be pointed out. First, decreasing the initial precipitate size becomes increasingly challenging in industrial practice, as it requires higher cooling rates after the solutioning heat treatment, which can result in damaged turbine components. Second, for most modern superalloys which possess a small, negative lattice mismatch at high temperatures, a decreasing particle size will eventually result in a shape change from cuboidal to spherical particles, which will lower creep strength [358, 463]. Third, the importance of initial particle size and of coarsening damage decreases as creep testing conditions become less severe. As shown previously in Figure 2.15, during isothermal service conditions, all coarsening curves will converge on a certain asymptotic particle size regardless of initial values [239, 646]. As such, it can be argued that while it remains important to consider $\bar{d}_0$ for modelling laboratory creep results, this value will be of less importance for industrial purposes.

Figure 5.11(c) and Figure 5.11(d) reveal an equivalent trend with regard to the evolution of mobile dislocation density, as described by Equation (5.20). Creep life is extended as the multiplication parameter, M , increases, or as the attrition parameter,

ϕ , decreases. This observation appears counterintuitive, since a rapid increase in the net rate of mobile dislocations is commonly expected to lead to higher strain rates [364–366]. However, this can be rationalised by considering Equations (5.21) and (5.22), which describe the net rates of climbing and gliding dislocations, and also the experimental results of Ram et al. [361]. These authors showed that the activation of several individual dislocation sources at low levels of creep strain will result in dislocation ‘avalanches’ within γ matrix channels and, eventually, in the formation of stable, equilibrium dislocation networks. For higher values of M , this drastic surge will be more pronounced and will first lead to a higher initial net rate of gliding dislocations, $\dot{\rho}_g$, in Equation (5.22). Second, this also implies a higher initial density of dislocations gliding through the matrix, ρ_g , which will then become arrested at particle interfaces. Third, following Equation (5.21), this will increase the initial net rate of climbing dislocations, $\dot{\rho}_c$, and their density, ρ_c . Fourth, the higher value of ρ_c will produce a strong negative feedback effect in Equation (5.22) and will outweigh the positive term for the generation of new gliding dislocations, dictated by M . Finally, this effect will markedly reduce the net rate of gliding dislocations, thus inducing an equilibrated state. A lower value of ϕ will have the same qualitative effect. Overall, this situation can be compared to other physical or biological systems which strive towards a state of equilibrium or homeostasis. In the present work, a higher value of M or lower value of ϕ will bring about this equilibrium more rapidly by, counterintuitively, causing more damage in very early stages.

Finally, it is critical to examine whether the model can reproduce the increasing creep performance of later-generation superalloys which contain higher amounts of rhenium. The same four compositions presented in Section 5.3.3.2 are compared at the design point of 900 °C and 400 MPa. All microstructural parameters are chosen to be constant, in order to isolate the effects of chemistry on solid solution strengthening and on the rate of particle coarsening. Thermo-Calc and TCNi8 are first used to calculate γ and γ' phase compositions at 900 °C. Individual chemistries are then slightly adjusted to yield the same γ' volume fraction of 64.3%, while maintaining the predicted phase compositions.

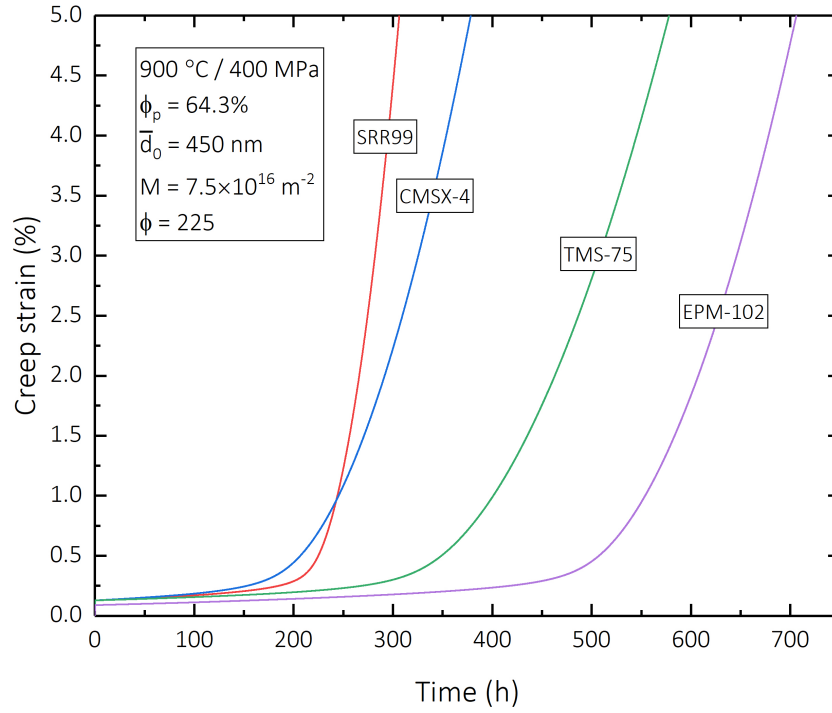


Figure 5.12: Comparison of simulated creep curves at 900 °C and 400 MPa for exemplary first- to fourth-generation single-crystal superalloys.

As shown in Figure 5.12, creep performance increases as expected in the order SRR99, CMSX-4, TMS-75, and EPM-102. This agrees with experimental results which show significant improvements in creep resistance associated with lower effective diffusivity values and with a retardation of diffusion-controlled deformation mechanisms. However, on the one hand, the predicted time to 1% strain is almost identical for SRR99 and CMSX-4, despite the 3 wt.% rhenium additions in the latter alloy. On the other hand, the model underestimates the time to 1% strain for TMS-75 and EPM-102 by about 50%. These discrepancies can be explained by the general inaccuracies associated with CALPHAD calculations and they underline the importance of improving and expanding thermodynamic parameter databases like TCNi8. Nonetheless, alloy performance remains in good qualitative agreement with published data and affirms the usefulness of the present model for alloy design.

5.5 Discussion: Choice of a Composition-Dependent Creep Merit Index

A significant goal of the present work is to provide an improved description of creep resistance for use in ABD calculations. In this context, model predictions must be critically assessed for a larger number of compositions and testing conditions. A survey of journal articles, patents, and grey literature yielded around 1500 data points for the time to 1% creep strain in different single-crystal superalloys. This set was filtered to include only the tertiary creep regime at intermediate levels of applied stress and temperature, resulting in 265 data points. Upper limits were set at 517 MPa (75 ksi) and 955 °C (1750 °F), following the results for CMSX-4 shown in Figure 5.1. Furthermore, alloys predicted by Thermo-Calc and TCNi8 to exceed a total TCP phase volume fraction of 5% were removed, since the effects of these deleterious phases have not been considered in the present work. Previous studies showed that a volume fraction of TCP phases of up to 2% is tolerable for shorter creep tests with rupture times in the range of 200 to 300 h [445, 696, 697], similar to most tests considered here. However, since Thermo-Calc provides estimates for thermodynamic equilibrium conditions, in which a higher volume fraction of TCP phases is expected, the critical limit was increased to 5%.

In Figure 5.13, experimental results are rendered on the x -axes as temperature-compensated time in the form of the Larson-Miller parameter $P_{\text{LM}}(\sigma) = T(20 + \log(t_{1\%}))$. The issues surrounding the use of the Larson-Miller parameter have been discussed in Section 2.2.2 and are again acknowledged. Nonetheless, this approach remains the most widely accepted within industry. Under the assumption that the same damage mechanisms are operating in all the tests considered here, the ‘merit indices’ or microstructural parameters rendered on the y -axes should provide relative measures of creep resistance and, in principle, should scale with Larson-Miller values.

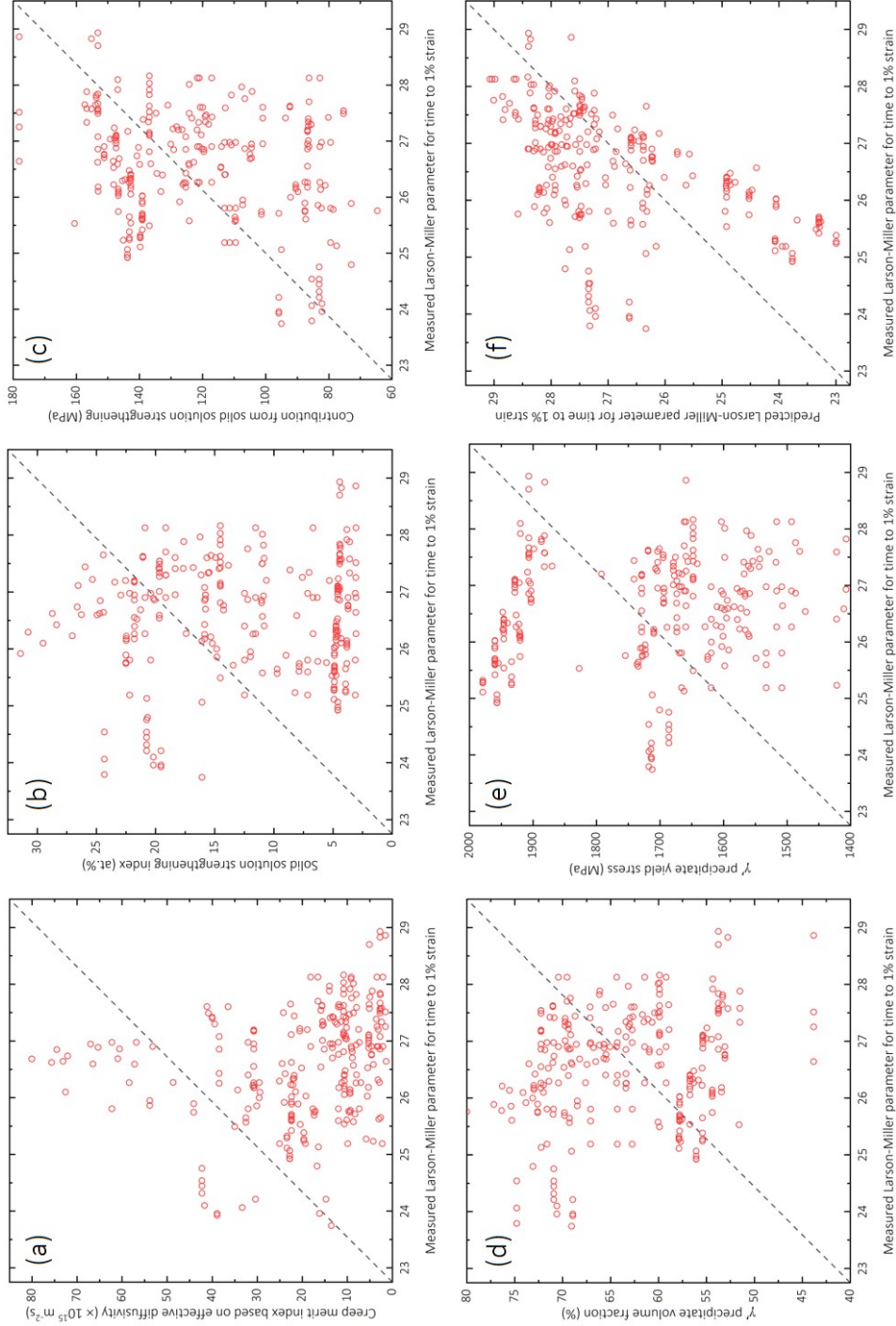


Figure 5.13: Comparison between experimentally measured Larson-Miller parameters for the time to 1% creep strain and different ‘merit indices’ for creep strength: (a) effective diffusivity index proposed by Reed et al. [52, 103], (b) solid solution strengthening index proposed by Rettig et al. [60], (c) yield stress contribution from solid solution strengthening as calculated by Roth et al. [698], (d) γ' volume fraction predicted by Thermo-Calc, (e) γ' precipitate yield strength as modelled by Crudden et al. [111], and (f) Larson-Miller parameters calculated with the present model.

Previous creep merit indices for alloy design consider a fixed microstructural architecture, with a set γ' volume fraction for all compositions, and neglect coarsening damage. Under this interpretation, creep resistance is primarily dictated by the effective diffusivity controlling climb processes at particle/matrix interfaces. Reed et al. [52, 103] proposed the inverse of D_{eff} as a suitable first-order merit index (Figure 5.13(a)). Similarly, Rettig et al. [60] proposed a weighted solid solution strengthening index which takes into account the relative contributions of molybdenum, rhenium, and tungsten in the γ phase, as derived from experiments on binary Ni-X (X=Mo,Re,W) alloys [315] (Figure 5.13(b)). When compared to experimental results, neither of these indices appears effective at predicting creep resistance. Rather, data points are clustered together at similar values of the respective index, but are scattered along the x -axes depending on experimental results. A further means of quantifying solid solution strengthening is estimating its contribution towards the total yield stress, as modelled, for example, by Roth et al. [698] (Figure 5.13(c)). Although this approach shows a somewhat better correlation with experiments, results again appear clustered in a certain range of this index.

The main reason for the poor performance of these three methods is that the underlying assumption of a constant microstructural architecture does not hold true for the range of commercial compositions compared here, or indeed for the range of microstructures one would like to consider during an alloy design process. Both the γ' volume fraction predicted by Thermo-Calc and TCNi8 (Figure 5.13(d)) and the individual strength of γ' precipitates estimated with the model of Crudden et al. [111] (Figure 5.13(e)) show large discrepancies within the data set. It can therefore be concluded that a reasonable estimate of creep resistance can only be achieved by considering all contributing factors.

The degrees of correlation between the experimental results and the merit indices or the microstructural parameters considered in Figure 5.13 are illustrated in the scatter plot matrix of Figure 5.14. To account for the highly non-linear relations, Spearman's ρ rank correlation coefficient is chosen instead of Pearson's r correlation coefficient. Spearman's coefficient assesses the measure of statistical dependence

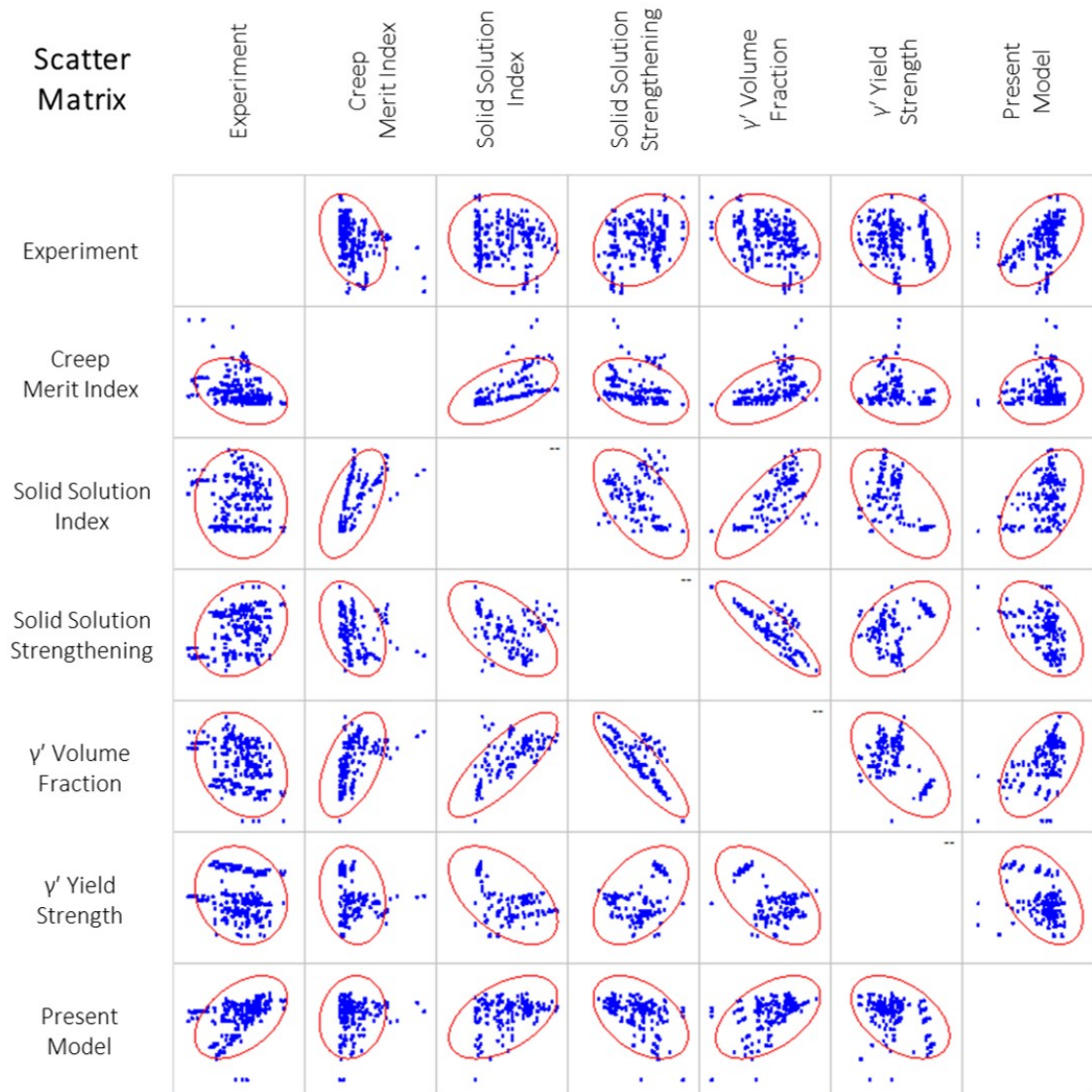


Figure 5.14: Scatter plot matrix showing Spearman correlations between experimental results and the six ‘merit indices’ considered previously. The red ellipses indicate 95% confidence levels.

between the rankings of two variables and expresses how well their relationship can be described using a monotonic function. It is less sensitive to strong outliers than Pearson’s coefficient, since it limits outlier effects to rank values rather than considering actual numerical values. This is beneficial in the present case, as some strong numerical discrepancies may arise from incorrect CALPHAD predictions. Coefficient values are shown in Table 5.5. Bold figures indicate correlations significant at the 0.05 level for the experimental results and for the present model.

	Correlation Parameters	Experiment	Creep Merit Index	Solid Solution Index	Solid Solution Strengthening	γ' Volume Fraction	γ' Yield Strength	Present Model
Experiment	Spearman's ρ p-value	1 –	-0.38124 1.25052E-10	-0.04559 0.45906	0.18384 0.00261	-0.20658 6.98836E-4	-0.23577 1.03611E-4	0.56255 1.33641E-23
Creep Merit Index	Spearman's ρ p-value	-0.38124 1.25052E-10	1 –	0.70783 9.66851E-42	-0.49482 7.79955E-18	0.64357 1.67699E-32	-0.06693 0.27673	0.05797 0.34631
Solid Solution Index	Spearman's ρ p-value	-0.04559 0.45906	0.70783 9.66851E-42	1 –	-0.65094 1.89876E-33	0.84756 1.327E-74	-0.40389 7.37103E-12	0.43936 -0.47141
Solid Solution Strengthening	Spearman's ρ p-value	0.18384 0.00261	-0.49482 7.79955E-18	-0.65094 1.89876E-33	1 –	1.17872E-84 0.39536	-0.87384 1.17872E-84	-0.87384 1.17872E-84
γ' Volume Fraction	Spearman's ρ p-value	-0.20658 6.98836E-4	0.64357 1.67699E-32	0.84756 1.327E-74	-0.87384 1.17872E-84	1 –	-0.43714 7.69633E-14	-0.43714 7.69633E-14
γ' Yield Strength	Spearman's ρ p-value	-0.23577 1.03611E-4	-0.06693 0.27673	-0.40389 7.37103E-12	0.39536 2.19425E-11	-0.43714 7.69633E-14	1 –	-0.45842 3.1566E-15
Present Model	Spearman's ρ p-value	0.56255 1.33641E-23	0.05797 0.34631	0.43936 5.57271E-14	-0.47141 4.02182E-16	0.51511 1.98712E-19	-0.45842 3.1566E-15	1 –

Table 5.5: Spearman correlation values between experimental results and the six microstructural variables considered previously. Bold coefficient values indicate correlation is significant at the 0.05 level.

Statistical analysis confirms that among the examined merit indices, the present model offers the highest degree of correlation with experiments, with a Spearman's ρ of 0.56. The present model also shows positive correlations to the solid solution strengthening index proposed by Rettig et al. and to the γ' volume fraction. This is unsurprising considering the importance of retarding diffusion-controlled deformation mechanisms and of decreasing the size of the matrix channels. Interestingly, no significant correlation can be found for the model and the creep merit index based on effective diffusivity. The negative correlations between the model and the two factors associated with yield strength bring to mind the necessary trade-offs in alloy design studies, in this case balancing mechanical strength at low and high temperatures.

Overall, results from the present model (Figure 5.13(f)) are shown to be in reasonable agreement with experimental results and largely differ by less than one-half of a Larson-Miller parameter. It is acknowledged that the logarithmic term in the Larson-Miller parameter will blur some differences between model and experiments. Nonetheless, unlike other creep merit indices, the model captures the relative performance of commercial compositions and — from a pragmatic point of view — is a suitable benchmark for ABD calculations. Furthermore, the prediction range of one-half of a Larson-Miller parameter is of the same magnitude as the scatter observed in experimental creep datasets due to (1) variations in chemistry between heats, (2) variations in heat treatment between specimen batches, and (3) variations in crystal orientation between individual specimens [699].

Even so, the influence of several inputs and calculated alloy properties on the modelling results is assessed in Figure 5.15 to rationalise some of the observed discrepancies. Colour scales illustrate across five evenly spaced major levels whether parameters are beneficial (green) or detrimental (red) to creep life.

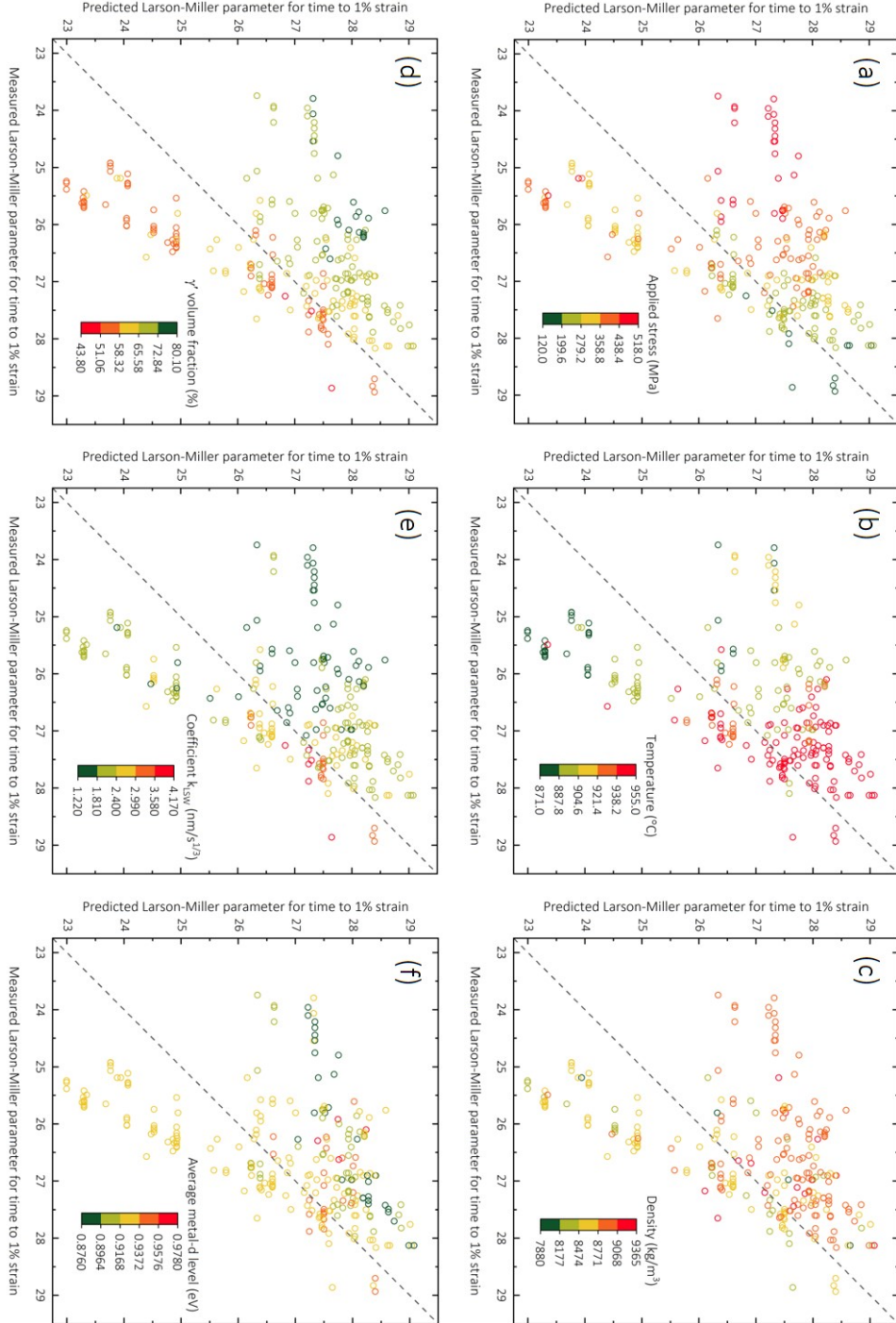


Figure 5.15: Qualitative assessment of the influence of creep testing conditions — (a) applied stress and (b) temperature — and calculated material properties — (c) density, (d) γ' volume fraction, (e) coarsening rate coefficient, and (f) average metal-d level — on the accuracy of model predictions.

As the colour maps only offer a qualitative indication of the sign and magnitude of these influences, the following approach is taken to also obtain quantitative values. First, a linear relation is assumed between modelling predictions and experimental results of temperature-compensated time, both expressed in the form of the Larson-Miller parameter $P_{LM}(\sigma) = T (20 + \log(t_{1\%}))$. Second, residual values are calculated for each data point based on the linear fit. A histogram of residuals and a normal probability plot of residuals are used to check whether the variance is normally distributed. This is found to be the case, as the resulting histogram shows a symmetric bell-shaped distribution around zero and as the normal probability plot is almost linear. Last, residual values are plotted in Figure 5.16 against several parameters, in complement to Figure 5.15.

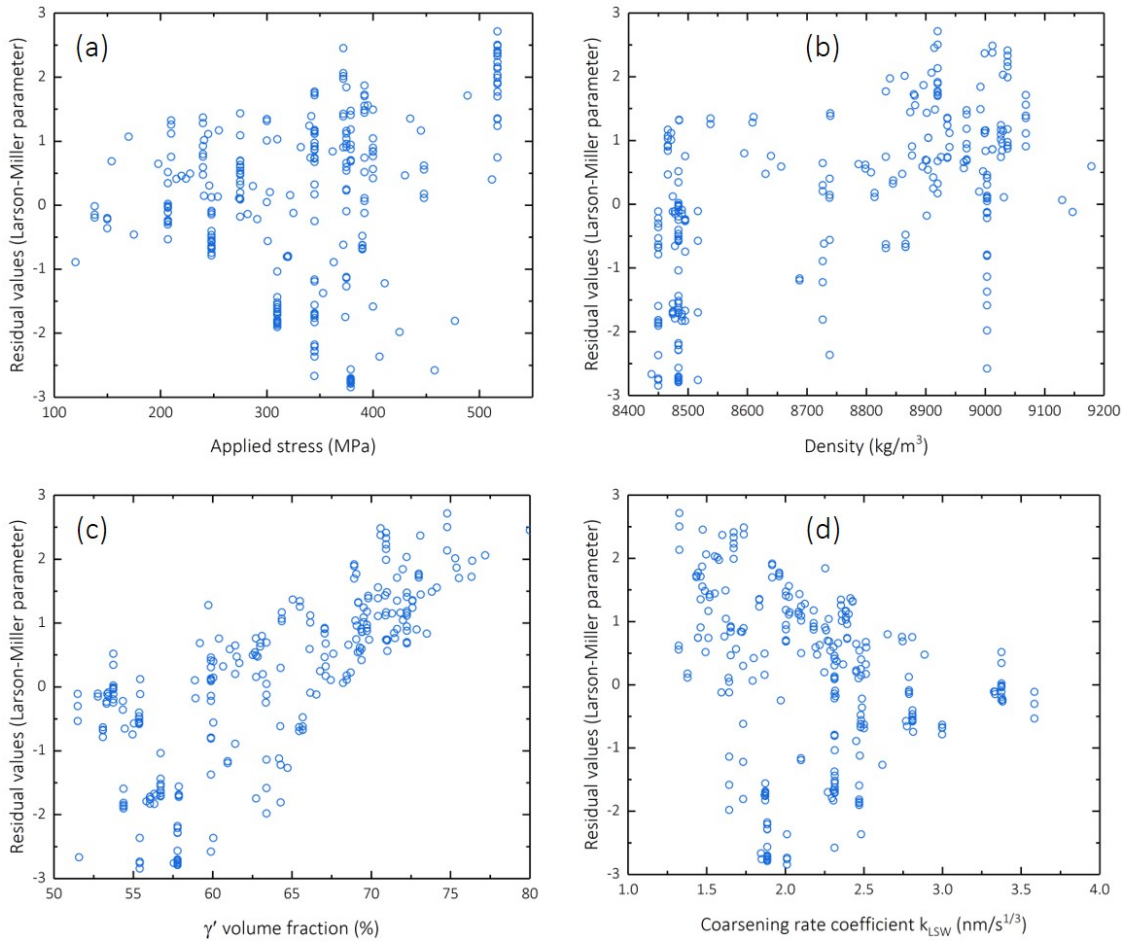


Figure 5.16: Quantitative residual values, obtained after assuming a linear relation between model predictions and experimental results, plotted against (a) applied stress, (b) density, (c) γ' volume fraction, and (d) coarsening rate coefficient.

The present model appears to overestimate the performance of alloys tested at the higher stress/lower temperature limit of the tertiary creep regime, as shown in Figure 5.15(a&b) and Figure 5.16(a). Test results at applied stresses above 500 MPa have associated residual values of around +2 to +3 units of the Larson-Miller parameter, indicating that model predictions for the time to 1% creep strain are too high. At these stress levels, shearing of γ' precipitates becomes feasible [237]. Although this mechanism may not be dominant, it represents an additional source of damage which remains unaccounted for and which explains this overestimation.

Likewise, overpredicted values for γ' volume fraction and/or underpredicted values for the coarsening rate parameter lead to an overestimation of creep life in Figure 5.15(d&e) and Figure 5.16(c&d). In both cases, residual values are clearly scaling with these parameters. This highlights the importance of extending and improving CALPHAD thermodynamic databases and coarsening models in order to obtain accurate estimates of microstructural evolution at high temperatures for a wide range of alloy compositions.

As further guidance for alloy design studies, the impact of density and of microstructural stability is considered in Figure 5.15(c&f). Density is calculated using a corrected rule-of-mixtures approach, which also accounts for bonding characteristics in superalloys [52, 103]. For increased performance in service, new alloys must possess a higher specific creep strength. This means that the beneficial effects of adding slow-diffusing, but heavy refractory elements like rhenium or tungsten must offset the detrimental effects of higher density and, consequently, of higher stresses arising from centrifugal forces [450]. The average metal-d level, denoted as $\overline{\text{Md}}$, provides a basic estimate for the probability of deleterious TCP phase formation. It is calculated with a rule-of-mixtures using the average energy levels of d-orbitals expected for each chemical element from elementary band theory [68, 70]. Although it has been established that using a critical cut-off value for $\overline{\text{Md}}$ as a design criterion is too simplistic [106], this parameter remains a useful first-order estimate of long-term microstructural stability. In an ABD study, compositions combining high specific creep strength and low $\overline{\text{Md}}$ values would be investigated

in more detail. Presuming other design requirements — e.g. oxidation resistance, hot corrosion resistance, castability, and cost — are met, these alloys would become candidates for small-scale trial castings and rapid property assessment campaigns.

5.6 Summary and Conclusions

1. A critical assessment of models for the tertiary creep deformation behaviour of single-crystal superalloys is presented.
2. With the assumptions that the applied stress is too small to enable γ' particle shearing and the temperature is too low to induce directional coarsening and thus the formation of rafted γ' structures, the two main damage mechanisms occurring in the tertiary regime are the coarsening of strengthening γ' precipitates and the accumulation of mobile dislocations in γ matrix channels; creep cavitation does not play a significant role.
3. For accurate modelling, it is shown that it is necessary to account for the influence of mean alloy chemistry on microstructural parameters such as γ' fraction and matrix composition. These serve as inputs for sub-models predicting precipitate coarsening and the accumulation of creep strain.
4. Several methods for calculating coarsening rates in superalloys have been compared. It is shown that using available CALPHAD-based methods, it is possible to accurately estimate both the interfacial energy between the γ and γ' phases and the coarsening rate parameter.
5. Effective drag coefficients for dislocation climb and dislocation glide are demonstrated to be important for the prediction of the creep strength imparted by slow-diffusing elements. The ratio of these coefficients is in good agreement with values from literature and can be used to rationalise improvements in creep strength of single-crystal superalloys spanning different generations. These advances are ultimately related to a retardation of diffusional flow at γ' particle interfaces.

6. Good agreement of the present model with the performance of the benchmark alloy CMSX-4 is demonstrated, without the use of excessive fitting.
7. An improved modelling strategy is proposed. One important advantage is the ability to provide reasonable estimates of creep strain life for given applied stress and temperature conditions. A critique using creep data from literature demonstrates that this new approach provides a more accurate merit index for creep resistance, when compared to existing alternatives. It is deemed suitable for alloy optimisation efforts.

Like the progress of the creep phenomenon, our rate of understanding has been slow. It will accelerate though if research is design driven.

— R.K. Penny & D.L. Marriott, “Design for Creep”

6

Conclusions and Future Work

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In the introductory chapter, the key goal of accelerating the design–make–test–analyse development cycle for new NBSA was discussed, with a focus on the design and testing of new single-crystal superalloys with improved creep properties. Within this scope, the main achievements and contributions of the present work are reviewed. Furthermore, future research activities are identified to complement and refine this investigation.

6.1 Rapid Assessment of Mechanical Behaviour using Small-Scale Testing

To address the lack of suitable rapid testing methods for NBSA, a novel ETMT system is introduced in Chapter 3 as a viable tool for assessing high-temperature

mechanical properties. Miniaturised tests are carried out on a prototype IGT single-crystal superalloy and are compared to full-scale methods on specimens of more standard geometry. The ETMT approach is advantageous owing to its increased speed, degree of simplicity, and use of smaller quantities of material. Furthermore, tensile properties are found to be comparable to those obtained from conventional tests over a wide range of temperatures and strain rates.

Two novel rapid testing methodologies are proposed. First, it is shown that changes in athermal plastic deformation with temperature can be determined with a single test by ramping up the temperature during deformation at a constant strain rate. This allows for an estimate of the variation of flow stress with temperature. Second, stress relaxation tests enable a rapid assessment of time-dependent deformation. Changes in operating mechanisms are revealed through deformation mechanism maps, generated using data measured at different temperatures.

These approaches are currently being applied in studies of additively manufactured superalloy components *via* selective laser melting (SLM). The advantage of only requiring small material volumes is critical in this context. Insights gained from ETMT testing have enabled a rapid optimisation of chemical compositions and manufacturing parameters and have led to a significant improvement in properties over several SLM production iterations. This case study represents a good example of the industrial benefits of an accelerated design–make–test–analyse cycle, which reduces the time for qualification and insertion of new grades of superalloys.

Future research should focus on improving the current ETMT setup and on expanding its capabilities:

1. A key advancement would be to achieve full, stable control using the DIC strain channel. As shown in Figure 3.4, this channel has been set up as an input for the Instron ETMT as part of the present work. Extensive preliminary tests were also carried out in an attempt to establish a strain control procedure. Unfortunately, it was found that even when all hardware and software options are maximised to yield a video frame rate of around 500 fps, this value remains too low for stable control of the much more dynamic ETMT, which normally

uses sampling rates on the order of 10 kHz. Continued research partnerships with both Instron and Imetrum Ltd will be vital for achieving this goal.

2. The modelling of the parabolic temperature distribution introduced in the present investigation can be further refined and expanded to a three-dimensional problem which also accounts for radiative heat loss. The new model can be calibrated for specific compositions and specimen geometries using data recorded by several thermocouples attached along the gauge length.
3. Once the temperature distribution has been understood and can be accurately estimated, further rapid testing methodologies with the ETMT become possible. A single creep test will effectively yield data over a wide range of temperatures. The specimen can then be sectioned and metallographically prepared following the procedures described in Chapter 4 to assess the influence of temperature variations on active deformation mechanisms. Similarly, extensive heat treatment studies can be carried out on a single sample and the influence of temperature on local microstructure can be determined.
4. The 2D strain maps shown in Chapter 3 provide important insights into the distribution and evolution of plasticity during ETMT tests. These results can be compared to FEM predictions from software packages such as ABAQUS to better understand deformation mechanisms in single-crystal specimens.

6.2 Experimental Assessment of Creep Damage Evolution in Single-Crystal Superalloys

Building on the novel rapid testing methodologies of Chapter 3, a key next step towards the development of improved superalloy compositions is to gain an in-depth understanding of high-temperature damage mechanisms at the microscale and to relate these to the macroscopic mechanical response of miniaturised specimens. The work of Chapter 4 addresses this topic, with a focus on the creep regime at intermediate levels of applied stress and temperature, which is most representative for the operating conditions of IGT.

Interrupted creep tests are carried out using the novel ETMT system combined with DIC strain measurements. Analogue to Chapter 3, this setup offers significant benefits over conventional testing methods. The evolution of dislocation density with creep strain is analysed for three single-crystal superalloys with distinct γ' volume fractions and levels of solid solution strengthening using a combination of HR-EBSD and cECCI. Experimental analyses are rationalised by DDD simulations. Dislocation densities are quantified between 0.02% and 1% plastic strain, with standard deviations on the order of $3 \times 10^{13} \text{ m}^{-2}$ for HR-EBSD and of $1 \times 10^{13} \text{ m}^{-2}$ for cECCI. Differences between HR-EBSD and cECCI are in good agreement with previous reports of GNDs representing between 10% and 50% of the total dislocation density. Both methods yield the same trend of a strong initial rise in mobile dislocation density, followed by an exponential decay over time. A simple evolution law of the form $\rho_m = (\rho_0 + M\varepsilon) \exp(-\phi\varepsilon)$ can accurately describe the experimental data and DDD simulation results. This law holds true for all investigated alloys and appears to be independent of chemistry.

Critically, LAGB are not the main sources of mobile dislocations. Instead, individual dislocation sources become active emitters once a critical local shear stress is reached. Dislocations can at first move with little constraints through the matrix channels, resulting in the high initial multiplication rate. DDD modelling reveals that after several sources have become operative, dislocation ‘avalanches’ result in the formation of equilibrium networks at macroscopic creep strains on the order of 0.1%. Further dislocation movement through matrix channels is then impeded and the dislocation multiplication rate decreases exponentially. The fashion in which this occurs is determined primarily by the γ' volume fraction. Quantitative descriptions of the change in dislocation density with creep strain represent a critical input for creep damage modelling and can inform improved alloys design models.

The present work can be expanded and complemented in several ways, leading to a more comprehensive understanding of creep deformation in superalloys:

1. A straightforward next step is to expand the initial test matrix to include a wider range of stress, temperature, and total plastic strain conditions. This

applies not only to the tertiary creep regime considered here, but also to the primary creep and rafting regimes. As the required testing, characterisation, and modelling methods have been set up and their utility has been proven, this work can be carried out with relative ease.

2. Testing campaigns can also be expanded to include additional single-crystal compositions, thus allowing a closer examination of distinct strengthening mechanisms. Furthermore, different crystal orientations besides the technically relevant $\langle 001 \rangle$ direction can be considered.
3. A critical, but challenging task is to elucidate the exact mechanisms by which individual dislocations become active sources. This was attempted as part of the present work, however, preliminary results were inconclusive, which can be explained by several factors. First, as shown in Chapter 4, a few individual sources suffice to generate large-scale dislocation ‘avalanches’. As such, it will be challenging to accurately locate one such source in a cECCI micrograph. Second, even if the source is captured on an image, it will be non-trivial to identify it, since characteristic features for Frank-Read or double cross-slip mechanisms may not be clearly visible depending on the chosen sample orientation. Third, dislocation lines propagating through the matrix channels will gradually obscure their sources. A proposed solution is to focus on just one material and one deformation condition at a low plastic strain level and to characterise this specimen extensively with cECCI. A large image data set thus collected will be more likely to contain features of interest.

6.3 Modelling of Tertiary Creep Damage in Single-Crystal Superalloys

Insights gained from the extensive HR-EBSD, cECCI, and DDD analyses of Chapter 4 are of paramount importance for the novel numerical model for creep damage accumulation in single-crystal NBSA introduced in Chapter 5. Analogue to Chapter 4, this work focuses on the tertiary creep regime. Under the assumption that

the applied stress is too small to enable γ' particle shearing and the temperature is too low to induce directional coarsening and thus the formation of rafted γ' structures, the two main damage mechanisms occurring in the tertiary regime are the coarsening of strengthening γ' precipitates and the accumulation of mobile dislocations in γ matrix channels; creep cavitation does not play a significant role.

For accurate modelling, it is shown that it is necessary to account for the influence of mean alloy chemistry on microstructural parameters such as γ' volume fraction and matrix composition. These serve as inputs for sub-models predicting precipitate coarsening and the accumulation of creep strain. Several methods for calculating coarsening rates in superalloys are compared. It is shown that using available CALPHAD-based methods, it is possible to accurately estimate both the interfacial energy between the γ and γ' phases and the coarsening rate parameter. Effective drag coefficients for dislocation climb and dislocation glide are demonstrated to be important for prediction of the creep strength imparted by slow-diffusing elements. The ratio of these coefficients is in good agreement with values from literature and can be used to rationalise improvements in creep strength of single-crystal superalloys spanning different generations. These advances are ultimately related to a retardation of diffusional flow at γ' particle interfaces. Good agreement of the present model with the performance of the benchmark alloy CMSX-4 is demonstrated, without the use of excessive fitting. An improved modelling strategy is proposed. One important advantage is the ability to provide reasonable estimates of creep strain life for given applied stress and temperature conditions. A critique using creep data from literature demonstrates that this new approach provides a more accurate merit index for creep resistance when compared to existing alternatives. It is deemed suitable for alloy optimisation efforts.

For any given model, a suitable balance must be struck to provide a clear, simple, and understandable description of the considered system, while still accounting for all critical factors. With this in mind, several improvements and amendments to the present work can be suggested:

1. Additional thermodynamic simulation packages can be incorporated within the process flow diagram of Figure 5.2. The Thermo-Calc precipitation module TC-PRISMA allows a treatment of concurrent particle nucleation, growth, dissolution, and coarsening mechanisms under given temperature conditions and can be used to analyse the effects of chemistry and heat treatments on the size evolution of γ' precipitates. The diffusion module DICTRA enables simulations of diffusion-controlled reactions and can be applied to obtain more accurate estimates of effective diffusivity parameters. It should, however, be noted that such additional packages will require more computational power.
2. Further research into modelling of compositional effects on lattice misfit is required. As shown in Figure 5.4, current methods cannot make accurate predictions and would lead to incorrect conclusions regarding optimal compositions. The CALPHAD-based approach of calculating lattice parameters using the molar volumes of phases shows most promise in the long run. However, this will require significant further development of CALPHAD parameter databases and modelling frameworks.
3. The stress redistribution around particles during tertiary creep has not been fully understood. Further research on the evolution of the internal stress and its dependence on testing conditions and on microstructure is critical in this context. Given that suitable experiments are difficult to implement, it can be ascertained that modelling approaches will be more likely to offer new insights.
4. Similarly, additional dislocation dynamics modelling is required to gain an in-depth understanding of the operating mechanisms during creep. This applies to all deformation regimes shown in Figure 5.1. Recent work combining phase field and continuum dislocation dynamics models showed good promise within this scope. The mechanisms by which individual dislocation sources become active emitters can then be investigated and compared to new experimental studies, as discussed in Section 6.2.

5. Finally, a more comprehensive model can be envisioned, which also accounts for the primary creep and rafting deformation regimes. As a first step, a novel ABD subroutine is currently being developed to encompass the APB shearing, stacking fault shearing, twin shearing, and dislocation climb bypass deformation mechanisms. The aim is to enable the design of superalloys with balanced high-temperature mechanical properties for operating conditions ranging from 600 to 900 °C and from 250 to 900 MPa.

6.4 Effects of Chemistry Variations on Elemental Phase Partitioning and Physical Properties

Considering the critical role of reliable parameter databases as inputs for ABD models, such as the one discussed in Chapter 5, the work of Appendix A attempts to improve the accuracy of CALPHAD predictions, with a focus on the design space for IGT alloys introduced in Figure 1.3. A set of six trial IGT alloys combining high chromium and aluminium contents for optimised hot corrosion and high-temperature oxidation resistance is investigated. Extensive experimental analyses of alloy microstructure, phase transition temperatures, and phase microchemistry reveal a complex influence of composition on alloy properties and an intricate interaction between different elemental additions. Throughout the study, comparisons are made to CALPHAD predictions made by the Thermo-Calc software package and two thermodynamic databases for NBSA, TCNi8 and TTNi8.

Thermo-Calc predictions for the equilibrium γ' volume fraction are in good agreement with results from image analysis of SEM micrographs. Predictions for γ' solvus and solidus temperatures are in reasonable agreement with DSC experimental results. For alloys without hafnium, the span of the HTW can be estimated to within 20 °C by combining the γ' solvus from TTNi8 and the solidus from TCNi8. As revealed through APT analyses, slight changes in chemistry can have profound effects on the alloy microchemistry. Thermo-Calc predictions for phase compositions using both TCNi8 and TTNi8 consistently underestimate $K_{\text{Ni}}^{\gamma'/\gamma}$, $K_{\text{Mo}}^{\gamma'/\gamma}$, $K_{\text{W}}^{\gamma'/\gamma}$, and $K_{\text{Al}}^{\gamma'/\gamma}$, while overestimating $K_{\text{Cr}}^{\gamma'/\gamma}$. It is imperative to adjust and update thermodynamic

database parameters for this region of the alloy design space if CALPHAD methods are to provide reliable and accurate inputs for ABD tools.

Proxigram analyses across γ/γ' interfaces reveal a diffuse, non-uniform transition between plateau concentrations over several nm. The average width of interfacial profiles correlates well with the atomic size difference between the respective element and nickel, as described by the empirical Vegard coefficients. γ/γ' lattice misfit values estimated using phase compositions determined by APT or predicted with TCNi8 are in good agreement with the observed changes in precipitate morphology, which becomes increasingly rounded as the absolute misfit value decreases. Misfit estimates based on CALPHAD predictions of the molar volumes of γ and γ' phases are inaccurate. Finally, several guidelines and recommendations for IGT alloy design within this novel compositional space are drawn.

To capitalise on these advances into the new proposed design space for IGT alloys, future work should focus on CALPHAD database improvements and additional experimental and modelling validation steps:

1. Existing databases for NBSA such as TCNi8 and TTNi8 should be updated to take the results of the present experimental campaign into consideration. However, this can only be achieved through research cooperations with the database providers, in this case Thermo-Calc and ThermoTech, meaning that an open dialogue is key.
2. The origins of some unclear APT results, for example the wide interfacial profile of chromium and the unexpectedly high γ' volume fractions obtained from lever rule plots, must be clarified. As APT can only probe limited material volumes, it is worth repeating the experiments of the present work and checking for differences due to chemical segregation or statistical fluctuations.
3. Preliminary results show that Monte Carlo methods can be successfully applied to NBSA to predict the nucleation and growth of γ' precipitates and the sublattice site preferences of different elements. However, further work is required to optimise phase composition estimations. In particular,

the cluster analysis algorithm currently used to assign atoms to either γ or γ' can be improved by expanding the analysis to more distant neighbouring atoms. Additional points worth considering are the choice of Lennard-Jones potential parameters, the implementation of random number generators, and the statistical description of atomic exchanges between neighbouring atoms.

4. The design guidelines drawn in the present work are currently being used to optimise and tailor IGT alloy chemistries for different operating environments. The next step will be to start a new design iteration by casting a set of new alloys and by subsequently testing them to validate the predictions of this study. In particular, it will be important to complement measurements of thermophysical properties discussed here with mechanical tests for tensile, creep, and TMF strength and with oxidation and hot corrosion tests.
5. On a slightly longer timescale, a key goal will be to test the new compositions in an actual service environment. So-called ‘rainbow tests’, in which several alloy substrate and coating combinations are tested simultaneously, will yield crucial information regarding the suitability of these alloys for industrial applications.

Appendices

The dream of the microscopy and materials science communities is to see, identify, accurately locate, and determine the fundamental physical properties of every atom in a specimen. With this knowledge together with modern computer models and simulations, a full understanding of the properties of a material can be determined. This fundamental knowledge leads to the design and development of more advanced materials for solving the needs of society.

— M.K. Miller, T.F. Kelly, K. Rajan & S.P. Ringer,
“The Future of Atom Probe Tomography”



Effects of Chemistry Variations on Elemental Phase Partitioning and Physical Properties

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A.1 Introduction

‘Classical’ IGT alloys like IN-792 [181] and Mar-M247 [185] were developed more than 45 years ago and can no longer fully satisfy industry requirements. A clear necessity exists to develop new IGT alloys with improved resistance to creep, TMF, hot corrosion, and oxidation damage and which can operate under increased turbine inlet temperatures, as discussed in Chapter 1. The proposed design space above 12 wt.% Cr* and 4 wt.% Al, shown previously in Figure 1.3, is reproduced for clarity in Figure A.1. A recent foray into this space was made with the development of the single-crystal alloy STAL15SX [32, 495, 550] and of the conventionally cast derivative STAL15CC [286, 287]. These alloys contain 15 wt.% Cr for high hot corrosion resistance and also provide excellent oxidation resistance due to their ability to form a continuous Al_2O_3 surface layer at high temperatures. This enables both high turbine inlet temperatures and high fuel flexibility, while minimising the risk of component failure should protective thermal barrier coatings crack. STAL15SX possesses sufficient creep strength for use in IGT first-stage blades, while STAL15CC is aimed at hot stator components.

There is an obvious possibility to design further derivatives at lower Cr and higher Al contents. This would increase creep and oxidation resistance, while retaining Cr levels above the traditional threshold of 12 wt.% for sufficient hot corrosion resistance [69, 78, 489]. The ABD methodology presented in Chapter 1 offers a suitable means of achieving this goal and of balancing various properties. However, an important caveat is that several key input parameters for ABD are derived from thermodynamic CALPHAD calculations, which in turn depend on

*In this section only, chemical elements are often abbreviated as their chemical symbols for better legibility.

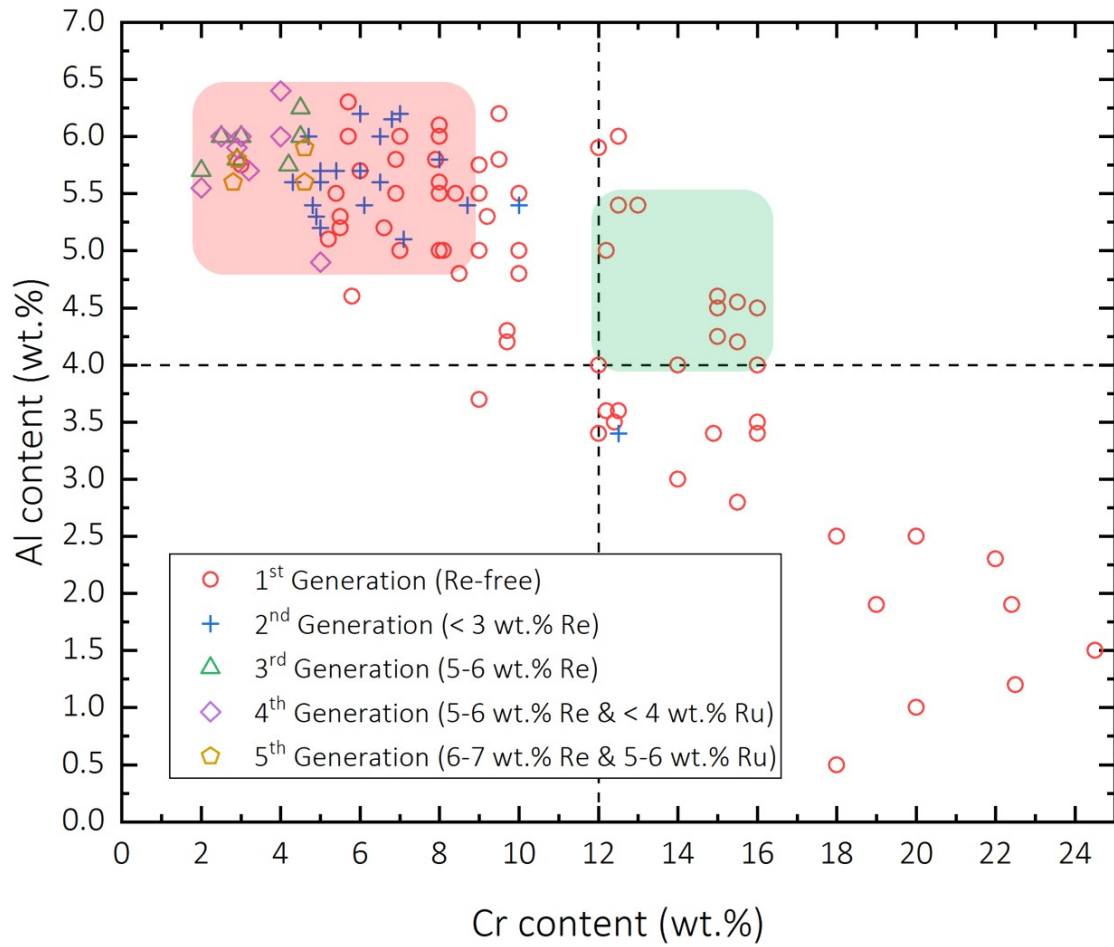


Figure A.1: Comparison of the proposed design space for new IGT superalloys (green rounded rectangle) and the general compositional space occupied by Re-containing aerospace alloys (red rounded rectangle), reproduced from Figure 1.3.

commercial parameter databases. The reliability and validity of modelling results are dictated by the accuracy of these databases and any significant errors will give rise to false conclusions regarding optimal alloy compositions. This issue is especially acute for new regions of the alloy design space, such as the one considered here, since experimental data will be scarce or missing altogether. As such, it is imperative to improve and expand the performance of CALPHAD tools and to gain a better understanding of the influence of chemistry on thermochemical and physical alloy properties and on microstructure.

The present chapter aims to remedy this situation by investigating a set of trial IGT alloys with carefully designed chemistries, which isolate the influence of individual additions. Results from an extensive experimental characterisation

campaign are compared to CALPHAD predictions using the Thermo-Calc software package and with Monte Carlo Simulations (MCS) for the spatial and temporal evolution of atomic arrangements. Insights gained from this study are used to derive guidelines for optimised IGT alloy design and to improve the reliability of CALPHAD techniques.

A.2 Experimental Method

A.2.1 Material

A set of six trial alloys, denoted in the following as SX1 to SX6, were pre-alloyed either from pure elements (Al, Cr, Co, Fe, Ni, Si, Ti) or from binary Ni–X alloys for refractory metals (Ni–Hf, Ni–Mo, Ni–Ta, Ni–W). Batches of 120 g were weighed, arc-melted under argon using an Edmund Bühler AM 500 Arc Melter, and poured into water-cooled copper moulds. The resulting ‘cigars’ were turned around and re-melted up to 3 more times to ensure complete smelting and to reduce microsegregation. Only minor differences to the total weight of raw input materials on the order of 10 mg were observed. The as-cast microstructures exhibit a large grain size of about 2 cm equivalent diameter. As such, although the castings are not perfect single-crystals, they are referred to in the following as ‘SX’, since all investigated specimens were extracted from individual grains.

Nominal chemical compositions are presented in Table A.1. The base composition of the investigated alloy series, denoted as SX1, was derived from STAL15SX to the design point of 12.5 wt.% Cr and 5.5 wt.% Al using an ABD-type MATLAB-based programme. Four compositions were designed to assess the influence of adding 1 wt.% Hf (SX2), 5 wt.% Fe (SX3), and 0.5 wt.% Si (SX6) and of increasing the Co content from 5 to 10 wt.% (SX5). Finally, a composition with lower Al and Ta levels and containing 2.4 wt.% Ti (SX4) was also included as a ‘combination’ between the base alloy and IN-792.

Alloy	Method	Chemical composition (wt.%)													
		Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe	±σ	±σ	
SX1 (Base)	Nominal	63.8	12.5	5	1.5	3.5	5.5	0	8	0	0	0			
	ICP-OES	64.5	12.3	4.93	1.46	3.4	5.57	0	7.7	0	0.03	0.02			
	EPMA	65.4	0.28	13.04	0.19	5.2	0.06	0.1	5.44	0.21	—	—			
SX2 (+Hf)	Nominal	63	12.5	5	1.5	3.5	5.5	0	8	1	0	0			
	ICP-OES	64.1	11.6	4.82	1.64	2.78	5.35	0	8.59	1.03	0.04	0.02			
	EPMA	63.74	0.57	12.67	0.58	5.15	0.09	0.13	0.37	0.97	0.14	—			
SX3 (+Fe)	Nominal	59	12.5	5	1.5	3.5	5.5	0	8	0	0	5			
	ICP-OES	58.4	12.3	4.99	1.46	3.39	5.38	0	7.71	0	0.03	6.31			
	EPMA	58.25	0.28	13.2	0.34	5.1	0.09	0.12	8.08	0.14	—	5.04	0.07		
SX4 (+Ti)	Nominal	64.1	12.5	5	1.5	3.5	5	2.4	6	0	0	0			
	ICP-OES	64.4	12.5	4.97	1.47	3.46	4.93	2.38	5.76	0	0.03	0.03			
	EPMA	63.64	0.34	13.08	0.29	5.15	0.06	0.1	4.72	0.09	2.69	0.16	0.31	0.15	—
SX5 (++Co)	Nominal	58.8	12.5	10	1.5	3.5	5.5	0	8	0	0	0			
	ICP-OES	58.8	12.5	10.4	1.48	3.45	5.58	0	7.67	0	0.03	0.03			
	EPMA	58.64	0.31	13.02	0.12	10.28	0.05	0.05	8.21	0.12	—	—			
SX6 (+Si)	Nominal	63.9	12.5	5	1.5	3.5	5	0	8	0.1	0.5	0			
	ICP-OES	66.24	11.71	4.46	1.51	3.48	4.9	—	7.1	0.07	0.5	0.03			
	EPMA	65.17	0.36	12.25	0.19	5.11	0.05	0.09	8.42	0.23	0.05	0.35	0.03		

Table A.1: Chemical compositions of the alloys in fully heat treated condition. Nominal values are compared to measurements from ICP-OES and EPMA analyses.

A.2.2 Differential Scanning Calorimetry

DSC testing was carried out using a Netzsch DSC 404 F1 Pegasus. While DSC provides a simple and well-established means of studying precipitation and phase change kinetics in superalloys, it is imperative to account for several sources of uncertainty [540, 700]; these are addressed in the following.

The temperature and heat flow signals of the Netzsch DSC were first calibrated following the ASTM E967 and E968 standards [701, 702] with several high-purity metals at heating/cooling rates of 2.5, 5, 10, 20, and 40 K/min. It should be noted that there is a gap in the range of 1100–1400 °C, as the calibrant with the highest melting point is gold at 1064 °C. All measurements are carried out under an inert, high-purity argon atmosphere at a purge flow rate of 40 mL/min, in accordance with ASTM standard E1269 [703]. Argon is chosen here over helium, as it provides the highest signal gain and therefore also highest precision. The furnace chamber is evacuated and backfilled with argon three times prior to testing in order to remove any oxidising impurities. To further ensure the highest possible sensitivity during testing, PtRh crucibles with PtRh lids and thin-walled Al₂O₃ liners are used in combination with a high-accuracy sample carrier system with type S thermocouples. Thin sapphire spacers are added on the sensor plates to avoid the crucibles sticking at high temperatures [700].

Selected ramp rates have a significant impact on measured transformation temperatures [704]. Higher rates give rise to a stronger DSC signal and better resolution of phase changes, but deviate more from thermodynamic equilibrium. Conversely, lower rates agree more closely with metallographic studies, but pick up inordinate amounts of noise. Furthermore, they result in much longer test durations and exacerbate errors associated with sample oxidation and the loss of volatile elements [700, 705, 706]. Rate effects can be accounted for by extrapolating to an idealised zero rate [704], as shown in Figure A.2 for pure calibration materials. The quantitative values in Table A.2 reveal that results from ramp rates of 10 and 20 K/min are in good agreement with ideal melting temperatures, whereas extrapolated values consistently underestimate them by around 2 °C. With the

	Ramp rate (K/min)	Melting temperature (°C)					
		In	Sn	Bi	Zn	Al	Au
Ideal	0	156.6	231.9	271.4	419.6	660.6	1064.4
Extrapolated	0	155.1	229.9	269	417	658.5	1061.1
Measured	2.5	155	230.5	269.5	417.2	658.2	1061.4
	5	155.4	231.1	269.9	417.3	658.4	1061.4
	10	155.9	232.1	270.5	417.4	658.5	1062.3
	20	158.4	235.3	272	418.1	660.1	1062.9
	40	158.6	239.8	275.6	419	658.8	1064.9

Table A.2: Measured, extrapolated, and ideal melting temperatures for pure calibration materials from DSC analyses at different ramp rates.

above in mind and following previous DSC studies on NBSA [700, 705, 706], heating/cooling rates of 10 K/min were chosen.

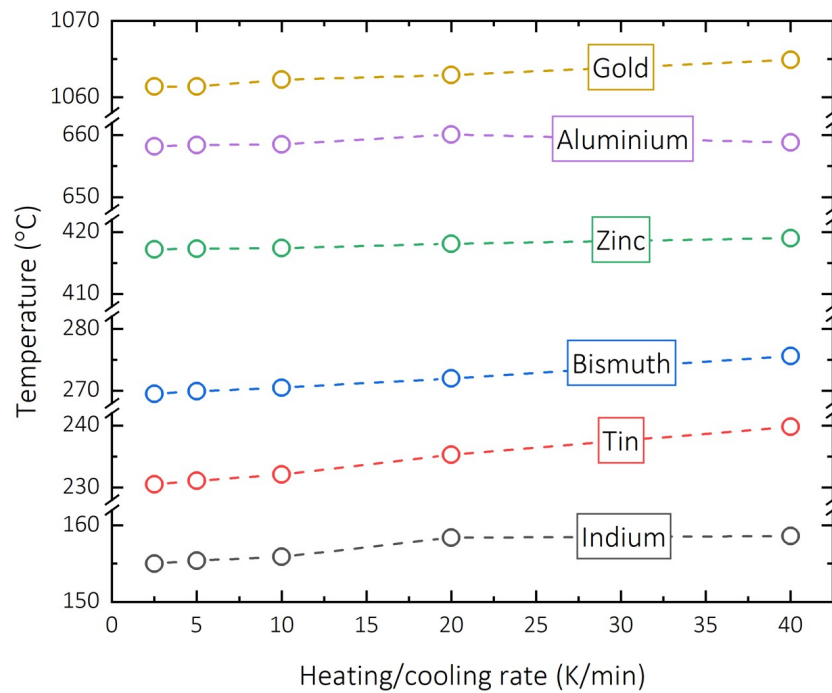


Figure A.2: Measured melting temperatures for pure calibration materials at different ramp rates.

For DSC testing of the IGT alloys, disc specimens of 3 mm diameter and 1 mm thickness were manufactured by wire-guided EDM. The selected dimensions are a trade-off between a larger sample, which yields sufficient measurable signal and thus minimises temperature errors, and a smaller one, which has lower internal temperature gradients and thus ensures that phase transitions occur simultaneously

throughout the entire volume [700, 705]. Both circular surfaces were polished down to 4000 grit silicon carbide grinding paper to achieve a good thermal contact with the sensor. Each specimen was ultrasonically cleaned in ethanol and weighed before the test. Given only slight differences in geometry, all specimens weighed about 63 mg.

For each test, two heating/cooling cycles are performed between 700 and 1450 °C to assess the influence of prior melting/solidification and of reduced segregation on the second cycle. To equalise the temperature in the system, constant temperature segments of 15 min duration are added between ramp steps. Following the ASTM E1269 method [540, 703], three measurements are carried out as part of each test: (1) a baseline measurement with an empty sample pan, (2) a calibration measurement with a synthetic sapphire disc of known mass and heat capacity, and (3) a sample measurement with the actual superalloy disc. The reference pan remains empty during all three runs. Finally, changes in alloy heat capacity, C_p , with temperature, T , are calculated using the Netzsch Proteus analysis programme.

A.2.3 Heat Treatment and Chemical Analysis

Preliminary DSC studies on as-received material gave an indication of the γ' solvus and solidus temperatures for each alloy. Using this information, solutioning heat treatments were carried out to reduce the microsegregation between dendrite core and interdendritic regions, while avoiding incipient melting. Samples were placed in a pre-heated furnace at 1170 °C. The temperature was then slowly ramped up at a constant rate of 6 °C/h up to 20 °C below the expected solidus, following the method proposed by Hegde et al. [707, 708]. After reaching the peak temperature, specimens were cooled down at 600 °C/h to 850 °C and were then removed from the furnace and air-cooled. Such solutioning steps of up to 17 hours duration are significantly longer than commercial standards, however, they lead to a nearly complete homogenisation and dissolution of γ' eutectics. Subsequent primary and secondary ageing heat treatments were chosen at 1120 °C for 4 h and 845 °C for 24 h, both completed by air-cooling.

The chemistries of fully heat treated specimens were checked at an independent laboratory using inductively coupled plasma optical emission spectrometry (ICP-OES) for metallic elements and combustion analysis for C and S impurities. Results are shown in Table A.1 below the nominal values. Chemical compositions and the remaining degree of microsegregation were further checked on polished specimens by EPMA using a JEOL JXA 8800 Superprobe equipped with four wavelength-dispersive X-ray spectrometers (WDS) for parallel detection of elements. Line scans of 200 points were carried out at a spacing of 10 μm , a probe diameter of 10 μm , an accelerating voltage of 25 keV, a beam current of 32 nA, and a dwell time for each point of 100 ms. The diffracting crystals used for WDS were LIF for Ni, Co, W, Ta, Hf, and Fe, PETJ for Cr, Mo, and Ti, and TAP for Al and Si. X-ray counts were converted to concentration values using standard correction procedures and signals from pure element standards. Average compositions obtained from EPMA and associated standard deviations are presented in Table A.1.

A.2.4 Electron Microscopy

Metallographic preparation was carried out on a Struers Tegamin-25 system down to 1 μm diamond suspension. An optimal finish was achieved by polishing for 5 min with a 1 to 1 mixture of Struers OP-S 0.04 μm colloidal silica suspension and water on a Struers MD-Chem polishing cloth. Specimens were cleaned in an ultrasonic bath with acetone and then with ethanol.

BSE images of fully heat treated microstructures were obtained using a Zeiss Merlin FEG SEM operating at an accelerating voltage of 10 keV and a probe current of 500 pA. The working distance was set at 8.5 mm to yield optimal EDX results using an Oxford Instruments X-Max^N silicon drift detector with a size of 150 mm². EDX data was processed using the TruMap function of the Oxford Instruments AZtec 3.3 software package to eliminate artefacts, correct background and peak overlaps, and enhance compositional variations.

A.2.5 Atom Probe Tomography

Matchsticks of $0.5 \times 0.5 \times 2 \text{ mm}^3$ were manufactured by EDM from fully heat treated material. Sharp tips for APT with a radius below 100 nm were produced in a two-stage electro-polishing process [709]. The matchsticks were first coarse-polished in a solution of 10 vol.% perchloric acid in acetic acid at a voltage of 12–20 VDC and then fine-polished in a solution of 2 vol.% perchloric acid in 2-butoxyethanol at 8–12 VDC. APT data was collected using a CAMECA local electrode atom probe (LEAP) 5000 XR [710, 711] at a specimen base temperature of 50 K and an ambient gauge pressure of less than 10^{-10} Pa. Samples were run in laser-assisted mode with an ultraviolet laser wavelength of 355 nm, a pulse energy of 50 pJ, a pulse frequency of 125 kHz, and a constant ion detection rate of 0.5%. 3D reconstructions were generated using the CAMECA IVAS 3.8.2 software package. Peak overlaps of multiple elemental species were deconvolved using the standard IVAS decomposition parameters.

A.2.6 CALPHAD Predictions

Throughout the present study, experimental results are compared to predictions made using version 2018b of the Thermo-Calc software package and two associated databases for NBSA — TCNi8, provided by Thermo-Calc Software AB, and TTNi8, provided by ThermoTech Ltd. The chemical compositions measured by ICP-OES were used as inputs. Phase diagrams were generated between 600 and 1400 °C. Equilibrium phase compositions were calculated at the final ageing temperature of 845 °C. In both cases, a simplified three-phase system consisting of γ , γ' , and liquid at high temperatures was assumed and all other phases were suspended. SEM results support this assumption, as only insignificant levels of small MC carbides and no TCP phases were observed after heat treatment.

A.3 Results

A.3.1 Alloy Microstructure

Chemical compositions determined by ICP-OES and EPMA are in good overall agreement with nominal values. Trace levels of Fe were detected, but no other impurities are present. Furthermore, EPMA line scans show little variation across the samples, implying good homogenisation and low microsegregation after the heat treatment. Nonetheless, some discrepancies can be noted; the levels of Cr in SX2 and SX6, Co in SX6, W in SX2, and Ta in SX6 are somewhat lower than intended, while the levels of Ta in SX2 and Fe in SX3 are higher.

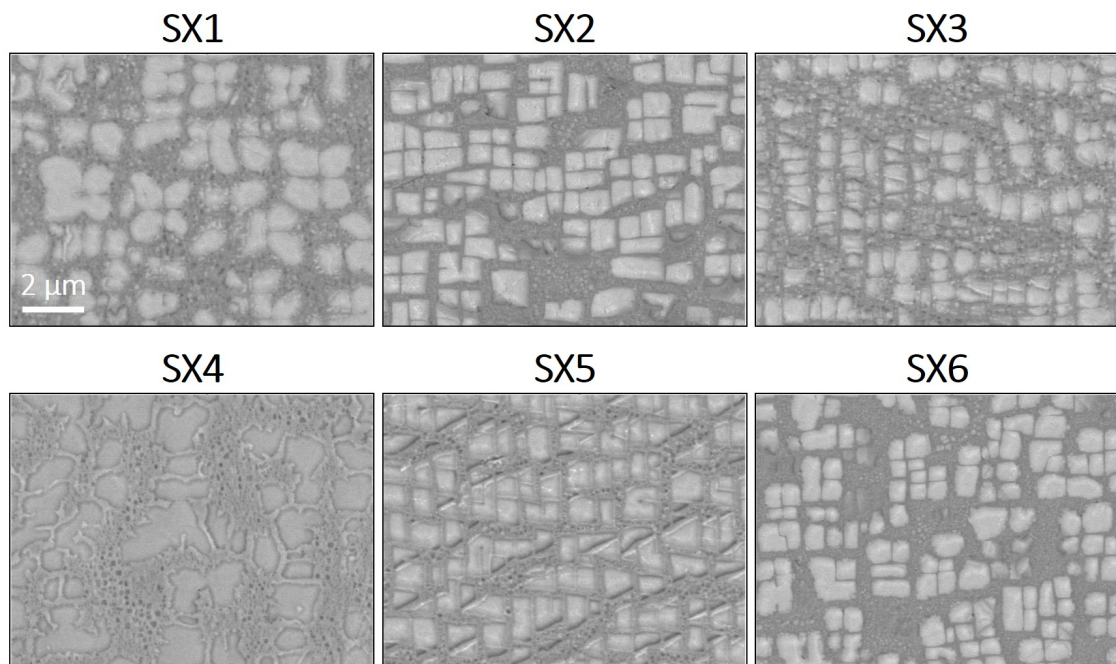


Figure A.3: SEM micrographs of the trial IGT alloys. The illustrated scale bar applies to all images.

The microstructures shown in Figure A.3 are characteristic of IGT superalloys and are composed of cuboidal, secondary γ' precipitates with side lengths on the order of 1 μm and spherical, tertiary γ' particles with diameters on the order of 10 nm, embedded in the γ matrix. Secondary particles form after the homogenisation step during cooling from around 1260 $^{\circ}\text{C}$, while tertiary ones precipitate during the subsequent ageing heat treatments at 1120 $^{\circ}\text{C}$ and 845 $^{\circ}\text{C}$. Particle size distributions

Alloy	γ' volume fraction ϕ_p (%)				
	SEM	TCNi8	TTNi8	APT	MCS
SX1	59.17	57.84	57.79	64.40	59.48
SX2	56.18	59.69	59.46	64.34	
SX3	51.45	48.33	51.01	53.44	60.01
SX4	62.68	60.79	62.59	66.75	56.46
SX5	58.47	52.40	56.45	63.45	60.92
SX6	54.43	50.65	50.95	63.99	

Table A.3: Comparison of γ' volume fractions measured in SEM micrographs, predicted by Thermo-Calc and the TCNi8 and TTNi8 databases for equilibrium conditions at 845 °C, extrapolated from APT data by rearranging the lever rule, and determined from MCS results.

were analysed using the image processing software package MIPAR [497]. Cross sectional area fractions comprising both secondary and tertiary γ' were measured for each BSE micrograph. These can be considered equal to γ' volume fractions from a stereological standpoint as long as the precipitates do not have a preferred orientation [712]. Values obtained by averaging the results from at least five micrographs are shown in Table A.3 along with Thermo-Calc predictions for γ' volume fractions under equilibrium conditions at 845 °C. Secondary precipitate morphology varies between the alloys and appears more cuboidal for SX2, SX3, SX5, and SX6 and more rounded for SX1 and SX4. The substitution of Ta for Ti in SX4 results in a marked reduction in contrast between γ and γ' , as the heavy Ta makes precipitates appear lighter in BSE micrographs.

EDX maps of the regions shown in Figure A.3 are presented in Figure A.4. As expected from previous studies, the γ' -formers Ni, Al, and Ta partition to the precipitates in SX1 while Cr, Co, Mo, and W are enriched in the γ matrix. With regard to additions made to the base composition, Hf and Ti are found to partition preferentially to γ' , whereas Fe partitions to γ . Results for Si in SX6 are inconclusive, as the EDX method erroneously detects low levels of Si within γ' due to overlaps with Ta peaks.

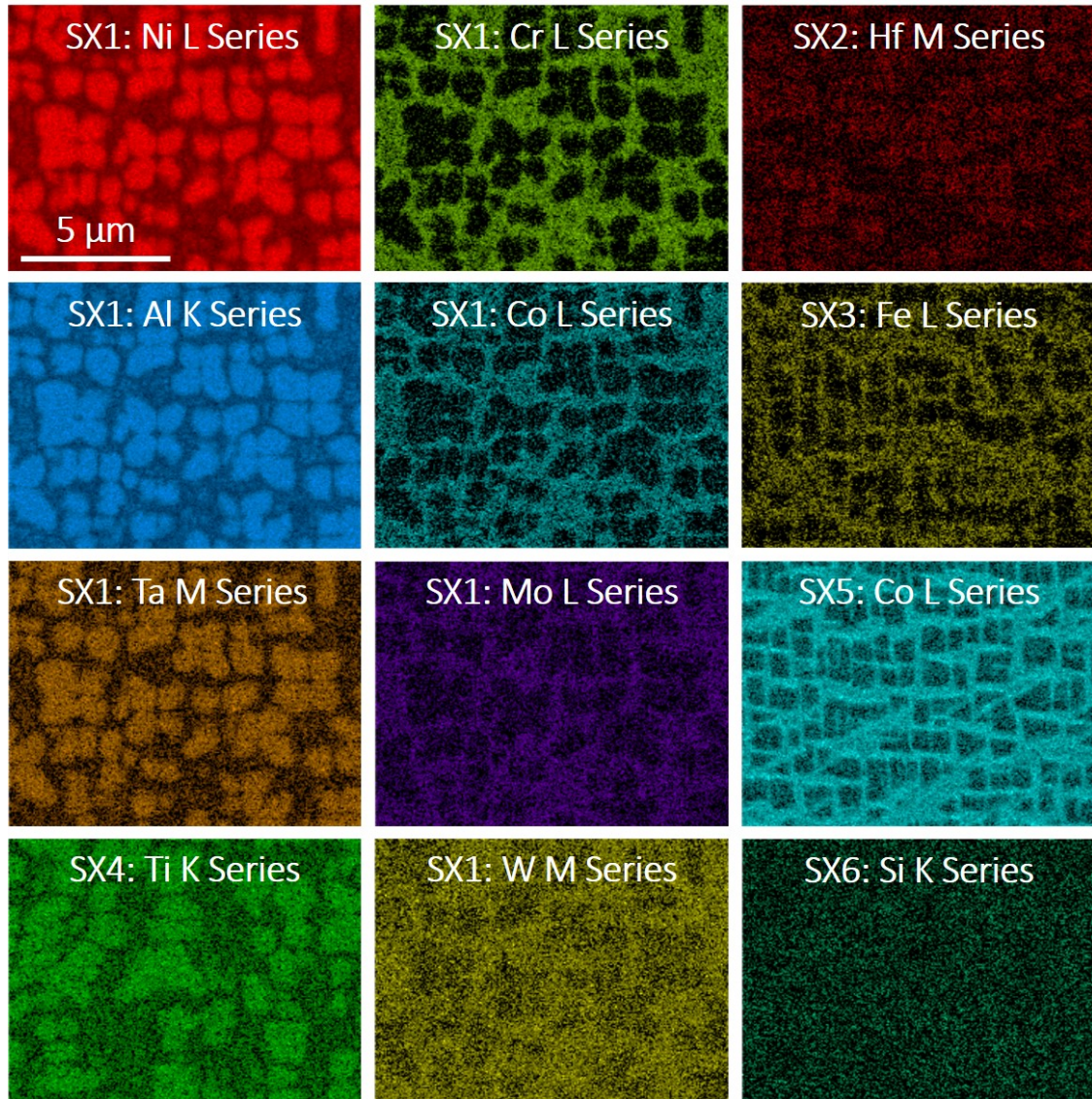


Figure A.4: EDX maps showing preferential partitioning of elements in the base alloy SX1 and of different additions in alloys SX2–SX6. The illustrated scale bar applies to all images.

A.3.2 Phase Transition Temperatures

A.3.2.1 Interpreting C_p – T Curves from DSC

Curves of heat capacity illustrated in Figure A.5 reveal several transitions with increasing temperature. Between 700 and 1100 °C, there is a gradual increase in C_p due to coarsening of the γ' phase [538, 540]. This is followed by a gradual dissolution of γ' into the γ matrix, which culminates in a peak at around 1200 °C. Once all precipitates have dissolved, a single-phase plateau regime is observed up to about

1300 °C, at which point melting of the specimen initiates and gives rise to a strong endothermic peak. The melting stage concludes at around 1350 °C and C_p values return to similar levels to the beginning of the test.

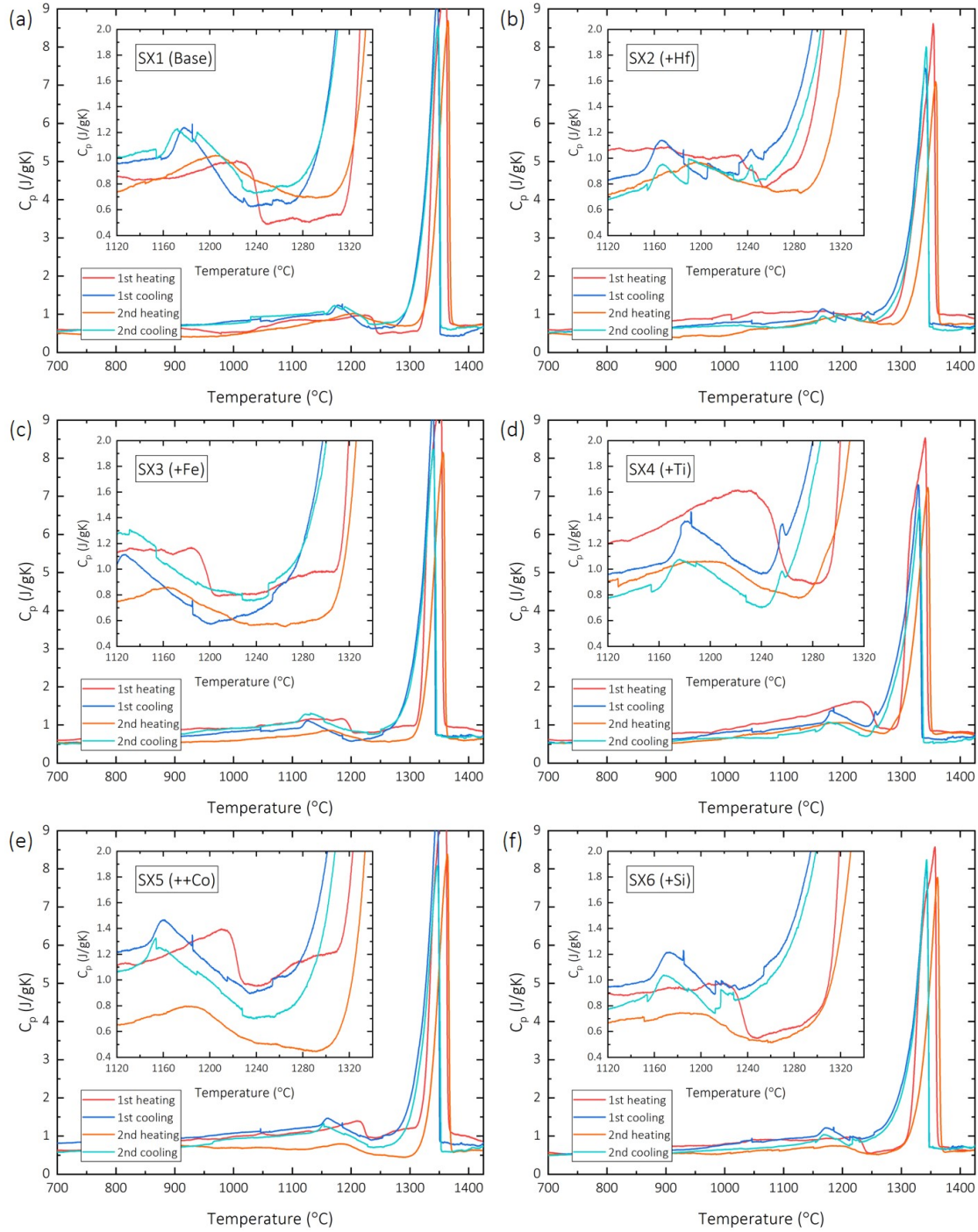


Figure A.5: Calculated changes in heat capacity, C_p , with temperature, T , during the two heating/cooling stages carried out for each DSC test. Insets show enlarged views of the heat treatment window sections.

Significant differences are observed between heating/cooling curves due to the dynamic nature of the DSC technique. During heating, transitions take place at higher temperatures due to instrument lag. Conversely, data from cooling steps is significantly affected by undercooling effects which suppress transitions and cause them to occur more abruptly at lower temperatures [700, 706]. As such, eutectic reactions which produce a weaker signal are only detected during cooling, with distinct peaks appearing at 1240 °C for SX2 and at 1255 °C for SX4. Because of the improved clarity of the DSC signal, many articles on NBSA only include data from cooling stages [372, 713–715]. However, in the context of comparing experimental data to ideal CALPHAD predictions, the undercooling effect can lead to significant discrepancies of up to 20 °C [705, 706]. This is especially true for alloys that lack GB elements like C or B, which would reduce the undercooling by precipitating carbides or borides as nucleation points [700]. Finally, differences can also be noted between the first and second heating/cooling steps. Owing to homogenisation of the material during the first cycle, the strength of endothermic/exothermic peaks during dissolution/precipitation decreases, as seen in Figure A.6.

Interpreting C_p - T curves to extract transition temperatures remains a matter of debate given the sluggish nature of solid state transitions. Sponseller [706] recommends taking the γ' solvus as the ‘recovery point’ in a C_p - T curve at which the signal returns to the baseline during heating or departs from it during cooling. The argument for this choice is that the location of the endothermic/exothermic peak is not only influenced by the actual location of the γ' solvus, but also by microsegregation between dendrite cores and interdendritic regions and by heating/cooling rate effects. However, Burton [705] argues that peak temperatures are more indicative of the solvus, as the locations of ‘recovery points’ will be affected by instrument lag and by the finite sample size. In the present work, this latter interpretation is preferred and the γ' solvus is reported as the observed endothermic peak of dissolution during the second heating. In like manner, following Quested et al. [540], the liquidus temperature is reported as the endothermic melting peak. Finally, following Chapman [700] and Quested et al. [540], the

solidus temperature is determined by extrapolating the C_p - T baseline until it meets the slope of the front of the endothermic melting peak during second heating. Temperatures were evaluated using the built-in ‘peak’ and ‘onset’ functions of the Netzsch Proteus analysis programme.

A.3.2.2 Effects of Chemistry on the Heat Treatment Window

Quantitative values are compared to Thermo-Calc predictions in Table A.4. Both databases give accurate estimates of liquidus temperatures, with differences of 10 °C or less. DSC results tend to lie between TTNi8 values, which slightly underestimate the liquidus, and TCNi8 values, which slightly overestimate it. Predictions for the solidus show less agreement, with both databases largely underestimating experimental results. Discrepancies on the order of 10 to 20 °C can be attributed to heating rate effects and to the challenging curve analysis when determining the ‘onset’ of melting. Overall, solidus values from TCNi8 are closer to DSC data. Conversely, TTNi8 predictions for the γ' solvus show much better agreement with experiments. TCNi8 strongly overestimates the solvus, even though the non-equilibrium DSC results from heating stages are expected to yield higher values. The heat treatment window (HTW), obtained as the difference between solidus and γ' solvus, is a key alloy design feature [12, 52]. It provides a measure for the potential of post-casting heat treatments, which should ideally allow for a full homogenisation in the single-phase γ regime without any incipient melting. The best estimates of experimental HTWs are obtained by combining γ' solvus predictions from TTNi8 and solidus predictions from TCNi8.

The effects of changes in chemistry on HTWs are presented in Figure A.6 using data from the first and second heating stages. Comparisons are made to Thermo-Calc phase diagrams in Figure A.7, using TTNi8 and TCNi8, respectively, to estimate changes in γ' and liquid volume fractions with temperature.

The addition of 1 wt.% Hf in SX2 significantly decreases the solidus temperature, while having little impact on the solvus. This is in good agreement with previous reports of Hf acting as a strong melting-point depressant and restricting the HTW

Alloy	γ' Solvus ($^{\circ}\text{C}$)			Solidus ($^{\circ}\text{C}$)			Liquidus ($^{\circ}\text{C}$)			Heat treatment window ($^{\circ}\text{C}$)			
	DSC	TCNi8	TTNi8	DSC	TCNi8	TTNi8	DSC	TCNi8	TTNi8	DSC	TCNi8	TTNi8	TC/TTNi8
SX1	1209	1273	1214	1333	1334	1321	1365	1369	1360	124	61	107	120
SX2	1200	1303	1222	1322	1286	1274	1358	1362	1353	122	-17	52	64
SX3	1164	1257	1153	1324	1305	1293	1357	1347	1352	160	48	140	152
SX4	1211	1231	1188	1311	1301	1308	1345	1346	1346	100	70	120	113
SX5	1185	1221	1207	1331	1330	1303	1364	1372	1356	146	109	96	123
SX6	1195	1259	1179	1330	1328	1317	1362	1371	1361	135	69	138	149

Table A.4: Comparison of DSC experimental results and Thermo-Calc modelling predictions for γ' solvus, solidus, and liquidus temperatures. Heat treatment windows are calculated using values from DSC, TCNi8, TTNi8, and a combination of the two databases taking the γ' solvus from TTNi8 and the solidus from TCNi8.

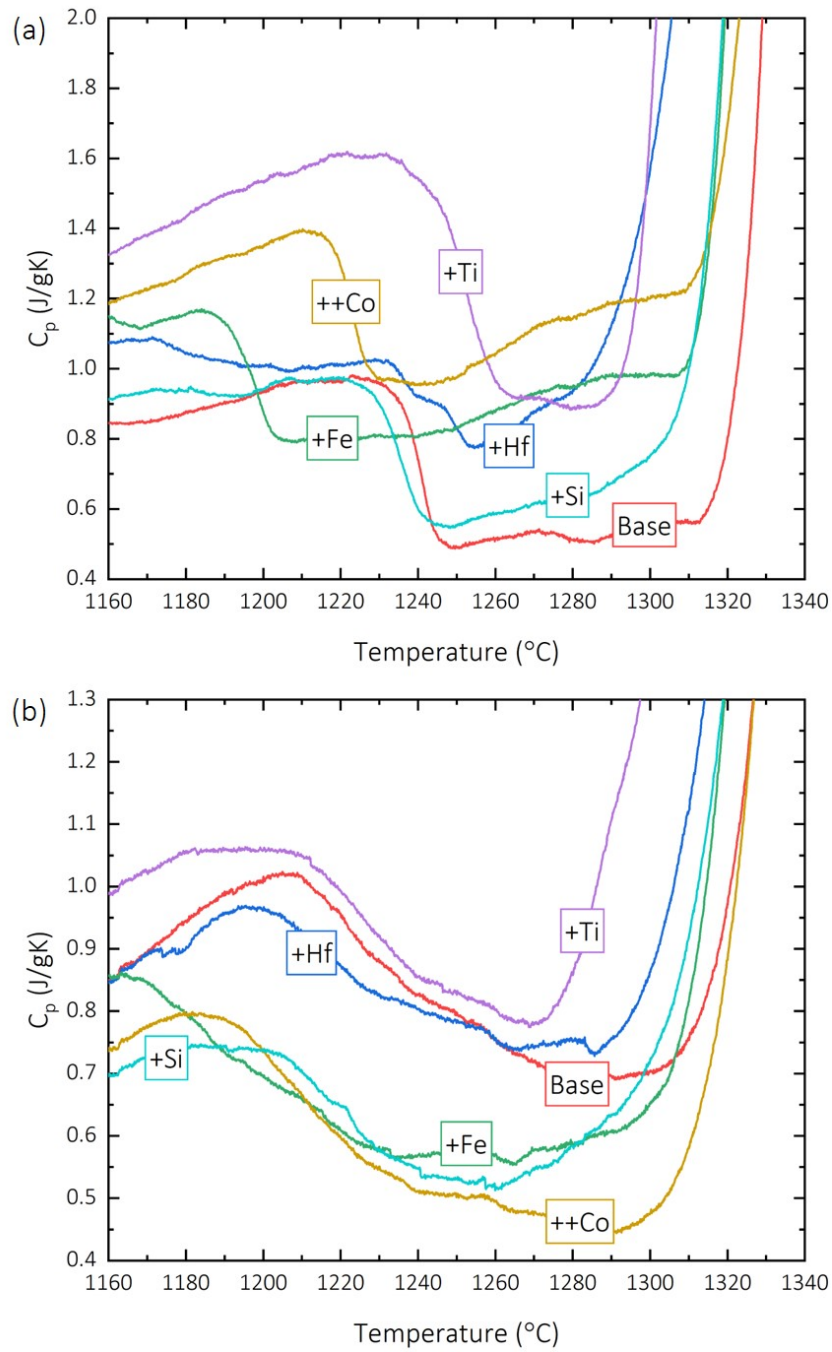


Figure A.6: Comparison of heat treatment window sections obtained during (a) first and (b) second heating stages.

[465, 705, 706, 714, 716, 717]. Nonetheless, the same reports also indicate that Hf additions up to around 1 wt.% raise the solvus temperature due to the preferential partitioning of Hf to the γ' phase [238, 705, 718], also observed in the EDX maps of Figure A.4. This discrepancy can be attributed to the lower level of W in SX2

compared to the nominal composition, as W is also known to raise the γ' solvus [465, 706, 719, 720]. Finally, it should be noted that Thermo-Calc correctly captures the reduced HTW as well as the tapered slope for the remaining liquid fraction during the final stages of solidification, as observed in Figure A.7. Studies on hot tearing susceptibility of superalloys have shown that adding Hf increases the time available for liquid feeding and for stress relaxation, thus improving castability [372, 713, 721].

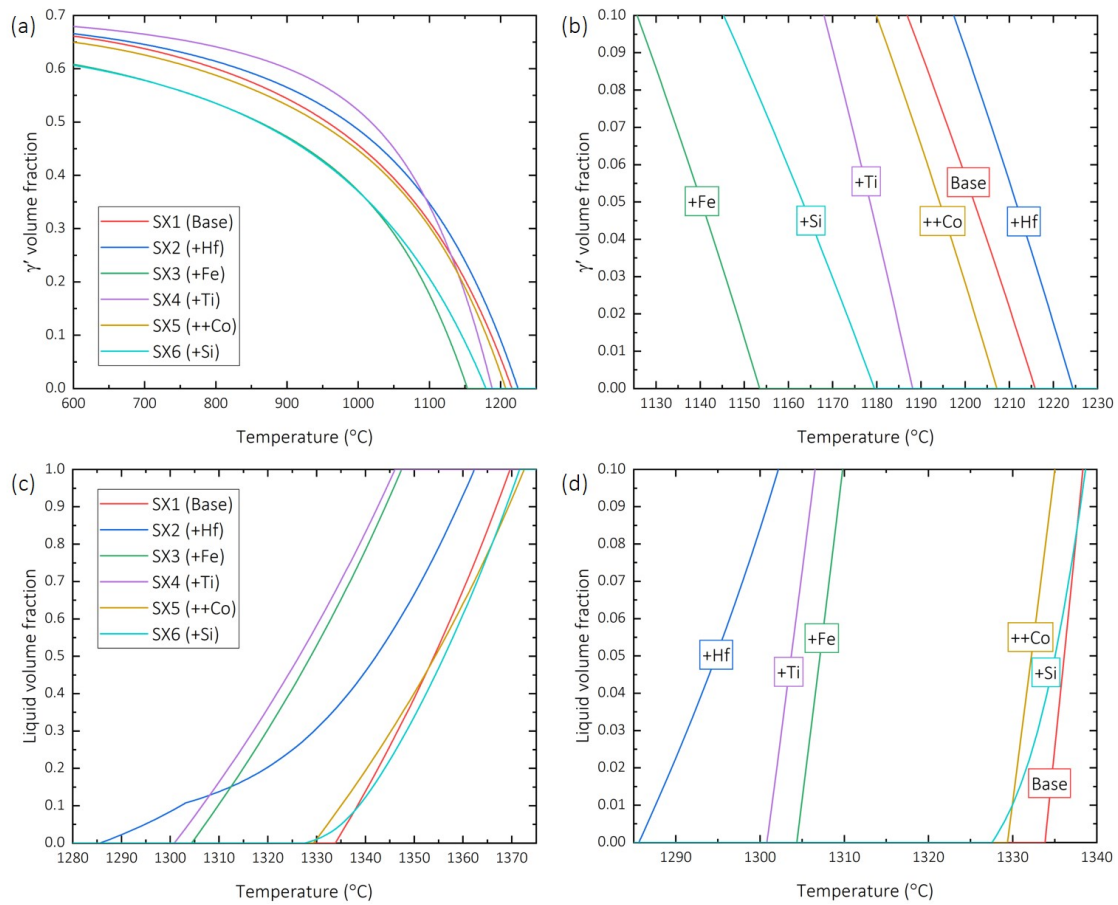


Figure A.7: Thermo-Calc predictions for the influence of temperature on (a) γ' volume fraction using the TTNi8 database and (c) liquid volume fraction using the TCNi8 database. The images in (b) and (d) present enlarged views between 0 and 10% volume fraction.

A similar reduction of the HTW is observed for alloy SX4, in which 0.5 wt.% Al and 2 wt.% Ta are substituted with 2.4 wt.% Ti. Extensive differential thermal analysis work by Sponseller [706] showed that Al and Ti are the most potent γ' -formers for raising the solvus and lowering the solidus and liquidus temperatures. A comparison of model IGT alloys with carefully controlled chemistries revealed

that the liquidus decreases at a rate of $-15.5\text{ }^{\circ}\text{C}/\text{wt.}\%$ Ti, $-12.2\text{ }^{\circ}\text{C}/\text{wt.}\%$ Al, and $-5.6\text{ }^{\circ}\text{C}/\text{wt.}\%$ Ta, respectively [706], in agreement with the present results for SX4. Thermo-Calc correctly predicts the reduced solidus and a higher γ' volume fraction up to around $1000\text{ }^{\circ}\text{C}$, however, this value falls rapidly at higher temperatures and results in an incorrect, lower solvus prediction compared to SX1.

The third chemical modification expected to restrict the HTW is the additional $0.35\text{ wt.}\%$ Si in SX6. An early study by Miner [722] showed that Si has a similar effect to Ti by lowering the solidus and liquidus and raising the solvus. This finding was confirmed by several later studies [495, 723–725]. While the solidus does decrease for SX6, the solvus is also reduced, which can be related to the lower measured Al content in this alloy. These findings are in agreement with Thermo-Calc predictions in Figure A.7.

A substantial widening of the HTW is obtained by increasing the Co content from $5\text{ to }10\text{ wt.}\%$ in SX5. The effects of Co in superalloys have been studied at length during the 1980s following critical supply shortages and revealed a complex influence of Co on alloy microstructure and properties [128, 726]. For example, the addition of $5\text{ wt.}\%$ Co to a Co-free variation of alloy René N6 significantly raises both the solvus and the solidus, but maintains the same HTW [706]. Further additions up to $12.5\text{ wt.}\%$ and $20\text{ wt.}\%$ Co slightly lower the solidus, but strongly reduce the solvus, resulting in a wider HTW. Similar results were obtained for Udimet 700 containing between $0\text{ and }17\text{ wt.}\%$ Co, however, the solvus showed a continuous decrease with increasing Co content [727–729]. These same trends were found for alloy Mar-M247 when increasing the Co level from $0\text{ to }10\text{ wt.}\%$ [719, 730] and for a set of model Ni–Cr–Co–Al–Ti alloys containing between $0\text{ and }57\text{ at.}\%$ Co [731]. Thermo-Calc predictions are in line with the experimental results from the literature and with the DSC data for SX5.

An even stronger effect of depressing the solvus is observed for SX3 after $5\text{ wt.}\%$ Ni is substituted with Fe. As the solidus is only slightly lowered, the overall HTW expands by almost $40\text{ }^{\circ}\text{C}$. In commercial nickel- and nickel-iron-based superalloys, Fe is either (1) completely avoided, as it promotes the precipitation of deleterious TCP

phases and it lowers high-temperature strength and environmental resistance, or (2) it is added in significantly higher quantities in low-cost, high-toughness materials for low-temperature applications [117, 239]. The only commercial composition similar to SX3 is the wrought alloy Haynes 214, which contains 3 wt.% Fe and which has been designed for components operating in carburising and/or oxidising environments [732–735]. As such, DSC data for comparable materials with around 5 wt.% Fe is lacking. Nonetheless, Thermo-Calc correctly reproduces the strong decrease in solvus, although it also overestimates the lower solidus in Figure A.7.

A.3.3 APT Analysis of Alloy Microchemistry

APT techniques have been essential for providing a deeper understanding of the microchemistry of phases and interfaces in NBSA [736–739]. The composition dependence of partitioning coefficients, of interfacial chemical profiles, and of interactions between elements at an atomic scale have been studied in-depth. Investigated materials range from ternary Ni–Cr–Al alloys [740–744], to quaternary Ni–Al–Ta–Mo [745–747], Ni–Al–Co–Ti [748], Ni–Cr–Al–W [547, 548, 720, 749, 750], Ni–Cr–Al–Ta [750–753], Ni–Cr–Al–Re [144, 145, 750, 754, 755], and Ni–Cr–Al–Ru alloys [750, 755], and, finally, to complex quinary and senary model alloys [547, 548, 731, 750, 756–758] and multi-component materials [41, 158, 454, 759–777]. Special attention has been given to elucidating the role played by Re additions in improving creep resistance [137–139, 141, 315, 778, 779], however, the influence of other slow-diffusing refractory additions like Mo, W, and Ta has also been considered [747, 750, 758, 777].

For each of the six trial alloys of the present study, 3D APT datasets with at least 20 million ions were reconstructed and analysed. Figure A.8 illustrates an exemplary dataset collected for SX1. The γ matrix and a γ' precipitate are identified unambiguously as a result of the preferential partitioning of Cr, Co, and Mo to γ and of Al, Ta, and W to γ' . To highlight the γ/γ' interface, an iso-concentration surface was generated at 20 at.% Cr. This cut-off value is used consistently for all six alloys.

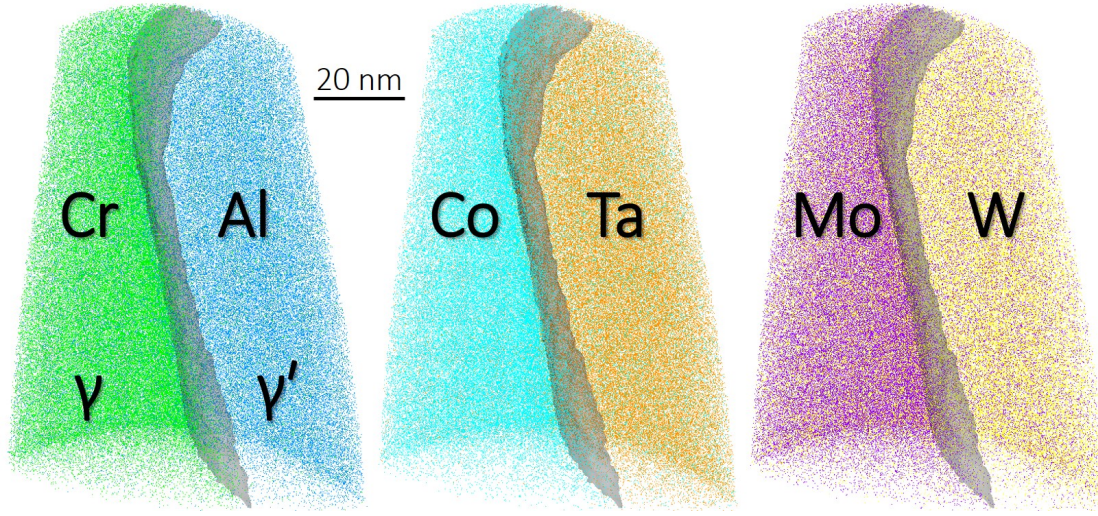


Figure A.8: 3D reconstruction of an APT dataset of around 21 million ions from the base alloy SX1. For clarity, only a fraction of the Cr/Al, Co/Ta, and Mo/W atoms are shown and Ni atoms are omitted altogether. The γ/γ' interface is shown in grey at an iso-concentration of 20 at.% Cr.

A.3.3.1 Phase Compositions and Element Partitioning

Phase compositions were estimated by generating cylindrical regions of interest at distances of at least 5 nm from the γ/γ' interfaces. Results are shown in Table A.5, where they are compared to Thermo-Calc predictions for equilibrium conditions at 845 °C. Using this data, partitioning coefficients are calculated and are presented in Table A.6. The observed partitioning behaviours are in good agreement with the EDX maps of Figure A.4, with the exception of W in alloys SX1, SX3, and SX6, where it is found to partition to γ' . Reasons for this discrepancy are unclear, as the M electron shell series of W should be identified unambiguously by EDX.

CALPHAD predictions and experimental results show a reasonable level of agreement. Whether TCNi8 or TTNi8 provides more accurate estimates depends on both the particular alloy and the element considered. Nonetheless, some trends emerge when considering the values of $K_i^{\gamma'/\gamma}$ for each element i in Table A.6. CALPHAD methods consistently underestimate $K_{\text{Ni}}^{\gamma'/\gamma}$, $K_{\text{Mo}}^{\gamma'/\gamma}$, $K_{\text{W}}^{\gamma'/\gamma}$, and $K_{\text{Al}}^{\gamma'/\gamma}$, while overestimating $K_{\text{Cr}}^{\gamma'/\gamma}$. These differences could be related to phases not having attained their equilibrium compositions after heat treatment [776, 777, 780] and/or to changes in chemistry during the final cooling after secondary ageing

Alloy	Method	γ' composition (at.%)										γ composition (at.%)											
		Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe
SX1	TCNi8	71.67	4.26	1.45	0.21	0.57	17.56	4.25	4.25	0.01	0.01	54.78	27.07	9.64	1.82	1.79	4.63	0.09	0.09	0.14	0.04	0.14	0.04
	TTNi8	70.97	3.47	2.34	0.41	1.03	17.56	4.19	4.19	0.02	0.01	55.77	28.13	8.42	1.55	1.15	4.65	0.18	0.18	0.12	0.04	0.12	0.04
	APT	70.61	2.78	2.55	0.53	1.75	18.80	2.81	2.81		0.17	50.62	33.59	9.30	1.54	1.16	3.51	0.08	0.08			0.19	0.19
	MCS	66.08	10.64	4.68	0.98	0.99	13.82					62.56	18.64	5.22	0.76	1.22	9.58		2.04				
SX2	TCNi8	72.02	3.87	1.31	0.22	0.45	16.88	4.66	4.66	0.57	0.01	0.01	54.41	27.15	10.11	2.20	1.56	4.23	0.10	0.00	0.20	0.04	0.04
	TTNi8	71.27	3.08	2.31	0.42	0.80	16.92	4.60	4.60	0.56	0.03	0.01	55.61	28.17	8.60	1.89	1.04	4.24	0.21	0.02	0.16	0.04	0.04
	APT	70.50	2.15	2.14	0.69	0.42	18.24	5.38	5.38	0.32	0.16	51.53	32.94	9.11	2.60	0.50	2.64	0.16	0.01			0.50	0.50
	MCS	69.67	2.87	1.12	0.14	0.35	18.53	5.09	5.09		0.01	2.22	47.75	24.14	8.55	1.59	1.77	5.28	0.07	0.11	10.73		10.73
SX3	TCNi8	68.85	2.76	2.34	0.40	1.05	17.95	4.74	4.74		0.02	1.89	47.40	25.42	7.69	1.41	1.11	5.16	0.16	0.16	0.10	11.55	10.24
	APT	69.95	2.14	2.49	0.34	1.49	17.99	3.66	3.66		1.94	46.08	28.43	8.34	1.41	1.17	4.21		0.12			10.24	10.24
	MCS	59.82	11.16	4.75	0.94	0.97	13.14	2.84	2.84		6.39	56.29	17.94	5.28	0.81	1.25	9.49	2.00	2.00			6.95	6.95
	TCNi8	71.68	2.99	1.84	0.10	0.37	15.42	4.61	2.98		0.00	0.01	51.45	30.94	9.63	2.11	2.22	3.14	0.21	0.09	0.15	0.06	0.06
SX4	TTNi8	70.57	3.29	2.68	0.22	0.91	14.94	4.48	2.87		0.04	0.01	52.33	31.79	8.60	2.01	1.40	3.35	0.21	0.14	0.11	0.07	0.07
	APT	70.98	1.73	2.31	0.30	0.77	16.13	4.68	3.08		0.03	46.11	37.88	9.70	1.61	1.35	2.95	0.23	0.07			0.09	0.09
	MCS	65.56	10.43	4.53	0.97	0.96	12.14	3.33	2.08			46.11	37.88	9.70	1.61	1.35	2.95	0.23	0.07				
	TCNi8	70.14	3.11	2.83	0.19	0.40	18.65	4.65	4.65		0.01	0.01	46.37	26.20	18.63	1.69	1.87	4.95	0.10	0.10	0.12	0.05	0.05
SX5	TTNi8	68.10	3.06	5.11	0.39	1.02	17.96	4.32	4.32		0.02	0.01	46.81	28.41	17.14	1.57	1.21	4.57	0.11	0.11	0.12	0.06	0.06
	APT	68.09	2.45	5.02	0.38	1.19	18.96	3.87	3.87		0.04	40.67	35.28	17.16	1.36	1.15	4.20	0.10	0.10			0.08	0.08
	MCS	60.53	11.06	9.86	0.96	1.00	13.80	2.80	2.80			56.44	18.87	11.09	0.81	1.25	9.53	2.00	2.00				
	TCNi8	72.39	3.67	1.21	0.26	0.65	17.18	4.46	4.46	0.05	0.13	0.01	59.93	23.02	7.76	1.61	1.59	3.96	0.09	0.09	1.99	0.05	0.05
SX6	TTNi8	71.84	3.03	1.97	0.43	1.03	16.97	4.23	4.23	0.04	0.45	0.01	60.43	23.80	7.01	1.44	1.20	4.11	0.30	0.30	1.66	0.05	0.05
	APT	71.01	2.51	2.47	0.57	1.58	16.95	3.79	3.79		0.94	0.19	53.02	30.80	8.44	1.85	1.11	2.69	0.15	0.15	1.56	0.37	0.37
	MCS	65.56	10.43	4.53	0.97	0.96	12.14	3.33	2.08			46.11	37.88	9.70	1.61	1.35	2.95	0.23	0.07				
	TCNi8	70.14	3.11	2.83	0.19	0.40	18.65	4.65	4.65		0.01	0.01	46.37	26.20	18.63	1.69	1.87	4.95	0.10	0.10	0.12	0.05	0.05

Table A.5: Comparison of phase compositions determined experimentally by APT with predictions made by Thermo-Calc and the TCNi8 and TTNi8 databases and by MCS for equilibrium conditions at 845 °C.

Alloy	Method	Partitioning coefficient $K_i^{\gamma'/\gamma}$											
		Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe	
SX1	TCNi8	1.31	0.16	0.15	0.12	0.32	3.79		49.87				
	TTNi8	1.27	0.12	0.28	0.27	0.90	3.78		23.63				
	APT	1.39	0.08	0.27	0.34	1.51	5.36		35.49				
	MCS	1.06	0.57	0.90	1.29	0.81	1.44		1.38				
SX2	TCNi8	1.32	0.14	0.13	0.10	0.29	3.99		45.96	165.17			
	TTNi8	1.28	0.11	0.27	0.22	0.77	3.99		21.43	25.20			
	APT	1.37	0.07	0.23	0.27	0.83	6.91		33.17	51.91			
SX3	TCNi8	1.46	0.12	0.13	0.09	0.20	3.51		75.66			0.21	
	TTNi8	1.45	0.11	0.30	0.28	0.95	3.48		28.76			0.16	
	APT	1.52	0.08	0.30	0.24	1.27	4.27		30.70			0.19	
	MCS	1.06	0.62	0.90	1.16	0.77	1.39		1.42			0.92	
SX4	TCNi8	1.39	0.10	0.19	0.05	0.17	4.90	22.17	32.08				
	TTNi8	1.35	0.10	0.31	0.11	0.65	4.46	21.53	20.50				
	APT	1.54	0.05	0.24	0.18	0.57	5.46	19.98	44.07				
	MCS	1.06	0.56	0.85	1.25	0.76	1.41	1.43	1.34				
SX5	TCNi8	1.51	0.12	0.15	0.11	0.21	3.77		46.29				
	TTNi8	1.45	0.11	0.30	0.25	0.84	3.93		41.17				
	APT	1.67	0.07	0.29	0.28	1.03	4.51		39.61				
	MCS	1.07	0.59	0.89	1.18	0.80	1.45		1.40				
SX6	TCNi8	1.21	0.16	0.16	0.16	0.41	4.34		48.31	215.51	0.06		
	TTNi8	1.19	0.13	0.28	0.30	0.86	4.13		13.99	20.64	0.27		
	APT	1.34	0.08	0.29	0.31	1.42	6.31		24.71		0.60		

Table A.6: Comparison of partitioning coefficients determined using the data in Table A.5.

at 845 °C. However, considering the discrepancies observed between Thermo-Calc phase diagrams and experimental DSC results and the general lack of data for this region of the alloy design space, it is not surprising that phase compositions differ. Finally, it should be noted that while a slight Hf addition was made to alloy SX6, its presence could not be confirmed by APT.

Partitioning characteristics also emerge from the plots of Figure A.9, constructed using phase compositions, C_γ and $C_{\gamma'}$, from APT and nominal compositions, C_n , from ICP-OES chemical analysis. These plots provide graphical estimates for the γ' volume fraction of each alloy, ϕ_p , by rearranging the lever rule $C_n = C_{\gamma'} \times \phi_p + C_\gamma \times (1 - \phi_p)$. Values for ϕ_p are obtained by measuring the gradients from linear regression analysis [778] and are compared with SEM observations and Thermo-Calc predictions in Table A.3.

The underestimated preferential partitioning of Ni and Al to the γ' phase explains why Thermo-Calc values for ϕ_p in Table A.3 are lower than the SEM measurements and the gradients from linear regression analysis of lever rule plots. TTNi8 offers more precise estimates, in line with it predicting the γ' solvus temperature more accurately. However, discrepancies between SEM and Thermo-Calc values can also be rationalised following the considerations of Maier and Bürgel [239], who showed that area fractions from SEM micrographs tend to overestimate γ' volume fractions due to a preferential orientation of the precipitates. Finally, it is not entirely clear why APT gradient values are consistently higher by several percent, although, they correctly reproduce the trends observed in SEM micrographs. One possible reason is that small, tertiary precipitates with a potentially different chemistry are not considered in the calculation. Furthermore, the average local chemistry may differ from the one measured by ICP-OES due to dendritic segregation effects.

A.3.3.2 Lattice Misfit Effects on γ/γ' Interface Width

Elemental partitioning profiles across γ/γ' interfaces set at iso-concentrations of 20 at.% Cr are investigated by means of proximity histogram (proxigram) analyses [781]. Proxigrams were computed 10 nm either side of the interface using

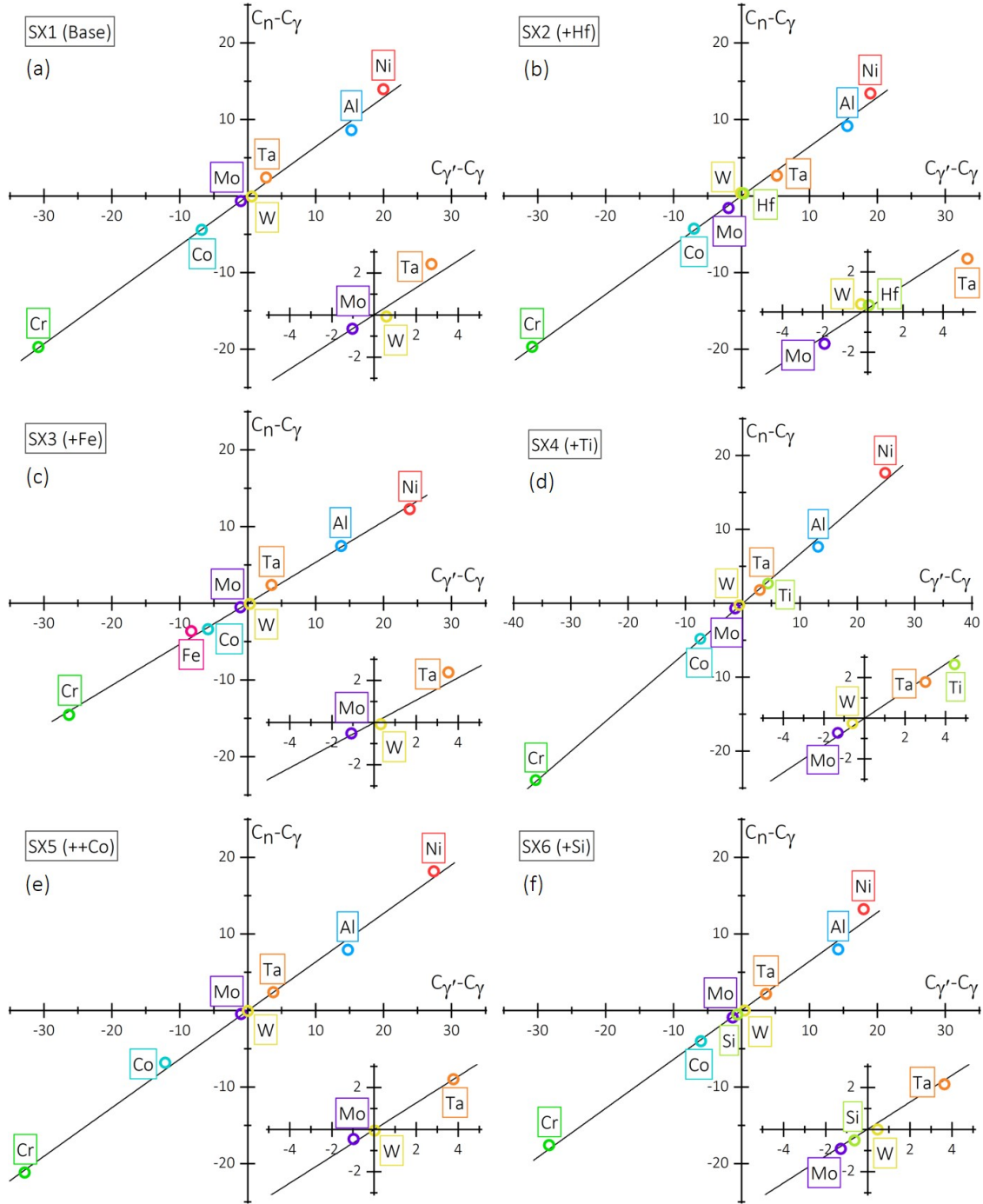


Figure A.9: Lever rule plots estimating γ' volume fractions as gradients from linear regression analysis. Insets show enlarged views of the elements centred around the origin.

a bin size of 0.1 nm. Error bars represent one standard deviation calculated as $\sigma = \sqrt{(C_i(1 - C_i))/N}$, where C_i is the atomic fraction of element i and N is the total number of atoms in the bin.

The results in Figure A.10 reveal diffuse, non-uniform interfaces between the

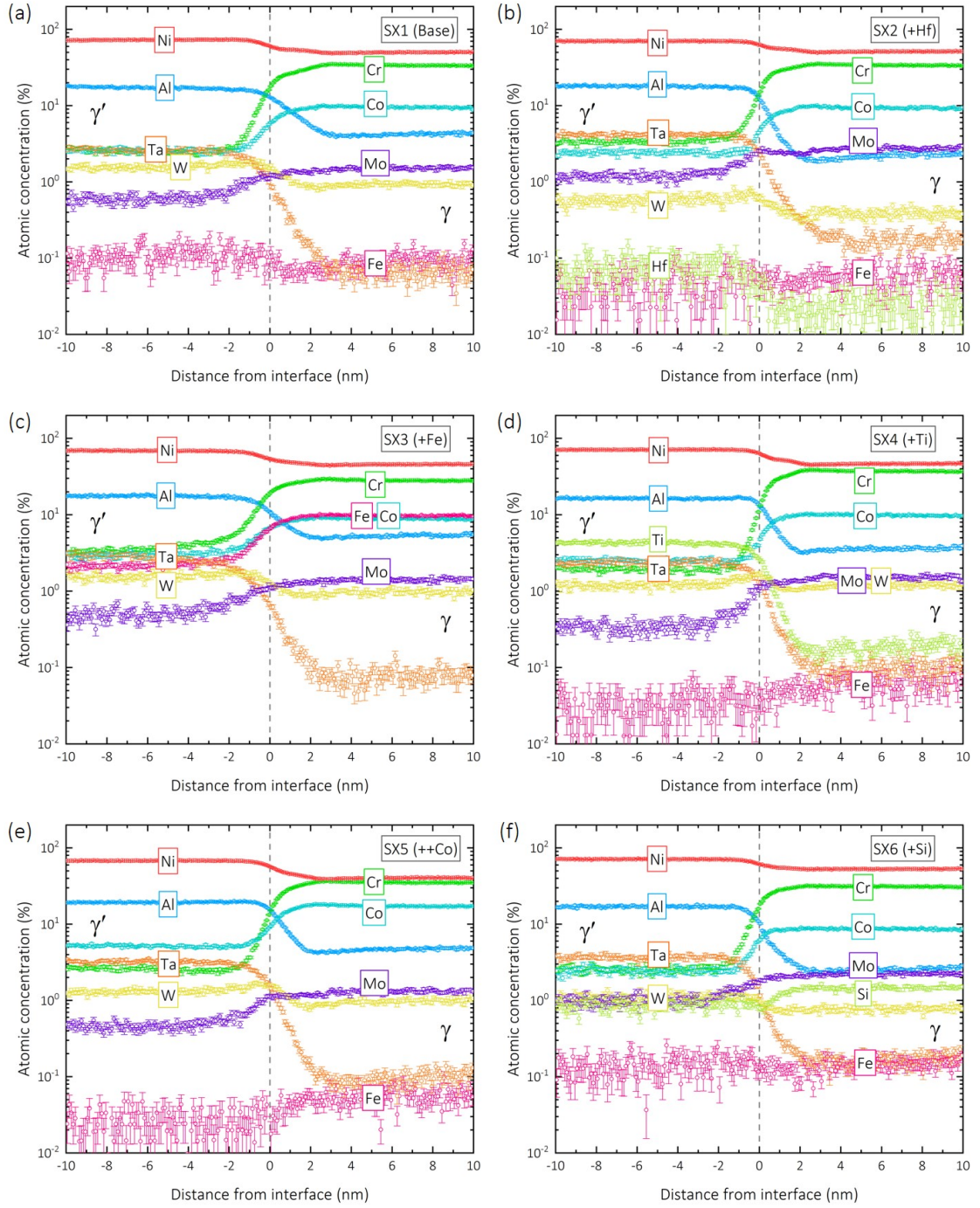


Figure A.10: Proximity histograms across γ/γ' interfaces set at iso-concentrations of 20 at.% Cr. Negative distance values are into a γ' precipitate and positive ones are into the γ matrix. Errors bars represent $\pm\sigma$ confidence intervals; for some elements these overlap with the solid symbols and are not visible.

plateau concentrations of γ and γ' . Interfacial widths, Δ_i , for the profile of each element i were calculated following the method proposed by Zhou et al. [755]. First,

plateau concentration values were obtained using least-squares averaging. Second, non-linear curve fitting to hyperbolic tangent functions was performed using an Orthogonal Distance Regression algorithm. Adjusted R^2 values are close to unity for all cases. Third, Δ_i was calculated by assuming that each interface begins 10% above the minimum and ends at 90% of the maximum plateau values.

As shown in Table A.7, the magnitude of Δ_i correlates with the Vegard coefficients Γ_i^γ and $\Gamma_i^{\gamma'}$. These indicate how the presence of element i will influence phase lattice constants and the misfit between γ and γ' , and are effectively measures of the size difference between solute i and solvent Ni atoms [12, 450]. Mo, Ti, and Ta all exhibit high interfacial widths, in agreement with recent APT reports on wrought disc superalloys [776, 777]. Exceptions are observed for W, which shows a rapid transition from γ' to γ and for Cr, which reaches the plateau value in γ more sluggishly than expected based on its relatively low Vegard coefficients. In the case of W, this difference can be rationalised by its partitioning coefficient being close to unity. For Cr, this discrepancy has recently been related to possible field evaporation artefacts caused by moving through the interface [777]. Similar interfacial profiles of Cr were observed by Booth-Morrison et al. [751–753] in model Ni–Cr–Al–Ta alloys, but were not discussed by the authors.

Following the previous considerations in Section 5.3.2.3, it is possible to estimate the effects of composition on the lattice constants a_γ and $a_{\gamma'}$ at room temperature using the phase compositions in Table A.5 and Vegard coefficients reported in the literature [242, 243] as:

$$a_\gamma = a_0^\gamma + \sum_i \Gamma_i^\gamma C_i^\gamma; \quad a_{\gamma'} = a_0^{\gamma'} + \sum_i \Gamma_i^{\gamma'} C_i^{\gamma'} \quad (\text{A.1})$$

where a_0^j is the lattice constant of pure Ni or pure Ni₃Al and Γ_i^j and C_i^j are the Vegard coefficient and the atomic fraction of chemical element i in phase j . Following Caron [450], a_0^γ and $a_0^{\gamma'}$ are taken as 3.524 Å and 3.57 Å, respectively. The room temperature (RT) values shown in Table A.8 are then scaled to the secondary ageing temperature of 845 °C using empirical relations reported by Kamara et al. [671]. Finally, the lattice misfit, δ , can be obtained as $\delta = 2(a_{\gamma'} - a_\gamma) / (a_{\gamma'} + a_\gamma)$.

Alloy	Interfacial width Δ_i (nm)										
	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe
SX1	0.90	3.50	2.46	4.90	0.71	3.99		5.18			
SX2	0.71	2.82	1.87	3.39	0.48	2.58		3.49	1.80		
SX3	1.42	3.79	2.80	5.03	0.65	2.71		8.48			3.33
SX4	0.91	2.45	1.63	3.98	0.04	1.35	3.49	3.41			
SX5	1.25	2.65	1.73	4.02	0.19	1.51		4.55			
SX6	0.67	2.81	1.60	3.41	3.41	2.45		2.97		0.91	
$\overline{\Delta}_i$ (nm)	1.17	3.60	2.42	4.95	1.10	2.92	3.49	5.61	1.80	0.91	3.33
Γ_i^γ (-)	-	0.11	0.0196	0.478	0.444	0.179	0.422	0.7	1.03	-	0.15
$\Gamma_i^{\gamma'}$ (-)	-	-0.004	0	0.208	0.194	0	0.258	0.5	0.78	-	-0.004

Table A.7: Widths of γ/γ' interfaces from Figure A.10 calculated following reference [755]. Average values, $\overline{\Delta}_i$, are compared to the unitless Vegard coefficients Γ_i^γ and $\Gamma_i^{\gamma'}$ obtained from references [242, 243].

Alloy	a_γ (Å)		$a_{\gamma'}$ (Å)		Lattice misfit δ ($\times 10^{-3}$)		
	RT	845 °C	RT	845 °C	(1) APT	(2) TCNi8	(3) V_m
SX1	3.582	3.645	3.588	3.643	-0.590	0.877	-2.448
SX2	3.583	3.646	3.602	3.656	2.737	2.490	-0.963
SX3	3.593	3.655	3.592	3.646	-2.471	-1.551	-0.536
SX4	3.588	3.651	3.599	3.654	0.864	0.640	-2.764
SX5	3.586	3.649	3.592	3.647	-0.528	0.987	-2.230
SX6	3.580	3.643	3.593	3.648	1.424	3.490	-0.276

Table A.8: Comparison of lattice misfit, δ , calculated (1) using the Vegard coefficients in Table A.7 and phase compositions from APT, (2) with the same approach as (1) but using phase compositions from TCNi8, and (3) based on predicted molar volumes of the phases from TCNi8.

Comparison is also made in Table A.8 to misfit values estimated using the same general approach, but with phase composition data predicted by TCNi8 at 845 °C. Furthermore, the CALPHAD-based method introduced in Section 5.3.2.3 is considered, in which lattice constants are calculated from the molar volumes predicted by TCNi8. As both γ and γ' contain 4 atoms in each unit cell, lattice constants a_j can be obtained as $a_j = (4V_m^j/N_A)^{1/3}$, where V_m^j is the calculated molar volume of phase j and N_A is the Avogadro constant.

Misfit results in column ‘APT’ are in good qualitative agreement with the observed precipitate shapes in Figure A.2. It has been shown that γ' morphology changes from spheroidal to globular and eventually to cuboidal as the absolute value of misfit, $|\delta|$, increases [233, 258, 259, 782]. For alloys exhibiting irregular, rounded shapes — SX1 and SX4 — a relatively low magnitude of misfit is predicted, whereas higher absolute values are obtained for alloys with regular, cuboidal structures — SX2, SX3, and SX6. The only exception from this trend is SX5, which exhibits blocky precipitates with sharp edges despite its low predicted misfit. Reasonable agreement is also found when considering the values in the ‘TCNi8’ column based on Thermo-Calc phase compositions. This is, however, no longer the case when the simpler approach of estimating lattice constants from V_m is used, in agreement with a recent APT study on model Ni–Cr–Al–Ti–Mo alloys [758] which found this approach to be inaccurate.

A.4 Discussion

A.4.1 Chemical Element Interactions in IGT Alloys

Results from electron microscopy, DSC, and APT analyses have revealed complex interactions between different chemical additions in the six investigated alloys. Understanding how these interactions in turn influence microstructure and material properties is crucial for increasing the accuracy and reliability of ABD tools. In the following, these aspects are discussed separately for each chemical variation, with some overarching trends also emerging.

A.4.1.1 On the Effects of Hf in SX2

Hf became a key addition to superalloys after it was found to significantly increase creep ductility and the time to rupture by influencing GB microstructure in both conventionally cast and directionally solidified components [238, 240, 718, 783–785]. Further advantages of adding Hf include improved castability, as the probability of hot tearing is reduced [372, 713, 721], and increased resistance to sulphidation and to isothermal and cyclic oxidation, as Hf acts as a getter of S and improves the adherence of oxide scales and of thermal barrier coatings [786–791]. A main downside of Hf is its strong reduction of the available HTW, although for SX2 this has been shown to remain large enough to enable full homogenisation.

The results in Table A.6 reveal a further benefit of Hf in SX2, as the partitioning coefficients of Mo and W are reduced. A higher content of slow-diffusing Mo and W in the γ matrix implies a reduced rate of diffusion-controlled processes such as the rate of dislocation climb at γ/γ' interfaces, which constitutes a key damage accumulation mechanism during service for IGT alloys [52]. The effect of Hf on partitioning behaviours can be understood by considering the preference of different elements for either Ni α -sublattice sites or Al β -sublattice sites within the γ' phase. Results of previous APT studies on NBSA are compiled in Table A.9, while ThermoCalc predictions for equilibrium conditions at 845 °C are shown in Table A.10. It emerges that Hf, Mo, and W all prefer Al sublattice sites, suggesting that Mo and W are displaced by Hf into the γ matrix in SX2.

Study	Material	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Fe	Other
Blavette & Bostel [759]	CMSX-2	α	α	α		β	β	β^*	β			
Blavette et al. [760]	ONERA alloy	α	α	α	β		β	β^*				Nb: β
Miller & Horton [792]	Ni-Al-B-X (X=Co/Hf/Fe)	α		α			β			β	β^*	
Blavette et al. [778]	CMSX-2 & PWA1480	α	α	α		β	β	β	β			Re: β
More & Miller [793]	Udimet 720	α	α	α	β	β	β	β				
Harada et al. [761]	TMS-63	α	α		β		β	β	β			
Duval et al. [762]	MC2	α	β^*	$=$	β	β	β	β	β			
Miller et al. [763]	PWA1480	α	α^*	α		β	β	β	β			
Murakami et al. [764]	CMSX-4	α	α	α^*	β	β	β	β^*	β	β		Re: β
Jayaram & Miller [747]	Ni-Al-Ta-Mo	α			$=$	β	β	β				
Wanderka & Glatzel [779]	CMSX-4	α	α	α		$=$	β	α	β			
Murakami et al. [766]	TMS-79	α	α		β		β		β			Ir: β
Cadel et al. [768]	N18	α	β	α	β		β	β				
Booth-Morrison et al. [752]	Ni-Al-Cr-Ta	α	β^*				β		β			
Zhou et al. [794]	Ni-Al-Cr-X (X=Re/Ru)	α	β				β					Re, Ru: β
Tu et al. [795]	Ni-Al-Mo	α			β		β					
Tiley et al. [796]	René 88	α	β	$=$			β	β				
Lin et al. [797]	Ni-Al-X (X=Cr/Co/Ru)	α	β	$=$			β					Ru: β
Oni et al. [748]	Ni-Al-Co-Ti	α		$=$			β	β				
Bagot et al. [776]	RR1000	α	α	α	β^*		β	β	β	β		

Table A.9: Site preferences of elements in the γ' phase for either Ni α -sublattice sites or Al β -sublattice sites. Results are compiled from literature reports on model alloys and commercial materials and are ordered chronologically. An asterisk symbol denotes only a weak preference, while an equality sign denotes a lack of preference.

Alloy	Method	Probability of element on Al β -sublattice sites (%)										
		Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Si	Fe
SX1	TCNi8	0.19	68.63	6.92	93.88	95.21	96.05		99.41			12.91
	TTNi8	0.31	52.59	0.24	91.69	90.19	99.25		99.99			22.34
	MCS	2.00	51.57	4.52	95.65	84.28	98.06		97.54			
SX2	TCNi8	0.16	69.07	8.91	93.13	94.85	96.30		99.41	99.96		13.23
	TTNi8	0.37	52.91	0.23	90.77	89.87	99.38		99.98	99.67		23.20
SX3	TCNi8	0.11	58.54	5.19	88.66	89.75	94.11		99.23			11.31
	TTNi8	0.16	36.00	0.12	85.84	82.19	98.59		99.96			12.04
	MCS	2.66	38.64	5.64	91.20	73.14	95.83		96.50			32.10
SX4	TCNi8	0.12	60.15	0.91	85.75	89.60	98.11	99.84	98.96			12.16
	TTNi8	0.38	46.50	0.16	82.83	87.34	99.33	99.99	99.97			13.87
	MCS	1.97	46.72	5.25	94.33	82.43	97.26	96.65	95.99			
SX5	TCNi8	0.12	62.78	5.53	94.48	95.16	94.88		98.79			9.25
	TTNi8	0.25	46.99	0.20	90.12	89.88	99.18		99.98			18.00
	MCS	2.12	48.82	4.93	95.08	82.20	97.73		97.35			
SX6	TCNi8	0.21	72.21	8.72	94.70	95.87	96.91		99.55	99.97	73.79	15.73
	TTNi8	0.39	58.74	0.31	92.47	91.23	99.46		99.99	99.72	100.0	25.54

Table A.10: Site preferences of elements within the γ' phase, expressed as the percentage of atoms occupying Al β -sublattice sites. Predictions made for equilibrium conditions at 845 °C by Thermo-Calc and the TCNi8 and TTNi8 databases are compared to MCS results.

Study	Material	Cr	Co	Cr/Co	$K_{\text{Hf}}^{\gamma'/\gamma}$
Present work	SX2	13.26	4.86	2.73	51.91
Murakami et al. [764]	CMSX-4	7.60	9.80	0.78	>1
Yoon et al. [767]	René N6	4.96	12.96	0.38	4.75
Reed et al. [769]	RR2100	3.00	12.85	0.23	2.20
	RR2101	3.06	12.97	0.24	4.50
Amouyal et al. [799, 800]	ME-9	8.18	7.74	1.06	0.14
	ME-15	7.73	7.31	1.06	0.16
Bagot et al. [776]	RR1000	16.50	17.90	0.92	≈ 8

Study	Material	Cr	Co	Cr/Co	$K_{\text{Si}}^{\gamma'/\gamma}$
Present work	SX6	13.22	4.44	2.98	0.60
Yeh et al. [724]	TMS-138A-Cr+Si	2.90	6.20	0.47	1.14
Yeh et al. [725]	KC-3, KC-4, KC-5	8.18	7.74	1.01	0.82
Segersäll et al. [41]	STAL15SX	17.87	4.90	3.65	0.33

Table A.11: Comparison of the ratio of nominal Cr and Co contents in at.% with the partitioning coefficients of Hf and Si, $K_{\text{Hf}}^{\gamma'/\gamma}$ and $K_{\text{Si}}^{\gamma'/\gamma}$, for several trial and commercial superalloys analysed in APT studies. EPMA results for Si-bearing alloys KC-3, KC-4, and KC-5 are also included for better comparison.

From an alloy design perspective, it must be pointed out that the preferential partitioning of Hf towards γ' in SX2, which directly influences its efficiency at displacing Mo and W, has been shown to vary with alloy chemistry. Recent studies [776, 798] proposed that $K_{\text{Hf}}^{\gamma'/\gamma}$ depends on the ratio of Cr to Co additions. At a high Cr/Co ratio, it is anticipated that Cr will increase the solubility of Hf in the γ matrix and will reverse partitioning, whereas at a low Cr/Co ratio, Co will stabilise the γ' phase for Hf [799, 800]. However, the data compiled from literature in Table A.11 suggests that this mechanism is not as simple as previously suggested. Alloy SX2 with double the Cr/Co ratio compared to ME-9 and ME-15 exhibits a $K_{\text{Hf}}^{\gamma'/\gamma}$ value two orders of magnitude higher. Furthermore, alloys CMSX-4 and RR1000 with similar Cr/Co ratios to ME-9 and ME-15 still exhibit clear partitioning of Hf towards γ' . It is therefore suggested that the dependency of $K_{\text{Hf}}^{\gamma'/\gamma}$ on the Cr/Co ratio only holds true for low Hf additions on the order of 0.1 wt.%.

A.4.1.2 On the Effects of Ti in SX4

With regard to the reversed partitioning of W, APT observations and first-principle calculations of substitutional formation energies in γ and γ' have shown an even stronger effect caused by Ta additions [547, 548, 801] and related this to the high affinity of Ta for the γ' phase and to the repulsive interatomic interactions of Ta–W dimers. More recently, a similar, albeit weaker effect was found for Ti [113, 114], in agreement with the site preferences in Tables A.9 and A.10. Despite potential downsides of lowering the oxidation resistance [802–806] and the available HTW [450, 706], Ti has the advantage of much lower density and cost compared to Ta and has been given preference in recent alloy design studies on new superalloys with optimised solid solution strengthening [61, 113, 114].

Analogue to SX2, the HTW of SX4 was found to be lower than for SX1, but nonetheless adequate for achieving full homogenisation. The results from image analysis of SEM micrographs and the estimates from lever rule plots, compared in Table A.3, indicate a significant increase in the γ' volume fraction of SX4, in agreement with the raised solvus temperature [450, 719] and with Thermo-Calc predictions. As such, the reduced partitioning coefficients of Mo and W can be related to both a higher precipitate volume fraction and to the effects of Ti and Ta atoms occupying Al sublattice sites [114]. The value of $K_{Cr}^{\gamma'/\gamma}$ also decreases, indicating that Cr might preferentially occupy β -sites in the alloys considered here. However, it should be noted that the sublattice preference of Cr can vary strongly with composition and heat treatment [752], as summarised in Table A.9. Changes in the partitioning coefficients of Al and Ta in SX4 are more likely related to the altered levels of these elements rather than to the presence of Ti.

A.4.1.3 On the Effects of Fe in SX3 and Co in SX5

A weaker, but nonetheless noticeable reduction of $K_{Mo}^{\gamma'/\gamma}$ and $K_W^{\gamma'/\gamma}$ is observed for alloys SX3 and SX5. In agreement with the reduced solvus temperatures and with Thermo-Calc predictions, the γ' volume fractions of these alloys are lower than for SX1, especially in the case of SX3. As such, it might be expected that the

concentrations of refractory elements in the γ matrix will decrease with added Fe and Co. Furthermore, Table A.9 shows only a weak preference of Fe for Al sublattice sites in a model Ni–Al–B–Fe alloy, while Co is found to either occupy Ni sites preferentially or both Al and Ni sites in an equal measure. Despite this, the values of $K_{\text{Mo}}^{\gamma'/\gamma}$, $K_{\text{W}}^{\gamma'/\gamma}$, and also $K_{\text{Al}}^{\gamma'/\gamma}$ are reduced in both SX3 and SX5, warranting a careful analysis.

A review of relevant literature reports reveals a complex and highly composition-dependent influence of Co on the partitioning coefficients of other elements. For Udimet 700 alloys with Co contents between 0 and 17 wt.%, Jarrett & Tien [727] found using STEM-EDX that $K_{\text{Cr}}^{\gamma'/\gamma}$ decreases and $K_{\text{Ni}}^{\gamma'/\gamma}$ increases with added Co, in agreement with the present work, while the partitioning behaviours of Co, Al, Ti, and Mo were not affected. Surprisingly, Harf [729] found no significant changes in partitioning for the same set of Udimet 700 compositions, when these were prepared by a powder metallurgical route. In an extensive study on the influence of Co, Ta, and W on the microstructure of single-crystal superalloys similar to NASAIR 100, Nathal & Ebert [719] measured phase chemistries after electrolytic phase extractions and only found significant changes for Ni, which partitioned more strongly to γ' as the Co content was increased from 0 to 10 wt.%. The same results were found by Zhi'An et al. [807], who examined a set of Udimet 500 alloys with 0 to 25 wt.% Co. A recent APT study on model Ni–Cr–Co–Al–Ti alloys containing between 0 and 57 at.% Co [731] found that, between 0 and 19 at.% Co, $K_{\text{Cr}}^{\gamma'/\gamma}$ decreases and $K_{\text{Ni}}^{\gamma'/\gamma}$ strongly rises, in accordance with results for SX1 and SX5, however, also contrarily that $K_{\text{Al}}^{\gamma'/\gamma}$ increases. The best agreement is found with a report by Nathal et al. [730] on conventionally cast Mar-M247 containing between 0 and 10 wt.% Co. These authors found that $K_{\text{Ni}}^{\gamma'/\gamma}$ strongly increases and that $K_{\text{Cr}}^{\gamma'/\gamma}$, $K_{\text{Al}}^{\gamma'/\gamma}$, and $K_{\text{W}}^{\gamma'/\gamma}$ gradually decrease as more Co is added. All in all, this brief review demonstrates that the impact of Co in superalloys has not yet been fully understood and that its effects are highly dependent on composition and even heat treatment [728]. These same conclusions were made in a recent review on the effects of Co on the microstructure and mechanical properties of NBSA [117].

The scarcity of data on alloys containing relatively low Fe levels like SX3 makes it difficult to assess its influence. The seminal review by Ochiai et al. [249] on determining site preferences in Ni₃Al from the directions of solubility lobes in a ternary region showed a mixed behaviour for Fe. An earlier study by Nicholls & Rawlings [808] on Ni₃Al(Fe) alloys found the site preference of Fe changes from Al β -sublattice sites at 2.5 at.% Fe to mixed at 9.3 at.%. This is in agreement with the work of Miller & Horton [792], who found a weak β preference in a Ni–Al–B–Fe alloy with 6 at.% Fe. As such, it can be expected that most of the 2 at.% Fe measured for the γ' phase of SX3 will occupy Al sublattice sites, thus explaining why the partitioning coefficients of Mo, W, Al, and Ta all decrease. From an alloy design perspective, potential improvements in oxidation resistance associated with Fe must be carefully considered against the significant reduction in γ' volume fraction, which will negatively impact high-temperature mechanical properties.

A.4.1.4 On the Effects of Si in SX6

A similar situation to Fe emerges for Si additions in superalloys, as previous research has shown that while Si improves hot corrosion and oxidation resistance [495, 496, 722, 724, 725, 809–811], it can also negatively affect mechanical properties and promote the formation of deleterious TCP phases [240, 495, 722–725]. As such, an optimal Si level of around 0.25 wt.% was found for STAL15SX [495, 496], which possesses a similar chemical composition to the trial IGT alloys considered here.

Analogue to Hf, the partitioning preference of Si towards γ or γ' is influenced by the overall chemical composition. Furthermore, based on the results of several APT studies compiled in Table A.11, a better correlation is found between $K_{\text{Si}}^{\gamma'/\gamma}$ and the Cr/Co ratio of nominal compositions in at.%. As such, the aforementioned considerations regarding the stabilising effects of Cr and Co on γ and γ' , respectively, can explain the stronger partitioning of Si towards γ with increasing Cr/Co ratio. It should be noted that Yeh et al. [725] had related this shift towards γ to the presence of Ti, however, this hypothesis is not supported by the present work or the APT results for STAL15SX [41].

A comparison of partitioning coefficients for alloy CM247LC without Si and with additions of 0.25 and 0.5 wt.% suggested that Si shifts all values towards unity [725]. This is also observed in SX6 for Ni, W, and Ta, but other results are inconclusive. Given the reduced nominal level of Al in this alloy, it is challenging to isolate the effects of Si. Furthermore, the lower γ' volume fraction can undoubtedly be explained by the lower Al content.

A.4.1.5 On the Interfacial Enrichment of W in SX2, SX4, and SX5

An interesting result observed in Figure A.9 for alloys SX2, SX4, and SX5 is an enrichment of W at γ/γ' interfaces. No such effect could be observed for SX1, SX3, or SX6, suggesting it is related to the reversed partitioning of W towards the γ matrix. Extensive work on the partitioning behaviour of W and the influence of Ta by Amouyal et al. [547, 548, 801, 812] showed clearly that W segregation only occurs in alloys with a high enough Ta content to effectively displace W atoms from their preferred Al β -sublattice sites in γ' and into the γ phase. Conversely, no W enrichment was observed in model ternary, quaternary, and quinary alloys with lower levels of Ta or in the Ta-depleted dendrite core regions of multi-component superalloys [547, 548, 801, 812]. This indicates that a critical level of Ta is required to displace W and this value was predicted by Thermo-Calc to decrease with temperature [547]. Considering the literature reports compiled in Table A.12, it appears the condition $K_X^{\gamma'/\gamma} < 1$ is a pre-requisite for the enrichment of solute X at γ/γ' interfaces, but it does not guarantee this will indeed occur.

From an alloy design perspective, it is important to assess what gives rise to interfacial solute segregation and, more so, how this might impact high-temperature creep resistance. Early APT studies hypothesised that slower-diffusing solutes like Ta, W, or Re might preferentially segregate to γ/γ' interfaces and this was indeed observed for the case of Re in several single-crystal superalloys [137, 141, 765, 767, 779]. However, it was concluded that this enrichment does not simply arise for reasons of thermodynamic equilibrium, but rather that it is related to the growth of γ' precipitates during cooling [137, 141]. Phase field modelling showed conclusively

Study	Material	W	Re	Segregation?
Present work	SX2, SX4, SX5	✗		Yes: W
Delargy & Smith [813]	IN-939			No
Blavette & Bostel [759]	CMSX-2	✗		Yes: Cr
Blavette et al. [760, 814]	ONERA alloy			No
Hopgood & Martin [815, 816]	SR99	✗		Yes: Cr
Harada et al. [761]	TMS-63			No
Duval et al. [762]	MC2	✗		Yes: Cr
Miller et al. [763]	PWA1480	✗		No
Wanderka & Glatzel [779]	CMSX-4	✗	✗	Yes: Re
Murakami et al. [765]	CMSX-4	✗	✗	Yes: Re
Murakami et al. [766]	TMS-79			No
Warren et al. [137]	RR3000	✗	✗	Yes: Re
Yoon et al. [767]	René N6	✗	✗	Yes: Re
Reed et al. [769]	RR2100 & RR2101	✗	✗	No
Tin et al. [771]	C17-1, C17-2, C17-3	✗	✗	Yes: Re, Co
Amouyal et al. [547, 548]	ME-9 & ME-15	✗	✗	Yes: W
Mottura et al. [139, 141]	CMSX-4	✗	✗	Yes: Re
Muraleedharan et al. [774]	DMS4	✗	✗	No
Lapington et al. [777]	ABD-2, ABD-4, ABD-6	✗		Yes: W

Table A.12: Compilation of APT reports on solute segregation at γ/γ' interfaces in trial and commercial superalloys. Cross marks indicate the presence of slow-diffusing W or Re in the material. Any elements observed to segregate are identified in the last column.

that the diffusion rate of Re is too slow to allow equilibrium particle growth and that, as the γ/γ' interfaces migrate during cooling, a Re ‘bow wave’ forms ahead of them [137, 141]. The same type of profile is observed in the present work and has been reported previously for W segregation [547, 548, 777]. Further support comes from a report of W enrichment occurring only at $\{100\}$ -interfaces of secondary, cuboidal precipitates, of the type investigated in the present study, but not at the curved interfaces of tertiary, spheroidal precipitates [812]. As the latter form during isothermal ageing heat treatments, there is no comparable supersaturation as during cooling that might give rise to interfacial segregation. These considerations suggest the excess W will no longer be present at interfaces during long-term creep testing, as the alloy microchemistry gradually approaches an equilibrium state. Nonetheless, the higher mole fraction of W in the γ phase of alloys like SX2, SX4, and SX5 is expected to play a key role in increasing creep resistance.

As discussed in detail in Chapter 5, modelling studies of creep damage accumulation in single-crystal superalloys predict that slow-diffusing atom species have a strong beneficial effect by pinning dislocations while these are overcoming γ' precipitates by series of climb events at γ/γ' interfaces [364–366]. A first-order approximation suggests that the time to 1% creep strain, which constitutes a key design parameter for turbine blade materials [37], is inversely proportional to the effective diffusivity for climb-assisted creep deformation in the γ matrix [364]. Creep tests on single-crystal, single-phase alloys carried out to isolate the solid solution strengthening effects of Mo, W, and Re revealed that the same creep rates are obtained when 1 at.% Re, 2 at.% W, or 2.44 at.% Mo are present within the γ matrix [112, 315]. This experimental finding is supported by first-principles calculations based on density functional theory, which predict that within a Ni_{31}X system at 0 K, where X denotes the solute impurity, a Re atom is twice as effective as W and 3.4 times as effective as Mo at reducing the creep rate [313, 817]. Furthermore, these values are in good agreement with extrapolated interdiffusion coefficients for binary Ni–Mo, Ni–W, and Ni–Re systems, which will directly affect the effective diffusivity of the matrix [314, 681]. These results highlight the importance of

carefully considering alloying effects on the partitioning behaviour of refractory elements when designing new compositions.

A.4.2 Atomistic-Scale Analysis using Monte Carlo Simulations

Currently ongoing work is attempting to rationalise some of the unexpected and intriguing results from APT by employing MCS to predict the temporal and spatial evolution of atomic arrangements [818] and the kinetics of ordering [819]. Several studies have successfully adapted and applied the MCS methodology to the case of single-crystal NBSA and reported good agreement with APT experimental results [765, 766, 820–822].

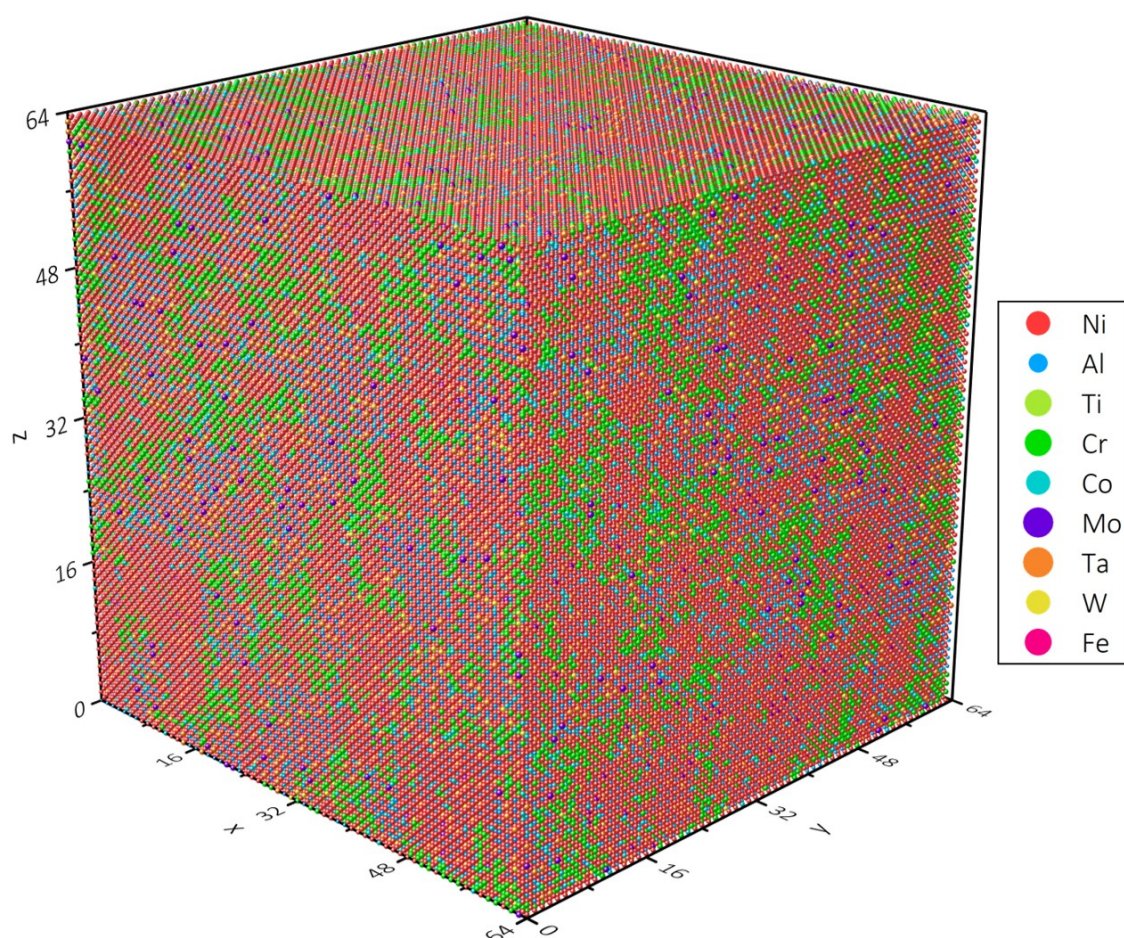


Figure A.11: 3D representation of the simulation system for alloy SX1 after 10^6 Monte Carlo steps. The symbols of individual elements are scaled based on empirically measured atomic radii in pm.

MCS are performed on a 64^3 FCC unit cell mesh containing 1,048,576 atoms, as illustrated in Figure A.11, while applying periodic boundary conditions. All lattice positions in this system are fixed and relaxation effects are not considered. The number of atoms included for each element is calculated based on the chemical compositions determined with ICP-OES in Table A.1. The initial structure is generated by randomly assigning atoms to lattice sites. The kinetics of ordering are controlled *via* Kawasaki dynamics [823] by the direct exchange of randomly selected atoms with one of their respective neighbours. The probability W that an exchange trial will be accepted is calculated as:

$$W = \frac{\exp(-\Delta H/k_B T)}{1 + \exp(-\Delta H/k_B T)} \quad (\text{A.2})$$

where ΔH is the change in total energy associated with the exchange of atoms, k_B is the Boltzmann constant, and T is the absolute temperature. ΔH is calculated by considering only the contributions from the first nearest neighbouring atoms. In order to minimise the computational load for this relatively large system, phenomenological Lennard-Jones pair potentials are employed to describe atomic interactions as:

$$e_{ij}(r) = e_{ij}^0 \left(\left(\frac{r_{ij}}{r} \right)^{m_{ij}} - \frac{m_{ij}}{n_{ij}} \left(\frac{r_{ij}}{r} \right)^{n_{ij}} \right) \quad (\text{A.3})$$

where $e_{ij}(r)$ represents the potential energy between atomic species i and j separated by a distance r . The exponents for the repulsive and attractive potentials of metals, m_{ij} and n_{ij} , are taken as 8 and 4, respectively, following the work of Sanchez et al. [824]. The values of potential parameters e_{ij}^0 and r_{ij} are summarised in Table A.13. They were estimated for multicomponent superalloy systems by Enomoto et al. [825–827] from thermochemical data on enthalpy and/or semi-empirical descriptions of cohesive energies and lattice parameters in pure metals, binary alloys, and compounds. Some values were slightly adjusted to yield a better agreement with γ/γ' phase boundaries reported in the literature for commercial superalloys [827].

The temperature of the system was set to 1118 K (845 °C) to correspond to the final heat treatment step. Calculations for alloys SX2 and SX6 have been omitted, as Lennard-Jones potential parameters for Hf and Si have not been

	$e_{ij}^0/e_{\text{NiNi}}^0$									
	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Fe	
r_{ij}/r_{NiNi}	1.000	0.982	1.002	1.275	1.560	0.990	1.384	1.543	1.057	Ni
		0.900	0.968	1.200	1.459	0.760	1.089	0.900	0.911	Cr
	Ni	1.000	0.998	1.365	1.509	0.910	1.248	1.600	1.057	Co
	Cr	1.018	1.032	1.556	1.791	1.035	1.336	1.787	1.230	Mo
	Co	1.017	1.014	1.006	1.960	1.238	1.549	1.901	1.530	W
	Mo	1.028	1.070	1.062	1.095	0.800	0.909	1.262	0.790	Al
	W	1.029	1.041	1.030	1.126	1.132	1.095	1.095	1.130	Ti
	Al	1.053	1.073	1.031	1.147	1.150	1.149	1.797	1.400	Ta
	Ti	1.035	1.080	1.037	1.156	1.151	1.122	1.174	0.924	Fe
	Ta	1.049	1.073	1.074	1.187	1.155	1.165	1.186	1.180	
Fe	1.017	1.037	1.017	1.077	1.046	1.031	1.085	1.098	1.014	

Table A.13: Lennard-Jones potential parameters used for MCS calculations, adapted from reference [827]. Parameters are normalised with respect to the values for pure Ni, with $N_A \times e_{\text{NiNi}}^0 = 17.13$ kcal/mol and $r_{\text{NiNi}} = 2.91$ Å, where N_A is the Avogadro constant.

reported in the literature and as the solute levels may be too low to be correctly captured by MCS [765, 820].

After 10^6 Monte Carlo steps, atomic configurations will be close to an equilibrium state and further minimisation of the total free energy will be negligible [821]. Figure A.11 illustrates the condition of the 3D FCC unit cell mesh at the end of the simulation for the case of alloy SX1. The formation of γ and γ' regions and the partitioning characteristics of different elements are revealed by plotting successive 2D layers, chosen here to be normal to the z -axis of Figure A.11, in Figure A.12. The formation of ordered γ' particles is unambiguously revealed by alternating pure Ni and mixed Ni–Al layers, while γ regions are identified through the preferential partitioning of Cr. A cluster analysis algorithm based on examining nearest neighbouring atoms is used to assign each atom to a Ni or a Al sublattice site within γ' or otherwise to γ . This then yields information on phase volume fractions, partitioning coefficients, and site preferences [765].

Preliminary MCS results of phase compositions and partitioning coefficients have been added to Tables A.5 and A.6 and show reasonable agreement with APT experiments and with Thermo-Calc predictions. Nonetheless, some clear discrepancies are observed. Most prominent are the high levels of Ni and Al in the γ

matrix and of Cr, Co, and Mo in γ' precipitates. These can be associated with the difficult separation of phase regions during MCS analysis and warrant an improved cluster analysis algorithm. The predicted sublattice site preferences of individual elements within the γ' phase are very close to Thermo-Calc equilibrium calculations, as summarised in Table A.10. Finally, the γ' volume fractions determined by MCS agree well with SEM measurements and with Thermo-Calc estimates in Table A.3. Future work will focus on improving the MCS methodology and applying it to a wider range of alloy compositions.

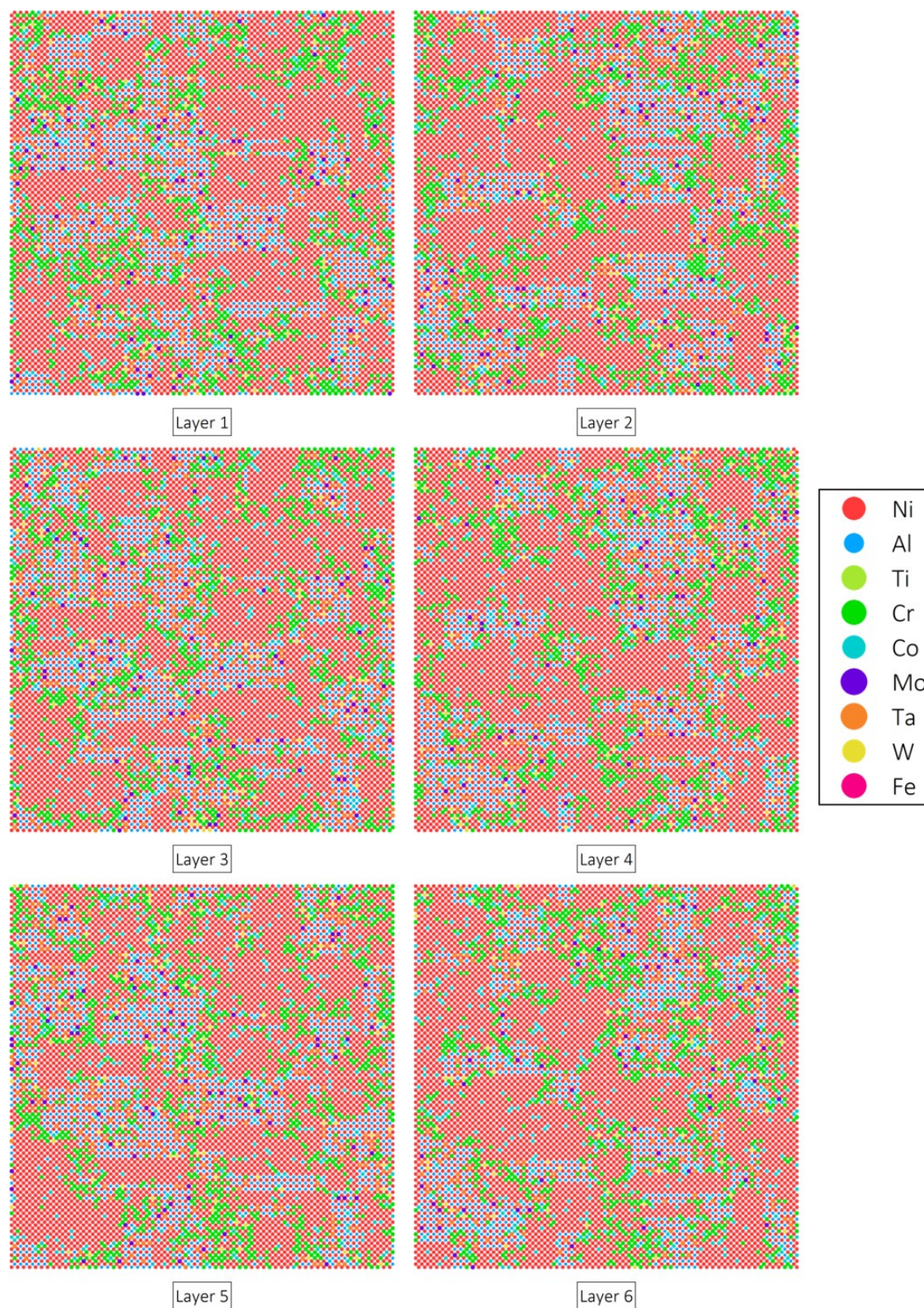


Figure A.12: 2D representations of the 1st to 6th atomic layers normal to the z -axis in Figure A.11. The symbols of individual elements are scaled based on empirically measured atomic radii in pm. Precipitate and matrix regions are clearly identified by the preferential partitioning of Ni and Al to γ' and of Cr to γ .

A.5 Summary and Conclusions

A set of six trial IGT alloys combining high Cr and Al contents for optimised hot corrosion and high-temperature oxidation resistance has been investigated. Extensive experimental analyses of alloy microstructure, phase transition temperatures, and phase microchemistry reveal a complex influence of composition on alloy properties and an intricate interaction between different elemental additions. Throughout the study, comparisons are made to predictions from CALPHAD and MCS. Several general observations have been made:

1. The alloy microstructure is composed of cuboidal, secondary γ' precipitates and spherical, tertiary γ' particles, embedded in the γ matrix. Thermo-Calc predictions for the equilibrium γ' volume fraction at 845 °C are in good agreement with results from image analysis of SEM micrographs.
2. Collecting and analysing C_p - T data from DSC measurements remains a challenging task, prone to experimental errors and subjective interpretation. A best practice approach has been outlined based on previous reports from the literature and ASTM standards.
3. Thermo-Calc predictions for γ' solvus and solidus temperatures are in reasonable agreement with DSC experimental results. For alloys without Hf, the span of the HTW can be estimated to within 20 °C by combining the γ' solvus from TTNi8 and the solidus from TCNi8.
4. As revealed through APT analyses, slight changes in chemistry can have profound effects on alloy microchemistry. Thermo-Calc predictions for phase compositions using both TCNi8 and TTNi8 consistently underestimate $K_{\text{Ni}}^{\gamma'/\gamma}$, $K_{\text{Mo}}^{\gamma'/\gamma}$, $K_{\text{W}}^{\gamma'/\gamma}$, and $K_{\text{Al}}^{\gamma'/\gamma}$, while overestimating $K_{\text{Cr}}^{\gamma'/\gamma}$. It is imperative to adjust and update thermodynamic database parameters for this region of the alloy design space if CALPHAD methods are to provide reliable and accurate inputs for ABD tools.

5. Proxigram analyses across γ/γ' interfaces reveal a diffuse, non-uniform transition between plateau concentrations over several nm. The average width of interfacial profiles correlates well with the atomic size difference between the respective element and Ni, as described by the empirical Vegard coefficients.
6. γ/γ' lattice misfit values estimated using phase compositions determined by APT or predicted with TCNi8 are in good agreement with the observed changes in precipitate morphology, which becomes increasingly rounded as the absolute misfit value decreases. Misfit estimates based on CALPHAD predictions of the molar volumes of γ and γ' phases are inaccurate.

Furthermore, several guidelines and recommendations for IGT alloy design within the compositional space considered here can be drawn:

1. Additions of elements restricting the available HTW such as Hf, Ti, and Si must be carefully controlled to allow a full microstructural homogenisation. This has been achieved in the present work using an optimised solutioning heat treatment with a constant temperature ramp in the HTW regime.
2. Additions of elements with a preference for the Al β -sublattice like Ta, Ti, Hf, and Si are effective at displacing slow-diffusing solutes such as Mo and W from these sites and into the γ matrix. This effect is expected to lead to improved creep resistance, as the higher molar fraction of Mo and W in the matrix will help reduce the rate of diffusion-controlled dislocation climb at γ/γ' interfaces.
3. An enrichment of W at γ/γ' interfaces is only found in alloys with $K_{\text{W}}^{\gamma'/\gamma} < 1$, in agreement with the literature. It results from the growth of secondary γ' particles under non-equilibrium conditions during cooling after the solutioning step. The W ‘bow wave’ formed ahead of the precipitates is expected to dissipate during high-temperature service and will not impart additional creep strengthening. Nonetheless, the higher mole fraction of W in the γ phase of these alloys will play a key role in reducing the effective diffusivity.

4. The preferred partitioning of Hf and Si is shown to be influenced by the ratio of Cr and Co additions. At a high Cr/Co ratio, it is anticipated that Cr will increase the solubility of Hf or Si in the γ matrix and will reverse partitioning, whereas at a low Cr/Co ratio, Co will stabilise the γ' phase for Hf or Si. However, this trend does not extend to higher Hf contents, as Hf is observed to partition preferentially to γ' despite a high Cr/Co ratio. The partitioning behaviours of Hf and Si must be carefully considered during alloy design, as both elements have the potential of occupying β -sublattice sites and of displacing slow-diffusing solutes.
5. The interactions of Co with other elements and its influence on microchemistry have not been fully understood and warrant further investigations. Effects of Co depend on the overall chemical composition and on the selected heat treatment steps. For the alloy design space considered here, increasing the Co level has a beneficial effect of widening the HTW and of promoting the partitioning of Mo and W towards γ .
6. Fe additions have a similar effect to Co and significantly widen the HTW by depressing the γ' solvus. However, this also leads to a marked reduction in γ' volume fraction, which is expected to negatively impact high-temperature mechanical properties. As such, Fe additions for improved oxidation resistance must be carefully considered against possible detrimental effects.
7. The levels of Mo, Ti, and Ta, which strongly influence the lattice misfit, must be carefully balanced, as the sign and magnitude of this mismatch will affect particle morphology and creep damage accumulation. For IGT alloys, a low misfit value which will limit the driving force for precipitate coarsening during long-term service is desirable.

Few metals, particularly those in common technological applications, are stable when exposed to the atmosphere at both high and low temperatures. [...] Some metals, such as iron, will rust and oxidise very rapidly whereas other metals, such as nickel and chromium, are attacked relatively slowly. It will be seen that the nature of the surface layers produced on the metal plays a major role in the behaviour of these materials in aggressive atmospheres.

— N. Birks, G.H. Meier & F.S. Pettit, “Introduction to the High-Temperature Oxidation of Metals”

B

High-Temperature Corrosion of Single-Crystal Superalloys

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B.1 Introduction to High-Temperature Corrosion Damage

High-temperature corrosion is defined, in contrast to aqueous corrosion, as any type of reaction at elevated temperatures between the material in question and its surrounding environment which does not involve aqueous electrolytes [239]. Depending on the chemical elements present in the environment, high-temperature corrosion encompasses a wide range of processes including oxidation, carburisation,

nitridation, sulphidation, and chlorination. A special form involving the presence of molten salt deposits is denoted as hot corrosion. These clarifications regarding nomenclature are important to clearly delimit the dominating form of environmental degradation. In the context of IGT, oxidation predominates when cleaner fuels are used, whereas hot corrosion becomes critical in harsher environments [828]. For brevity, only oxidation damage is considered in further detail in this section. The basic mechanisms of hot corrosion, as well as design guidelines for resistant alloys are discussed in extensive reviews in references [828–831].

For all types of high-temperature corrosion, an alloy with acceptable resistance must react with the environment to form an adherent, continuous, protective scale with adequate mechanical properties [832]. The kinetics of such a reaction must be fast enough to prevent initial failure, but slow enough to offer protection throughout the intended component life. In the case of NBSA, the scale of interest was at first Cr_2O_3 , due to the high chromium levels adopted from stainless steels, and later on Al_2O_3 , as oxidation resistance at higher temperatures became imperative and the benefits of adding more aluminium were noted [116].

As design constraints became more challenging, the functions of load bearing and environmental resistance were ultimately divided between the superalloy substrate and specialised coatings, leading to the development of MCrAlY coatings [42] and later of ceramic thermal barrier coatings (TBC) [833]. The importance of TBC for increased oxidation resistance is illustrated in Figure B.1 and has been discussed for the case of gas turbines in the work of Padture et al. [834–836]. However, coatings bring about several problematic issues, and should not be seen as a panacea which absolves designers from taking environmental damage into account. Considering the rules of safe design, the base alloy must be able to form a protective scale in case the coating should fail and this scale must effectively avert component failure.

A final illustrative point is to compare the prevalence of creep- and oxidation-related articles on superalloys, along with several other keywords in Figure B.2. It is acknowledged that such a simple search cannot hope to encompass all publications of interest and will also include work on nickel-iron- and cobalt-based materials;

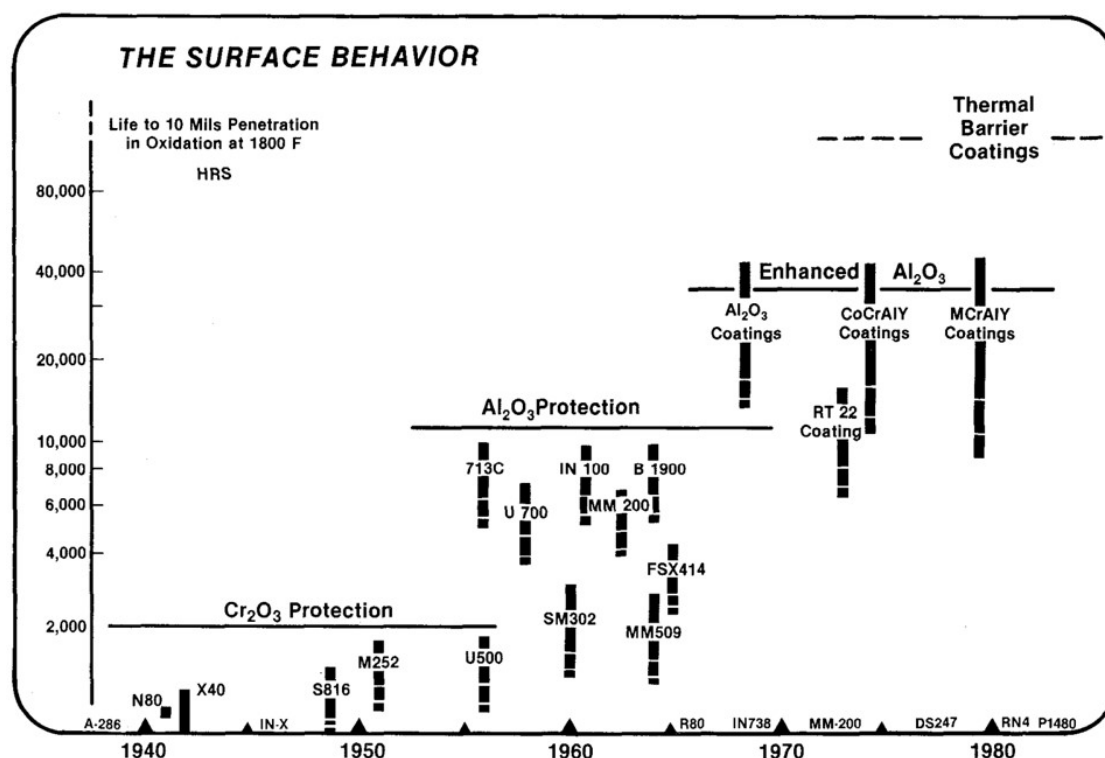


Figure B.1: Advances in oxidation resistance, expressed as time until 10 mm penetration of the superalloy substrate due to surface oxidation at 1800 °F (982 °C) [116]. Major improvements were achieved initially by designing alloys which formed more oxidation-resistant scales and later by developing and improving protective coatings.

nonetheless, several trends emerge. Work on oxidation and corrosion has long been secondary to mechanical damage and the ratio of articles on these distinct topics has largely remained constant. It is also interesting to note how studies on microstructural evolution and microstructure analysis have spiked in recent years, as novel characterisation techniques have been developed to elucidate material properties and performance. It can be ascertained that fundamental theories and models for environmental damage are far less developed than their mechanical damage counterparts, thus warranting increased research activities.

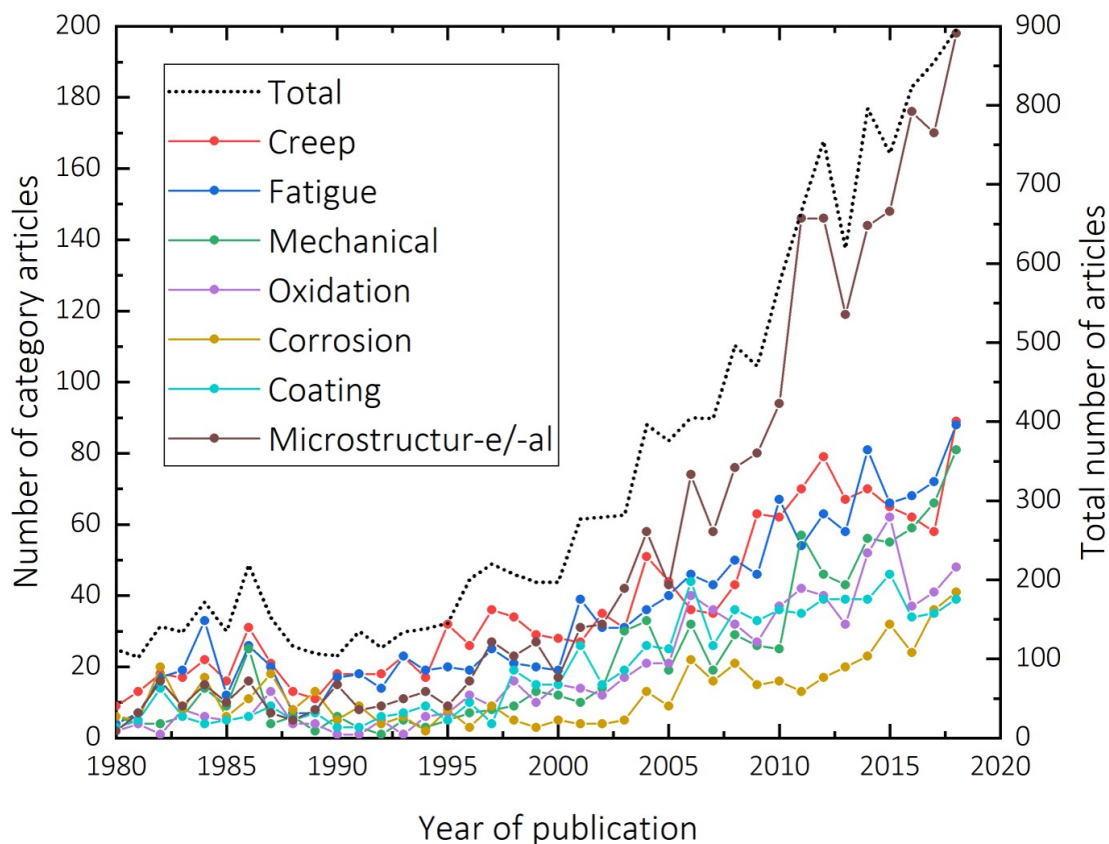


Figure B.2: Comparison of the number of journal articles published in different years which contain certain keywords in their title. The right y -axis shows the total number of articles containing the word “superalloy”, while the left y -axis shows separate categories containing the words “superalloy” AND “creep” / “fatigue” / “mechanical” / “oxidation” / “corrosion” / “coating” / “microstructure” OR “microstructural”. Results were obtained and analysed using the Elsevier Scopus database; status as of December 2018.

B.2 Selective Oxidation Mechanisms

Desired protective scales are obtained by controlling and adjusting the chemical composition to promote a selective oxidation process, in which a solute oxidises preferentially to the alloy base material and forms a continuous surface layer [837, 838]. The general case is presented in Figure B.3 for a model A–B alloy, where the oxides of both A and B are stable under the given conditions, but BO is more stable than AO. In superalloys, A generally represents the nickel or cobalt base and B corresponds to aluminium, chromium, tantalum, or titanium additions.

For lower concentrations of B, as seen in Figure B.3(a), an external layer of AO will form along with internal BO oxides. If the concentration of B exceeds a

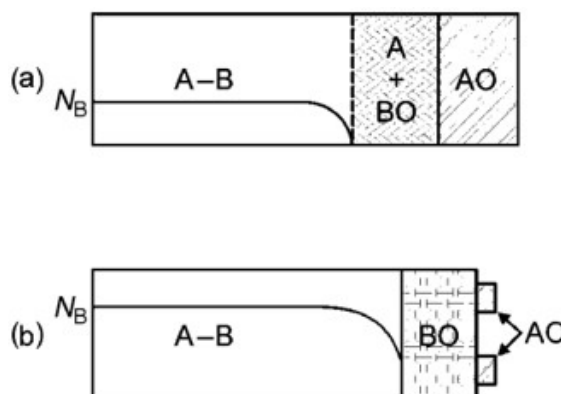


Figure B.3: Schematic cross sections and concentration profiles of an A–B alloy in which both components form stable oxides, but BO is more stable than AO [839]. (a) A small concentration of B results in the internal oxidation of B and an external layer of AO. (b) A large concentration of B results in a continuous external layer of BO, with some AO having formed during the initial, transient stage.

certain critical value, as is the case in Figure B.3(b), a continuous layer of BO will form instead, although some initial AO can be expected during the transient stage. It should be noted that continued selective oxidation of B will deplete it from under the scale, resulting in an enrichment of A-rich oxides with time [805, 839]. The characteristic timescale for this transition from BO to AO will depend on alloy chemistry, operating conditions, and specimen geometry [805]. As such, the alloying element B must form an oxide scale that is both stable and slow growing and the internal reservoir for B must be large enough so that B is not fully depleted from the substrate during the intended service lifetime. Furthermore, it must be acknowledged that Figure B.3 presents an oversimplified view of oxidation processes. Alloys often undergo additional degradation in the form of thermal cycling damage, internal oxidation, and void formation, which reduce both corrosion resistance and mechanical properties [805, 832]. These negative aspects are discussed further in references [832, 839].

B.2.1 Chromia-Forming Alloys

The oxidation behaviour of chromia-forming alloys is captured well by the schematic in Figure B.3, with A representing nickel and B representing chromium in this

case. Following the work by Giggins and Pettit [840], nickel-chromium alloys can be separated into three oxidation groups, as illustrated in Figure B.4.

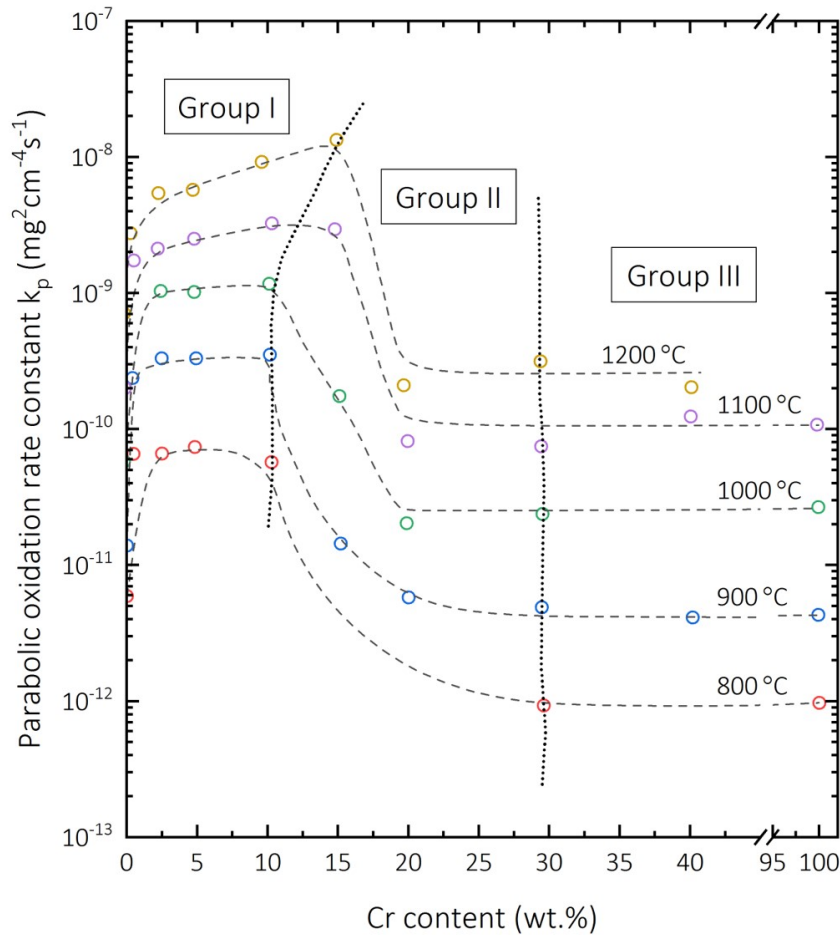


Figure B.4: Compositional effects on the oxidation behaviour of binary Ni–Cr alloys at different temperatures, adapted from reference [840]. Alloys exhibiting similar oxidation characteristics are separated into groups which correlate with the level of chromium.

Group I corresponds to the situation of Figure B.3(a), with an external NiO scale and internal Cr_2O_3 precipitation. Continuous Cr_2O_3 layers are observed for Group III alloys, analogue to Figure B.3(b), and lead to significantly lower oxidation rates compared to pure nickel. In the intermediate regime of Group II, external Cr_2O_3 is observed at GB, while NiO forms over the grains. Such observations have led to the proposal that GB provide short-circuit diffusion paths [841] and that the microstructure has a significant influence on oxidation resistance [842]. Furthermore, rare-earth element additions such as cerium or yttrium have been found to improve the oxidation resistance of chromia, leading to continuous layers at lower chromium

levels, reductions in the rate of oxide growth, and improved adhesion [843–845]. A critical problem which prevents the use of chromia at very high temperatures is the fact that above 1000 °C it oxidises to volatile CrO_3 , which leads to accelerated degradation [832, 839]. In the presence of high-velocity gases, for example within an IGT environment, this critical temperature limit is further reduced [805].

B.2.2 Alumina-Forming Alloys

The shortcomings of chromia volatilisation led to Al_2O_3 becoming the oxide of choice for high-temperature applications. While the thermodynamically stable form of alumina is the α corundum structure, several other metastable polymorphs such as γ and θ exist and can precede α under certain conditions, as illustrated in Figure B.5 [846]. Compared to model Ni–Cr alloys, Ni–Al exhibits negligible amounts of nickel-containing transient oxides of the metastable phases. The transition to the desirable α form brings about a significant decrease in oxide growth rate, as well as a change in oxide morphology, and is of great technological significance [847, 848]. Birks et al. [839] and Edmonds [849] reviewed the existing literature on the conditions leading to this transition and concluded that an overlapping regime is observed for all alumina-forming alloys and that it is sensitive to further alloying additions. Chromium and titanium were found to aid θ – α transformations, while minor elements including yttrium, zirconium, lanthanum, and hafnium retard it [850, 851]. It is important to note that α - Al_2O_3 grows mainly by inward diffusion of oxygen at GB to the interface between the alloy substrate and the oxide scale, therefore posing a potential problem for the formation of an external layer [839].

In like manner to Ni–Cr, three separate regimes influenced by temperature and composition are found for the oxidation of binary Ni–Al alloys, as shown in Figure B.6(a). Alloys of region I develop external NiO scales and internal Al_2O_3 precipitates, some of which convert to NiAl_2O_4 . For region II, a protective Al_2O_3 scale develops initially, but as the aluminium is gradually consumed it is replaced by a thick scale containing NiO and spinel. Finally, when the temperature and/or the aluminium content are increased, a transition to group III behaviour is observed,

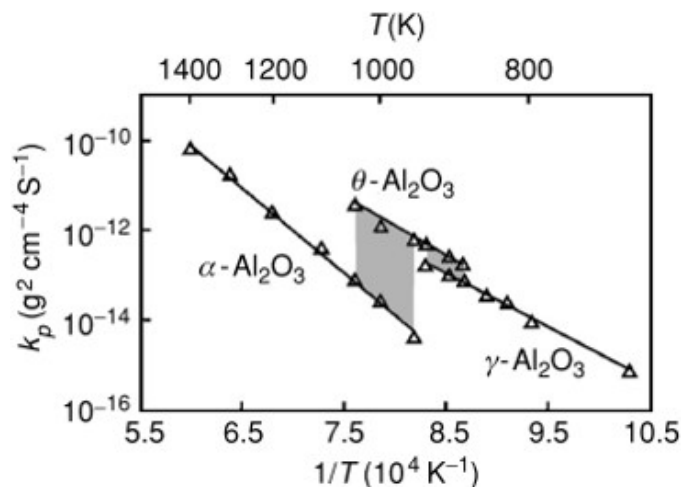


Figure B.5: Arrhenius plot showing a comparison of oxidation rate constants for the α -, γ -, and θ -alumina polymorphs, with the general transition regions between different forms shown in grey [850].

for which an alumina scale is the only reaction product [330, 849]. The broad bands separating these regions are influenced by surface preparation and a given specimen may develop different scales at different locations on its surface [839]. As shown in Figure B.6(b), transitions between the three groups yield significant changes in oxidation kinetics, with parabolic growth rates dropping by several orders of magnitude from region I to region III [805].

Critically, the level of aluminium necessary to ensure Al_2O_3 formation is much higher than that normally found in NBSA and lies outside the $\gamma + \gamma'$ phase field. The reason why such scales can nonetheless be attained is the truly fortuitous synergistic effect of chromium additions within the ternary Ni–Cr–Al system. For example, adding 10 wt.% chromium reduces the critical aluminium content for alumina formation at typical service temperatures from around 10 wt.% [854–856] to as low as 5 wt.% [805, 839]. A concise way of describing the oxidation behaviour of Ni–Cr–Al alloys is to construct an oxide map, in which experimental oxidation results are plotted onto the ternary composition triangle, as shown in Figure B.8. Although empirical in nature, such maps prove very useful for visualising compositional effects on the predominating oxide scales [330]. The oxide maps of Figure B.8 were constructed by Smialek & Meier [805] based on several studies on ternary Ni–Cr–Al alloys [853, 857, 858]. Once again, three primary regions emerge; they correspond

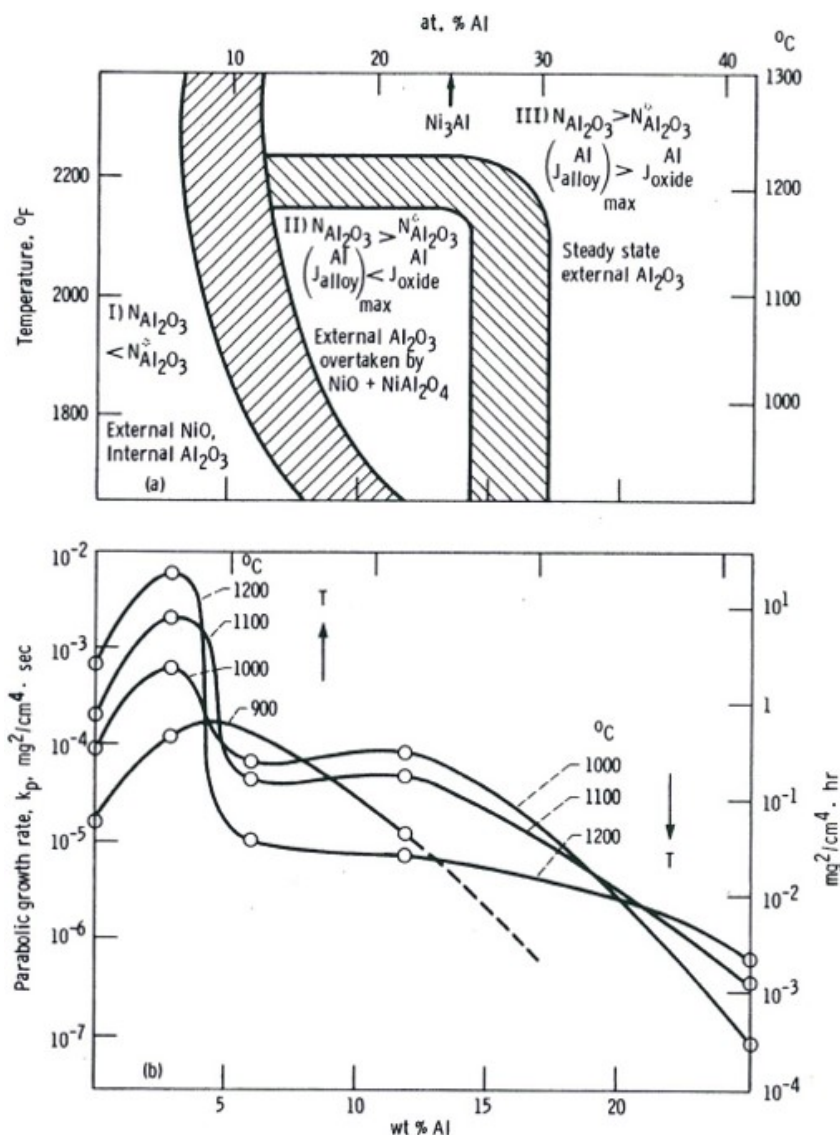


Figure B.6: Compositional effects on the oxidation behaviour of binary Ni–Al alloys at different temperatures [852]. Distinct regimes are delimited within the oxide phase map in (a) and the scale growth rates of alloys corresponding to these regimes are plotted in (b), showing a dependency on aluminium content analogue to Figure B.4. Cross-hatched regions in (a) mark regions in which variable results are obtained based on surface conditions.

to NiO external scales and Al_2O_3/Cr_2O_3 subscales in region I, Cr_2O_3 external scales and Al_2O_3 subscales in region II, and external scales of only Al_2O_3 in region III. It should be noted that the boundaries in Figure B.8 will shift depending on temperature, heating rate, and alloy grain size [12, 805].

As shown in Figure B.7(a), the oxidation of Ni–Cr–Al alloys always begins with the formation of an external NiO and $Ni(Cr,Al)_2O_4$ scale. Diffusion of O

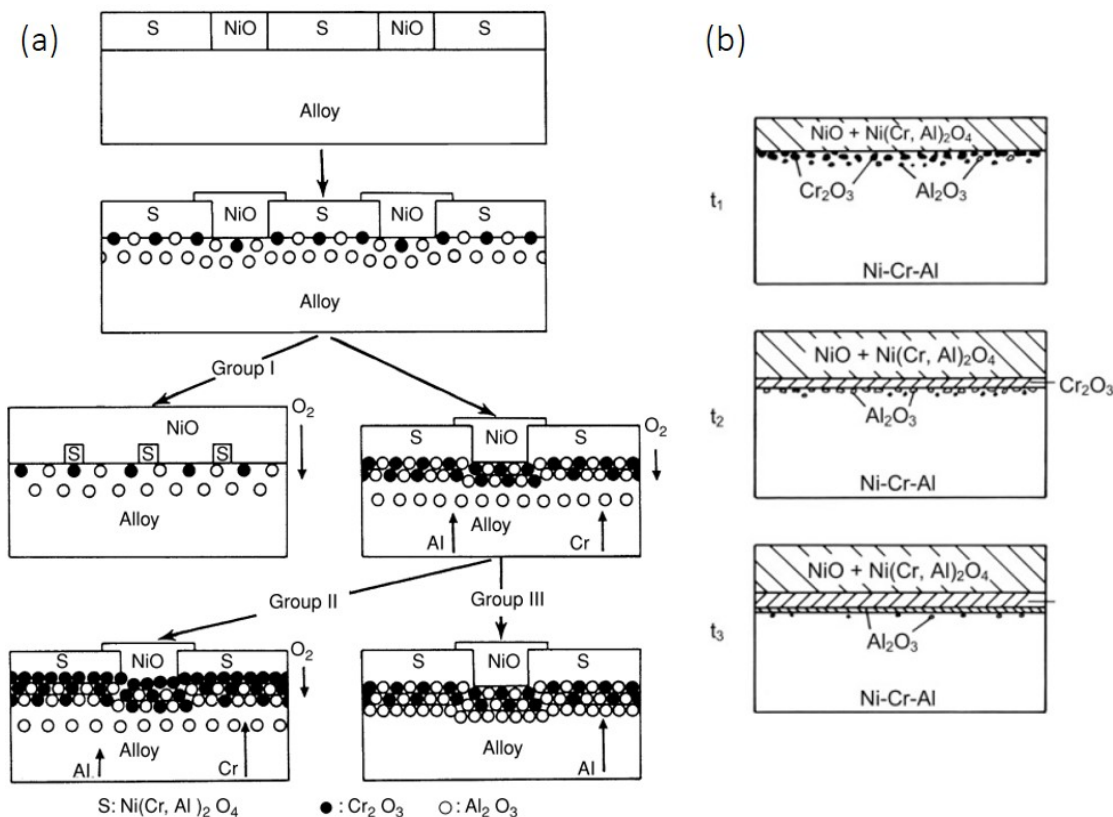


Figure B.7: (a) Schematic diagram illustrating oxide scale development of different Ni–Cr–Al alloys as a function of time [853]. (b) Schematic diagram of oxide scales at increasing exposure times $t_1 < t_2 < t_3$ for a group III alloy with 10 wt.% chromium and 5 wt.% aluminium [239].

into the alloy substrate results in the formation of Cr_2O_3 and Al_2O_3 subscales. Further developments and the nature of the steady-state oxide scale will depend on temperature and chemical composition [853]. For group I alloys that are rich in nickel, the insufficient flux of aluminium and chromium leads to the formation of a brittle, outward-growing NiO scale. For group II materials containing higher levels of chromium but low aluminium, the initial transient NiO/ $\text{Ni}(\text{Cr}, \text{Al})_2\text{O}_4$ external scale gives way to a mixed chromia and alumina layer. The flux of chromium is sufficient to give rise to an external Cr_2O_3 scale, underneath which internal precipitation of Al_2O_3 occurs. Finally, in group III alloys which possess appreciable amounts of both chromium and aluminium, the transient scale is directly replaced by a continuous, compact Al_2O_3 scale. Furthermore, no internal precipitation occurs, as the alumina layer reduces the oxygen activity to levels at which nickel and

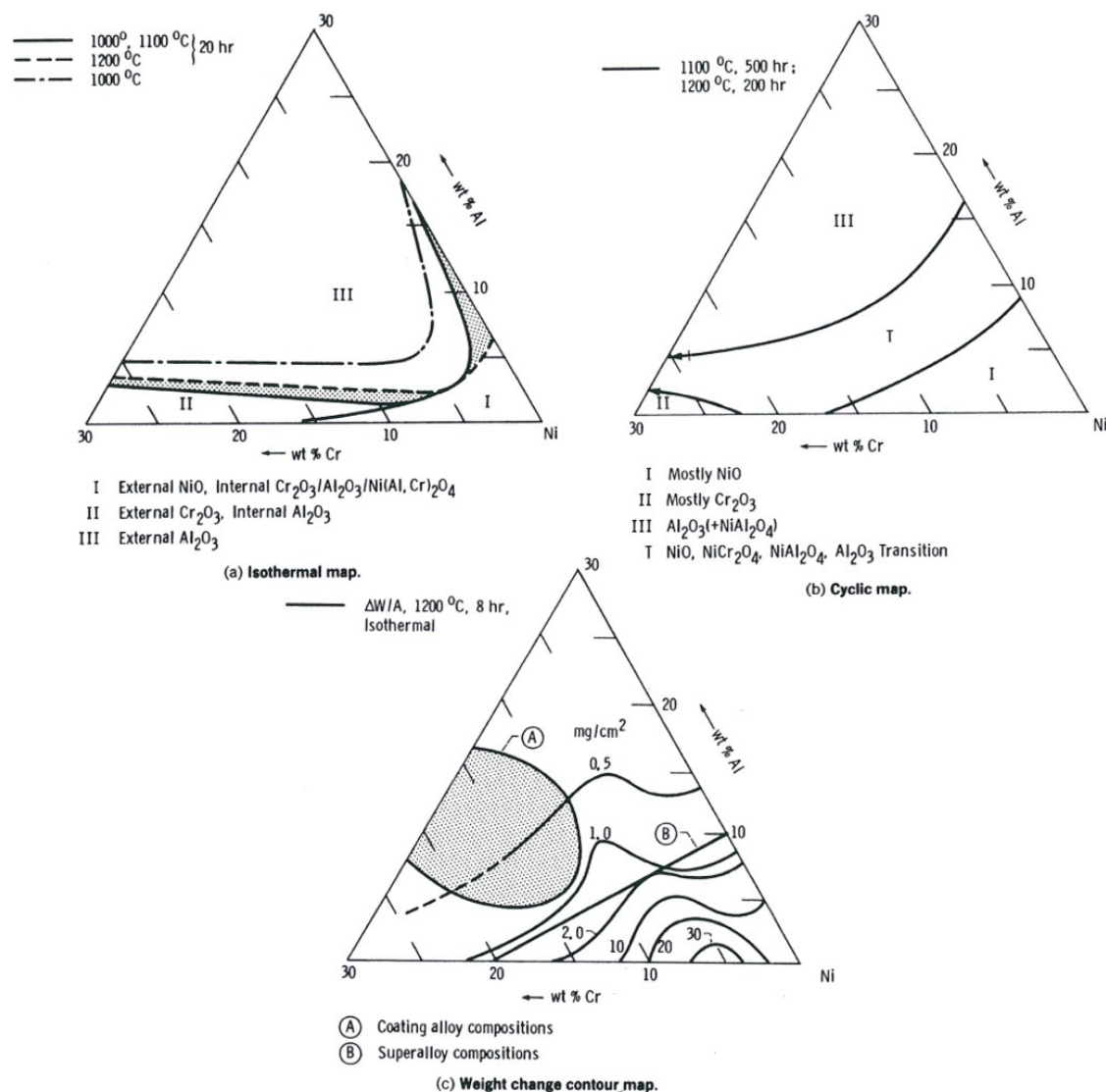


Figure B.8: Compositional effects on the oxidation behaviour of ternary Ni–Cr–Al alloys in terms of (a) isothermal oxidation, (b) cyclic oxidation, and (c) weight change [805]. Regions which encompass alloys with similar properties are labelled accordingly. The lines delimiting these regions have been traced by Smialek & Meier based on values reported in the literature [853, 857, 858].

chromium cannot oxidise internally. Figure B.7(b) illustrates changes in the oxide layer composition with exposure time for a group III Ni–Cr–Al alloy with 10 wt.% chromium and 5 wt.% aluminium.

It must be noted that the beneficial influence of chromium has not yet been fully understood [832, 859]. Initially, this effect was described in purely thermodynamic terms as ‘gettering’ and it was proposed that the chromia scale reduces the activity of oxygen and prevents the internal oxidation of aluminium [860]. However, further

work showed that interactions in the Ni–Cr–Al system are more complex and suggested that chromium both reduces the solubility of oxygen in an alloy and alters the concentration profiles in the subsurface region [853, 859, 861, 862]. As such, a more appropriate term is a ‘third element effect’ [12].

B.2.3 Single-Crystal Superalloys

The oxidation behaviour of modern superalloys is much more complex than that of binary or ternary model alloys and is markedly influenced by different chemical additions. These lead to the formation of diverse oxidation products including titanium-, tantalum-, and tungsten-rich oxides and spinels [496, 637, 839, 863]. Nonetheless, it is instructive to plot the range of commercial cast superalloy compositions presented in Figure 1.3 on the oxide map reported by Wallwork and Hed [857] for isothermal oxidation at 1000 °C. The proposed design space for new IGT materials is highlighted by a green triangle. Higher-generation, rhenium-containing alloys possess (1) high aluminium contents to precipitate high γ' volume fractions and (2) low chromium levels to accommodate increased levels of slow-diffusing refractory metals, while reducing the probability of TCP phase precipitation. This leads to a transition from a group II to a group III oxidation behaviour. However, latest-generation materials retain so little chromium that only a weak ‘third element effect’ is observed and protective scales will barely form [12, 849].

First-generation single-crystal compositions including PWA1480 [864], René N4 [194], SRR99 [865], CMSX-2 [866], and CMSX-3 [866], along with second-generation alloys PWA1484 [867, 868], René N5, and CMSX-4 [866, 869] were all found to exhibit sufficient oxidation resistance for turbine blade applications. An example of the complex layers observed for CMSX-4 at different temperatures is shown in Figure B.10 and it reveals a transition from a group II to a group III behaviour above 1000 °C. Below 900 °C, the γ' phase is insoluble in the matrix, thus limiting the diffusion of aluminium and the formation of an Al_2O_3 scale [866]. Between 900 and 1000 °C, some dissolution is possible, giving rise to a precipitate-denuded zone and a discontinuous alumina layer [869]. Finally, at higher temperatures, this

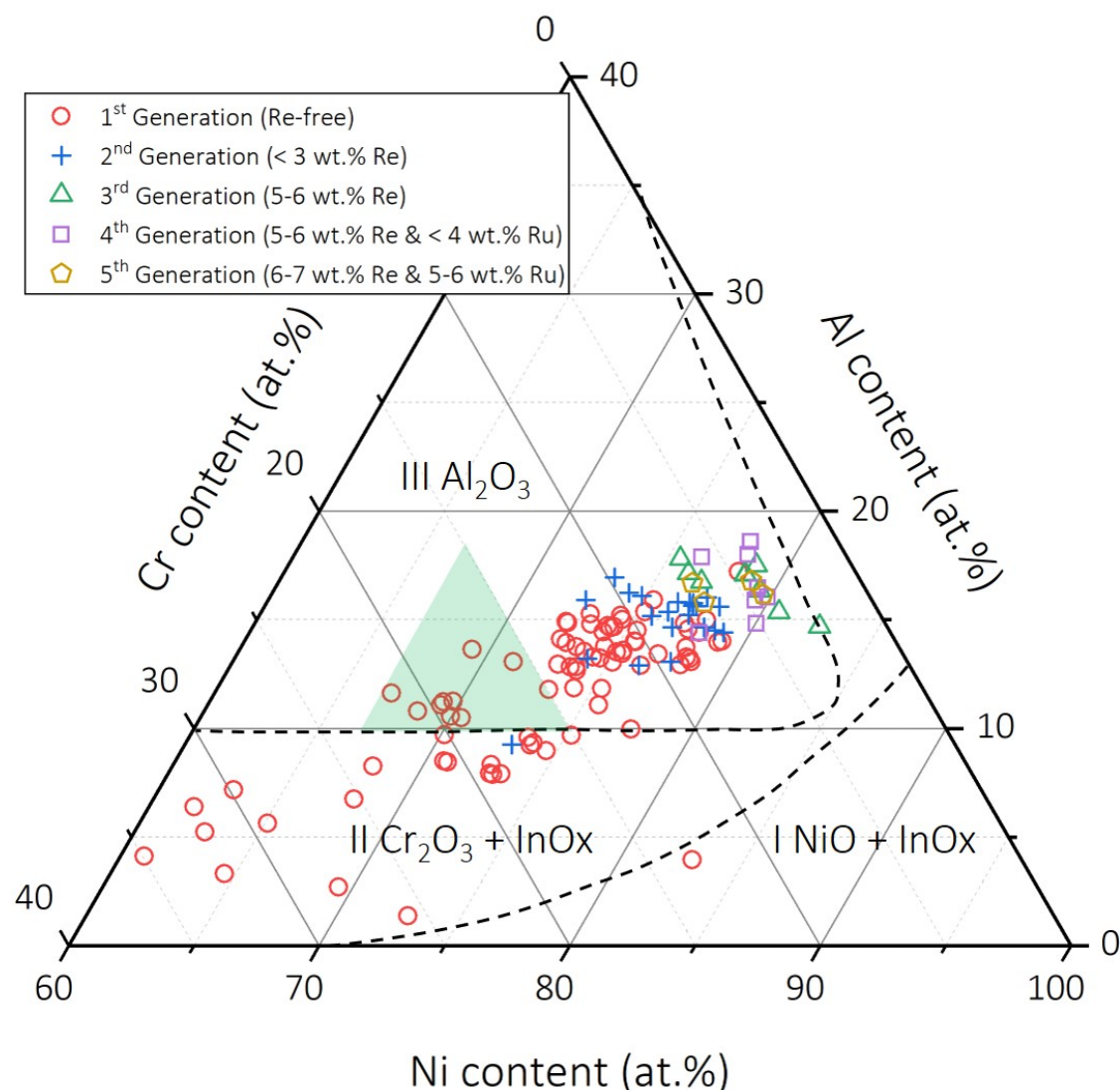


Figure B.9: Ternary Ni–Cr–Al diagram showing the positions of different NBSA compositions presented in Figure 1.3 on the isothermal oxidation map reported by Wallwork and Hed [857]. Based on this simplified treatment, it can be seen that commercial superalloys have transitioned over time from a group II to a group III behaviour. The proposed design space for new IGT superalloys is represented by a green triangle and lies just above the transition line from Cr_2O_3 to Al_2O_3 formation.

subscale becomes continuous [869] and acts as a diffusion barrier for the oxidation of other elements [865]. These changes give rise to an unexpected trend of lower mass gain at higher temperatures [863].

Third-, fourth-, and fifth-generation single-crystal compositions including CMSX-10 [870], TMS-75, TMS-138A, TMS-173 [869, 871], and UCSX2 [872] generally exhibit poor oxidation resistance and form thick NiO and spinel layers instead of

alumina scales. The necessity of adding protective coatings and the risk of component damage should these coatings fail locally has provided an incentive for the design of new materials with balanced chromium contents. Recently developed superalloys like René N6 [219], DD32 [873, 874], TMS-196 [227, 869], and TMS-238 [229] were designed to combine good creep strength and oxidation resistance and contain around 4.5 wt.% chromium, which enables Al_2O_3 formation at service temperatures.

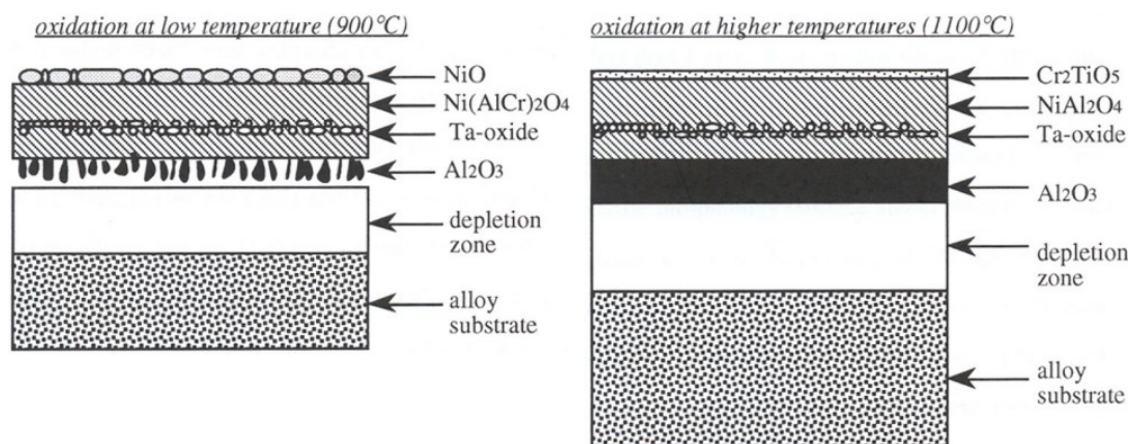


Figure B.10: Schematic of the oxide layers and sub-surface γ' -denuded zones forming on the single-crystal superalloy CMSX-4 at different temperatures [865]. A transition from a group II to a group III behaviour takes place above 1000 °C.

B.3 Extrapolation of Oxidation Parameters

Measurements of oxidation kinetics are commonly based on three parameters — (1) the amount of metal consumed, assessed by observing the weight loss of the specimen or the residual metal thickness, (2) the amount of oxygen consumed, and (3) the amount of oxide produced [839]. Of these, only methods (2) and (3) offer the possibility of obtaining continuous results through weight gain or oxygen consumption measurements. Conversely, for method (1) tests must be interrupted, thus requiring a larger number of samples when assessing long-term isothermal behaviour. The present review focuses only on weight gain measurements during isothermal tests, as these are more accessible than gas consumption monitoring [839]. Typical experimental setups for this approach, including the simpler spring balance and the more accurate automatic recording balance, have been reviewed by Birks

et al. [839]. An automatic balance with high sensitivity and reduced noise levels is recommended for tests aiming at a fundamental description of oxidation mechanisms.

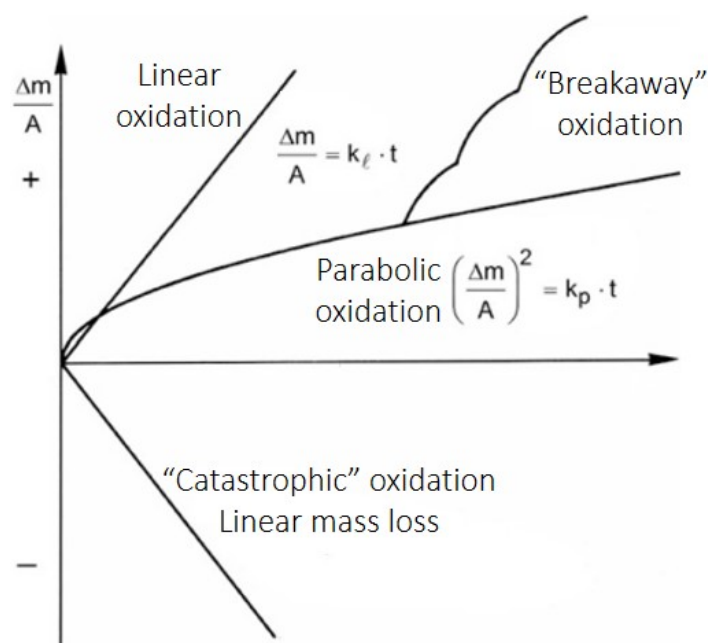


Figure B.11: Idealised kinetic oxidation rates for the cases of linear and parabolic growth, adapted from reference [239]. The special case of breakaway oxidation is also illustrated, wherein oxide scale formation and spallation alternate. The case of linear mass loss through catastrophic oxidation can be normally excluded for Al_2O_3 , however, it can occur for Cr_2O_3 at temperatures above around 1000 °C.

Weight gain experiments help reveal the rate law governing the growth of an oxide scale over time, as shown in Figure B.11. The most important types are the linear, parabolic, and logarithmic laws, and their characteristics and theoretical basis have been discussed at length by Birks et al. [839]. Logarithmic growth is observed at low temperatures, normally below 500 °C, while linear oxidation is only observed for highly oxidising metals like tantalum or niobium. Figure B.11 presents two additional special cases. The first is breakaway oxidation, wherein growing oxide scales fail periodically and lead to direct contact of the oxidising atmosphere and the metal substrate. The second is catastrophic linear mass loss, which occurs when transformation reactions to volatile products take place, as is the case for molybdenum oxides or for chromia scales at high temperatures. The critical rate law in the context of protective scales for gas turbine materials is

B	A	k'_p (cm ² s ⁻¹)	k_p (g ² cm ⁻⁴ s ⁻¹)	k_c (cm ² s ⁻¹)	k_r (eq. cm ⁻¹ s ⁻¹)
k'_p (cm ² s ⁻¹)	1	1	$2 \left(\frac{M_X}{\bar{V}Z_X} \right)^2$	$\left(\frac{\bar{V}_M}{\bar{V}} \right)^2$	$\frac{1}{\bar{V}}$
k_p (g ² cm ⁻⁴ s ⁻¹)	$\frac{1}{2} \frac{(\bar{V}Z_X)^2}{M_X^2}$	$\frac{1}{2} \left(\frac{\bar{V}}{\bar{V}_M} \right)^2$	1	$\frac{1}{2} \left(\frac{\bar{V}_M Z_X}{M_X} \right)^2$	$\frac{\bar{V}}{2} \left(\frac{Z_X}{M_X} \right)^2$
k_c (cm ² s ⁻¹)	$\left(\frac{\bar{V}}{\bar{V}_M} \right)^2$	$2 \left(\frac{M_X}{\bar{V}Z_X} \right)^2$	1	1	$\frac{\bar{V}}{\bar{V}_M^2}$
k_r (eq. cm ⁻¹ s ⁻¹)	$\bar{V}$	$\frac{2}{\bar{V}} \left(\frac{M_X}{Z_X} \right)^2$	$\frac{\bar{V}_M^2}{\bar{V}}$	$\frac{\bar{V}_M^2}{\bar{V}}$	1

Table B.1: Relationships between variously defined parabolic oxidation rate constants for an oxide scale with stoichiometry $M_\nu X$, adapted from reference [839]. Relating factors F are given according to $A = F \times B$, with A listed horizontally and B vertically. Symbols have the following meaning: $\bar{V}$ is the equivalent volume of oxide scale (cm³ eq.⁻¹), $\bar{V}_M$ is the equivalent volume of metal (cm³ eq.⁻¹), M_X is the atomic mass of non-metal X (oxygen, sulphur, etc.), and Z_X is the valency of X (eq. g-atom X⁻¹).

parabolic growth [805]. It implies that oxidation processes become more sluggish with time, but never stop. For a specimen with a total surface area A , the mass change Δm after an exposure time t can be obtained as:

$$\left(\frac{\Delta m}{A} \right)^2 = k_p t \quad (\text{B.1})$$

with k_p as the key rate-governing parameter for parabolic oxide growth. The derivation of Equation (B.1) by Wagner [875] is based on a simplified oxidation process. It is assumed that the oxide layer is a compact and perfectly adherent scale, that the oxidation rate is controlled by the migration of ions or electrons across the scale, and that thermodynamic equilibrium is established at the oxide/gas and metal/oxide interfaces, as well as locally throughout the scale [805]. In reality, however, one or several of these assumptions will not be fully satisfied, and, especially during initial stages of oxidation, scale growth mechanisms can differ substantially from idealised ones.

Several amended relations have been proposed in order to capture further degradation effects such as volatilisation or thermal cycling [832, 876]. Furthermore, Monceau and Pieraggi [877] proposed a novel method for calculating variations of k_p throughout the duration of a test, whereas the singular values cited in the literature are normally obtained from steady-state equilibrium regimes, in which

the mass gain curve has substantially shallowed in gradient. As shown in Table B.1, k_p can also be expressed in terms of rate coefficients for the oxide scale thickness, k'_p , for metal surface recession, k_c , or for the growth rate of an oxide scale unit, k_r [239, 839]. Conversions can be made readily using the factors within the table. Results from different oxidation studies must be compared with care, as there are no 'official' physical units for k_p or similar coefficients, and this choice is left to the discretion of the respective authors.

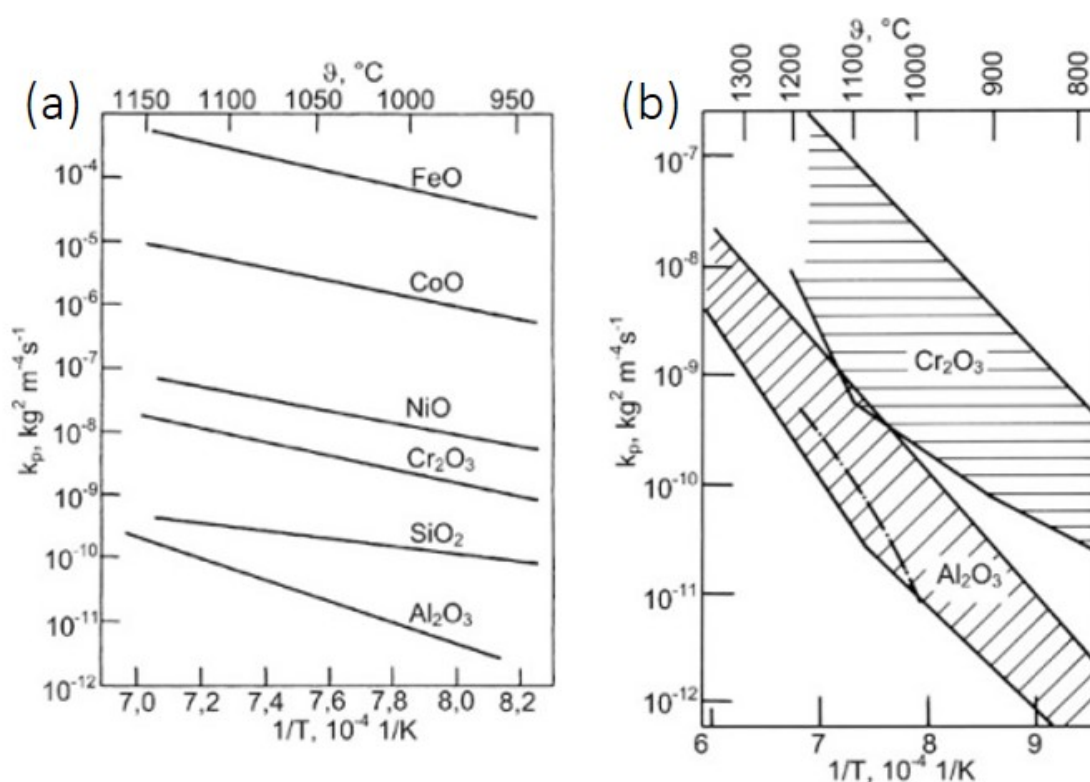


Figure B.12: (a) Comparison of changes in k_p with temperature for selected oxide scales [805]. (b) Similar plot to (a) showing the scatter in experimental data obtained for chromia- and alumina-forming alloys [878]. Results in (b) are based on extensive oxidation studies of commercial iron-, cobalt-, and nickel-based alloys.

As k_p is directly proportional to the diffusivity of rate-controlling ions, its dependence on temperature can be captured well by an Arrhenius plot, as shown for several industrially relevant oxides in Figure B.12(a). Once again, the importance of Al_2O_3 becomes clear, as it exhibits the lowest rate values across the entire temperature range. Nonetheless, as illustrated in Figure B.12(b), commercial alloys exhibit a broad range of parabolic growth rate constants, as these are affected

by additional chemical and structural factors pertaining to both the oxide scale and the alloy substrate [878].

B.4 Design for Oxidation

As expressed by the broad bands in Figure B.12(b), k_p values for engineering alloys can vary by up to two orders of magnitude for both chromia- and alumina-formers, and will depend on complex interactions between different chemical additions [805]. A comparison of rate constants for several conventionally cast compositions in Figure B.13(a) indicates that these fall between the rates for pure Cr_2O_3 growth in Ni-30Cr and pure Al_2O_3 growth in Ni-14Cr-12Al. No clear trends can be discerned based solely on the Al/Cr ratios shown in the brackets. Comparing the relative oxidation resistance of single-crystal alloys is even more complicated, as shown in Figure B.13(b). These materials contain a wider range of elements and can exhibit anomalous trends of their Arrhenius plots due to transitions between dominant steady-state oxide scales at different temperatures. Nonetheless, several design guidelines can be gleaned from experimental studies of oxidation damage.

B.4.1 Major Element Effects

Analyses of precise compositional effects on oxidation mechanisms are scarce in comparison to similar work on high-temperature mechanical properties. The most extensive studies were carried out on correlating chemical variations with cyclic oxidation performance [804, 871, 884]. It is acknowledged that cyclic oxidation experiments, which are periodically interrupted after pre-determined cycle lengths, cannot be directly compared to isothermal oxidation behaviour. Cyclic tests are more arduous due to the combined effects of spallation, re-oxidation, and solute depletion [805, 849], which makes a fundamental mechanistic understanding very difficult. Nonetheless, some noteworthy compositional trends emerge, as observed in Figures B.14 and B.15.

Cyclic oxidation results obtained by Barrett et al. [804] for nearly 100 different conventionally cast compositions exposed at 1100 and 1150 °C for 100 h with 1 h

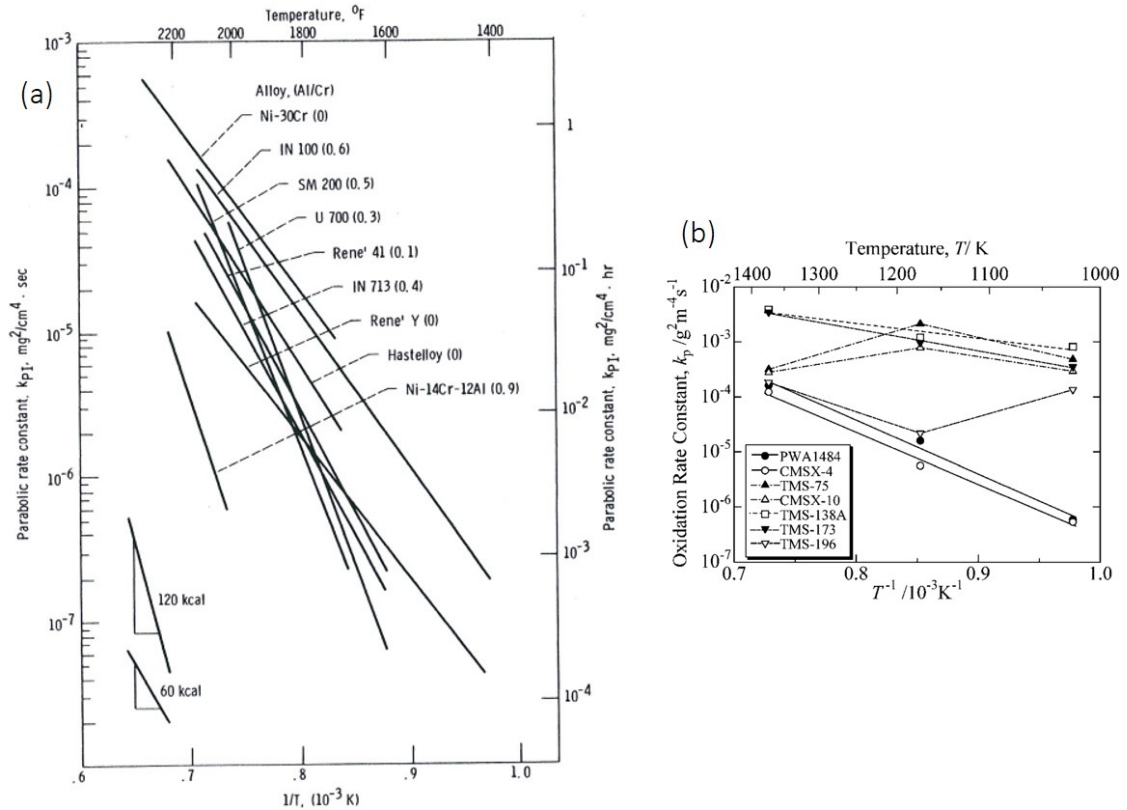


Figure B.13: Arrhenius plots showing the temperature dependence of the parabolic rate constant k_p for (a) different polycrystalline commercial superalloys [879–883] and (b) modern second- to fourth-generation single-crystal superalloys [869].

cycles are presented in Figure B.14(a). The level of oxidation damage is captured by an attack parameter, k_A , which takes into account both the growth and the spallation of scales. Several conclusions can be drawn based on these three-dimensional oxidation charts [805]. First, a high aluminium content of 6 wt.% and above is the most important factor for good performance. Second, a high level of chromium on the order of 15 wt.% is not mandatory for optimal results and it cannot compensate for low aluminium levels of 2 to 4 wt.%. Third, higher tantalum and lower titanium contents can be associated with improved performance. However, tantalum also cannot fully compensate for lower aluminium additions. The influence of other refractory metals was not entirely clear, however, it appears that higher molybdenum and tungsten and lower niobium levels are beneficial [804].

Smialek & Meier [805] carried out a similar ranking analysis of about 20 commercial superalloys, illustrated in Figure B.14(b). While the lack of systematic

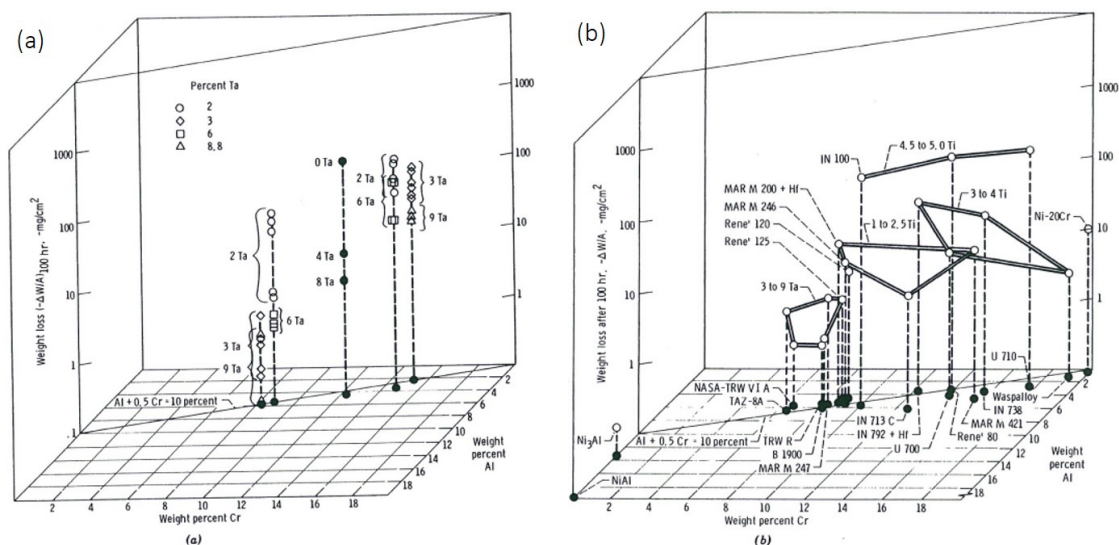


Figure B.14: Multicomponent oxidation maps showing the influence of aluminium, chromium, tantalum, and titanium levels on cyclic oxidation resistance at 1100 and 1150 °C for (a) about 100 model alloys [804] and (b) around 20 commercial materials [805].

variations makes it more challenging to isolate and identify compositional effects, similar broad trends emerge. Alloys with increased oxidation resistance contain relatively high levels of aluminium and tantalum and low titanium. The Al/Cr ratio does not exhibit a clear influence on cyclic oxidation performance; alloys with more aluminium perform the best irrespective of chromium content. The observed beneficial effects of lower titanium and higher tantalum levels are in reasonable agreement with other reports from the literature [802, 803, 806, 885]. However, the proposed mechanisms by which these elements affect oxidation resistance differ between studies and may indeed depend on the overall chemical composition and on testing conditions. A further study on commercial materials with different levels of cobalt showed that increasing its content from around 5 to 20 wt.% decreases scaling resistance due to the growth of highly defective cobalt oxides [886].

A recent study revisited the cyclic oxidation databases compiled by Barrett et al. and Smialek & Meier and focused on a thorough statistical analysis to uncover compositional effects [887]. Most of the aforementioned conclusions are confirmed, as observed in Figure B.15. Aluminium shows the strongest beneficial effect, followed by tantalum, and these two elements also exhibit a clear positive synergistic effect,

though the exact mechanisms involved remain unclear. Titanium and niobium are especially detrimental to oxidation resistance and further show a strong negative synergy, perhaps due to the formation of a combined TiNbO_4 scale. As shown in the surface plots of Figure B.15(c) and (d), the negative impact of tungsten and niobium can be significantly reduced if sufficient aluminium and tantalum are present. Tungsten appears to be only moderately detrimental, while molybdenum and cobalt exhibit negligible effects. Finally, this study could relate the measured weight changes and the observed compositional effects to a ratio of beneficial to detrimental oxide scales, as measured by quantitative X-ray diffraction [887]. Beneficial scales include $\alpha\text{-Al}_2\text{O}_3$, $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ spinel, and NiTa_2O_6 tri-rutile, while the detrimental ones for high-temperature cyclic oxidation are $\alpha\text{-Cr}_2\text{O}_3$, NiCr_2O_4 spinel, NiO , and NiTiO_3 .

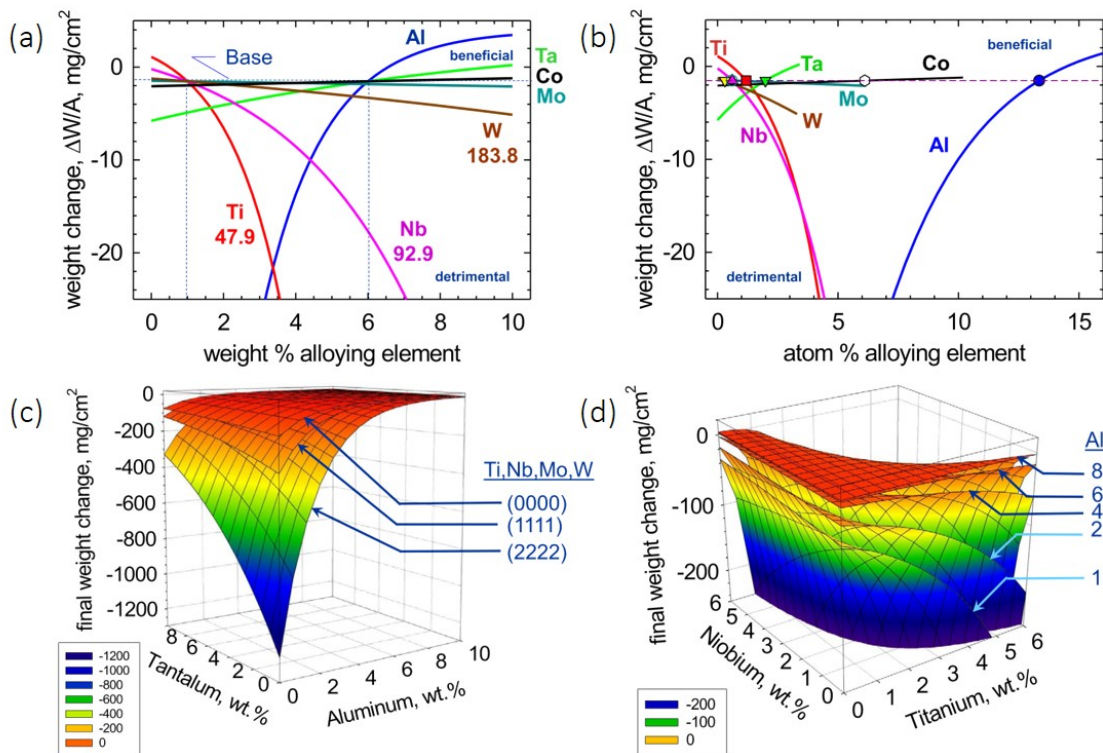


Figure B.15: Total specimen weight change after 200 h exposures at 1100 °C with 1 h cycles, based on multiple linear regression modelling of cyclic oxidation experiments [887]. Predictions are shown as a function of composition changes in (a) wt.% and (b) at.%. Synergistic effects of (c) beneficial aluminium and tantalum and (d) detrimental titanium and niobium additions in different base compositions are further identified.

Less attention has been given to single-crystal compositions, which have been primarily developed and optimised for high-temperature mechanical strength. A

recent comparative study of the cyclic oxidation performance of first- to fourth-generation single-crystal superalloys exposed at 1100 °C with 1 h cycles confirms that earlier variants possess superior oxidation resistance, as observed in Figure B.16(a). Both tantalum and hafnium are reported to have a beneficial effect by improving scale adhesion and by forming stable oxide particles in the surface layer. Conversely, rhenium and ruthenium degrade oxidation resistance due to the vaporisation of their respective oxides [871]. These results are in agreement with isothermal and cyclic oxidation tests carried out by Moniruzzaman et al. [888] on model Ni–Cr–Al–Ti–Re alloys with different contents of aluminium and rhenium. It was reported that at lower aluminium levels, rhenium has a detrimental effect by limiting the formation of dense alumina scales and by producing volatile rhenium-rich oxides.

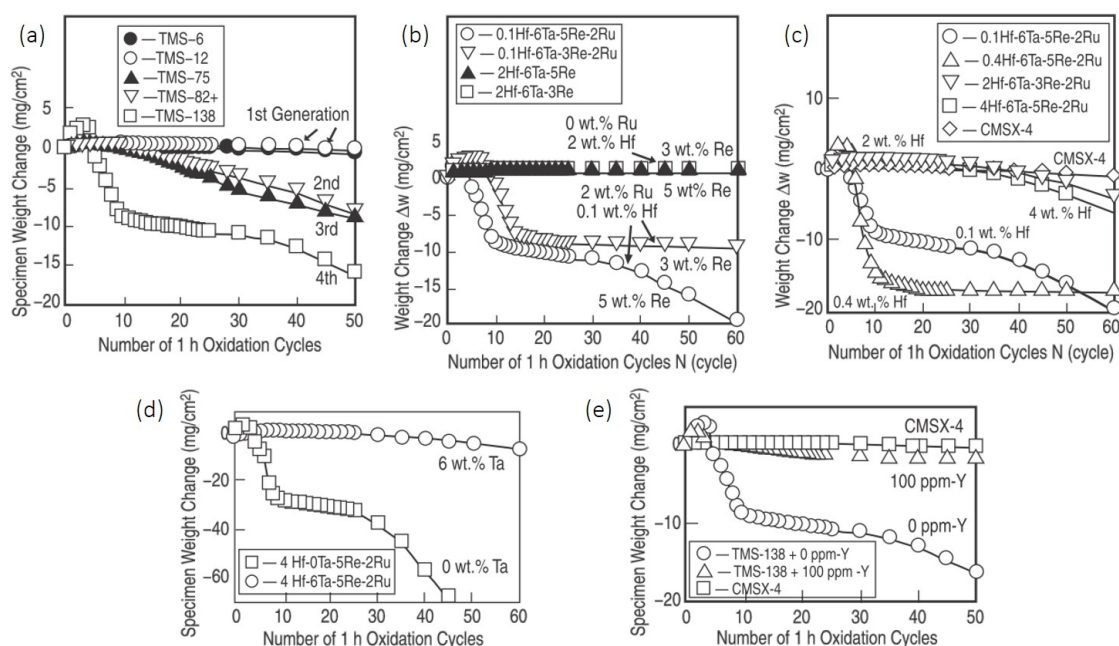


Figure B.16: (a) Comparison of the cyclic oxidation performance of first- to fourth-generation single-crystal superalloys at 1100 °C. (b)-(e) Effects of major (tantalum, rhenium, ruthenium) and minor (hafnium, yttrium) element additions on the cyclic oxidation resistance of fourth-generation superalloys [871].

Finally, it is worth noting that compositional trade-offs have been found not just for mechanical and oxidation properties at high temperatures, but also for oxidation and hot corrosion resistance. Murata et al. [490] reported a nearly inverse relation between the material weight loss measured during continuous, isothermal

oxidation tests and that observed after burner-rig tests for a set of trial IGT alloys. It was found that a high Al/Ti ratio and low tungsten levels are beneficial for oxidation resistance, but significantly decrease hot corrosion properties.

B.4.2 Minor Element Effects

A much clearer view emerges for the role played by minor elements in superalloys, as these are often added specifically to impart higher oxidation and/or hot corrosion resistance. The most prominent example is the addition of rare-earth elements including cerium, lanthanum, scandium, and yttrium [12, 117, 805, 889, 890]. Of these, yttrium is commonly considered to be most beneficial for oxidation resistance [864, 871, 891–893], although optimal combinations and levels of rare earths have been shown to depend on the alloy in question and on oxidation conditions. For example, for alloy CMSX-4 co-doping with yttrium and lanthanum yielded better results than adding these elements separately [209], as illustrated in Figure B.17. Other oxygen-active minor additions including zirconium [894–896] and hafnium [789–791, 864] can also provide significant improvements.

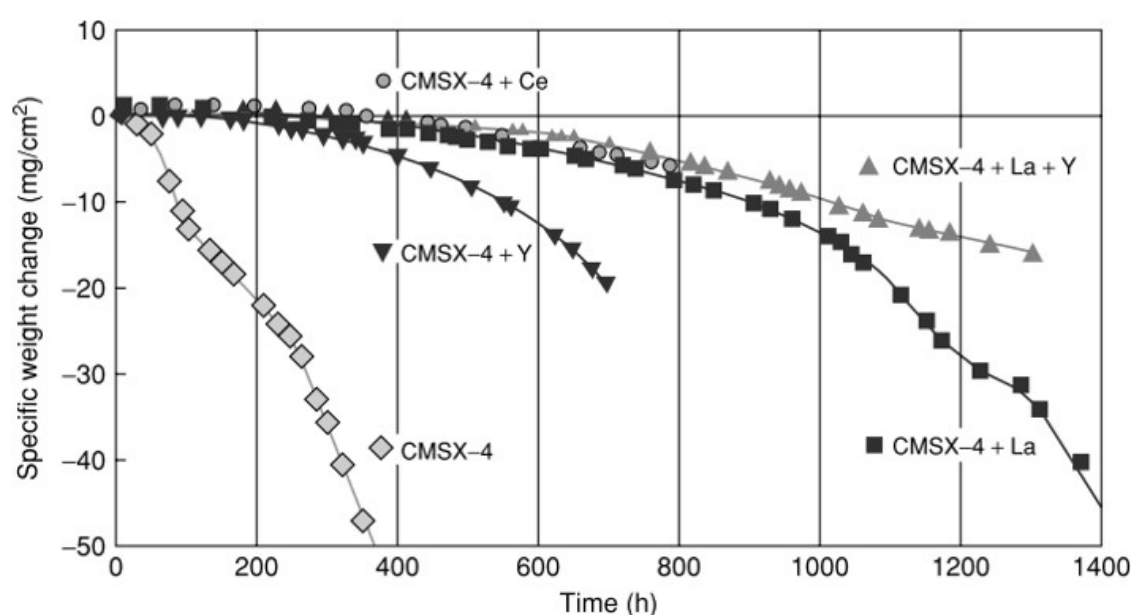


Figure B.17: Effects of rare-earth element additions on the cyclic oxidation resistance of CMSX-4 at 1093 °C [209].

This group of so-called ‘reactive elements’ (RE) has been shown to confer an improved adherence of oxide scales by means of several mechanisms, which have been critically reviewed and discussed in the literature [889, 897–901]. First, oxide intrusions, commonly denoted as ‘pegs’, can mechanically ‘anchor’ the oxide scale to the substrate [889]. Second, RE may act as vacancy sinks and prevent vacancy coalescence at the substrate/scale interface [902]. Third, they may also enhance scale plasticity by promoting finer Al_2O_3 grains and stress relief through Coble creep mechanisms [903]. Fourth, RE have been suggested to improve the cohesive energy between the metal substrate and the oxide scale and to reduce oxide growth stresses [889, 904]. As discussed by Smialek & Meier [805], it appears that all four mechanisms have a partial contribution towards improving scale adherence and no single model can be regarded as definitive. Furthermore, these authors point out a fifth mechanism which has been increasingly accepted and highlighted in recent years, namely a ‘gettering’ effect of RE which counteracts the deleterious effects of sulphur [905, 906]. RE are potent sulphide-formers and can therefore effectively bind the sulphur that would have otherwise decreased scale adherence by segregating to the metal/oxide interface and breaking the strong van der Waals bonds between them [899, 907]. Nonetheless, positive effects have also been observed in materials containing very little sulphur, suggesting the aforementioned four models will still play a role [908].

An important caveat is that RE additions must be carefully controlled to yield optimal oxidation resistance, as summarised schematically in Figure B.18 using results for model ternary Ni–Cr–Al and Co–Cr–Al alloys [894, 909, 910]. Low concentrations below 100 ppm reduce compressive growth stresses and buckling effects within the scale. This is beneficial for isothermal oxidation, but it does not impact scale adherence properties and cyclic resistance. An ideal regime is found at around 0.1 wt.% RE, as isothermal growth rates remain minimal and oxide pegs improve mechanical scale adherence. Finally, levels above 0.5 wt.% are detrimental for all oxidation tests, as the solubility limits for the RE dopants are exceeded, which causes non-protective RE-rich oxides to form [890, 911]. It should be noted

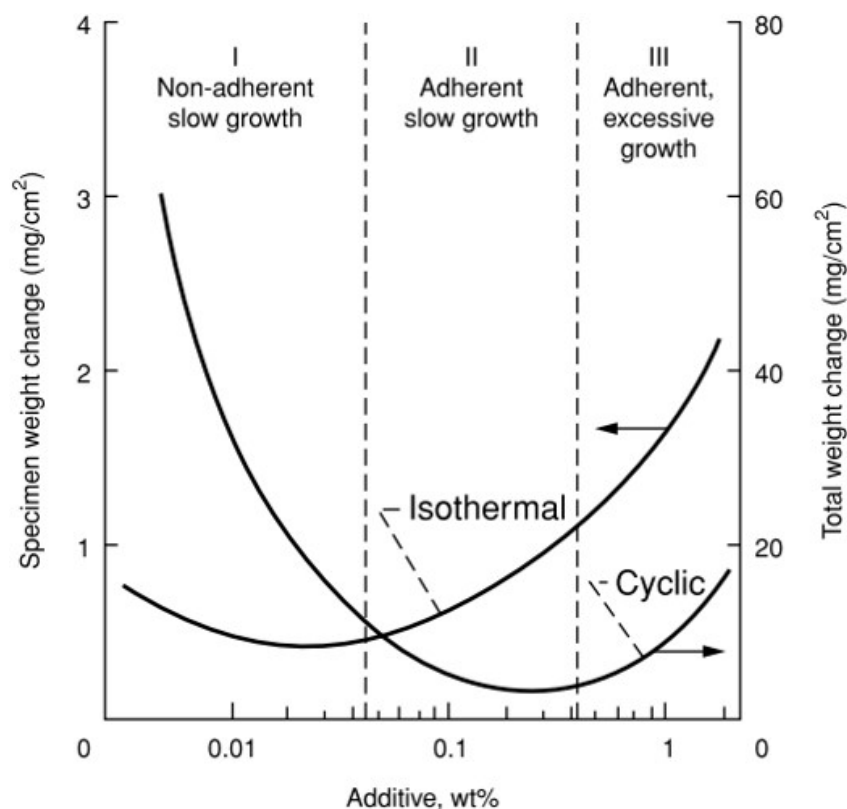


Figure B.18: Schematic comparison of the effects of zirconium, hafnium, and yttrium dopants on the isothermal and cyclic oxidation resistances of Ni–Cr–Al and Co–Cr–Al alloys [894, 909, 910], adapted from reference [805].

that over-doping with RE can also decrease mechanical properties, owing to the formation of low-melting Ni–Ni₅M eutectics, where M includes yttrium, cerium, and lanthanum [912–916]. A promising approach towards avoiding such detrimental effects is co-doping with more than one RE [890, 900], since this will reduce the probability that the solubility limit of any one RE will be exceeded. Furthermore, it has been suggested that co-doping could provide an overall improved oxidation resistance since individual RE may interact with tramp elements in different ways and may segregate at different types of GB [890].

Finally, a special mention must be made for silicon, which has been reported to be most beneficial for oxidation resistance of all the elements with an oxygen reactivity intermediate to aluminium and nickel [805]. A range of studies have reported improvements in both hot corrosion and oxidation resistance caused by silicon additions of up to 1 wt.% [495, 496, 722, 724, 725, 809–811]. These have been

related to an increase in aluminium activity [724] and to the formation of silicon-containing pegs which improve scale adhesion [21]. However, higher silicon contents may affect mechanical properties and may promote the formation of deleterious TCP phases [240, 495, 722–725]. As such, an optimal level of around 0.25 wt.% has been recently suggested for IGT superalloys [495, 496].

Bernard of Chartres used to compare us to puny dwarfs perched on the shoulders of giants. He pointed out that we see more and farther than our predecessors, not because we have keener vision or greater height, but because we are lifted up and borne aloft on their gigantic stature.

— John of Salisbury, “The Metalogicon”

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