

MICROMECHANICAL TESTING OF OXIDIZED GRAIN BOUNDARIES



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To my family

PREFACE

This dissertation is the result of my own work carried out in the Department of Materials, University of Oxford, under the supervision of Prof. Sergio Lozano-Perez, Dr. David Armstrong and Dr. Edmund Tarleton. No part of this dissertation has been previously submitted for a degree at this or any other university. Work carried out in collaboration with other authors is dully acknowledged in the text. A list of references is given at the end of the dissertation.

Some of the work and content in the dissertation has been reported in the following conferences and publications:

CONFERENCES

Oral presentations:

Recent insights in the deformation and fracture of oxidized grain boundaries in austenitic alloys; at 17th Int. Conference on Environmental Degradations of Materials in Nuclear Power Systems-Water Reactors, Ottawa, CA (2015)

Understanding how oxidized grain boundaries fail: A combined experimental and crystal plasticity finite element approach; at 7th International Conference on Multiscale Materials Modeling (MMM14), Berkeley, US (2014)

Stress Corrosion Cracking: Micromechanical testing of oxidized grain boundaries; at MAI-SN meeting at EDF Research and Development (closed meeting; invitation only), Écuellen, FR (2014)

Understanding the failure of oxidized grain boundaries; at 9th International Congress on the Microscopy of Oxidation, Nottingham, UK (2014)

PUBLICATIONS

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Judith Dohr, Edmund Tarleton, David E.J. Armstrong, Thierry Couvant, Sergio Lozano-Perez. *Recent insights in the deformation and fracture of oxidized grain boundaries in austenitic alloys: A synergistic experimental and finite element study*. In proceedings of the 17th international Conference on Environmental Degradations of Materials in Nuclear Power Systems-Water Reactors, Ottawa, CA (2015), ISBN 978-1-926773-19-3

Sergio Lozano-Perez, **Judith Dohr**, Martina Meisnar, Karen Kruska. *SCC in PWRs: learning from a bottom-up approach*. Metallurgical and Materials Transactions E., Volume 1a, Issue 2 (2014) pp. 194-210

Sergio Lozano-Perez, Martina Meisnar, **Judith Dohr**, Karen Kruska. *Reviewing the internal oxidation mechanism as a plausible explanation for SCC in PWR primary water*. In proceedings of the 16th international Conference on Environmental Degradations of Materials in Nuclear Power Systems-Water Reactors, Asheville, North Carolina, USA (2013)

ABSTRACT

Primary water stress corrosion cracking (SCC) of metals in pressurized water reactors (PWRs) is known to be one of the most challenging and cost intensive modes of failure in the nuclear industry. Even though it is known that cracking in Ni-base alloys proceeds mainly intergranular (IG), the initiation and propagation of cracks in ductile metals are not yet understood and a much-desired accurate prediction of SCC related failure seems unobtainable.

In this thesis, a combination of microcantilever fracture experiments, scanning electron- (SEM) and transmission electron microscopy (TEM) techniques was employed to study and compare the failure of oxidized grain boundaries of Ni-base Alloy 600 with high and low intergranular carbide coverage and different sample history.

A new technique for lifting-out whole cantilevers after testing and for performing 3D focussed ion beam sequencing (3D FIB-SEM) while preserving a thin central region of the cantilever for further TEM sample preparation was developed and is presented.

In lieu with recent efforts of the main project sponsor Électricité de France (EDF) to build a predictive model for IGSCC based on localized/microscopic information, one of the main objectives was the extraction of the stress at failure of individual oxidized GBs. Supported by finite element simulations, microcantilever fracture tests revealed that surface oxides on top of individual GBs have the capability to alter the mechanical response by delaying/suppressing the onset of failure. An overestimation of the failure stress (> 230 MPa) was observed, proving that the presence of the surface oxide on top of the test structures cannot be neglected. The failure stress on both samples, tested without influence of the surface oxide, was found to cover a range of 300 – 600 MPa,

which agreed well with finite element simulations of the tests and further demonstrates the reliability of the obtained data.

The second objective was to gain a better understanding of the observed fracture behaviour and the role of local microstructure. Using the gathered microscopy data, it was found that the crack clearly favours a progression along the IG oxide-metal interface in the presence of carbide precipitates. Electron energy loss spectroscopy (EELS) revealed that the observed crack path can be linked to compositional and density variations of the IG oxide. In the presence of carbides the oxide was layered. An oxide close to the stoichiometry of chromia was located at the original GB and next to the carbides. Next to this Cr-rich oxide, Fe-rich mixed spinel oxides of varying composition and density were found. An explanation for density variations based on the possible formation of defective spinel oxides of the type $A^{2+}B^{3+}_2O_4$, due to an unavailability of certain cation species is presented. No clear interface preference was observed in the absence of precipitation, where the IG oxide was found to be thin and often incomplete with Cr-richer oxides preferentially located at the original GB. While these observations were consistent on both samples (high and low carbide coverage), bigger void-like defects were located at the Fe-richer oxide-metal interface of the cold worked sample with high IG carbide precipitation only. These weak spots seemed to be the preferred path for crack propagation on this sample. The sample with low intergranular carbide coverage showed no obvious porosities at this interface but a Cr-depleted region was seen.

Introducing a multi-faceted investigation strategy, supported by finite element simulations, the presented thesis provides the most accurate determination of the failure stress of oxidized GBs on Alloy 600 to date and adds new valuable insights to our understanding of IGSCC and the future prediction of SCC related failures.

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LIST OF ABBREVIATIONS AND ACRONYMS

ALPHABETICAL ORDER

A600	Alloy 600
A690	Alloy 690
ADF	Annular dark field
AIDE	Adsorption-induced dislocation emission
AISM	Adsorption-induced slip mechanism
APT	Atom probe tomography
ATEM	Analytical transmission electron microscopy
BF	Bright field
CGR	Crack growth rate
CPFEM	Crystal plasticity finite element model
CRSS	Critical resolved shear stress
CSLB	Coincidence site lattice boundary
CW	Cold work
CZM	Cohesive zone model
DF	Dark field
DP	Diffraction pattern
EAC	Environmentally assisted cracking
EBSD	Electron backscatter diffraction
EDF	Électricité de France
EDS	Energy dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EELS SI	EELS spectrum imaging
EGBD	Extrinsic grain boundary dislocations
F-D	Force-Displacement
FCC	Face-centred cubic
FEA	Finite element analysis
FEG	Field emission gun
FEM	Finite element method
FIB	Focussed ion beam
FRM	Film rupture model
GB	Grain boundary
GIF	Gatan image filter
GNDs	Geometrically necessary dislocations
HAADF	High-angle annular dark field
HAB	High angle boundary
HAC	Hydrogen assisted cracking

HE	Hydrogen embrittlement
HELP	Hydrogen-enhanced local plasticity
HRTEM	High resolution transmission electron microscopy
IAEA	International atomic energy agency
IG	Intergranular
IGSCC	Intergranular stress corrosion cracking
INSS	Institute of Nuclear Safety Systems
LAB	Low angle boundary
LPSCC	Low potential stress corrosion cracking
MAADF	Medium-angle annular dark field
MAXS	Maximum stress
MLI	Mean Lineal Intercept
MM	Micromanipulator needle
MSA	Multivariate statistical analysis
ND	Normal direction
PWR	Pressurized water reactor
PWSCC	Primary water stress corrosion cracking
RD	Rolling direction
RSS	Resolved shear stress
RT	Room temperature
SCC	Stress corrosion cracking
SDV	Solution dependent state variables
SE	Secondary electron
SEM	Scanning electron microscope
SIMS	Secondary ion mass spectrometry
SIO	Selective internal oxidation
SMM	Surface mobility model
SSDs	Statistically stored dislocations
STEM	Scanning transmission electron microscope
T-EBSD	Transmission electron backscatter diffraction
TD	Transverse direction
TEM	Transmission electron microscopy
TG	Transgranular
TKD	Transmission Kikuchi diffraction
UEL	User-defined element
UMAT	User-defined material

1 INTRODUCTION

In 2014, 440 nuclear reactors spread over 31 countries produced over 11% of the world's electricity.^[1] Despite its dangers, which became once more apparent during the nuclear disaster in Fukushima in 2010, many countries rely on nuclear power to satisfy their ever-increasing electricity needs. The safe and economical use of any nuclear power system, besides depending on a reliable fuel source, relies strongly on the integrity of the materials used for their construction.^[2] Materials used in nuclear reactors, like pressurized water reactors (PWR), which make up the majority of worldwide nuclear systems, are thereby exposed to extreme conditions, including a corrosive environment, high temperatures, pressure and radiation. In the light of the nuclear disaster in Fukushima and its negative effect on public acceptance of new nuclear facilities and projects, one of the main endeavours in the community is to achieve a safe extension of the lifetime of already existing plants to optimize cost-performance of these complex and expensive constructs. In the US over 70 facilities have already been granted an extension from 40 to 60 years of service.^[2] As a consequence, accurate lifetime predictions are needed more than ever. These however rely strongly on a better understanding of material degradation associated with the harsh reactor conditions. Stress corrosion cracking (SCC) is one such form of catastrophic material failure, and has been degrading Nickel-base alloys like Alloy 600 in the primary circuit and secondary circuit of PWRs for decades. To date, despite extensive efforts to better understand and predict the occurrence of the formation of

CHAPTER 1 Introduction

microcracks associated with this localized form of corrosion, the mechanisms governing SCC crack initiation and propagation are not yet understood.^[3] In an effort to enable a more realistic prediction of SCC via engineering models, Électricité de France (EDF) has recently introduced a physical-based model of SCC, which combines extensive experimental efforts (diverse microscopy techniques and mechanical testing) with large-scale simulations, to tackle the challenges faced with predicting SCC.^{[4], [5]} For this, an accurate parameterization of certain local input factors is needed, one of which being the stress necessary to fail oxidized GBs. Building upon the relative young field of micromechanics this thesis, besides giving a comprehensive review of SCC-related literature and research on Alloy 600, provides relevant new insights in SCC crack initiation and propagation by testing oxidized GBs via micromechanical cantilever bend tests. Two Alloy 600 coupons with different microstructural properties - high and low intergranular carbide coverage - oxidized under simulated PWR primary water conditions have been tested. Next a new preparation and investigation strategy, involving 3D FIB-SEM sequencing and conventional (S)TEM investigations is presented. Following the presented multi-technique approach, which was combined with finite element simulations, it was not only possible to extract the desired stress at failure of oxidized GBs for the use in EDF's local SCC model but to also provide new valuable insights about the role of intergranular oxides and sample microstructure in SCC.

2 STRESS CORROSION CRACKING: A REVIEW

The following review is dedicated to stress corrosion cracking (SCC) of Ni-base Alloy 600 exposed to PWR primary water. As such, it focuses on the literature evolving around this specific alloy and environment. Parts of the review have been published in an invited review paper, co-authored by the author of this thesis.^[3]

2.1 Pressurised water reactors: Current issues and challenges

Pressurised Water Reactors (PWRs) are the most common type of nuclear power plants worldwide. According to the latest Nuclear Technology Review provided by the International Atomic Energy Agency (IAEA), 63.2% of the 438 operational nuclear reactors worldwide are PWRs.^[6] In the primary circuit (red circuit in Figure 1) of this reactor type, the heat generated by the fission of atoms in the core heats the pressurized water.^[8] The water in the primary loop is purified water and acts as heat transfer fluid as well as moderator. The primary water is usually heated up to 280 – 345 °C^[7] and kept under a pressure of 150 bar to avoid boiling within the core.^{[8], [9]} The primary water circulates to a steam generator, where the heat from the primary loop is used to transfer heat to a secondary water circuit to generate steam. This steam is then used to generate electricity by turning a steam turbine. One big advantage of PWRs is that the reactive sections of the plant, the reactor and primary loop, are separated from the rest of the system.^[9]

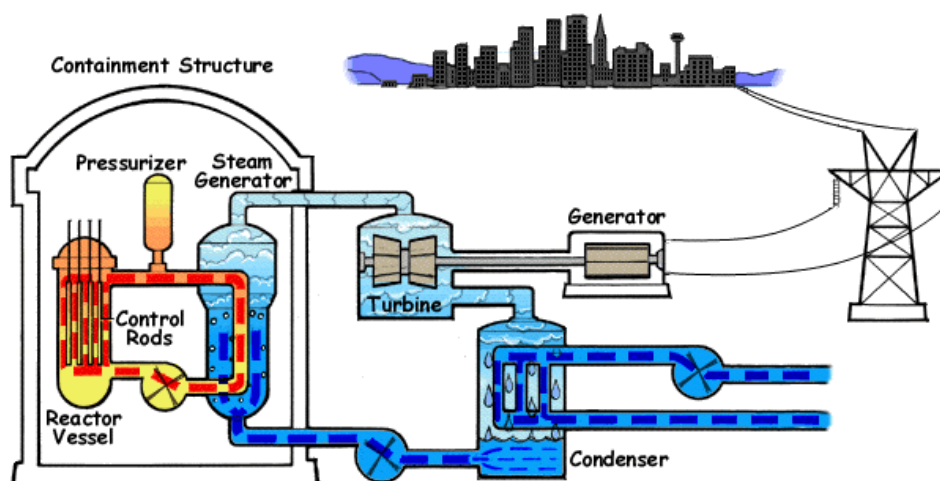


Figure 1: Setup of a Pressurized Water Reactor (PWR).^[10]

Depending on the PWR circuit (primary or secondary), materials used in PWRs are exposed to extreme conditions, including irradiation, high temperatures, pressures and corrosion. Consequently, the PWR environment poses many challenges for its structural materials and it is no surprise that they are susceptible to material related failures, caused by for instance irradiation-induced hardening and environmentally assisted forms of failure, like SCC. Incidents like the failure of the David-Besse PWR plant in 2002, which led to an undetected SCC-caused leakage of water and left behind a football-sized corrosion pit (see Figure 2) highlight the fact that SCC is hard to detect and predict.^[11] It is a major concern for the nuclear industry because associated issues are not only expensive but pose a threat to the health and safety of nature and our society. Consequently, studying and predicting SCC behaviour of structural materials used for key components of PWRs (*e.g.* zirconium, steel and Ni-base alloys) is a prime interest to the nuclear industry to ensure a safe and economic operation of nuclear plants. The following work is concerned with Ni-base Alloy 600 used in the primary circuit of the PWR and its failure via stress corrosion cracking.



Figure 2: Top-view picture of the leakage and hole in the David-Besse PWR plant in Ohio.^[11]

2.2 Alloy 600

The material investigated in this project is Alloy 600 (A600), also called Inconel 600. The typical composition of this austenitic Ni-base alloy is shown in Table 1. A600, which has a face-centered cubic (FCC) structure, is known for its good mechanical properties, strength and toughness throughout a range of temperatures (from cryogenic to above 1095 °C) and also for its high ductility, good workability and resistance to corrosion and oxidation ^[12], see Table 2. As such A600 is of particular interest to the nuclear industry, which uses A600 in many key components in commercial power plants (*e.g.* steam generator tubes, anti-vibration bars and control rod driving mechanisms ^{[11], [13] - [16]}). In the case of PWRs, which use H₂O as coolant and moderator, this means A600 is permanently exposed to an environment that promotes SCC at temperatures between ca. 280 °C and 350 °C.^[15] Figure 3 shows the areas of applications for A600 in the PWR primary system. Contrary to its otherwise good

CHAPTER 2 Stress corrosion cracking: a review

properties, A600, like the rest of the Ni-base alloy family, is known to be susceptible to SCC since 1959.^{[14], [16], [18] - [21]} Today, new alloys, like Alloy 690 or Alloy 800, are replacing A600 in the newer nuclear plants due to their superior resistance to SCC. Nonetheless, A600 is still in use in many of the older plants and in order to better understand, predict and control the crack initiation and propagation of SCC of Ni-base alloys in the PWR primary side at the micro- and nano-scale and to ensure an elongated lifetime of the plants, the nuclear industry aims to gather as many details about the internal oxidation and failure mechanisms of A600 as possible.

CHEMICAL COMPOSITION (WT.%)	
Nickel (+ Cobalt)	72 min
Chromium	14 - 17
Iron Fe	6-10
Carbon	0.15 max
Manganese	1 max
Sulfur	0.015 max
Silicon	0.5 max
Copper	0.5 max

Table 1: Limiting chemical composition of A600 in (wt.%). Adapted from J R Davies ^[22].

MECHANICAL PROPERTIES	
Young's Modulus	207 GPa
Poisson's ratio	0.29
Tensile Strength	552 - 690 MPa
Yield Strength (0.2% offset)	172 - 345 MPa

Table 2: Mechanical properties of A600 at RT. Adapted from J R Davies ^[22].

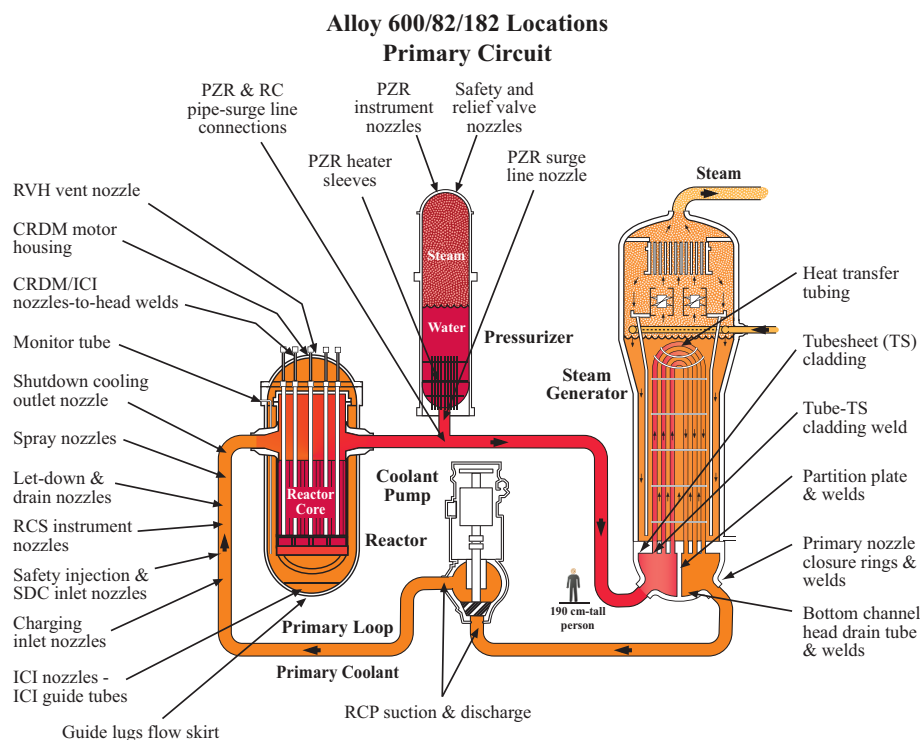


Figure 3: Use of A600 and/or its weld metal versions in PWR primary systems. Taken from R W Staehle ^[11]. [*Courtesy of EPRI*]

2.3 Corrosion of Alloy 600 under PWR primary water conditions

“Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.” Definition adapted by J R Davies ^[23]. In the case of A600, which consist of different elements with varying nobility (corrosion probability), this means that many reactions can take place simultaneously and that more than one oxide species might form as a consequence of corrosion.^[24] Corrosion and oxidation depend strongly on what is known as the “8 primary variables” ^[11], which include alloy composition, alloy structure, irradiation, stress, environmental species, temperature, pH and electrochemical potential (H₂ and O₂ availability). So-called Pourbaix diagrams, which are obtained with thermodynamic corrosion software, can be used to visualize stable phases of the alloy and to “predict” the possible formation of oxide species under

specific aqueous conditions.^{[25], [26]} It is also known as E-pH diagram (corrosion potential in Volts vs. potential of Hydrogen) and the example in Figure 4 shows stable species of A600 oxides at 580 °F (ca. 300 °C).^[25] The PWR regime is located close to the Ni/NiO phase transformation, as highlighted in purple.

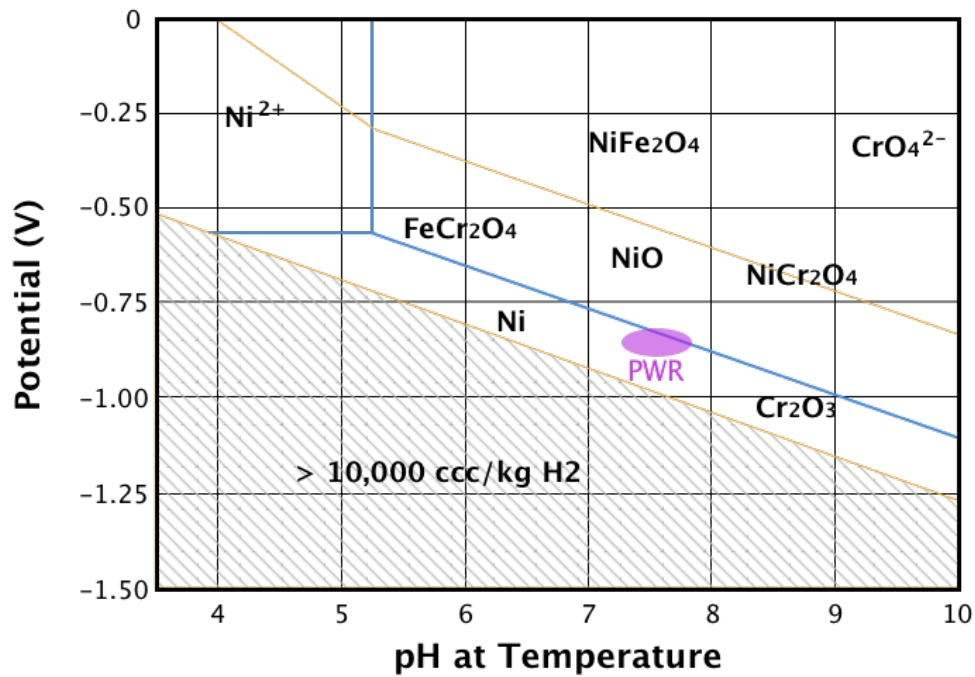


Figure 4: Exemplary E-pH (Pourbaix) diagram for A600, showing oxides formed based on the major alloy constituents Ni, Fe and Cr at 300 °C. As seen in Thompson *et al.*^[25].

2.4 Alloy 600 oxide layers formed under PWR primary water conditions

Upon contact of the alloy with the environment (*e.g.* PWR primary coolant), layers of insoluble corrosion products might form. The forming layers are also known as passivation layers and separate the metal from its environment. This gives the material a certain corrosion resistance. Many applications in industry (*e.g.* the nuclear industry) rely on the stable passivation behaviour of their engineering alloys. However, if for any reasons (*e.g.* a possible fracture of brittle oxides, stress or a change in the corrosive

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environment) the layer loses its integrity, fatal forms of localized corrosion, like SCC, may occur.^[23] Oxidation mechanisms are rather complex due to a multitude of influencing variables and their interdependencies. The kinetics of oxidation makes up a complete field of research and exceeds the scope of this thesis. Comprehensive literature is available elsewhere.^{[27] - [29]} To date, the oxidation of A600 in primary water is not yet fully understood. Different oxide species and layers of diverse thickness form depending on the element concentration and environmental conditions. Factors, like element reactivity and the ability of atoms to move through the oxide/alloy (diffusivity), all affect the behaviour.^[24] This in turn depends on factors like, GBs and defects (point defects, vacancies, interstitials, dislocations, *etc.*) and impurities in the material as well as carbides, grain size and increased diffusion rates at higher temperatures. Last but not least, one must also consider the influence of stress and strain on the diffusion of atoms^{[30], [31]} along with the fact that oxides might crack, grow intergranularly, contain voids and be brittle. Besides the on-going debate about the validity of existing models of SCC, which will be discussed in chapter 2.7, it is widely acknowledged that the oxidation process of A600 is likely to play a crucial role in the initiation and propagation of IGSCC.^{[7], [32] - [38]} Hence, oxide formation in PWR primary water is a prime subject of investigation to the community. Several studies based on different techniques, including HRTEM, SEM, EDX and APT, have addressed the structural composition and formation of oxides formed on Ni-base alloys and the general structure represented in Figure 5 seems commonly accepted.^{[39] - [46]} The individual layers displayed in Figure 5 will be discussed next.

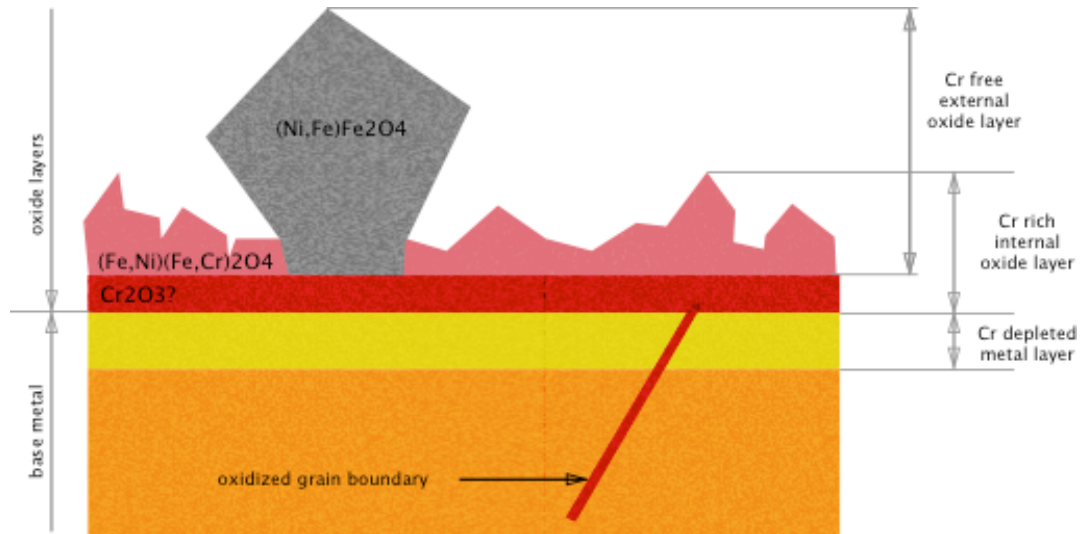


Figure 5: General oxide structure formed on A600 under PWR primary water conditions. As seen in Combrade *et al.* ^[36].

2.4.1.1 External oxide layer

The outer Cr-free layer has been shown to consist of nucleated crystallites, which mainly consist of Ni and Fe oxides with little or no Cr content and which can exceed the size of 1 μm . According to a study carried out by Combrade *et al.* ^[36] this layer does not seem to fulfill a protecting role for the base metal and depending on the testing conditions it might not form at all. Carette *et al.* ^[39], who carried out oxide formation studies on A690, has for instance shown that the formation as well as growth of this external layer depends strongly on the environment's saturation with Fe and Ni cations. Sennour *et al.* ^[41] have moreover demonstrated that the surface condition (*e.g.* surface defects) has an influence on the oxide, as crystallites seem to nucleate preferentially along polishing scratches present at the surface.

2.4.1.2 Cr-rich inner layer

The Cr-rich inner layer however is believed to be of protective nature and has been shown to usually be less than 100 nm thick. ^{[33] - [35], [41] - [43]} According to several studies ^{[34], [36], [40], [47]}, the Cr-rich inner layer can moreover be divided into 2 sub layers. ^[36]

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- A Cr-rich spinel type oxide, which makes up the majority of the inner layer
- A compact Cr oxide layer, which is situated at the metal-oxide interface

Panter *et al.* ^[34] have revealed that this 5 nm thick sublayer's Cr content is in fact too high to be of spinel type nature and that it seems to be composed of Cr_2O_3 , as also reported in other studies.^{[41], [42], [47]} Panter *et al.* ^[35] moreover suggest that this thin layer, due to it being the first “continuous” layer, has the ability to act as the main protective barrier and questions the protective nature of the overlying Cr-rich spinel. Combrade *et al.* ^[36] pointed out that the protective nature of the spinel oxide is still to be determined. Additionally, a Ni-rich (chromium-depleted) zone beneath the Cr oxide layer has been observed frequently.^{[35], [36], [40], [46]} During research on Alloy 690, which has a higher Cr content, Sennour *et al.* ^[41] and Lefaix-Jeuland *et al.* ^[32] observed periodically dispersed Cr_2O_3 nodules at the oxide/metal interface rather than a continuous Cr_2O_3 layer. Contrary to work carried out by other research teams the authors ^{[41], [32]} could not confirm the existence of a Cr depleted zone at the base metal under the oxide. The reason for an occurrence or non-occurrence of such a Cr depleted zone at the metal/oxide interface and the formation of Cr_2O_3 layers or nodules is still to be examined. However the existence of a critical chromium content, which promotes a rapid formation of a protective Cr_2O_3 scale, has been established. Additionally, Carette *et al.* ^[39] pointed out that the fluctuations in composition, morphology and microstructure of the oxide layers seem to also depend on the test conditions and corrosion test duration.

2.4.1.3 Intergranular oxides

Multiple studies have demonstrated that oxygen is able to diffuse inwards (below the metal/oxide interface) along GBs of Ni-base alloys and build up what is known as intergranular oxides.^{[7], [34], [36], [38]} Generally, intergranular oxides are believed to be

very similar to the protective Cr-rich layer in the previous category and are believed to have a direct influence on SCC in A600, by embrittling its GBs and thus influencing its mechanical properties, including the failure stress. On A600 these intergranular oxides have been shown to reach penetration depths of several microns and multiple studies [34], [35], [40], [47] have observed that oxide diffuses much faster and deeper along triple junctions and penetrations of around 10 μm have been reported.^[36] Moreover, a dependency between the Cr content and penetration depth has been established by Delabrouille *et al.* ^[40], stating that the penetration depth decreases as a function of increasing Cr content but quantitative estimations were not given. Another interesting observation concerns the occurrence of intergranular oxides in form of nodules, which seem to be isolated from the metal/oxide interface.^{[35], [47], [48]} Although the authors emphasize that the resolution of their experiments might not be sufficient for proofing a total isolation of the nodules from the intergranular oxide connected to the surface/oxide interface, the importance of their findings has to be highlighted as these isolated nodules might play a crucial role in IGSCC of A600 and hence deserve further investigations. Recently, it has been shown that the intergranular oxide is often of inhomogeneous nature with regions of lower density, voids and pores ^{[44], [49]} (see Figure 6), which were also found ahead of the oxidation front.^[46] While the role and nature of these weak spots in the oxide is not yet understood, theories about their formation evolve around a possible link to local defect density ^[50] and a formation of defective spinel oxides due to stoichiometric fluctuations.^[46]

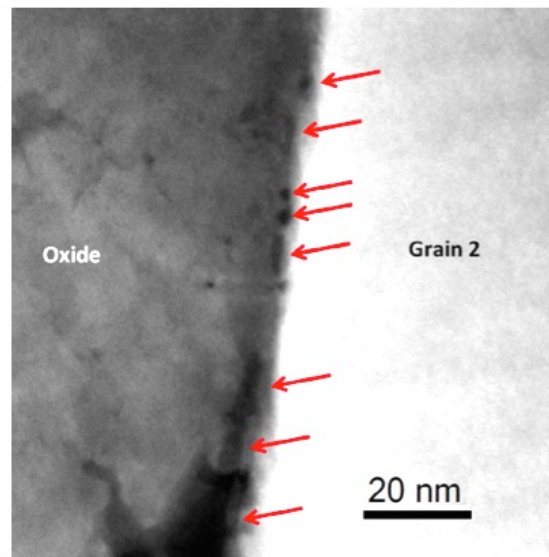


Figure 6: High-angle ADF image showing the oxide–metal interface in grain 2. The darker regions (arrowed) at the oxide near the interface can be interpreted as having a lower density than the oxide further away. [Taken from Dugdale et al. ^[49] and printed with permission from Elsevier]

2.5 Definition and evolution of SCC in PWR environments

SCC is a microscopic and localized form of corrosion-related failure, which manifests itself as microscopic cracks which are known to proceed intergranularly (IG), transgranularly (TG) or in mixed modes.^[21] This environmentally assisted form of material degradation occurs during service time, often without any obvious visual signs of corrosion present. This results in catastrophic failures of the components made of susceptible alloys, like A600. The SCC type relevant for A600 used on the primary side of PWRs is known as low potential SCC (LPSCC) or primary water SCC (PWSCC), often also referred to as intergranular SCC (IGSCC), as the cracking of Ni-base alloys under primary water SCC conditions has been identified to predominantly progress along the GBs of the alloy.^[51] Since this thesis is mainly concerned with understanding intergranular PWSCC failure of oxidized A600 grain boundaries, the terms SCC, LPSCC, PWSCC as well as IGSCC won't be distinguished

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and refer to the same phenomenon. Researchers have widely acknowledged that the occurrence of SCC in PWRs is dependent on the interplay between 3 main factors, which are prerequisites of SCC.

- A material susceptible to SCC
- A specific chemical environment (aqueous)
- A certain tensile/compressive stress (applied or residual)

In general, SCC can be described as the sudden occurrence and proceeding propagation of cracks in a material exposed to a trigger environment, which at the same time is also exposed to a certain stress level. Generally this type of cracking tends to proceed in the direction normal to the stresses, which initiate SCC.^[51] This includes secondary stresses (*e.g.* due to machining, deformation, heat gradients *etc.*) as well as applied stresses. The dependence on those 3 factors can be displayed in a Venn diagram (see Figure 7), which serves as a conceptual visualization of the conditions necessary for SCC to occur. If one of the necessary factors is not present, SCC will not occur.^[11]

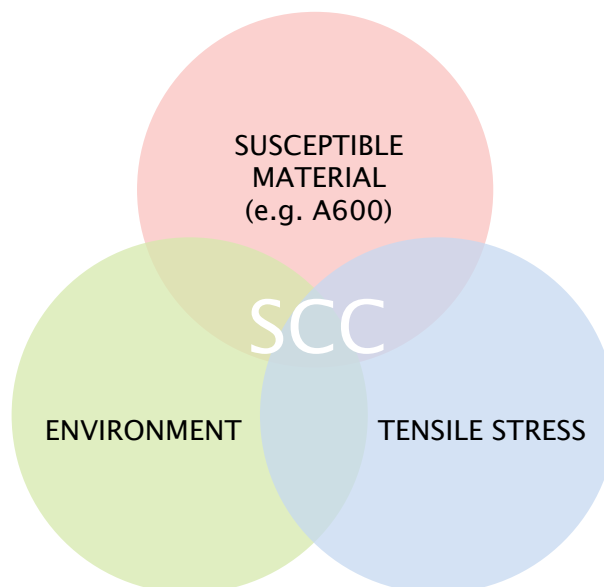


Figure 7: Venn diagram of the conditions necessary for SCC occurrence.

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The evolution of SCC after long enough exposure to the environment can be divided into 3 different segments; (1) INCUBATION, which might take from a few hundred to thousands of hours of exposure and provides the necessary conditions for, (2) CRACK INITIATION, where first microscopic cracks appear on the alloy surface and preferentially nucleate at pre-existing defects (Figure 8) ^[52] and a CRACK PROPAGATION phase, which might be further divided into a slower (initial) crack growth stage, where so-called proto-cracks form and coalesce until a critical transition point is reached at which the rate increases rapidly and which is usually associated with the point at which the stress intensity factor K_I exceeds a critical threshold value called K_{ISCC} ($K_{ISCC} = 9 \text{ MPa m}^{1/2}$ at 330 °C and 30 kPa H_2 partial pressure ^[53]). This then initiates the fast propagation stage at which intergranular cracks penetrate the alloy at a certain rate and then plateaus until final rupture occurs at the fracture toughness K_{IC} of the material. ^{[11], [54]}

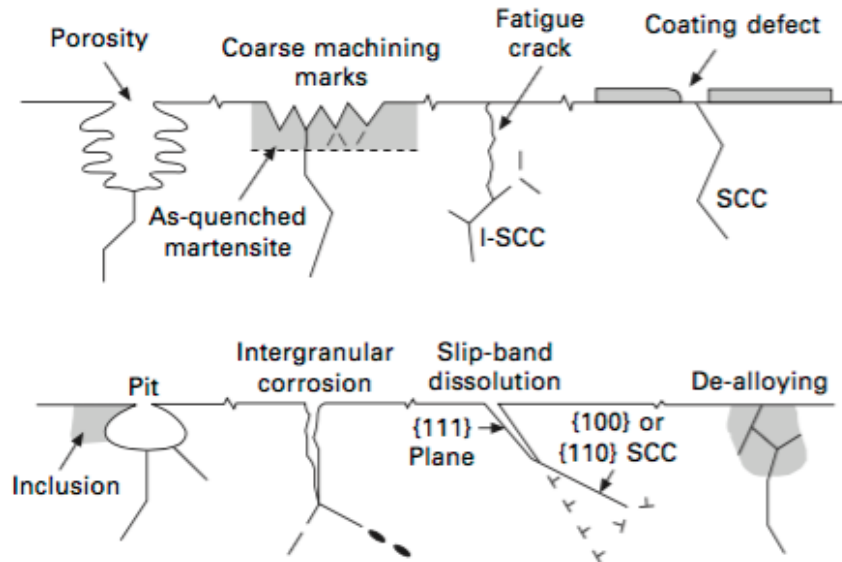


Figure 8: Representation of potential SCC initiation sites. [Taken from Raja and Shoji ^[52] and printed with permission from Elsevier]

2.6 Influencing parameters

As defined earlier, IGSCC is a phenomenon occurring upon a conjoint interaction between a susceptible material, a specific aggressive environment and stress. Several interdependent factors (metallurgical, mechanical, electrochemical) influence these 3 parameters and SCC.^{[51], [52]}

- **Material specific factors:** A600 composition and microstructure (*e.g.* Ni and Cr content, intra and/or intergranular carbide precipitation, heat treatment), grain boundaries (GBs), cold work, *etc.*
- **Environment specific factors:** Primary water composition and species (Lithium, Boron), corrosion potential (H_2 and O_2 concentrations and pH) and temperature
- **Stress:** Applied (external) and residual stress (*e.g.* cold work, plastic deformation from manufacturing)

It should be noted that the effect of these parameters is difficult to understand and determine because of their synergy and interdependencies. This represents a major challenge for engineering models when trying to predict SCC initiation and failure. Nonetheless, some of the most relevant findings and factors will be discussed in the following sub-sections and have moreover been partially summarized in our review paper.^[3]

2.6.1 Nickel (Ni) and Chromium (Cr) content

In 1989, Yonezawa *et al.* ^[55] published a study about the influence of Ni (68 – 88 % wt.) and Cr (1 – 20 % wt.) contents on IGSCC in PWR primary conditions. While the Ni content, with Cr being held constant at 5%, has been shown to have no significant impact, the chromium content revealed significant influence on SCC resistance. The results are presented in Figure 9. It can be seen that SCC resistance

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increased with increasing Cr percentage (from 3 – 17 % wt.). Consequently, the resistance of A600 in PWR primary coolant to SCC is improved drastically with increasing chromium levels. This is in good agreement with work published approximately ten years later ^[56], which reported a peak in susceptibility for 5 – 10 % of chromium, an increase in SCC resistance from 10 – 17 % Cr and no cracking at all from Cr contents higher than 17%.

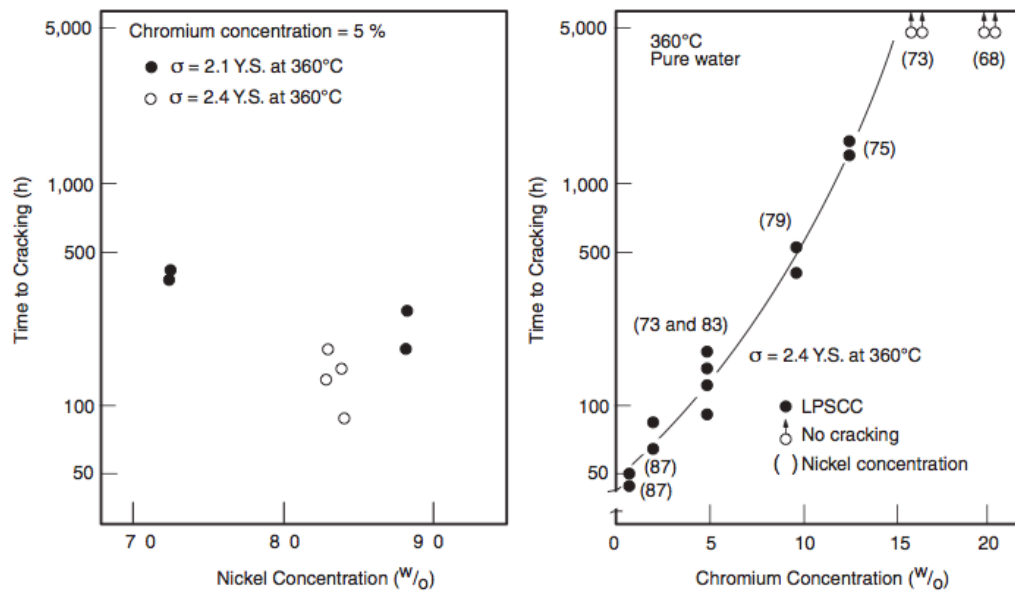


Figure 9: Impact of Nickel and Chromium contents on PWSCC (at 360°C). [Provided by Yonezawa and Onimura ^[55]]

Moreover, their results support the observed better resistance of A690 (with over 30% Cr) to SCC as compared to A600. ^{[40], [57], [58]} While an increase in Cr content led to an increased resistance to SCC, as also reported in a review by Rebak and Hua ^[58] for A600 under PWR conditions, it did not significantly change the alloy microstructure (grain size and carbides) or its mechanical properties. It was also reported that in caustic environments a higher Cr content does not reveal the same increase in resistance, which led to the conclusion that the beneficial effect must be an oxide formation related effect. As reported by Angeliu and Was ^[59], an increase of Cr from

5 – 17 % leads to a change of the surface oxide $\text{Ni}(\text{OH}_2)$ to being mainly a more protective Cr_2O_3 oxide. It was shown that oxide films on alloys with higher chromium content are generally thinner and richer in chromium and have a better shielding capability and mechanical resistance.^{[40], [59]}

2.6.2 Carbon and carbide precipitates

Carbon is an impurity element of A600 and it usually amounts up to 0.015%. Carbon mainly influences the microstructure of A600 in the form of so-called carbide precipitates. The amount of carbon in solution, heat treatment duration and temperature affect the alloy microstructure and its carbide precipitation.^{[51], [60]} A high-temperature anneal ($> 1000\text{ }^\circ\text{C}$) usually results in more Carbon in solution and IG carbide precipitation. In addition the precipitation might be further supported by a secondary thermal treatment (*i.e.* at temperatures between $600 - 720\text{ }^\circ\text{C}$).^[60] Carbide precipitates in A600 are rich in chromium and they are mainly Cr_{23}C_6 and Cr_7C_3 carbides (depending on the chromium content), with the latter being usually more dominant in A600.^{[61], [62]} They can be intragranular, intergranular or both. Multiple studies have reported that networks of intergranular carbides result in an improved resistance to SCC.^{[13], [49] - [61]} Intragranular carbides on the contrary seem to make the material more susceptible.^[6] Norrington *et al.*^[63], demonstrated the increased resistance to SCC with increased GB carbide density of reverse steam generator U-bend tubes. Later work by Hertzberg and Was^[64] considered both the effect of carbon in solution and precipitates and looked at their separate effect. They came to the conclusion that alloys with GB precipitates have inferior SCC resistance compared to the beneficial effect of carbon in solution alone. Another study supporting the beneficial role of carbides has been published by Alexandreanu *et al.*^[65], who focussed on the influence of special GBs (*e.g.* coincident site lattice boundaries (CSLB), low angle and high angle boundaries

(HABs), carbon in solution and GB carbides. They came to the conclusion that higher carbon content in solution increases IGSCC resistance and that GB carbides, on top of an increased resistance of special GBs and increased carbon content in solution, provide additional resistance to SCC. The implication is that carbides might not only be beneficial for inhibiting crack initiation but also crack propagation.^[65] Bruemmer *et al.*^[60] believe carbides are a source of dislocation activity and attribute IG carbides a stress-relieving role, including the blunting of crack tips, resulting in an overall reduction in crack growth rates and IGSCC susceptibility. Another theory is the preferential oxidation of Cr-rich carbides together with the formation of more compact chromia (Cr_2O_3) or Cr-richer oxides (*e.g.* chromite), which might help to slow down intergranular oxide penetration.^{[46] - [66]} A recent paper from Dugdale *et al.*^[49], which focussed on the micromechanical testing of oxidized GBs via microcantilever tests, states that crack paths might be modified by the presence of carbides along the GBs. They stated that carbides do not oxidize but are surrounded by a chromium-depleted region, which oxidizes preferentially. The interface between the carbide and the relatively dense oxide surrounding it was never observed to fracture during their tests. Moreover, they simulated the fracture of carbide free GBs and found that in comparison to GBs with carbides, the stress to failure of the carbide free GBs is slightly lower (5%). Hence, they suggest that carbides might have a minor strengthening effect. The authors assumed that the rather complex crack paths caused by carbides, as compared to the rather straight GB paths when obstacles are present, to be the origin of the strengthening.^[49] Vaillant^[67] and Bruemmer^[68] moreover suggests that intergranular carbides are obstacles which might help to decrease GB phenomena like sliding by hindering GB dislocation motion and limiting the number of sliding boundaries, and hence, reducing crack initiation and crack growth. Other studies from 2015 and 2016^{[69], [70]}, carried out in hydrogenated steam at 480 °C, pointed out the consumption of

carbides by oxidation and the formation of a Cr and Fe rich oxide above the surface near carbide and a Ni enrichment (Cr-Fe depletion) below. Evidence of localized carbon enrichment along the GB was found ^[69], which even though mainly associated with the presence of the IG carbides, extended into the matrix hence suggesting an increased concentration of C in solid solution caused by carbide consumption. As demonstrated by Hertzberg *et al.* ^[71] this results in increased GB activation energy and lowered dislocation motion and climbing. Another interesting fact is the observation of chromium-depleted zones associated with Cr rich carbides. Depleted zones, associated with this “sensitised” microstructure, form within a temperature range where precipitates are thermodynamically stable and the diffusivity of chromium is high enough for nucleation to carbides. The role of carbides and the depleted zone is still subject of much discussion. Kai *et al.* ^[72] reported that the depth of the chromium-depleted region plays a role but the width and shape seem to be of no crucial significance. Bruemmer ^[60] on the other hand stated that depletion is not an essential factor in the IGSCC of A600 under deaerated or caustic environments since its effect is too minor as compared to the positive effect of IG carbides.^{[60], [72], [73]}

2.6.3 Grain boundaries (GBs)

The microstructure of the alloy’s GBs, including grain size, structure, chemistry and character are of high relevance to SCC susceptibility.^[65] In 1984 ^{[74], [75]}, the idea of grain boundary design and control was born and the effect of GB properties on SCC has been subject to investigations ever since. From an atomistic point of view there are two types of GBs: Low Angle Boundaries (LABs, misorientation $< 15^\circ$) and High Angle Boundaries (HABs, misorientation $> 15^\circ$).^[76] High angle GBs can be further divided using the coincident site lattice model, which has been established by Kronberg and Wilson in 1949.^[77] This model describes the GB energy as a measure of the number of

coinciding atomic positions between the grains. If the number of coincident sites is high (low number of broken bonds) then the GB energy is low.^[76] GBs with a high number of coinciding atomic positions are called coincident site lattice boundaries (CSLB) or special grain boundaries. Several studies have revealed that an increased number of CSLB in the alloy structure has a positive effect on SCC resistance.^{[65], [73], [75], [78], [79]} As mentioned in the previous section, Alexandreanu *et al.*^[65] found that regardless of the microstructure or testing conditions, CSLBs are always more resistant to cracking when compared to HABs. The authors report that the best microstructure seems to consist of a high fraction of CSLBs, mixed with HABs that are preferentially precipitated by GB carbides and thus profit from the positive influence of carbides on IGSCC resistance.^[65] Preferential precipitation of HABs has been suggested by previous work^{[80], [81]}, which is based on the assumption that precipitates form preferentially on GBs with a higher energy state (like HABs). It was moreover found that cracking propagates preferentially along HABs^{[45], [78]}, that oxide penetration at HABs is deeper^[82], coherent twins ($\Sigma 3s$) don't crack and might act as obstacles to crack propagation.^[79] Explanation for the better SCC behaviour of CSLBs might be provided through the behaviour of extrinsic grain boundary dislocations (EGBD), which are created through the interaction of lattice dislocations with GBs during high temperature deformation. According to the type and structure of the GBs those EGBDs might be dissociated, absorbed or trapped at the boundaries.^[83] As reported by Thaveeprungsriporn^[83] and Alexandreanu *et al.*^[84] the highly ordered CLSBs show a higher density of EGBDs because the absorption of dislocations is more difficult as compared to HABs. Both studies report a 3-times higher annihilation rate of EGBDs at HABs. Alexandreanu *et al.*^[84] moreover observed higher hardness near CSLBs, as a result of the reduced ability to absorb EGBDs and an overall increase of grain-average hardness with an increasing fraction of contiguous CSLBs. CSLBs are trapping sites for grain boundary dislocations. They act as obstacles

to matrix dislocations, leading to matrix hardening and an increased internal stress in the alloy.^[84] This results in a reduction in the creep rate. A quite recent study from Stratulat *et al.*^[85] focussed on the determination of the critical stress intensity factor of oxidized A600 via microcantilever bend-tests and a potential correlation between obtained values and GB character. While a range of 0.73 – 1.83 MPa m^{1/2} was found for the critical stress intensity, no direct correlation to GB misorientation could be established.

2.6.4 Primary water conditions and hydrogen content

The purified water (dissolved oxygen < 10 ppb) in the primary loop is usually kept within an operating temperature range of 280 – 345 °C.^{[7], [86]} Hydrogen (typically 30 cc/kg^[87]) is used to control/suppress coolant radiolysis by maintaining a minimum concentration of dissolved oxygen (inhibit corrosion), and to maintain low redox potentials (near the Ni/NiO equilibrium, Figure 4). The addition of species like boron and lithium further helps to control the reactivity and to adjust pH values.^[88] The pH is usually kept at 6.8 – 7.4 at operating temperature.^[7] It is known that SCC is most severe in the regions where temperatures exceed 300 °C, whereas no SCC occurrence has been reported for temperatures lower than 250 °C.^[73] Crack growth rates (CGRs) are moreover strongly dependent on temperature^{[73], [89], [90], [91]} and follow an Arrhenius type relationship.^[95] Amongst literature there seems to be a large scatter in activation energies for A600 in PWR primary water.^{[90] - [93]} As reported by Marcus^[94] average accepted/trusted values used for predictions by the community (*e.g.* EDF) are 180 kJ/mol for crack initiation and 130 kJ/mol for crack propagation. Several studies^{[45], [46], [90], [91], [94] - [96]} have reported that the hydrogen content in high temperature water plays an important role in SCC behaviour of Ni alloys. As reported by Morton *et al.*^[90], studies in literature agree that the peak for the crack growth rate is observed in the

proximity to a key phase transition, the nickel to nickel oxide (Ni/NiO) phase transition and extends ca. ± 80 mV from the equilibrium potential.^[95] Morton *et al.*^[90] reported that, depending on the level of deviation from this transition, the level of dissolved hydrogen has an up to 7x effect on the CGR of Ni Alloys. Additions of Boric acid and lithium hydroxide on the other hand do not seem to play a crucial role in IGSCC, although high Li concentrations have been suspected to enhance IGSCC rates.^{[95], [96]} Using SEM and ATEM, it has been found that there is a correlation between surface oxide thicknesses and H₂ content. The higher the corrosion potential (lower H₂) the more increase in surface oxide thickness. Caballero Hinostroza *et al.*^[45] performed oxidation tests on non-stressed samples in a Ti autoclave with varying hydrogen levels (3, 30 and 60 cc/kg H₂O) and reported an effect on the morphology of the external oxide scale. At the lowest H₂ level the surface was depicted with large Ti-rich crystallites of several 100 nm in size and some needle-like oxides, rich in Ni and O, which were randomly distributed on top. At the medium and high H₂ level the crystallite distribution became more inhomogeneous and the crystallite size decreased as well (ca. 100 nm) along with variations in Ni and Cr content of the crystallites. It was moreover found that IG oxide penetration depth decreased slightly with increasing H₂ levels, whereas Pimentel *et al.*^[46] found an increase in IG oxidation depth in their study of varying H₂ levels (10.43 and 945 cc/kg H₂O). An additional effect has been reported concerning the effect of increasing H₂ levels and their relation to carbide coverage and size. In another study^[97], using H₂ charged A690 samples, it has been reported that the fracture toughness decreases with increasing H₂ levels and that hydrogen embrittlement seems to become more severe with increasing carbide precipitation of the alloy.

2.6.5 Stress

As defined in chapter 2.5, tensile stress, besides a susceptible material and environment, is a prerequisite of SCC occurrence. The threshold stress needed for IGSCC to occur is usually close to the yield stress (strength) of the respective alloy and made up of applied and residual stresses.^[98] Applied stresses are introduced by external factors (e.g. reactor pressure and temperature gradients) and are usually considered of minor influence since they are low compared to threshold stresses for SCC of A600. Residual stresses, on the other hand, which are usually associated with the alloy's metallurgical and manufacturing history, including welding, cold work, heat treatments, surface polishing/grinding and design related defects, are considered to be the driving force of SCC because they cause local stress concentrations which are close to or even higher than the yield strength of the material.^[11] This is true even though the overall nominal stress might be well below a given threshold.^[99] For Alloy 600 it has been reported that SCC won't occur at stresses lower than 250 MPa.^[100]

2.6.5.1 Stress and stress intensity

The concept of stress intensity in fracture mechanics can be used to determine the stress state near the apex of a crack caused by an applied stress (external and/or residual). It is described by the stress intensity factor K , which is a function of overall stress and crack length for 3 different cracking modes (I: normal opening, II: in-plane shear and III: anti-plane shear, as depicted in Figure 10). If a critical stress intensity factor K_C is reached, a crack propagates.

$$K = \sigma_{total} \sqrt{\pi a} \quad \text{Equation 1}$$

For SCC type failure, which usually occurs perpendicular to the applied stress, mode I failure is considered most common^[11] and usually K_{IC} is lower than K_{IIC} or K_{IIIC} .

However, shear (mode II) or a mixed mode (I and II) might occur locally upon the activation of local plasticity.

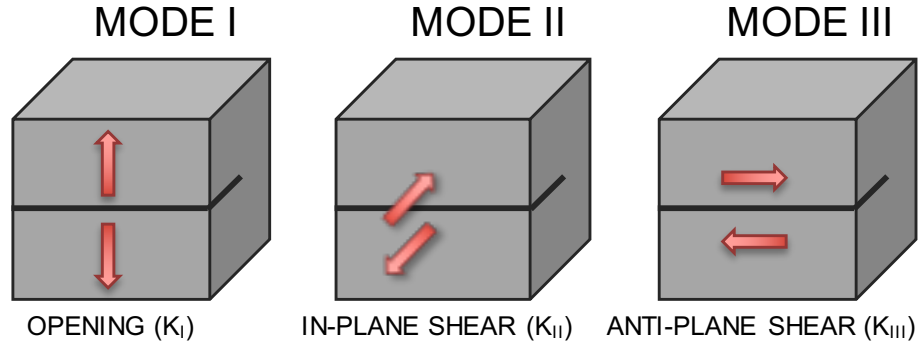


Figure 10: Modes of failure (I, II and III) as defined by conventional fracture mechanics.

As discussed in section 2.5, the SCC community makes use of the correlation between crack growth rate and stress intensity factor (Figure 11) to determine what is called the threshold critical stress intensity factor K_{ISCC} . At some point during the SCC initiation stage, the K_I value needed to coalesce the small subcritical proto-cracks reaches K_{ISCC} and cracks propagate. In theory this means that as long as stress and proto-cracks in the material are small enough ($K_I < K_{ISCC}$) SCC is prevented.^[99] Different macroscopic CGR tests of A600, as summarized by Chopra et al. ^[57], have shown that there is a significant dependency of CGRs for stress intensity values between 5 – 25 MPa m^{1/2} and that this dependence plateaus for values > 25 MPa m^{1/2} (see Figure 11). No relationship between H₂ fugacity and stress intensity factor could be established.^[90] In accordance with a threshold stress intensity $K_{ISCC} = 9 \text{ MPa m}^{1/2}$ at 330 °C and 30 kPa H₂ partial pressure reported by Raja and Shoji ^[52], a stress intensity threshold of 5 - 10 MPa m^{1/2} for Alloy 600 seems commonly accepted. In reality however there is no such thing as a unified, global threshold value for K_{ISCC} since the stress state varies with varying SCC conditions due to the already mentioned interdependencies of the usual influence factors (material and environment specific).

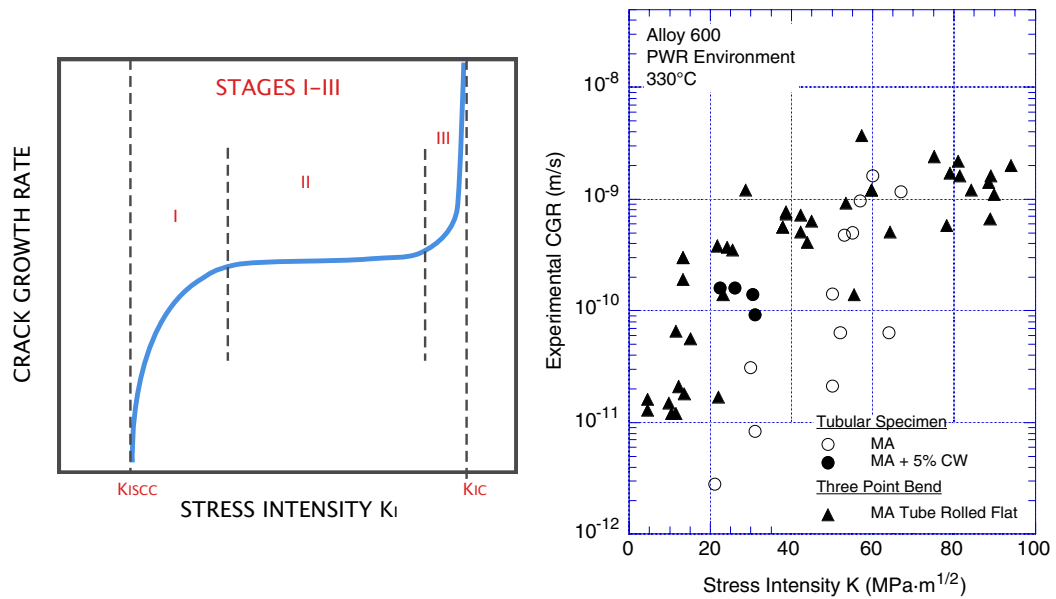


Figure 11: Relationship between crack growth rate and stress intensity factor K . (left) Theoretical behavior and (right) laboratory data taken from Chopra *et al.* [57] (stage I and stage II only). A significant K dependence was only reported for values between 5 - 25 $\text{MPa}\cdot\text{m}^{1/2}$ (stage I).

A proper treatment or differentiation between crack initiation (slow crack growth) and crack propagation stages for SCC seems moreover rather difficult and especially the early stages of crack growth, which are usually considered sub-critical, are hard to understand on a macroscopic level. SCC is a local and microscopic phenomenon. Nonetheless, most predictive SCC models rely on global parameters, macroscopic in nature. As pointed out by Couvant *et al.* [4] there is a need to obtain more information about local conditions and to build new, more realistic models for SCC prediction, which are based on local parameters. However, since oxide penetrations are usually shallow an accurate determination of the stress necessary to fail individual GBs and their toughness is difficult and remains subject to on-going efforts in *e.g.* the quite young field of small-scale micromechanical testing, which is discussed in more detail in chapter 2.8.

2.6.6 Cold work

Cold work (CW), like thickness reduction via cold rolling (in %), changes the microstructure of the alloy through the application of external stresses and results in higher yield strength, meaning that ultimately a higher stress is needed to deform the alloy permanently (plastically). Hence CW is closely related to the yield strength of a material. Its strengthening effect originates in its injection/introduction of dislocations and the consequent suppression of plastic deformation (dislocation motion) in the alloy. The introduced higher defect density in the material hinders further dislocation generation/motion, resulting in the observed higher strength. Consequently more stress is needed for the onset of plastic deformation. It has been reported that CW and higher yield strength lead to increased CGRs in A600.^{[101] - [104]} Nonetheless, the quantification of the effect is challenging. Not only the amount of cold work seems to have a detrimental effect but also the processing orientation.^[102] Bruemmer *et al.* ^[101], in agreement with Moshier ^[102], established that CW always increases SCC susceptibility when compared to the as-received alloy condition. The researchers moreover found that low amounts of CW might result in a significantly higher SCC susceptibility than high amounts of cold work (*e.g.* 20%). It is believed that the influence originates in the higher concentration of defects close to the GB, which changes the deformation ahead of the crack tip. The consequent increased hardness might counteract the stress relaxation at the crack tip.^{[101], [105]}

2.7 SCC models and mechanisms

Over the decades many experiments have been conducted on numerous materials in order to gain a complete understanding of the mechanisms initiating and promoting SCC in PWR environments. As a result, many models and mechanisms have been

proposed but the broad range of factors that contribute to SCC, as discussed in section 2.6, makes it difficult to propose a unified theory.^{[87], [106]} The next sections give brief overviews of the most important mechanistic models in literature. To date, none of which have been able to link all factors that influence SCC initiation and propagation of A600 in PWR primary water and thus, only provide an incomplete, if not speculative answer. Nowadays it becomes more and more acknowledged that SCC might involve several different mechanisms, which initiate depending on the conditions. Already in 1996 Rebak *et al.*^[66] acknowledged that “The intricate case of A600 SCC can be better understood if it is assumed that a continuous spectrum of mechanisms operate, that is, in some cases the mechanical factors would be dominant and in others the chemical or environmental factors would be dominant.”

2.7.1 *Film-rupture model (FRM)*

The origins of the FRM, which is also known as slip dissolution model or slip oxidation model, reaches back to 1944 when Mears *et al.*^[107] postulated that corrosion occurs preferentially along anodic (film-free) pathways in a metal (*e.g.* along GBs) as a result of an electrochemical mechanism. His general concept served as a base for the general idea of a film rupture based SCC mechanism (Figure 12), as proposed by Logan^[108] in 1956, and many of the SCC proposals based on a film rupture mechanism that came later^{[109] - [120]} are derived from this initial concept. In the FRM, a sufficiently high and localized plastic strain at a passivated SCC tip (1) tears apart the protective oxide film and reveals the unprotected metal (2). As shown in Figure 12, which depicts a sequence of the FRM, shear of slip planes might be involved in uncovering the bare metal.^[109]

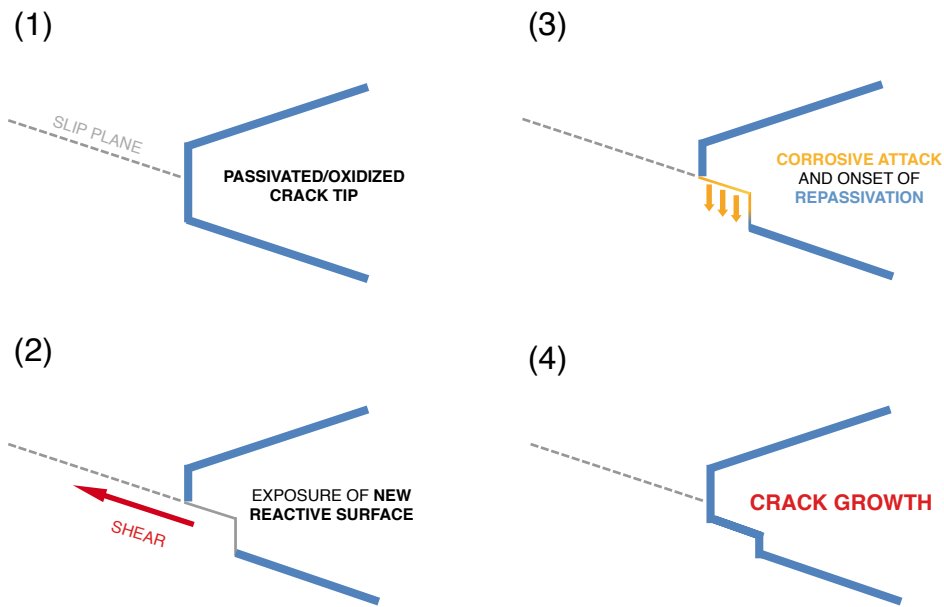


Figure 12: Exemplary sequence of FRM steps occurring at the tip of a propagating stress corrosion crack. (1) Passivated crack tip with intersecting slip plane. (2) Shearing of the slip plane by plastic strain and creation of a new unprotected (reactive) surface. (3) Corrosion attack of the reactive surface and onset of repassivation at the outer edge. (4) Repassivation of crack flanks after sufficient corrosion attack and plastic deformation. This ensures that an increment of crack growth occurs and will recur.

The exposed bare metal initiates the onset of very localized anodic dissolution (corrosion) in the exposed areas (3) before a repair process of the protective layer comes into action. With strain and corrosion working hand in hand, the consequent advancement of the crack (4) is explained as a repetition of the mentioned steps. Whilst strain accelerates the corrosion via film rupture, corrosion removes the most strain hardened material right ahead of the crack tip.^[109] Whilst film rupture seems more plausible for applied strain/loading rates, the case of a static load is more complex.^[110] Vermilyea *et al.*^[111] postulated a discontinuous treatment of the model, whereby crack advancement is treated by a discrete electrochemical sequence (dissolution, passivation and film rupture) and concomitant calculation of the strain rate at the crack tip based on

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continuum fracture mechanics. He explained that under static load the corrosion/passivation mechanism of the crack tip itself doesn't result in the plastic deformation but that the deformation is introduced by a following, transient creep deformation step. The CGR would thereby be dependent on the corrosion and repassivation rate in the crack. However, it appears that crack growth rate and strain rate are the crux of the FRM and subject of much discussion within the SCC community^{[110], [113] - [120]}, as to gain realistic plastic strain distributions, the FRM relies on large corrosion depths which would need to be achieved with every film rupture sequence and could not be confirmed experimentally. As a consequence, the inapplicability of the FRM for intragranular SCC was acknowledged and research associated with FRM started to focus more on explaining IGSCC mechanisms, where corrosion is directional along paths of minor repassivation rate (*e.g.* GBs).^{[110], [112]} Nonetheless, Ford and Andresen^{[113], [114]} made use of Vermilyea's concept and successfully applied their so-called fundamental CGR equation, which is an explicit function of the crack tip strain rate and showed that, at least for the conditions prevailing in light water reactors, the model has been statistically validated for certain stainless steels, low alloy steels as well as A600 and A182 in high temperature water.^[113] However, they insist that the accurate prediction of the CGR is strongly dependent on a complete understanding of the individual conditions.^[114] As a consequence the FRM and derived equations are still subject to ongoing developments.^{[115] - [120]} In a critical paper published in 2007, Gutman^[120] proclaimed his general scepticism about its ability to explain and predict SCC in its full scope and suggests that dividing SCC into sub-phenomena and trying to decipher those seems to be the better route towards SCC prevention. He concludes that there is *no such thing as a unified mechanism or theory*^[120], which explains all the complex factors that influence SCC behaviour.

2.7.2 *Film induced-cleavage model*

In 1985, Sieradzki and Newman ^[121] developed a model for the transgranular SCC behavior of ductile alloys (alpha brass and copper). They based their concept on the occurrence of intermitted cleavage-like fracture events, which they believe to originate from the formation of a thin, brittle surface film formed around the crack tip due to a de-alloying process. In their later work ^[122], which includes the discussion of this concept for *e.g.* stainless steel, Cu-Al alloys, alpha brass and pure copper, they've called this process the film-induced cleavage mechanism. This model will not be further discussed due to its focus on transgranular SCC.

2.7.3 *Surface mobility model (SMM)*

The so-called surface mobility model (SMM), established by Gavele in 1987 ^[123], proposes that increased surface mobility, due to a high surface diffusion coefficient (D_s), is involved in the SCC mechanism. The model suggests that stresses caused by an increased, environment-induced surface mobility, due to the formation of surface oxides (contaminants), will be released by the formation of surface vacancies at the alloy surface. Crack advancement is then either promoted by a surface vacancy exchanging places with a metal atom at the stressed crack tip or by the emission of adatoms from the crack base.^[123] Figure 13 shows the concept of this mechanism. The SMM has been subject to criticism ever since its first introduction and represents one of the more controversial proposals in literature.^{[124] - [127]} In 1994 a paper ^[125] was published which pointed out that Galvele's model overestimates the crack rate by at least 14 orders of magnitude. Galvele ^[128] points out his critics usually focus on mechanical aspects of the mechanism only and concludes that assumptions made by his critics couldn't be valid because they simply neglect the contribution of the complex chemical environment, necessary for SCC to occur. In an attempt to clarify the issues

with his concept, Galvele re-discussed the 4 postulates his model is based on (see ^[129] for further information) and pointed to data demonstrating a successful application of the model in theory and experiments.

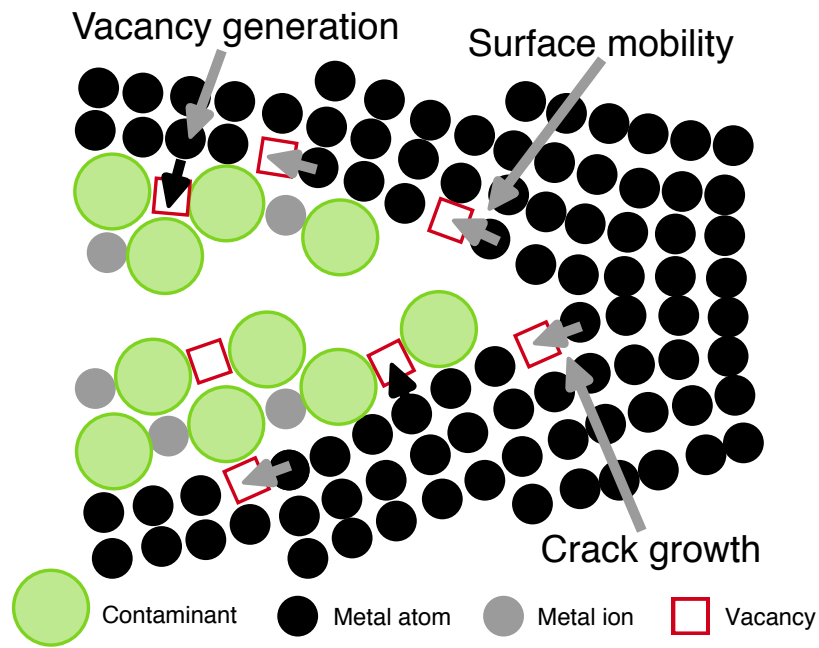


Figure 13: Crack propagation by surface mobility, in the presence of an ionic contaminant. As seen in the original publication by Galvele.^[123]

2.7.4 Hydrogen embrittlement (HE)

Hydrogen embrittlement, like SCC, is a form of environmentally assisted materials degradation. Hydrogen has been reported to embrittle materials for many years. In the case of Ni-base alloys in primary water several studies have been conducted and as discussed in section 2.6.4, H_2 has detrimental effects on SCC behaviour. It has been shown that whilst A600 is generally prone to HE ^{[58], [94]}, carbide precipitation on A690 significantly contributes to the HE effect, as the metal/carbide interface is believed to be a major trapping site for H_2 .^[97] Even though not subject of this review and the investigations in this work the role of HE is an important part of solving the equation

and should be mentioned. Based on the early work carried out by Troiano in 1960^[130], Hirth *et al.*^[131] suggested that hydrogen preferentially diffuses into the triaxial tensile stress region ahead of a crack where a critical combination of stress and hydrogen concentration is reached, which in turn promotes cracking.^[131]

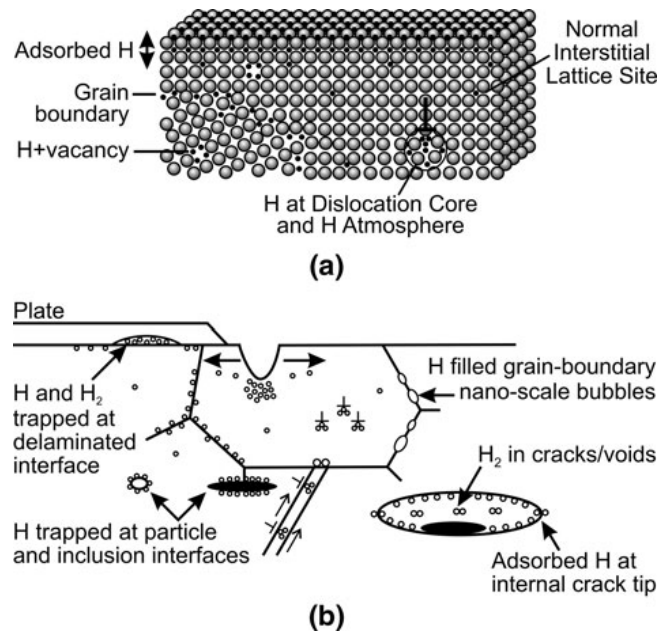


Figure 14: Representation of possible H₂ trapping sites in metals. H₂ adsorbed at the crack tip surfaces and interfaces (GBs, inclusion *etc.*) is main source of HE. [Taken from Lynch^[133] and reprinted with the permission of The Minerals, Metals and Materials Society]

To date, there seems to be no universal explanation for the degradation caused by such HE but considering the multitude of trapping sites for the small H₂ atoms in a metal^[133] (see Figure 14) and its capability to not only adsorb at cracks but diffuse ahead of them, a conjoint action of several proposed HE mechanisms, *e.g.* the adsorption induced dislocation emission (AIDE) or adsorption induced slip mechanism (AISM)^[132],^[133],^[134] or hydrogen enhanced local plasticity (HELP)^[135] - ^[140], could contribute to the overall, comprehensive process of HE and its role in SCC. As pointed out by Lynch^[132] the accuracy of these mechanisms might depend on material composition, testing

conditions and other variables. It moreover appears that, even though certainly part of the whole story, an H_2 based mechanism alone can not account for environmentally induced phenomena like SCC. Depending on the material system and conditions other mechanisms or a conjoint influence might be rate controlling.

2.7.5 *Selective internal oxidation (SIO)*

The name selective internal oxidation refers to a mechanism, involving preferential oxidation along GBs at temperatures $< 400\text{ }^{\circ}\text{C}$. It is based on a well-known phenomenon, the internal oxidation of Ni-base alloys, which has been mainly observed at very high temperatures ($500 - 1200\text{ }^{\circ}\text{C}$) and involves the inwards diffusion of oxygen and the preferential oxidation of the less noble alloying elements below the metal/oxide interface.^[7] The SIO model of SCC for temperatures below $400\text{ }^{\circ}\text{C}$ (see Figure 15) has been introduced by Scott and Le Calvar in 1993^[37] and describes the formation of brittle oxides along GBs as a result of such a selective oxidation process. The embrittlement is thereby caused by corrosive damage to the surface (surface oxidation) and the consequent inwards diffusion of oxygen along GBs. Brittle GB oxides form, which are usually rich in Cr (e.g. Cr_2O_3), and are believed to fail periodically under stress. This leads to intergranular microcracking and crack growth upon exceeding of a critical stress intensity value. Due to the crack opening, oxygen is able to diffuse deeper into the alloy, consequently oxidizing deeper sections of the GB, which then also suffer from cracking.^{[95], [141], [142]} Scott and Le Calvar suggest that possible origins of GB embrittlement via oxygen diffusion include not only internal oxide formation but also gas bubble formation (CO/CO_2) and oxygen adsorption at GBs are a possibility.^[37] As already mentioned earlier and shown in the Pourbaix diagram in Figure 4, SCC in PWR primary water conditions evolves around the Ni/NiO phase transformation and hence supports the concept of a selective internal oxidation of the less noble A600 alloying

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elements (Cr, Fe and C), as the environment does not allow for a major oxidation of the solvent metal itself (Ni). As a consequence the nobler matrix element Ni is rather stable in this region, thus promoting the idea of SIO.

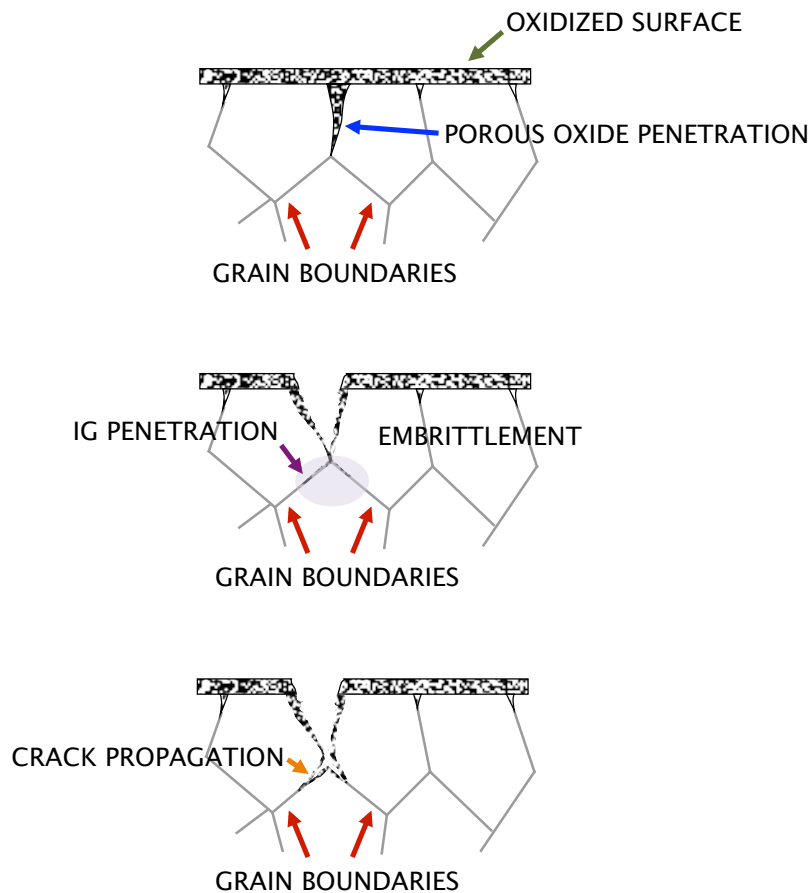


Figure 15: Schematic of the selective internal oxidation model.

Due to the fact that A600 has been shown to fail intergranular in PWR primary circuit conditions, including demonstration of the internal oxidation along GBs, it is to date one of the better-accepted models in the literature. It is moreover the only model mechanism describing both, initiation, via oxidation of GBs to a critical depth, and propagation of cracks, via periodic rupture of film under stress. As pointed out by Dugdale *et al.* ^[49] and Lozano-Perez *et al.* ^[50], the mechanism relies on the fact that the Cr-rich oxide within the GBs is indeed brittle and grows faster than the crack itself.

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Although the intergranular oxidation and failure of GBs has been addressed in multiple studies ^{[13], [37], [45], [46], [49], [69], [85], [95], [141] - [143]}, experimental evidence, besides the observation of an intergranular failure, which would underline the assumption made by the SIO model is still scarce. As a consequence, the mechanism governing a supposedly brittle failure of oxidized GBs and a potential relationship to local microstructure and degree of oxidation has not yet been clarified. However, the fact that intergranular fracture has been observed by individual researchers, as well as the quite recent observations of oxides present ahead of crack fronts in Ni alloys ^{[31], [48], [144] - [146]}, seem to favour a SIO mechanism. Nonetheless, as pointed out by Capell and Was ^[141], one major flaw of the model is the discrepancy concerning the diffusion of oxygen along the GBs, as the values for the diffusion coefficient of oxygen are still a few magnitudes too low to account for the observed crack growth rates. They conclude that the diffusion coefficient of oxygen for conditions relevant to IGSCC does not yet have a consensus value.^[141] A possible explanation is given by the observed presence of porosities within the intergranular oxide and ahead of the cracks.^[50] This would support enhanced oxide diffusivity along GBs, which might account for the SIO mechanism's discrepancies with the oxide diffusion coefficients found in literature but proof is lacking. As reported by Lozano-Perez *et al.* ^[50], recent studies from 2011 and 2012 ^{[48], [147]} have revealed that, if measured along GBs and deformation bands only, localized deformation (high dislocation density) seems to have an accelerating effect on intergranular oxide penetration depths and that applied stress further accelerates this process. This contribution of localized plasticity is however not accounted for by the original SIO mechanism. Lozano-Perez *et al.* ^[50] note that due to experimental observations in support of a SIO mechanism, the SIO model has to be considered as plausible explanation for IGSCC even though it can't explain all the observations made

in experiments. Especially the observation of localized plasticity near the crack fronts, the role of hydrogen and local microstructure remain unexplained.

2.8 Micromechanical testing

2.8.1 Introduction

Microscopic events are often driving macroscopic material response. Consequently, research has shifted towards the investigation of material properties and features at the micro-scale and beyond. With the introduction of the FIB, the high precision fabrication of micron-sized test specimens has improved tremendously and has successfully been used in *e.g.* micro-tensile tests ^{[148], [149]}, micro-compression tests ^[150] and microcantilever bend tests ^{[49], [151] - [153]}, with the latter being the method used in this study which will be highlighted in the following sections. It involves the use of nanoindentation equipment ^[154] to load micron-sized test structures and record load-displacement data. Subsequently, mechanical properties such as yield and fracture stress or Young's modulus can be calculated. The microcantilever bend technique itself is an important step forward in understanding the local mechanical behaviour of alloys and combined with other techniques (*e.g.* TEM) it can help to establish links to individual microstructural features, like GBs, oxidation, precipitates *etc.*, which influence the material's mechanical response.

2.8.2 Microcantilevers

25 years ago, Johansson *et al.* ^[155] and Weihs *et al.* ^[156] reported the first tests of micron-sized cantilevers. Their approach involved the fabrication of freestanding Si-beams with lithographic techniques. The freestanding beams were tested by applying force to the free end of the beam with a nanoindenter.^[156] Doing so, the force-

displacement behaviour of the material under bending could be recorded. Nowadays, cantilevers are preferentially prepared using the milling option of the FIB, simply because not all materials can be etched using etching techniques and because the structures can be produced directly onto selected areas of the bulk material. This FIB-based technique consequently allows site-specific preparation and testing of individual microstructural features ^{[49], [85], [152]} and their influence on material properties directly on the bulk material and prevents the necessity to study materials in form of deposited thin films. Nonetheless, besides the different fabrication of the test specimen and eventual variations in cantilever shape (rectangular, triangular, pentagonal, *etc.*) the main principle of the test hasn't really changed much. In 2004 Di Maio and Roberts ^[151], for the first time, used the FIB-based approach to estimate the fracture toughness of tungsten carbide coatings, using pentagonal microcantilevers. Thereby the authors made use of a sharp notch, which was milled onto the cantilever near the fixed end, to serve as initial flaw for crack propagation (pre-crack). Using linear elastic fracture mechanics, the fracture toughness K_{IC} was calculated based on the beam dimensions, notch depth and load at failure.

$$K_{IC} = \sigma_c \sqrt{\pi a} F\left(\frac{a}{b}\right), \quad \text{Equation 2}$$

with σ_c being the stress at failure, a being the length of the notch and $F(a/b)$ being a geometry dependent, dimensionless shape factor.^[151] Armstrong *et al.* ^[152] adapted this approach, using triangular beams (no notch) and simple beam theory for stress-strain analysis to study the anisotropy of the Young's modulus of copper. Combining microcantilever tests with EBSD, the authors found that the orientation dependent results for E are in good agreement with values calculated from bulk data available in literature. Also focussing on the influence of the effective length, defined as the distance between the fixed end and load point, the authors moreover found that a width

to length ratio of 6 should be kept to optimize simple beam theory estimations of the Young's modulus. Another study from 2011 ^[153] focussed on determining the fracture toughness of bismuth embrittled copper GBs. It was possible to show that micron-sized cantilevers, together with EBSD to obtain the misorientation angles and the initial approach by Di Maio and Roberts ^[151], can be used to study the fracture toughness of individual GBs (bi-crystals) and their possible relation to misorientation. No obvious relationship between K_{IC} and the misorientation of the tested GBs, nor the plane normal of the grains, could be established. Another study by Daniel *et al.* ^[157] from 2016 investigated nanocrystalline monolithic TiN thin films in the context of grain boundary engineering. Micromechanical fracture tests were carried out on notched and unnotched cantilevers, which were prepared on differently oriented nanostructured version of the material, as shown in Figure 16. While the unnotched beams were used to extract information about Young's modulus and fracture stress (as performed in the context of this thesis), K_{IC} was extracted via the usual notched-beam approach.

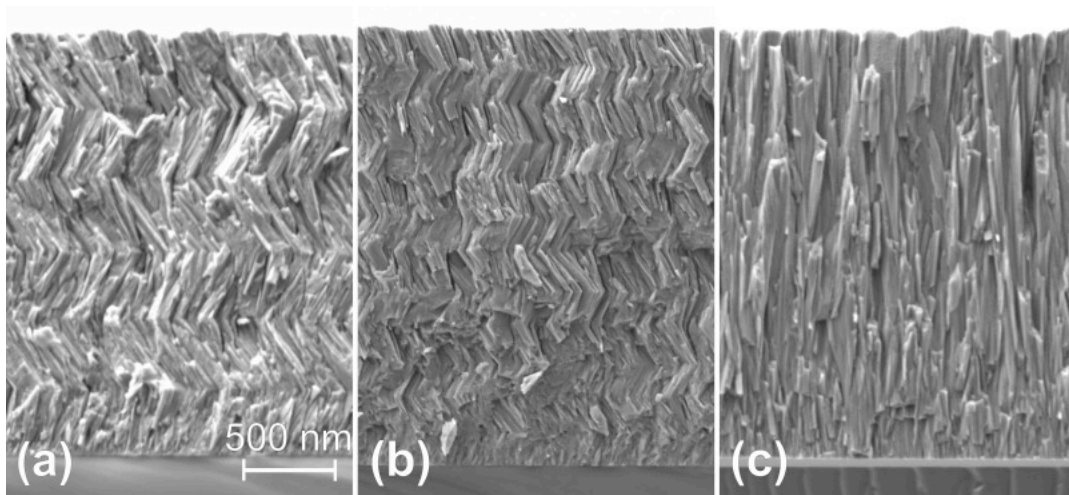


Figure 16: SEM cross-sectional micrographs of representative TiN films with chevron-like microstructure consisting of (a) 6 and (b) 12 layers and (c) a reference TiN film grown on a rotating Si substrate with columnar microstructure oriented perpendicular to the substrate surface. [Taken from Daniel *et al.* ^[157] and reprinted with permission from Elsevier]

A study by Jaya *et al.* ^[158] compared results of different fracture tests on Si, including single cantilever bending, clamped cantilevers, double cantilever beams and micro-pillar splitting, and showed that fracture toughness results are constant and in good agreement with bulk values. This moreover, highlights the suitability of micro-cantilevers for studying failure responses.

2.8.2.1 Microcantilever testing and SCC

The use of micromechanical fracture testing in the context of SCC research is a quite young field. As a consequence, literature is not very comprehensive. In the context of nuclear materials research, Fujii ^[159], ^[160] and Dugdale ^[49] are one of the first to apply such micromechanical strategies for studying the intergranular failure stress of oxidized GBs. Fujii ^[159] studied the influence of phosphorus segregation on aged and unaged Fe-Mn-P alloys, using a microscopic tensile test specimen and found that the failure load decreased with increasing phosphorous levels. In a second study Fujii ^[160] applied his strategy to test A600 GBs and found that intergranular oxidation significantly weakens the GB strength (ca. 300 MPa) whereas unoxidized GBs did not experience fracture, not even at 900 MPa. Besides the mentioned work, only Prof. Sergio Lozano-Perez's group in Oxford has attempted to test oxidized GBs on Alloy 600 in the context of SCC. Concerning the extraction of mechanical properties via micromechanical testing to study the supposedly brittle nature of oxidized GBs, a study from Prof. Lozano-Perez's group in Oxford from 2012 ^[49] on A600 coupons, oxidized in simulated PWR primary water, has addressed some of the open questions. Using a multifaceted approach, evolving around micromechanical cantilever bend-tests of oxidized GBs, the authors have been able to present valuable new insights:

1. The experimental response of tested GBs can be divided into 2 categories:
 - Cantilevers that do not fracture but are subject to plastic deformation

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- Cantilevers that experience brittle fracture along GBs
- 2. The cracking stops where the oxide vanishes
- 3. A Cr depleted oxide is formed next to the metal-oxide interface and a Cr-rich oxide is located at the centre of the IG oxide
- 4. In agreement with the SIO model, GB fracture is directly linked to the presence of internal oxides
- 5. Contrary to the SIO model, the fracture does not propagate through the oxide but always along the metal-oxide interface, where the less dense Fe-rich oxide is observed
- 6. Intergranular carbides modify the crack path and do not oxidize but are surrounded by a Ni-rich (Cr-depleted) region, which seems to oxidize preferentially

In lieu with EDF's efforts ^[4] to build a new model for predicting SCC initiation and propagation, based on more localized (microscopic) information about oxidation rates, stress intensities and the toughness of oxide weakened GBs, the authors of reference [49] have been able to provide quantitative information about the stress needed to fail an oxidized GB on A600 for the first time, supporting their results via Finite Element Analysis (FEA). A value of 1.35 GPa has been reported for the stress at failure (σ_{fail}), which corresponds to an interfacial fracture energy G of 3.4 J m⁻².

Even though this research peaked the interest of EDF and others in the community, it has to be emphasized that only one of the tested GBs (cantilevers) has been fully characterized and modelled by the authors, meaning that the result clearly lacks statistical significance. Also closely related to SCC research, Stratulat *et al.* ^[85], in collaboration with Prof. Lozano-Perez, recently used notched, pentagonal microcantilevers to successfully estimate the fracture toughness of oxidized Alloy 600

GBs. Using cantilever fracture test data, individual cantilever dimensions and the initial approach by Di Maio and Roberts^[151] the authors report values of $0.73 - 1.83 \text{ MPa m}^{1/2}$ for K_{IC} . Using EBSD to obtain misorientation data of the tested GBs, the authors moreover found that there is no direct correlation between the fracture toughness K_{IC} of the oxidized GBs and misorientation angle.

2.8.2.2 Size effects

Ever since the establishment of the field of microcantilever testing, size effects have been an important phenomenon. However, work has mostly focussed on size-effects in the context of plasticity measurements.^{[161] - [165], [166] - [169], [170]} According to Chen *et al.*^[168], a reduction of the thickness of metallic cantilever beams to the order of micron results in the observation of a strong size effect of the mechanical behavior. Motz *et al.*^{[164], [169]} for instance reported that copper beams at this scale usually exhibit a “smaller is stronger” trend, meaning that the yield stress increases with decreasing beam thickness. Whilst at present there is no unified explanation for the observance of size-effects, most existing theories base their occurrence on the ability of dislocations to move freely within a given crystal volume. This becomes even more complex when complex microstructures (oxides, GBs, precipitates *etc.*) are involved. While the theory behind size-effects exceeds the scope of this thesis, usually two different explanations for the “smaller is stronger” phenomenon for beams under bending are given. First, the increase in strength can thereby be explained in the context of strain gradient crystal plasticity. Thereby the size-effect is caused by strain gradients in the beam upon bending, whereby the crystal accommodates the deformation (tensile at top part and compressive at the bottom) via so-called geometrically necessary dislocations, which impede the plastic flow. If two identical crystals of different size are subjected to the same amount of deformation, the same amount of GNDs needs to be accommodated by their crystal lattice. However, due to the smaller crystal having a smaller volume to

accommodate all the necessary GNDs, the likelihood of dislocation mobility (plastic flow) is hindered, hence resulting in increased hardening of the smaller crystal. The second explanation is based on a backstress, originating from the dislocation pile-up at the neutral axis of the beam under bending, where the shear turns sign (top = tensile, bottom = compressive), which hinders further plasticity, as more force is needed for dislocations to move. In his experiments on single crystal copper cantilevers Motz reported that the flow stress scales with the beam thickness as $t^{-1.14}$. Motz^[169] later confirms this experimental observation via dislocation dynamics modelling, giving a simulated factor of t^{-1} . This is moreover in good agreement with Gong *et al.*^[165] who reported a scaling factor of $t^{-1.1}$ for prismatic slip in Ti. As expected the Young's modulus itself seems to be size-effect free, as it is a merely elastic property, as *e.g.* reported by Gibson^[167]. Nonetheless, a “one size fits all” explanation for the occurrence of size-effects does not yet exist. Moreover, even though a size-effect on the failure properties of materials with mostly brittle response seems unlikely, as supported by Armstrong *et al.*^[153] and Jaya *et al.*^[158] whose studies agree well with bulk values, comprehensive studies focussing on the potential influence of size-effects on fracture properties are widely lacking. Most of the work involving microcantilever fracture tests does not mention any size-effects on the fracture stress or toughness of tested beams. However, at least on the nanoscale ($< 1\mu\text{m}$), theoretical and experimental evidence of an increase in toughness with decreasing sample size has been reported.^[171] In a manuscript entitled “Smaller is tougher”, Beaber *et al.*^[171] suggest that the toughness is inversely proportional to the square root of size for thin films, nanopillars and nanospheres, using experimental results published elsewhere and in-situ electron microscopy nanoindentation experiments of Si nanospheres. However, the authors acknowledge that the presented results are still provisional and that more simulations and additional experiments are needed to confirm their findings. In the context of the

microcantilever fracture tests performed in this study, a major size-effect on the failure stress is not expected, as most beams experience no or hardly any plasticity before failure (see chapter 5). However, to keep any potential effect at bay, when comparing results on individual coupons, the microcantilever size of tests performed on each coupon was kept consistent to ensure comparability of the obtained results.

2.8.2.3 FIB-damage

Several studies in literature have dealt with the potential influence gallium (Ga^+) damage induced during FIB-based sample preparation. However, studies have been mainly carried out in the context of micropillar compression tests and smaller samples (*e.g.* TEM lamellas). The influence mainly originates from the introduction of additional defects (dislocations), Ga^+ implantation as well as re-deposition on the flanks of the milled samples, which might alter the measured properties (*e.g.* higher stress). Kiener *et al.* ^[172] for instance found that depending on the applied milling current, Ga^+ ions might penetrate into the sample to a depth of up to 50 nm. He suggests the use of lower kinetic energies and milling currents for final thinning steps as well as the use of grazing incident ions. Other studies ^{[173], [174]} compared two different micropillar preparation strategies. One involved the use of a FIB the other the chemical growth of the pillars. This allowed a direct comparison of the effect caused by the ion damage of the FIB. It was found that the ion damage induced a significantly lower yield strength (0.85 GPa), while the damage free, chemically grown structures exhibited a yield strength close to the theoretical values (9.2 GPa). The only study dealing with the effects of gallium bombardment on microbeams concerns the preparation of Si cantilevers. It was observed that the beams deflected once a width smaller than 300 nm is approached. However, neither the milling conditions nor a sufficient explanation was given. While an influence can't be ruled out with a 100% certainty, a significant influence caused by the FIB-based preparation of the microcantilevers in this study is

not expected as the beam dimensions are significantly bigger than the reported 300 nm of the Si beams and also exceed typical micropillar dimensions or dimensions of in-situ TEM test structures. Moreover, during the final preparation steps of the cantilevers, as detailed in section 3.3.2, the edges of the cantilevers were mill-polished using line-by-line “polishing” boxes and decreasing beam currents (*e.g.* 1000 – 100 pA) until clean edges and the desired cantilever width and length are obtained. The use of decreasing beam currents moreover prevents any significant re-deposition of gallium at the cantilever flanks, as can be seen in Figure 22 in section 3.3.2, where no re-deposition is seen on the edges of the triangular beams.

2.1 ATEM and SCC research

For SCC research ATEM represents an indispensable tool. In 1980 Thomas and Bruemmer published one of the first studies, providing ATEM analysis of GB oxides.^[175] 20 years later, the same group observed short, oxidized zones ahead of crack tips and narrow (~ 40 nm wide), deeply penetrated, oxidized zones along GBs of U-bend Ni alloy samples. By applying high-resolution imaging and fine-probe analysis, they were able to gather information about local chemistries and structures of those regions.^[176] In 2002 the group^[177] used ATEM to identify the corrosion products and environmental impurities along attacked GBs of PWR secondary-side A600 steam generator tubing. At approximately the same time Lozano-Perez and Titchmarsh^[178] performed a high quality ATEM study on initiation of SCC in A600 under simulated PWR primary water conditions, which underlined the huge potential of this method to study IGSCC and crack tips of Ni-base alloys. As recently demonstrated by Sennour *et al.*^[41], ATEM also plays a very important role in deciphering the structural and

chemical composition of oxide layers formed on the alloy and in identifying their crystallographic details.

2.2 Finite element simulations of micromechanical cantilever bend tests

In recent years materials modelling based on the finite element method (FEM), has proven to be a valuable supplement to the study of SCC of materials used in nuclear power plants. The potential of such models for studying various aspects of SCC is huge and the range of possible applications is wide spread.^{[4], [5], [49], [179] - [181]} The FEM is a numerical approach, which allows for the approximate solution of physical problems using partial differential equations. As described by Jacob Fish^[182], the FEM consists of 5 steps:

1. Pre-processing: Subdividing the problem domain into finite elements.
2. Element formulation: Development of equations for elements.
3. Assembly: Obtaining the equations of the entire system from the equations of individual elements.
4. Solving the equations.
5. Post-processing: Determining quantities of interest, such as stresses and strains, and obtaining visualizations of the response.

For further information about this method see reference [182].

However, as stated by Roters *et al.*^[183], “The finite element method is just the solver; to build a model it has to be combined with some physics. In the case of simulations in the field of solid mechanics a model consists of the geometry of some part (or several parts), mechanical boundary conditions and most important a material model.”

2.2.1 *The cohesive zone model*

Based on early work by Dugdale and Barenblatt ^{[184], [185], [186]}, the cohesive zone model (CZM) represents a well-established concept for explaining the initial linear elastic behaviour and consequent failure of interfaces based on the progressive decohesion of a cohesive zone ahead of a crack. The exact failure response, is thereby defined by a so-called traction-separation law (T- Δ), which relates the tractions (t_n , t_s , t_t) in normal and shear directions to the surface with the corresponding relative displacements (δ_n , δ_s , δ_t) across nodes or segments of the cohesive surfaces in the zone at which failure occurs and propagates.^[187] One big advantage of this method is the combination of crack initiation and propagation within one model ^[188], which makes it useful for the simulation of brittle SCC related GB decohesion. In the literature several different shapes and formulations of T- Δ laws can be found.^{[189] - [192]} The theory behind the cohesive zone model is detailed in section 4.2.

In the frame of this thesis the cohesive zone FEM has been used to simulate the brittle failure of the micromechanical bend tests and to achieve the major goal of quantifying the local stress at failure of a range of GBs for A600 (section 8.1).

2.2.2 *The crystal plasticity model*

Alloys, like A600, are built of polycrystals. The crystals are anisotropic and the exact elastic-plastic response of an alloy is dependent on the individual crystal orientations of the grains. Consequently, many mechanical phenomena like shape changes in the alloy, crystallographic texture, strength, strain hardening and deformation induced surface damage are also orientation dependent.^{[183], [193]} The crystal plasticity FEM has been developed in an attempt to utilize the extensive knowledge collected from experimental and theoretical studies of single-crystal deformation and dislocations to further the advancement of continuum field theories based on deformation.^[193] As such, this

CHAPTER 2 Stress corrosion cracking: a review

method, which has been introduced by Peirce *et al.* ^{[193], [194]} in 1982, serves as sophisticated tool for describing the mechanical response of crystalline materials, ranging from single crystals and polycrystals to whole parts.^{[183], [193]} To date various constitutive and numerical formulations have been developed ^{[180], [183], [193], [195] - [197]} to solve a broad range of crystal-mechanical problems. For instance a recent study from 2010 ^[181], which combines nanoindentation, EBSD experiments and CPFEM, made use of a strain-gradient CPFEM approach to study the anisotropy in the indentation behaviour of individual grains within a α -Ti polycrystal. This revealed the capability of such a method to correctly capture the orientation dependence of the load–displacement response.^[181]

The crystal plasticity simulations in the context of this work (see section 8.2) are based on the same strain gradient crystal plasticity formulation, as initially developed by Dunne *et al.* ^{[180], [181]}, who developed a user-defined element (UEL) in FORTRAN which was later transformed into a user-defined material (UMAT) by Dr. Edmund Tarleton. The FORTRAN based UMAT, which was implemented into the FEA software Abaqus 6.14-2, was provided by Dr. Tarleton for testing its applicability in the frame of this thesis. The theory behind the formulation and computational plasticity theory in general exceeds the scope of this thesis but the key principle and idea as well as the slip-rule used to determine the slip rates on all 12 slip systems in the fcc crystals are briefly highlighted in chapter 4.3. For more detailed information about crystal plasticity theory, the developed formulation and its underlying implicit integration scheme, please refer to the original work and the book published by Dunne.^{[180], [198]}

2.3 Motivation and goals

“The penetration of oxygen into grain boundaries has been shown to promote intergranular embrittlement and this suggests that oxidized grain boundaries could be the initial surface flaws for crack initiation. However, it is not clear if oxidized grain boundaries can be considered simply as microcracks with no mechanical resistance.”
Combrade et al. (2005) [36]

As made clear in the provided literature review, the exact mechanisms of crack initiation and propagation of SCC remain unknown and even though mechanisms have been suggested it seems to become more and more accepted that the phenomenon can't be explained by one mechanism alone. The nature of the “brittle” failure associated with SCC, a potential fracture through the GB oxide as suggested by the SIO model, the influence of oxidation level and local microstructure (carbide precipitation) on the mechanical resistance of the GBs are not yet proven nor understood. Due to its unprecedented capability to extract local mechanical parameters, like the stress at failure of individual oxidized GBs, micromechanical testing of SCC via cantilever bend-tests of individual oxidized GBs has been used to study intergranular SCC initiation and propagation. The investigation of local SCC conditions and the extraction of local parameters like the failure stress are crucial for advancing the nuclear industry's effort of realizing more accurate, physics-based component lifetime prediction on the engineering scale and for predicting and understanding SCC related failures in component materials. Most models in industry are based on macroscopically determined quantities whereas SCC represents a local and microscopic phenomenon. From this it is clear that models based on local parameters, as developed by EDF [4], [5], are needed to achieve more accurate predictions. To date, due to the challenging nature and lack of experience with testing oxidized GBs at the microscale, only 2 publications,

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directly dealing with the extraction of the stress at failure of oxidized GB on Alloy 600 have been reported in literature. Fujii ^[159] reported an experimental value of 300 MPa for oxidized A600 GBs, obtained via a micro tensile test strategy, whereas Dugdale ^[49] reported a single quantified value of 1.35 GPa for one oxidized GB, obtained via microcantilever bend tests, which the authors obtained via cohesive zone finite element simulations of the actual experiment. Due to the obvious lack of statistical significance of the existing work, main goals of this thesis included:

- The testing of a higher number of oxidized GBs via microcantilever bend tests
- The advancement of the overall methodology of investigations
- The extraction and quantification of the stress at failure from experiments as well as via finite element simulations to prove their accuracy
- The provision of a failure stress range, based on the performed test results for use in EDF's "local" model for IGSCC prediction ^[4]
- The acquisition of a better understanding of the SCC fracture mechanism and mechanical response of oxidized GBs by trying to relate it to the local microstructure (*e.g.* role of carbides, role of oxide chemistry and composition)

As such, chapter 5 gives some preliminary investigations of the two oxidized A600 coupons.

Chapter 6 addresses the microcantilever tests and results carried out on the Alloy 600 coupons detailed in section 3.2. The importance of considering external oxide scales when extracting the stress at failure at the microscale is also covered and supported by finite element simulations.

Chapter 7 extends the micromechanical results by electron microscopy investigations, including the introduction of a new lift-out preparation and investigation strategy for microcantilevers, which allows for an almost complete reconstruction of the tested

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sample volume via 3D FIB-SEM while still being able to prepare a TEM lamella for additional high-resolution investigations. Electron energy loss spectroscopy of the intergranular oxide, carbides and interfaces is also addressed and linked to the observed crack path.

Chapter 8 introduces the use of finite element models in the context of the finite element analysis software suite Abaqus to simulate the performed tests. Cohesive zone models are used to quantify the stress at failure and to proof the accuracy of the failure stress results, extracted via stress-strain analysis and simple beam theory, as described in chapter 6. Finally, a strain gradient crystal plasticity subroutine is used to simulate the plastic response of an unoxidized GB.

Chapter 9 concludes the observations made in the frame of this thesis and provides some final remarks.

Chapter 10 provides recommendations and details about possible future research directions.

3 EXPERIMENTAL ASPECTS

3.1 A multi-faceted investigation strategy

All experiments carried out within the frame of this thesis evolve around a multi-faceted investigation strategy, which includes experimental as well as computational means. Figure 17 gives an overview of the investigation cycle employed on the prepared microcantilevers, which combines micromechanical cantilever bend tests with electron microscopy (SEM as well as (S)TEM) and realistic FEM simulations and represents a sophisticated strategy, which, to the best of the author's knowledge, provides the most accurate way of studying the failure of oxidized GBs and to extract their local failure stress to date.

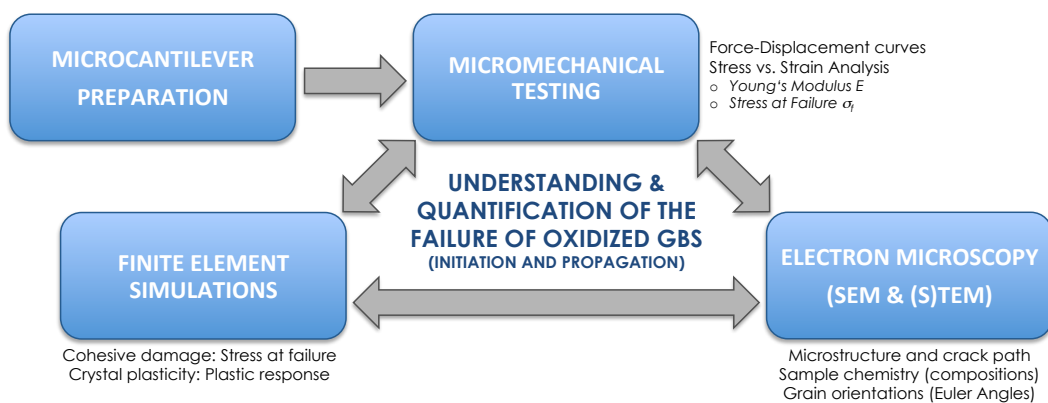


Figure 17: Overview of the multi-faceted investigation strategy to understand SCC crack initiation and propagation of oxidized GBs on Alloy 600.

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Due to the broad range of machines used in this thesis, their fundamental principles and functionality won't be covered in detail. References to relevant introductory literature for each technique and machine will however be provided. Before giving an overview of all sample preparation strategies and applied techniques, the next chapter will introduce the different samples used in the frame of this thesis and highlight some preliminary observations.

3.2 Materials

In the course of this thesis 3 Alloy 600 coupons, with different microstructure and thermal history have been investigated, 2 of which have been oxidized (*A600-INSS* and *A600-EDF*) and are the main subjects of investigation of this work. The third was an unoxidized A600 coupon (*A600-NOX*), used for crystal plasticity FEM only (see section 8.2). All coupons used in this research were provided by external institutions. Oxidation was achieved by exposing them to simulated PWR primary water in an autoclave. Details about sample composition, heat treatment and autoclave conditions of the provided samples are presented in the following sections.

3.2.1 Oxidized Alloy 600

3.2.1.1 Alloy 600 with high intergranular carbide coverage

The first sample was a mill-annealed Alloy 600 coupon provided by the Institute of Nuclear Safety Systems (INSS), Japan, who also performed the corrosion test of the sample in an autoclave. The main research of this thesis was carried out on this sample, which will be further referred to as *A600-INSS*. The chemical composition of *A600-INSS* is shown in Table 3 (top). Prior to autoclave testing the sample has been mill annealed for 30 minutes at 1050 °C to promote intergranular carbide precipitation. The

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sample also received 20% cold work via cold rolling. The autoclave testing itself was carried out under simulated PWR primary water conditions, as described in Table 3 (bottom).

CHEMICAL COMPOSITION (WT.%)				
Ni	Cr	Fe	C	Mn
74.03	16.21	8.57	0.017	0.32

AUTOCLAVE CONDITIONS		
DH2	Li	B
30 cc/kg	2 ppm	500 ppm

Table 3: Chemical composition of *A600-INSS* (top) and simulated primary water autoclave conditions (bottom). The sample was exposed to the environment at 340 °C for 2000 hours.

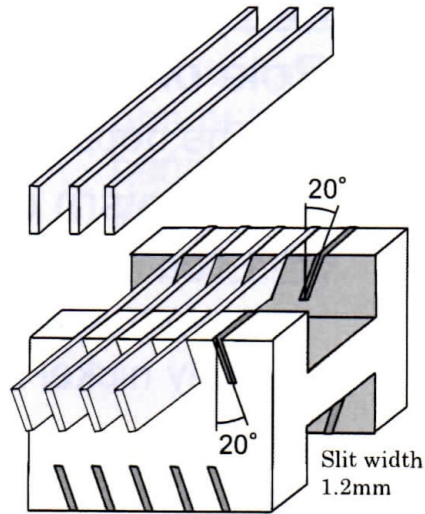


Figure 18: Demonstration of the special jig design, which was used to apply stress to *A600-INSS* in form a 40° twist. [Provided by INSS, Japan]

To promote the oxidation of the sample, the sample was exposed to the environment at 340 °C for 2000h. Moreover, in order to accelerate the intergranular oxidation, the sample was stressed by applying 40° twists via a special jig designed by INSS. The

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design is demonstrated in Figure 18. Unfortunately, the sample provider did not document any detailed information about the applied stress conditions.

3.2.1.2 Alloy 600 with low intergranular carbide coverage

The second sample investigated in this thesis was a hot-forged Alloy 600 coupon provided by Électricité de France (EDF), France. All sample information was provided by EDF, who provided the sample and carried out the pre-examinations. EDF also carried out the autoclave testing of this sample. The sample will be further referred to as *A600-EDF*. The chemical composition of *A600-EDF* is shown in Table 4 (top). The forging was carried-out at 1100 °C – 1200 °C and the sample was given a final 2h heat-treatment at 820 °C. This resulted in a relatively high number of intragranular carbides, which indicate the original location (ghost microstructure) of the grain boundaries before recrystallization, as can be seen in Figure 19. In contrast only 15% of GBs were covered with intergranular carbides, as reported by EDF. The average grain diameter provided by EDF, excluding twin boundaries, has been reported as 10 µm. Nonetheless, Figure 19 suggests an average grain size of 20 - 30 µm to be more realistic.

CHEMICAL COMPOSITION (WT.%) (%)											
Ni	Cr	Fe	C	Mn	Si	S	Cu	Co	Al	Ti	P
73.2	16.05	8.8	0.058	0.81	0.45	<0.001	0.02	0.04	0.24	0.29	0.007

AUTOCLAVE CONDITIONS		
DH ₂	Li	B
20 cc/kg	2 ppm	1000 ppm

Table 4: Chemical composition of *A600-EDF* (top) and simulated primary water autoclave conditions (bottom). The sample was exposed to the environment at 360 °C for 1004 hours.

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Information about the mechanical properties of the sample in the as-received condition was provided by EDF and is summarized in Table 5 (bottom). The autoclave testing itself was carried out under simulated PWR primary water conditions, as described in Table 4 (bottom). The sample was exposed to the simulated PWR primary water environment for 1004h at a high temperature of 360 °C to accelerate the oxidation.

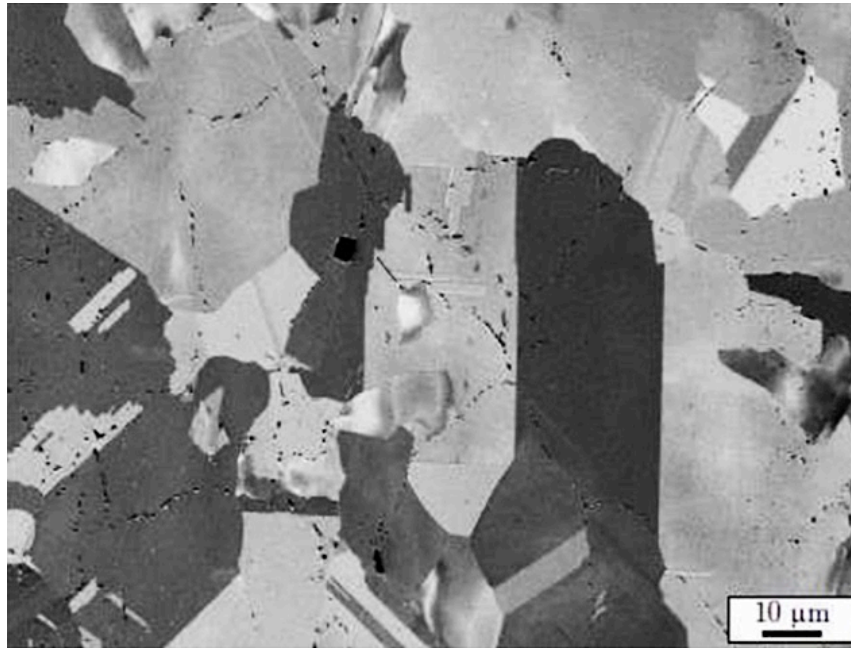


Figure 19: SEM SE image of the microstructure of hot-forged *A600-EDF* before exposure to the environment, revealing the location of grain boundaries before recrystallization. [Provided by EDF, France]

Temperature (°C)	YS _{0.2} (MPa)	UTS (MPa)	El. (%)
20	468	729	33
360	430	462	30

Table 5: Mechanical properties of *A600-EDF* in the as-received condition at room temperature and 360 °C.

3.2.2 Alloy 600 with no oxidation

The third sample was a pre-strained, hot-forged Alloy 600 coupon, with no oxidation present (polished). The sample, which received a final 2h heat treatment at 820 °C, was also provided by EDF. It was polished using the procedure described in chapter 3.3.1 and served as a simplified system for simulating cantilever bending, using crystal plasticity FEA modelling (see section 8.2). It will be further referred to as *A600-NOX*. The chemical composition of *A600-NOX* is shown in Table 6 (top) and the mechanical properties at room temperature are summarized in Table 6 (bottom). The mean size of the alloy grains was reported to be ca. 60µm with relatively poor intergranular carbide coverage (~ 15%), similar to *A600-EDF*.

CHEMICAL COMPOSITION (WT.%)											
Ni	Cr	Fe	C	Mn	Si	S	Cu	Co	Al	Ti	P
73.03	16.02	8.8	0.058	0.81	0.45	<0.001	0.02	0.04	0.16	0.6	0.007

Temperature (°C)	YS _{0.2} (MPa)	UTS (MPa)	El. (%)
20	428	729	33

Table 6: Chemical composition (top) and mechanical properties at room temperature (bottom) of *A600-NOX*.

3.3 Sample preparation

3.3.1 Initial bulk sample preparation

To obtain a clean and scratch-free surface on the unoxidized *A600-NOX* coupon, suitable for obtaining EBSD maps to extract the Euler angles of the grains, the sample surface was polished with diamond paste (grit size: 1µm) for about 15 – 20 min. Next the sample received a 10 – 12 min long mirror finish with colloidal silica, using water as lubricant. This procedure was performed on the *A600-NOX* sample only. Due to the

requested preservation of the surface oxide films on the samples provided by INSS, Japan, proper surface polishing was no option for *A600-INSS*. *A600-EDF* was the only other sample experiencing a slight polish via colloidal silica alone. This was necessary due to the thick and inhomogeneous outer surface oxide layer present on this sample, as described in section 5.2. Several gentle, hand-applied rubs of ca. 10 seconds were applied until the oxidized GBs of the alloy underneath the surface oxide scale became visible. This was checked in a conventional optical microscope. The only purpose of this treatment was to enable an easier preparation of micro-cantilevers at GBs, as described in the next section. Details about all samples are given in section 3.2.

3.3.2 Microcantilever preparation

The FIB-based fabrication of micron-sized cantilevers used in this thesis makes use of the site-specific sputtering capability (ion milling) provided by the Ga^+ ions of conventional FIB or dual beam FIB systems. In the frame of this thesis 3 different FIB systems have been used, as summarized in Table 7. For details about the functionality and principles behind FIB microscopes please refer to Yao ^[199] and Latif ^[200]. The presented strategy is based on an approach first used by Di Maio and Roberts ^[151] and Armstrong *et al.* ^{[152], [153]} for pentagonal and triangular beams respectively. Dugdale *et al.* ^[49] adapted this approach for testing of oxidized GBs on Alloy 600 for the first time. All cantilevers tested, across all sample coupons investigated within the frame of this thesis, were manufactured according to the described guidelines. As a general rule, the ratio between L_{eff} (GB to load point) and the cantilever width in this work was kept greater than 6 to allow for most accurate estimations of Young's modulus E and stress at failure σ_f via simple beam theory. This is based on findings by Armstrong *et al.* ^[152], who reported on the influence of the effective length (loading position) on the mechanical behaviour of single crystal copper beams and was able to show that 6 is a

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critical aspect ratio which needs to be kept in order for beam theory estimations to work and to prevent an underestimation of obtained values of Young's modulus E .

MACHINE	COLUMN TYPE	ION-SOURCE	GIS	MM NEEDLE
FEI FIB 200	Single Beam	Ga^+	Pt	Static
Zeiss NVision 40	Dual Beam (FIB+SEM)	Ga^+	W, C, SiO_2	Kleindiek
Zeiss Auriga	Dual Beam (FIB+SEM)	Ga^+	Pt, C, W	Kleindiek

Table 7: Single and dual beam FIB systems used in this thesis.

As a first step of cantilever preparation, suitable GBs were located by milling small local trenches into the oxidized specimen surface, using the sputtering and tilting function of the FIB as shown in Figure 20. Ideally, the chosen oxidized GBs should be as perpendicular to the sample surface as possible.

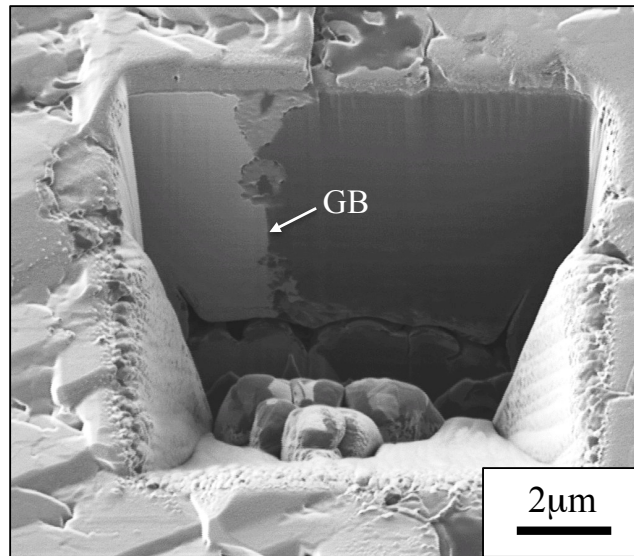


Figure 20: FIB SE image showing a FIB-machined local trench revealing an oxidized A600 GB (A600-INSS), which runs perpendicular to the sample surface. Dark spots are observed at the oxide-metal interface of the untested material.

Depending on the machine, (single or dual-beam FIBs), the necessary contrast to reveal the sample features, including *e.g.* the GB, carbides and the intergranular oxide where

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some darker regions were visible at the oxide metal interface of the untested material, is provided by their different channelling interactions with the beam (ion or electron beam). With the patterning option of the FIB, 3 trenches (U-shape) were milled onto the sample in such a way, that the GB was included approximately 1 μm away from the fixed end of the cantilever, where the stress is high. High beam currents of 4000 – 7000 pA are recommended. The trenches used for obtaining the initial U-shape are schematically shown in Figure 21. The region in-between the trenches should be at least 1 – 2 μm wider and longer than the desired cantilever width and length in order to allow for sufficient fine-tuning and polishing of the cantilever edges. For a desired final beam width of 4 μm this would for example mean a region of at least 5 – 6 μm in width in-between the initial trench arrangement. By tilting the stage of the FIB to a 30° angle, the long side of the cantilever was then undercut from one side. Following a 180° rotation the beam length was also undercut from the other side to achieve the desired triangular shape. Beam currents of 2000 – 3000 pA are suggested for this step.

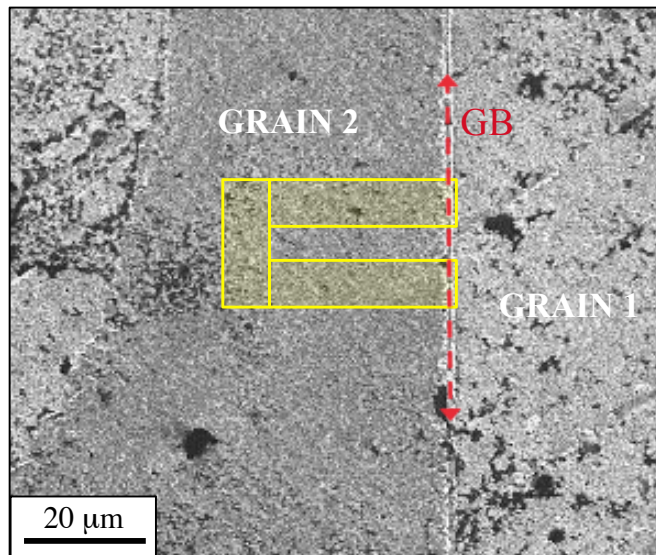


Figure 21: FIB SE image showing the schematic of the trench arrangement needed to mill the initial U-shaped cantilever pattern (*A600-INSS*). The GB is included ca. 1 μm away from the fixed end.

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Considering the often complex surface state of the samples, *e.g.* a severe surface oxidation (roughness) on *A600-INSS*, a triangular shape was preferred to pentagonal cantilevers due to it needing less milling time and not needing for two vertical sides of identical depth, which, especially on samples with high surface roughness, are difficult to obtain and might lead to torsion of the beams. After the undercut the three beam edges were finished off, using small line-by-line “polishing” boxes and decreasing beam currents (*e.g.* 1000 – 100 pA) until clean edges and the desired cantilever width and length were obtained. An example of a finished triangular cantilever after preparation is shown in Figure 22.

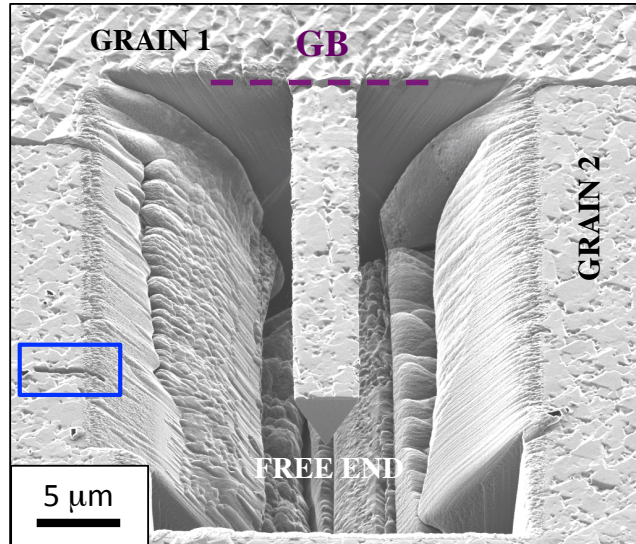


Figure 22: Representative SEM SE image of a triangular microcantilever (*A600-INSS*). The milled line, highlighted by the blue box, marks the desired height of the loading point (L_{eff}).

As can be seen in the image, a small line (highlighted by a blue box) was milled next to one of the trenches to mark the desired loading point in preparation for the following micromechanical bending test with a Nanoindenter (section 3.4). The line was moreover useful to determine the effective length (L_{eff}), defined as distance between the GB and point of contact between the indenter and cantilever, which was needed for simple beam theory estimations, as described in section 3.5. To keep reported size-

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effects ^{[161] - [165]} (which might influence the reliability and reproducibility of the obtained data) at a constant level, consistent cantilever dimensioning throughout the experiments on each sample was important. Consequently, all cantilevers in this thesis showed a triangular shape, undercut at 30°, and cantilever length and width were kept as consistent as possible to ensure comparability of the results on each coupon. However, depending on the grain size of each investigated coupon, the dimensions of the test structures needed to be adjusted. Average cantilever dimensions on each individual sample are summarized in Table 8. Moreover, it was found that the beams were not perfectly and comparably equilateral. Consequently, beam dimensions were measured individually for each cantilever in this study using a range of SEM images taken from different perspectives and angles to determine a good average. The finished cantilevers were then tested and analysed, as described in section 3.4 and 3.5.

AVERAGE CANTILEVER DIMENSIONS (μm)			
<i>Coupon ID</i>	<i>Length (L)</i>	<i>Width (w)</i>	<i>Effective Length (L_{eff})</i>
<i>A600-INSS</i>	28	3.8	> 6*w
<i>A600-EDF</i>	28	3.8	> 6*w
<i>(2 beams)</i>	20	3	> 6*w
<i>A600-NOX</i>	20.8	2.9	> 6*w

Table 8: Table showing the average dimensions of the beams prepared on each coupon. All samples are undercut at 30°.

3.3.3 Microcantilever lift-outs and TEM sample preparation

3.3.3.1 Conventional TEM sample preparation

For the performance of structural and chemical investigations of tested beams (GBs) via analytical transmission electron microscopy (ATEM), and for the extraction of the local microstructure and geometry for realistic modelling purposes, electron transparent samples (thickness between 50 – 100 nm) had to be prepared. This can be achieved by

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using advanced FIB-based TEM lift-out methods, as reported in literature.^{[201], [202], [203]}

Nowadays, state of the art dual beam FIB systems, which incorporate both a FIB and a scanning electron microscope (SEM) ^[204], represent a very common and convenient tool for sample preparation and investigations. The FIB's ability of site-specific material removal paired with the SEM's capability of non-destructive imaging and analysis, has numerous benefits ^[205] like being able to track the milling progress damage free or allowing 3D FIB-SEM tomography of the sample (see section 3.6).

Conventional TEM sample preparation in this thesis was based on work published by Huang *et al.* ^[206] and Lozano-Perez *et al.* ^[207], who use an in-situ lift-out technique based on dual-beam FIB systems for TEM sample preparation. The method involves the deposition of a protective platinum strip (1 μm thick) onto the area of interest to prevent Ga^+ ion implantation and undesired milling of the sample area. This is followed by the consequent removal of the material from 3 sides (3 trenches) around the area of interest, leaving behind an approximately 1 – 2 μm thick region, which is only fixed at one end (Figure 23 a). This region is then undercut from 2 sides (45°) using 2 boxes (Figure 23 b). The sample is then approached and lifted-out with a micromanipulator needle, using Pt as weld material (Figure 23 c - d). The lamella is then directly transferred to a special copper support grid (Omniprobe 3 or 5 post TEM grid) and cut loose from the micromanipulator (Figure 23 e - f). The final thinning to achieve electron transparency is then carried out directly on the support grid. In this thesis, the single beam FIB system described in Table 7 was used for the lift-outs, whereas the final thinning was carried out in either of the described dual-beam FIBs.

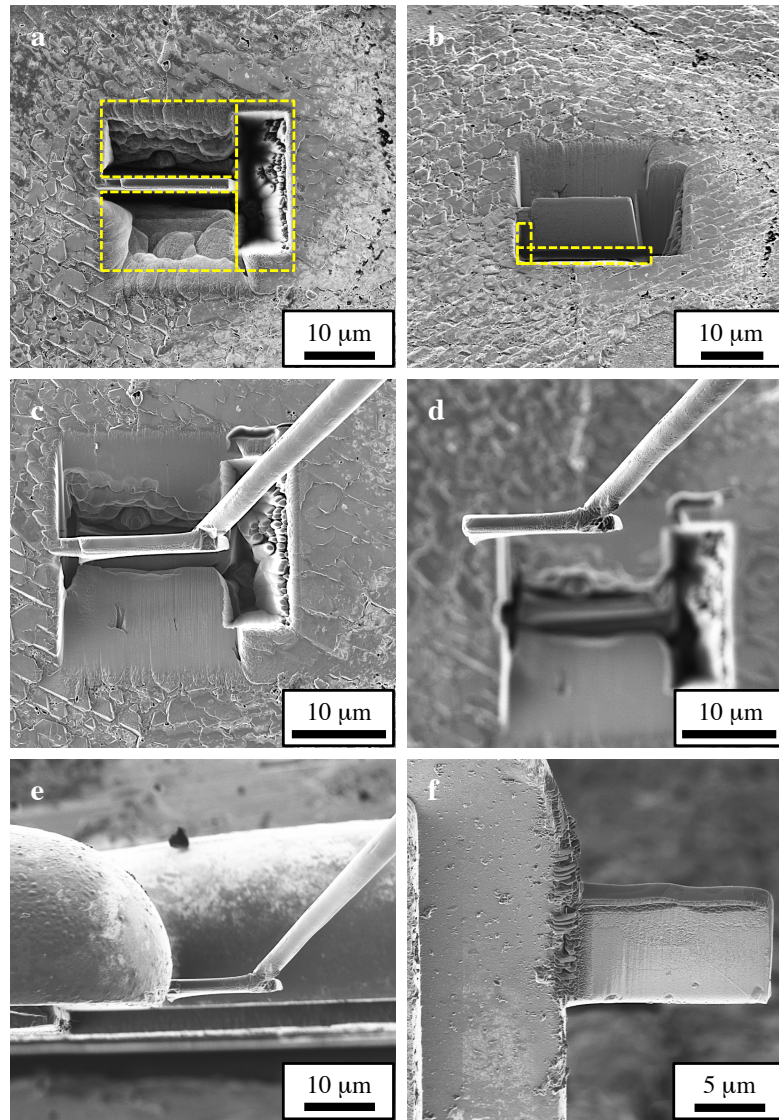


Figure 23: Conventional TEM sample lift-out steps, performed in the FEI FIB200.

3.3.3.2 A novel strategy for lifting out whole microcantilevers

As described in section 3.3.2, the cantilever is a freestanding, triangular beam fixed only at one end. This is similar to the conventional TEM sample condition right before the lift-out. Consequently, if carried-out with care, the above-described technique is perfectly applicable for obtaining a TEM sample of the central portion of tested cantilevers. Nonetheless, most of the sample volume is destroyed in the progress and no information about the local 3D microstructure along the GB can be gained.

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Consequently, a novel strategy for preparing TEM samples from whole cantilever volumes directly on the copper grid has been developed and will be discussed next. The presented technique for lifting-out whole cantilevers originated from the idea to combine a conventional sample preparation step with advanced sample characterization via 3D FIB-SEM sequencing from 2 sides of the sample volume directly on a TEM grid, leaving approx. 300 nm untouched for final TEM sample preparation. As detailed in section 3.6, this allowed for the very first time the extraction of information about the local 3D microstructure and crack path of micromechanically tested cantilevers, which incorporate oxidized GBs, in addition to conventional TEM sample preparation, which allowed further analytical TEM investigations (*e.g.* STEM, EELS) where necessary. The single beam FIB system described in Table 7 was used for the cantilever lift-outs, whereas the 3D FIB-SEM sequencing and final thinning was carried out in either of the described dual-beam FIB systems. The starting point was a typical freestanding cantilever with a GB included approx. 1 μm away from the fixed end (Figure 24 a). Keeping in mind the performance of 3D FIB-SEM sequencing and the final aim of obtaining a TEM sample of the GB region from the central portion of the beam, the first step was to deposit a protective Pt layer onto the area of interest which covers the whole beam width and includes plenty of area from both grains as indicated by the green box in Figure 24 a ($L_{box} = \sim 12 \mu\text{m}$). Whilst the deposition of a smooth Pt layer onto the whole cantilever width might be considered time intensive, it ensured a minimization of eventual FIB curtaining effects encountered during 3D FIB-SEM sequencing and further stabilized the crack during the lift-out procedure. The next step was the expansion of the trench regions on the long side of the beam close to the fixed end to access more area of the fixed end grain (Figure 24 b, yellow boxes). Following the usual preparation procedure described in section 3.3.3.1 the sample was then tilted and undercut at 45° , using 2 boxes. These boxes were placed in such a way that the width

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of the beam near the fixed end was reduced to the typical 1 – 2 μm thickness of a typical TEM sample before the lift-out (Figure 24 c) to enable an easy detachment during the lift-out process (Figure 24 d, indicated by pink arrows). Due to the fact that the whole cantilever volume needed to be undercut, great care was taken to make sure that the undercut was successful and that no issues (*e.g.* an eventual re-attachment from Ga^+ redeposition) were encountered during the actual lift-out process. For the lift-out process the sample was usually aligned with the free end looking away from the micromanipulator. The reason for this was to simply use the free-end side of the beam as extension arm for the attachment to the copper grid to minimize its influence when performing further analytical microscopy characterizations like *e.g.* EDX elemental mapping. Moreover, this made further time-intensive chopping of the cantilever's long side unnecessary. To help with a later locating of the mid-point of the cantilever width during the later 3D FIB-SEM sequence, a shallow line was milled central onto the Pt free long-side of the cantilever. The sample was then approached by the micromanipulator, using Pt as weld material (Figure 24 e, green box) and the attachment to the bulk was cut loose (Figure 24 e, yellow box). After the lift-out, the sample was attached to a conventional 3-post TEM copper grid, as usual using Pt as weld material. Keeping in mind the dimensions of the whole beam, care was taken that during all welding steps the actual weld was strong enough to hold the sample before cutting it loose from the bulk or micromanipulator needle. Figure 24 f shows the final cantilever lift-out after attachment to the copper grid. The blue arrow indicates the tested GB region, which will be used for further 3D FIB-SEM sequencing and TEM sample preparation. In order to prepare a TEM sample out of the whole cantilever volume, 3D FIB-SEM sequencing was performed from 2 sides of the beam, leaving behind approximately 300 nm for the usual, final TEM sample thinning. The 3D FIB-SEM sequencing procedure is described in section 3.6.

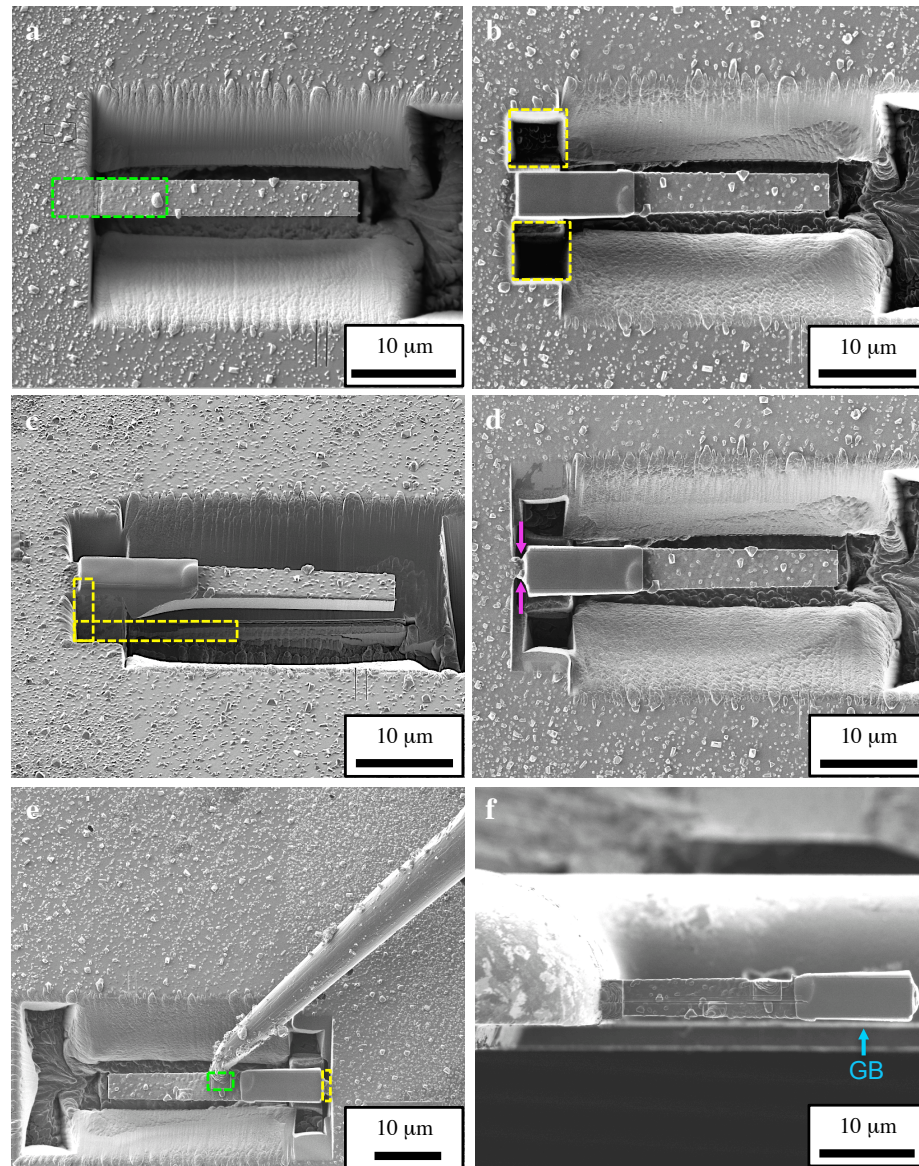


Figure 24: Microcantilever lift-out procedure. (a) Protective Pt-layer deposition (green box). (b) Undercutting of grain 1 (yellow boxes). (c) Undercut at 45° to be done from both sides (yellow boxes). (d) Top view of the undercut cantilever, which was attached to the bulk by an only 1 – 2 μm wide region, as indicated by the pink arrows. (e) Welding of the sample to the MM needle via Pt-deposition (green box) and consequent detachment from the bulk (yellow box). (f) Whole cantilever lifted-out onto a TEM Cu grid (top view). The Pt-protected region of interest (GB region), used for further 3D FIB-SEM and TEM sample preparation, is indicated in blue.

3.4 Micromechanical testing of FIB-machined cantilevers

A FIB-based preparation strategy, based on early work by Di Maio and Roberts ^[151] was used within this thesis. The FIB-based fabrication of the microcantilevers is described in section 3.3.2. After microcantilever fabrication, the respective sample was put onto the piezoelectric stage of a Agilent NanoIndenter G200 (Agilent Technologies, Wokingham, UK), as shown in Figure 25 (top), and the prepared cantilevers were identified with its built-in optical microscope, using either the 10x or 40x magnification lens provided in this machine. After careful calibration of the microscope to the indenter, the cantilevers were scanned with the scanning option of the nanoindenter. Thereby the tip was brought into contact with the sample and the piezoelectric stage then rasters the sample under the tip in x-y direction, whilst maintaining a pre-set constant load. The coil-magnet assembly shown in Figure 25 (top) controls this load and the displacement of the shaft-tip assembly is measured with the built-in capacitive plates (50 nN force and 0.02 nm depth resolution). Plotting the x-y-data against the tip displacement resulted in a topological image of the cantilever surface, as shown in Figure 25 (bottom). The resulting maps allowed a placement of the indenter tip with 2 nm accuracy. This was crucial for an accurate and central placement of the indenter tip (diamond Berkovich tip) onto the free end of the cantilever at the desired effective length L_{eff} , which marks the load point (black X). The height of the load point (tip-cantilever contact point) was indicated by marker lines (blue), which were milled next to the trenches of the beam during the cantilever preparation procedure, as also detailed in section 3.3.2 (blue box in Figure 22). The quality of the scan however was strongly dependent on the surface quality (*e.g.* surface roughness due to varying degrees of surface oxidation), as can be seen in Figure 26. A constant scan load of 3 μ N was found to work best on the samples used in this study.

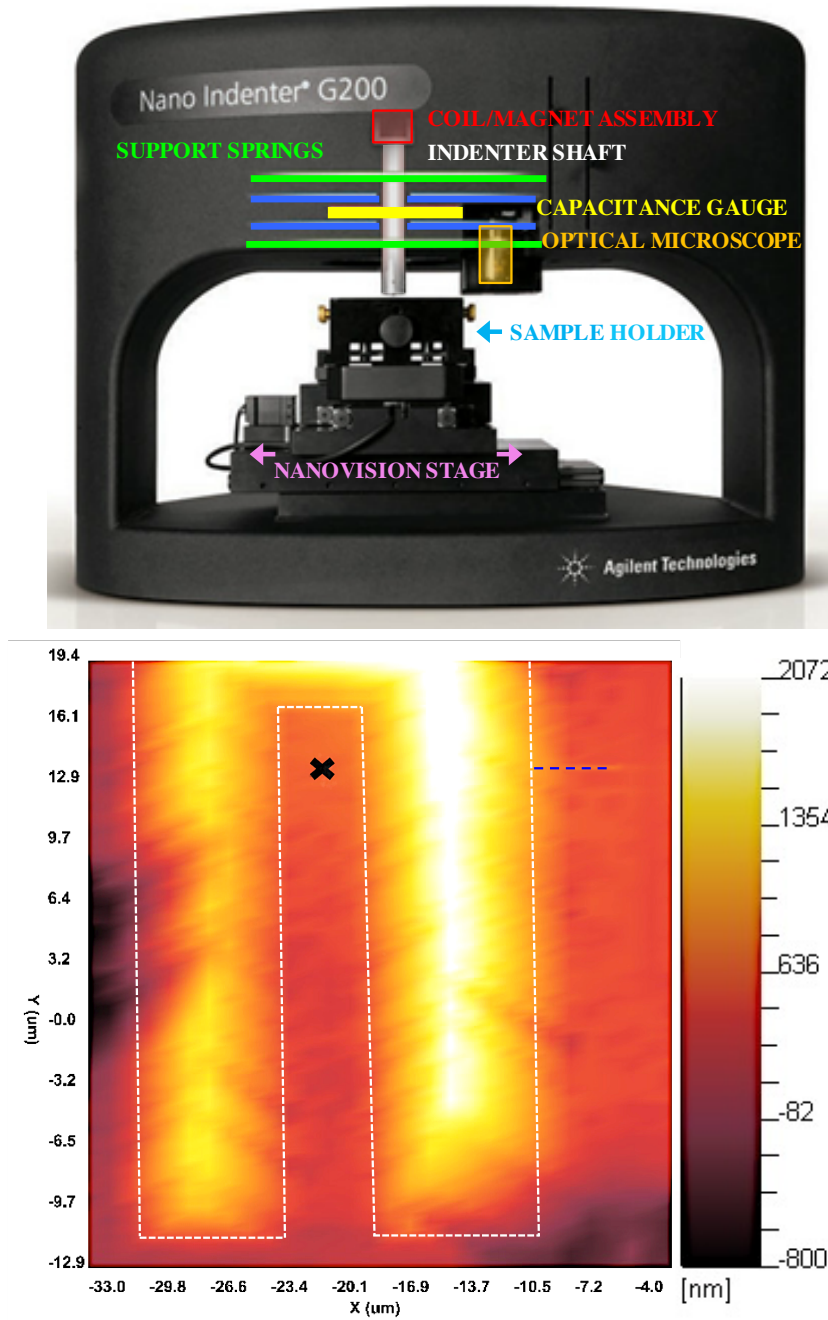


Figure 25: (top) Representation of the Agilent NanoIndenter G200 set-up. (bottom) Scan of a cantilever on *A600-EDF* obtained with the Agilent NanoIndenter G200. The brighter U-shaped shades in the scan represent the trenches around the actual cantilever. The X represents the loading point at the desired effective length L_{eff} , which was found by a milled line (blue) next to the trench, usually seen as lines of lighter colour.

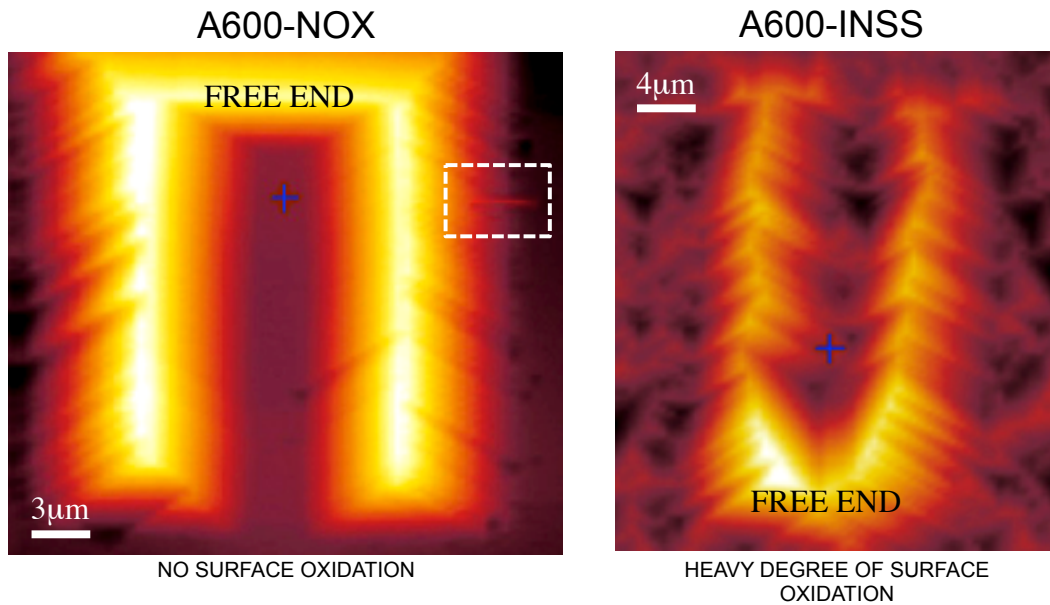


Figure 26: Comparison of the scan quality of 2 samples with different surface roughness conditions. While the example on *A600-NOX* was flat (no surface oxides) and the cantilever and marker line (white box) were easily identified, the example on *A600-INSS* showed a heavy degree of surface oxidation and roughness, leading to scan artifacts (tip convolutions) and a bad scan quality.

After central placement of the Berkovich tip at the height of the pre-marked loading point, a constant displacement rate of 5 nm/s was applied until failure or until a certain pre-set displacement (*e.g.* 2000 nm) was achieved. Simultaneously, the force-displacement (F-D) behaviour was recorded. Information about the failure mechanisms (*e.g.* brittle fracture, plastic deformation *etc.*) of individual GBs was extracted from the data and the desired stress at failure was determined, as will be described in the next section. A representative F-D curve, showing no fracture event, is shown in Figure 27. The F-D data of all tested beams was analysed, using simple beam theory to perform stress-strain analysis (see section 3.5), and partially supported by FEA, as described in chapter 8.

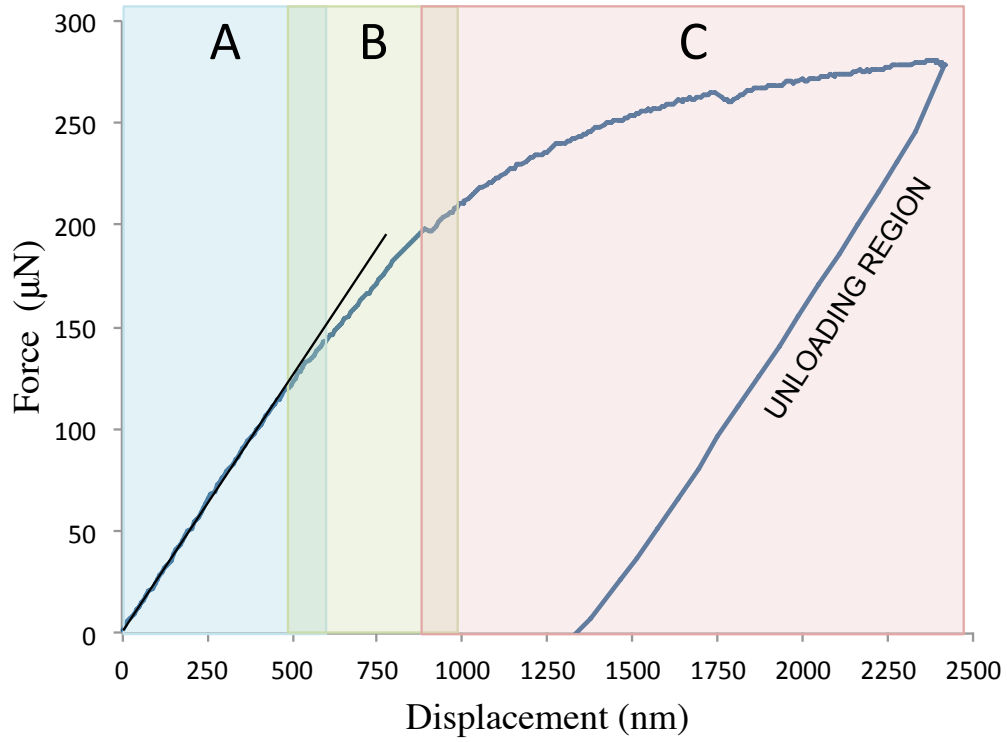


Figure 27: Representative F-D curve. Region A corresponds to the merely elastic region of the curve. The point of onset of plastic deformation presumably lies within the overlap of region A-B but it is not always clearly identifiable on first sight. Region B - C represents the plastic regime (non-linear behavior).

3.5 Simple beam theory for stress-strain analysis

Throughout this thesis, simple beam theory^{[170], [208]} was used to perform stress-strain analysis of the acquired data. This was done by converting the recorded F-D data (Figure 27) into maximum stress-maximum strain plots (Figure 28, right). A set of beam dimensions and mathematical relations was needed for this undertaking and will be discussed next. Figure 28 (left) represents a simplified representation of the triangular cantilever set-up used in this thesis. The width and height of the beam were measured in a SEM before the test. The effective length L_{eff} was defined as the distance between the GB and the loading point and was measured using dedicated FIB-milled

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markers, as detailed in section 3.3.2. The GB was incorporated approx. 1 μm away from the fixed end and represents the region of highest stress at which failure will initiate.

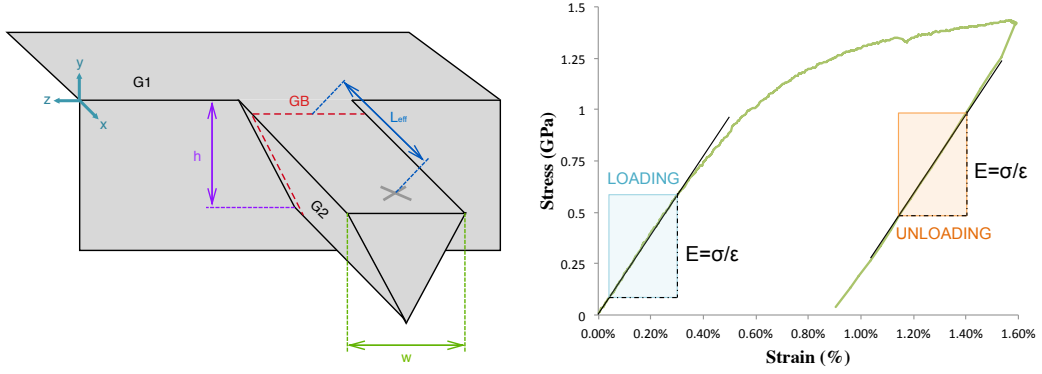


Figure 28: (left) Schematic of the triangular microcantilever dimensions needed for simple beam theory stress-strain analysis and (right) stress-strain curve corresponding to F-D data in Figure 27. The gradient of the elastic regions in the loading and unloading regime give the Young's modulus E .

In theory one can recognize that when a load P is applied at a defined loading point at the free end of the beam (grey X in Figure 28, left), the beam experiences a displacement δ and is subject to an uniaxial force in the plane of bending, where all stress elements are zero besides the stress in xy and xx direction. This however relies on ideal conditions, meaning “perfectly symmetric” beam dimensions and symmetry of the triangular cross-section of the beam about the plane of loading.

The maximum stress via simple beam theory is defined as

$$\sigma = \frac{My}{I} = \frac{Ey}{R} \quad \text{Equation 3}$$

With M being the bending Moment, defined as $M = PL$ (Force x Length) and y being the distance from the beam edge in loading plane to the neutral axis of the beam, which for a triangular shape is located at $y = \frac{2}{3}h$. So the neutral axis for beams, as depicted in

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Figure 28 (left), is located one-third from the top surface of the beam. The second moment of area I for a triangular beam cross-section is consequently defined as

$$I = \frac{wh^3}{36} \quad \text{Equation 4}$$

As detailed in Equation 3, the stress σ caused by M at a distance y from this neutral axis might also be expressed in terms of the Young's modulus E and the radius of curvature R from the neutral axis induced by the bending.

The stress is then found to be,

$$\sigma = \frac{My}{I} = \frac{M}{I} \frac{1}{3}h = \frac{PL}{\frac{wh^3}{36}} \frac{1}{3}h = \frac{12PL}{wh^2} \quad \text{Equation 5}$$

The strain in the elastic regime is then defined by its relationship to stress and the Young's modulus E via,

$$\varepsilon = \frac{\sigma}{E} \quad \text{Equation 6}$$

With the modulus being $E = \frac{PL^3}{3I\delta}$ and the displacement being $\delta = \frac{PL^3}{3IE}$.

For maximum strain ε it follows

$$\varepsilon = \frac{h\delta}{L^2} \quad \text{Equation 7}$$

A representative stress-strain curve, which was constructed using F-D data and beam dimensions and the described calculations, is shown in Figure 28 (right). In simple beam theory, the maximum stress σ_{max} , is located at the fixed end of the beam (top = tensile, bottom = compressive). Simple beam theory assumes the beam to be fixed at one end and it does not consider a non-static attachment of the beam to the base material, as is the case in the experiments. This often leads to an underestimation of the obtained Young's modulus E . This is due to the fact that the stress field created at the

“fixed end” stretches into the base and leads to an additional slope θ_0 and displacement δ_0 of the fixed end and hence a contribution to the overall deflection of the beam. As found by Armstrong ^[152], assuming that the additional contributions to the overall displacement are proportional to bending moment as well as local shear force, the compliance S (flexibility), can be defined as shown in Equation 8.

$$S = \frac{\delta}{P} = \frac{L^3}{3EI} + \theta_{m0}L^2 + (\theta_{p0} + \delta_{m0})L + \delta_{p0} \quad \text{Equation 8}$$

The not fully constrained fixed end in the experiment scales with L_{eff}^2 , where L_{eff} stretches from the fixed end to the loading point. However, for beams with a width to length aspect ratio greater than six the effect caused by the slope of the fixed end becomes negligible and the L_{eff}^3 term (bending term), as is the case in simple beam theory considerations, prevails. Errors of about 5 – 7 % for E due to this “base-effect” have been reported.^{[152], [170]} Consequently, care was taken that all beams in this thesis showed a width to length ratio of ≥ 6 . The beams tested in the frame of this work were not simple single crystals but composed of 2 grains (bicrystal) with a weakened GB present near the fixed end from which L_{eff} was measured and which represented the region of highest stress where failure initiated.

3.6 3D FIB-SEM sequencing

3D FIB slicing presents a powerful tool, which enables the 3D reconstruction of a selected volume of interest (up to 20 μm x 20 μm x 20 μm ^[209]) with nanometre resolution. By performing a series of layer-by-layer milling with a dual-beam FIB, together with conjoint 2D SEM imaging of each layer, the sample proportion can be reconstructed by aligning the image slices and using dedicated reconstruction software (FEI Avizo 9.0). 3D information with a high level of detail can be obtained in a matter

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of hours.^[209] For detailed information on how such volume reconstructions are done please refer to the references given in [147], [210] and [211]. A more detailed description of the 3D FIB slicing technique can be found in work by Yao ^[199]. The technique has already been used to successfully reconstruct the surface oxidation of stainless steels and to learn about the role of cold work and applied stress on oxidation behaviour.^{[147], [210]} Even the 3D reconstruction of individual stress corrosion cracks ^[209] and the successful reconstruction of the crack path, oxide and carbides along GBs of A600 ^[49] has been demonstrated. Even though 3D FIB-SEM sequencing represents a powerful tool for studying the 3D microstructure and degree of oxidation, it has the major disadvantage of not leaving any sample volume behind for further examinations with different techniques, like *e.g.* TEM. In the frame of this thesis the method was consequently incorporated in the TEM sample preparation of the central portion of tested GBs, as described in section 3.3.3.2, which describes the novel lift-out strategy. In short, a whole cantilever was lifted-out onto a conventional TEM Cu-grid, aligned properly and a layer-by-layer 3D FIB-SEM image series was recorded from one side until about 150 nm away from the central point (Figure 29, top), which was marked with a milled line on the Pt protection free cantilever length. The sample was then rotated 180° and the procedure was repeated from the other side, leaving behind about 300 nm of the central GB region to prepare an electron transparent lamella, suitable for advanced high-resolution electron microscopy characterizations and for building realistic finite element models. Figure 29 (bottom) shows an example of the resulting reconstructions for the respective sides of the beam volume. The blank region in the middle represents the volume used for TEM sample preparation. The sequences were recorded using either of the 2 dual-beam machines, described in Table 7 with a 300 pA milling current. All reconstructions were performed using Gatan Digital Micrograph

(Gatan) for pre-processing of the slices (*e.g.* drift corrections and slice alignment) and FEI Avizo 9.0 3D software for the reconstructions itself.

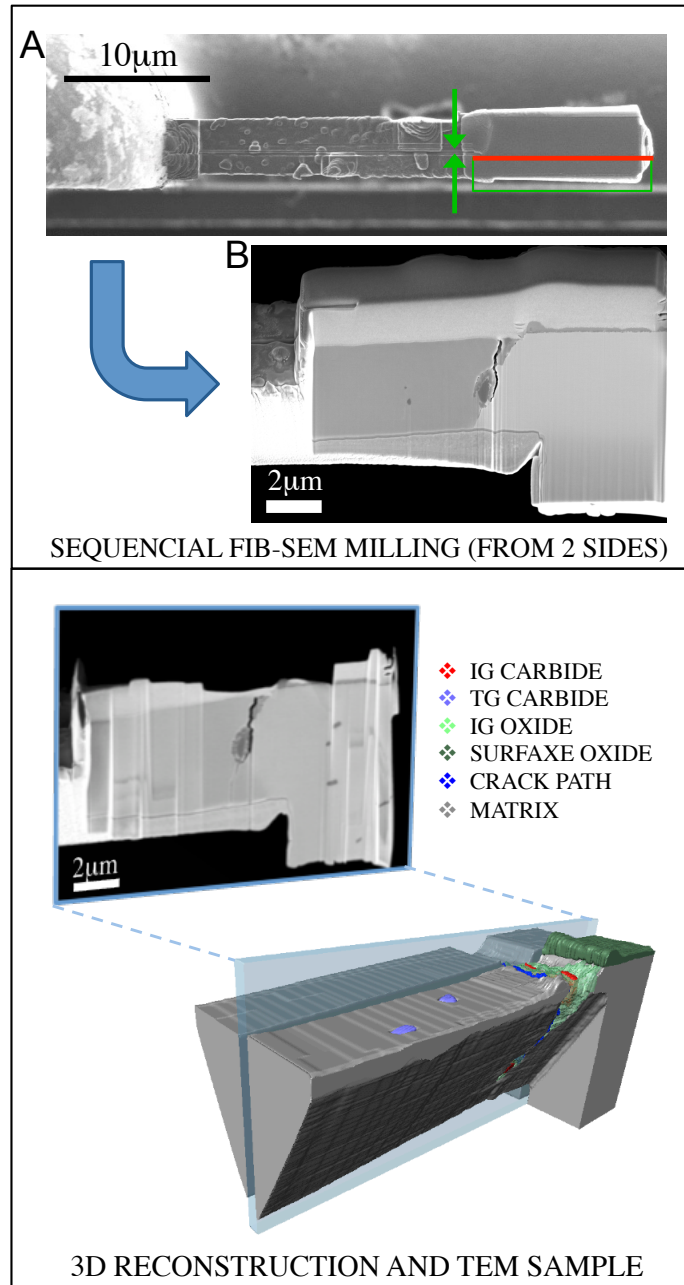


Figure 29: (top, A) Microcantilever attached to the TEM stub. The box indicates the milling sequence performed at the first side. (top, B) SEM image of the GB region after the first milling sequence was performed. The same procedure was performed from the other side. (bottom) 3D reconstruction of the FIB-SEM milling sequence of both sides. The blank region (light blue) indicates the small volume left for TEM sample preparation.

3.7 Determination of grain orientation data (Euler angles)

As described in section 8.2, the plastic response of cantilever tests was modelled via a crystal plasticity finite element approach. For this approach information about the crystallographic orientation and relationship of the 2 grains incorporated in each beam was needed in form of a set of rotation angles, the crystal's so-called Euler angles (φ_1 , Φ , φ_2).^[212] The Euler angles are the set of rotation angles needed to bring the sample coordinate system, with all Euler angles at zero, to overlap with the crystal coordinate system. The necessary sequence of rotations was performed using a $ZZ'Z''$ -convention (Bunge convention). As detailed in Figure 30, this involved a rotation of φ_1 about the sample's Z-axis (normal direction; ND), bringing the original X (rolling direction; RD) and Y (transverse direction; TD) to their new positions X' and Y'. This was followed by a rotation of Φ around the new X'-axis, again leading to new axis positions. The final rotation of φ_2 was then performed around the again newly oriented Z''.^[213] This way the sample reference frame was brought to overlap with the corresponding crystal orientation. The set of Euler angles for each grain was then transformed into the respective inverse rotation matrix G , which is a product of each of the performed rotations (matrices in Figure 30) and allowed an expression of crystal coordinates in terms of specimen coordinates as needed for the crystal plasticity FEM (CPFEM). A Matlab script (see APPENDIX A) was written by the author of this thesis, which helped to transform the Euler angles of the grains into their respective rotation matrices and determined their misorientation angles. Euler angles were extracted using electron backscatter diffraction (EBSD) techniques on either a bulk sample or on a TEM lamella via Transmission Kikuchi Diffraction (TKD). For further information about EBSD please refer to references [214] - [218]. For TKD, previously known as T-EBSD^[219], please refer to reference [214], [218] and [219].

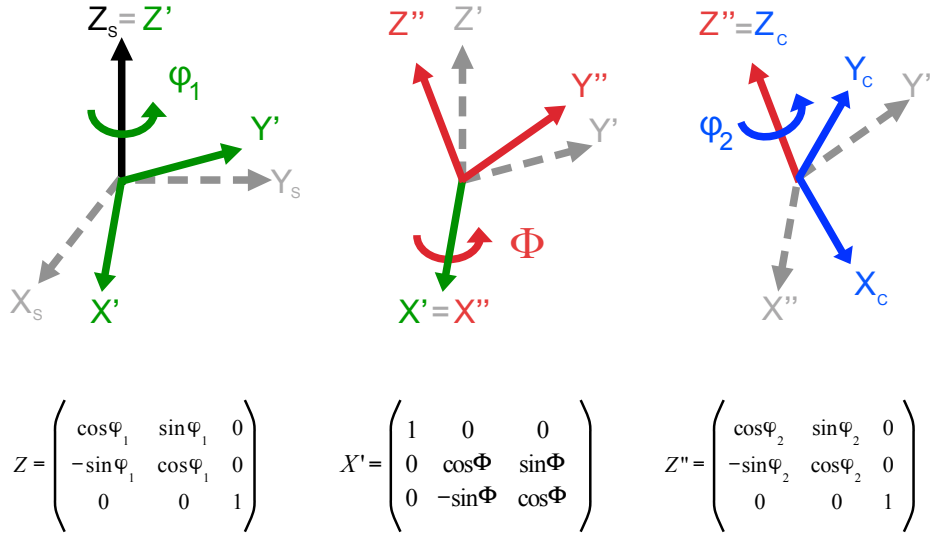


Figure 30: Bunge convention of the Euler angles (φ_1 , Φ , φ_2) with the rotations (Z , X' , Z'') necessary to transfer the sample reference coordinate frame (X_s, Y_s, Z_s) into the respective crystal coordinate system (X_c, Y_c, Z_c). The individual rotations can be expressed in matrix form.

Note: All Euler angles were acquired with the help of Dr. Hamidreza Abdolvand and Dr. Arantxa Vilalta-Clemente, who helped with EBSD and TKD respectively.

3.7.1 Electron backscattered diffraction (EBSD)

Conventional bulk EBSD measurements were performed on *A600-NOX* (no surface oxide). The machine used was a ZEISS EVO, at 18 mm working distance and 16 mm detector distance. An acceleration voltage of 30 kV and probe current of 10 nA was used and data was analysed using Bruker's Esprit 2.0 software. Figure 31 (left) shows a schematic of a typical EBSD set-up. For unpolished samples with surface oxides present (*e.g. A600-INSS*) an alternative to bulk sample EBSD was necessary. Due to the applied strategy of lifting-out TEM samples from whole cantilevers, this alternative was provided in the form of Transmission Kikuchi Diffraction (TKD), which allows the EBSD-technique to be performed on the thin TEM lamellas.

3.7.2 Transmission Kikuchi diffraction (TKD)

The TKD set-up used in this work followed work by Meisnar *et al.* ^[218], carried out on 316 stainless steel, and is schematically displayed in Figure 31 (right). To extract the grain's Euler angles via TKD, a Zeiss Merlin FEG-SEM and eFlashHR Bruker EBSD detector was used to record either a full TKD map of the GB region or just 2 small maps in each grain. A special TKD sample holder (Bruker) was used, which places the TEM sample at a 45° tilt. The stage was then tilted to 35° towards the detector, decreasing the overall tilt between the sample and incident beam to only 10°. A working distance of 7.5 mm was chosen whilst the distance between the detector and sample was 12 mm. The operating conditions were set at 30 kV accelerating voltage and 3.5 nA probe current. Step size and magnification were varied and a pattern resolution of 160 x 120 pixels was chosen. The data was analysed using Bruker Esprit 2.0 software.

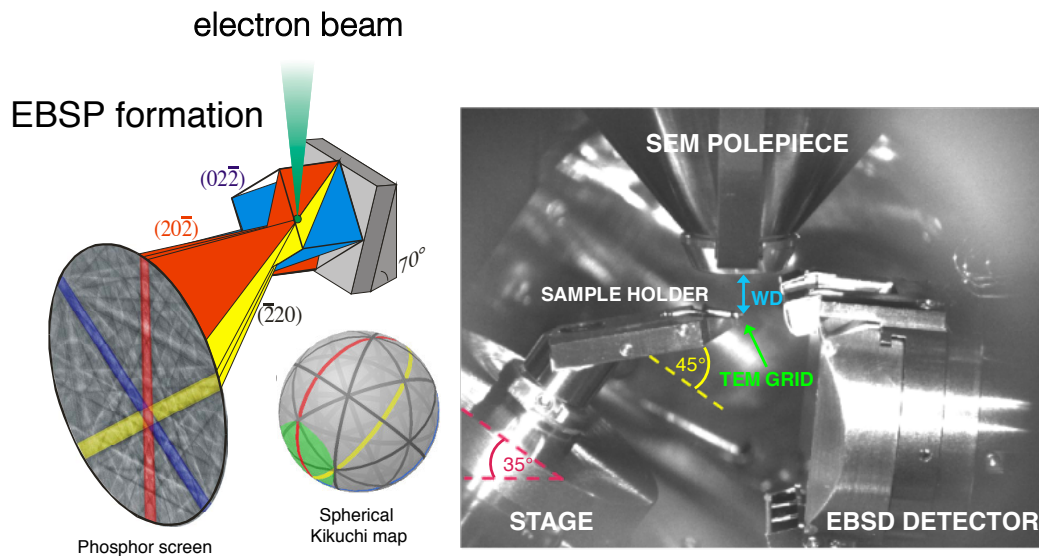


Figure 31: (left) Schematic of the EBSD setup and pattern formation.^[216] The sample is tilted 70° toward the phosphor screen, where the diffracted electrons generate the characteristic Kikuchi bands and patterns, which are then indexed in dedicated software. (right) TKD setup as seen in the SEM chamber. Due to the indicated sample holder and stage tilt, the sample is tilted only 10° tilt from the incoming electron beam.^[218]

3.8 Analytical TEM (ATEM)

Transmission electron microscopy (TEM) enables the characterization of materials down to the atomic limits.^[220] For this an electron beam produced by a suitable electron source (*e.g.* thermionic or field emission guns) is accelerated to 200 kV and focussed by a set of magnetic electron lenses and apertures onto the electron transparent sample (30 – 100 nm thickness). The multiple signals that are generated by the interaction of the electron beam with the sample are based on different scattering mechanisms, *e.g.* elastic (energy conservation) and inelastic scattering events (energy lost as heat). Conventional TEM (stationary beam), together with a scanning TEM option, offers a broad spectrum of characterisation techniques, which provide structural, crystallographic and chemical information. Electrons leaving the electron transparent sample are collected by an objective lens and can be used to generate an image in its image plane or to access its diffraction pattern (DP) in its back focal plane. Focussing either on the image or back focal plane, one can switch between imaging mode and diffraction mode (crystallographic information). Depending on the chosen objective aperture, which sits in the diffraction plane, bright field (BF) and dark field (DF) images can be obtained. Equipped with suitable detectors, changes caused by the electron-sample interaction, like deviations from the original electron path (imaging and diffraction) or energy loss can be detected. The work in this thesis mainly utilized ATEM in the scanning mode of conventional TEMs, known as scanning transmission electron microscopy (STEM), to acquire supplementary data and high-resolution images to better understand the failure response of the micromechanical bend tests. Hence, investigations were carried out on TEM cross-sectional samples of the GB region of tested cantilevers where necessary. As such, only STEM will be explained in more detail along with information about the microscopes, conditions and software

used. For more general information about TEM, its versatile sub-techniques and the use of diffraction in TEM mode, please refer to the well-known TEM bible by Williams and Carter.^[220]

3.8.1 Scanning transmission electron microscopy (STEM)

In STEM mode, a highly focussed electron beam is used to raster/scan the sample surface. In the frame of this research it was used to identify regions of higher or lower atomic number (Z-contrast), using a so-called high-annular dark field detector to detect electrons, which are incoherently-inelastically scattered at high angles, where the contribution from diffraction contrast becomes negligible. The contrast in high angle annular dark field imaging (HAADF) consequently originates in the specific energy loss and wavelength change of the incident electron upon interaction with atoms of high atomic number Z . Atoms with high Z scatter the electrons more strongly (higher energy loss) and the regions associated appear bright in the HAADF image. Contrast in HAADF is consequently proportional to atomic number variations, assuming that thickness and density remain constant. Moreover, 2 different annular darkfield detectors were used for imaging in STEM mode. The first detector (ADF1) had a 72.80 mrad inner and 235.75 mrad outer collection angle, whereas the second detector (ADF2) had a 32.50 mrad inner and 51.37 mrad outer collection angle (these values correspond to 12 cm camera length on the Oxford ARM). Using both detectors simultaneously a HAADF Z-contrast image was obtained with the first detector and a diffraction contrast MAADF image from the second detector. For the EELS mapping a Gatan ADF detector was used at 82.30 mrad inner and 194.15 mrad outer collection angle at 2 cm camera length on the Oxford ARM.

3.8.1.1 Chemical analysis via EELS

STEM and its possibility to raster the sample with a highly focussed electron beam allows the gathering of highly localized analytical data. This includes the possibility to study local element distributions and composition of the tested specimens via energy dispersive X-ray spectrometry (EDX) or electron-energy loss spectroscopy (EELS). Since only the latter was used in the frame of this work, EDX won't be discussed in detail. The interested reader might find more information about EDX in reference [220]. The EELS performed in this thesis allowed a determination of the sample's elemental composition by using the characteristic loss of energy experienced by electrons when inelastically scattered from specific elements. In each point on the sample the corresponding energy loss spectrum, as shown in Figure 32 for the A600 matrix material, was recorded.

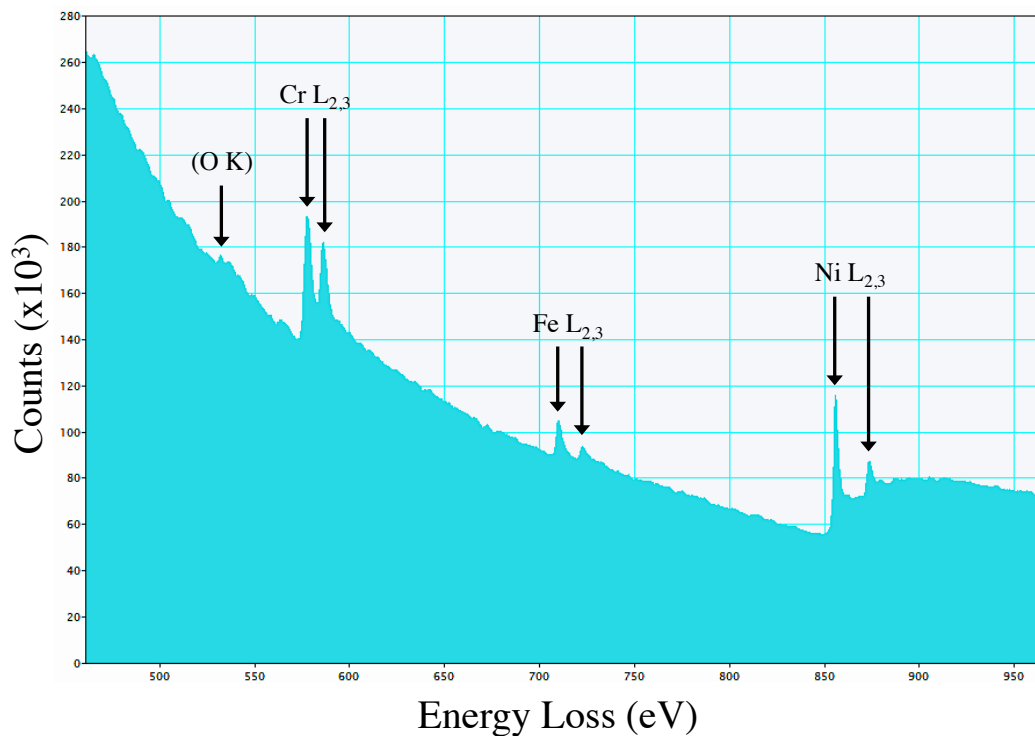


Figure 32: EELS core loss spectrum of Alloy 600 matrix, showing adsorption edges for the main constituents (Ni, Fe and Cr). As indicated, the oxygen edge is also noticeable.

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When rastering the electron beam over the sample, the majority of electrons pass through the sample without losing energy. They contribute to what is called the zero loss peak. All other peaks are generated by electrons, which have lost an amount of energy which is directly associated with a certain element. The usual energy loss range for elements of interest in A600 is shown in Table 9.

ELEMENT	EDGE	ENERGY (eV)	Z
C	K	284	6
O	K	532	8
Cr	L _{2,3}	575	24
Fe	L _{2,3}	710	26
Ni	L _{2,3}	855	28

Table 9: Energy loss range, corresponding energy edges and atomic number of some constituent elements of A600.

Detecting/recording an energy loss spectrum in each point on the sample whilst scanning it with the pointed electron beam, chemical variations were mapped. To avoid multiple energy losses in the sample via multiple scattering, the TEM sample thickness was chosen to be sufficiently thin ($t/\lambda \ll 1$). For A600 a thickness of ≤ 70 nm was found to be sufficient, since the inelastic mean free path (λ) can be estimated to be ~ 100 nm.

3.8.1.2 Microscopes, conditions and software

Throughout this thesis 2 state of the art TEMs were used. A JEOL 2100 LaB₆ TEM operated at 200 kV, mainly used for imaging, and a JEOL ARM200F (cold-FEG) TEM at 200 kV equipped with a Gatan GIF spectrometer and a JEOL Centurio 100 mm² EDX detector, needed for analytical techniques, like EELS. All EELS data was recorded at a collection angle of 40 mrad and a convergence angle of 30 mrad was used with an energy resolution of ~ 0.4 eV. Extraction of individual elemental EELS

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maps was performed in Gatan Digital Micrograph. Further EELS data processing, like alignment of the spectra using the zero loss peak and a correction for noise via multivariate statistical analysis (MSA) was performed using the dedicated MSA open-source software Hyperspy 0.8.^[221] The MSA processing thereby helped to reduce the experimental error, associated with the compositional information gathered via EELS by applying principal component analysis and factorial analysis of correspondence to differentiate between relevant data, which was finally used to generate a new “clean” spectrum and the noise/artefacts inherent in the as-recorded dataset.^{[221] - [223]} It should be noted that compositional information from very small regions is generally to be treated as qualitative. Errors might arise from the fact that even the electron transparent TEM lamellas are in reality a 3D volume with a complex 3D microstructure in the GB region, which might vary throughout the volume. This might result in the blurring of the actual compositional profile. Additionally surface oxidation of the TEM sample surface might contribute to an overestimated O content from matrix regions. A relative error of 10% for all elements is usually reasonable.

4 COMPUTATIONAL ASPECTS

4.1 Extraction and implementation of real microstructures

Whilst simple microstructures, like the GBs on *A600-NOX* in section 6.3, were directly recreated in the FEM software (Abaqus v6.14-2), using measurements taken from SEM images, more complex microstructures of the GBs enclosed in the tested beams needed to be extracted, using a Matlab- and Python-based algorithm developed by Tarleton *et al.* ^[224]. For this an SEM image of the surface geometry (2D) obtained close to the centre of the beam during the 3D FIB-SEM sequencing was converted into a binary image (black and white pixels only) and then processed in Matlab. By comparing next neighbour pixels (4 point pixel connectivity) the vertices of the features were calculated, using the end point locations of diagonals, and the positions were stored in a text file. The sketch was thereby calibrated against the scale bar of the experimentally obtained SEM image to keep consistent dimensioning. A Python script was then used to read in the vertices stored in the text file into the finite element software Abaqus (v6.14-2) and to partition the mesh. The thereby generated sketch of the particle was then projected onto the beam, brought to the right position relative to the cantilever dimensions and extruded in the 3rd dimension. Hence, a simplified but representative 3D mesh of the experimentally observed GB microstructure was obtained. The steps of the extraction process are shown in Figure 33. The assumption that the geometry did not significantly change through the thickness of the beam is a simplification and

ideally needs to be checked (kept in relation) with the 3D FIB-SEM data. For details about the theory behind this method please refer to the original work.^[224]

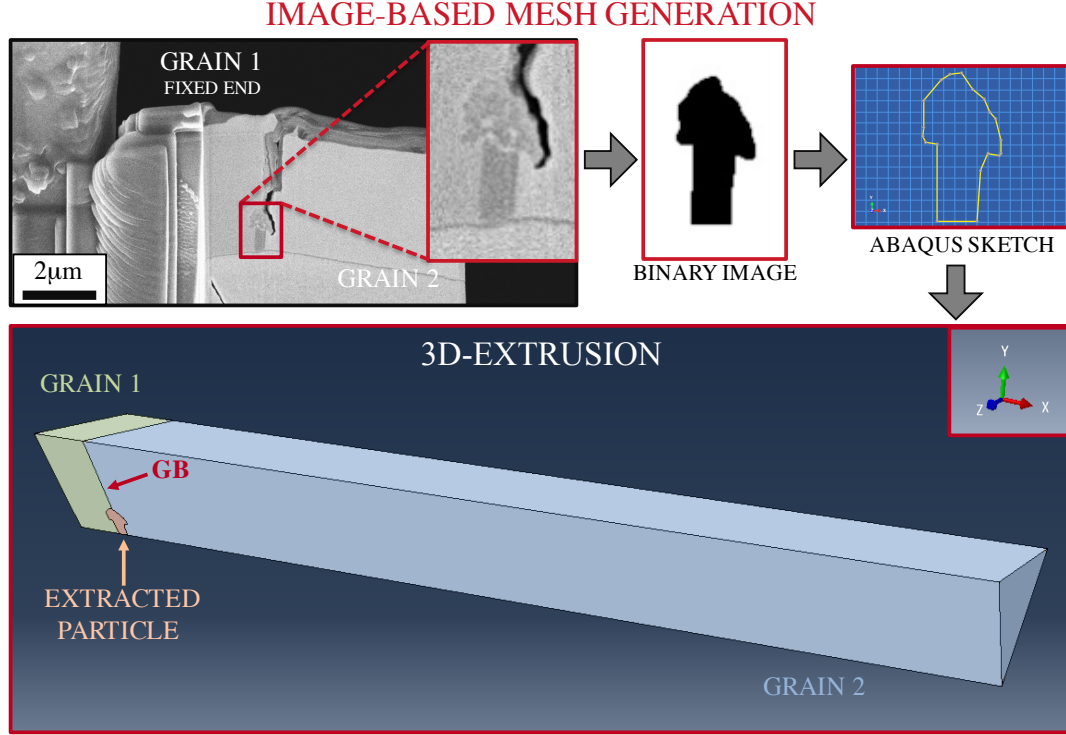


Figure 33: Steps involved in the image based mesh-generation of realistic GB microstructures.

4.2 The cohesive zone model

In the context of this thesis, a linear elastic cohesive softening law, as provided in Abaqus Standard (6.14-2), was used as a constitutive law for simulating the failure of oxidized GBs and is depicted in Figure 34.^[225] A maximum nominal stress (MAXS) criterion was chosen for damage initiation. According to this criterion damage initiates once the nominal stresses (tractions t_n , t_s and t_t) reach a critical damage initiation value - the user-defined maximum nominal stress σ_f - and the ratio between the current stress values and pre-defined damage initiation stress becomes equal to 1.

$$\max \left\{ \frac{\langle t_n \rangle}{t_n^0}, \frac{t_s}{t_s^0}, \frac{t_t}{t_t^0} \right\} = 1 \quad \text{Equation 9}$$

As shown in the curve in Figure 34, the initial response of the material is linear elastic, with an initial effective stiffness K . The penalty (contact) stiffness K_i ($i = n, s, t$) is thereby defined as

$$K_i = \frac{\sigma_i}{\Delta_{0i}} \quad \text{Equation 10}$$

Upon reaching the critical traction level at the pre-defined maximum nominal stress σ_f , which denotes the maximum strength of the interface and the end of the elastic regime, the bonds between the 2 cohesive surfaces ahead of the crack start to come apart, in other words the stiffness K decreases, and failure initiates. A scalar damage variable D , ranging from 0 to 1, is used to reflect the state of damage, with 0 representing no failure and 1 representing full failure at the point of total separation between the 2 surfaces, as defined by the pre-set critical opening displacement Δ_f .

The damage evolution is expressed via

$$D(\delta) = \begin{cases} 0 & ; \Delta < \Delta_o \\ \frac{\Delta_f(\Delta - \Delta_o)}{\Delta(\Delta_f - \Delta_o)} & ; \Delta \geq \Delta_o \end{cases} \quad \text{Equation 11}$$

Thereby Δ is the effective displacement defined as Euclidean norm of the displacement vector respective to the crack face.

$$\Delta = \sqrt{\langle \delta_n \rangle^2 + \delta_s^2 + \delta_t^2} \quad \text{Equation 12}$$

The effective traction would be given as $T = \sqrt{\langle t_n \rangle^2 + t_s^2 + t_t^2}$.

From Figure 34 it can be seen that the linear elastic law is fully defined by 3 interdependent cohesive parameters.

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1) The material's initial stiffness per unit area K , which starts to decrease upon reaching
 2) the maximum nominal stress σ_f , which indicates the point of softening and 3) the
 critical opening displacement Δ_f at which failure has occurred and the material's initial
 stiffness K goes to zero.

The parameters make up the traction tensor $\mathbf{T}$ and are related by the following equation:

$$\mathbf{T} = \begin{Bmatrix} t_n \\ t_s \\ t_t \end{Bmatrix} = \begin{bmatrix} K_{nn} & K_{ns} & K_{nt} \\ K_{ns} & K_{ss} & K_{st} \\ K_{nt} & K_{st} & K_{tt} \end{bmatrix} \begin{Bmatrix} \delta_n \\ \delta_s \\ \delta_t \end{Bmatrix} = \mathbf{K}\boldsymbol{\Delta} \quad \text{Equation 13}$$

For the uncoupled T- Δ law used in this thesis, as commonly used for investigations of
 mechanical behaviour, only the diagonal terms K_{nn} , K_{ss} and K_{tt} need to be defined and
 all other values in the matrix are zero.^[226] The general constitutive relation between the
 tractions and separations can then be expressed by

$$\mathbf{T} = (1 - D)\mathbf{K}\boldsymbol{\Delta} \quad \text{Equation 14}$$

The critical fracture energy G_c , which is represented by the total area underneath the
 curve, can then be expressed by

$$G_c = \frac{1}{2} \sigma_f \Delta_f \quad \text{Equation 15}$$

It is related to the fracture toughness of the material via

$$G_c = \frac{K_{IC}^2}{E} \Rightarrow K_{IC} = \sqrt{G_c E} \quad \text{Equation 16}$$

A cohesive-type surface-to-surface contact formulation available within the FEA
 software package Abaqus (v6.14-2) was chosen.^[225] As proven for the simulation of
 intergranular failure of polycrystalline aggregates by Simonovsky et al.^{[227], [228]} this
 formulation is a numerically stable alternative to the use of an interfacial layer of
 cohesive elements. The relation between tractions and separations, as usually defined
 for cohesive elements, are thereby understood as contact separations, meaning as

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relative displacements of node areas at the chosen slave surface, in normal and shear directions, to their corresponding projection points on their master surface.^{[225], [228]} To accurately capture the point of failure and strength of the material via the cohesive zone formulation, the chosen cohesive parameters were individually calibrated against the experimental F-D data for each modelled beam. Moreover, in order to successfully obtain accurate results, care was taken that the mesh along the cohesive zone was fine enough in relation to the length of the cohesive zone ahead of the proceeding crack, which is defined as the length from the crack tip to the region of maximum traction (stress)^[229], as shown in Figure 34 and might be determined via

$$l_{cz} = ME \frac{G_c}{(\sigma_f)^2} \quad \text{Equation 17}$$

M being a parameter close or equal to 1, E being the material's Young's modulus, G_c the critical energy release rate and σ_f the maximum nominal stress. The necessary number of elements N_e in the cohesive zone can then be determined via

$$N_e = \frac{l_{cz}}{l_e} \quad \text{Equation 18}$$

With l_e giving the mesh size along the cohesive zone^{[229], [230]}, which must satisfy

$$l_e \leq \frac{l_{cz}}{N_e} \quad \text{Equation 19}$$

Nonetheless, whilst the above equations help to estimate mesh size and element number along the cohesive zone, an exact number of elements is not established in literature.^[231]

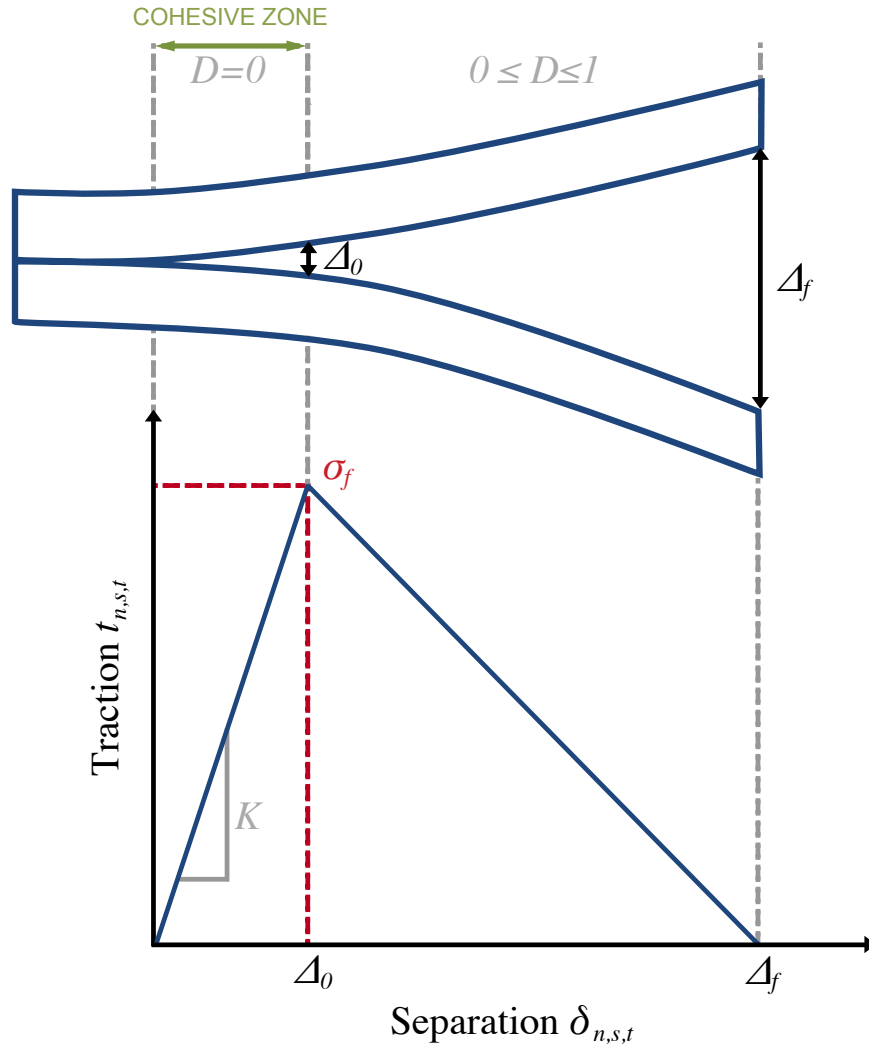


Figure 34: Linear elastic traction-separation law as implemented in Abaqus 6.14-2 and corresponding definition of the cohesive zone ahead of the crack tip (at Δ_0) to the point of maximum traction.

4.3 The crystal plasticity model

4.3.1 A strain gradient crystal plasticity formulation

The strain gradient crystal plasticity concept describes the deformation of a crystal or poly-crystal of known orientation upon application of stress via the motion and glide of dislocations (crystallographic slip). If a body is deformed beyond the elastic limit,

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upon meeting the yield criterion, the resulting unrecoverable deformation (plastic deformation) can be described via crystallographic slip taking place at a certain rate on all activated slip systems. These slip systems activate upon exceeding a certain threshold value known as the critical resolved shear stress τ_c . In A600, which is fcc, there are 12 possible slip systems which might activate. An increasing dislocation density on each activated slip system, is the cause of the experimentally observed strain hardening. The slip rate is thereby determined by the amount of dislocations able to move freely (mobile dislocations) as well as the presence of any obstacles, which impede the motion of the dislocations. These immobile obstacles might come in the form of statistically stored dislocations (SSDs) and/or geometrically necessary dislocations (GNDs), which are needed to accommodate the curvature of the crystal lattice during bending.

THE SLIP RULE [180], [198], [232], [233]

The flow kinematics of the formulation relies on the spatial deformation gradient $\mathbf{F}$.

The deformation gradient is a second order tensor.

$$\mathbf{F}_{ij} = \frac{\partial \mathbf{x}_i}{\partial \mathbf{X}_j} \quad \text{Equation 20}$$

For a better understanding it can be thought of as a mapping function ($d\mathbf{x} = \mathbf{F}d\mathbf{X}$). So if we *e.g.* assume that the vectors describing the edges of a material element are aligned with the laboratory basis (reference coordinate system), as shown for 2D in Figure 35, the deformation gradient would map the initial edge vectors of the element in the undeformed configuration to their counterpart in the deformed configuration, hence expressing the deformed location vector $d\mathbf{x}$ in multiples of the undeformed vector $d\mathbf{X}$. The deformation gradient $\mathbf{F}$, is then decomposed multiplicatively into elastic and plastic

parts, to describe the full deformation of a crystal of certain orientation, including stretch (elastic part) and any plastic deformation and rigid body rotations (plastic part).

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p \quad \text{Equation 21}$$

The rate of the deformation gradient can thereby be expressed as $\dot{\mathbf{F}} = \mathbf{L}\mathbf{F}$, where $\mathbf{L}$ is the velocity gradient ($\mathbf{L} = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} = \dot{\mathbf{F}}\mathbf{F}^{-1}$), which can be divided into symmetric ($\mathbf{d}$) and asymmetric parts ($\mathbf{w}$).

$$\mathbf{L} = \mathbf{d} + \mathbf{w} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T) + \frac{1}{2}(\mathbf{L} - \mathbf{L}^T)$$

The symmetric part is known as the rate of deformation $\mathbf{d}$, whereas the asymmetric part is known as continuum spin $\mathbf{w}$.

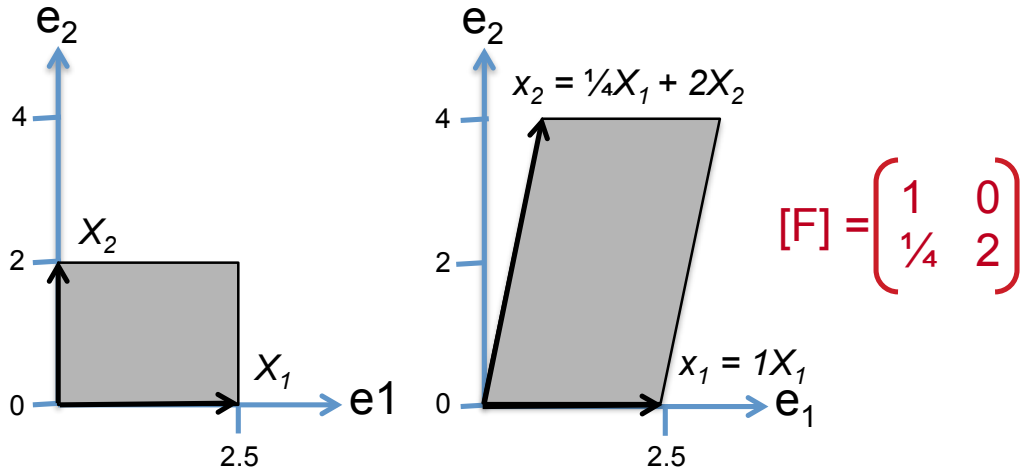


Figure 35: Graphical description of the deformation gradient of a 2D material element, which in the undeformed configuration (left) aligns with the lab basis. The vector components in the deformed state (right), here describing pure shear, can be expressed in terms of the vectors in the undeformed state via the deformation gradient $\mathbf{F}$.

Same as the deformation gradient $\mathbf{F}$, the velocity gradient $\mathbf{L}$ is decomposable into elastic and plastic parts. Hence, the rate of plastic deformation due to dislocation glide (slip) can be defined as

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$$\dot{\mathbf{F}}^p = \mathbf{L}^p \mathbf{F}^p, \quad \text{Equation 22}$$

where the plastic velocity gradient $\mathbf{L}^p$ is a summation over the crystallographic slip rate on all active slip systems ($i = 1 - 12$ for fcc).

$$\mathbf{L}^p = \sum_{i=1}^{12} \dot{\gamma}^i \mathbf{n}^i \otimes \mathbf{s}^i \quad \text{Equation 23}$$

$\mathbf{n}^i$ is thereby the respective normal vector on the i^{th} slip plane and $\mathbf{s}^i$ the slip direction. To consider size effects the GND density in the formulation is fully coupled with the slip rate via an activation volume term, using the following flow rule:

$$\dot{\gamma}^i = \rho_{SSD}^m b^{i2} v \exp\left(-\frac{\Delta F}{kT}\right) \sinh\left(\frac{(\tau^i - \tau_c^i) \gamma_0 \Delta V^i}{kT}\right) \quad \text{Equation 24}$$

ρ_{SSD}^m is the mobile SSD density, b^i the burgers vector magnitude, v the attempt frequency of the dislocations, ΔF the Helmholtz free energy, k the Boltzman constant, T the absolute temperature in Kelvin (K), τ^i the shear stress of i^{th} slip system and τ_c^i the corresponding critical resolved shear stress, γ_0 is the work conjugate to the resolved shear stress, ΔV is the activation volume. The activation volume is proportional to the burgers vector b and pinning distance l .

$$\Delta V^i = l b^{i2}$$

Where l is a function of the sessile dislocations (SSDs and GNDs).

$$l = \frac{1}{\sqrt{\psi(\rho_{SSD}^s + \rho_{GND})}} \quad \text{Equation 25}$$

ψ is a coefficient indicating that not all sessile dislocations (SSD or GNDs) act as pinning points, ρ_{SSD}^s the sessile SSD density and ρ_{GND} the GND density. The pinning distance l given in Equation 25 is defined as the distance between two sessile dislocations and is visually depicted in Figure 36.

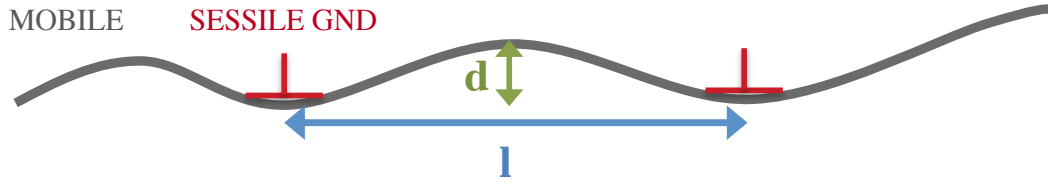


Figure 36: Definition of the pinning distance l , which is defined as the distance between two sessile (immobile) dislocations (e.g. GNDs).

So if we consider two crystals of same type but different length-scale both still need to accommodate the same amount of deformation and same number of GNDs. However, due to the smaller crystal having a smaller volume the local density of the GNDs is higher and thus the pinning distance is shorter, making it harder for mobile dislocations to move. This results in increased strain hardening of smaller grains in comparison to grains with a larger activation volume.

Whilst the SSD density of the material is an estimated constant, which might be changed in the code, the GND density of a slip system i can be obtained via the following relationship

$$\mathbf{G} = \sum_i (\mathbf{b}^i \otimes \boldsymbol{\rho}_{GND}^i) = \text{curl} \mathbf{F}^p \quad \text{Equation 26}$$

To capture gradient effects, access to the local state of plastic deformation at each integration point within an element is needed. In the UMAT, this is accomplished by using $\mathbf{F}^p$ at each of the element integration points from each of which $\text{curl} \mathbf{F}^p$ can be computed. In the code the data between integration points is thereby shared via a so-called common block (shared memory).

FINDING A SOLUTION ^{[180], [198], [232], [233]}

Considering the initial crystal orientations of the grains, found via the experimentally obtained Euler angles, and the elastic constants of the system (e.g. for A600), the GND

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density evolution and flow rate (strain rate) upon the onset of plastic deformation is established at the each increment in time. Thereby, Abaqus provides the deformation gradient at the beginning ($\mathbf{F}_t$) and end of the time increment ($\mathbf{F}_{t+\Delta t}$), as well as the state variables (SDVs) at the beginning of the time increment. At each time increment, Abaqus calls the UMAT, passes on its information, and the UMAT updates the values for the end of the time increment (at $t+\Delta t$) with a new stress $\boldsymbol{\sigma}_{t+\Delta t}$ estimate, material Jacobian $\frac{\partial \Delta \boldsymbol{\sigma}}{\partial \Delta \boldsymbol{\varepsilon}}$ and the SDVs. At the start Abaqus uses the initially merely elastic deformation gradient ($\mathbf{F} = \mathbf{F}^e$, as $\mathbf{F}^p = \mathbf{I}$) in the elastic regime) to calculate the velocity gradient $\mathbf{L}$. Since we define the overall time-step, usually from 0 - 1, to achieve a known final displacement (e.g. 2 μm in negative y direction), which we also define in Abaqus, we can calculate the velocity gradient via its relationship to the rate of deformation.

$$\dot{\mathbf{F}} = \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{x}}{\partial \mathbf{X}} \right) = \frac{\partial \mathbf{v}}{\partial \mathbf{X}} = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \frac{\partial \mathbf{x}}{\partial \mathbf{X}} = \mathbf{L} \mathbf{F}$$

The strain $\boldsymbol{\varepsilon}$, deformation gradient $\mathbf{F}$ and velocity gradient $\mathbf{L}$ are moreover related and the strain increment $\Delta \boldsymbol{\varepsilon}$, which upon exceeding the elastic limit needs to be decomposed into $\Delta \boldsymbol{\varepsilon} = \Delta \boldsymbol{\varepsilon}^e + \Delta \boldsymbol{\varepsilon}^p$, can be determined by the symmetric part of the velocity gradient

$$\Delta \boldsymbol{\varepsilon} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T) \Delta t, \text{ with } \mathbf{L} = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} = \dot{\mathbf{F}} \mathbf{F}^{-1}$$

Now initially the plastic contribution to the stress at $t+\Delta t$ will be zero, as all previous mentioned values are the elastic part of their respective decomposition only. Hence, while still in the elastic regime (no slip activation), the elastic stress estimate, known as the trial stress $\boldsymbol{\sigma}^{tr}$, will be the solution such that all plastic contributions and the plastic corrector term (red) in

$$\boldsymbol{\sigma}_{t+\Delta t} = \mathbf{D}(\boldsymbol{\varepsilon}_t^e + \Delta \boldsymbol{\varepsilon}^e) = \mathbf{D}(\boldsymbol{\varepsilon}_t^e + \Delta \boldsymbol{\varepsilon} - \Delta \boldsymbol{\varepsilon}^p) = \boldsymbol{\sigma}^{tr} - \mathbf{D} \Delta \boldsymbol{\varepsilon}^p \quad \text{Equation 27}$$

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are zero and

$$\boldsymbol{\sigma}_{t+\Delta t} = \mathbf{D}(\boldsymbol{\varepsilon}_t^e + \Delta \boldsymbol{\varepsilon}^e) = \boldsymbol{\sigma}^{tr}$$

This is also apparent from the definition of $\boldsymbol{\sigma}^{tr}$

$$\boldsymbol{\sigma}^{tr} = \boldsymbol{\sigma}_t + \mathbf{D}\Delta \boldsymbol{\varepsilon} + (\boldsymbol{\omega}\boldsymbol{\sigma}_t + \boldsymbol{\sigma}_t\boldsymbol{\omega})\Delta t$$

$\mathbf{D}$, in the above equations, is the global elastic constitutive matrix, which is calculated via

$$\mathbf{D} = \mathbf{T}_\sigma \mathbf{C} \mathbf{T}_\sigma^T$$

Where $\mathbf{C}$ is the local stiffness matrix, which is composed based on the knowledge of the elastic constants of the material and the experimentally obtained grain orientations (Euler angles), which we feed into Abaqus. $\mathbf{T}_\sigma$ is the incrementally updated rotation matrix (as defined in APPENDIX B), due to on-going rotation of the grains during deformation. In each time increment the trial stress is used to calculate the resolved shear stress τ^i (RSS), on each of the 12 slip systems for fcc crystals.

$$\tau^i = (\mathbf{n}^i \otimes \mathbf{s}^i) : \boldsymbol{\sigma}_{t+\Delta t} \quad \text{Equation 28}$$

where $\mathbf{n}^i$ and $\mathbf{s}^i$ are the slip plane normal and direction on the i^{th} slip system ($i = 1 - 12$).

It is then compared to the pre-set critical value, the critical RSS τ_c . According to the slip rule in Equation 24, glide on each of the 12 individual slip systems in the fcc lattice of A600 ($\{111\} \langle 110 \rangle$) initiates if the resolved shear stress τ^i of a slip system is equal to or greater than the critical resolved shear stress τ_c^i . As soon as the RSS becomes bigger than the critical RSS, yield occurs as the yield criterion is met.

$$\frac{\tau^i}{\tau_c} > 1$$

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At this stage the imposed trial stress at $t+\Delta t$ and its corresponding RSS won't be the actual solution anymore as the plastic contribution $\Delta\epsilon^p$ becomes non-zero ($D\Delta\epsilon^p > 0$) and needs to be considered. Hence, there will be a discrepancy between the initially imposed deformation gradient (and stress) and the one calculated under consideration of any activated slip. This results in a stress residual, which is derived from Equation 27.

$$\psi = \sigma_{t+\Delta t} - \sigma^{tr} + D\Delta\epsilon^p \quad \text{Equation 29}$$

Whereby $\psi < 0$ means elastic response and $\psi = 0$ a plastic response.

Since the imposed and the calculated solution are not in equilibrium, a new more accurate solution for the stress $\sigma_{t+\Delta t}$ needs to be found. This is done via a Newton's approximation method, by iteratively/incrementally changing the stress within the current time increment ($t+\Delta t$) until the residual becomes close to zero within a defined tolerance ($\leq 10^{-12}$ MPa). This is the so-called Newton Raphson equilibrium iteration loop, as depicted in Figure 37 for one increment in time. At the start of the loop the elastic trial stress at $t+\Delta t$ is changed incrementally ($n = 0 - 50$ within one time increment), hence updating the resolved shear stress in Equation 28, which is used to determine updated strain rates on the active slip systems, which in turn adjusts the plastic velocity gradient and hence the plastic strain increment $\Delta\epsilon^p$. The loop is repeated until the residual is within the specified tolerance. The new, more exact solution for the stress found at iteration n of the loop is then updated at the end of the time increment ($t+\Delta t$), and the solution is passed on to Abaqus to obtain the new material Jacobian and to give an updated estimate for the deformation gradient, which is then used in the next time increment to estimate the next incremental solution.

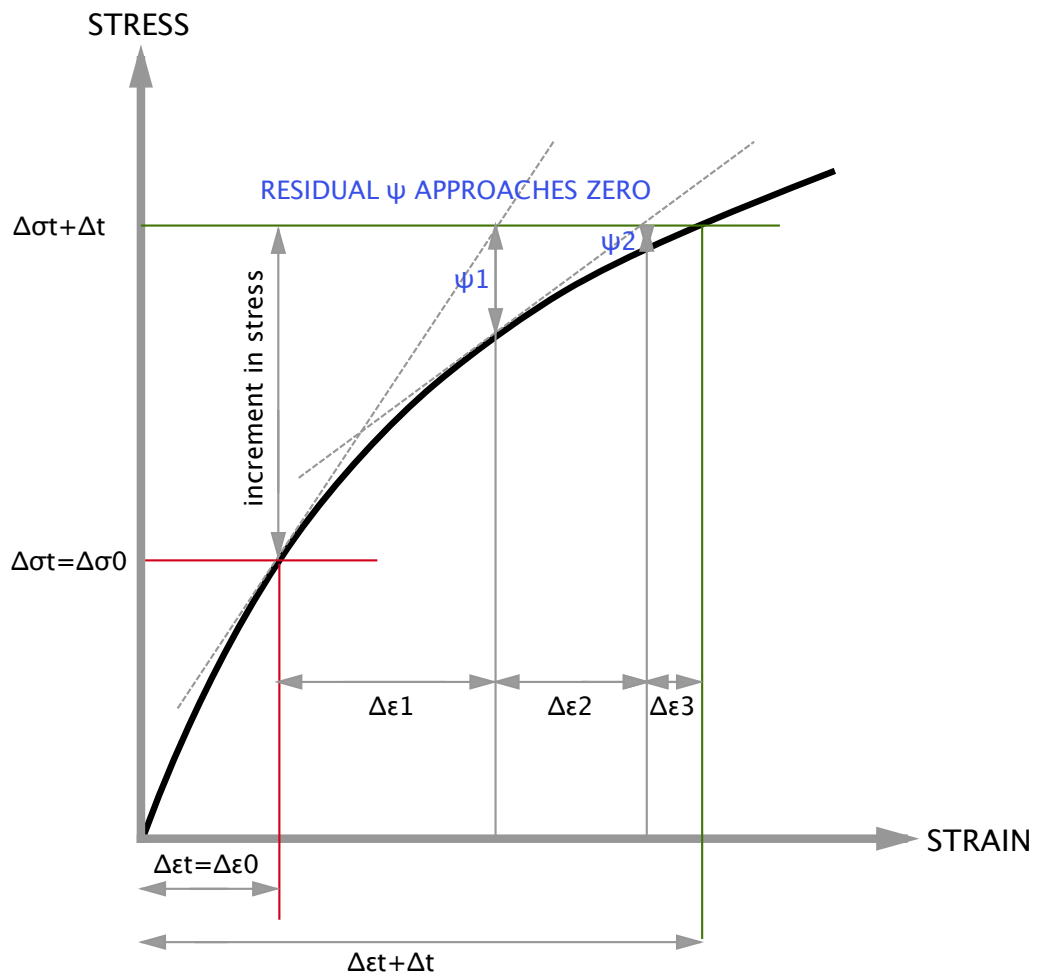


Figure 37: Schematic of the Newton Raphson equilibrium iteration, carried out within one time increment to bring the stress residual close to zero, within a specified tolerance, to find a more accurate solution. Once the equilibrium solution is found the loop is terminated and the solution is used to calculate the next increment in time.

5 PRELIMINARY INVESTIGATIONS

5.1 Preliminary observations on A600-INSS

Information about average grain size and carbide coverage was not provided by INSS. Consequently, the average grain diameter was estimated via the mean lineal intercept (MLI) method, by which 10 lines of equal length were randomly drawn across the sample and the GB intersections were counted and brought in relation with the total length of the test lines according to Equation 30. The obtained average length is proportional to the equivalent grain diameter, which was found to be ca. 67 μm .

$$\overline{R_{GB}} \sim \overline{L_{mli}} = \frac{1}{N_{total}} = \frac{L_{total}}{N_{GB}M} \quad \text{Equation 30}$$

R_{GB} is the average grain diameter, L_{mli} is the mean linear intercept length, N_{total} is the number of intercept per total test line length L_{total} , N_{GB} is the total number of counted GBs and M is the used magnification. The SEM images in Figure 38 were taken from a polished piece of sample, which was cut off the oxidized *A600-INSS* coupon, to determine carbide coverage. Average carbide coverage at the GBs was estimated to be ca. 45% $\pm$ 12, by manually measuring (ImageJ processing software) and adding up the length of all individual carbides found over the total length of a number of GBs and bringing the total carbide length into relation with the overall GB length in terms of percentage. The carbides distributed along the GBs were usually elongated in shape with the IG oxide growing around them and extending along the GB portions in-between.

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Investigations in the SEM revealed the presence of small TG carbides, which showed no signs of oxidation.

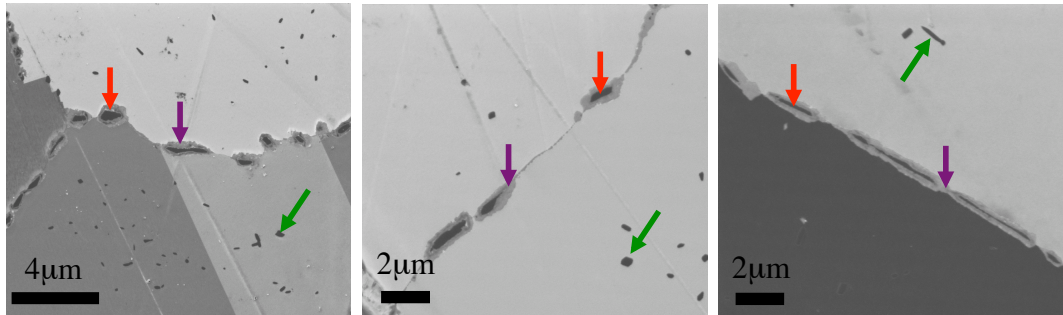


Figure 38: Top view SE SEM images of the carbide precipitated grains. The majority of carbides is seen at the GBs with transgranular carbides (green arrows) also enclosed in the grains. The preferential oxidation at the GBs (purple arrows) seems to grow around the elongated carbides (red arrows).

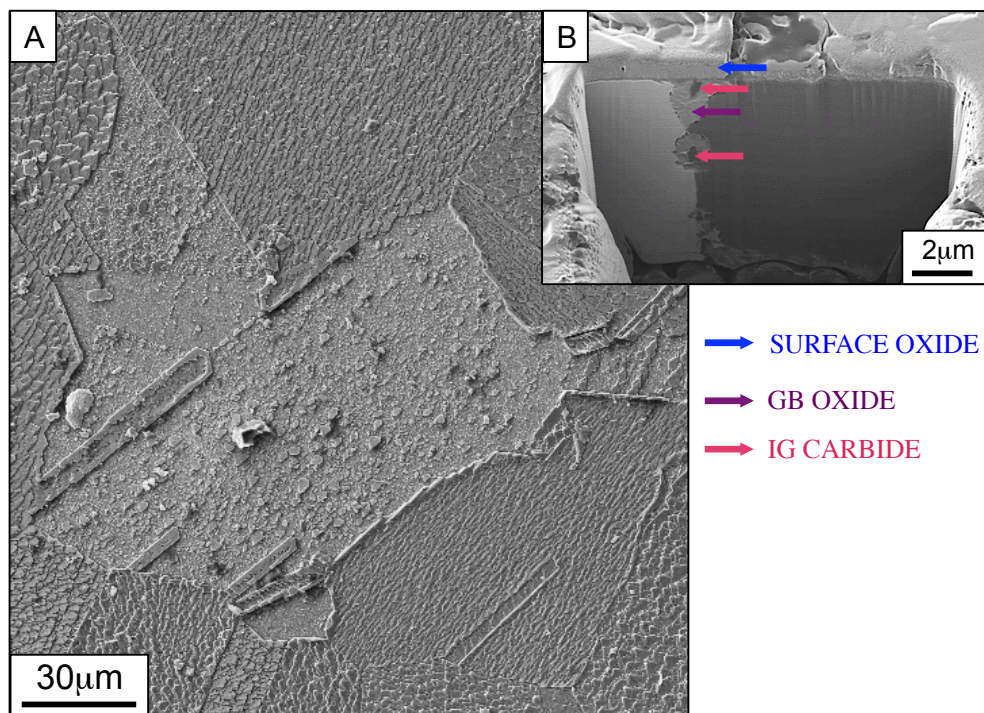


Figure 39: (A) SE SEM image of the surface oxide layer present on *A600-INSS*. Size, thickness and density of the crystallites vary across the differently oriented grains. (B) SE SEM image of an oxidized GB on *A600-INSS*. Features of interest are marked out in different colors.

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As can be seen in Figure 39 (A), an inhomogeneous Fe-rich surface oxide on *A600-INSS*, composed of a layer of crystallites, which varied in size, density and thickness across the grains, was observed after exposure to the autoclave at 30 cc/kg H₂ (Table 3). This is attributed to different oxidation rates of the differently orientated grains and helped to locate the underlying GBs on this sample for microcantilever preparation. Moreover, autoclaving induced intergranular oxidation, as shown in Figure 39 (B), which shows a trench milled into the untested material. Dark regions were visible at the oxide-metal interface before the microcantilever test. In accordance with previous work on Alloy 600 [36], [143], [234] oxidized under simulated PWR conditions and as shown in the example in Figure 40, which shows a HAADF image of a *A600-INSS* beam cross-section after testing, a dual oxide layer structure was observed, which was composed of an outer (Fe,Ni)₃O₄ spinel layer and an inner (Cr,Fe,Ni)₃O₄ spinel.

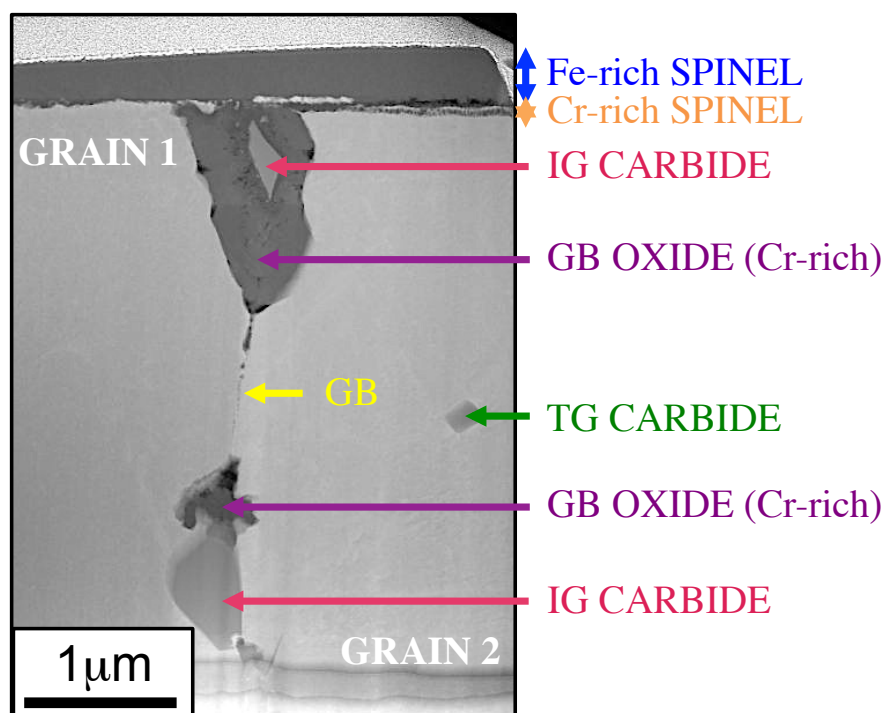


Figure 40: HAADF scanning TEM images (Jeol ARM200f) of a cantilever cross-section after testing (C4), showing the oxidized surface, preferential oxidation along the GB and intergranular carbide precipitation. Grain 1 corresponds to the fixed end of the cantilever.

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As shown in this example, the Cr-rich GB spinel was seen to reach the bottom of the beams in some cases. Consequently, IG oxidation was expected to exceed 4 μm , which agreed well with the $\sim 5 \mu\text{m}$ of depth, reported by Dugdale^[49], who performed their study on the same sample. Again, dark spots were seen at the oxide-metal interface. Preliminary EELS investigations of the unoxidized and untested GB (Figure 41) and carbide-metal interfaces (Figure 42), revealed the presence of a sensitized (Cr-depleted) region at the GB and the carbide-metal interface of about 100 nm in width.

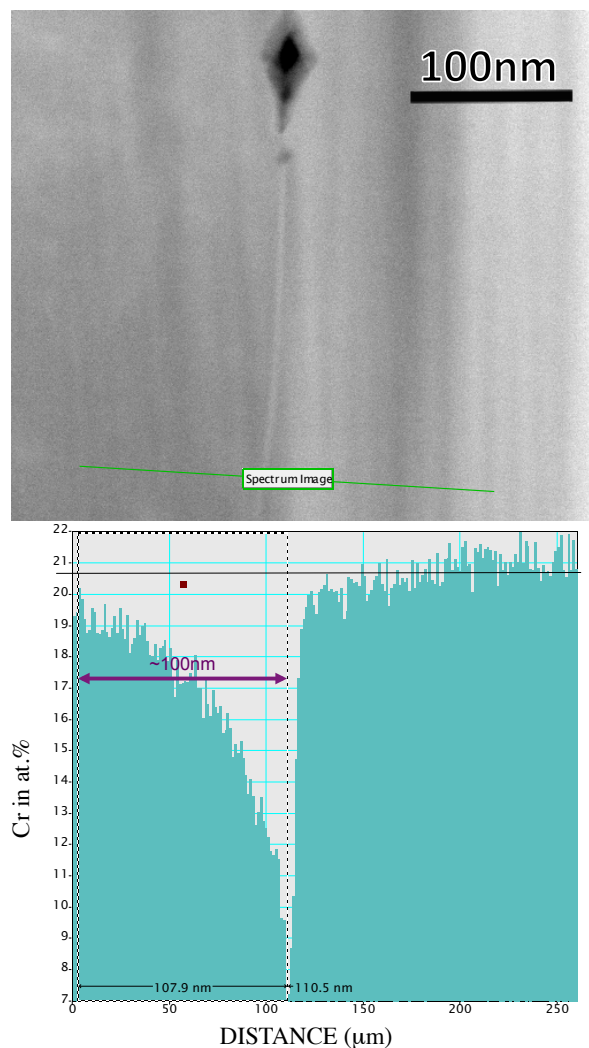


Figure 41: EELS spectrum image, line profile (top) and corresponding spectrum (bottom) of an unoxidized and untested GB region in-between to intergranular carbides. The Cr content distribution is asymmetric across the GB, with one grain (left) more sensitized than the other. The sensitized region drops to $\sim 7\%$ and extends to at least 100 nm.

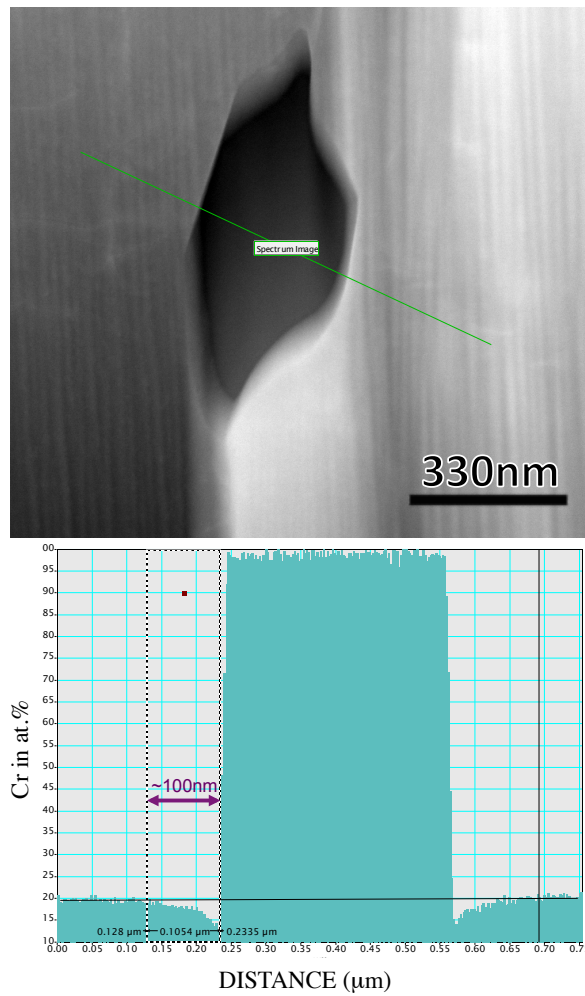


Figure 42: EELS spectrum image, line profile (top) and corresponding spectrum showing the Cr content in at% (bottom). There is a clear Cr concentration drop within 100 nm from the carbide.

5.2 Preliminary observations on A600-EDF

Initial observations of the sample revealed that oxidation in the autoclave at 20 cc/kg H_2 (Table 4) resulted in the growth of a thick surface oxide layer, consisting of differently sized Fe-rich crystallites. In addition to these crystallites the surface was additionally covered with Ni-rich needle-like oxides (Figure 43 A and B).

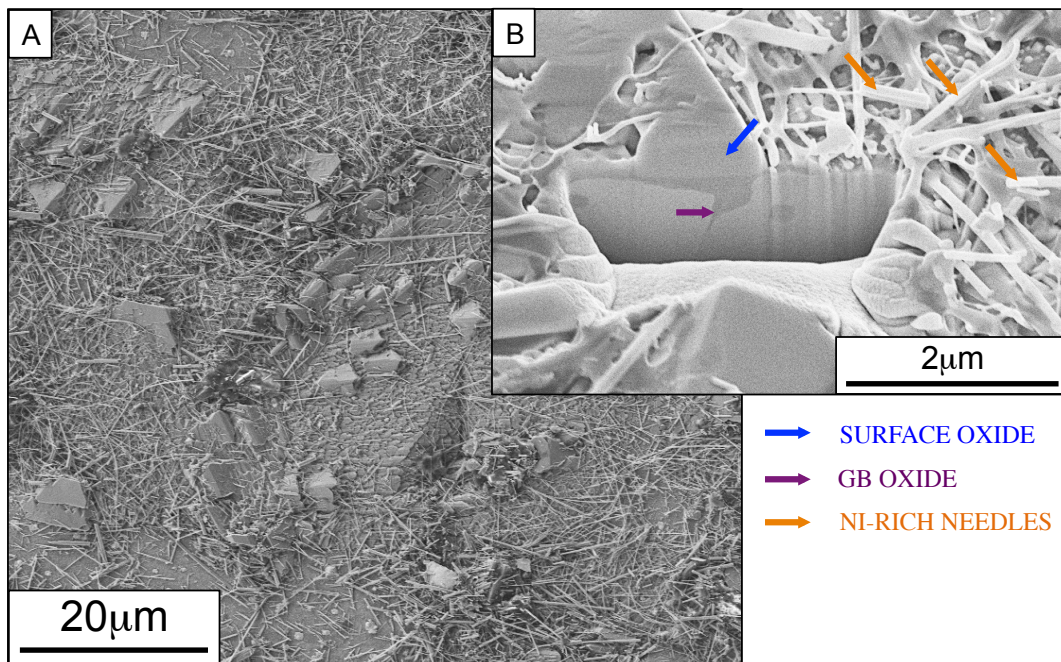


Figure 43: SEM overview image of the surface oxide on *A600-EDF* after autoclaving. A thick surface oxide layer, consisting of differently sized Fe-rich crystallites was found along with Ni-rich needle-like oxides. (B) SEM image of an oxidized GB on *A600-EDF*. Main features are marked out in different colors.

This is in agreement with observations made by EDF on the same material, using same autoclave conditions.^[235] Besides the precipitation of the Ni-rich needles, which are assumed to be a by-product of the autoclaving conditions, the oxide layers on *A600-EDF* were in overall agreement with those observed on *A600-INSS*. As apparent in Figure 43 A, the presence of the thick surface oxidation and the Ni-rich needles made an identification of the underlying GBs very challenging and hence time-consuming. Consequently, the surface was gently polished, as described in section 3.3.1, to expose the underlying oxidized GBs for further micro-cantilever preparation. The surface after the polish is shown in Figure 44 A and B. The majority of the carbides were transgranular (green arrows, Figure 44 B) with some intergranular carbides (pink arrows) at the GBs. Besides the oxidation of the GBs (purple arrows, Figure 44 B) some of the surface near IG and TG carbides showed signs of oxidation themselves.

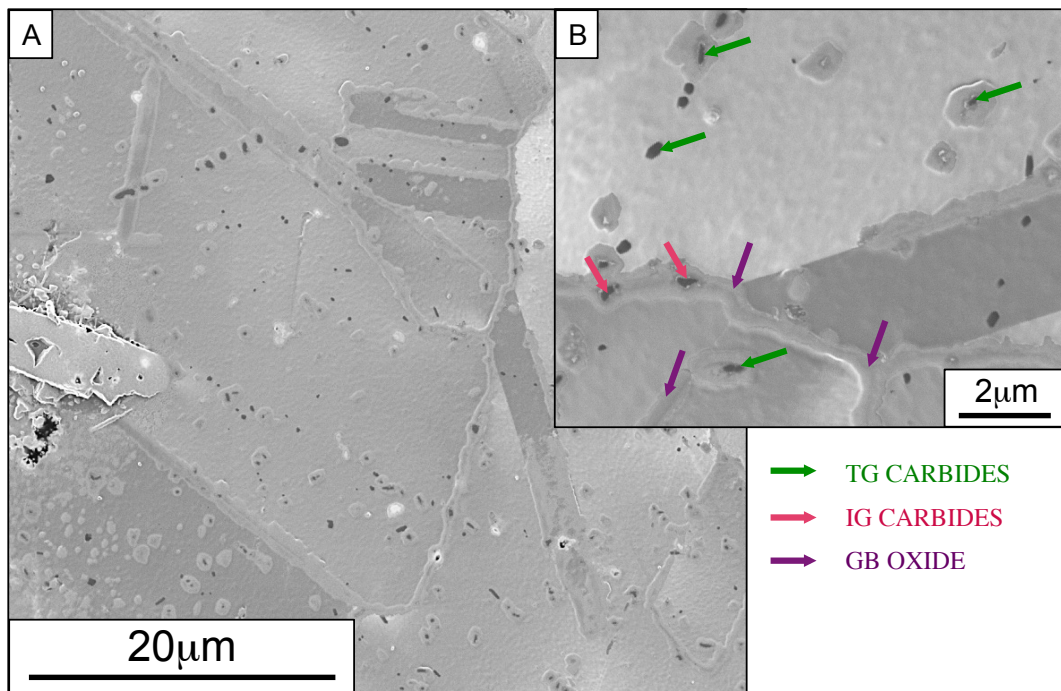


Figure 44: SEM overview image of the surface oxide on *A600-EDF* after a gentle polish with colloidal Si. The oxidized GBs were exposed along with TG carbides, some of which showed signs of oxidation. Some IG carbides embedded in the GB oxide were also seen.

5.3 Summary

Initial observations of both oxidized A600 coupons revealed a quite different surface appearance, which most likely originates in the slightly different autoclave conditions, as summarized in Table 3 for *A600-INSS* and Table 4 for *A600-EDF*. While *A600-INSS* revealed a surface oxide layer, which varied in thickness and crystallite appearance across the individual grains, hence allowing an easy identification of the underlying GBs, *A600-EDF* showed a more compact surface oxide, which was depicted with elongated needle-like oxides. The complicated surface of *A600-EDF* did not allow a direct localization of the underlying GBs so the surface oxide was polished back to expose the underlying grains and GBs. Finally, the surface state of the 2 oxidized A600

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coupons before cantilever preparation and micromechanical tests can be summarized as follows:

- *A600-INSS*: As-oxidized condition (not polished)
- *A600-EDF*: Polished condition (no surface oxide layer)

6 CANTILEVER FRACTURE TESTS ON ALLOY 600

6.1 *A600-INSS* with high intergranular carbide coverage

6.1.1 *Beams tested in the as-oxidized condition*

10 oxidized grain boundaries were tested on the sample denoted *A600-INSS*, using micromechanical cantilever bend tests. Figure 45 shows an example of a beam manufactured on *A600-INSS* before the test.

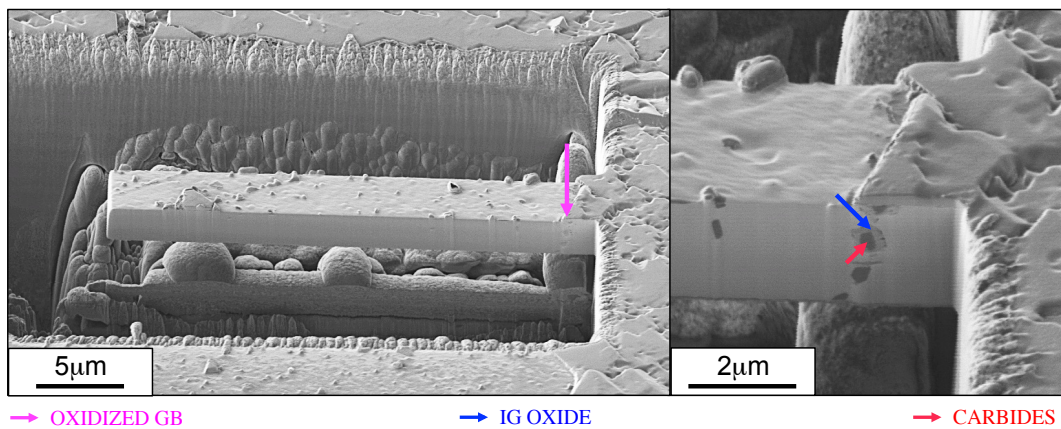


Figure 45: Microcantilever prepared on *A600-INSS* in the as-oxidized condition, incorporating an oxidized GB close to the fixed end (pink arrow). The IG oxide (blue arrow) and IG carbides (red arrow) can be seen in the close up image.

Table 10 shows an overview of the test results for all 10 cantilevers, obtained using the extracted beam dimensions and stress-strain analysis, as described in section 3.5. The range of Young's moduli E for the beams tested on *A600-INSS* covers approximately 120 – 300 GPa, thus revealing an elastic anisotropic behaviour. As shown in Table 10,

CHAPTER 6 Cantilever fracture tests on alloy 600

and in accordance with SEM investigations, also detailed in chapter 7.1, only 4 out of 10 tested cantilevers on *A600-INSS* exhibited cracking, as indicated by major fracture events (load-drops) present in the recorded F-D curves. In the examples shown in Figure 46, which are representative of the fractured cantilevers, it can be seen that the GBs were overall very brittle with an immediate onset of failure at a critical load and no or minimal plastic deformation present before failure. A yellow arrow highlights the crack in the corresponding SEM SE images taken after the test. Considering all beams, which revealed fracture after testing, the stress at failure σ_f , which was defined as the stress-strain equivalent of the point of failure highlighted in the F-D curves, was found to cover a range of $\sim 330 - 770$ MPa.

CANTILEVER	FRACTURE	SURFACE OXIDE	E (GPa)	σ_f (MPa)
C1	YES	YES	192	734
C2	NO	YES	171	-
C3	YES	YES	142	765
C4	NO	YES	139	-
C5	YES	YES	116	326
C6	NO	YES	136	-
C7	NO	YES	135	-
C8	NO	YES	232	-
C9	YES	YES	148	437
C10	NO	YES	302	-

Table 10: Overview of microcantilevers tested on *A600-INSS* at room temperature. The Young's modulus E was found to be anisotropic and not all beams experienced failure during testing.

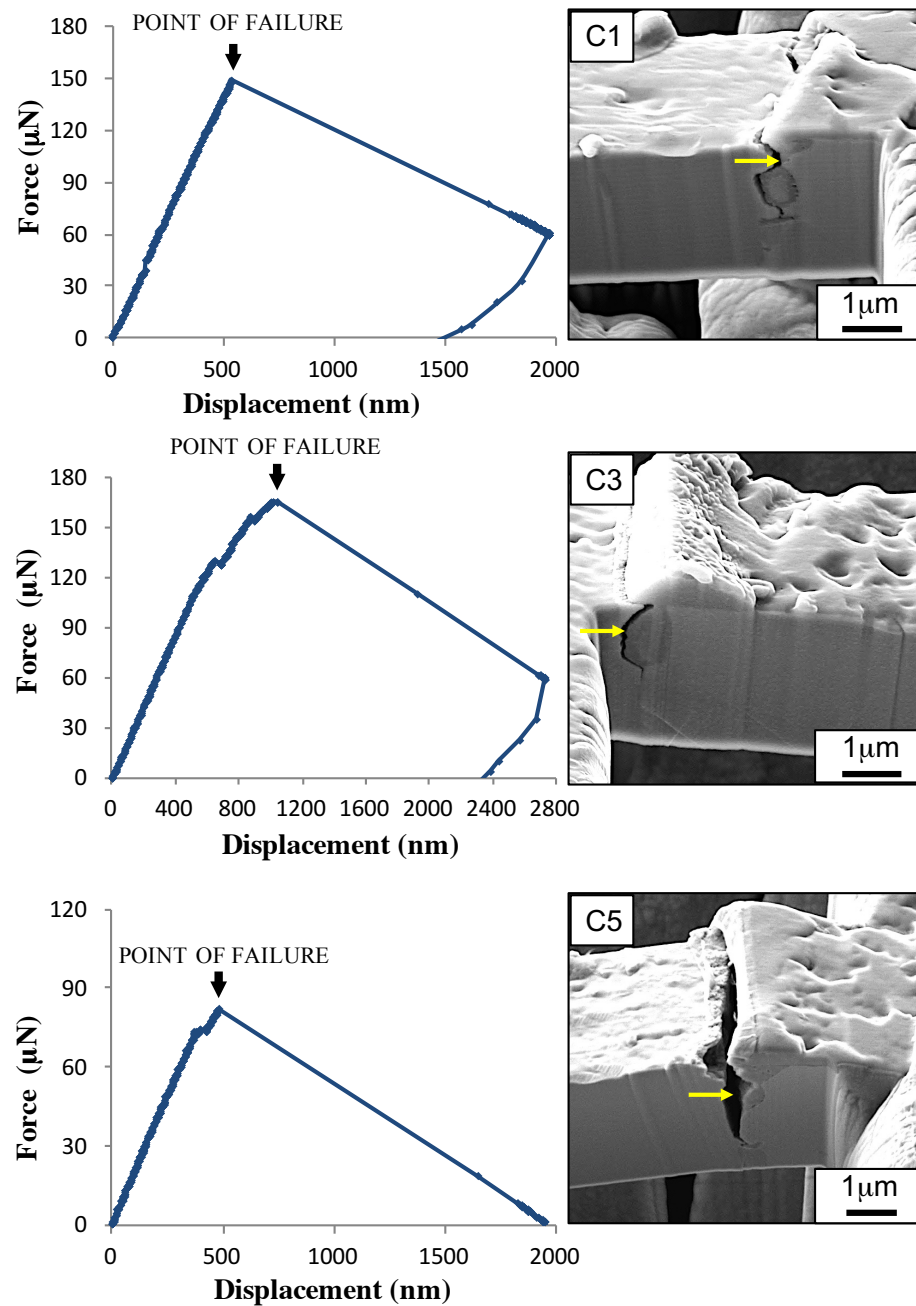


Figure 46: F-D data of oxidized GBs on *A600-INSS*, including C1 C3 and C5. A major fracture event (displacement jump) at a critical load is clearly present in the graphs on the left and a crack is visible in the SEM SE images taken after the test (yellow arrow).

The remaining cantilevers showed no obvious signs of fracture after testing but plastic deformation only. This was supported by the F-D curves of these cantilevers, as shown in Figure 47, which lack the presence of a clear, major displacement jump but show a

rather step-like curve progression with many smaller load-drops. These drops most likely originate from slip events, as clearly visible in the corresponding SEM SE close-ups (green arrows), as they resemble the load drops associated with slip by Gong and Wilkinson^[236] for micromechanical bend tests on single crystal α -Titanium.

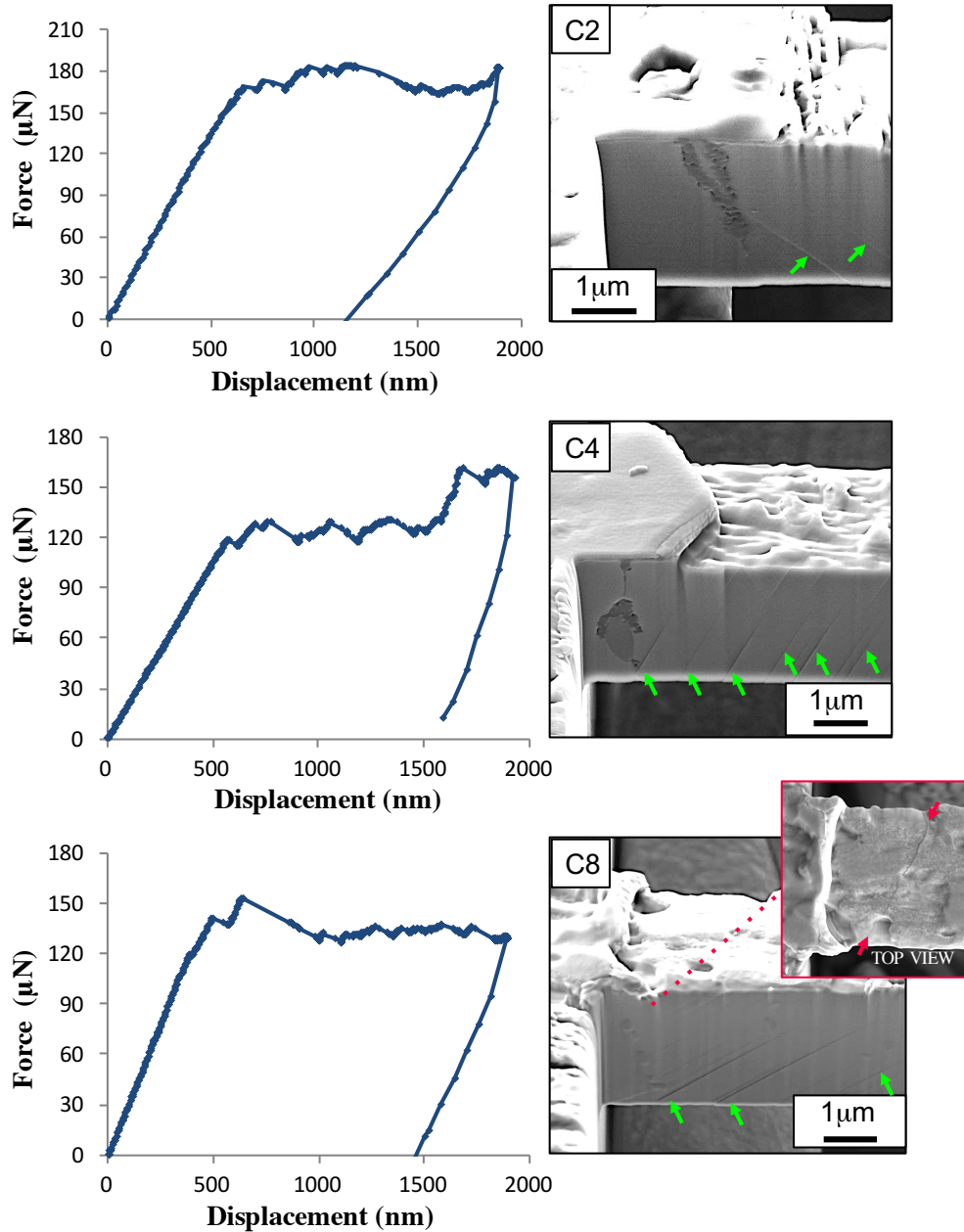


Figure 47: F-D data of oxidized GBs on *A600-INSS*, including C2, C4 and C8. No major fracture event (displacement jump) is identifiable but multiple smaller load drops are seen in the F-D curves. The presence of slip lines (green arrows) can be observed in the SEM SE images taken after the test that are most likely the origin of these drops.

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The rather low yield of only 4 fractured cantilevers out of 10 led to the question of why some cantilevers seem to fail while others only deform plastically, despite the presence of the GB oxide in all cases. This question will be addressed next.

6.1.2 The influence of surface oxides on the mechanical response of oxidized GBs on A600-INSS

Considering the tests performed on *A600-INSS* in chapter 6.1.1, 2 modes of failure were observed; 1) beams showing fracture and little to no plastic deformation and 2) beams undergoing plastic deformation with no apparent fracture. The following section is dedicated to explaining why only 4 out of 10 GBs fractured whilst the other 6 exhibited no obvious visual signs of cracking. Figure 48 shows a range of close-up images of beams tested on *A600-INSS* in the as-oxidized condition. In all cases the presence of a surface oxide layer of varying thickness on top of the grains was found. For beams with no apparent fracture present after testing (Figure 48, C2 and C4), the surface oxide overlapped the oxidized GBs to a greater extent than in the cases where fracture occurred (Figure 48, C1 and C3). This suggested that the overlap of the surface oxides might act as stiff bond, keeping the GBs closed and hence influencing the overall mechanical response of the beams and the extracted stress at failure. To demonstrate an influence of the stiff surface oxide overlapping the GBs, a new test series was performed. The aim was the direct comparison of results obtained on the same grain boundaries with and without a surface oxide present. An additional cantilever was prepared on the same GBs as C3 and C4 (GB 3 and 4 respectively). The 2nd cantilever on GB 3 and 4 is denoted R3 and R4. To enable a direct comparison, the surface oxide of R3 and R4 of each of these pairs, was removed by careful milling of the oxide in the grain boundary region, before final preparation to obtain the triangular cantilever shape.

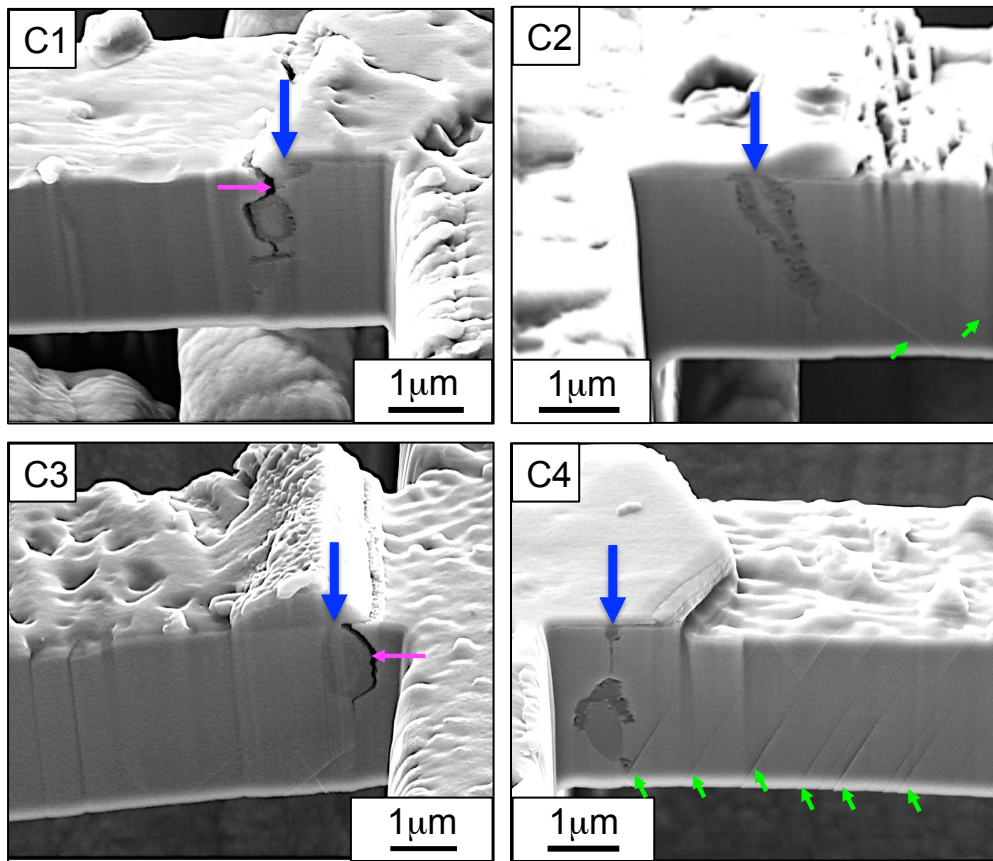


Figure 48: SEM SE images of oxidized GB regions after testing with the nanoindenter. A thick surface oxide layer, overlapping the original GB (blue arrows) is seen. In C2 and C4, which showed no obvious fracture after testing, the surface oxide overlaps the oxidized GB to a greater extent than in the fractured cases (C1 and C3), where failure is clearly present. Pink arrows mark the cracks in C1 and C3 while green arrows indicate slip lines in C2 and C4.

This was achieved via the milling function of the FIB at low beam currents (10 – 30 pA). That way it was possible to expose the underlying GB close to the fixed end. The milling-box setup used for this procedure is shown in Figure 49. Thereby, after successful location of the oxidized GB (Figure 49 A) and milling of the typical U-shape, the outer surface layer was carefully removed, using a milling box (Figure 49 B - C) before the usual 30° undercut of the cantilever, as described in section 3.3.2, was performed to obtain final shape and width of the beams (Figure 49 D). The reason for performing this step before undercutting the cantilever was to achieve a uniform

removal of the surface layer and to prevent preferential milling of the thinner material edges of a triangular cantilever. Each cantilever was then tested with the Nanoindenter, as described in 3.4, and test results were compared (Table 11).

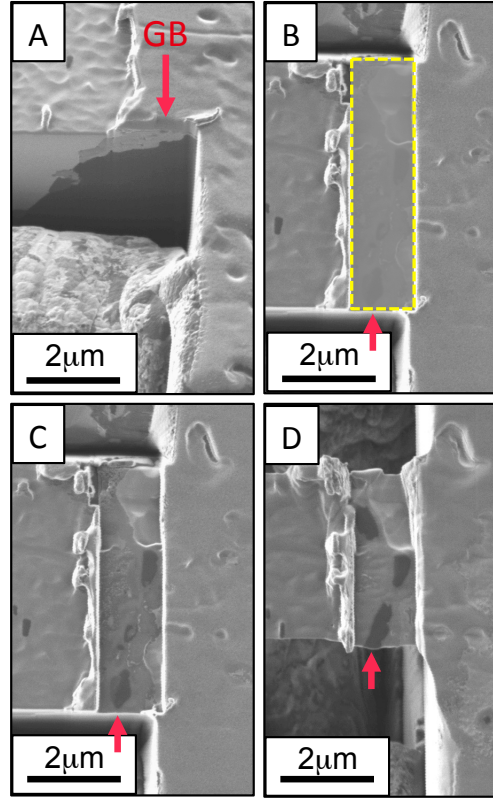


Figure 49: FIB-based surface oxide removal. After identification of the oxidized GB (A), here demonstrated on cantilever R4, a small milling-box (yellow) is used to remove the surface oxide overlap (B - C) before final cantilever preparation (undercutting) to obtain the desired width and triangular shape (D).

Beam/GB	Surface Oxide	Fracture	E (GPa)	σ_f (MPa)
C4	Yes	No	153	-
R4	No	Yes	121	362
C3	Yes	Yes	142	765
R3	No	Yes	128	527

Table 11: Young's Modulus E and stress at failure σ_f calculated via simple beam theory for GB pairs 3 and 4, each tested with and without the influence of surface oxide.

The following observations were made:

- Cantilever pair C4 and R4

In case C4, a surface oxide overlaps the oxidized GB (Figure 50) and no cracking along the oxide-metal interface was seen after testing. Nonetheless, slip lines were visible. R4, whose surface oxide had been removed, experienced fracture along the oxide-metal interface with a normal failure stress σ_f of 362 MPa. The behaviour was reflected in the corresponding stress-strain curves (Figure 51). C4 showed no obvious failure event but multiple smaller stress drops, which were probably associated with the slip events, whereas a main fracture event, indicated by the major stress drop after reaching the failure stress σ_f in Figure 51 was seen for cantilever R4. Moreover, C4 showed a slightly increased stiffness as compared to R4.

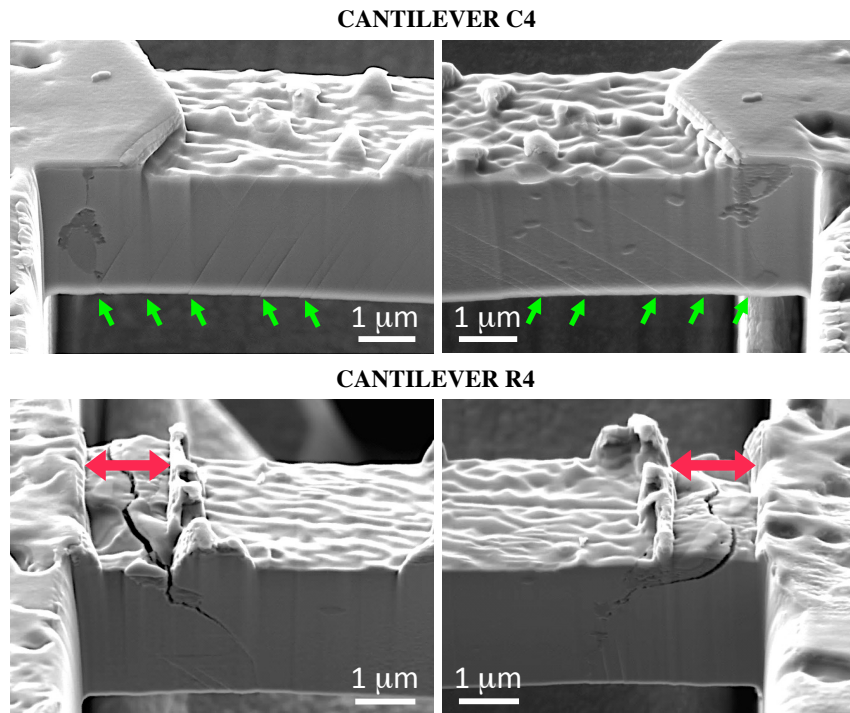


Figure 50: SEM images of cantilever pair C4 and R4 after testing. Whilst C4 shows no obvious signs of cracking but plastic deformation only (slip lines, green arrows), fracture is clearly visible in R4 (no surface oxide, red arrows).

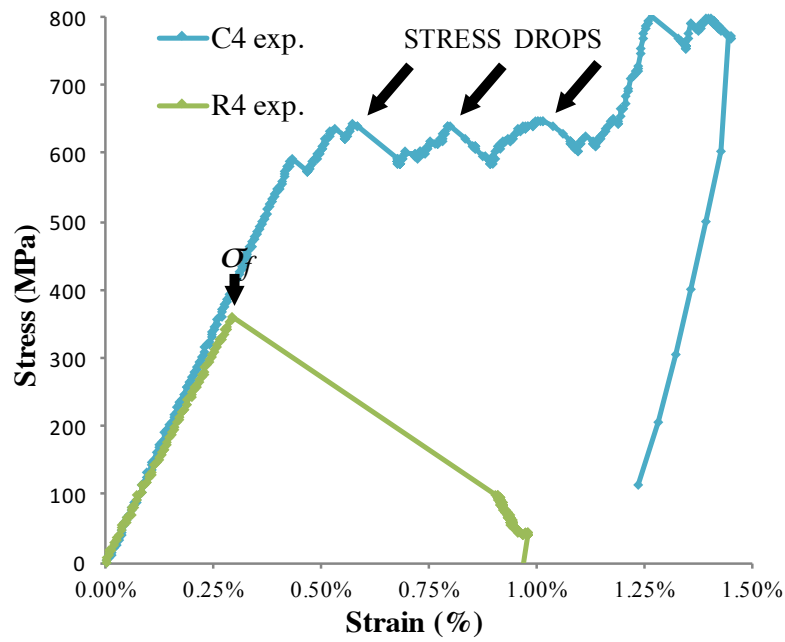


Figure 51: Stress-strain curves of cantilever pair C4 (surface oxide), showing multiple smaller stress drops (slip events) and R4 (no surface oxide), showing a clear fracture event.

○ Cantilever pair C3 and R3

Both cantilevers showed fracture after testing (Figure 52). Nonetheless, with the surface oxide present on C3, the stress at the point of failure σ_f was 238 MPa higher (Table 11), as for R3 with no surface oxide overlapping the GB. The drop of the failure stress σ_f and a slight decrease in stiffness for R3 (no surface oxide) when compared to C3 were reflected in the corresponding stress-strain curves of the tests, as shown in Figure 53. The observed behaviour clearly demonstrated an influence coming from the presence of the surface oxide atop of the GBs. A higher failure stress ($\Delta\sigma_f = 238$ MPa) was observed, suggesting an enhanced resistance to cracking due to the presence of the stiff surface oxide overlapping the GB or, in the case of cantilever pair C4 and R4, an overall suppression or delay of the onset of fracture.

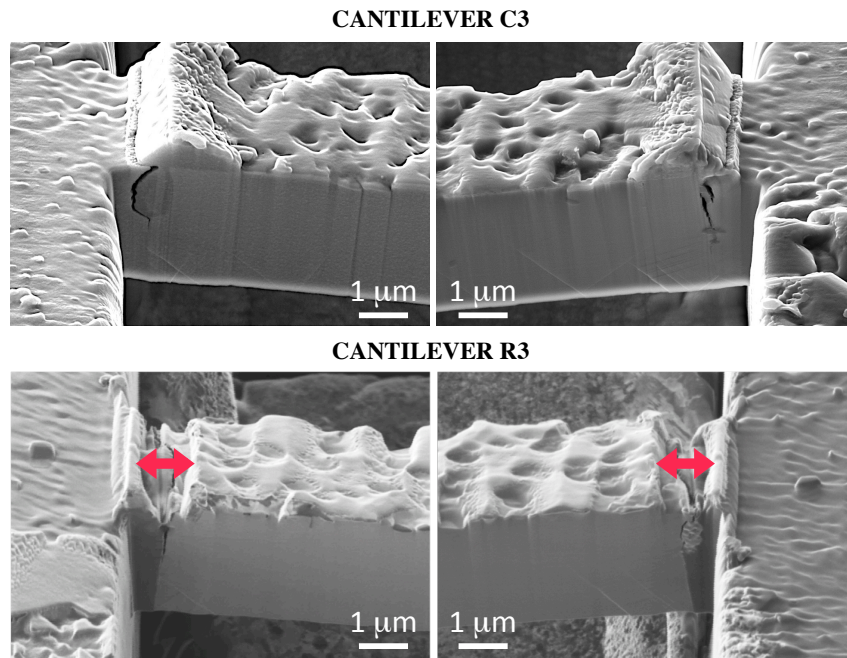


Figure 52: SEM images of cantilever pair C3 (surface oxide) and R3 (no surface oxide, red arrows). Cracking can be observed in both cases.

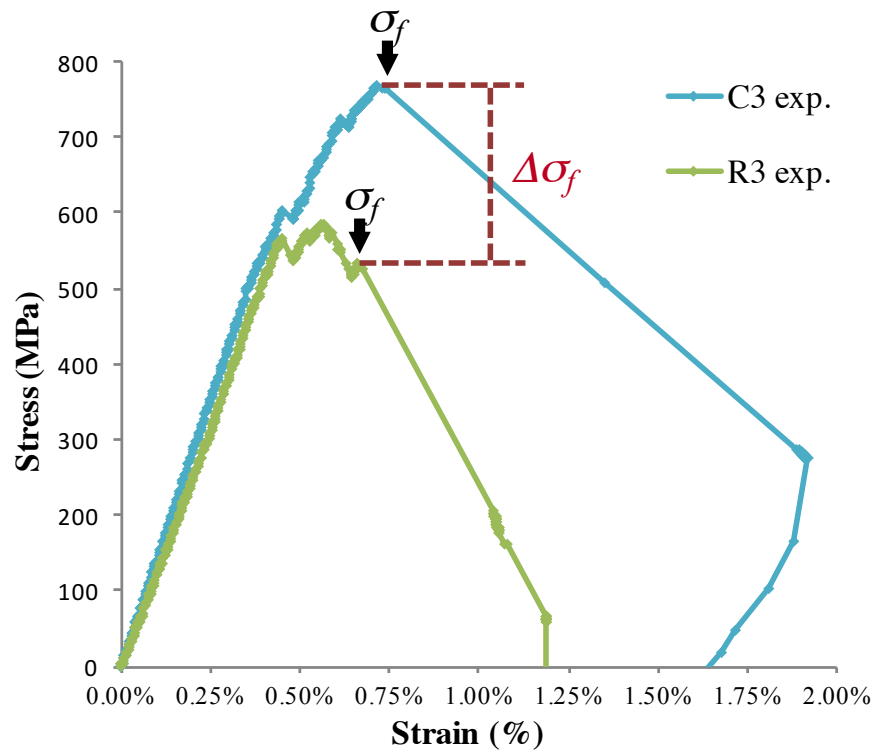


Figure 53: Stress-strain curves of cantilever pair C3 (surface oxide) and R3 (no surface oxide). A main fracture event at failure stress σ_f can be observed in both cases.

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To quantify the experimental behaviour, the fracture tests of cantilever pair C3 and R3 were simulated, using their real dimensions, an image based mesh generation (see chapter 4.1) and a cohesive surface based FEM approach (chapter 4.2) whereby cohesive parameters were calibrated for R3 (no surface oxide) and were then used for model C3 (surface oxide) to see whether the experimentally observed influence of the oxide overlap can be accounted for. In addition to the surface oxide crystallite overlapping the GB in the case of C3, a thinner surface layer on top of the free end grain of both beams was included in the model. For reasons of simplicity it was treated as a thin continuous layer of Fe-rich oxide with a constant thickness of 120 nm. To obtain this averaged thickness, several measurements of the non-uniform oxide layer thickness were taken from (S)TEM images and averaged. As also detailed in chapter 8.1.1, the surface oxide layer on R3 and the surface oxide crystallite atop of the GB in C3 was assumed to have a Young's modulus E of 230 GPa and $\nu = 0.262$ ^[237] as found for magnetite. The carbide/oxide inclusion present in R3 was assumed to have a Young's modulus E of 302 GPa and $\nu = 0.336$, as found for Cr_7C_3 carbide precipitates ^[238] and also within the range reported for Cr_{23}C_6 . ^{[239], [240]} For the Young's modulus E of the beams a value of 118 GPa was found to be the best fit. This agrees well with R3's value of E , calculated via simple beam theory after adding an additional height h' of 120 nm to the overall beam height h , which corresponded to the averaged surface oxide layer covering the beam length. Young's modulus E , the stress at the first noticeable load drop σ_{drop} and stress at failure σ_f , estimated with and without the presence of the additional 120 nm are summarized in Table 12. As an example, the full mesh and model of cantilever R3 is shown in Figure 54, showing grain 1 (green), grain 2 (grey), the average 120 nm thick surface oxide layer (blue) as well as the loading condition at the free end, a distance L_{eff} away from the GB, and the fixed boundary condition (fixed end) which has been applied (pink) to the other.

Beam/GB	Surface	E (GPa)	σ_{drop} (MPa)	σ_f (MPa)
C3	Yes	142	604	765
R3	No	128	558	527
		$E_{(h+h')}$ (GPa)	$\sigma_{drop(h+h')}$ (MPa)	$\sigma_{f(h+h')}$ (MPa)
		130	569	721
		115	522	490

Table 12: Young's Modulus E , stress at the first load drop σ_{drop} and stress at failure σ_f calculated for cantilever pair C3 and R3. For comparison with simulations, results were calculated with and without the consideration of an averaged surface oxide layer ($h' = 120$ nm).

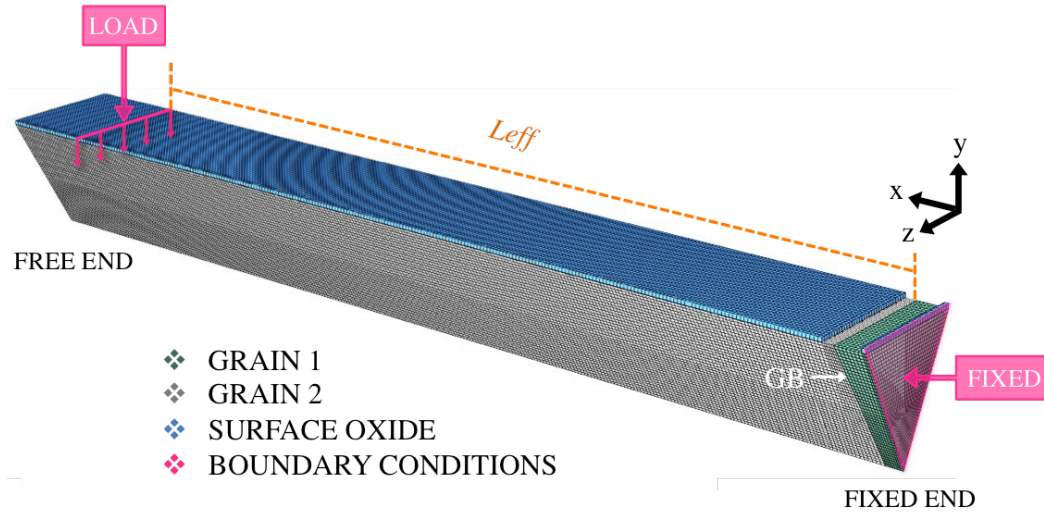


Figure 54: Full model and mesh of cantilever R3 before testing.

The cohesive laws and respective parameters, used in both models were calibrated against the experimental behaviour of R3, as shown in Figure 53 and Figure 57, and are summarized in Table 13. Due to cohesive damage FEM only being applicable to brittle failure, the stress at the first noticeable load drop σ_{drop} , has been used as a reference for the calibration of the model. To achieve the correct crack path in the model, 3 different laws needed to be defined. *Law 1*, corresponded to the oxidized interfaces along the GB, *Law 2* to the surface oxide interface and *Law 3*, the strongest of cohesive laws, was applied to unoxidized regions to achieve the experimentally observed crack arrest.

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Based on the cohesive parameters used for the 1st law at the oxidized regions in the model, an interfacial fracture energy G of 1.44 J m^{-2} for the oxide/metal interface and an estimated fracture toughness of $K = \sqrt{2EG} = 0.58 \text{ MPa m}^{1/2}$ was found. These were calculated based on Equation 15 and Equation 16 in chapter 4.2. A significantly higher interfacial fracture energy of $G = 19 \text{ J m}^{-2}$ was found for the unoxidized regions. This highlights the GB oxide's contribution to the weakening of the interface. The same Young's modulus and cohesive parameters used in R3 (Table 13) were then used for the cohesive model of C3 to validate whether the experimentally observed increase in stiffness and delay of the point of failure reflected in the experimental data, as seen in Figure 53 and Figure 57, can be reproduced. Close up images of both models (see Figure 55) show the interfaces along the oxidized GB at which *Law 1* was applied (oxidized law) highlighted in yellow and *Law 2* (surface oxide interface) in pink. In all other regions along the GB, *Law 3* (unoxidized regions, black) was used to capture the experimentally observed crack arrest. The laws are summarized in Table 13. The models were then displaced at the experimentally obtained load point, as indicated by the loading boundary condition (pink arrows in negative y direction) in Figure 54.

	Δ_f (nm)		σ_f (MPa)	K (GPa/ μm)
Law 1:	5	Normal:	575	1180
(Oxidized)		Shear _{1,2} :	575	453.85
Law 2:	5	Normal:	575	1180
(Surf. Ox)		Shear _{1,2} :	260	453.85
Law 3:	5	Normal:	7830	1180
(Unoxidized)		Shear _{1,2} :	7830	453.85

Table 13: Cohesive parameters as used for the oxidized (*Law 1*) regions, surface oxide interface (*Law 2*) and unoxidized regions (*Law 3*) in model C3 and R3. Δ_f is the opening displacement, σ_f the maximum nominal stress in normal and shear directions and K the initial stiffness in normal and shear directions.

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As demonstrated in Figure 56, which compares the simulated fracture path at the end of the displacement step and the corresponding SEM images of the fractured GBs after testing, the cohesive damage simulation captures the experimentally observed behaviour accurately.

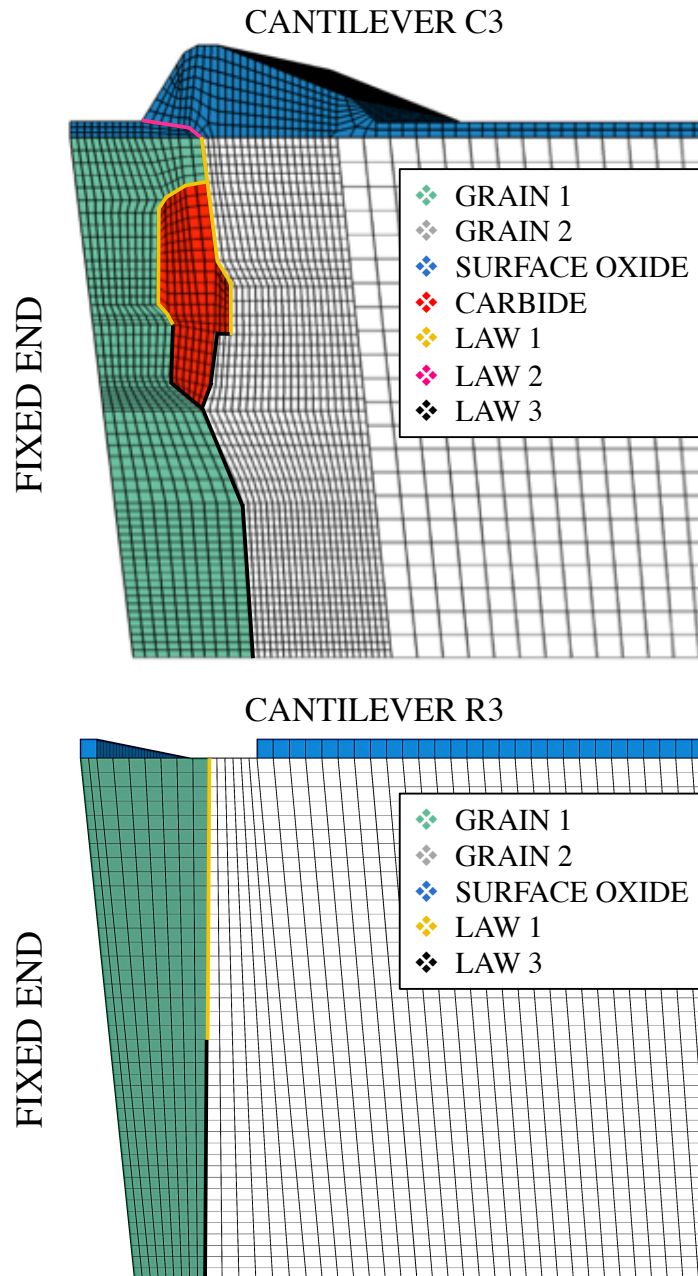


Figure 55: Close-up of the model and mesh of C3 (top) and R3 (bottom). Interfaces at which cohesive *Law 1* (oxidized), *Law 2* (surface oxide interface, R3 only) and *Law 3* (unoxidized) have been applied are highlighted in different colours.

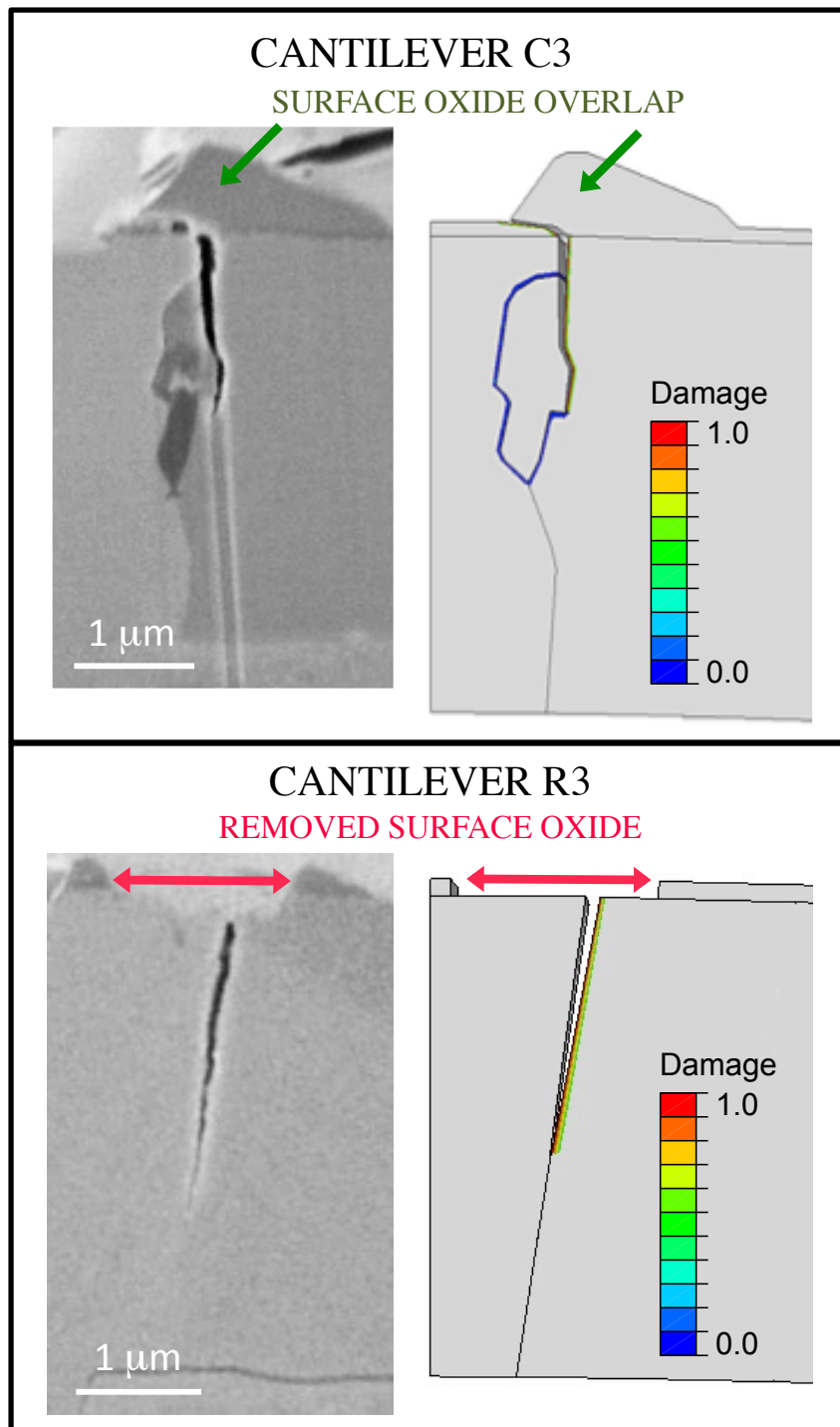


Figure 56: SEM SE images of the central GB portion of cantilever C3 (top) and R3 (bottom) after testing. The corresponding FEM models are shown on the respective right side. Green arrows mark the surface oxide overlap and the red arrows indicate the area where the surface oxide had been removed. Using realistic cantilever geometry and microstructure and cohesive surface FEM simulations the experimentally observed fracture path was reproduced.

Figure 57, which compares the experimentally and computationally obtained F-D curves, shows that by applying the same cohesive parameters to the models, the experimentally observed increase in stiffness and fracture stress can be predicted/captured well. A normal stress at failure of $\sigma_f = 575$ MPa was predicted for tested grain boundaries C3 and R3. Considering the fact that this value was calibrated against the stress at the first noticeable load drop in the experimental F-D curve of R3, which corresponded to $\sigma_{drop} = 522$ MPa, the error when compared with beam theory estimations was within $\sim 10\%$. This highlighted the accuracy of the stress at failure values of the beams tested in this study, obtained via simple beam theory estimations.

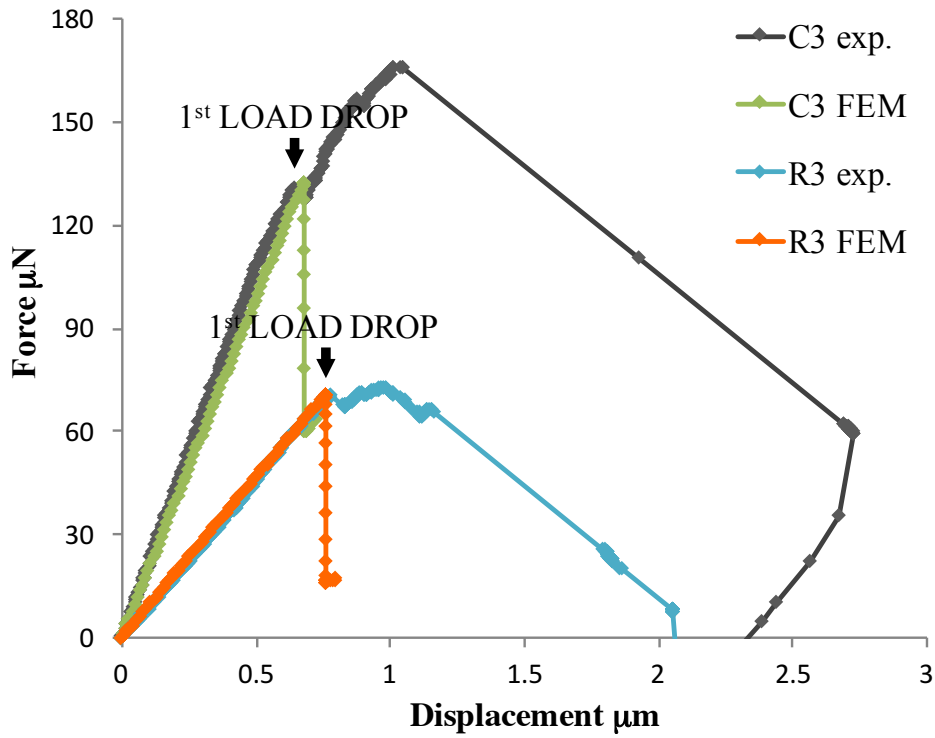


Figure 57: Comparison of the experimental and computational F-D curves of cantilever C3 and R3. The FEM curve for C3 has been predicted, using the cohesive parameters of R3, which were calibrated against the experimental data of R3.

Even though no data has been provided in their publication, Dugdale *et al.* ^[49] claim that the presence of GB carbides, considering their shape and location along the GB,

increased the stress at failure by $\sim 5\%$. This leaves the question of whether the rather complex oxide/carbide particle enclosed along the GB path in model C3 (red particle in Figure 55, top), when compared to the rather simple microstructure of model R3, was actually the cause for the increase in stiffness and stress at failure. To verify that the predicted increase in stiffness and fracture stress was not a result of the presence of the inclusion, the simulations for C3 were repeated with varying material properties for the precipitate. First it was treated as the same as the surface oxide layer, with $E = 230$ GPa and $\nu = 0.262$. Next the modulus was increased ($E = 400$ GPa) to make it stiffer and finally the particle was treated same as the matrix material ($E = 118$ GPa), to simulate what happens if the particle did not exist. As shown in the graph in Figure 58, the particle's contribution to the failure stress was found to be negligible (suppressed) in the presence of the overlapping surface oxide crystallite. Hence, it can be concluded that the precipitate played no role in the observed increased stiffness and failure stress and that it was merely a result of the surface oxide overlapping the GB. This aligns with the assumption that a significant enough oxide cover, might act to shift the stress concentration away from the oxidized GB, which otherwise represents the actual stress concentrator and weak spot in the tensile region of the beam. The main load is thereby accommodated by the stiff surface oxide layer, which reduces the overall stress in the beam. The opening stress on the grain boundary, which otherwise is the weakest spot with highest stress, is believed to remain below the critical value required for crack growth. Hence fracture is suppressed and the crack kept closed. In addition, the presence of the stiff oxide cover might provide an initial obstacle, as the initiated crack needs to propagate along a crack path normal to the main axis of applied load (delamination like) before reaching the actual GB and propagating along the oxide-metal interface.

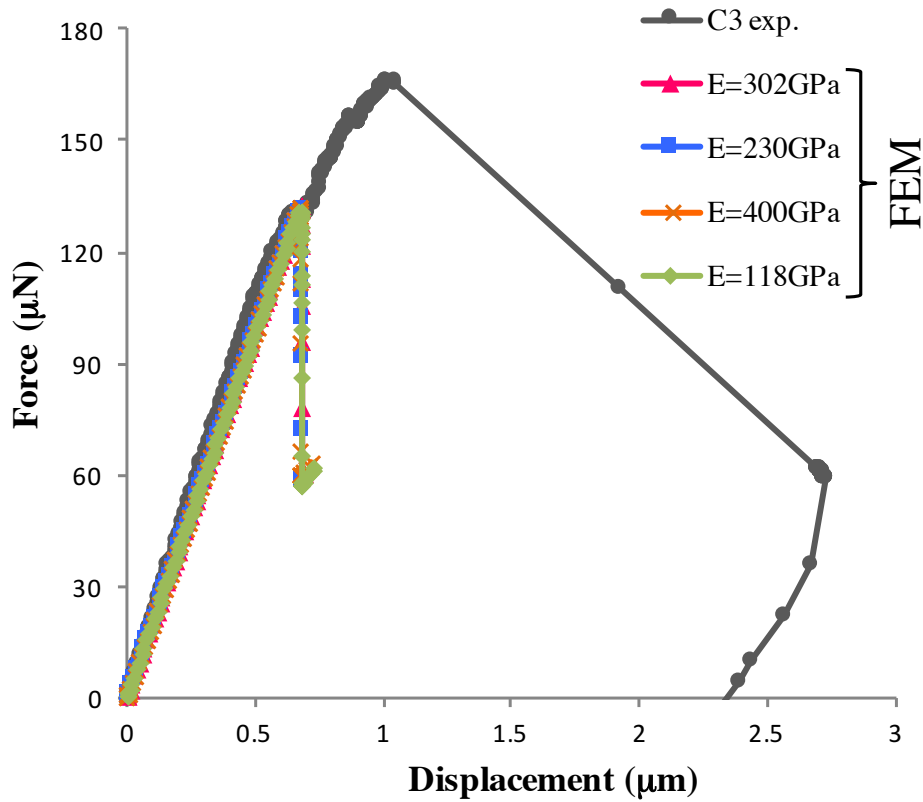


Figure 58: Influence of the oxide-carbide particle (red particle in Figure 55, top) on the F-D behavior of C3 (*A600-INSS*), as discussed in section 6.1.2. As can be seen, different values for E do not alter the materials stiffness or failure stress.

6.1.3 Beams tested after surface oxide removal on top of the GBs

Due to the proven influence of the surface oxide found in the previous section, 4 more surface-oxide free GBs were tested in addition to the two, which already had the surface oxide atop of the GBs removed. Figure 59 shows an example of such a beam before the test. A black arrow marks the region where the surface oxide had been removed, according to the FIB-based procedure described in section 6.1.2 (Figure 49). Table 14 shows the test results of all 6 cantilevers, obtained using the extracted beam dimensions and stress-strain analysis, using simple beam theory as described in section 3.5. The range of Young's moduli E for the beams tested on *A600-INSS* covered approximately 120 – 185 GPa, again demonstrating elastic anisotropic behaviour.

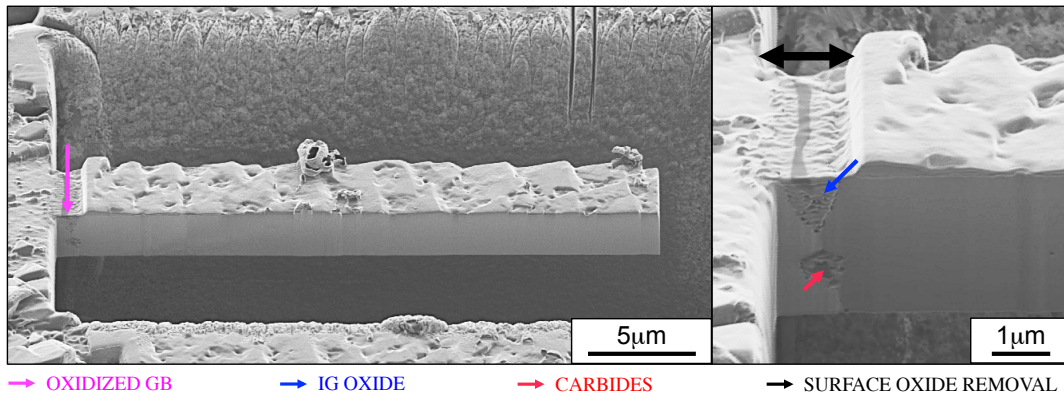


Figure 59: SEM SE image of a microcantilever prepared on *A600-INSS*, incorporating an oxidized GB (pink arrow) close to the fixed end. The black arrow marks the region where the surface oxide had been removed. A blue arrow indicates the IG oxide and a red arrow a carbide.

CANTILEVER	FRACTURE	SURFACE OXIDE	E (GPa)	σ_f (MPa)
R1	YES	Removed	167	420
R2	YES	Removed	144	472
R3	YES	Removed	128	527
R4	YES	Removed	121	362
R5	YES	Removed	129	380
R6	YES	Removed	185	494

Table 14: Overview of microcantilevers tested on *A600-INSS* at room temperature. The Young's modulus E was found to be anisotropic. All beams experienced failure during testing.

In accordance with major fracture events (load-drops) present in the recorded F-D curves, all beams experienced failure, as can be seen in the representative examples in Figure 60. Cracks were clearly visible in the SEM SE images after testing, as also discussed in chapter 7.1. A yellow arrow marks the cracks in Figure 60. It can be seen that the tested GBs were very brittle with no or minimal plastic deformation present before the onset of failure. The stress at failure σ_f , defined as the stress-strain equivalent of the point of failure marked in the F-D curves, did not exceed 530 MPa (Table 14), as

compared to a peak failure stress of 765 MPa for beams tested in the as-oxidized condition in section 6.1.1.

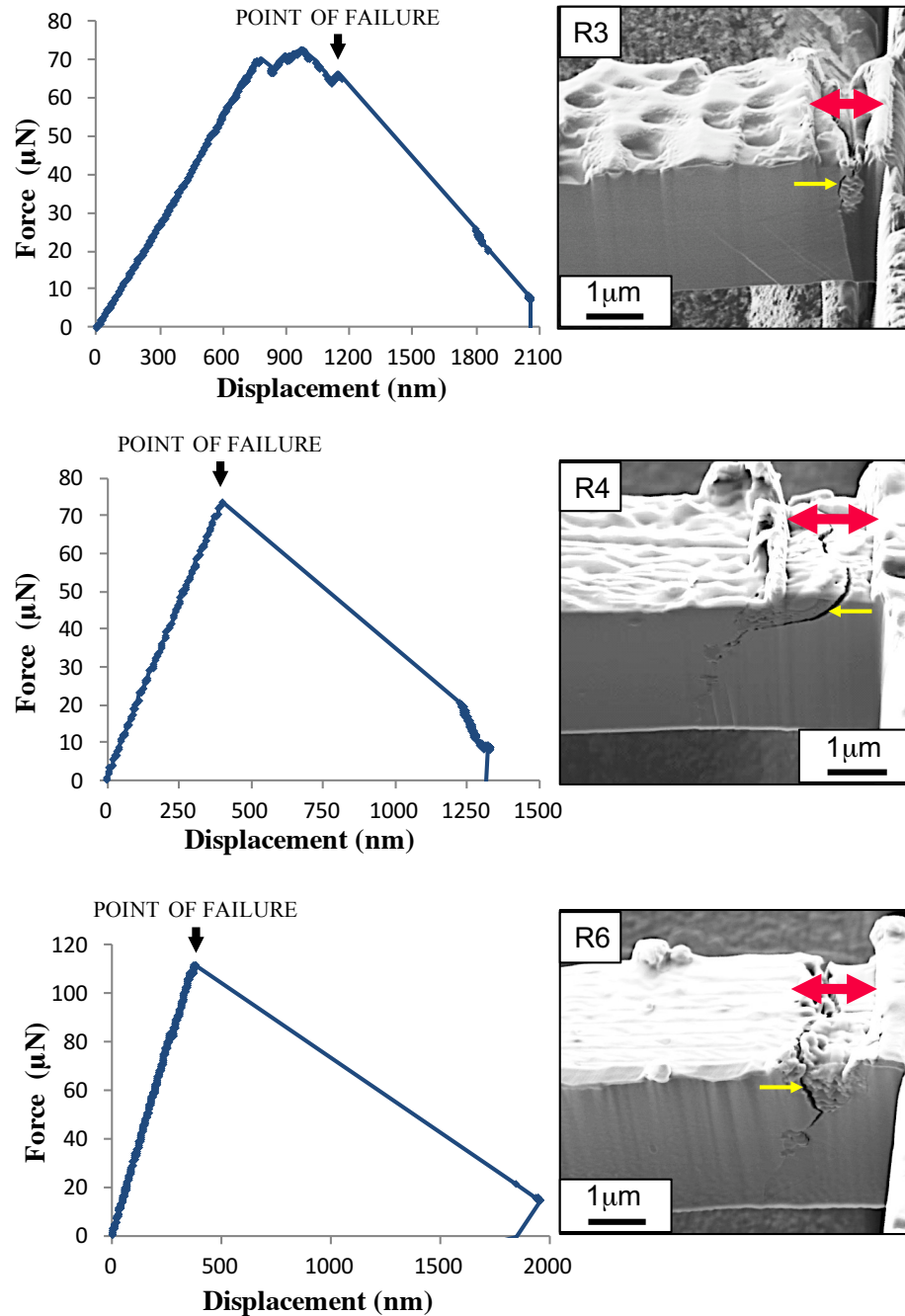


Figure 60: F-D data of oxidized GB tested on A600-INSS with no surface oxide atop of the GBs, including R3, R4 and R6. Major fracture events are visible upon reaching a critical load (point of failure). A crack is visible in the SEM SE images after testing (yellow arrow). Red arrows mark the area where the surface oxide had been removed.

6.1.3.1 Failure stress and GB misorientation

After the removal of the surface oxide atop of the GBs, stress at failure was still different across the tested beams. Values varied between 362 – 527 MPa. In 2015, Stratulat *et al.* ^[85] found that there is no direct correlation between GB toughness (K_{IC}) and misorientation on oxidized A600. Nonetheless, to investigate whether the variation of the failure stress observed in this thesis was in any way related to GB misorientation, transmission Kikuchi diffraction (TKD) was performed on 5 of the GBs tested on *A600-INSS* (see section 6.1.3) to extract the Euler angles of the grains, G1 at the fixed end and G2 at the free end, which make up the beam and to calculate the respective misorientations. To calculate the misorientation based on the extracted Euler angles, a Matlab script was written in the frame of this thesis. The script and some explanations are attached in APPENDIX A. As can be seen in Table 15, the 5 GBs were all HABs.

BEAMS	G1: ($\varphi_1, \Phi, \varphi_2$) in (°)	G2: ($\varphi_1, \Phi, \varphi_2$) in (°)	γ (°)	σ_f (MPa)
R2	(251, 28, 251)	(325, 49, 47)	53,64	479
R3	(356, 41, 346)	(242, 26, 147)	55,71	527
R4	(4, 28, 313)	(300, 44, 48)	55,88	362
R5	(10, 30, 31)	(298, 39, 41)	54,38	380
R6	(308, 32, 61)	(125, 52 231)	47.41	494

Table 15: Euler angles ($\varphi_1, \Phi, \varphi_2$) for the grains at the fixed (G1) and free (G2) end of the cantilevers, corresponding misorientation angle (γ) and failure stress (σ_f) of the surface oxide free GBs R2, R3, R4, R5 and R6 tested in section 6.1.3.

This was not surprising considering that GBs, which revealed a strong degree of IG oxidation, were chosen for the tests. When plotting the stress at failure as a function of the misorientation, as shown in Table 15, no obvious trend was observed. Even though from a statistical point of view only very limited misorientation data was available, the finding seemed in overall agreement with the findings by Stratulat *et al.* ^[85].

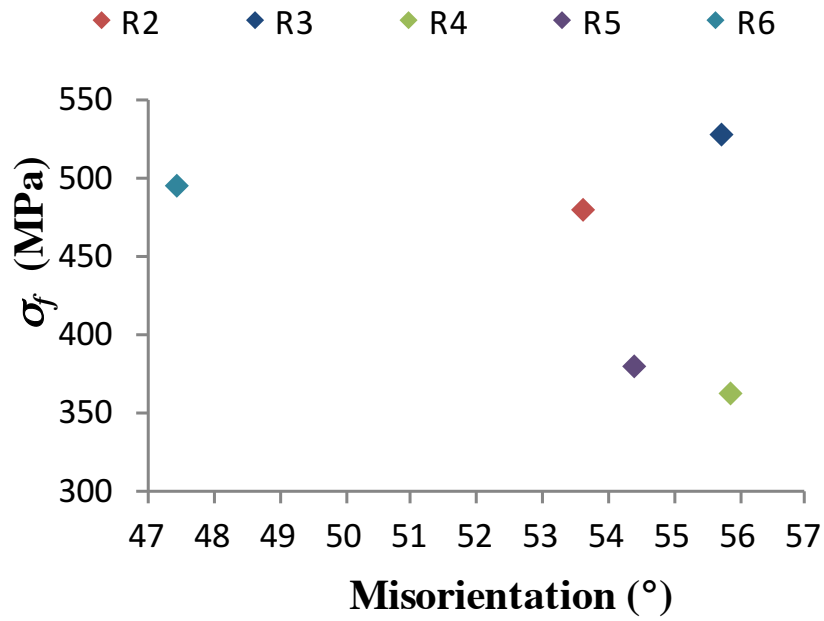


Figure 61: Failure stress σ_f plotted as a function of misorientation angle γ for 5 GBs, tested on *A600-INSS* (see section 6.1.3) without a surface oxide cover.

6.2 A600 with low intergranular carbide coverage

A total of 9 oxidized grain boundaries were tested on the sample denoted *A600-EDF*, using micromechanical cantilever bend tests. Figure 62 shows an example of a beam manufactured on *A600-EDF* before the test.

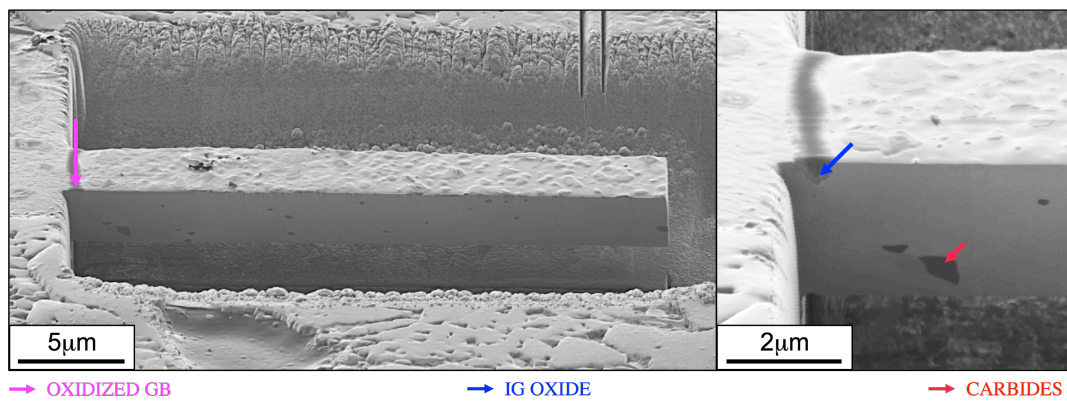


Figure 62: SEM SE image of a microcantilever prepared on *A600-EDF*, incorporating an oxidized GB (pink arrow) close to the fixed end. A blue arrow indicates the IG oxide and a red arrow a carbide.

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Table 16 shows a summary of all micromechanical test results for the 9 cantilevers prepared on *A600-EDF*, obtained using the extracted beam dimensions and stress-strain analysis, using simple beam theory as described in section 3.5. The range of Young's moduli E for the beams tested on *A600-EDF* was in good agreement with the range found on *A600-INSS*. It covered approximately 135 – 320 GPa. As shown in Table 16, even though no surface oxide was present on *A600-EDF*, only 4 out of 9 tested cantilevers exhibited obvious fracture events.

CANTILEVER	FRACTURE	SURFACE OXIDE	E (GPa)	σ_f (MPa)
C1	YES	No	172	776
C2	YES	No	148	665
C3	YES	No	143	644 (?)
C4	YES	No	141	627
C5	YES	No	138	651 (?)
C6	YES	No	166	495 (?)
C7	NO	No	164	-
C8	NO	No	140	-
C9	YES	No	320	598

Table 16: Overview of microcantilevers tested on *A600-EDF* at room temperature. The Young's modulus E was found to be anisotropic. 7 out of 9 cantilevers experienced failure during testing.

In Figure 63, it can be seen that the GBs were relatively brittle with only minimal plastic deformation present before failure, as indicated by a clear and isolated displacement jump in the respective F-D curves. The failure was followed by a plateau, which corresponds to almost perfectly plastic behaviour with either minimal strain hardening or slight strain softening only. For three tested beams (Figure 64) it was not clear whether fracture occurred looking at the F-D curves alone. Due to the shallow IG

oxidation of this coupon (300 – 1000 nm only), the fracture jumps appeared well-hidden in-between the load-drops from plastic deformation (slip).

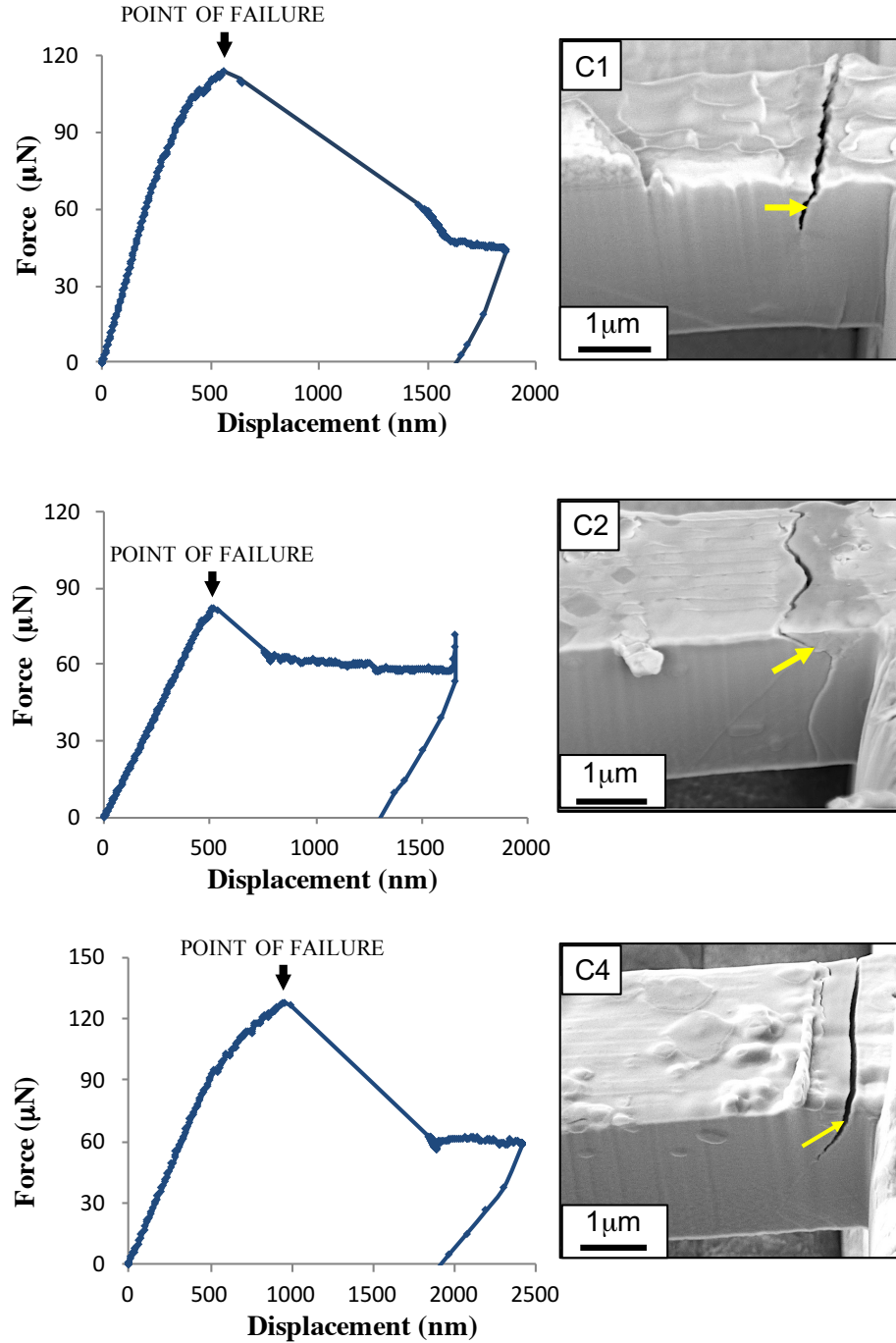


Figure 63: F-D data of oxidized GBs on *A600-EDF*, including C1, C2 and C4. A major fracture event upon reaching a critical load (point of failure) is clearly present in the graphs. A plateau-like plastic region can be seen, with minimal strain hardening or strain softening. Cracks are visible in the corresponding SEM in-lens images taken after the test (yellow arrows).

Nonetheless, as indicated by the yellow arrows in Figure 64, fracture was visible in the SEM images after testing, as also discussed in section 7.1.2. The first bigger isolated load drop in each of those curves was assumed to correspond to the point of failure.

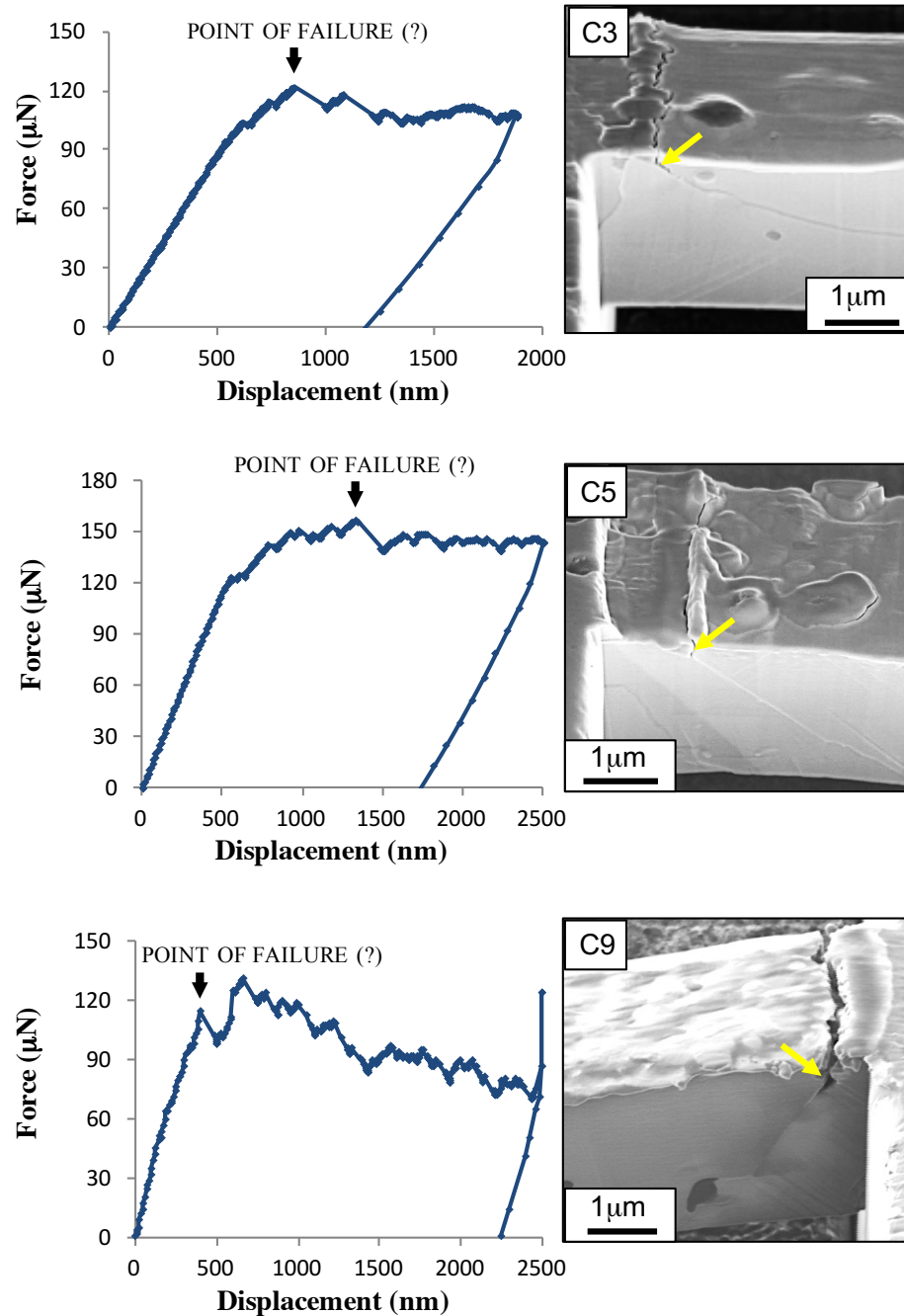


Figure 64: F-D data of oxidized GBs on *A600-EDF*, including C3, C5 and C9. Multiple load-drops are seen, which make a certain determination of the point of failure difficult. The first big and isolated load-drop in the curve has been defined as point of failure. Subtle cracking (yellow arrows) is seen in the SEM in-lens images taken after the test.

Hence, the extracted stress at failure σ_f in Table 16 was marked with (?), as it was impossible to identify the load-drop, which corresponds to the fracture event, with 100% certainty. For all 7 beams, which revealed fracture after testing, the stress at failure σ_f , which was defined as the stress-strain equivalent of the point of failure marked in Figure 63 and Figure 64, was found to cover a range of $\sim 495 - 780$ MPa. As also confirmed by SEM imaging, 2 cantilevers deformed only plastically, showing no obvious sign of fracture. This was reflected in the corresponding F-D curves shown in Figure 65. No major fracture events but multiple smaller load drops were present in the curves.

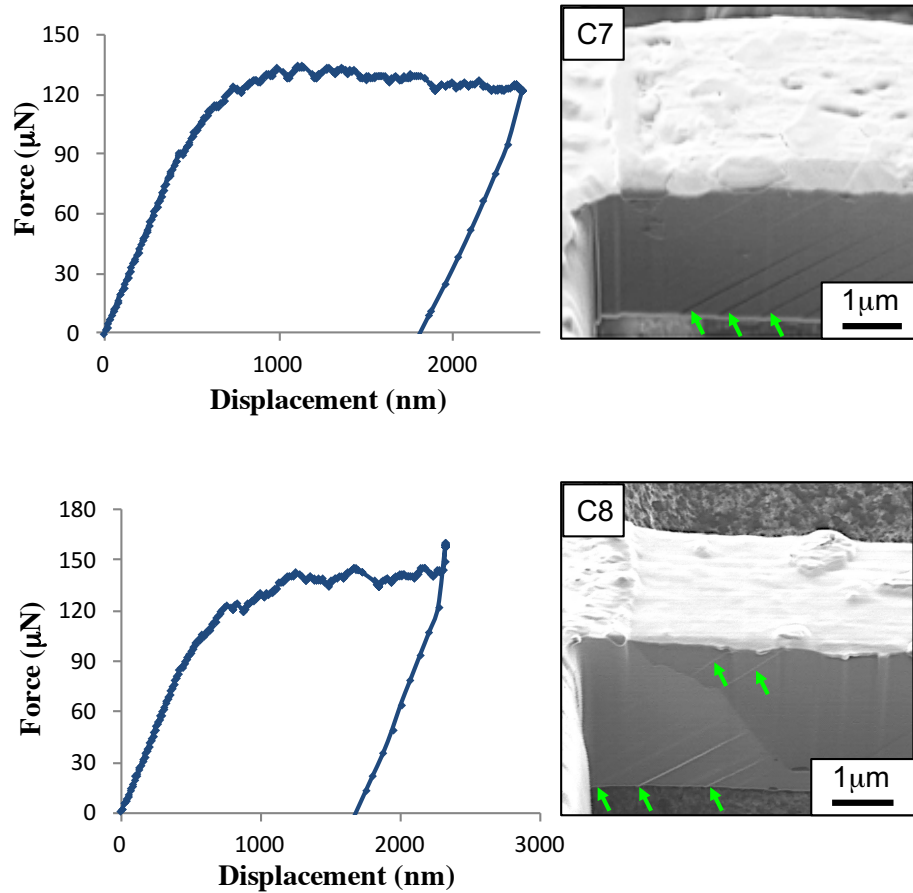


Figure 65: F-D data of oxidized GBs on *A600-EDF*, including C7 and C8. No fracture has been observed but plastic deformation only. The smaller load-drops in the curves are most likely associated with slip, as indicated (green arrows) in the corresponding SEM in-lens images taken after the test.

6.3 A600 with no oxidation and low intergranular carbide coverage

A total of 5 unoxidized grain boundaries was tested on the sample denoted *A600-NOX*, using micromechanical cantilever bend tests. Figure 66 shows an example of a beam manufactured on *A600-NOX* before the test. A pink arrow marks the unoxidized GB, which was included near the fixed end. Table 17 shows an overview of all micromechanical test results on *A600-NOX*, obtained using the extracted beam dimensions and stress-strain analysis, as described in section 3.5. The range of Young's moduli E was found to be $\sim 120 - 194$ GPa.

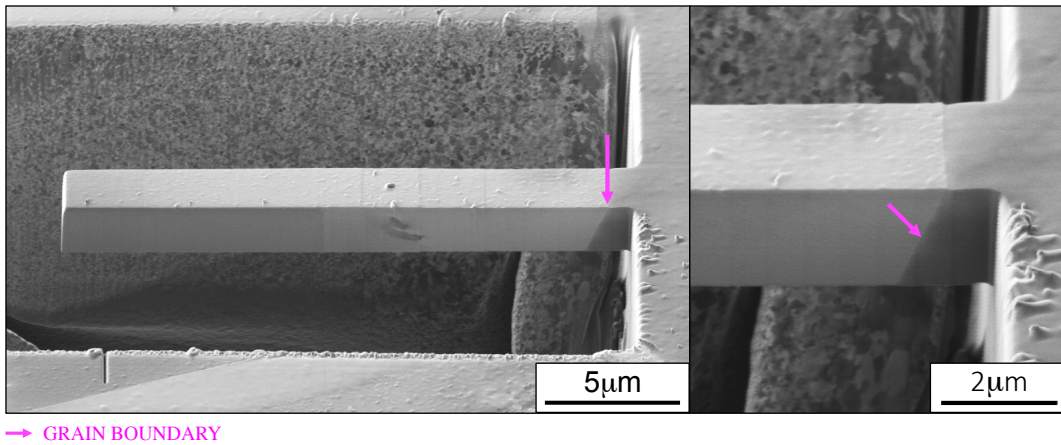


Figure 66: SEM SE image of a microcantilever prepared on *A600-NOX*, incorporating an unoxidized GB (pink arrow) close to the fixed end.

As detailed in Table 17, none of the tested beams exhibited cracking, as also seen in the recorded F-D curves in Figure 67. After reaching the yield point, which has been highlighted by a red X and corresponds to σ_{yield} , strain hardening occurs until a peak load, marked by the orange arrow in each F-D curve in Figure 67 and also highlighted in the corresponding close ups, was reached and was then followed by strain softening.

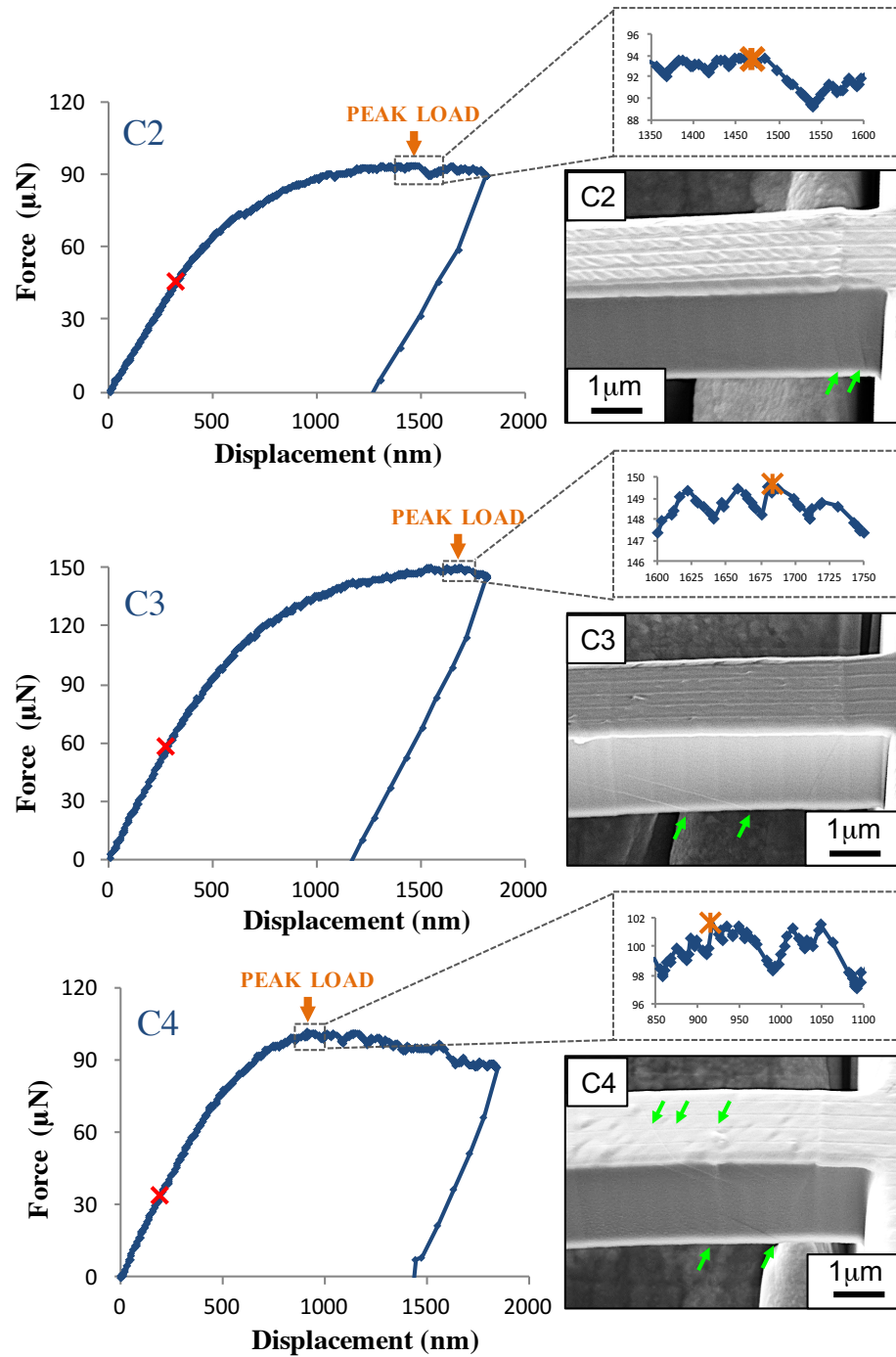


Figure 67: F-D data of GBs on *A600-NOX*, including C2, C3 and C4. No fracture has been observed. A red X marks the yield point, after which strain hardening takes place until a peak load (orange arrow and close-up) is reached and the material softens. The subtle load-drops in the curves are most likely associated with slip, as indicated (green arrows) in the SEM SE images taken after testing.

Multiple subtle load drops were present in the curves, which are likely associated with slip events, as indicated by the green arrows in the SEM SE images taken after the test. Since none of the beams fractured during the tests, the σ_{yield} has been estimated instead (Table 17). In accordance with Armstrong ^[170], σ_{yield} was defined as the point at which the initial E had dropped by 2%. The yield stress σ_{yield} was found to cover a range of $\sim 308 - 490$ MPa.

CANTILEVER ID	FRACTURE	E (GPa)	σ_{yield} (MPa)
C1	NO	148	411
C2	NO	117	359
C3	NO	189	489
C4	NO	194	326
C5	NO	136	308

Table 17: Overview of microcantilevers tested on *A600-NOX* at room temperature. The Young's modulus E was found to be anisotropic. None of the beams experience failure during testing. The yield stress σ_{yield} is given instead.

6.4 Discussion and summary

Two different oxidized Alloy 600 coupons were micromechanically tested and analysed, using microcantilever bend tests and simple beam theory estimations. The aim was the extraction of the oxidized GBs' stress at failure σ_f . Moreover, one unoxidized coupon was tested to obtain deformation data on a simplified system, suitable for crystal plasticity considerations, as described in section 8.2.

6.4.1 *A600-INSS with high intergranular carbide coverage*

6.4.1.1 *Fracture behaviour*

10 out of 16 oxidized GBs on *A600-INSS* with high intergranular carbide coverage experienced fracture during testing (see section 6.1). 4 of which were cantilevers tested

in the as-oxidized condition whereas the other 6 were cantilevers whose surface oxide atop of the GBs had been removed, as described in chapter 6.1.2. The stress at failure of all beams was found to cover a range of $\sim 330 - 770$ MPa. Considering only those beams whose surface oxide atop of the GBs had been removed, σ_f did not exceed 530 MPa. All beams whose surface oxides had been removed fractured during testing. A relationship between failure stress and GB misorientation could not be established. The Young's modulus E of the cantilevers was found to be anisotropic, covering a range of 120 – 300 GPa.

6.4.1.2 Surface oxide influence

The influence of the surface oxides atop of oxidized grain boundaries on the micromechanical test results on *A600-INSS* was studied by experimental and computational means (see section 6.1.2). Two pairs of cantilevers on 2 different GBs were tested with the nanoindenter and test results compared. Each pair included one cantilever with and one without an influence of the surface oxide overlapping the grain boundary. The following conclusion can be drawn:

- The presence of the surface oxide leads to an overestimation of the extracted stress at failure values (ca. 230 MPa for cantilever pair C3 ($\sigma_f = 765$ MPa) and R3 ($\sigma_f = 527$ MPa)).
- The presence of the surface oxide overlap can act to delay/suppress fracture, as seen for cantilever pair C4 (no fracture) and R4 (fracture, $\sigma_f = 362$ MPa).

These are interesting observations, considering the fact that the influence of the surface oxide has been neglected in the only other comparable microcantilever study on the fracture behaviour of oxidized Alloy 600 GBs available in literature ^[49], which was carried out on the same sample coupon and in which the presence of a surface oxide is

clearly apparent, *e.g.* in Fig. 2 c - f in their paper (shown here in Figure 68), but ignored.

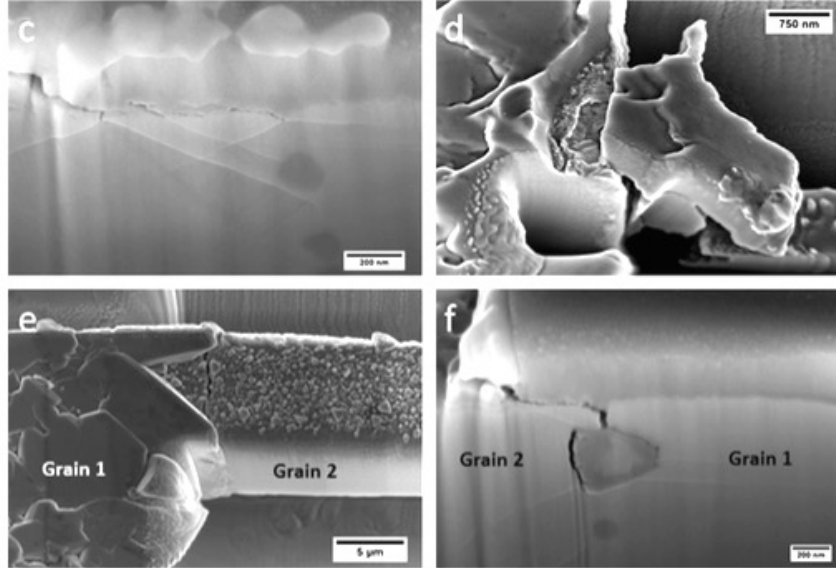


Figure 68: SEM images of tested GBs, adapted from Dugdale *et al.* ^[49]. Tests on *A600-INSS* performed by Dugdale *et al.* ^[49] clearly show the presence of the surface oxide overlap and the interaction between the oxide and cracks, which has been ignored in their study and considerations.

This can explain the relatively high value of $\sigma_f = 1.35$ GPa reported in their study, which is also higher than any other values reported in literature. Micro-tensile work performed by Fujii *et al.* ^[160] reported failure stress values of $\sim 180 - 300$ MPa and a recent macro-scale study by EDF ^[235], performed on the same material as *A600-EDF* in this study, reported a value of 825 MPa. The EDF study is however based on simulations and statistical predictions only.

- Beam theory estimations and values quantified via cohesive surface FEM are generally in good agreement. The stress at the first noticeable load drop of 522 MPa for R3, obtained via simple beam theory, under consideration of an additional height $h' = 120$ nm from the averaged surface oxide layer atop of the beam length, was roughly 50 MPa lower than the simulated value. With a value

CHAPTER 6 Cantilever fracture tests on alloy 600

of $\sigma_{drop} = 575$ MPa, quantified via cohesive damage modelling, this is within 10% of error.

- An estimated fracture toughness of $K = \sqrt{2EG} = 0.58$ MPa m^{1/2} was obtained via cohesive zone simulations, assuming an initial flaw size of 5 nm.

Even though at the lower end of the fracture toughness range, the value agrees well with an estimated fracture toughness of $0.73 - 1.82$ MPa m^{1/2}, as reported by Stratulat *et al.* ^[85], for notched pentagonal cantilevers tested on oxidized Alloy 600..

6.4.2 A600-EDF

7 out of 9 cantilevers on the surface-oxide free A600-EDF with low intergranular coverage experienced fracture during testing (see chapter 6.2). 4 of which showed clear, isolated fracture events. A plateau like region in the corresponding F-D curves was seen after fracture, with little to no strain hardening or softening. Most likely caused by the shallow oxidation of the sample, additional visual confirmation of the fracture from SEM imaging was necessary for the other 3 fractured cantilevers, as their point of failure was hidden within multiple load-drops in the F-D curves. The first big and isolated load-drop was defined as point of failure for these beams. Two beams deformed plastically only. Since no surface oxides were present on the slightly polished A600-EDF surface, a partial oxide cover overlapping the GBs, as was the case for A600-INSS, was ruled out as explanation. However, considering the rather shallow oxidation depth of this coupon, it is likely that the IG oxidation depth of the 2 deformed beams GBs was simply insufficient for failure to occur. In a recent study carried out by EDF ^[235] it was observed that the probability of fracture in oxidized grain boundaries could be dependent on the oxidation depth. They found that the likelihood of fracture of GBs with an IG oxidation depth less than 300 – 400 nm is low compared to more deeply oxidized GBs. The stress at failure of all 7 fractured beams was found to cover a

range of 495 – 780 MPa. The Young's modulus of the cantilevers was found to be anisotropic, covering a range of 135 – 320 GPa.

6.4.3 *A600-NOX*

5 beams were tested on the unoxidized coupon *A600-NOX*, with low intergranular carbide coverage (see page 147). The range of Young's moduli E was found to be $\sim 120 - 194$ GPa, thus revealing an elastic anisotropic behaviour. None of the beams experienced failure. The yield stress σ_{yield} was determined instead and was found to cover a range of 308 - 489 MPa. This gives a mean yield stress $\overline{\sigma_y}$ of 379 MPa with a standard deviation of 73.1 MPa. The yield stress σ_{yield} , as reported by EDF for the as-received alloy at RT, was 428 MPa (see Table 4). Considering an underestimation of the obtained Young's moduli by simple beam theory, with an assumed error $< 7\%$, in agreement with Armstrong ^[170] (see also chapter 3.5), and the limited amount of 5 beams which have been tested, a $\sim 13\%$ error for the yield stress is a good agreement.

6.4.4 *Young's modulus of Alloy 600*

The range of Young's moduli E of all 3 tested Alloy 600 samples seems in good agreement. Covering an overall range of 120 – 320 GPa, it compares well to an average bulk literature value of 207 GPa.^[22] It is moreover in good agreement with the orientation dependent data found for single crystal nickel-based super alloys in $\langle 111 \rangle$ ($\sim 290 - 320$ GPa), $\langle 001 \rangle$ ($\sim 115 - 130$ GPa) and $\langle 011 \rangle$ ($\sim 210 - 230$ GPa) direction.^{[241], [242]}

6.4.5 *Stress at failure of oxidized GBs on Alloy 600: A summary*

Taking only into account beams with no surface oxide layers atop of the GBs, *A600-EDF* resulted in a mean fracture stress $\overline{\sigma_f}$ of 633 MPa, with a standard deviation of

82.9 MPa, while *A600-INSS* resulted in a mean fracture stress $\overline{\sigma_f}$ of 443 MPa, with a standard deviation of 65.7 MPa. It should be mentioned that two of the beams on *A600-EDF* (C1 and C2) had slightly smaller dimensions. This might result in an overestimation of the mean fracture stress on this sample. Taking only into account beams with comparable dimensions, the mean $\overline{\sigma_f}$ on *A600-EDF* reduces to 603 MPa, with a standard deviation of 63.7 MPa. Nonetheless, there is still a difference of about 150 MPa between the average failure stress obtained on *A600-EDF* and *A600-INSS*. A possible explanation might be the more shallow oxidation depth of the EDF sample due to the shorter exposure to the environment. The average failure stress obtained on both samples is significantly lower than the single value of 1.35 GPa reported by Dugdale *et al.* ^[49] for the same coupon as *A600-INSS*. However, it should be remembered that, while using the same testing method, they simply neglected the presence and now proven influence of a surface oxide on their small-scale micromechanical cantilever tests. The range obtained is however in reasonably good agreement with a range of 180 – 300 MPa, obtained via micro-tensile testing at room temperature, as reported by Fujii *et al.* ^[160] and with a reported threshold stress range of 350 – 600 MPa at high temperature (> 290 °C) with increasing exposure times for SCC of MA Alloy 600 SG tubes under primary coolant condition, as reported by the IAEA.^[51] A recent study by EDF ^[235] carried out on a sample coupon from the same material as *A600-EDF* in this study, to study the critical failure stress of the material. The result is based on simulations and a statistical determination of a critical fracture stress based on a Gaussian distribution of the stress. Assuming an average stress of 531 MPa in the specimen upon reaching 2.5% elongation, which corresponds to a fracture of 13% of all grains and a standard deviation of 361 MPa, the critical failure stress was assumed to be at 87% (100% – 13%) of the Gauss curve, which was reported to be 825 MPa.

6.4.6 Modes of failure of oxidized GBs on Alloy 600

In accordance with the recorded F-D data two main modes of failure were identified for the oxidized samples *A600-INSS* and *A600-EDF*.

1. Beams undergoing fracture and little to no plastic deformation.
2. Beams undergoing plastic deformation with no apparent fracture.

This observation was made irrespective of a high (*A600-INSS*) or low (*A600-EDF*) carbide precipitation, suggesting that the two main modes of failure, observed via microcantilever bend tests, are independent of carbide precipitation. The modes remain the same in the presence of a surface oxide layer on top of the beams, even though it was found that a significant surface oxide overlap might suppress failure, as observed on *A600-INSS*. This is also true for the less severe IG oxide penetration on *A600-EDF* with low IG carbide precipitation, which might also increase the chances of observing plastic deformation only. The identified modes are in agreement with the modes of failure reported by Dugdale *et al.* ^[49]. To better understand the micromechanical response, identified failure modes and crack path on both samples, beams were additionally examined by means of electron microscopy, including scanning electron microscopy (SEM) and well as transmission electron microscopy (TEM) techniques, as discussed in the following chapter.

7 ELECTRON MICROSCOPY OF TESTED CANTILEVERS ON OXIDIZED ALLOY 600

7.1 SEM of fracture surfaces

To study the deformation behaviour of the GBs tested in section 6.1 and 6.2, the cantilevers were additionally examined in a SEM. Pictures were taken before as well as after the micromechanical tests to make sure that the features observed can be related to the microcantilever testing.

7.1.1 A600-INSS with high intergranular carbide coverage

Figure 69 shows before and after images of 2 deformed beams on *A600-INSS* after testing in the as-oxidized condition. As previously mentioned in section 6.1.1, signs of plastic deformation in form of slip lines were clearly present after the test, which were not seen before testing. However, even though carbides were present along all tested GBs, as seen on the cantilevers' sides, indicated by the red arrows in Figure 69 and Figure 70, and the degree of oxidation was comparable to those which exhibited cracking, no obvious signs of fracture were visible in the SEM images. As discussed in chapter 6.1.2, a more extensive surface oxide, overlapping the as-oxidized GBs in Figure 69 to a greater extent than the ones shown in Figure 70, is believed to be the root cause for this behaviour.

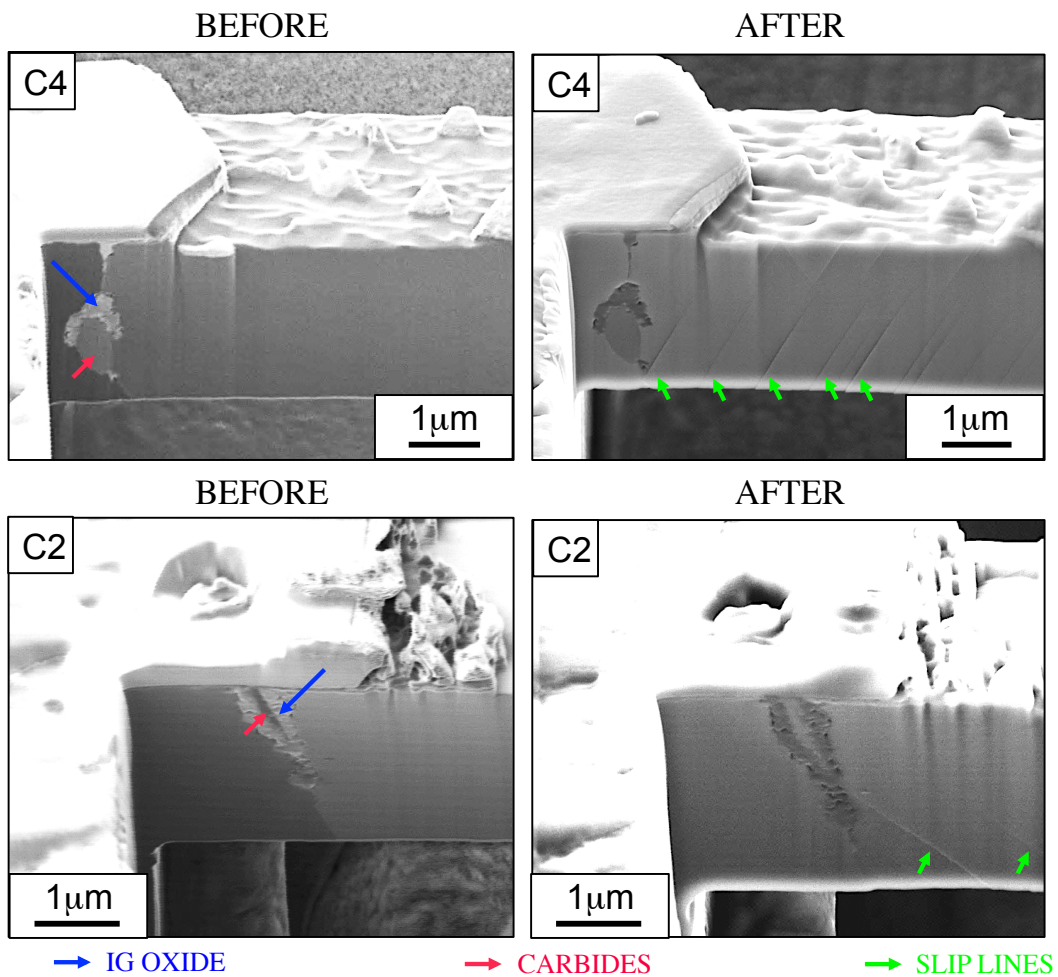


Figure 69: Representative SEM SE images of beams C4 (top) and C2 (bottom) on *A600-INSS* in the as-oxidized condition. No fracture is seen but plastic deformation only. Important features are marked with arrows of different color. As indicated by the green arrows, slip lines are visible after the test.

Figure 70 shows a before and after image of a fractured beam, tested in the as-oxidized condition (C5, top) and a before and after image of a beam tested after the removal of the surface oxide (R2, bottom). In both cases and in all other fractured beams shown in Figure 71, failure was clearly visible after the test. Cracking appeared to proceed along the oxide-metal interface rather than through the IG oxide and appeared to stop where the IG oxide ended (yellow arrows). The carbide-metal and carbide-oxide interface was never seen to fracture during testing.

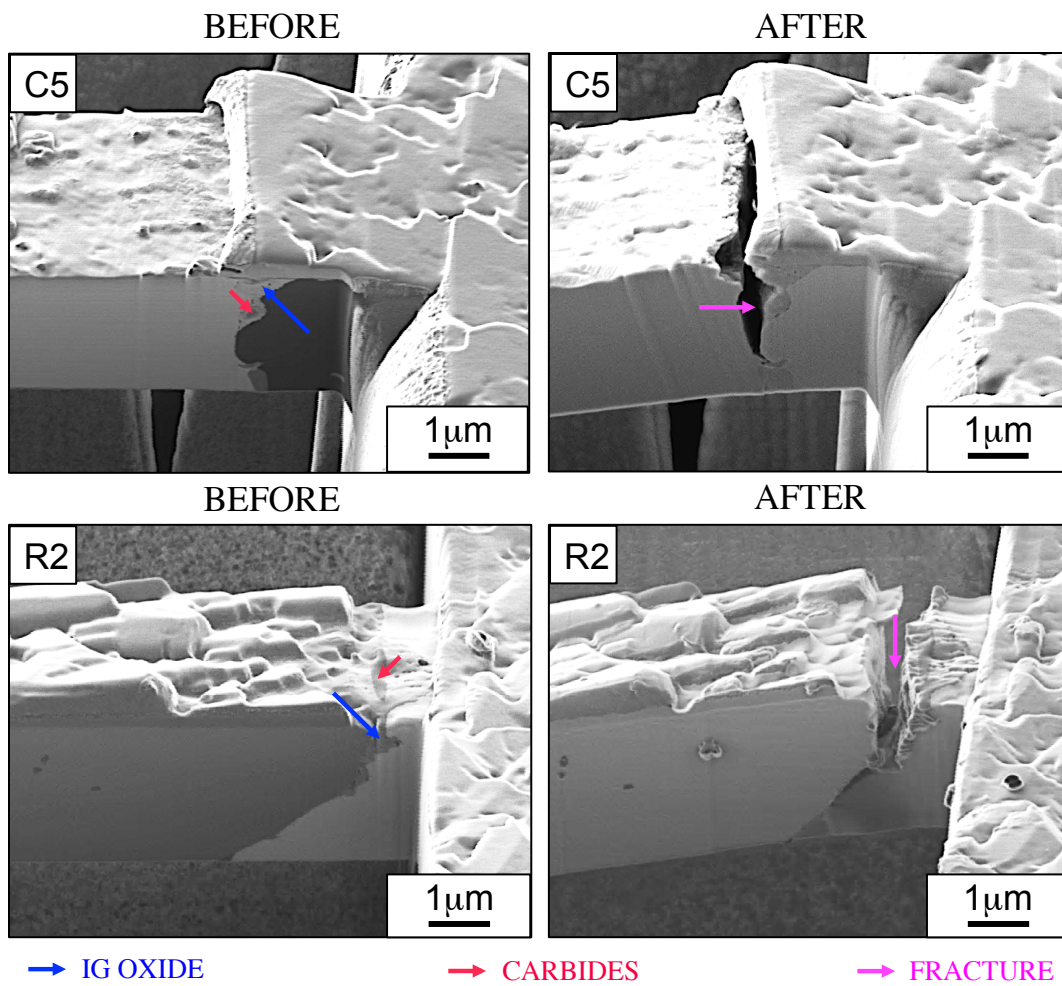


Figure 70: Representative SEM SE image of a fractured beam before and after testing on *A600-INSS* in the as-oxidized condition (top) and after surface oxide removal (bottom). Fracture is clearly observable after the test. Important features are marked with arrows of different color.

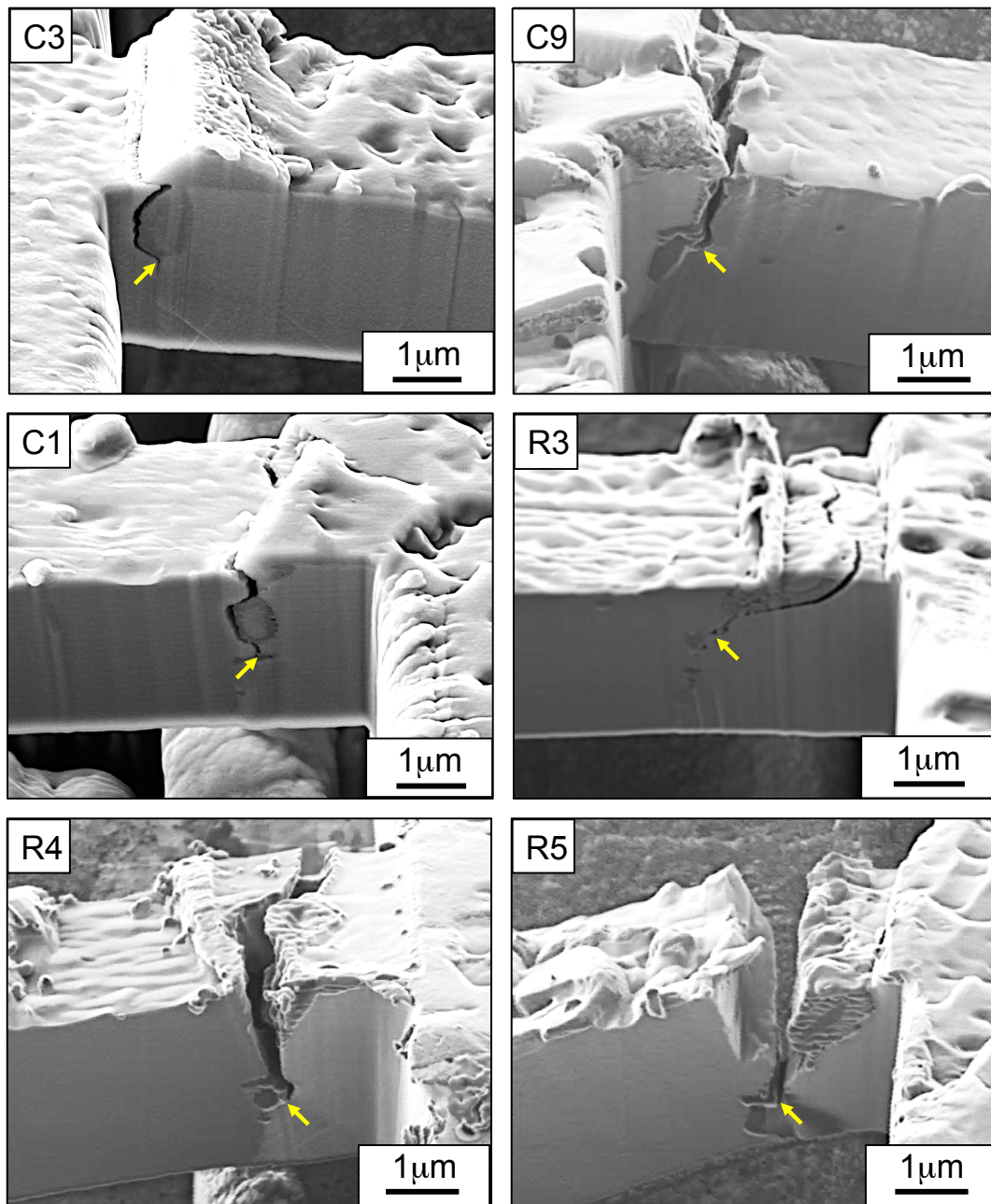


Figure 71: SEM SE images of fractured beams on *A600-INSS* after testing in the as-oxidized condition (C1, C3 and C9) and after surface-oxide removal (R3, R4 and R5). Failure along the oxide metal interface is visible. The crack stops in accordance with the IG oxidation (yellow arrows).

7.1.2 A600-EDF with low intergranular carbide coverage

Figure 72 shows before and after images of the 2 beams (C7 and C8), which deformed plastically only. As supported by multiple smaller load-drops in the F-D curves of these cantilevers (Figure 65, chapter 6.2), signs of plastic deformation in form of slip lines (green arrows) were clearly present in the SEM SE images taken after testing, which were not present before the test. No fracture was visible after the test.

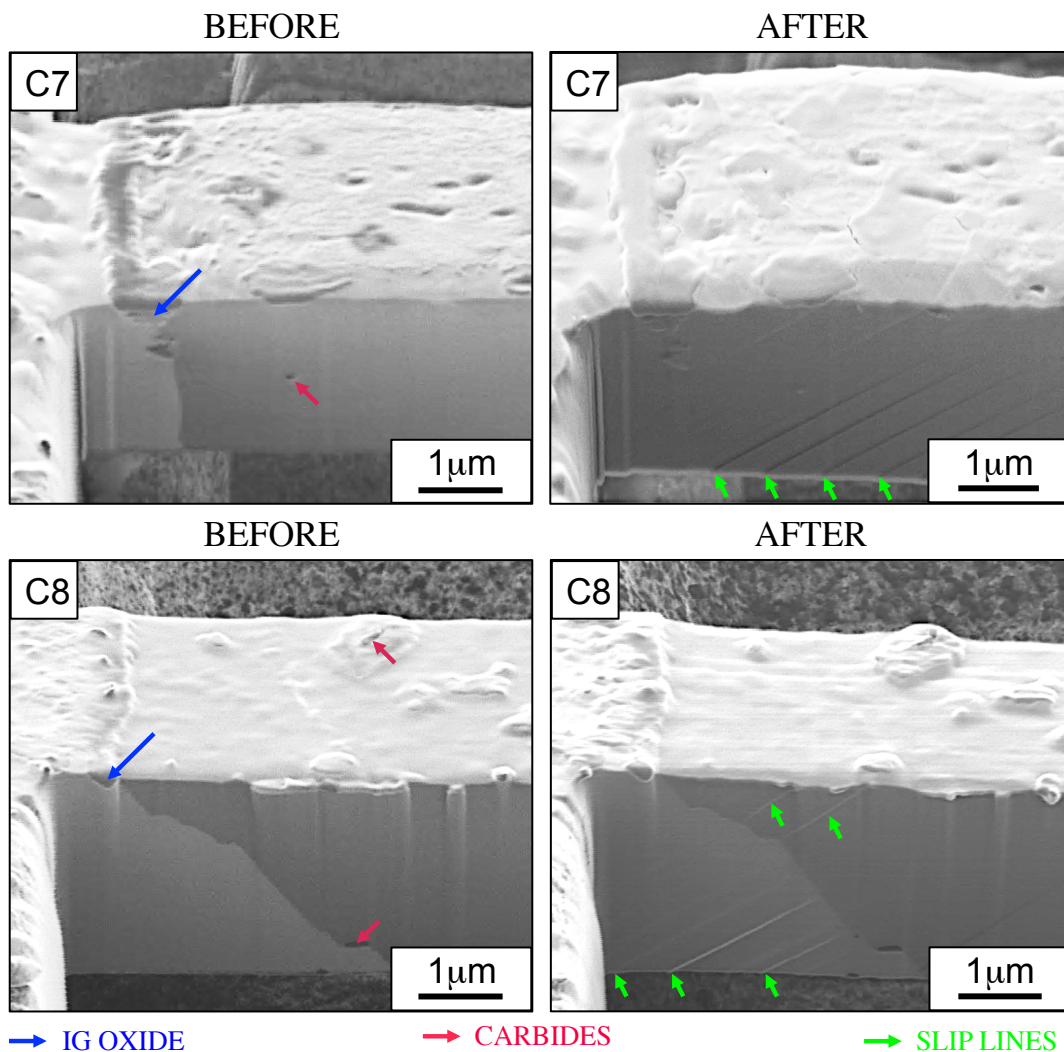


Figure 72: Representative SEM SE images of beams C7 (top) and C8 (bottom) on A600-EDF. No fracture is visible. Important features are marked with arrows of different color. As indicated by the green arrows in the after images, slip lines are visible after the test.

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Figure 73 (a) and (b) show before and after images of cantilever C4, which cracked during the test. Fracture along the oxide-metal interface was seen on both sides of the IG oxide after testing, as indicated by 2 pink arrows, suggesting a weaker cohesive strength of this interface. The IG oxidation is overall thicker close to the sample surface and progresses down the GBs. Figure 73 (c) and (d) shows cantilevers C1 and C2 after the test. Fracture along the oxide metal interface was clearly visible. This was in agreement with their F-D curves (left column in Figure 63, chapter 6.2), which showed a clear fracture jump (major load-drop). C3 and C5 (Figure 73 (e) and (f)) on the other hand, showed only very subtle fracture, which was in agreement with a less deep oxide penetration and the visibility of multiple slip lines in the SEM in-lens images after the test. The visible examination agreed with a difficult to define fracture event in the associated F-D curves of these beams, as discussed in chapter 6.2 (right column in Figure 63), which, rather than showing one big fracture jump (major load-drop), showed multiple load-drops. From SEM investigations it moreover appeared that certain beams, it was especially apparent in the images of C2 and C3 (black arrows), seemed to include triple points.

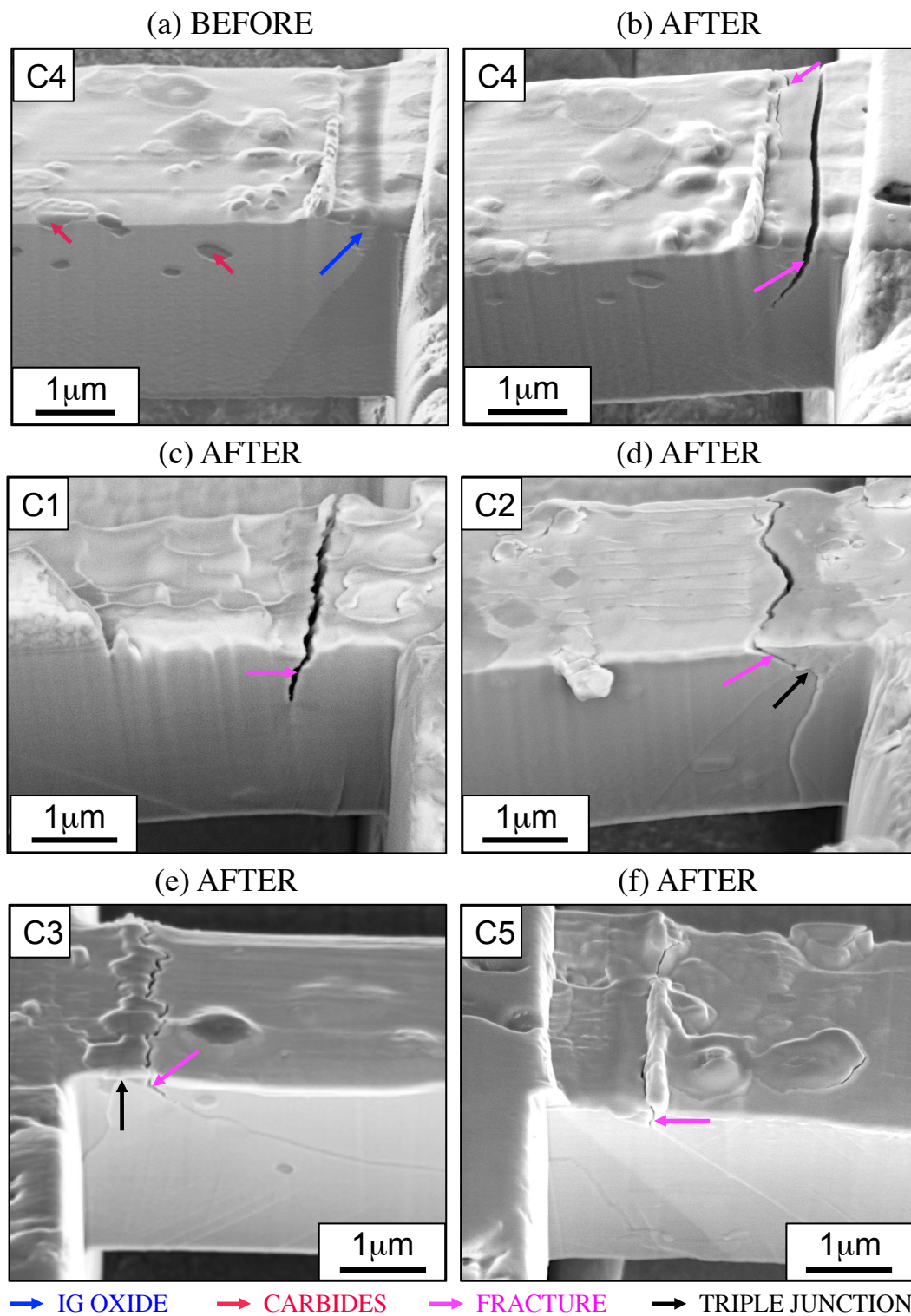


Figure 73: (1st row) Images of beams C4 before (FIB SE) and after the test (SEM SE). (2nd row) SEM in-lens images of C1 and C2 after the test. Fracture is clearly visible (pink arrows). (3rd row) SEM in-lens images of beams C3 and C5 after testing. Even though shallow, fracture is visible (pink arrows). C2 and C3 show presence of triple junctions (back arrows).

7.1.3 3D FIB-SEM of fractured cantilevers

7.1.3.1 A600 with high intergranular carbide coverage: A full reconstruction

Figure 74 shows the 2 sides of cantilever R6 after testing. Fracture was clearly visible and seemed to propagate along the oxide metal interface, stopping mid-way through the beam on the 1st side but reaching the bottom of the beam on the 2nd side (Figure 74, yellow arrows). Nonetheless, from the SEM images alone it was hard to draw any final conclusions, as features like thin crack regions, carbides and IG oxides were not always easily distinguishable.

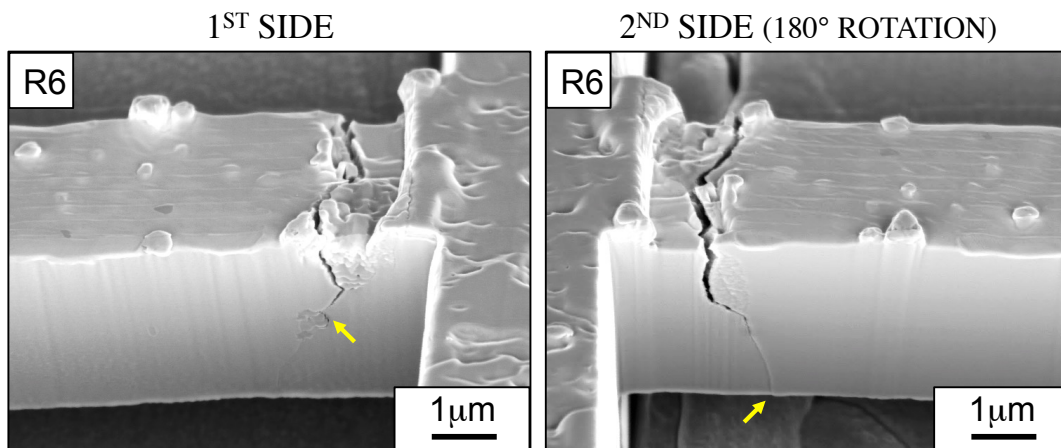


Figure 74: SEM images of cantilever R6 (no surface oxide) after testing. The crack, which proceeds along the oxide metal interface, appears to stop mid-way through the beam on the 1st side but reaches the bottom of the beam on the 2nd (yellow arrows).

To better understand the observed behaviour and to obtain additional proof of the initial observation that cracking proceeds along the oxide-metal interface and stops where the oxide vanished, more information about the 3D crack path, local degree of oxidation, carbide precipitation as well as the individual fracture interfaces and sample composition (chemistry) was needed. 3D FIB-SEM (see section 3.6.) alone has the major disadvantage that all the sample volume is destroyed during the destructive procedure. In contrast, for the first time, the new cantilever lift-out strategy presented in

chapter 3.3.3.2 enabled an almost complete 3D reconstruction of a tested oxidized GB, in addition to obtaining a TEM sample from the central portion of the microcantilever for further structural and chemical investigations via (S)TEM (see chapter 7.2 and 7.3).

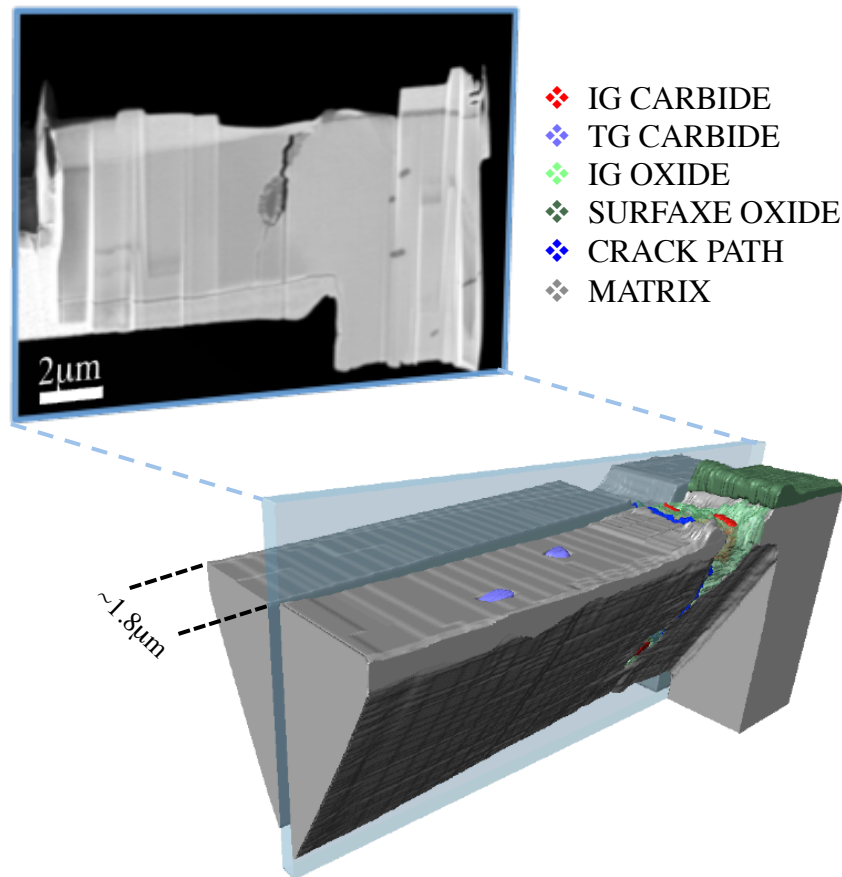


Figure 75: Full reconstruction of cantilever R6, showing the middle section, which has been left for TEM sample preparation (approx. 270 nm).

The full reconstruction of cantilever R6, as shown in Figure 75, only misses a region of ca. 270 nm in the centre of the beam, which was retained for TEM sample preparation. The left column of images shown in Figure 76, denoted as 1st side, shows a small selection of the individual SEM image slices, taken during the sequential milling through the first cantilever volume of R6.

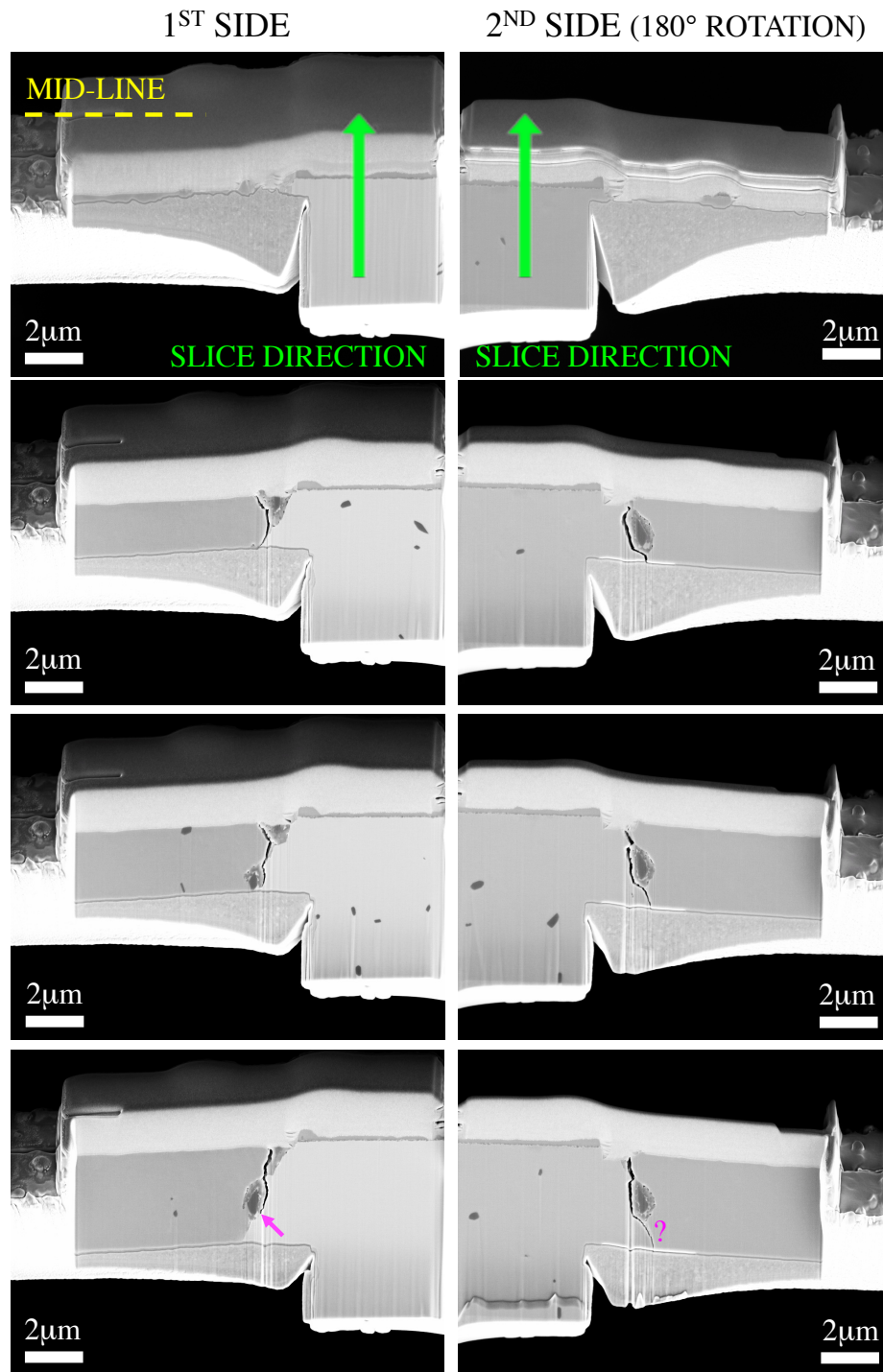


Figure 76: Selection of slices through the 1st side (left column) and 2nd side (right column) of the R6 after testing. The SEM in-lens image sequences have been generated via 3D FIB-SEM sequential milling performed on a TEM stub from 2 sides, starting at the cantilever edge and approaching a mid-line marker (yellow), as indicated by the green arrow, which marks the slicing direction. Whilst the crack tip can be seen on the 1st side (pink arrow) the crack proceeds further than the obvious oxidized portion on the 2nd side (pink question mark).

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As indicated by the green arrow in Figure 76, which marks the slicing direction, the sequence started at the edge of the beam and approached the centre of the cantilever towards a mid-line marker (yellow). The right column of images in Figure 76 shows the series of SEM images, taken during sequential milling through the 2nd side of the cantilever volume (180° rotation). From the SEM image sequence alone it can already be concluded that oxidation was rather inhomogeneous throughout the volume and thicker/more compact in regions around carbide precipitates. Moreover it was seen that whilst the crack tip was identifiable on the 1st side of the sequence, as indicated by the pink arrow in Figure 76, the crack proceeds further than the obviously visible portion of oxidized GB on the 2nd side (pink question mark). As shown in Figure 77 (A) and (B), multiple transgranular carbides (purple) were enclosed throughout the sample volume. Two big intergranular carbides are shown in red with a typical elongated shape. Whilst the transgranular carbides did not show any signs of oxidation, the intergranular oxide (light green) was found to encapsulate the IG carbides (red), following down the grain boundary. The oxide was thickest close to the surface of the beam and around the IG carbides, as also seen in Figure 77 (C), with regions of thinner oxidation where no carbides were located. As initially observed, the crack (blue) seemed to preferentially proceed along the oxide-metal interface but also found its way through in-between the IG oxide (yellow arrow in Figure 77 (C), indicating that a fracture through the intergranular oxide was possible. From the SEM image in (C) alone, it would have been hard to identify that the crack crosses the oxide since the oxide on the left side of the crack is hardly distinguishable from the matrix. However, from Figure 77, especially B, it can be seen that while cracking proceeds along the far end side of the beam for the carbide closer to the surface of the beam it changes path and proceeds around the fixed end side of the beam where the second oxidized IG carbide was located, which extended throughout the whole beam volume.

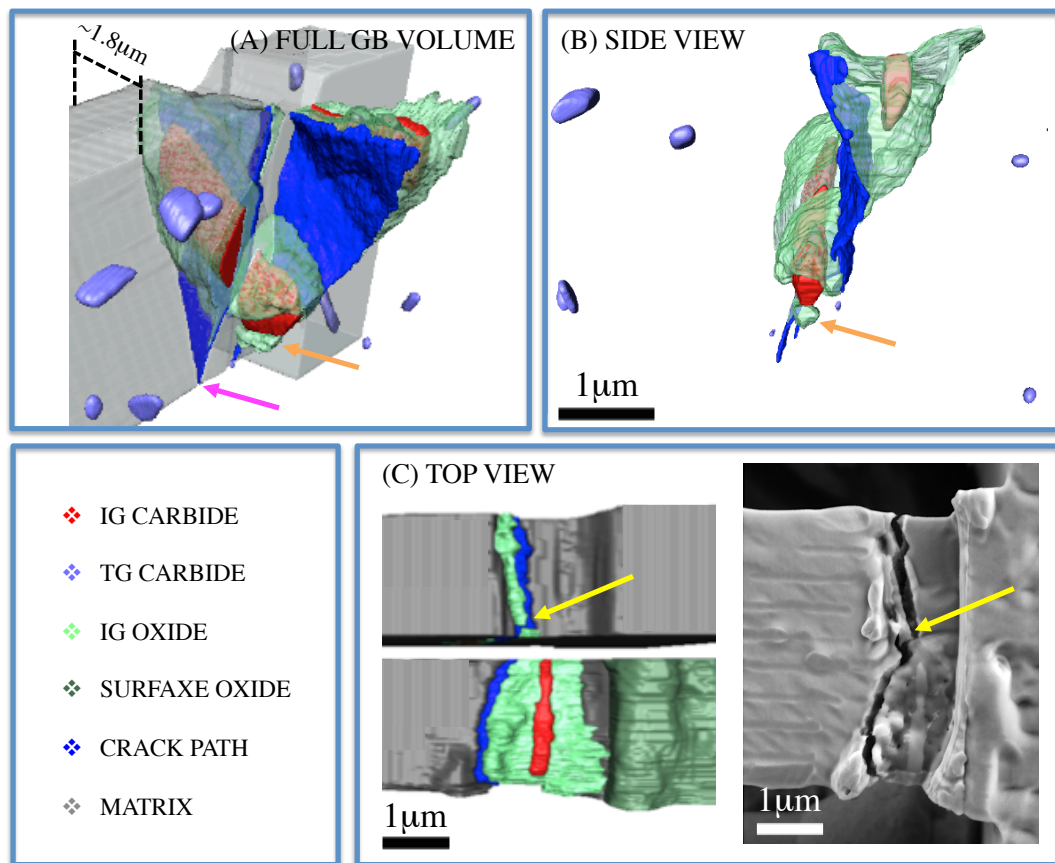


Figure 77: 3D FIB-SEM tomography reconstruction of cantilever R6 from different perspectives. (A) Full reconstruction of the GB volume, showing that the crack proceeds throughout the full volume, as indicated by the pink arrow. (B) Side view of the reconstruction showing the crack progression (blue) in-between the IG carbides (red). Orange arrows mark the oxidation of the GB region below the not fully encapsulates carbide. (C) Comparison of the reconstruction with the corresponding SEM SE image in top view. Whilst difficult to see in the SEM SE image, the reconstruction makes it clear that the crack crosses the IG oxidation at the point indicated by the yellow arrows.

Representative of all SEM sequences and images obtained on this sample, it was found that IG oxidation was able to reach the GB below the carbides even though the precipitates were not always fully encapsulated by the oxide. The oxide-carbide interface was never seen to fracture. Consequently, the cohesive strength of the oxide-metal and oxide-carbide interface must be different. However, the resolution provided by this method was not sufficient enough to determine any obvious differences and

even though the reconstruction implied that the crack (blue) hit the bottom of the beam, exceeding the in the SEM and reconstruction visible portion of IG oxide (light green) at some point, resolution and contrast was insufficient to clearly rule out the presence of a very thin IG oxidized layer down to the bottom of the beam. Consequently, thanks to the new lift-out strategy, TEM investigations were employed to complete the picture, as will be discussed in sections 7.2 and 7.3.

7.1.3.2 Alloy 600 with low intergranular carbide coverage

Even though no full 3D reconstruction of cantilever volumes were performed on *A600-EDF*, 3D FIB-SEM sequencing, as previously described for *A600-INSS* (section 7.1.3.1), of the fractured GB portions was performed on a TEM stub from 2 sides. Figure 78 shows a selection of slices through the 1st and 2nd side of the fractured oxidized GB portion of cantilever C3 after testing. Pink arrows indicate the crack. The green arrows next to the individual images of each side indicate the slicing direction, starting from the beam edge towards the mid-region of the beam, where a small region (~ 300 nm) was missing since it was left for TEM sample preparation. As indicated by the red arrow in the 1st side column of images in Figure 78, a triple point was included in cantilever C3. As shown in the close-up image (red box), the original location of the triple point was noticeable within the IG oxide. In agreement with the SEM investigations in section 7.1.2, fracture proceeded along the oxide metal-interface where the oxide was sufficiently thick, *e.g.* in the first 250 nm close to the surface. In thinner regions however the crack path seems not as clear, as indicated by the blue arrow in the 2nd close up image (blue box) in Figure 78. No obvious porosities were seen along the oxide-metal interface. In the 2nd side column of images it was moreover found that the crack changes direction, as indicated by the orange arrow in the close up image (orange box), in a region in-between 2 bigger oxide patches. A yellow arrow in

the same close-up (orange box) indicates the location of an IG carbide ahead of the oxidation front.

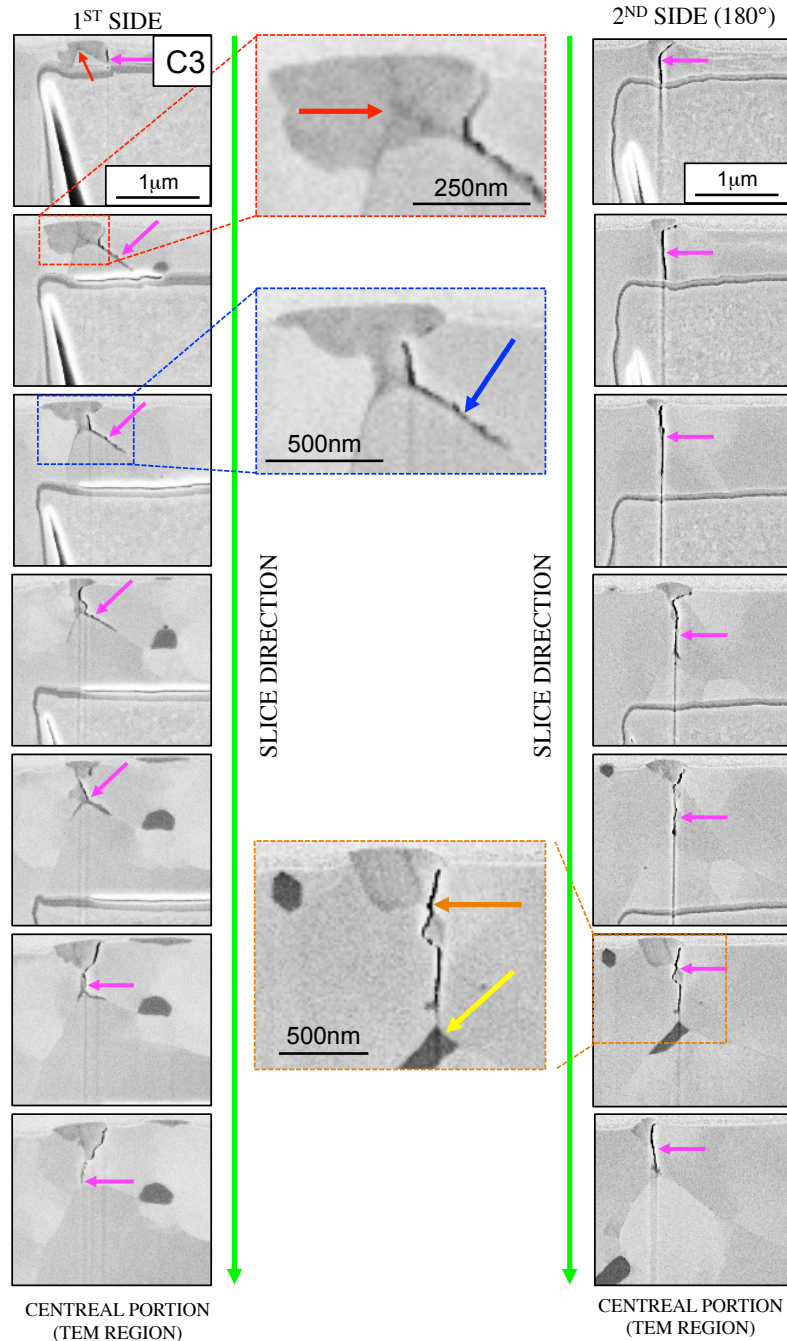


Figure 78: 3D FIB-SEM images of the 1st cantilever side of cantilever C3. The green arrow indicates the slicing direction towards a region in the center, which has been left for further TEM sample preparation. The original location of a triple point (red arrow in red box) is noticeable within the IG oxide. Fracture through the IG oxide is observed in the more thinly oxidized regions (blue arrow in blue box). Pink arrows indicate the fracture path.

7.2 (S)TEM imaging of oxidized GBs after testing

Initial SEM investigations of the fracture of oxidized GBs on *A600-INSS* with high intergranular carbide coverage and *A600-EDF* with low carbide coverage suggested that fracture predominantly proceeded along the oxide-metal interface where the oxide was sufficiently thick and in the case of *A600-INSS* never along the carbide-oxide interface. To obtain additional information as to why this was the case, ADF and HAADF scanning TEM (STEM) of the central portion of 4 fractured beams and 1 of the deformed beams in *A600-INSS* was performed and compared to 3 fractured beams on *A600-EDF*. This was used to study the local microstructure and crack at higher resolution.

7.2.1 *A600-INSS with high intergranular carbide coverage*

STEM images (ADF1) of the fractured GBs of cantilevers R1, R3, R6 and C5 are shown in Figure 79. The images of the cracked cantilever cross-sections confirmed that cracking never exceeded the oxidized GB portion. Even in the case of R6, which has been reconstructed in 3D in section 7.1.3 and where it was not possible to clearly determine the full degree of oxidation along the GB, it was now possible to confirm, due to the higher resolution of STEM, that oxidation did reach the bottom of the beam in accordance with the observed crack path. Moreover, in all 4 examples it can be seen that fracture followed the oxide/metal interface where the IG oxidation seems to be sufficiently thick, *e.g.* around the IG carbides and close to the surface. This is not surprising as sensitization (Cr depletion) of the matrix and GB next to the Cr-rich carbides is expected, which results in the formation of less protective oxides. In regions where the IG oxide was not sufficiently thick/wide, as *e.g.* apparent in case R1, failure through the oxide seemed possible. As indicated by the varying contrast in the ADF images (Z-contrast), the IG oxide revealed differences in density and composition.

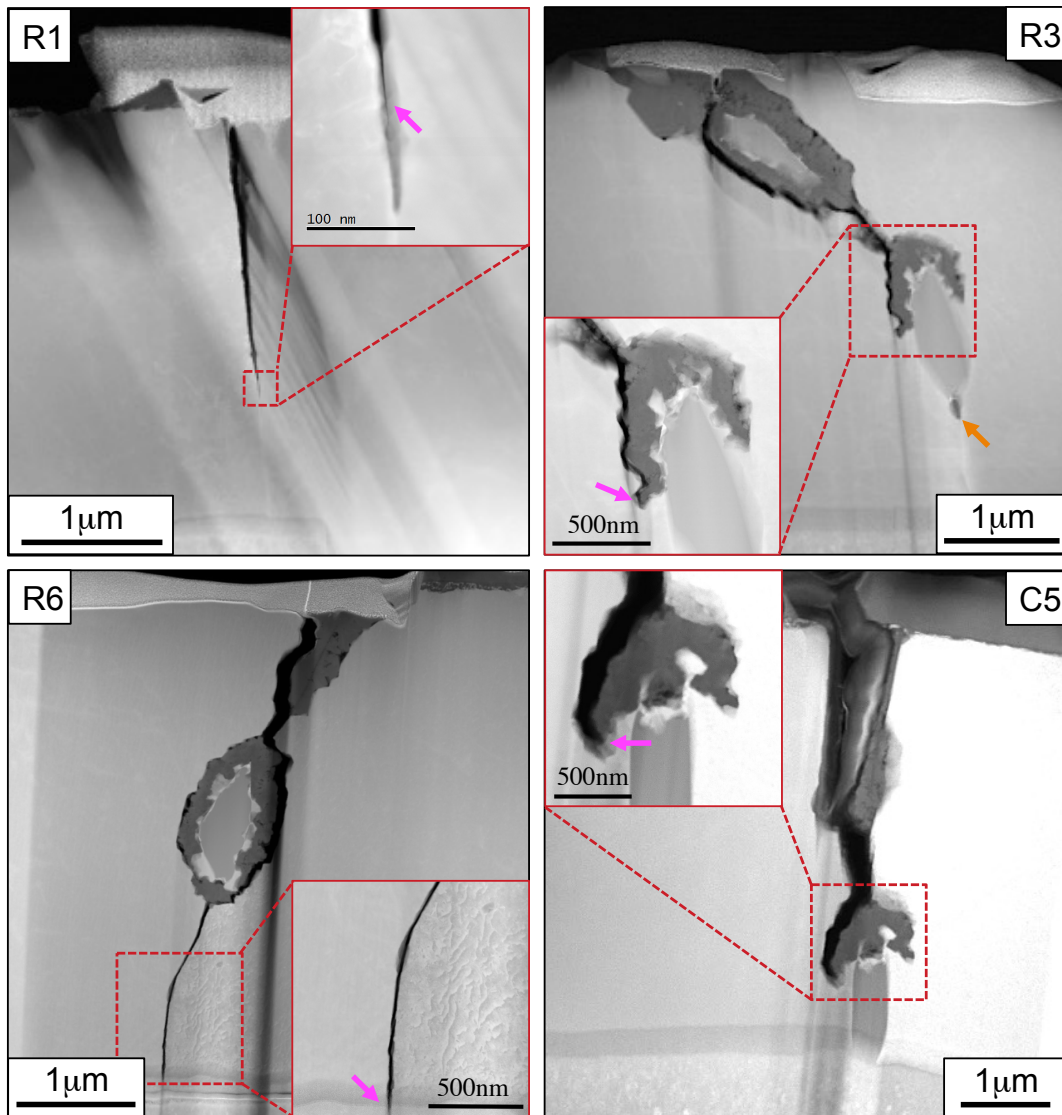


Figure 79: STEM ADF1 images of the crack paths in beams R1, R3, R6 and C5. The crack tip (pink arrows) does not exceed the oxidized GB portion, as made obvious in the close-up images of each cantilever. An orange arrow marks an oxidized region below the 2nd carbide of R3.

In all examples it was found that oxidation is thickest and potentially more compact next to IG carbides, while the oxide-metal interface and the thin oxidation in-between the carbides seemed to be rather inhomogeneous in nature. The preferential growth of thick/wider oxides next to IG carbides is most likely caused by sensitisation of the material (regions of less Cr) adjacent to the carbides, hence leading to the formation of less protective (Cr-deficient) oxides and subsequently an accelerated oxidation in these

less protected regions. In examples R3 in Figure 79 and C4 in Figure 80, oxidation below the 2nd not fully oxide-covered carbide was observed (orange arrows). As demonstrated in the ADF images of cantilever C4 in Figure 80, which deformed plastically only, an incomplete and inhomogeneous IG oxidation was especially visible in-between the preferentially oxidized carbide precipitates.

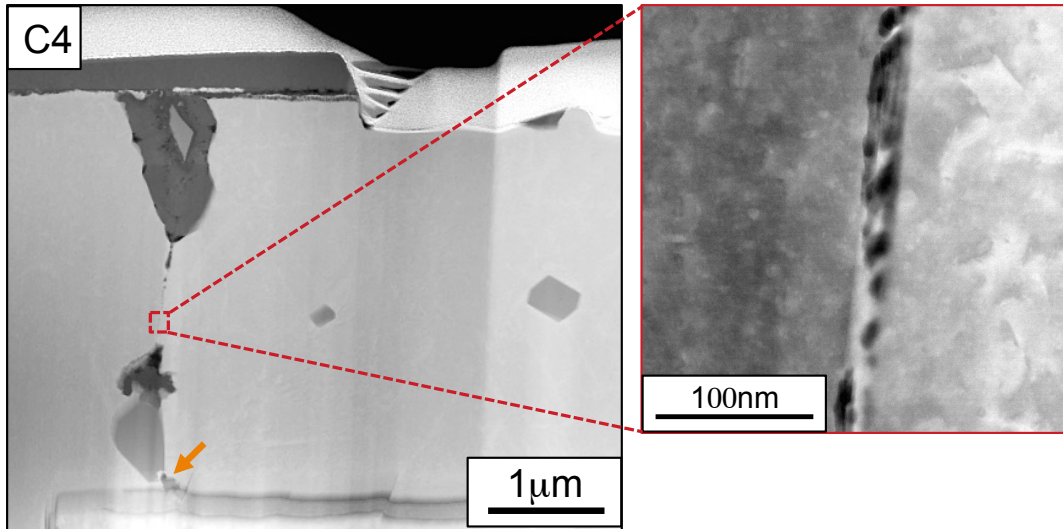


Figure 80: STEM ADF images of C4 recorded with ADF1 and close up of the thinly oxidized GB region in-between the 2 carbides, which reveals the inhomogeneous nature of the fine IG oxide located in these regions. An orange arrow marks an oxidized region below the 2nd carbide of C4.

This might explain why in thinly oxidized regions cracking did not favour a specific interface but progressed more randomly through the IG oxide, as seen on the fractured examples. Overall, the oxide appeared to be more dense close to the carbides whilst black regions of varying size, were preferentially located at the oxide-metal interface. This was also seen on the untested material (see Figure 20, page 71) and where no carbides were found along the GB, as indicated by the red arrows in Figure 81. The original GB path in Figure 81 also appeared to have a darker contrast while lighter regions at the carbide-oxide interface were seen in case of R6. The question at this point, which will be addressed in section 7.3.3, was whether these dark regions in the

ADF images in Figure 80 and Figure 81 were associated with less density (porosities or voids) or just varying composition (Z-contrast). In accordance with the preliminary SEM examinations of the deformed beam after testing (Figure 82, left), which revealed signs of slip induced by the deformation, the diffraction contrast provided by the ADF2 detector (Figure 82, right) showed dislocation arrangements along the activated slip planes in the crystal lattice of C4.

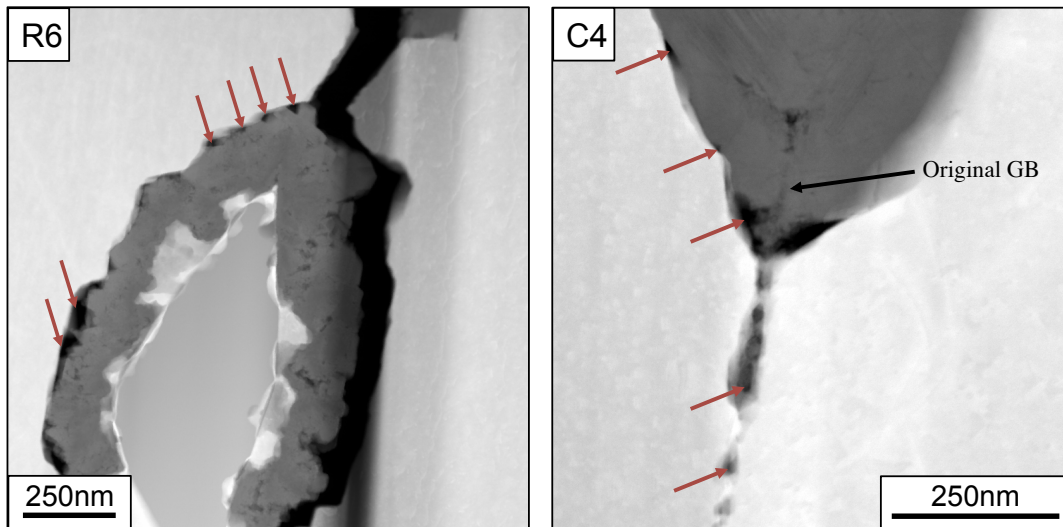


Figure 81: Representative close-up ADF1 images of 2 tested grain boundaries on Alloy 600. (R6, left) Fracture along the metal-oxide interface and (C4, right) no apparent fracture. The darker regions (red arrows) are assumed to correspond to regions of less density. Larger voids/porosities seem to be preferentially located at the oxide–metal interface.

It was also visible, using conventional bright field STEM imaging, as shown in Figure 83 (C6), where individual dislocations along these slip lines were seen at higher resolution (green box). In accordance with the fcc lattice of the alloy, which has 12 potential slip systems, these planes were identified to be of the $\{111\}$ family of planes, using electron diffraction for indexing, as shown in the DP of the left grain (yellow box) and the corresponding stereographic projection (CaRIne Crystallography software).

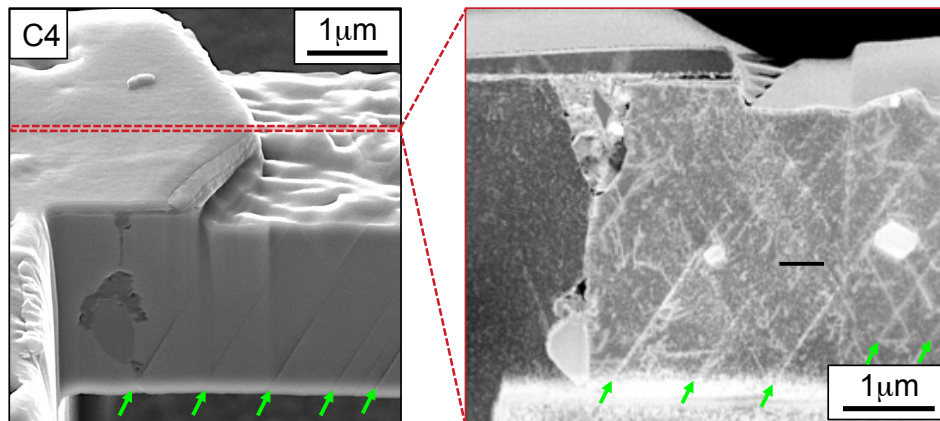


Figure 82: (left) SEM SE image of C4 after testing. (right) STEM image (ADF2) of the corresponding cross section of C4 taken from the central part of the cantilever. Dislocation motion along active slip planes, as indicated by the green arrows are clearly visible.

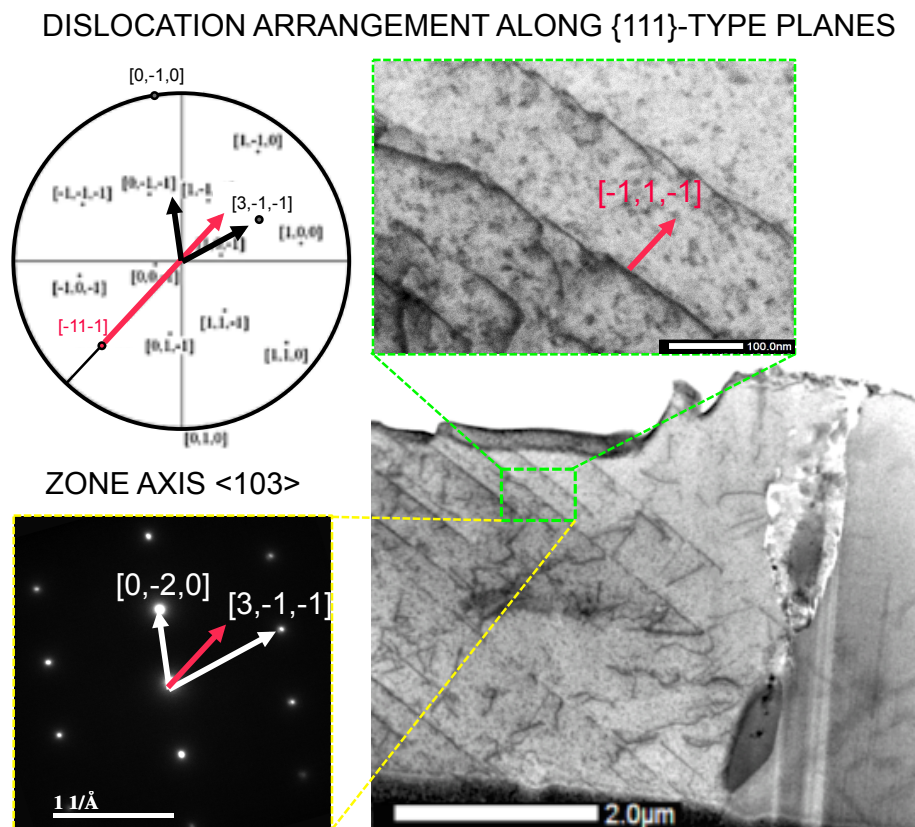


Figure 83: BF STEM image of cantilever C6 (*A600-INSS*) and close-up of the dislocation arrangement (green box). The DP of the left grain (yellow box), the angular relation of the spots and a stereographic projection (CaRIne Crystallography software) was used to index the pattern. It could be shown that that the dislocations align along $\{111\}$ type of planes, in accordance with the fcc lattice of the alloy, as indicated by the red arrow which marks the $[-1,1,-1]$ direction.

7.2.2 Alloy 600 with low intergranular carbide coverage

STEM images (ADF1) of the fractured GBs of beams C1, C3 and C5 on *A600-EDF* are shown in Figure 84. In agreement with the SEM images in 7.1.2, the STEM images of the cracked cantilever cross-sections confirmed that the crack never exceeded the oxidized GB portion. The pink arrows indicate the crack tip.

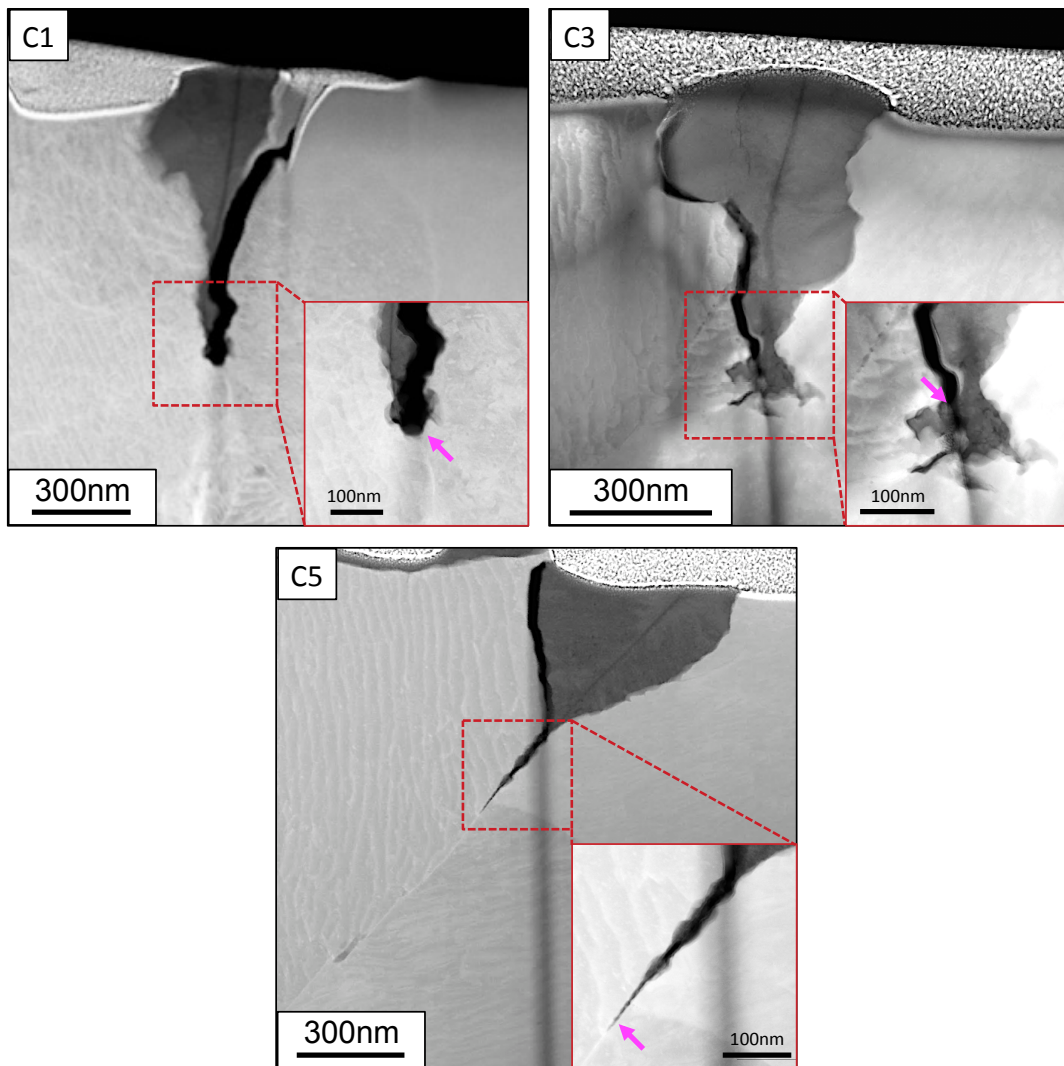


Figure 84: STEM ADF images (Jeol ARM200f, ADF1) of the crack paths in beams C1, C3 and C5. The crack tip (pink arrows) does not exceed the oxidized GB portion, as made obvious in the close-ups.

It can be seen that fracture follows the oxide/metal interface where IG oxidation seems to be sufficiently thick whereas in thinner oxidized regions ahead of the thicker oxide, as for example in the case of C5 in Figure 84, failure through the IG oxide was possible. The ADF1 images in Figure 85, revealed a potentially scarcely oxidized 2nd grain boundary next to the main crack path of C3. The potentially oxidized region appeared rather inhomogeneous in nature with smaller, not interconnected nodules dispersed along the GB (yellow arrows), which were later on identified as oxides via EELS (see Figure 92 on page 185). The inhomogeneous and incomplete oxidation of the 2nd GB might explain why it did not fracture during the test. Overall, the oxide appeared to be thickest and more compact close to the surface. As reflected by the varying contrast in the ADF images (Z-contrast), the IG oxide appeared to have differences in density and composition.

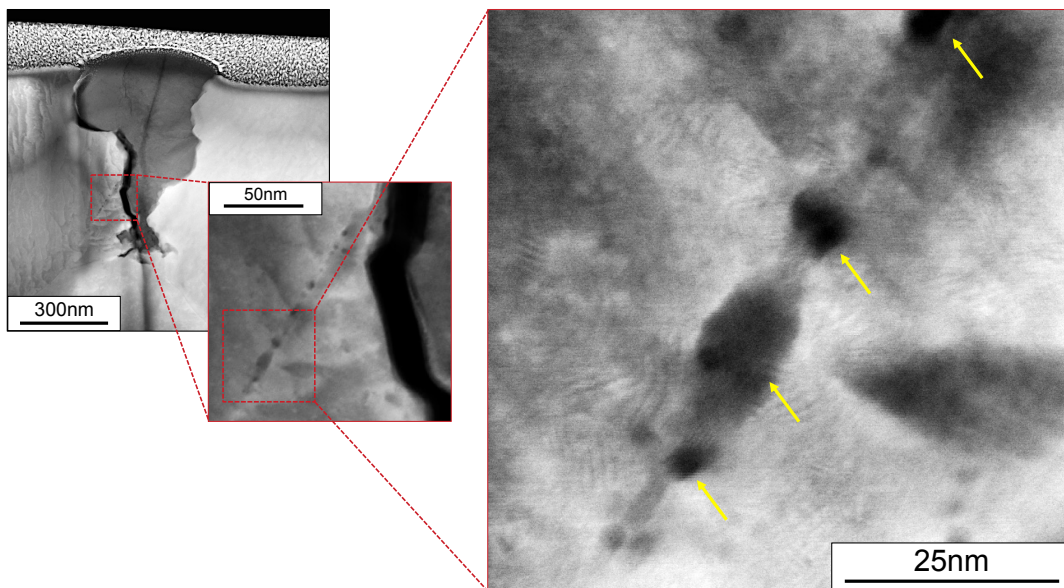


Figure 85: STEM images (ADF1) of the thinly oxidized GB region of a 2nd GB next to the crack path in cantilever C3. The close-ups show the inhomogeneous nature of this region. Small nodules (yellow arrows), potentially oxides, are noticeable.

7.3 EELS of oxidized GBs after testing

To obtain chemical information (composition) about the main elements of interest (O, Cr, Fe and Ni), to study the observed density variations and in the case of *A600-INSS* the observed weak spots (pores) within the IG oxide as well as to establish a possible link to the crack path, EELS was performed on *A600-INSS* and *A600-EDF*.

7.3.1 *A600-INSS with high intergranular carbide coverage*

3 examples will be discussed in the following sections. Whilst cantilever R1 and R6 fractured during testing, cantilever C4 deformed plastically only. Moreover, R6 and C4 both showed intergranular carbide precipitates and an intergranular oxidation down to the bottom of the beam, whilst the TEM lamella of R1 enclosed no carbides.

7.3.1.1 *Cantilever R1 (no carbide present)*

EELS maps of R1, as demonstrated in Figure 86 a) for the full crack path and b) for a close-up of the crack tip, show that O is present at both sides of the crack (EELS SI maps of O K edge in Figure 86 a) and b)), suggesting that the crack passed through the intergranular oxide, rather than choosing the oxide metal interface. This is also clear in the close-up STEM HAADF image of the oxidized crack tip portion in Figure 86 b). Cr is preferentially located at the right-side crack flank (EELS SI maps of Cr L edge in Figure 86 a) and b)), whilst Ni is slightly enriched on the left side crack flank and ahead of the crack tip, where Fe seems depleted (EELS SI maps of Fe and Ni L edge in Figure 86 a) and b)). Compositional profiles in at.% (atomic percentages) were taken at multiple locations on both regions (pink boxes in Figure 86). The following observations were made.

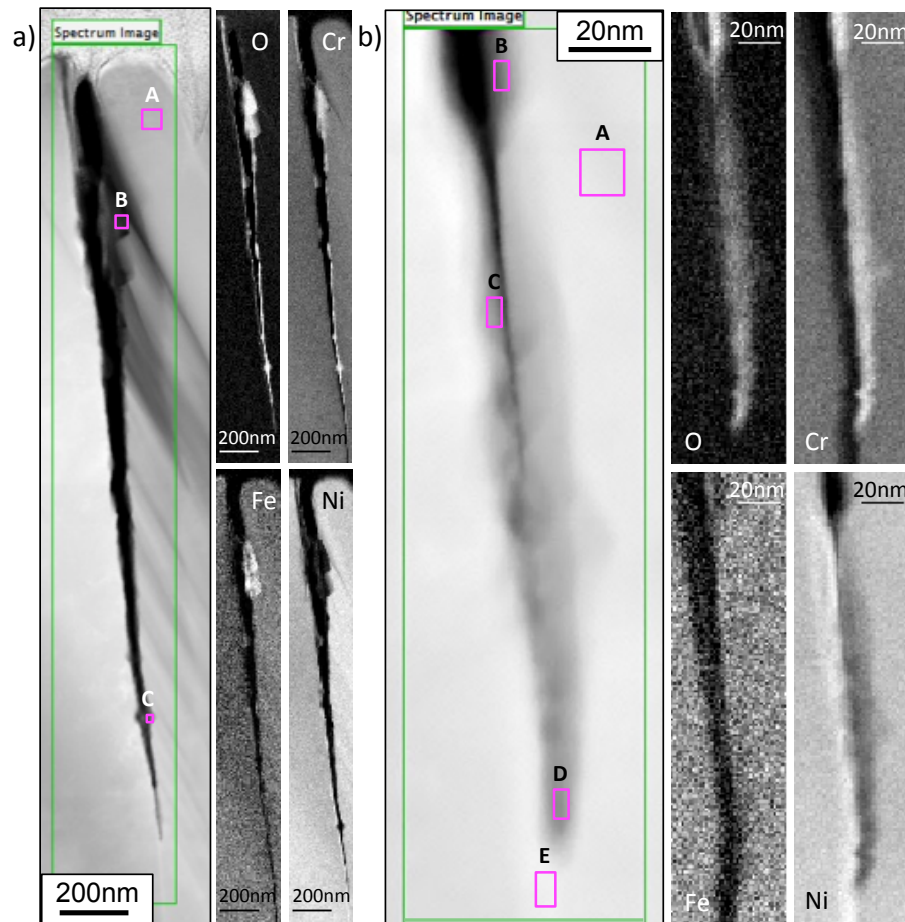


Figure 86: a) STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of R1. Pink boxes mark the labeled regions used for compositional profiling. b) STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of R1's crack tip. Pink boxes mark the labeled regions used for compositional profiling.

R1: Overview region (Figure 86 a), Table 18)

Region A corresponds to the matrix. With 65% Ni, 20% Cr, 8% Fe and 7% O, considering the natural error caused by the 3D volume and the fact that oxygen content in the matrix is overestimated due to a certain degree of surface oxidation of the TEM lamella, the compositional profile reflects the actual sample composition of 72.75% Ni, 17.98% Cr, 8.85% Fe in at.% well. The 2 regions taken within the IG oxide (Region B

and C) are mixed spinel oxides with a dominant Cr amount, especially in region C where the composition is closest to chromia (Cr_2O_3).

Region	Ni (at.%)	Cr (at.%)	Fe (at.%)	O (at.%)
A	65 ± 4	20 ± 3	8 ± 2	7 ± 1
B	6 ± 1	21 ± 4	10 ± 1	62 ± 4
C	-	27 ± 4	3 ± 1	70 ± 5

Table 18: Compositions corresponding to regions of R1, as marked in Figure 86 a).

R1: Oxidized crack tip (Figure 86 b), Table 19)

The close-up look at the oxidized crack tip region confirms an enrichment in Ni ahead of the oxide (Region E, 85% Ni) and on the left side of the crack flank (EELS SI map of Ni L edge in Figure 86 b)). The enrichment is associated with a depletion of Fe (only $\sim 4\%$ Fe, in region B, C, D and E), when compared to the matrix composition (Region A, 8% Fe). Moreover, it was seen that region C, located at the left side of the flank, is rather rich in Ni (63%) and clearly depleted in Cr (8%), whereas region B and D, located at the right side of the crack flank, are composed of a more Cr rich oxide (25% and 27% Cr respectively). The elevated Ni content in these two regions is likely an artefact caused by a blurring of the compositional profile of the ~ 25 nm wide GB region, as typical TEM samples are usually at least 50 nm thick and a certain matrix contribution can't be ruled out.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	67 ± 4	20 ± 3	8 ± 2	5 ± 1
B	16 ± 2	27 ± 4	3 ± 1	54 ± 4
C	63 ± 4	8 ± 2	-	29 ± 4
D	27 ± 4	25 ± 3	4 ± 1	44 ± 4
E	85 ± 4	6 ± 1	4 ± 1	5 ± 1

Table 19: Compositions corresponding to regions of R1, as marked in Figure 86 b).

7.3.1.2 Cantilever R6 and C4 (carbides present)

As can be seen in the STEM HAADF images and EELS elemental maps of cantilever R6 and C4, shown in Figure 87 and Figure 88 respectively, the composition varied quite significantly throughout the intergranular oxide. Whilst oxygen seems to be quite evenly distributed (EELS SI maps of O K edge in Figure 87 and Figure 88), Cr seems preferentially accumulated in regions around the intergranular carbides and along the original GB path (EELS SI maps of Cr L edge in Figure 87 and Figure 88), where Fe and Ni are scarce (EELS SI maps of Fe L and Ni L edge in Figure 87 and Figure 88). The iron on the other hand seems to be preferentially located on the outer edge of the oxide (oxide-metal interface) enclosing the IG carbides.

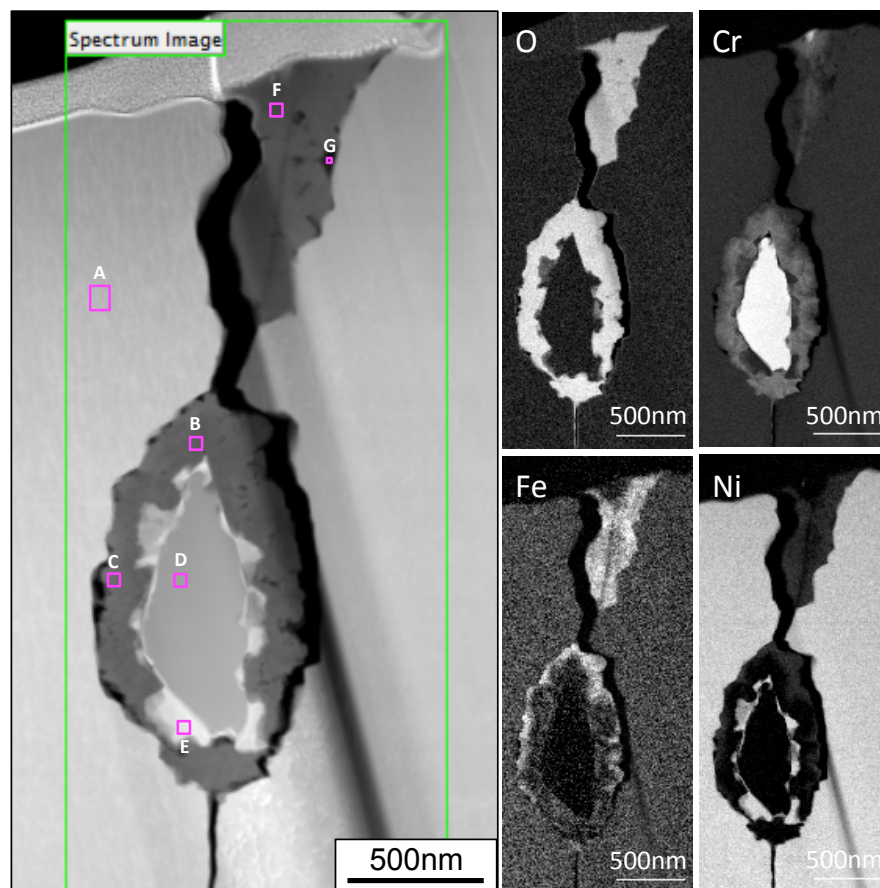


Figure 87: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of R6. Pink boxes mark the labeled regions used for compositional profiling.

Even though very subtle, the Ni content seemed higher in this Fe-rich oxide. There was generally little Ni in the oxide but small patches of metallic Ni were seen next to the oxide-carbide interface of beam R6 (EELS SI map of Ni L edge in Figure 87). No patches of metallic Ni next to the oxide-carbide interface were found in the case of C4 (EELS SI map of Ni L edge in Figure 88), besides a small Ni-rich region at the bottom of the not fully oxide-covered carbide, as indicated by the orange arrow in Figure 88.

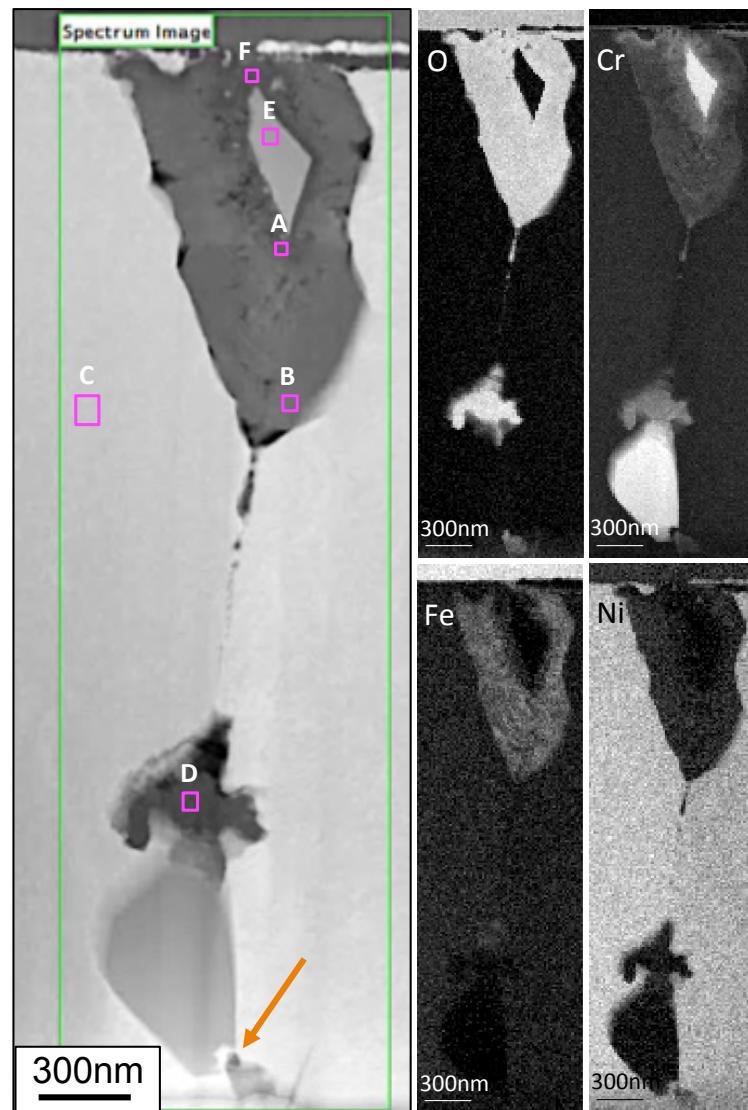


Figure 88: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of C4. Pink boxes mark the labeled regions used for compositional profiling. Below the not fully oxide-covered carbide, Ni-enrichment above an oxidized region was seen, as indicated by the orange arrow.

As for cantilever R1, the composition of different regions on R6 and C4 was extracted.

R6: Full GB region (Figure 87, Table 20)

Keeping in mind the previously mentioned artefact caused by the oxidation of the surface of the cross-section, the matrix composition of R6 (Region A Table 20) and C4 (Region C, Table 21) is in good agreement (62% Ni, 19% Cr, 7% Fe, 12% O and 61% Ni, 19% Cr, 10% Fe, 10% O respectively) with that of R1 (Table 18, Region A). In the STEM HAADF image in Figure 87, region B and F correspond to the oxide, which is located close to the IG carbides in R6, where Cr is rather abundant (31%) with low Fe content (3%). In region C, which is located further towards the oxide-metal interface, the Fe within the IG oxide is clearly dominant (30%), with only 11% Cr and 6% Ni. Region D, with a strong Cr signal (93%), corresponds to the carbide precipitate and Region E, with a composition similar to the matrix, corresponds to the Ni-rich patches located at the oxide-carbide interface. Region G is located within a black spot at the oxide-metal interface, showing the composition of a mixed Ni, Fe, and Cr spinel.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	62 ± 4	19 ± 3	7 ± 1	12 ± 2
B	-	31 ± 4	3 ± 1	66 ± 4
C	6 ± 1	11 ± 1	30 ± 4	63 ± 4
D	-	93 ± 4	-	7 ± 2
E	62 ± 4	17 ± 2	7 ± 1	14 ± 2
F	-	31 ± 4	3 ± 4	66 ± 4
G	13 ± 2	11 ± 1	17 ± 2	59 ± 4

Table 20: Compositions corresponding to regions on R6, as marked in Figure 87.

R6: Close up of original GB region within the IG oxide (Figure 89)

Due to the observed abundance of Cr and a depletion in Fe at the location where the original GB was located, as first seen in the EELS SI map of the Cr L edge in Figure

87, the region within the IG oxide, where the original GB used to be located, was extracted and looked at more closely. Figure 89 shows the EELS maps for O, Cr and Fe. It was found that Cr is accumulated at the GB, where Fe is depleted. Considering O and Cr only, the composition (at.%) in region A, was found to be very high in Cr with a content of 40% and oxygen holding 60%. This agrees with the stoichiometry and compositional profile of Chromia (Cr_2O_3) and, provided density variations can be ruled out as origin of contrast, as addressed in section 1.1.1, would explain the darker appearance of this region, as Cr and O, due to their lower atomic numbers, appear darker in the z-contrast provided by HAADF images.

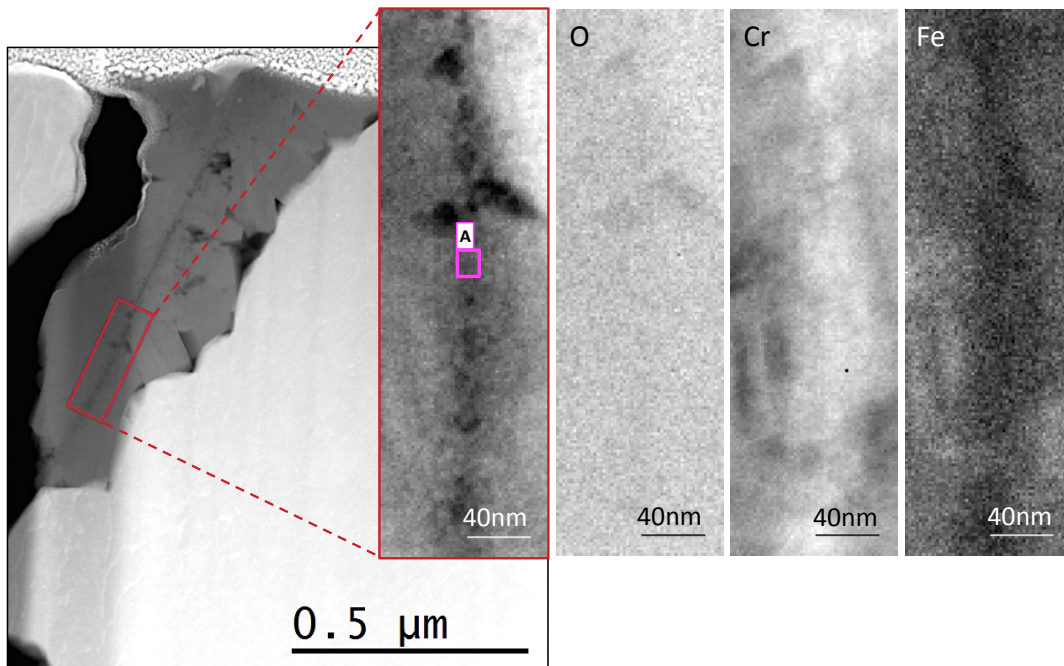


Figure 89: STEM HAADF image, associated spectrum region (red box) and EELS elemental maps (O K, Cr L, Fe L) of the region within the intergranular oxide of R6 where the original GB, which appears darker, used to be located. The pink box in the close-up marks the region used for compositional profiling (Ni and Fe not considered), which amounted to 40% Cr and 60% O.

C4: Full GB region (Figure 88, Table 21)

In the STEM HAADF image in Figure 88, region A, D and F correspond to the oxide, which is located close to the IG carbides in C4. In agreement with observations on R6, the oxide in these locations was found to be rich in Cr (31%, 29% and 37% respectively), whereas Fe and Ni contents seemed negligible. In region B, which corresponds to the oxide close to the metal interface, Ni (11%), Fe (15%) and Cr (15%) are more balanced, which is in good agreement with a mixed spinel composition found for R6 in similar regions located close to the oxide-metal interface (Region C and G in Table 20). Region E (92% Cr) corresponds to the IG carbide. In contrast to R6, no Ni-rich patches next to the oxide-carbide interface were observed at the oxide-carbide interface in C4.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	4 ± 1	31 ± 4	-	65 ± 4
B	11 ± 2	15 ± 2	14 ± 2	60 ± 4
C	61 ± 4	19 ± 3	10 ± 1	10 ± 1
D	4 ± 1	29 ± 4	5 ± 1	62 ± 4
E	-	92 ± 5	-	8 ± 2
F	-	37 ± 5	3 ± 1	60 ± 4

Table 21: Compositions corresponding to regions on C4, as marked in Figure 88.

C4: Close up of original GB region (Figure 90, Table 22)

As already shown in the ADF1 STEM image in Figure 80, the thinly oxidized GB region between the 2 carbides in C4 is rather inhomogeneous with regions rich in Cr and O. Consequently, EELS was performed in this region, as shown in Figure 90. As can be seen in the EELS SI maps of the O K, Cr L, Fe L and Ni L edges, nodule like patches of oxygen (30%) are distributed along the GB, which appear to align with regions rich in Cr (22%) in the otherwise seemingly Cr depleted GB. A light depletion

in Fe along the GB is also noticeable, whilst Ni only seems depleted in the locations where the Cr-rich oxide nodules are located. In terms of composition (Table 22) it appears that these oxide nodules are a mixed spinel oxide but blurring of the compositional profile of the ~ 25 nm wide GB region is likely, as a certain matrix contribution can't be ruled out. This would also explain the rather low oxygen percentage (30%) and relatively high Ni content of 43% found in this region. Overall the observation of these Cr-rich oxide nodules was align with the observed Cr abundance at the original GB observed on R6 (Figure 89).

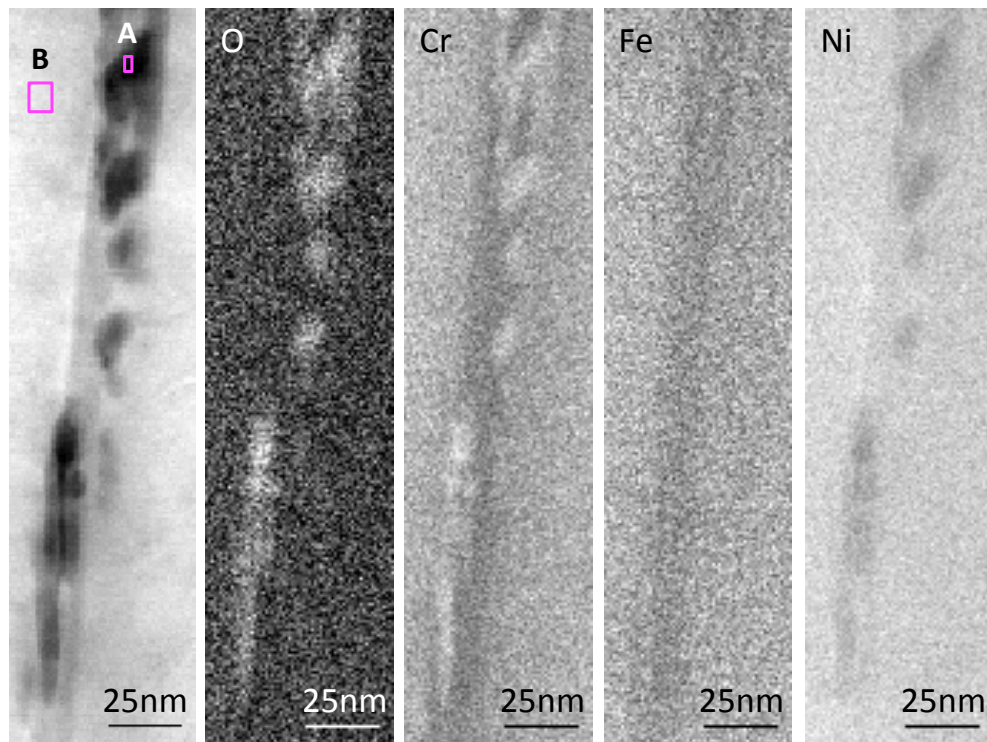


Figure 90: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) and regions used for compositional profiling (pink boxes) of the GB region located between the 2 carbides of C4.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	42 ± 4	22 ± 3	6 ± 1	30 ± 4
B	63 ± 4	19 ± 3	8 ± 2	10 ± 1

Table 22: Compositions corresponding to regions on C4, as marked in Figure 90.

7.3.2 *A600-EDF with low intergranular carbide coverage*

3 examples on *A600-EDF* will be discussed in the following. C3 and C5, which both fractured during testing, and example C5b which was a second region incorporated into cantilever C5, which did not fracture. As briefly explained in Figure 91, region C5b was located in the cantilever's base material of the fixed end grain, away from the tested GB region, and was only exposed during TEM sample preparation.

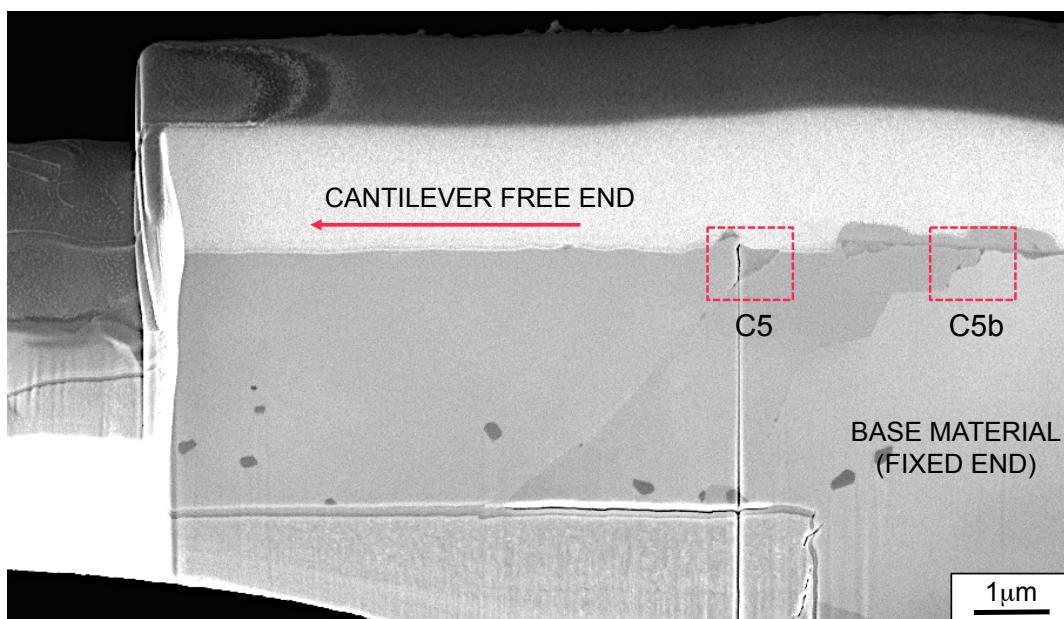


Figure 91: Separation of cantilever C5 into region C5 and C5b.

7.3.2.1 *Cantilever C3*

As can be seen in the STEM HAADF images and EELS elemental maps of cantilever C3, shown in Figure 92, composition varied throughout the intergranular oxide. Whilst oxygen seems to be quite evenly distributed (EELS SI maps of O K edge in Figure 92), Cr seems preferentially located along the original GB path and in a region right above a triple point (red arrow) where Fe and Ni are depleted (EELS SI maps of Cr L, Fe L and Ni L edge in Figure 92). The Fe and Ni on the other hand seemed to be randomly distributed in the rest of the IG oxide and Ni enrichment at the left GB ahead of the

oxidation front is also noticeable as well as some oxidation along a 2nd GB (yellow arrow) next to the crack path, which has already been highlighted in the ADF1 image shown in Figure 85. The Cr at the GBs generally comes from the unoxidized GB ahead, where Fe and Cr are diffusing towards the oxide, leaving behind the Ni enriched region ahead of the oxidation front. Compositional profiles in at.% (atomic percentages) have been taken at multiple locations (pink boxes in Figure 92).

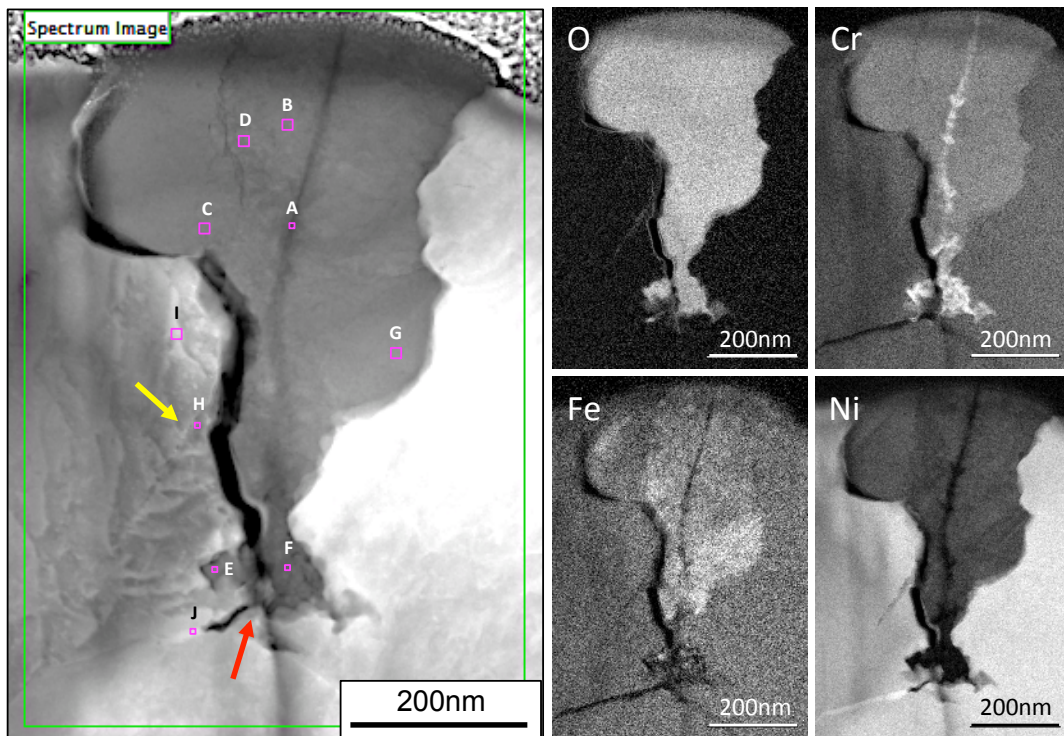


Figure 92: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of C3 on *A600-EDF*. Pink boxes mark the labeled regions used for compositional profiling. A mildly oxidized 2nd GB (yellow arrow) is seen next to the fracture path as well as a triple point (red arrow), located at the oxidation front.

The following observations were made and are summarized in Table 23. Region A corresponds to the original GB. With 42% Cr, 1% Fe and 57% O, the stoichiometry of the oxide located at the original GB is closest to chromia (Cr_2O_3). Region B, C, G and D are mixed (Ni, Fe, Cr) spinels with slightly varying compositional profiles. Region B showing the smallest Fe content (7%) but highest Ni content (17%) whereas region C

and G show the highest Fe content (10 and 13% respectively) and D the smallest Ni content (12%). Region E and F, which are located close to the oxidation front, are rich in Cr with 32% and 36% respectively and very similar Ni and Fe contents. Region H corresponds to an apparently partially oxidized 2nd GB (yellow arrow). With an O content of 41%, oxidation is clearly present. A slight falsification of the Ni, Cr and Fe composition (Region H, Table 23) is however likely due to matrix contributions in this region. However, the EELS elemental maps in Figure 92 show an enhancement in Cr and O while Fe and Ni are depleted, hence highlighting the Cr-rich nature of the oxide in region H. Region I represents the matrix, which with 70% Ni, 20% Cr and 10% Fe agrees well with the actual sample composition (see Table 4) of these elements converted into at.% (73.2% Ni, 16.05% Cr, 8.8% Fe), especially considering that no other matrix impurity elements have been considered. With a Ni content of 81%, region J corresponds to the Ni enriched region in the left grain ahead of the IG oxidation front.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	-	42 ± 6	1 ± 0.2	57 ± 5
B	17 ± 2	19 ± 3	7 ± 1	57 ± 4
C	14 ± 2	14 ± 2	10 ± 1	58 ± 4
D	12 ± 2	21 ± 3	9 ± 1	58 ± 4
E	5 ± 1	32 ± 5	5 ± 1	58 ± 4
F	4 ± 1	36 ± 5	5 ± 1	55 ± 4
G	13 ± 2	19 ± 3	13 ± 2	55 ± 4
H	32 ± 5	21 ± 3	6 ± 1	41 ± 5
I	70 ± 5	20 ± 3	10 ± 2	-
J	81 ± 5	10 ± 1	5 ± 1	4 ± 1

Table 23: Compositions corresponding to regions on C3, as marked in Figure 92.

7.3.2.2 *Cantilever C5*

As for cantilever C3, the composition of the intergranular oxide varied in the case of cantilever C5, as can be seen in the STEM HAADF images and EELS elemental maps shown in Figure 93. The crack proceeds along the oxide metal interface of the first thick IG oxidation patch, while the crack does not seem to clearly favour an interface in the more thinly oxidized region. Oxygen is quite evenly distributed (EELS SI maps of O K edge in Figure 93) and Cr preferentially located along the original GB path where Fe and Ni are depleted (EELS SI maps of Cr L, Fe L and Ni L edge in Figure 93). Fe and Ni are rather randomly distributed in the rest of the IG oxide. A triple point is also highlighted with a red arrow in the STEM HAADF image. No Ni enrichment is observed ahead of the oxidation front. Compositional profiles in at.% (atomic percentages) have been taken at multiple locations (pink boxes in Figure 93) on region C5, as well as the thinner oxide region close to the crack tip. The following observations have been made.

C5: Full GB region (Figure 93, Table 24)

Region A, B and D correspond to mixed (Ni, Fe, Cr) spinels with slightly varying composition. Whilst Ni and Cr contents are quite consistent, region A, located next to the original GB, showed a higher Fe content (7%) than B and D (3% and 4% respectively). Region C, which corresponds to the original GB is enriched in Cr (28%) with a depletion in Fe and Ni. Region E represents the matrix, which with 65% Ni, 21% Cr and 10% Fe, plus a 4% oxygen content most likely coming from surface oxidation of the cross-section, agrees well with the matrix composition obtained for cantilever C3 (Region I, Table 23).

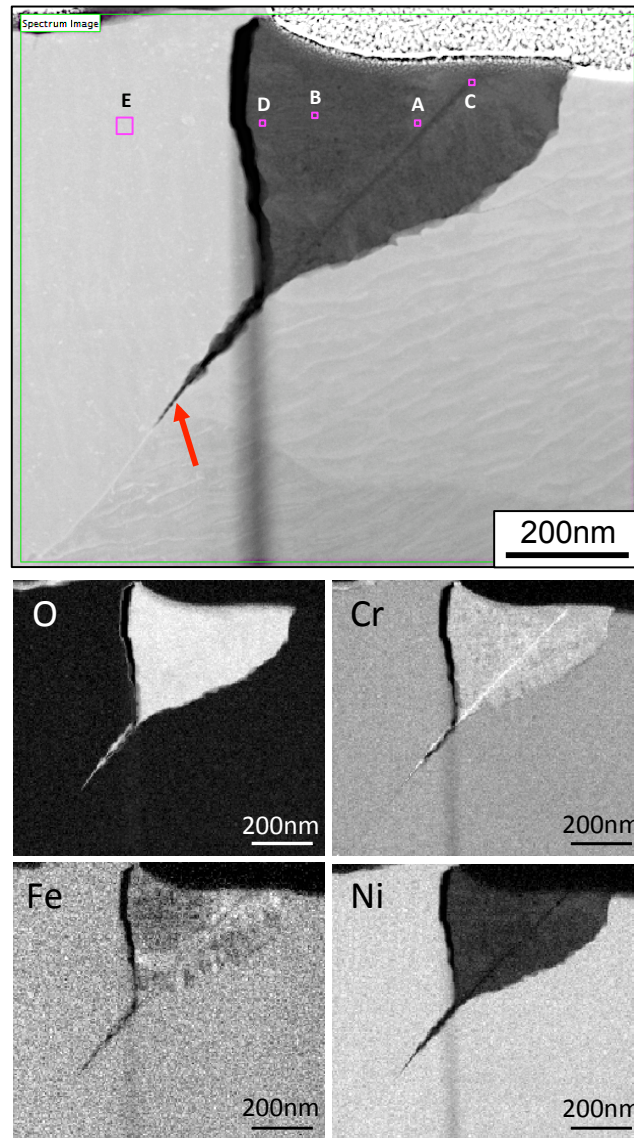


Figure 93: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of C5 on *A600-EDF*. Pink boxes mark the labeled regions used for compositional profiling. The red arrow marks a triple point.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	13 ± 2	18 ± 3	7 ± 1	62 ± 4
B	12 ± 2	18 ± 3	3 ± 0.4	67 ± 4
C	3 ± 0.5	28 ± 4	4 ± 1	65 ± 4
D	13 ± 2	18 ± 2	4 ± 1	65 ± 4
E	65 ± 4	21 ± 3	10 ± 1	4 ± 1

Table 24: Compositions corresponding to regions on C5, as marked in Figure 93.

C5: Close up of thinner IG oxide and crack tip (Figure 94, Table 25)

The STEM HAADF image and EELS elemental maps are shown in Figure 94. Oxygen is seen at both sides of the crack path (EELS SI maps of O K edge in Figure 94). The oxide located at the left side of the crack flank is Cr-rich, whereas Fe and Ni are depleted (EELS SI maps of Cr L, Fe L and Ni L edge in Figure 94). A triple point, highlighted with a red arrow can be seen in the STEM HAADF image. In the close up (red box) of this region it can be seen that small oxide nodules are dispersed along the 2nd GB, as highlighted by the yellow arrows. Compositional profiles in at.% (atomic percentages) have been taken and the following observations have been made and are summarized in Table 25. The oxide located at the left crack flank has 32% of Cr and only very small amount of Fe and Ni 2% and 3% respectively). Region B corresponds to the matrix and agrees well with the previously found matrix profile (Region E, Table 24). Region C corresponds to one of the oxide nodules dispersed at the 2nd GB. Even though a matrix contribution of these small nodules is clearly present, the amount of O (10%), when compared to the matrix (2%) increases by 8% and the Cr (23%) compared to the matrix (20%) is also slightly elevated (3%), suggesting a Cr-rich oxide in these regions.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	3 ± 1	32 ± 4	2 ± 1	63 ± 4
B	68 ± 4	20 ± 3	10 ± 1	2 ± 0.4
C	56 ± 4	23 ± 4	11 ± 1	10 ± 1

Table 25: Compositions corresponding to regions on C5, as marked in Figure 94.

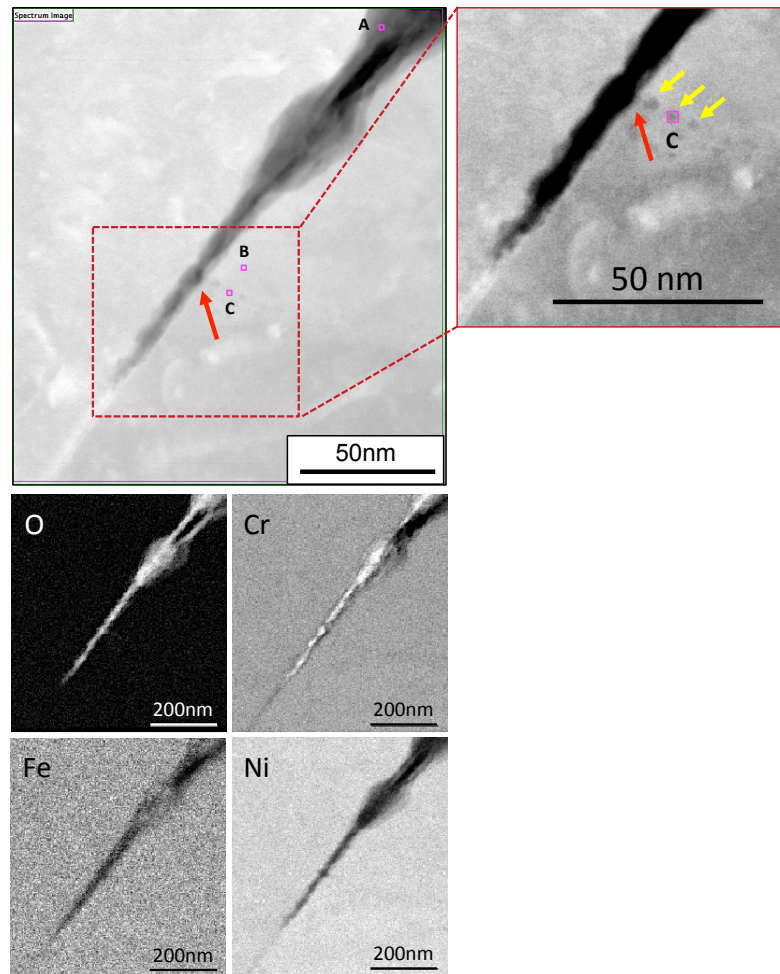


Figure 94: STEM HAADF image and close up, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of C5's crack tip region. Pink boxes mark the labeled regions used for compositional profiling. Small oxide nodules (yellow arrows) are seen along the 2nd GB of the triple point (red arrow).

7.3.2.3 Cantilever C5b (Figure 95, Table 26)

As for cantilever C3 and C5, region C5b, an unfractured oxidized triple boundary which was revealed in the cantilever base material of C5 during TEM sample prep, showed compositional variations within the IG oxide, as can be seen in the STEM HAADF images and EELS elemental maps in Figure 95. Consistent with previous observations on the 2 fractured GBs, O is quite evenly distributed (EELS SI maps of O K edge in Figure 95) while Cr is preferentially located along the original GB path as

well as in some other individual spots (Cr-rich triangular regions in the EELS SI maps of Cr L in Figure 95) within the IG oxide, where Fe and Ni are depleted (EELS SI maps of Fe L and Ni L edge in Figure 95). These Cr-rich spots strongly resemble the Cr-rich region atop of IG carbides on *A600-INSS*, as was seen in Figure 88 in section 7.3.1.2. Hence, it can be assumed that the triangular spots (EELS SI maps of Cr L in Figure 95) are associated to a close vicinity to IG carbides, which started to locally produce Cr-rich (Cr_2O_3) oxides, but were not covered in the TEM cross-section. Moreover, it appears that Cr is depleted at the metal-oxide interfaces. Interestingly, Fe and Ni are rather randomly distributed in the rest of the IG oxide, besides the 2nd biggest IG oxide patch, located on the left side of the triple boundary, which seems slightly richer in Fe and also indicated the potential presence of a carbide. The triple point is highlighted with a red arrow in the STEM HAADF image. The regions in-between the bigger IG oxide patches show small inhomogeneously dispersed oxide nodules (yellow arrows), which appear rich in Cr. Ni enrichment, caused by the local loss of Fe and Cr in these regions due to oxidation, is also observed ahead of the oxidation fronts.

Region	Ni (at. %)	Cr (at. %)	Fe (at.%)	O (at.%)
A	-	35 ± 5	3 ± 1	62 ± 4
B	68 ± 4	18 ± 3	7 ± 1	7 ± 1
C	62 ± 4	22 ± 3	10 ± 1	6 ± 1
D	84 ± 5	11 ± 2	5 ± 1	-
E	-	38 ± 6	2 ± 0.4	60 ± 4
F	6 ± 1	24 ± 3	6 ± 1	64 ± 3
G	12 ± 2	18 ± 3	7 ± 1	63 ± 4
H	12 ± 2	18 ± 3	7 ± 1	63 ± 4
I	16 ± 2	16 ± 2	8 ± 1	60 ± 4
J	14 ± 2	16 ± 2	11 ± 2	59 ± 4
K	12 ± 2	16 ± 2	15 ± 2	57 ± 4

Table 26: Compositions corresponding to regions on C5b, as marked in Figure 95.

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Compositional profiles in at.% (atomic percentages) were taken at multiple locations (pink boxes in Figure 95) of region C5b. The following observations were made and are summarized in Table 26. Region A corresponds to the location of the original GB and is a Cr-rich (35%) oxide with minor amounts of Fe. Region B and C are 2 locations in the matrix. Region B, being located close to the oxide metal-interface where a Cr-depletion was noticeable, showed a slightly higher Ni content (68%) compared to Region C (62%) as well as slightly lower Cr and Fe contents. Region E corresponds to an oxide rich in Cr (38%), almost close to the stoichiometry of chromia (Cr_2O_3), which might be associated to the presence of an IG carbide, which was not included in the TEM lamella. Region F on the other hand represents one of the oxide nodules found along the inhomogeniously oxidized GB in-between the thicker oxide patches. The oxidized nodules appear rich in Cr (24%) with minor Ni and Fe content of 6% each. Region G and region H are mixed (Ni, Cr, Fe) spinels, identical in composition and are located at or close to the sample surface. Region I is located further down the IG oxide and next to the original GB location. The oxide there is slightly richer in Ni (16%) when compared to region G and H (12% both). Region J and K are located in the apparently Fe-rich oxide patch, in agreement with the EELS elemental maps region K is richer in Fe (15%) than region J (11%), while the Cr content seems to be equal with 16% for both.

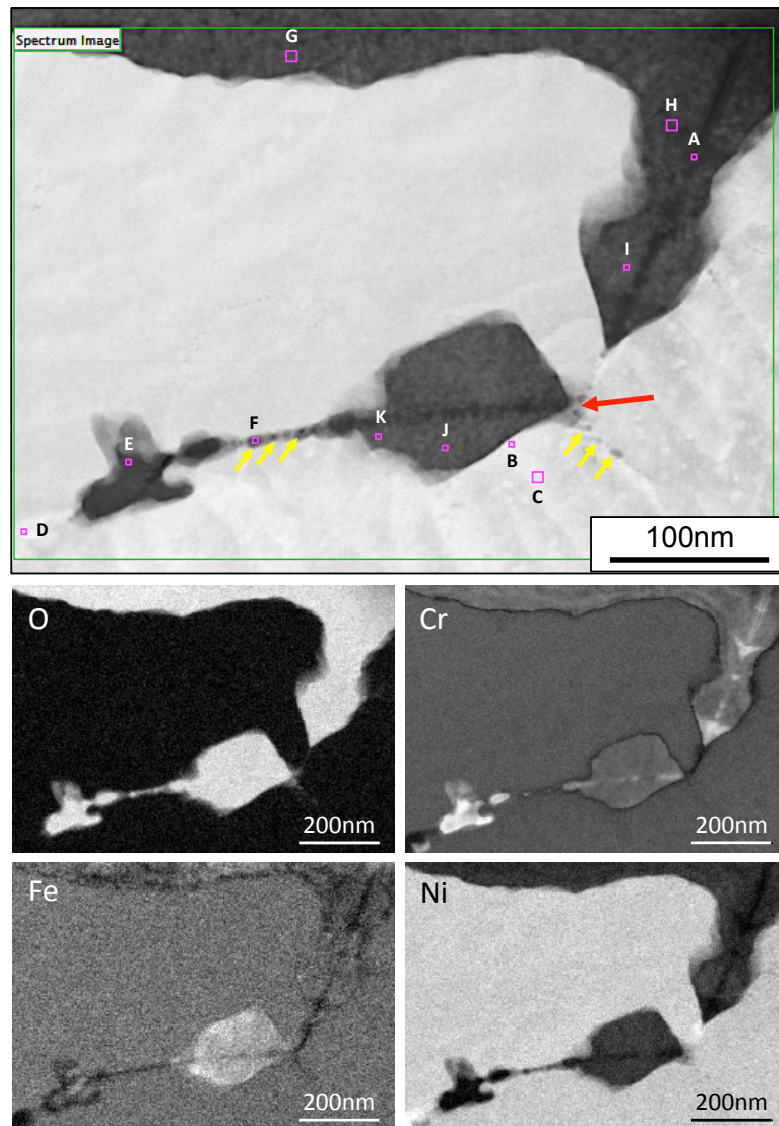


Figure 95: STEM HAADF image, associated spectrum region (green box) and EELS elemental maps (O K, Cr L, Fe L and Ni L edges) of region C5b. Pink boxes mark the labeled regions used for compositional profiling. Small oxide nodules (yellow arrows) are seen between the thicker IG oxide patches. A red arrow marks a triple boundary.

7.3.3 Density of the original GB region and oxide-metal interface

7.3.3.1 A600-INSS with high intergranular carbide coverage

The oxide closest to the stoichiometry of Chromia (Cr_2O_3) was mainly located at the original GB path and around Cr-rich carbides and appeared darker in the HAADF images. As explained in the course of chapter 3.8, the contrast generated by the

scattered electrons in STEM HAADF images is proportional to atomic number variations, assuming a constant thickness and density. Darker regions correspond to regions of low atomic number Z and brighter regions to high atomic numbers. Cr ($Z = 24$) and O ($Z = 8$) for instance have lower atomic numbers than Ni ($Z = 28$) and Fe ($Z = 26$) and appear darker in the HAADF images, which would align with a darker appearance of Cr-rich oxides found at the original GB. However, from the HAADF image alone it was not possible to determine whether the contrast was mainly associated to Z or also density variations (porosity). So before any final conclusions could be drawn, the origin of the dark regions had to be clarified first. The relative intensity I_{HAADF} in a HAADF image is approximately proportional to Z^2 , with Z being the atomic number.

$$I_{HAADF} \sim Z^2 \quad \text{Equation 31}$$

Using Equation 31, to compare the ratios between the intensity signals and atomic number of 2 regions, the origin of the contrast can be determined.

$$\frac{I_1}{I_2} = \frac{Z_1^2}{Z_2^2} \quad \text{Equation 32}$$

Therefore a line profile was drawn across a region of interest, as *e.g.* shown in Figure 96, which shows the inhomogeniously oxidized GB region in-between to carbides on *A600-INSS*. The average intensity of the matrix (*e.g.* $I_1 = 5650$) and oxidized GB (*e.g.* $I_2 = 4720$) was obtained. By using the weighted atomic number average (Z) of each region, which is based on the local atomic percentages, *e.g.* 63% Ni, 19% Cr, 8% Fe and 10% O for the matrix and 43% Ni, 21% Cr, 6% Fe and 20% O for the GB oxide nodule, as shown in the calculation in Figure 96, it was possible to show that the ratio between intensities and atomic numbers were the same.

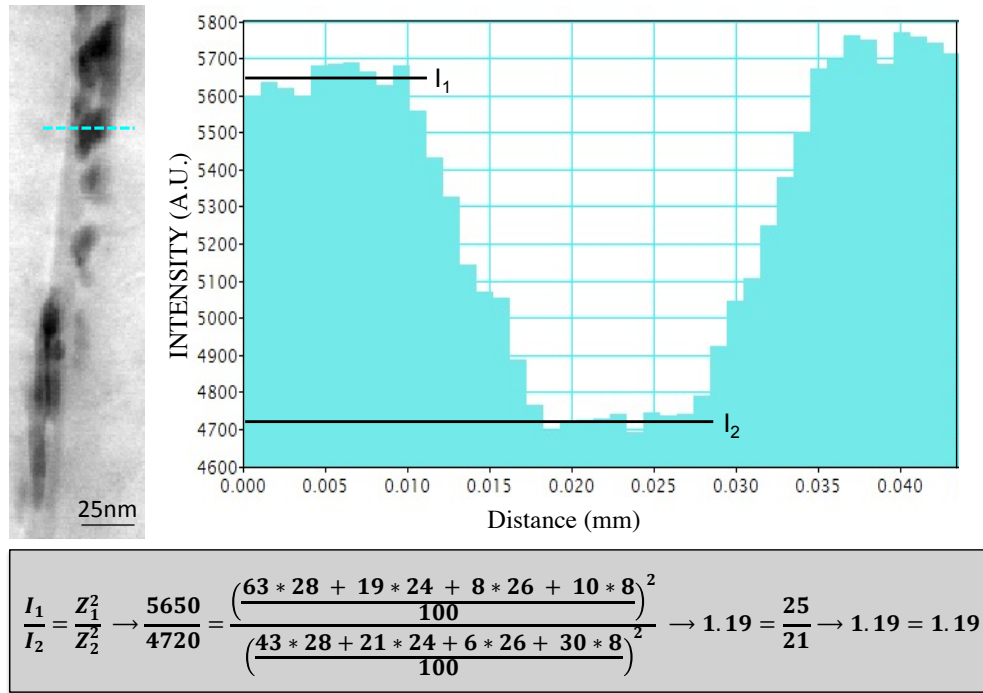


Figure 96: Line profile (dashed line) across the oxidized GB portion of C4 and corresponding intensity spectrum. The ratios between the intensities (I_1/I_2) and weighted atomic number average, which is based on Z for Ni (28), Cr (24), Fe (26) and O (8) and local composition in at.%, show that contrast is not associated with porosity. The weighted atomic number average is thereby found by multiplying the at.% of the respective elements from the EELS analysis in the regions with the respective atomic numbers Z. For Z1 in the above example, 63% are multiplied by 28 for Ni, 19% are multiplied by 24 for Cr, 8% multiplied by 26 for Fe and 10% multiplied by 8 for O. The results are summed up and divided by a total 100 %.

Hence, contrast at the GB of the example in Figure 96 was not associated with a greater porosity of the oxidized GB portion, when compared with the surrounding matrix material. The same procedure was repeated on a different sample (R6) to determine the origin of the contrast of the oxide at the original GB path, identified to be chromia, embedded in the mixed spinel oxide of *A600-INSS*, as was shown in Figure 89. With 0.75 (I_1/I_2) to 0.85 (Z_1^2/Z_2^2) it was found that the original GB path enclosed within the IG oxide was not an obvious weak spot due to a lower density caused by the presence of porosity and voids either. This moreover implied that the darker contrast in this region was merely a result of the Cr-rich oxide (lower Z) located in this region.

However, when comparing the matrix composition to a region at the oxide-metal interface where a bigger black spot was located (Region G in Table 20), as shown in Figure 97 (Region 1 and associated intensity spectrum), it can be seen that with $I_1/I_2 = 5.8$ and $Z_1^2/Z_2^2 = 2.55$, the contrast can be associated with a density variation.

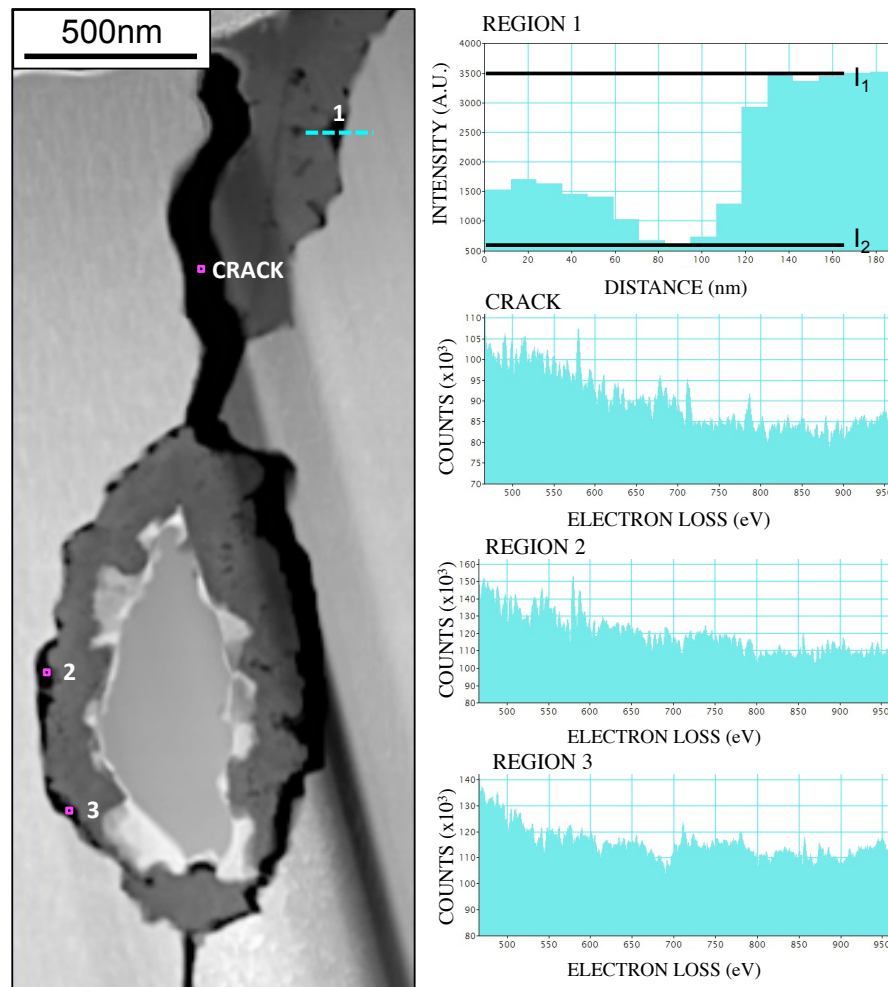


Figure 97: Line profile (dashed line) across a dark region, located at the oxide-metal interface of R6, denoted as region 1, and corresponding intensity spectrum. The ratios between the intensities and weighted atomic number average show that contrast is not associated with porosity. Comparison of the EELS signals in the CRACK region, as well as in REGIONS 2 and 3, revealed only noise, indicating porosity (voids).

Even more convincing was the fact that no signal was obtained in the big black regions, denoted 2 and 3, as shown in their respective energy loss spectra in Figure 97. Similar

to the crack region (Figure 97, CRACK plus corresponding energy loss spectrum) mainly noise was detected, proving that the black features at the oxide-metal interface were in fact voids (weak spots).

7.3.3.2 *A600-EDF with low intergranular carbide coverage*

Two line profiles (R1 and R2) on *A600-EDF* cantilever C3 were also investigated using the same procedure of comparing intensity and Z ratios based on local compositional percentages. The regions are shown in Figure 98.

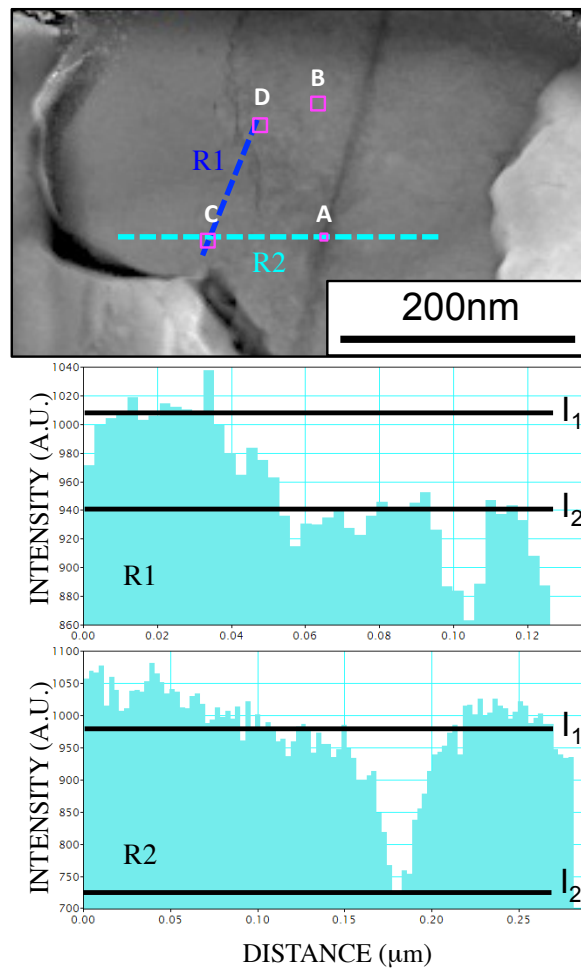


Figure 98: Line profile (dashed line) and corresponding intensity spectra of 2 regions on C3 (*A600-EDF*). R1 compares 2 regions within the IG oxide and R2 compares the original GB with the surrounding oxide.

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For R1 it was found that with $I_1/I_2 = 1.07$ and $Z_1^2/Z_2^2 = 0.99$ the 2 mixed spinel oxides, even though region D was richer in Cr (21%) than region C (14%), as summarized in Table 23, do not significantly differ in density and that contrast was mainly associated with Z variations. For R2 it was found that with $I_1/I_2 = 0.74$ and $Z_1^2/Z_2^2 = 0.78$ the GB was no obvious weak spot either and Z contrast was dominant.

7.4 Discussion and summary

To better understand the mechanical response, fracture behaviour and a possible link to the local microstructure and degree of oxidation of the beams tested on *A600-INSS* (high IG carbide coverage) and *A600-EDF* (low IG carbide coverage), electron microscopy investigations, including SEM, additionally supported by 3D FIB-SEM sequencing, as well as (S)TEM and EELS of the tested GBs, was performed, as discussed in section 7.1, 7.2 and 7.3 respectively. The findings will be discussed in the following sections, starting with a summary of the EELS data presented in chapter 7.3, which helps to put the findings into context.

7.4.1 EELS of oxidized GBs: A brief summary

The fracture path and observed compositional and density variations, indicated by the Z-contrast in the ADF images taken in section 7.2, were additionally examined via EELS (section 7.3). Based on the observations, considering the additional information gained by the analysis in section 7.3.3, the following statements can be made:

7.4.1.1 EELS on *A600-INSS* with high intergranular carbide coverage

- The oxide formed at the original GB is dense, rich in Cr and closest to the stoichiometry of chromia (Cr_2O_3). It is however not continuous along the GBs.

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- The IG oxide next to the GB and carbides seems to be composed of mixed spinel oxides with varying Ni, Fe and Cr contents. The oxide richest in Cr is located next to the IG carbides, whereas the oxide richest in Fe is located closer to the oxide-metal interface.
- Pores/voids are located at the oxide-metal interface.

7.4.1.2 EELS on A600-EDF with low intergranular carbide coverage

- The oxide formed at the original GB is dense, rich in Cr and closest to the stoichiometry of chromia (Cr_2O_3). It is however not continuous along the GBs.
- The IG oxide next to the GB seems to be composed of mixed spinel oxides with varying Ni, Fe and Cr contents.
- If carbides are present along or close to the GB, the oxide richest in Cr is located close to the Cr-rich precipitates, whereas a more Fe-rich oxide is found further towards the oxide-metal interface, as was found for A600-INSS.
- No detectable pores/voids are located at the oxide-metal interface but the interface is slightly depleted in Cr.

7.4.2 Fracture of oxidized Alloy 600 GBs

The SIO mechanism, as discussed in section 2.7.5, suggests a failure through a brittle Cr-rich intergranular oxide. Based on the SEM and especially the 3D FIB-SEM and STEM observations made on both specimens tested in this study, as described in the course of chapter 7, it was found that:

- Failure preferentially proceeds along the oxide-metal interface in regions where the IG oxide is sufficiently thick/wide.
- Failure through the intergranular oxide is observed in regions where GB oxidation is narrow and incomplete.

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On *A600-INSS* thicker oxide regions are often found close to the surface but also around the IG carbides dispersed along the GBs. Due to the sensitization around IG carbides (see APPENDIX A), which has been reported in literature before ^{[60], [49], [72]}, and a preferential oxide-consumption of the precipitates to form Cr-rich oxides, the IG oxide seems to be able to grow wider around carbide precipitates. This is in agreement with work reported by Bertali *et al.* ^{[69], [70]}, carried out in hydrogenated steam, and work by Gaslain *et al.* ^[243], carried out in a simulated primary water environment (325 °C, 1400 hours) comparable to the one in this study. However, it is in contrast to work by Dugdale *et al.* ^[49], who did not associate the wider oxide formation around IG carbides with a consumption of the precipitates but only with a preferential oxidation of the Cr-depleted region around it. The oxides formed in sensitized regions are usually Cr-deficient and hence less protective. This aligns with the observation of pores/voids along the oxide-metal interface where these less protective and Cr-deficient oxides are found. The reasons for void formation in these regions remains unproven and further investigations are suggested. Possible explanations are however proposed in section 7.4.2.1. The thinner and inhomogeneously-oxidized regions on *A600-INSS* were mainly seen in-between IG carbides, as oxide formation seemed to prefer close proximity to the Cr-rich inclusions. Considering the well-established concept that the least noble elements in the alloy, like Cr in A600, are oxidizing first, diffusion of oxygen towards Cr rich regions and vice versa seems plausible.

In the case of *A600-EDF*, IG oxide penetration was generally less deep due to a ca. 50% shorter exposure to the environment. While wider IG oxides were mainly associated with surface proximity it was moreover found that thick/wide oxide patches are located further down the GBs, as was shown in the HAADF (S)TEM image in Figure 95. Owing to the 3D FIB-SEM data of the tested beams on *A600-EDF*, as shown in Figure 99, it was however possible to show that even though this coupon had limited

IG carbide precipitation, smaller IG carbides are often found throughout the 3D volume of these regions or sometimes, even though transgranular in nature, they are located close enough to the GBs to suffer from oxide consumption.

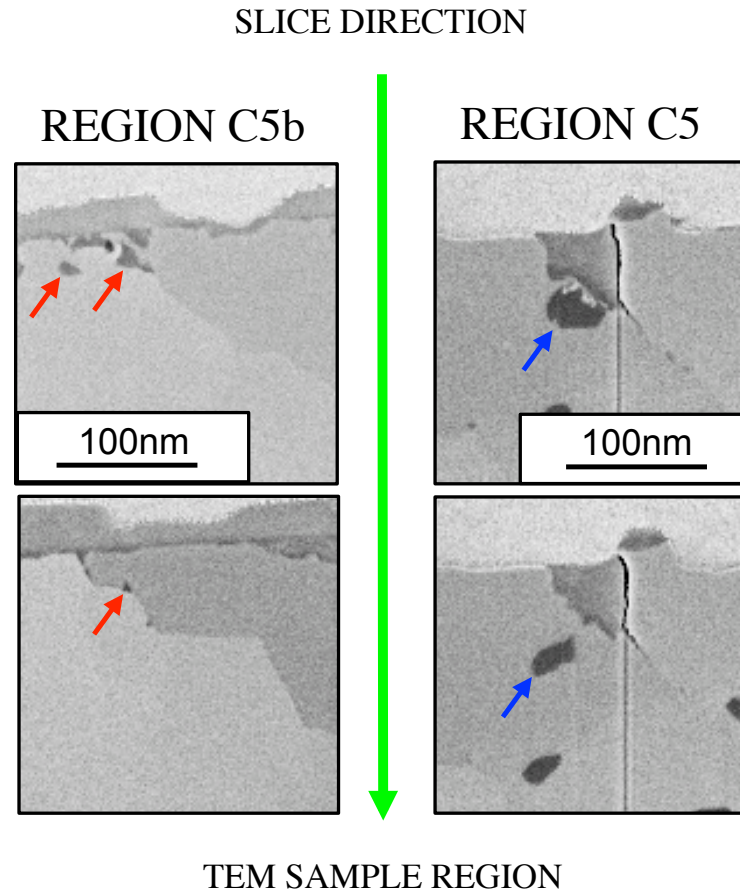


Figure 99: Two slices of the 3D FIB-SEM image stack of region C5b (left) and C5 (right), approaching the region which has been spared for TEM investigations, as shown in Figure 95 and Figure 93 respectively. (left) Red arrows mark the location of small intergranular carbides. Only a trace of the carbide is left in the second slice (bottom image) on C5b, which represents a slice taken close to the center of the beam before the actual TEM sample region. (right) The blue arrow marks the location of a transgranular carbide close to the GB path of C5 in both slices. As the center of the beam is approached (TEM sample region), the carbide loses contact with the oxidized GB.

This explains the observed patch-like and wider oxide formation on *A600-EDF*, which was also observed on surface near transgranular carbides, as shown in Figure 100, and

resembles the thicker oxidized regions around intergranular carbides seen on *A600-INSS*, as was *e.g.* seen in Figure 79 and Figure 80.

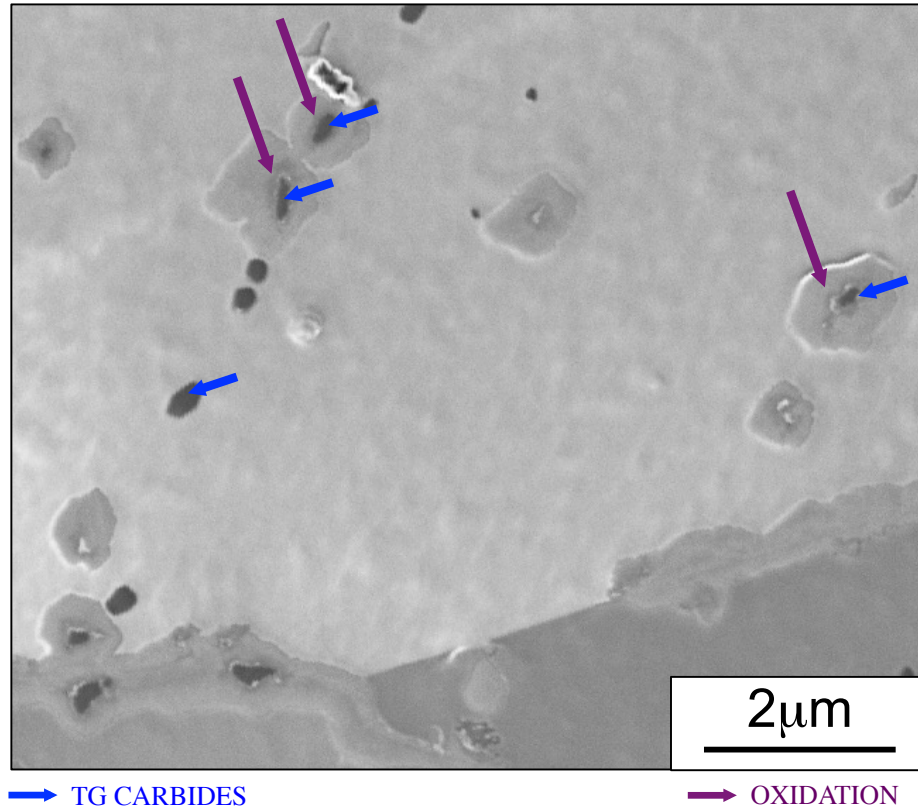


Figure 100: Surface-near transgranular carbides on *A600-EDF* (green arrows). A shell-like and wider oxidation (purple arrows) is growing around them. The behavior strongly resembles the wider oxidation seen around intergranular carbides along the oxidized GBs of *A600-INSS*, as *e.g.* shown in Figure 79 and Figure 80.

One noticeable difference is that on *A600-INSS*, the oxide-metal interface was clustered with pores/voids of varying size, whereas *A600-EDF* showed no obvious porosity at this interface. Instead, a Cr-depleted region was seen, leaving behind a finer, sensitized region at the interface (*e.g.* Figure 95 on page 193). This is likely due to the different heat treatment and defect density of the two samples. Whilst *A600-INSS* experienced a final mill-anneal at 1050 °C to promote IG carbide precipitation, which is known to cause different levels of sensitization, *A600-EDF* received a final heat-treated at 820 °C

to promote the growth of transgranular carbides. This lower temperature might have replenished some of the Cr lost at the interfaces of *A600-EDF*, which is usually known as healing. However, usually healing performed in literature reports thermal treatments at lower temperatures for up to $\sim 15\text{h}$ ^[244] and the wider oxidation found around the surface near carbides and around the few IG carbides found on this sample would also suggest otherwise. It seems more sensible that a higher defect density in *A600-INSS*, due to the cold working of this sample, might play a role, as cold work increases dislocation density, and IG carbides may activate dislocation sources to help relieve local stresses. The dislocations in turn are preferred sinks for vacancies. Nonetheless, *A600-EDF* has only been exposed to the environment for 1004h whereas *A600-INSS* has seen the environment for almost double the time (2000h). Hence, the observed fine Cr-depletion at the oxide metal interface of *A600-EDF* might still lead to the formation of less protective and less dense spinels upon longer exposure times. A study carried out on the same material for longer exposure times might be sensible to see whether porous regions might form. As was the case for *A600-INSS*, an inhomogeneous and thin oxidation seemed to be located ahead of and in-between the thicker oxide patches. Hence, for both samples, failure through the IG oxide can be linked to an incomplete interconnection of the oxides in these regions. This might explain why failure does not choose a particular interface but progresses randomly through the nodule-like oxides in these regions, as seen on both samples. This would agree well with the observed failure through an intergranular oxide observed by Fujii ^[160] on a carbide-free A600 coupon exposed to similar simulated primary water conditions for 1500 and 2700 hours at 360 °C, using 30 cc/kg DH2, 500 ppm B and 2ppm Li. Irrespective of the sample, failure in this study was never seen to proceed along the carbide-oxide interface or through the location of the original GB embedded within thicker IG oxides. In agreement with EELS data, as explained in section 7.3, oxides formed at the original

GB and directly adjacent to the IG carbides are usually very rich in Cr and show the stoichiometry of chromia (Cr_2O_3) or very close to chromia. The Cr at the GBs usually comes from the GB ahead, due to diffusion of Cr towards the oxide. The GB serves thereby as a fast diffusion channel. Fe also travels towards the surface but has seen to accumulate in regions away from the carbides and closer to the oxide-metal interface. The observation of Cr and to a lesser extend Fe diffusion is supported by the occasional observation of Ni enrichment ahead of the oxidation fronts, due to the local loss of Cr and Fe and a rejection of Ni from the oxide, as has been previously observed in the literature.^{[46], [69], [70]} In some cases a Ni rejection from the oxide was also seen at the oxide-carbide interface and in small regions within the oxide (Figure 101, turquoise arrows).

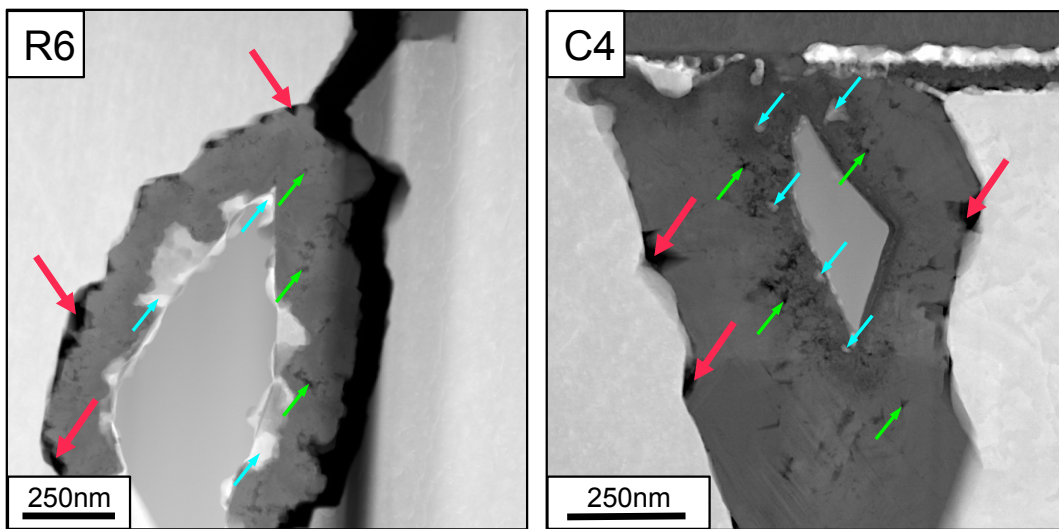


Figure 101: Small Ni-enriched patches (turquoise arrows) at the oxide carbide interface and within the IG oxide next to the carbides of R6 and C4. Tiny density fluctuations within the IG oxide (green arrows) can be seen and might be linked to a conversion of the Ni-rich patches to oxides of less density. Big voids (red arrows) are located at the oxide-metal interface.

It is possible that these patches are converted to tiny areas of less density (green arrows), a lot smaller than the voids at the interface (red arrows), as sometimes seen within the otherwise Cr-rich oxide formed in the vicinity of carbides. This might be

explained because the oxide next to the carbides is naturally Cr-rich, due to the local abundance of Cr to form this protective oxide species, which would slow down the consumption of the carbide itself so that the Ni-rich patches might be targeted first. The resulting tiny defects, whilst also adding some porosity, are too small compared to the voids at the interface to serve as weakest link for crack propagation. Pimentel *et al.* ^[46], who compared the oxide penetration depth of 2 different heat treatments of A600, both exposed to the environment for 1500h, observed that the IG oxide penetration seems to be slowed down by the presence of IG carbides. This aligns with the observed consumption of the Cr-rich carbides in this study and a shell-like growth of the IG oxide around the precipitates. Gaslain *et al.* ^[243] found that, while oxide penetration depth seems to be slowed down by the presence of Cr-rich carbides, the volume of the IG oxide growing on samples with and without the presence of carbide precipitation does not change, as the IG oxide simply grows wider around precipitates. Even though the volume of the IG oxidation has not been investigated, the observation of wider oxide formation around carbides has been confirmed in this thesis. Moreover, it was seen that the IG oxide does not necessarily need to fully circumvent the whole carbide in 3D before being able to further penetrate down the GB. This is again shown in Figure 102 and was also seen in the 3D- FIB reconstruction in section 7.1.3 (Figure 77) and in the STEM data shown in chapter 7.2. Keeping in mind that the carbides are 3D features it is enough for the oxidation to reach the carbide at some point in 3D to allow for an additional oxidation of the carbide from the bottom in regions where the IG oxide has not fully encapsulated the carbide yet. While some Ni-rich patches might again evolve due to a rejection of Ni (Figure 102, turquoise arrows), the formation of more protective Cr-rich oxides at the oxide-carbide interface would slow down the local carbide consumption, which in turn might further the oxidation of the GB underneath and a diffusion of oxygen further down the GB towards new, more vulnerable regions.

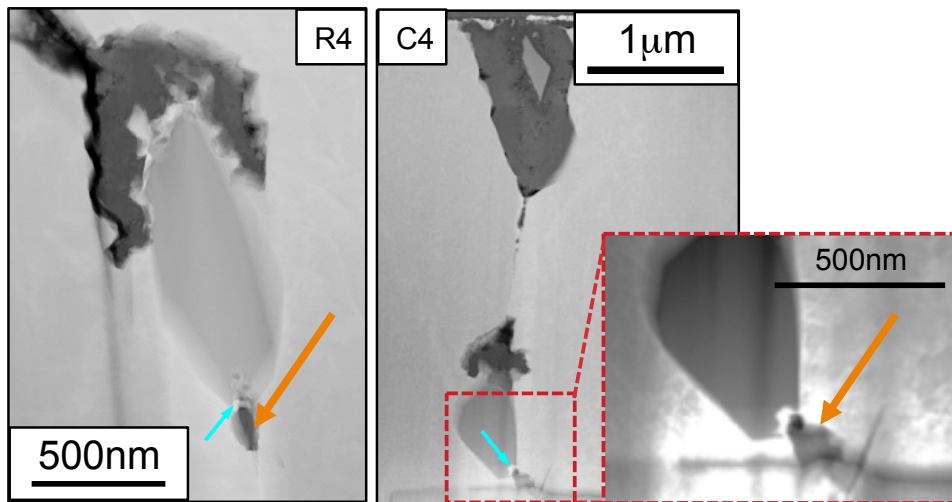


Figure 102: Oxidation at the bottom of IG carbides (orange arrows), showing the consumption of the carbide from the bottom up, as seen on R4 (left) and C4 (right). This allows for a further penetration of the GB ahead of the carbides.

This is also indicated in the 3D FIB-SEM tomography data of beam R6 (see section 7.1.3.1), which has been re-organized for easier visualization in Figure 103. The 2 SEM in-lens image slices seen in Figure 103 (top 2 images), correspond to the inner edges of the blank region in the centre of the beam's reconstruction, which has been left for TEM sample preparation. As indicated by the pink arrows it can be seen that the IG oxidation does not fully encapsulate the carbide in 3D yet but oxidation at the bottom of the carbide extends throughout the whole volume. Additionally, IG oxidation proceeds down the GB (orange arrow) as also indicated by the crack path (blue in the reconstruction), which aligns with the IG oxide penetration.

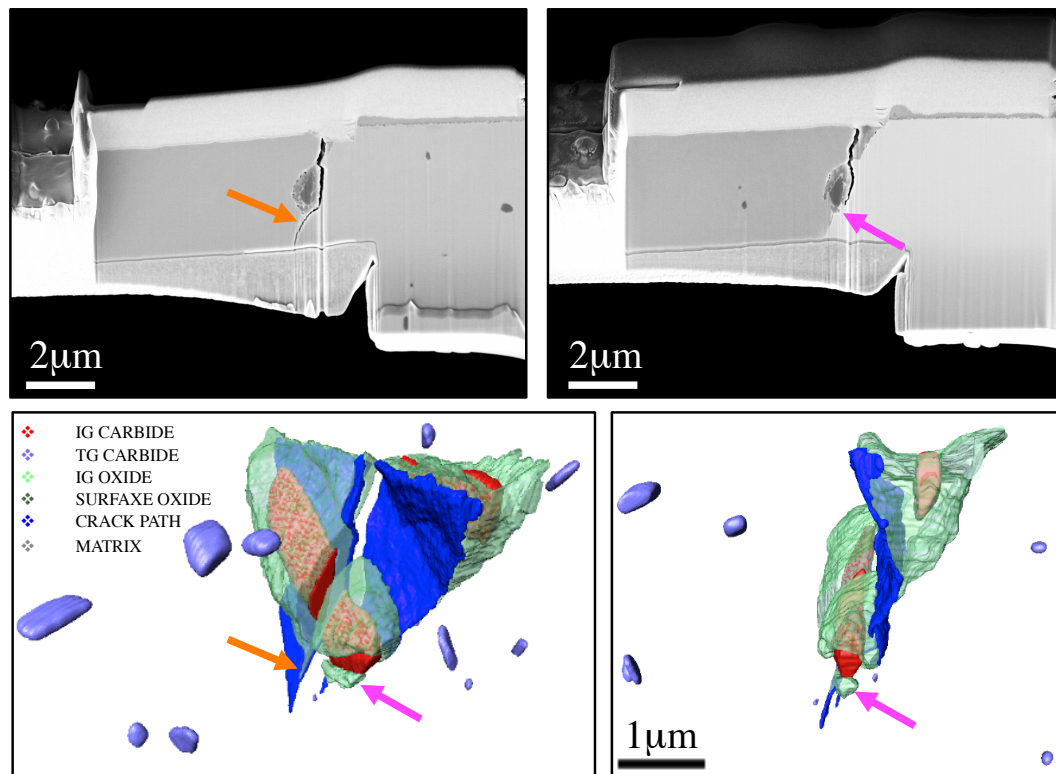


Figure 103: 3D FIB-SEM reconstruction of cantilever R6, showing the degree of IG oxidation of the carbides (red). At the carbide closer to the bottom it can be seen that while the carbide is not fully encapsulated in 3D yet, IG oxidation has reached the bottom of the carbide throughout the volume (pink arrow) and penetrates further down the GB (orange arrow), in agreement with the crack path (blue). The 2 SEM in-lens image slices shown on top correspond to the inner edges of the reconstruction, where the blank region is found which has been left for TEM sample preparation.

7.4.2.1 The role of voids in the fracture of oxidized GBs

As proven by the EELS investigations on *A600-INSS* in chapter 7.3, as summarized in section 7.4.1, the oxide next to the carbides is “layered”, with a compact Cr-rich oxide located at the oxide carbide interface and original GB and a more Fe-rich oxide located next to the oxide-metal interface. This is shown schematically in Figure 104. A thin Cr-depleted area (Figure 104 A, blue) is found around the GB and the carbide (~ 100 nm, as supported by EELS). O is diffusing inwards and the sensitized area and carbide oxidizes preferentially (Figure 104 B).

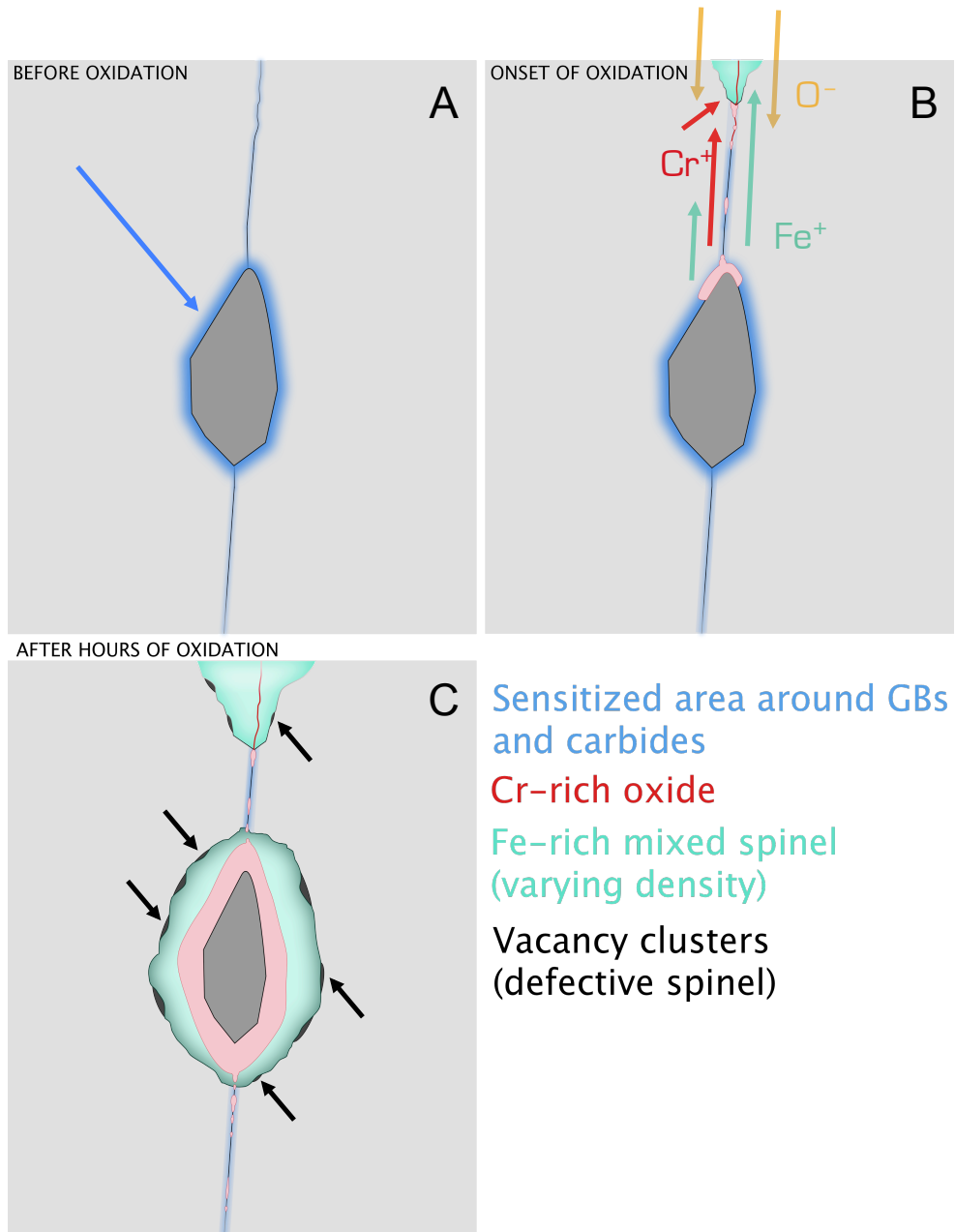


Figure 104: Schematic of the oxides formed, as seen on *A600-INSS*. A: A Cr deficient region of about 100 nm (blue) is found around the GB and around the carbide. B: Due to an inwards diffusion of O this Cr-depleted area and the Cr-rich carbide oxidizes preferentially. While Ni is mostly static during oxidation (Ni/NiO equilibrium), Fe and to a lesser extend Cr are diffusing outwards. The less noble Cr is mainly using the GBs as diffusion paths. B - C: Cr-rich oxide (red) is mainly formed at the original GB and close to carbide (grey particle). C: Fe-rich mixed spinel oxides ($A^{2+}B^{3+}_2O_4$) of varying composition form next to the Cr-rich layer. Fe is thereby preferentially found close to the oxide-metal interface, as indicated by the gradient of the mixed spinel layer (green), where defective spinel and vacancy clusters (black) are formed.

In the proximity of the Ni/NiO phase equilibrium, Ni is mostly static during oxidation. However, Fe and to a lesser extend Cr are diffusing outwards towards the surface. Since the less noble Cr is mainly using the GBs as diffusion paths, the Cr-rich oxide (red) is mainly formed at the original GB and close to the Cr-rich carbides, which are consumed by oxidation (Figure 104 B - C). C: While Cr-rich oxides (red) form preferentially next to carbides (grey particle in Figure 104) and at the original GB, Fe-rich mixed spinel oxides ($A^{2+}B^{3+}_2O_4$) of varying composition form next to the Cr-rich layer. Fe is thereby preferentially found close to the oxide-metal interface, as indicated by the gradient of the mixed spinel layer (green) in Figure 104 C. Defective spinel and vacancy clusters (black) preferentially form at this interface, potentially as a result of an unavailability of trivalent cations.

The oxide-metal interface, where the voids of varying size were located, has been identified as the preferred fracture path in regions where carbides are present, as indicated by the yellow arrows in Figure 105, whereas failure in-between these regions and ahead of wider oxidation fronts was associated with a thin and incomplete GB oxidation, as highlighted by the red circles in Figure 105 (R6 and C5).

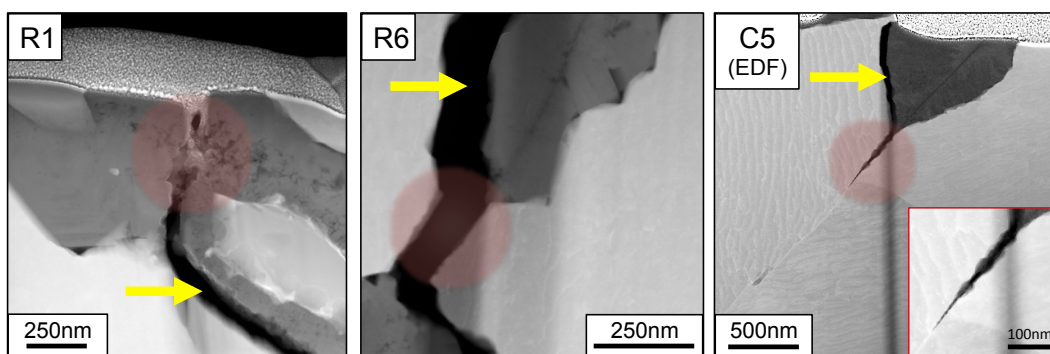


Figure 105: STEM ADF1 images of the fracture of oxidized Alloy 600 GBs. Yellow arrows mark regions where the crack progresses along the oxide-metal interface next to carbides, whereas red circles in R6 and C5 highlight fracture through thinly oxidized regions in-between or ahead of the wider oxide patches. The red circle in R1 moreover shows cracking through a porous region where the oxides of 2 IG carbides meet.

Whilst predominantly located at the metal-oxide interface, the red circle highlighted in Figure 105 R1 shows that a crack might also find its way through the IG oxide in regions where the Fe-rich oxides of two IG carbides meet.

As first suggested by Terachi *et al.* in 2000 ^[245] and more recently by Pimentel *et al.* in 2015 ^[46], it is likely that the formation of these porosities are linked to the formation of defective spinels due to the unavailability of trivalent cation species in Cr-deficient regions. Due to a local unavailability of trivalent cations, and potentially a supersaturation of divalent Fe cations, it would not be possible to complete the ratio of 1:2 for divalent (Ni, Fe, Cr) to trivalent (Fe and mainly Cr) cations, as required for the formation of stoichiometric spinels of the type $A^{2+}B^{3+}_2O_4$, as shown in Figure 106.

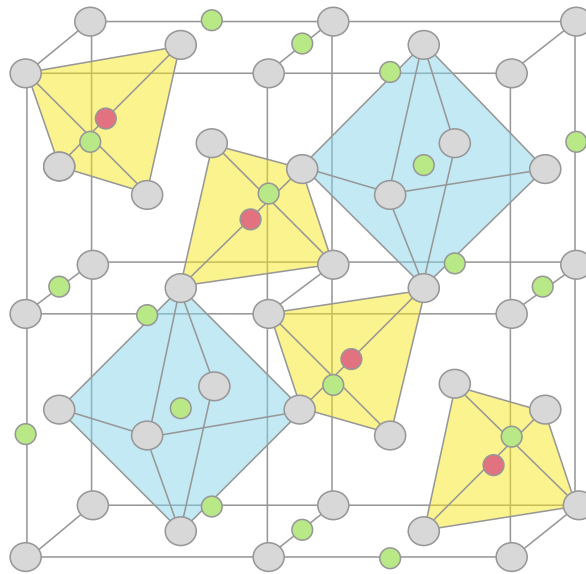


Figure 106: Stoichiometric structure of an oxide spinel, as typically found on Alloy 600. O is shown in grey, whilst A^{2+} species are located at the yellow tetrahedral sites in red and B^{3+} species are found at the blue octahedral sites in green. In a perfect spinel structure a 1:2 ratio of 2+ to 3+ is needed, meaning that for every 2+ two 3+ cations are needed.

This would consequently leave behind regions of defective oxides with less density, as observed in this study. The lesser density is thereby explained by the generation of cation vacancies. The vacancies can be of either the 2+ or 3+ type, since the

unavailability of 3+ cations in the structure would also mean that less 2+ cations are needed to finish the structure. The thereby generated cation vacancies in the defective spinel structure would then cluster to the observed voids/cavities. The formation of the vacancies to bigger volume defects, like voids, and ultimately the fracture of the interface could involve several mechanisms like *e.g.* vacancy migration, diffusion and defect nucleation at sinks like *e.g.* GBs and interfaces as well as their consequent link-up and coalescence.

The following scenarios, or a combination of either, might be proposed to explain the special role of the observed voids and their involvement in the SCC mechanism.

1. Usually the GBs act as sinks for defects like vacancies. However, as has been shown, the GBs, which prior to oxidation served as diffusion channels for the Cr cations, are converted to regions of a more compact and dense Cr_2O_3 , provided enough Cr is available. As a consequence, the weaker oxide-metal interfaces where the Cr-deprived and defective oxides are primarily located might take on the role as defect sinks. Vacancies, either coming from the oxide and/or the bulk, would get trapped at the interface, which serves as the new defect sink, and form clusters and consequently voids. In the case of Cr unavailability, *e.g.* if no intergranular carbides are present, porosity (vacancy clustering) might not be associated with an interface but could be randomly assembled within the IG oxide. This is also suggested by the nodule like Cr-rich regions seen at the GBs in between IG carbides and ahead of the wider oxidation fronts and might explain why failure through the intergranular oxide as suggested by the SIO, is possible. However, in contrast to the SIO mechanism a brittle Cr_2O_3 itself is not the mere cause of the embrittlement but the presence of defective, mixed spinel oxides and porosity.

2. While unproven, the voids at the oxide metal-interface of the INSS sample, might provide small interconnected pathways for further exposure to the environment, hence promoting IG oxidation of the already less protected regions at the oxide-metal interface. In addition to a diffusion of metal ions through the oxide scale via vacancies or interstitials this might promote the local corrosion via further vacancy injection at the additionally created nanosurface-environment interfaces of these cavities, hence initiating an oxidation of the metal as usually found at the initial stages of corrosion at the external metal-environment interface. However, due to a potential sensitization (Cr-depletion) at the internal metal-oxide interface, the oxides formed would not be protective (Cr-rich) but also of a less protective, defect-rich spinel nature.
3. Additional stress caused by the growth of the intergranular oxide layer might contribute to an increased diffusion/migration of defects, like vacancies, towards the interface. This in turn would further the formation of voids in these regions. An increased transport of vacancies towards the interface, potentially also from the bulk via dislocation climb, creates a susceptible region for cracking with an increased density of defects/voids. This in turn would again result in an exposure of the unprotected surface to the environment. As mentioned by Bertali *et al.* ^[246], the volume increase and stress associated with IG oxidation growth might moreover lead to an opening of the boundary ahead of the oxidation front, hence furthering its growth.
4. Assuming a water penetration or easy provision of O ions via a network of pores/voids is not possible, growth stresses and the formation of defective oxides seems still plausible. However, it could additionally mean that, due to a local shortage of O ions at the oxide-metal interface, additional anion vacancies are generated, which potentially affect the spinel structure and defect migration.

CHAPTER 7 Electron microscopy of tested cantilevers on oxidized alloy 600

A computational study published by Zamora *et al.* in 2016 ^[247], which is based on molecular dynamics theories, addressed the effects of cation-anion clustering on the defect migration in MgAl_2O_4 , which also has the typical $\text{A}^{2+}\text{B}^{3+}_2\text{O}_4$ structure as found on Alloy 600. Mg is thereby 2+, Al 3+ and O provides the anions. It was found that, when a 2+ vacancy clusters with an O vacancy, the defect cluster is frozen (immobilized) at temperatures ≤ 750 K. This is well within the relevant PWR temperature range. At higher temperature (2000 K) they become unstable and decay into a 3+ vacancy and O vacancy pair and a 3+ antisite defect (3+ taking a 2+ space). The clustering of 3+ vacancies and O vacancies on the other hand was found to significantly reduce the mobility of both defect components at all temperatures. Provided an exposure to the environment can be ruled out, this might explain why voids, which are essentially clusters of vacancies, are preferentially formed at the oxide-metal interface where a shortage of O, paired with the formation of cation vacancies due to a shortage of 3+ cations, might lead to a local pinning of these defects.

8 MODELLING OF THE MECHANICAL BEHAVIOUR

8.1 Quantification of the failure stress via cohesive damage FEM

8.1.1 *Material definitions and model specifications*

All cohesive zone models (see section 4.2) in this thesis were built, using representative cantilever dimensions and geometries as described in section 4.1 and were based on cohesive surface contact rather than cohesive elements. As found by Simonovski *et al.* [227], [228], a cohesive surface-based contact results in a significant increase in numerical stability when compared with its element-based counterpart. As shown in Figure 107, which compares the different discretization and tracking options, the results did not significantly change between the available options in Abaqus 6.14-2. However, as stated in the Abaqus user-manual [225], a surface-to-surface contact discretization is expected to yield the most accurate stress results. As such, a surface-to-surface discretization together with the computationally more stable and cost effective small sliding tracking option was chosen, as it was found that the finite sliding option for cohesive surfaces couldn't be used in conjunction with a surface-to-surface discretization when damage and cohesive contact interaction properties are defined. An isotropic elastic material definition was chosen for the alloy. The element type used to generate the mesh of the cohesive models was of the 3D linear brick type C3D8, as it is usually known to yield better performance for bending and contact problems than its reduced integration counterpart (C3D8R) and provides improved computational cost

when compared to *e.g.* elements of the linear quadratic, reduced integration type (C3D20R), which are usually preferred for bending problems but often cause numerical issues and non-convergence when used in problems involving contact surfaces.^{[248], [249]}

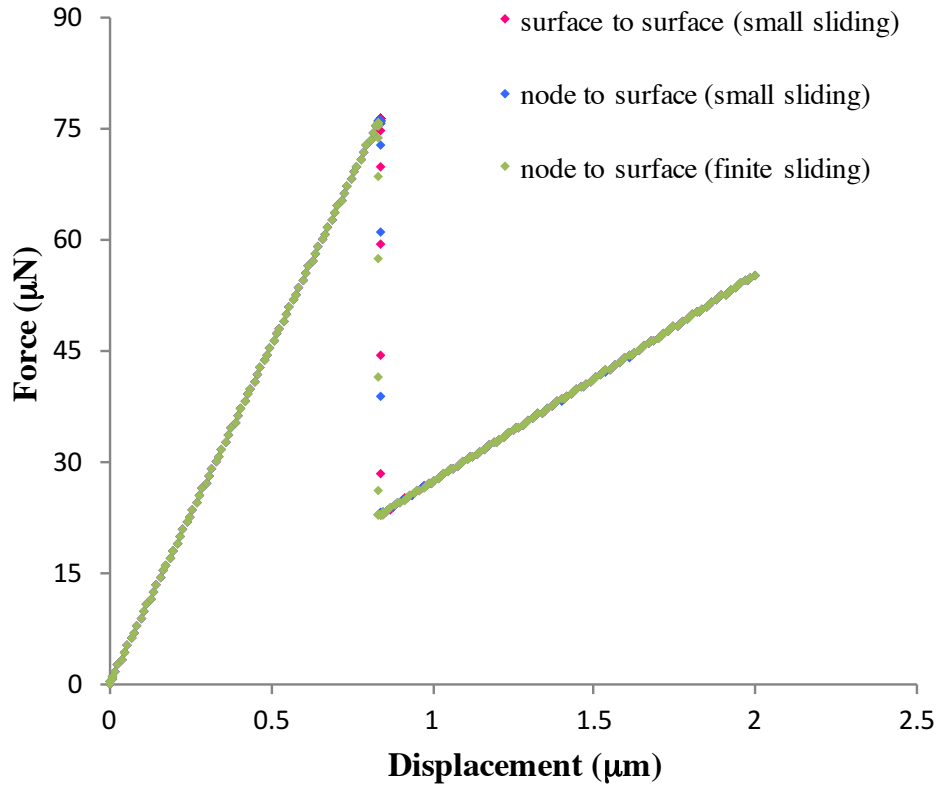


Figure 107: Comparison of the solution obtained via the different contact discretization and tracking options available in Abaqus 6.14-2.

The mesh and element size was chosen based on detailed mesh convergence studies, which allow optimization of result accuracy and computational cost. As shown in Figure 108, which shows a plot of the maximum load versus approximate global element size, a size of 100 – 200 nm was identified as sufficient for the cohesive zone models presented in this work, since the change in maximum load for elements smaller than 200 nm lied within a range of $\pm 0.1 \mu\text{N}$. Moreover, the element size along each cohesive zone of a model was validated against the required conditions for the element length (l_e) in a cohesive zone, as required by Equation 19 in section 4.2. Where

necessary, the element/mesh size was refined accordingly. Edge seeds, as defined in section 17.4 of the Abaqus user manual ^[225], satisfying the above-mentioned requirements for element size, were applied *e.g.* to make seeds of the initial slave and master surfaces line up.

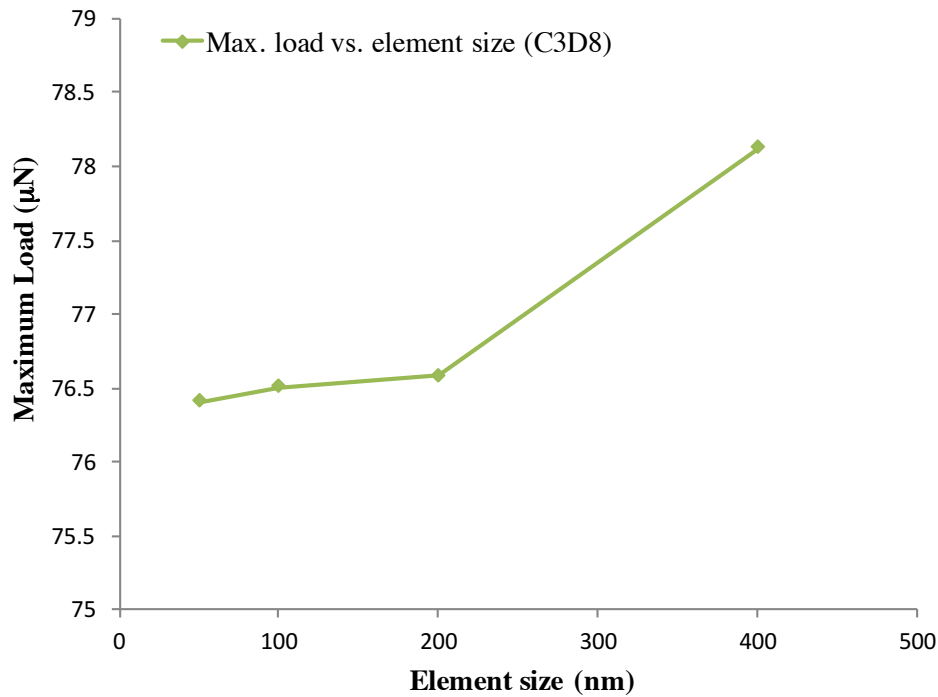


Figure 108: Maximum Load versus approximate global element size for element type C3D8.

To prevent well-known convergence issues ^[250] caused by the abrupt change of stiffness upon reaching the maximum nominal stress and the associated negative softening response, a small amount of viscous damping, as provided within the Abaqus 6.14-2 interaction property module, was applied. To prevent artificial damping the viscosity coefficient μ had to be sufficiently small. Based on the convergence of the solution, as shown in Figure 109, the viscous coefficient μ was chosen to be 10^{-6} . For details about the theory behind the cohesive zone method please refer back to section 4.2.

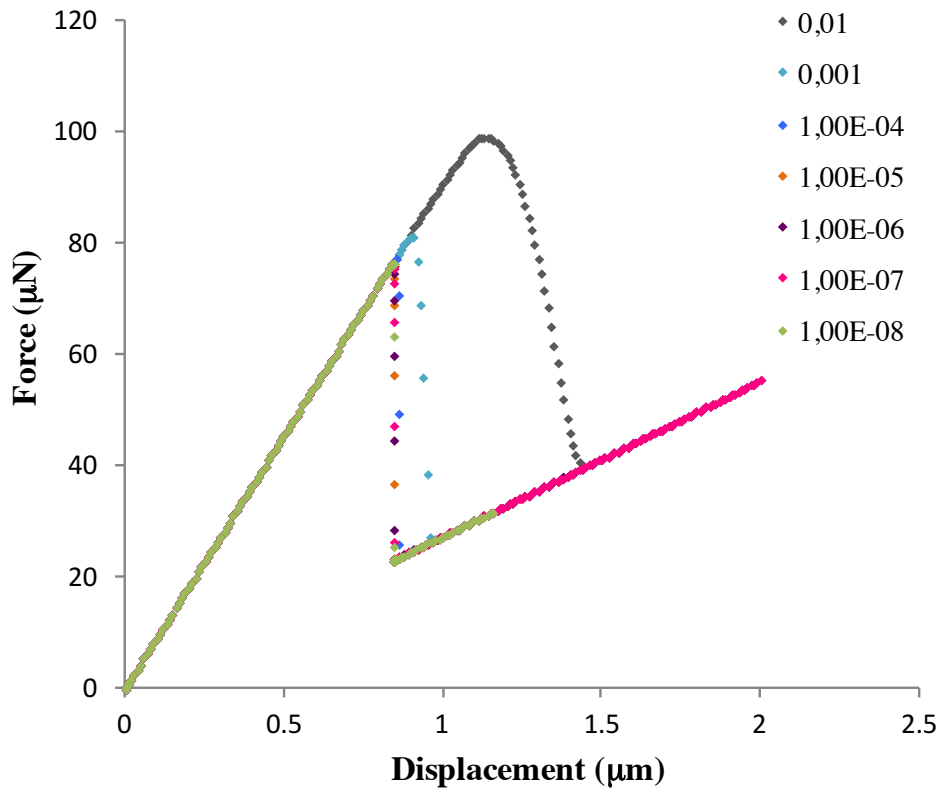


Figure 109: Influence of different viscosity coefficients μ on the convergence of the solution.

Due to the anisotropic nature of the grains for tests performed at this scale, rather than using a literature value of $E = 207 \text{ GPa}$ ^[22], the values for the elastic modulus E were individually calibrated, based on stress-strain analysis of the obtained F-D curves for each beam. In accordance with literature a Poisson ratio of $\nu = 0.29$ ^[22] was chosen. The iron-rich surface oxide layer was modelled using an elastic modulus of $E = 230 \text{ GPa}$ and Poisson ratio of $\nu = 0.262$, as found for magnetite.^[237] The carbide/oxide inclusions along the tested GBs were treated as stiff single elastic inclusions, using an elastic modulus of $E = 302 \text{ GPa}$ and Poisson ratio $\nu = 0.336$, as found for Cr_7C_3 carbides ^[238] and also close to the average of the range of values found for Cr_{23}C_6 in literature ($E = \text{ca. } 275 - 335 \text{ GPa}$ ^{[239], [240]}). To reflect the experimentally observed behaviour, linear elastic cohesive laws of diverse strength, had to be applied for different regions/interfaces along the GB (*e.g.* the metal-metal, oxide-metal and oxide-carbide

interfaces) as necessary. Details are pointed out for each model. In the cohesive zone models in this study the magnitude of the initial stiffness K was chosen to be 10 times the elastic modulus of the material, according to the following relationship established by Turon.^[251]

$$K = \alpha E t^{-1} \text{ in GPa}/\mu\text{m} \Rightarrow K_{nn} = 10 E; K_{ss} = K_{tt} = 10 \mu = \frac{10 E}{2(1+\nu)}$$

Where α is a parameter much larger than 1, E is the Young's modulus and t the thickness of the laminate, which is zero. As a consequence a unit thickness of $t = 1 \text{ mm}$ is assumed by Abaqus. The magnitude of K needs to be sufficiently high, to make sure that the resulting opening is negligible, but not too high as this might lead to numerical instabilities and a non-convergence of the solution^[229]. A non-convergence might occur when the elastic surface energy exceeds the cohesive surface energy. The opening displacement Δ_f was chosen to be 5 nm ^[252], considering $\frac{\sigma_f}{K_{ss,tt}} \leq \Delta_f$ and the damage initiation stress σ_f was calibrated against the F-D data for each modelled beam.

8.1.2 Results

As initially demonstrated in section 6.1.2, which dealt with the influence of surface oxides on the mechanical properties of the tested GBs, cohesive surface models are capable of reflecting the experimentally observed interfacial failure of oxidized GBs and can be used to quantify the stress at failure σ_f , which is otherwise estimated via simple beam theory (section 3.5). As detailed in section 6.1.2, a normal stress at failure σ_f value of 575 MPa was found, as compared to a beam theory estimate of 522 MPa . This suggested an error between the quantified FEM value and corresponding simple beam theory value of $< 10\%$. As a consequence, in addition to the model presented in section 6.1.2 for two cantilevers tested on the same GB, 3 more fractured cantilevers (R4, R6 and C5) were simulated via cohesive damage simulations to compare

experimental and simulated values and to further validate the accuracy of the overall stress results obtained within the frame of this thesis. It should be noted, that in contrast to the cantilevers in section 6.1.2, which showed a thicker and rather homogeneous surface oxide layer on top of the free end grain, as shown in Figure 110 (C3, no loosely distributed crystallites), the other beams, which will be discussed in the following, showed only scarcely distributed crystallites of varying size (red arrows in Figure 110) on top of their respective free end side grain. As these scarcely distributed crystallites were not suitable for averaging or treatment as a continuous layer, no averaged homogeneous surface oxide layer on top of the long end side of these beams was considered in the following simulations.

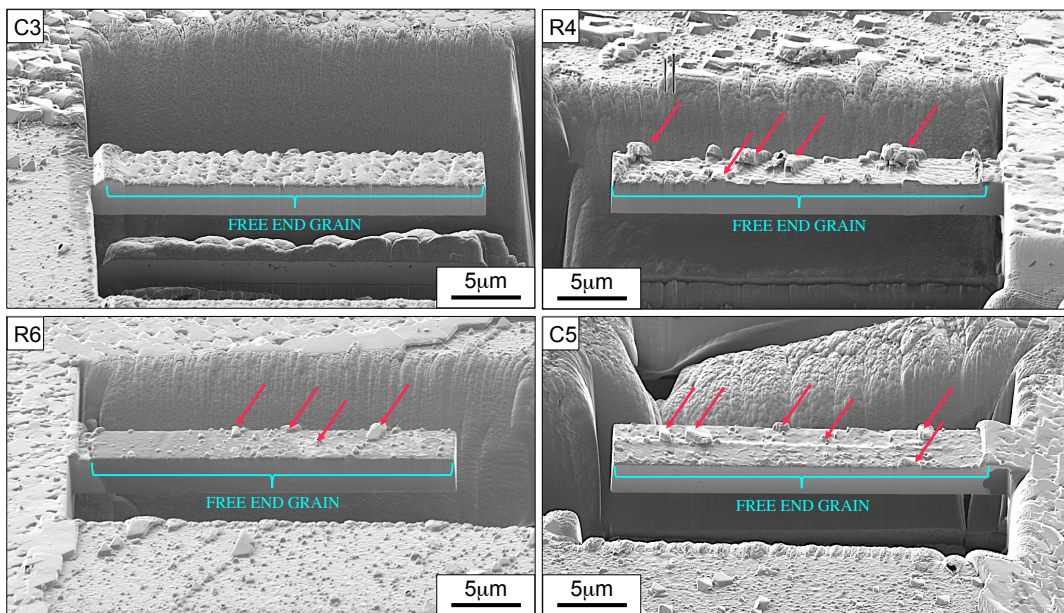


Figure 110: SEM SE images of the cantilevers, which have been simulated via cohesive zone FEM. C3, which was modeled and discussed in section 6.1.2, showed a rather homogeneous surface oxide layer along the free end grain of the cantilever, which was suitable for treated as an homogeneous surface oxide layer of ~ 120 nm thickness in the simulation. No homogeneously thick surface oxide layer on the free end side of the grains of R4, R6 and C5 has been included in the respective models, as the surface oxide only showed scarcely distributed crystallites of varying size (red arrows), which were not suitable for averaging or a treatment as homogeneous layer.

8.1.2.1 Stress at failure of cantilever R4 (A600-INSS)

The cantilever denoted R4 on A600-INSS had no surface oxide overlap, as it was removed according to the procedure described in section 6.1.2 (Figure 52). Using the experimental F-D curve of the beam shown in Figure 111 (R4 exp.), which revealed a merely brittle behaviour, the cohesive properties were calibrated against the experimental behaviour of the beam. As can be seen, the FEM model reflected the experimental curve (Figure 111, R4 FEM) and fracture path (Figure 112) really well.

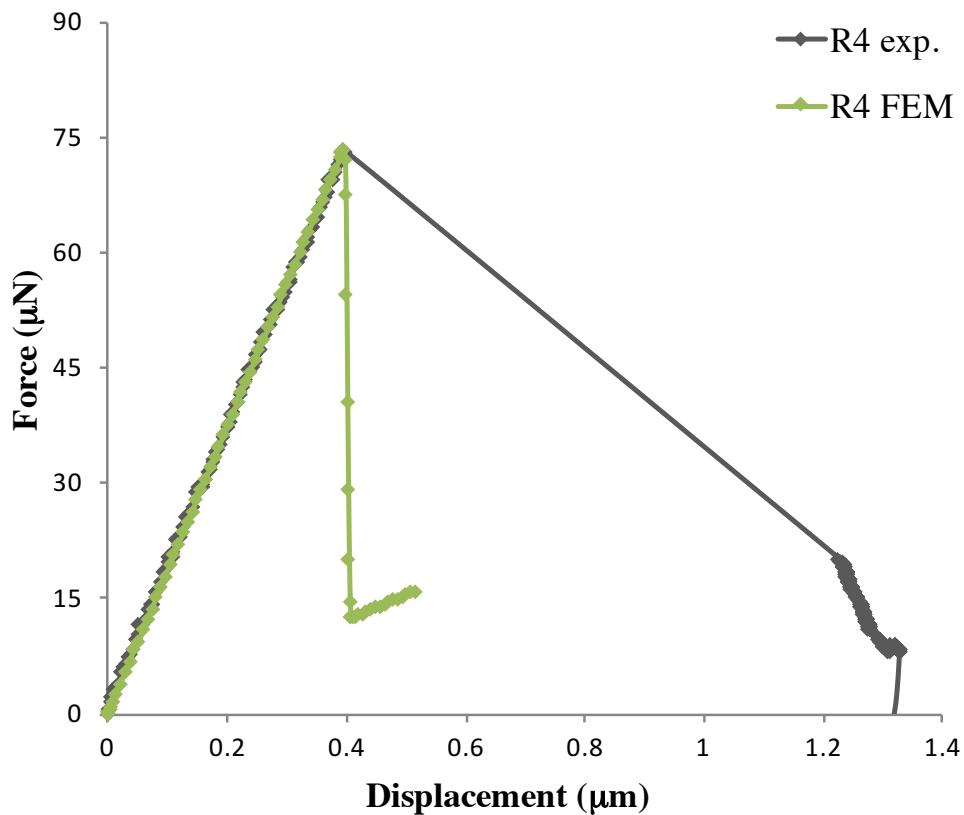


Figure 111: Comparison of the experimental and computational F-D curves of cantilever R4. The FEM curve has been predicted using the cohesive parameters summarized in Table 27.

Table 27 shows a summary of the 3 cohesive laws used in the model of R4. As indicated in Figure 113, besides the usual oxidized (*Law 1*, yellow) and unoxidized regions (*Law 3*, black), a second and stronger oxidized law (*Law 2*, blue) was needed to make the crack propagate as observed in the experiment. This indicated that individual

oxidized interfaces have different cohesive properties. This might be linked to the degree of porosity along the respective oxide-metal interfaces. A Young's modulus E of 130 GPa was found to be the best fit and the normal stress at failure σ_f was found to be 330 MPa. This is in good agreement with σ_f and E obtained via simple beam theory, which were 362 MPa and 121 GPa respectively, as summarized in Table 34, hence being within a 10% error between the simulated and experimental values.

CANTILEVER R4

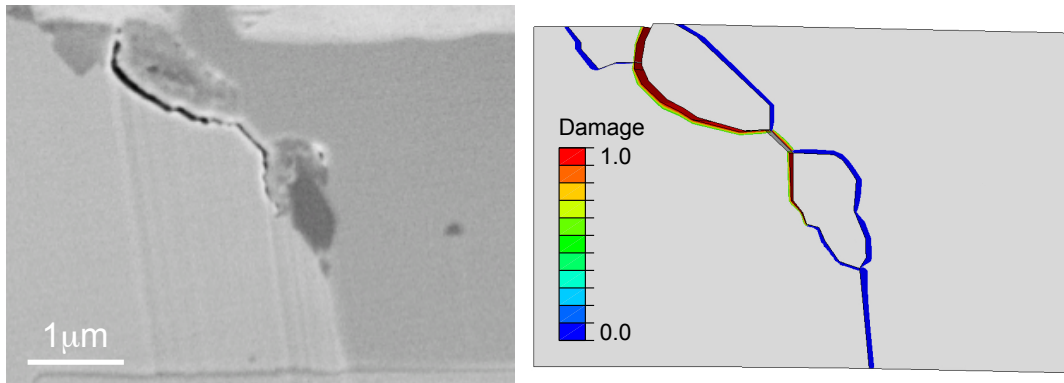


Figure 112: SEM SE image of the central GB portion of cantilever R4 after testing (left) and corresponding FEM model (right). Using realistic cantilever geometry and microstructure and cohesive surface FEM simulations the experimentally observed fracture path was reproduced.

	Δ_f (nm)		σ_f (MPa)	K (GPa/ μm)
LAW 1: (Oxidized)	5	Normal:	330	1300
		Shear _{1,2} :	330	503.88
LAW 2: (Ox. Strong)	5	Normal:	2000	1300
		Shear _{1,2} :	2000	503.88
LAW 3: (Unoxidized)	5	Normal:	5000	1300
		Shear _{1,2} :	5000	503.88

Table 27: Cohesive laws as used for the oxidized (*Law 1* and *Law 2*) and unoxidized regions (*Law 3*) in model R4. Δ_f is the opening displacement, σ_f the maximum nominal stress (stress at failure) in normal and shear directions and K the initial stiffness in normal and shear directions.



Figure 113: Cut through the center of the cohesive surface FEM model of cantilever R4 before the deformation. The 3 cohesive laws, applied at the individual interfaces, as also summarized in Table 27, are indicated in different colors.

8.1.2.2 Stress at failure of cantilever R6 (A600-INSS)

Same as cantilever R4 in the previous section, the cantilever denoted R6 had no surface oxide overlap. Using the experimental F-D curve of the beam shown in Figure 114, the cohesive properties were calibrated against the experimental behaviour of the beam. Again, the FEM model reflected the experimental curve (Figure 114) and observed fracture path (Figure 115) well. Table 28 shows a summary of the applied cohesive laws in the model, which were necessary to capture the real fracture path. Interfaces at which the laws were applied are moreover highlighted in Figure 116. Same as for model R4, 2 different laws were needed for the oxidized regions, indicating differences in cohesive properties of different interfaces. A Young's modulus E of 203 GPa was found to be the best fit and the normal stress at failure σ_f was found to be 445 MPa. This is in good agreement (within 10%) with the σ_f and E obtained via simple beam

theory estimations, which was 494 MPa and 185 GPa respectively, as also summarized in Table 34.

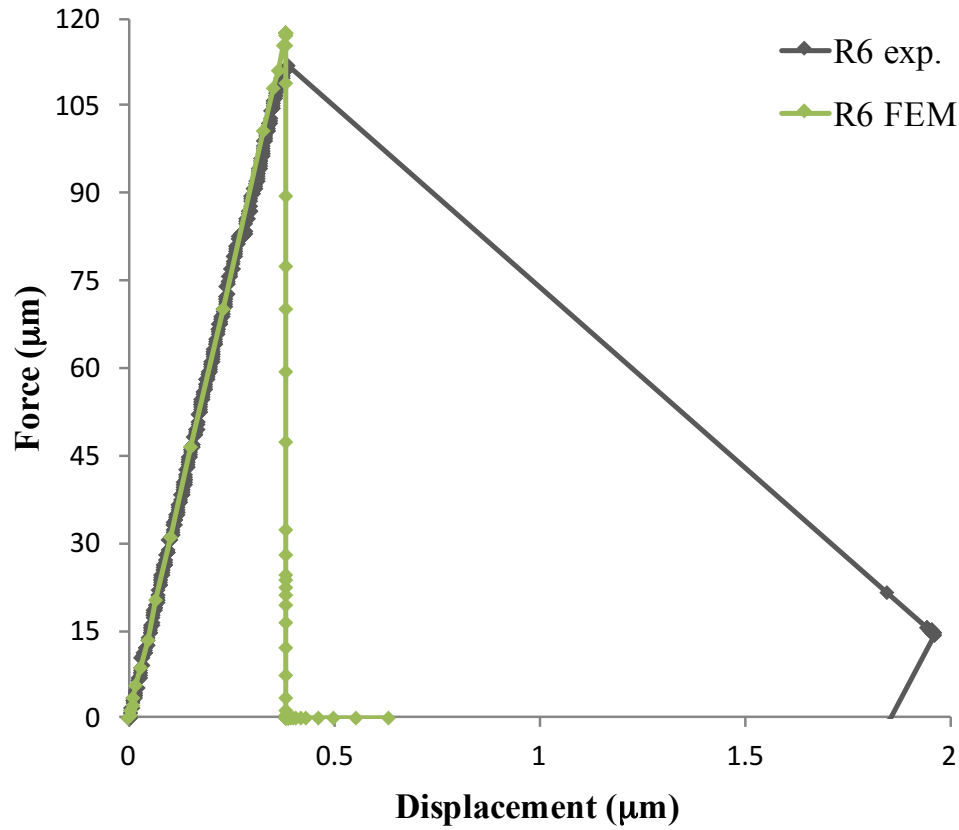


Figure 114: Comparison of the experimental and computational F-D curves of cantilever R6. The FEM curve has been calibrated against the experimental behaviour using the cohesive parameters summarized in Table 28.

	Δ_f (nm)		σ_f (MPa)	K (GPa/ μm)
LAW 1:	5	Normal:	445	2030
(Oxidized)		Shear _{1,2} :	445	786.82
LAW 2:	5	Normal:	2000	2030
(Ox. Strong)		Shear _{1,2} :	2000	786.82

Table 28: Cohesive laws as used for the oxidized (*Law 1* and *Law 2*) and unoxidized regions (*Law 3*) in model R6. *Law 1* was as used for the oxidized regions and *Law 2* was needed to capture the experimental crack path. Δ_f is the opening displacement, σ_f the maximum nominal stress (stress at failure) in normal and shear directions and K the initial stiffness in normal and shear directions.

CANTILEVER R6

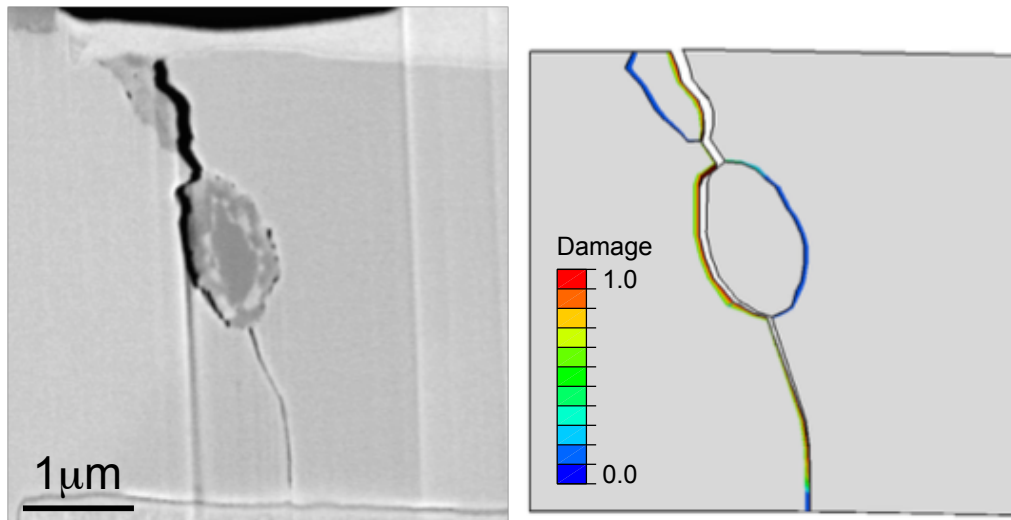


Figure 115: SEM SE image of the central GB portion of cantilever R6 after testing (left) and corresponding FEM model (right). Using realistic cantilever geometry and microstructure and cohesive surface FEM simulations the experimentally observed fracture path was reproduced.

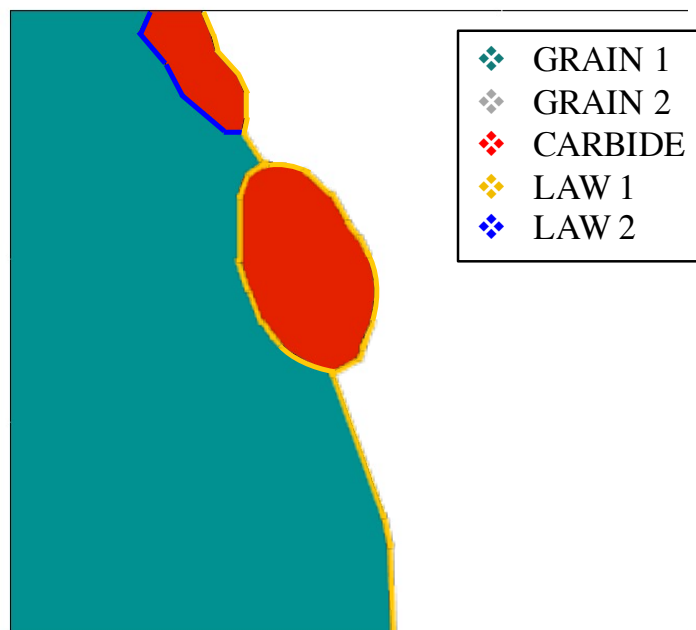


Figure 116: Cut through the center of the cohesive surface FEM model of cantilever R6 before the deformation. The 2 cohesive laws, applied at the individual interfaces, as also summarized in Table 28, are indicated in different colors.

8.1.2.3 Stress at failure of cantilever C5 (A600-INSS)

The cantilever denoted C5 on A600-INSS showed a minor surface oxide overlap, as can be seen in the ADF1 STEM image in Figure 117. Subsequently, the overlapping surface oxide crystallite had to be considered in the model. Using the experimental F-D curve (Figure 118, C5 exp.), which revealed minor plastic deformation before failure, the cohesive properties were calibrated against the major load-drop and the 1st noticeable load-drop in the experimental curve of the beam.

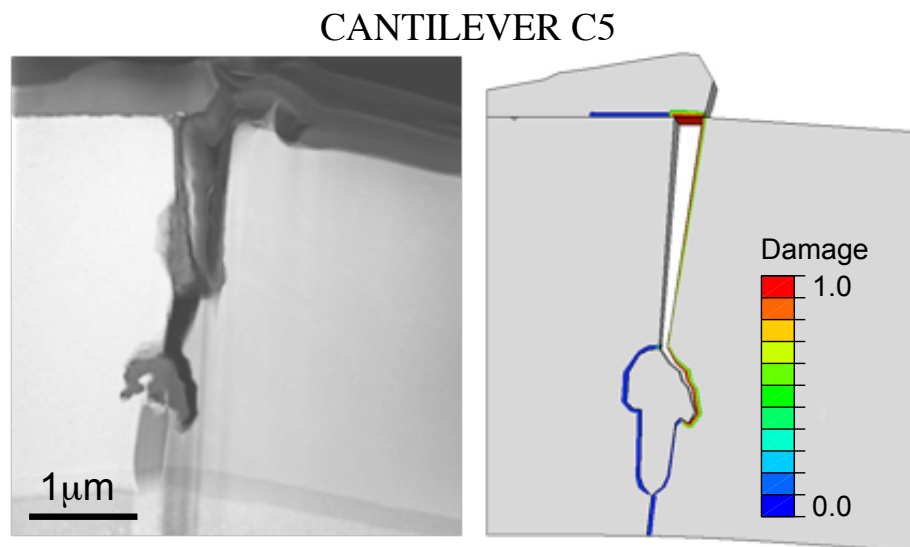


Figure 117: STEM ADF image of the central GB portion of cantilever C5 after testing (left). The corresponding FEM model is shown on the respective right side. Using realistic cantilever geometry and microstructure and cohesive surface FEM simulations the experimentally observed fracture path was reproduced.

As can be seen in Figure 118, the FEM model reflected the experimental curve and observed fracture path (Figure 117) really well. The 3 applied cohesive laws, which were needed to reflect the experimentally observed fracture path, are summarized in Table 29 and Table 30, for the major and 1st noticeable load-drop respectively. Areas at which the 3 cohesive laws were applied are moreover highlighted in Figure 119.

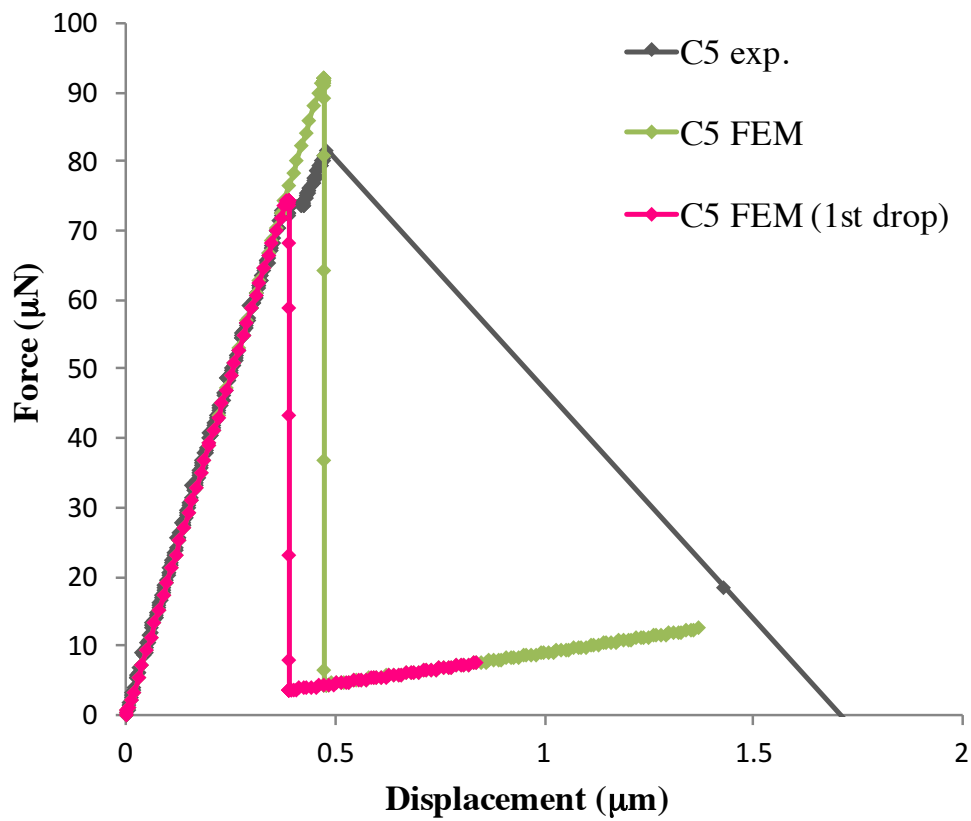


Figure 118: Comparison of the experimental and computational F-D curves of cantilever C5. The FEM curves for C5, including a second simulation calibrated against the 1st noticeable load-drop (pink curve), have been predicted using the cohesive parameters summarized in Table 29 and Table 30.

	Δ_f (nm)		σ_f (MPa)	K (GPa/ μm)
LAW 1:	5	Normal:	330	1270
(Oxidized)		Shear _{1,2} :	330	492.25
LAW 2:	5	Normal:	330	1270
(Surf. Ox.)		Shear _{1,2} :	125	492.25
LAW 3:	5	Normal:	5000	1270
(Unoxidized)		Shear _{1,2} :	5000	492.25

Table 29: Cohesive parameters used to calibrate the maximum nominal stress (failure stress) against the main load-drop in the experimental curve (Figure 118). *Law 1* was as used for the oxidized regions, *Law 2* at the surface-oxide interface and *Law 3* in unoxidized regions of model C5. Δ_f is the opening displacement, σ_f the maximum nominal stress (stress at failure) in normal and shear directions and K the initial stiffness in normal and shear directions.

	Δ_f (nm)		σ_f (MPa)	K (GPa/ μm)
LAW 1:	5	Normal:	265	1270
(Oxidized)		Shear _{1,2} :	265	492.25
LAW 2:	5	Normal:	265	1270
(Surf. Ox.)		Shear _{1,2} :	85	492.25
LAW 3:	5	Normal:	5000	1270
(Unoxidized)		Shear _{1,2} :	5000	492.25

Table 30: Cohesive laws used to calibrate the maximum nominal stress (failure stress) against the 1st noticeable load-drop in the experimental curve (Figure 118). *Law 1* was as used for the oxidized regions, *Law 2* at the surface-oxide interface and *Law 3* in unoxidized regions of model C5. Δ_f is the opening displacement, σ_f the maximum nominal stress (stress at failure) in normal and shear directions and K the initial stiffness in normal and shear directions.

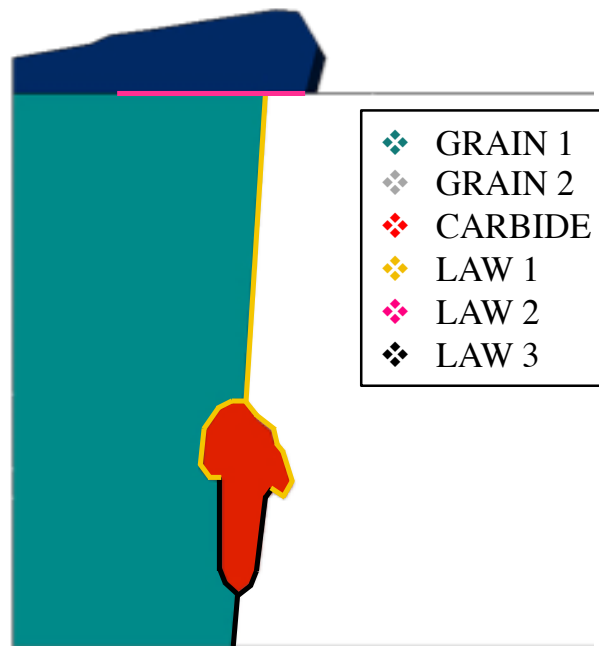


Figure 119: Cut through the center of the cohesive surface FEM model of cantilever C5 before the deformation. The 3 cohesive laws, applied at the individual interfaces, as also summarized in Table 29 and Table 30, are indicated in different colors.

A Young's modulus E of 127 GPa was found to be the best fit and the normal stress at failure σ_f was found to be 330 MPa at the major fracture event and 265 MPa at the 1st

noticeable load-drop. This is in good agreement with σ_f and E from simple beam theory estimations, where the stress was found to be 362 MPa (major load-drop) and 289 MPa (1st noticeable load-drop) respectively. The simple beam theory value for E was estimated to be 116 GPa.

8.2 Crystal plasticity FEM: Towards a more realistic simulation

The initial incentive for trying to use the strain gradient crystal plasticity formulation and code, as developed by Dunne *et al.* ^[180] and briefly described in section 4.3, was to try and combine it with the cohesive damage models in the previous chapter (8.1) for an even more realistic representation of the experiments and to not only capture the brittle (linear elastic) response of the beams but also any eventual plastic deformation taking place before the ultimate fracture event. Nonetheless, very early in the process it was found that the code couldn't be used in conjunction with cohesive surfaces, as convergence of the solution could not be achieved. The reasons are not entirely clear but might be related to the use of quadratic, reduced integration type elements (C3D20R), which are known to cause convergence issues in problems involving contact ^[248] but were the only element type currently supported by the provided UMAT. Though it would have been interesting to combine the cohesive damage models with the provided crystal plasticity subroutine, this would have needed for further development of the advanced UMAT subroutine, *e.g.* an extension to C3D8 type elements, and consequently exceeded the scope of this thesis. Nonetheless, as described in section 6.3, unoxidized A600 beams were tested and shown to never experience failure but plastic deformation only. Hence, one of the beams was used as simplified system to test the code and check whether it is possible to accurately reproduce the experimentally recorded F-D behaviour.

8.2.1 Material definitions, model specifications and relevant quantities

The anisotropic elastic material definition for the alloy in the crystal plasticity model was based on the cubic elastic constants of Alloy 600, which was adapted from published data available in literature.^[253] The constants are given in Table 31.

C11	C22	C44
234.6 GPa	145.4 GPa	126.2 GPa

Table 31: Elastic constants for Alloy 600, as given by ^[253].

In a cubic material $c_{11} = c_{22} = c_{33}$, $c_{12} = c_{21} = c_{13} = c_{31} = c_{23} = c_{32}$ and $c_{44} = c_{55} = c_{66}$ and all other terms are zero. Applying these rules, one can calculate elastic modulus E , poison ratio ν and shear modulus μ , using the following relationships:^{[254], [255]}

$$E_1 = E_2 = E_3 = E = \frac{c_{11}^3 + 2c_{12}^3 - 3c_{11}c_{12}^2}{(c_{11}^2 - c_{12}^2)} \quad \text{Equation 33}$$

$$\nu_{12} = \nu_{21} = \nu_{31} = \nu_{13} = \nu_{23} = \nu_{32} = \nu = \frac{(c_{12}c_{11} - c_{12}^2)}{(c_{11}^2 - c_{12}^2)} \quad \text{Equation 34}$$

$$\mu_{12} = \mu_{13} = \mu_{23} = \mu = c_{44} = \frac{1}{s_{44}} \quad \text{Equation 35}$$

This gives a Young's modulus $E = 123.3$ GPa, a Poisson's ratio $\nu = 0.38$ and a shear modulus of $\mu = 126.2$ GPa, as also summarized in Table 32. The element type used to generate the mesh of the model was of the 3D linear quadratic, reduced integration type C3D20R ^[225], as, besides yielding most accurate results for cantilever bending ^[249], it was the only element type implemented in the subroutine. Mesh/element size was chosen based on mesh convergence studies (Figure 120). Ultimately, an element size of 300 nm was chosen as it was found that a further decrease in element size leads to instability and an early non-convergence of the solution. The reasons are unclear.

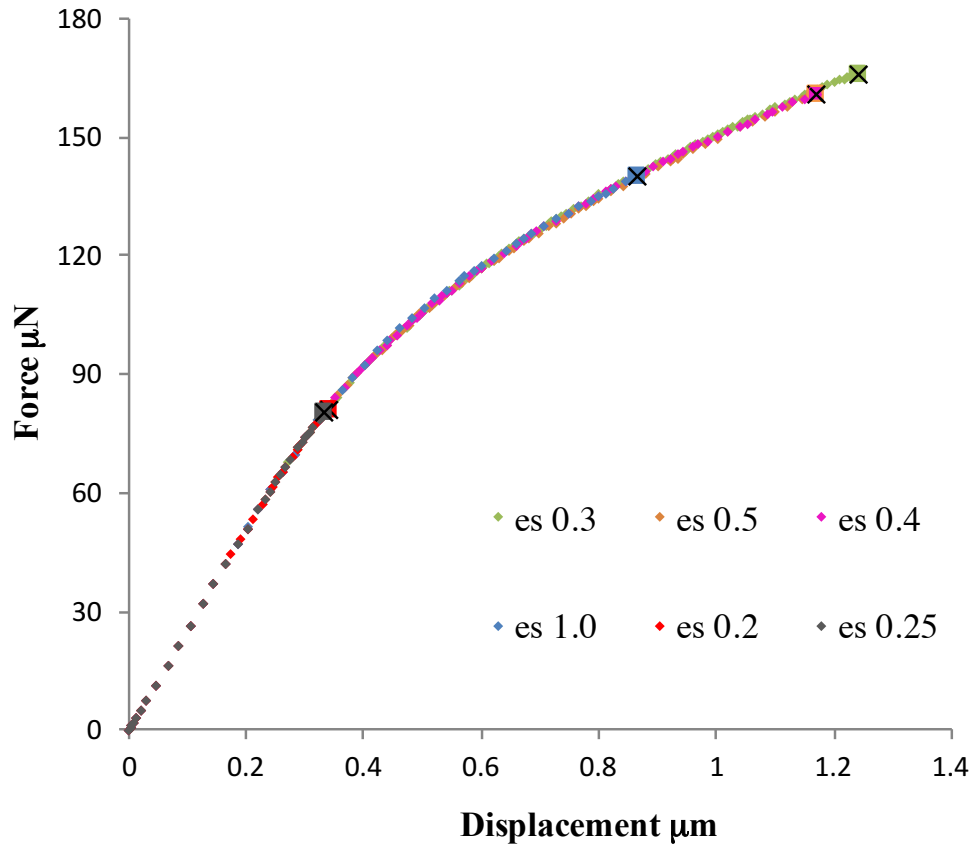


Figure 120: Mesh convergence study for crystal plasticity simulations of a deformed beam. Due to convergence issues (black X marks the crash point) for an element size smaller than 300 nm ($es = 0.3$), 300 nm was chosen for the simulation.

Besides implementing the real beam dimensions and GB path, the Euler angles (φ_1 , Φ , φ_2) of beam C3 tested on *EDF-NOX* were extracted via conventional bulk EBSD, as no surface oxide was present, and were found to be (145°, 20°, 258°) for grain 1 (G1, fixed end) and (61°, 54°, 322°) for grain 2 (G2, free end) in Bunge notation (ZX'Z''). The Matlab script in APPENDIX A was then used to transform the Euler angles into the rotation matrices, defined as R_G1 and R_G2 in the Matlab code, for G1 and G2. This corresponds to a misorientation of 37.6°. The matrix elements for G1 and G2 were then directly fed into Abaqus 6.14-2, by defining the materials for G1 and G2, using the materials property module and *General > Depvar* to give the number of solution dependent state variables (SDVs = 89) as defined by the code, and *General >*

CHAPTER 8 Modelling of the mechanical behaviour

User Material (mechanical) to select the material and add the mechanical constants for each grain (9 matrix elements). This way the real crystal orientations for both grains (before any displacement) were implemented, hence allowing the UMAT to determine any slip activation of the differently oriented grains, via the slip rule below (also shown in Equation 23 in section 4.3).

$$\dot{\gamma}^i = \rho_{SSD}^m b^{i2} v \exp\left(-\frac{\Delta F}{kT}\right) \sinh\left(\frac{(\tau^i - \tau_c^i) \gamma_0 \Delta V^i}{kT}\right)$$

$$\Delta V^i = l b^{i2}; l = \frac{1}{\sqrt{\psi(\rho_{SSD}^s + \rho_{GND})}}$$

Whilst most constants were taken from literature ^[232], the 4 values shown above in red could be altered in the code to calibrate the simulated curve against the experimentally recorded behaviour. The values were γ_0 , the shear strain that is work conjugate to the resolved shear stress, ψ , the likelihood of dislocation pinning, the mobile SSD density ρ_{SSD}^m and the critical resolved shear stress τ_c .^[233] While γ_0 and ψ , were used as found in Kartal *et al.* ^[232], ρ_{SSD}^m and τ_c were used to fit the model to the experiment. The critical resolved shear stress τ_c governs the yield point. As shown in Figure 121, the higher τ_c the bigger the linear elastic regime, as slip only initiates when the resolved shear stress exceeds the critical value.

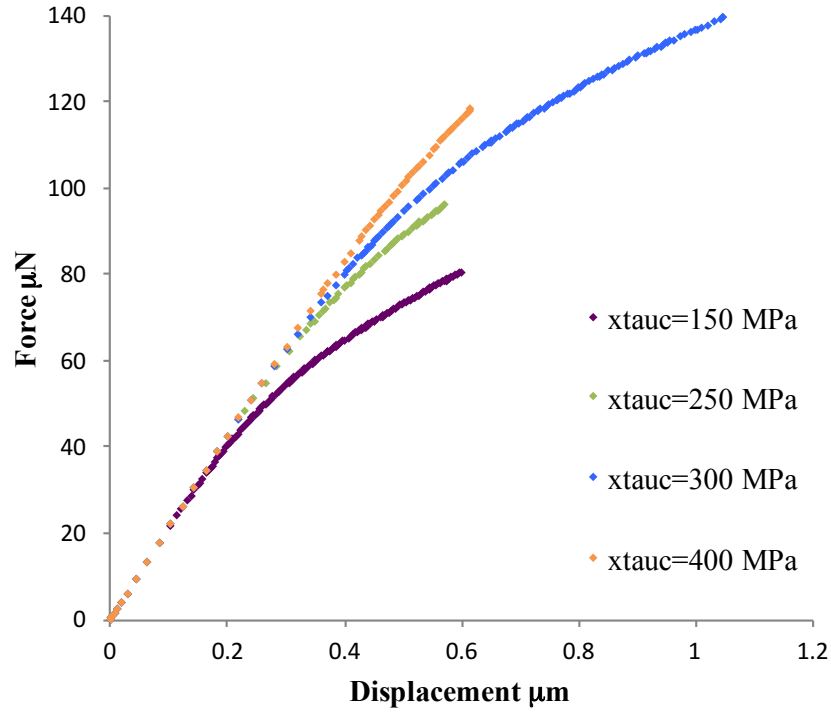


Figure 121: Variation of the critical resolved shear stress $\tau_c(x\tau_{auc})$ only, showing its influence on the linear elastic region. ρ_{SSD} was kept constant at 0.055 m^{-2} .

The variation of the ρ_{SSD}^m , same as γ_0 and ψ influenced the hardening region. Consequently, only ρ_{SSD}^m was changed during calibration. Figure 122 shows the influence of ρ_{SSD}^m on the hardening. It was found that for ρ_{SSD}^m and γ_0 , the higher the values were, the closer the hardening got to perfectly plastic behaviour, approaching a flat curve progression. The higher the mobile dislocation density, the easier the plastic flow. However, the higher ψ , the steeper the curve progression (Figure 123), as a higher pinning probability of dislocations means less plastic flow and hence increased strain hardening. In general one can see that different values for these constants resulted in different crashing points of the code. While the reasons for the crash were not 100% clear it was noticed that the less strain hardening occurred and the closer the curve progression got to ideal plastic behaviour the more likely an early crash was.

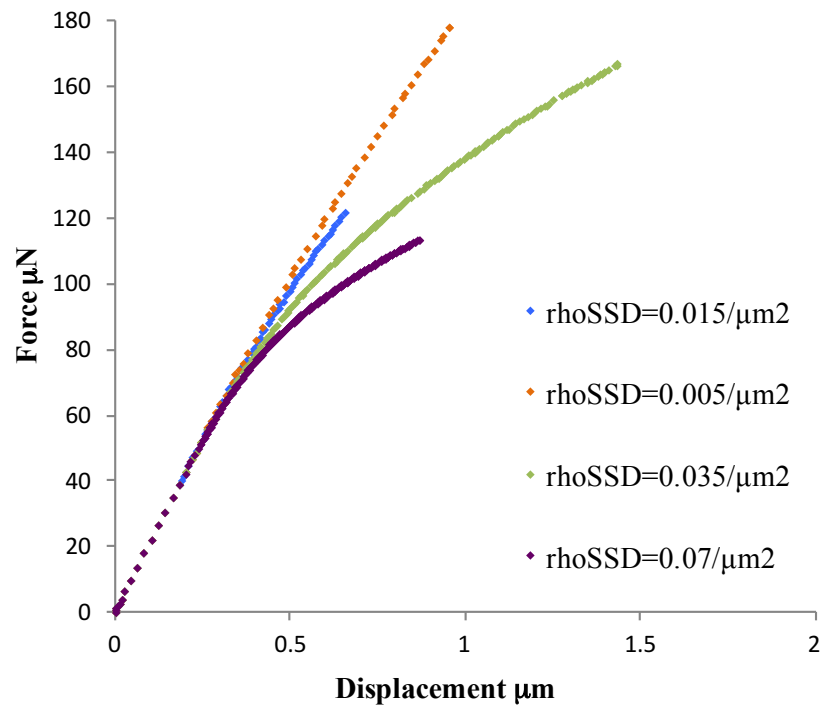


Figure 122: Variation of ρ_{SSD}^m (ρ_{SSD}), showing its influence on the hardening region. X_{tauc} was kept constant at 250 MPa.

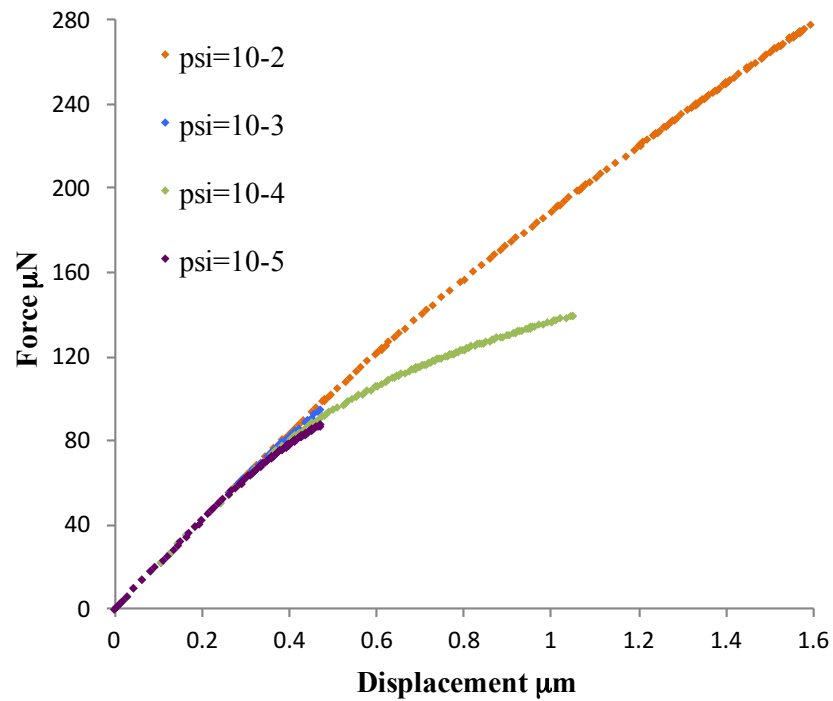


Figure 123: Variation of pinning probability ψ (ψ), showing its influence on the hardening region.

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All chosen values for the material properties are summarized in Table 32. As can be seen, the elastic constants were adjusted to reflect Alloy 600, using Equation 33, Equation 34 and Equation 35. ρ_{SSD}^m (plastic regime) and τ_c (elastic regime) were fitted against the experimental results, as discussed in the following section. The other constants were already implemented in the code by work performed by Dunne *et al.* [232] carried out on a Ni-base superalloy and needed no changing.

UMAT PROPERTIES VALUES		
Young's modulus E	123.3 GPa	Based on the elastic constants for A600 from [253]
Poisson's ratio ν	0.38	Based on the elastic constants for A600 from [253]
Shear modulus μ	126.2 GPa	Based on the elastic constants for A600 from [253]
Burger's vector b	3.5072 Å	Taken from [232]
Helmholtz free energy ΔH	3.45x10 ⁻²⁰ J	Taken from [232]
Boltzman constant k	1.381x10 ⁻²³ J K ⁻¹	Taken from [232]
Temperature T	293K	
Frequency of attempts ν	1x10 ¹¹ s ⁻¹	Taken from [232]
ρ_{SSD}	1x10 ¹⁰ m ⁻²	Taken from [232]
τ_c (xtauc)	300 MPa	Fitted
ρ_{SSD}^m (RhoSSD)	0.055 m ⁻²	Fitted
Nominal strain γ_0	8.33 10 ⁻⁶	Taken from [232]
Probability of pinning ψ	1.457x10 ⁻⁴	Taken from [232]

Table 32: Summary of the chosen values for the material properties required by the UMAT to achieve the fit shown in the F-D graph in Figure 124.

8.2.2 Results

Figure 124 shows the experimental F-D curve of beam C3 (*A600-NOX*), tested in section 6.3 of this thesis, and the corresponding, calibrated crystal plasticity FEM curve, which was obtained based on the values in Table 32. As can be seen the simulated curve (green) reflects the experimentally obtained behaviour well, proving

that the subroutine is suitable for accurately capturing the mechanic response of tested beams. This further highlights that a combination with cohesive damage is highly desirable even though the code in its current state often failed to converge, which needs to be investigated in future work.

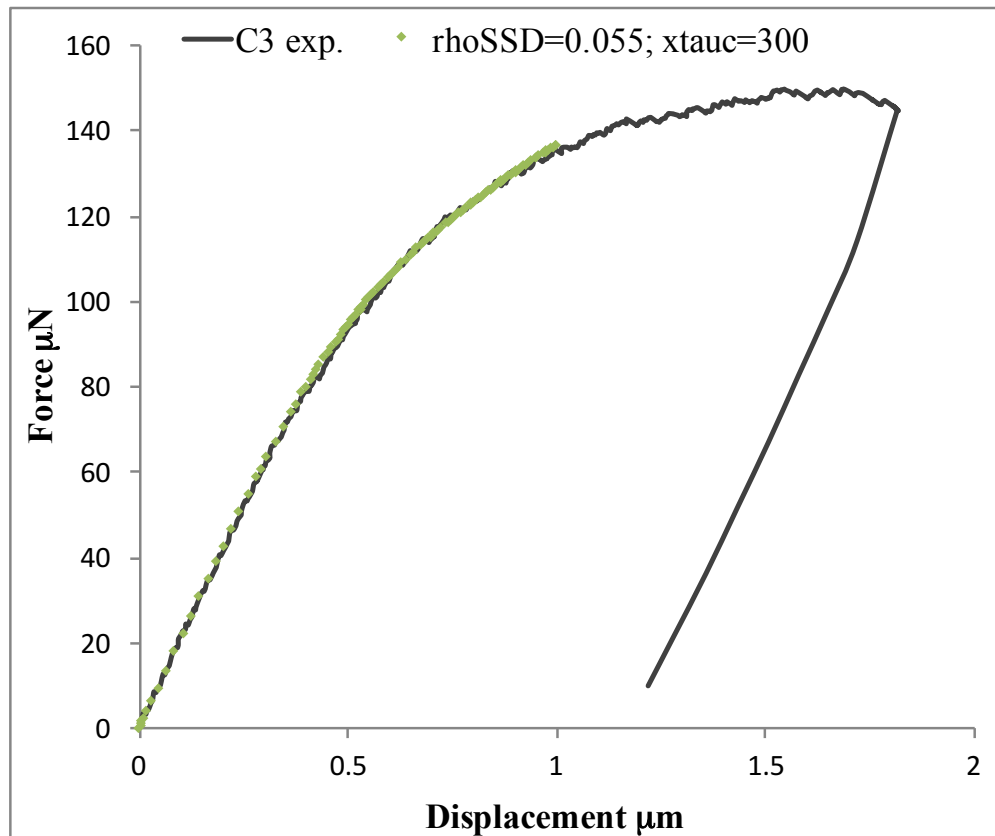


Figure 124: Comparison of the experimental and computational F-D curves of cantilever C3 (*A600-NOX*). The crystal plasticity FEM curve (green) has been predicted using the parameters given in Table 32.

As can be seen in Figure 125, slip lines were mainly found at the bottom of the beam after deformation. When compared to the simulated GND density, summarized over all active slip systems (Figure 126), it can be seen that the density is highest near the bottom of the beam where the slip lines were usually seen in the experiment (Figure 125 AFTER). For a 900 nm displacement a maximum GND density of $8.4 \times 10^3 / \mu\text{m}^2$ can be estimated using the following relationship.

$$\rho \approx \frac{1}{D^2} \approx \frac{b}{\theta} \approx \frac{bL}{u} \approx \frac{u^2}{b^2 L^2} \approx 8.4 \times 10^3 / \mu m^2, \quad \text{Equation 36}$$

with D being the dislocation distance, θ the angle of misorientation, u being the 900 nm displacement, burger's vector $b = 3.5 \times 10^{-4} \mu m$ and L being the length of the cantilever ($L = 28 \mu m$). Even though this is a very rough estimate, which lacks experimental significance, it showed that the simulated values for the GND density are sensible.

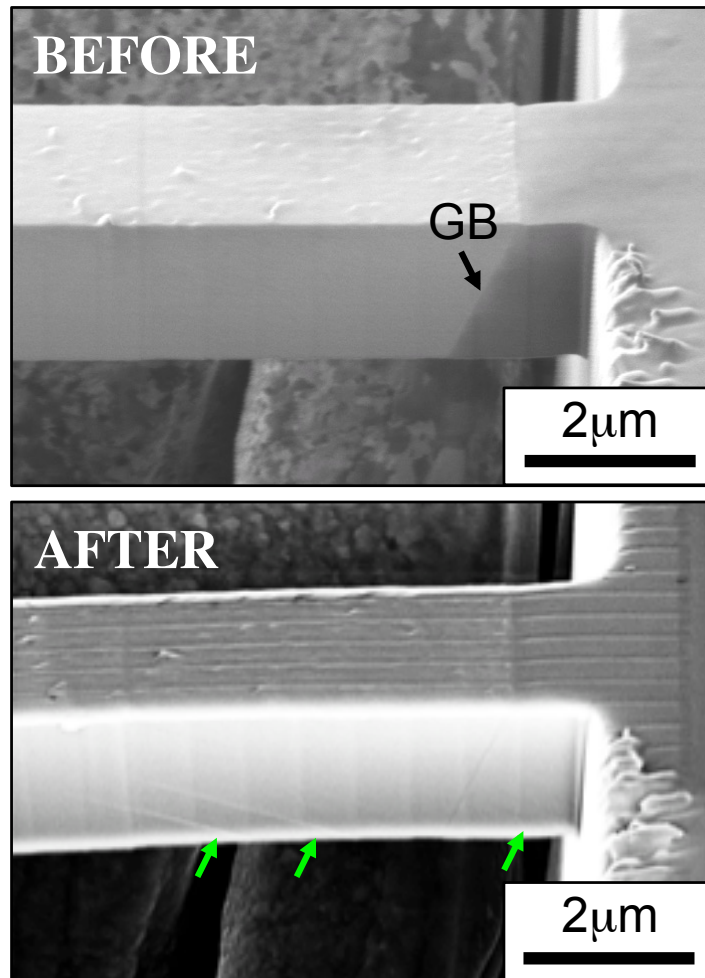


Figure 125: (top) SEM SE image of C3 before testing. (bottom) SEM in-lens image of C3 after testing. Slip lines (green arrows) are found at the bottom of the beam.

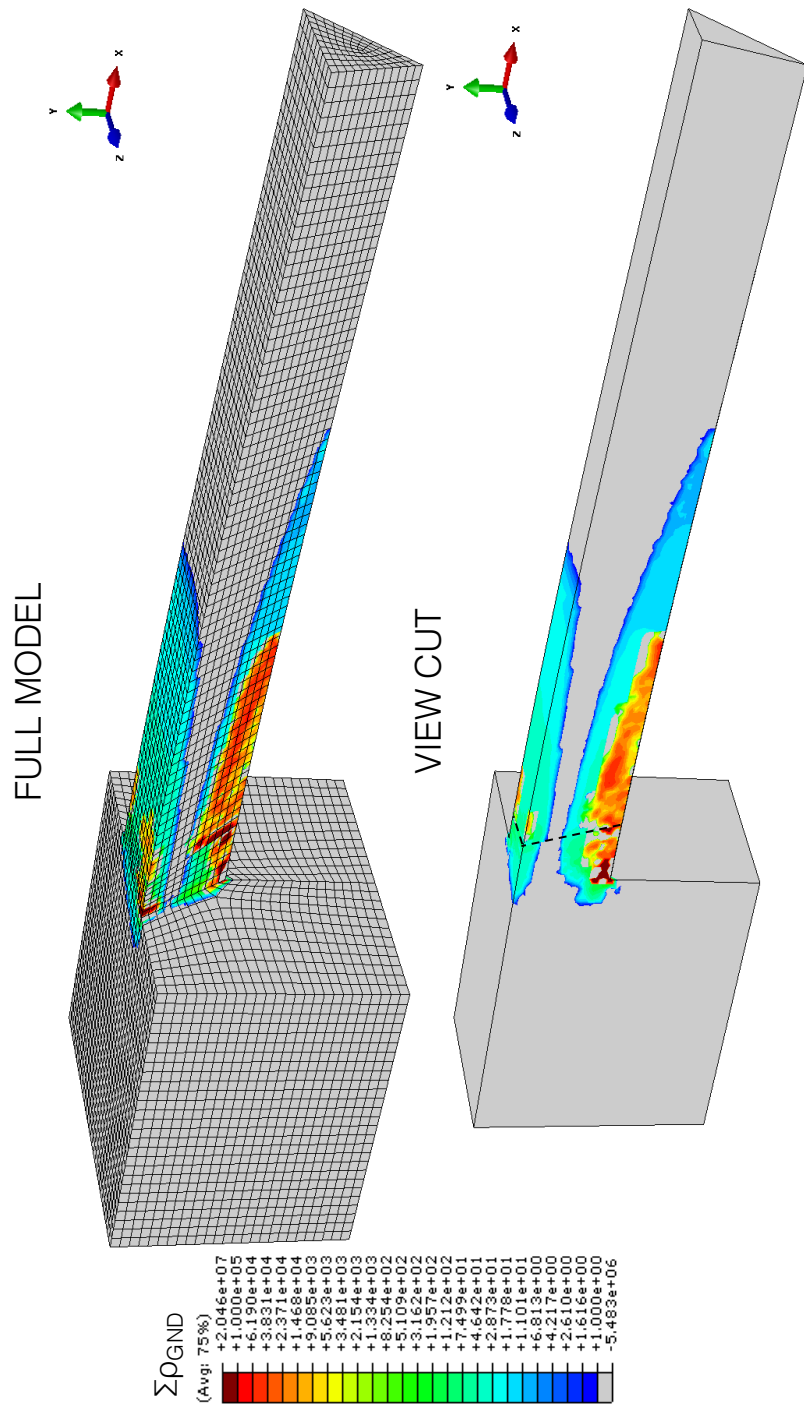


Figure 126: Full model and view cut of the crystal plasticity model of beam C3 on A600-NOX, showing the summation over all GND densities ($\Sigma\rho_{GND}$, SDV26) on all slip systems. As expected the density is highest near the compressed part of the beam under bending (bottom of beam) where slip lines are seen in the experiment (see Figure 125 AFTER). The maximum is located at the bottom fixed end of the beam where stress is highest.

It was moreover possible to confirm that several of the 12 possible slip systems in the fcc A600 activated in either grain 1 or grain 2 or both, as summarized in Table 33. Based on the Euler angles of the grains incorporated in the beam, (111)[01-1] and (-111)[101] were identified as slip systems with the highest Schmid factor on grain 2 (Euler angles (61°, 54°, 322°)) and grain 1 (Euler angles (145°, 20°, 258°)) respectively. Figure 127 shows a representation of SDV58 (red in Table 33) and SDV62 (blue in Table 33), which represent these slip systems and are clearly active in the simulation. Figure 127 moreover demonstrates that, at same displacement, different slip systems might be very active in one grain but not in the other depending on crystal orientation. This is also reflected by the different Schmid factors m in Table 33.

SDV	Slip normal	Slip	Grain 1	Grain 2
SDV57	111	1-10	$m = 0.1158$	$m = 0.4272$
SDV58	111	01-1	$m = 0.0739$	$m = 0.4320$
SDV59	111	10-1	$m = 0.0419$	$m = 0.0048$
SDV60	-111	110	$m = 0.0040$	$m = 0.0236$
SDV61	-111	01-1	$m = 0.4303$	$m = 0.0324$
SDV62	-111	101	$m = 0.4344$	$m = 0.0560$
SDV63	1-11	110	$m = 0.0054$	$m = 0.3656$
SDV64	1-11	011	$m = 0.3186$	$m = 0.3711$
SDV 65	1-11	10-1	$m = 0.3240$	$m = 0.0056$
SDV66	11-1	1-10	$m = 0.1063$	$m = 0.0380$
SDV67	11-1	011	$m = 0.0378$	$m = 0.0284$
SDV68	11-1	101	$m = 0.0685$	$m = 0.0664$

Table 33: Active slip systems in the simulation of beam C3 on A600-NOX. SDV58 (red) represents the slip system with the highest Schmid factor in G2 and SDV62 (blue) represents the slip system with the highest Schmid factor in G1.

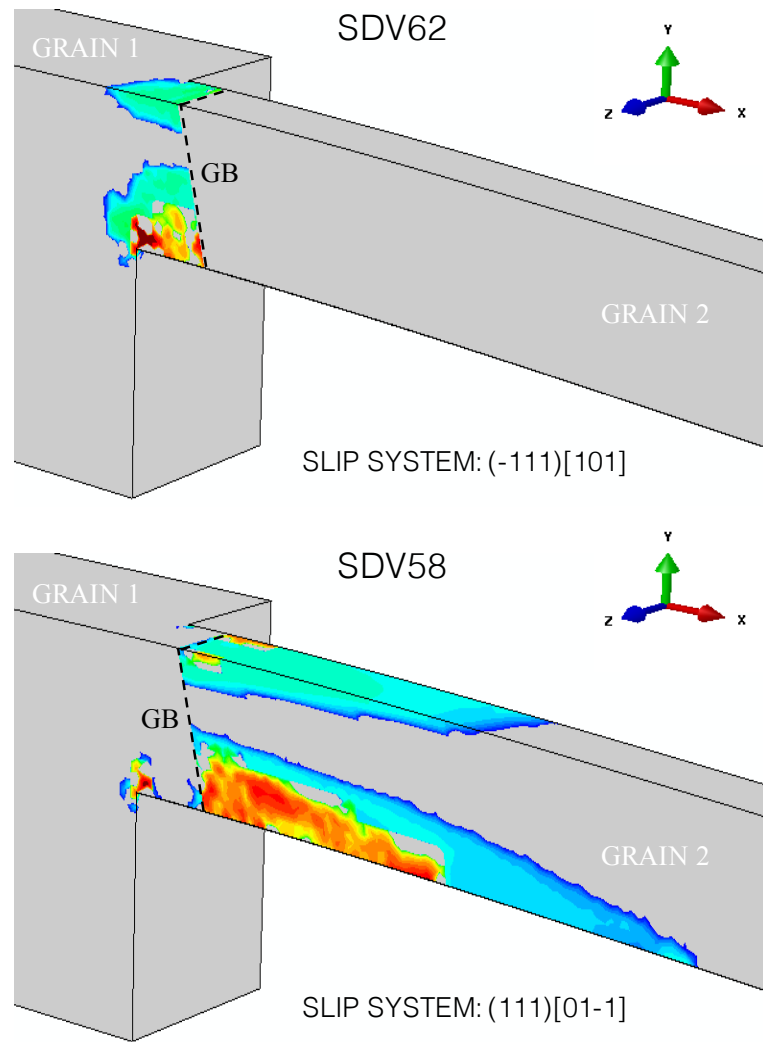


Figure 127: Slip system $(-111)[101]$ (SDV62) active on grain 1 and slip system $(111)[01-1]$ (SDV58) active on grain 2. The slip systems represent the slip system with the highest Schmid factor m on each grain. SDV62 with Schmid factor $m = 0.4344$ and SDV58 with Schmid factor $m = 0.4320$.

8.3 Summary and discussion

8.3.1 Stress at failure summary

As discussed in section 8.1, cohesive surface finite element simulations were used to quantify the stress at failure σ_f which was otherwise obtained via simple beam theory.

As summarized in Table 34, the quantified, normal σ_f for the simulated beams

compares well to the corresponding beam theory estimates. The table also shows a comparison of the Young's modulus E used for FEM and obtained via simple beam theory.

	BEAM THEORY		FEM	
Cantilever ID	E (GPa)	σ_f (MPa)	E (GPa)	σ_f (MPa)
R3 (see 6.1.2)	115	522 (1 st load drop)	118	575 (1 st load drop)
C3 (see 6.1.2)	130	569 (1 st load drop)	118	575 (1 st load drop)
R4	121	362	130	330
R6	185	494	203	445
C5	116	326	127	330
		285 (1 st load drop)	127	265 (1 st load drop)

Table 34: Comparison of Young's modulus E and stress at failure σ_f from simple beam theory estimations and cohesive surface simulations. R3, as discussed in section 6.1.2, and to a lesser extend C5 showed a clear onset of plastic deformation before the major fracture event. Consequently, the stress at the 1st noticeable load-drop has been considered for calibrations of the FEM models.

As initially indicated by the results discussed in section 6.1.2, the difference between the modelled and simple beam theory stress values was $\leq 10\%$ in all cases. This highlights the accuracy of the stress at failure values extracted in the frame of this thesis. The graph in Figure 128 compares the failure stress values obtained via simple beam theory estimations and cohesive surface FEM. An error interval of $\pm 10\%$ is used for the beam theory values to indicate that the difference between values lies always within $\leq 10\%$. Overall, to the best knowledge of the author, the cohesive zone models presented in this thesis, whilst still being an approximation, represent the most realistic case of simulating the fracture of oxidized GBs via micromechanical cantilever tests to date. Agreement with simple beam theory is good and gives additional confidence in the results obtained.

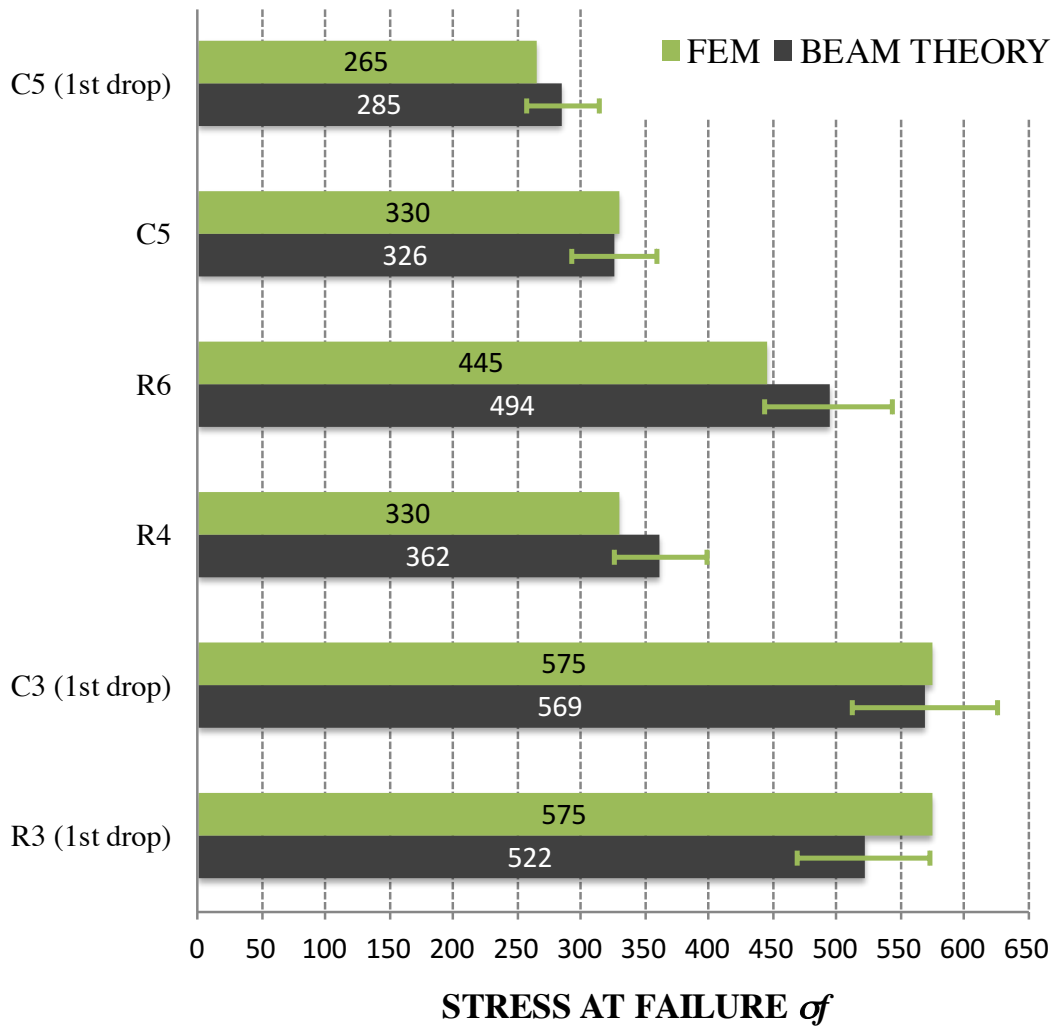


Figure 128: Graph comparing the failure stress σ_f , obtained for a range of cantilevers, as detailed in Table 34, via stress-strain analysis (beam theory) and cohesive zone FEM simulations. The error bar on the simple beam theory values shows a $\pm 10\%$ interval, indicating that the difference between the experimental and simulated value is always within $\leq 10\%$.

8.3.2 Crystal plasticity FEM of an unoxidized bi-crystal

As discussed in section 8.2, the strain gradient crystal plasticity UMAT developed by Dr. Tarleton, which is based on the UEL initially developed by Dunne *et al.* ^{[180], [232]}, together with elastic constants for A600 as found in literature ^[253] and an implementation of the bi-crystal's grain orientations as found by EBSD, enables us to reproduce the elastic regime of the Force-Displacement behaviour without any further

CHAPTER 8 Modelling of the mechanical behaviour

calibration. Moreover, the experimentally observed strain hardening (plastic regime) can be captured by calibrating the critical resolved shear stress, to fit the transition point between the linear and plastic regime, as well as the mobile dislocation density, to reflect the degree of strain hardening (plastic portion of the F-D curve). Moreover, an estimate of the evolving GND density can be obtained, which even though lacking real significance due to unavailability of comparable experimental data, is in good agreement with an experimentally observed preferred accumulation of slip lines at the bottom of the deformed beam. Finally, it could be shown that the slip systems with the highest calculated Schmid factors m (see Table 33) on either grain are active in the simulation and that, depending on orientation, different slip systems are more active in one grain than the other at the same level of displacement. From these first insights it can be concluded that even though the initial incentive of combining a cohesive zone model with crystal plasticity could not be achieved and the code itself often crashes, the results are promising and clearly show the potential for a future combination of the 2 methods.

9 FINAL SUMMARY AND CONCLUSIONS

9.1 Modes of failure of oxidized Alloy 600

In accordance with observations by Dugdale *et al.* ^[49], 2 main modes of failure were observed on both oxidized specimens tested in the frame of this thesis:

1. Beams undergoing fracture and little to no plastic deformation
2. Beams undergoing plastic deformation with no apparent fracture

9.2 Stress at failure of oxidized GBs

9.2.1 A600-INSS:

- With surface oxides present on top of the GBs, σ_f was found to cover a range of $\sim 330 - 770$ MPa.
- A mean failure stress of 443 MPa, with ± 65.7 standard deviation, can be reported for beams tested on A600-INSS (without surface oxide influence).
- The surface oxide present on top of the oxidized GBs, was shown to influence the micromechanical response of the tested beams, leading to an increase in failure stress (up to 230 MPa) as well as a delay of fracture.

CHAPTER 9 Final summary and conclusions

- While only 4 out of 10 beams failed with a surface oxide present, all 6 beams where the surface oxide on top of the GBs had been removed experienced failure.
- Realistic cantilever dimensions in conjunction with cohesive zone models can be used to quantify the stress at failure of oxidized GBs and have shown that simple beam theory analysis provides a good σ_f estimate for brittle failure. The difference between simulated and experimental values was always within 10%.
- A mean failure stress of 438 MPa, with ± 140.7 standard deviation, can be reported for the cohesive zone models.

9.2.2 A600-EDF:

- A mean failure stress of 603 MPa, with ± 63.7 standard deviation, can be reported for beams tested on A600-EDF.
- Even though no surface oxide was present, 2 out of 9 beams did not fail. It is believed that this is caused by a less deep oxide penetration due to the significantly shorter oxidation time of this sample but differences due to sample history and autoclave conditions can't be ruled out.

9.2.3 A600-NOX:

- In the unoxidized state no fracture was observed during testing.
- A mean yield stress of 379 MPa, with 73.1 MPa standard deviation was found. The yield stress σ_{yield} reported by EDF for the as-received alloy at RT was 428 MPa (see Table 4).
- Using realistic beam dimensions, the experimentally obtained grain orientations and elastic constants for Alloy 600 it is possible to capture the elastic response of the beams accurately. By adjusting the critical resolved shear stress (yield criterion, $\tau_c = 300$ MPa) and mobile dislocation density (plastic flow,

$\rho_{SSD}^m = 0.055/\mu\text{m}^2$), the onset and degree of the plastic deformation can be captured.

9.3 Cantilever lift-outs, 3D FIB-SEM and TEM sample preparation

- A new lift-out strategy was presented, which combines TEM sample preparation of tested microcantilevers with 3D FIB-SEM sequencing, hence enabling an even more complete examination of micromechanically tested cantilevers of any material. The strategy is described in section 3.3.3.2.

9.4 The failure of oxidized grain boundaries: A comparison

It was found that the IG oxide is layered, as explained in more detail in section 7.4.2.1 (Figure 104). Cr-rich oxide is formed around IG carbides, which are consumed by oxidation, and at the location of the original GB, which are the preferred diffusion path for Cr. A more Fe-rich, mixed spinel is found close to the oxide-metal interface.

- Defective spinel oxides (vacancy clusters) seem preferentially located at the oxide-metal interface where Cr is depleted and a Fe-rich oxide is located. However, smaller density variations were also randomly clustered within the IG oxide.
- The Cr-rich oxide (Cr_2O_3) at the original GB, enclosed in the more Fe-rich oxide, is no obvious weak spot.

CHAPTER 9 Final summary and conclusions

As discussed in section 7.4.2.1, the availability of certain ion species, especially trivalent cations of Cr, during the formation of stoichiometric oxides of the form $A^{2+}B^{3+}_2O_4$ is assumed to play a crucial role in the appearance of the oxide.

Cracking mainly proceeds along the oxide-metal interface where the IG oxide is sufficiently thick (e.g. around IG carbides) and where the defective (less dense) Fe-rich spinel is preferentially located.

- The carbide-oxide interface was never found to fracture.
- In regions in-between carbides, or where there is no IG carbide precipitation, oxidation was often thin and incomplete (nodule-like), hence allowing for a fracture through the oxide rather than choosing a particular interface.
- A600-EDF, which did not show voids at the oxide-metal interface, showed a ~ 160 MPa higher average failure stress (see section 9.2). This might be explained by a weaker adhesion caused by the presence of voids in case of *A600-INSS*. However, due to the different sample history and autoclaving time and conditions other possible explanations can't be ruled out. This includes a potential effect from H_2 , which was not studied in this thesis.

Summarizing, the research presented in this thesis, which is based on a combination of micromechanical cantilever bend tests, electron microscopy (SEM as well as (S)TEM) and realistic FEM simulations, represents a sophisticated strategy for the examination of oxidized GBs, which to the best of the author's knowledge provides the most accurate way of studying the failure and microstructure of oxidized GBs. This includes the provision of the most complete set of local failure stress values of oxidized A600 GBs available in the literature.

10 SOME THOUGHTS ON FUTURE RESEARCH

Before discussing some ideas for future studies in the field of SCC of oxidized GBs, the author wants to emphasize that SCC is a highly complex and broad field of research. In the author's opinion, it should be examined in a step-by-step approach. The studied systems need to be simplified rather than trying to test too many variables at once. Moreover, the SCC community should think about establishing better-structured and collaborative research routines, making use of the strengths of individual research labs to target and isolate different influence factors on the same samples. It seems that a lot of contradictory information found in literature has its roots in the consideration of too many variables on too many alloys, all of which tested under slightly different conditions. This makes comparability of individual results very difficult and complicates the drawing of more general conclusions. Research and samples should ideally be timed and shared without limitations to enable a successful investigation of different variables and conditions and to better understand their respective combinations. By making research and samples more accessible to peers or by at least agreeing on experimental conditions and by sharing results more rapidly, individual as well as collective progress in any field of research would most certainly accelerate.

“Knowledge is power. Knowledge shared is power multiplied”

–Robert Noyce

CHAPTER 10 Some thoughts on future research

The research presented in the frame of this thesis was aimed at providing novel insights in SCC crack initiation and propagation of oxidized GBs on Alloy 600 and at establishing the failure stress of oxidized GBs for use in predictive SCC models like the one developed by the project collaborator EDF.^[4]

Future studies dealing with the SCC related failure of oxidized GBs might target:

1. The determination of individual valence states of IG oxides

A determination of valence states via EELS, as demonstrated by Wang *et al.*^[256] for cobalt and manganese and more recently attempted by Pimentel *et al.*^[46] for oxides formed on A600 might be employed. This would be highly beneficial and help to prove the important role of ion species availability in the formation of different IG oxides.

2. A comparison of composition, valence and density of the IG oxides formed on A600 after elevating exposure times on the same coupon, using constant autoclaving conditions

Focussing on one sample with constant autoclave conditions, while elevating exposure time in the autoclave it could be shown whether carbides might actually determine the preferred crack path for propagation or not. Building upon the findings of this thesis it could for example be established whether voiding is observed in the absence of carbide precipitation and/or whether voids are linked to longer exposure times and deeper oxide penetration levels independent of carbide precipitation.

3. A computational study on defect interactions and oxide growth

A study on defect migration and cation-anion interactions, similar to the one carried out by Zamora *et al.*^[247] for MgAl_2O_4 , could be useful as well as a study on the interaction between dislocations and carbides. This might involve discrete dislocation plasticity and FEM analysis or a combination of both. A study focussing on the role of the stress

caused by the oxide expansion (growth stresses on the bulk) and its potential effect on dislocation/vacancy motion might moreover be useful.

4. In-situ micromechanical experiments of oxidized grain boundaries

The ability of observing the GB failure in-situ might be useful to prove a crack progression via micro-void coalescence, spallation and/or collapse. This could involve microcantilevers as well as micropillar testing. The presence of surface oxide scales, which might influence the failure response, needs to be considered in any case. As was shown in this study (section 6.1.2).

5. Simulations to study void-fracture interactions

For example the influence of the number of voids on the crack path should be studied. Does the crack choose the side with a higher void density for propagation? A simple FEA analysis of a GB showing different levels of voiding and void size could be performed to study the influence of voids on the cohesive properties of GBs. Another possibility involves a computational study on void count and size of an oxidized GB. By varying void count and size on the respective sides of the IG oxide, the preferred crack path might be determined.

6. Transmission Kikuchi diffraction ^[218] for an identification of stress/strain fields at the oxide-metal interface.

The identified regions of highest stress in the TKD maps could be further examined in a TEM in search of dislocations and to establish whether vacancies are preferentially found in these regions, which would indicate a preferential migration and clustering of the defects in the regions of highest stress.

7. *Studies concerning the role of hydrogen at the individual GB interfaces*

A thermal desorption analysis of the potential hydrogen traps (voids, dislocations and interfaces) seems plausible to prove the presence/nucleation of hydrogen in these regions. However, as it is a bulk technique, interpretation and designation of the obtained hydrogen data might be a limiting factor.

8. *Microcantilever fracture tests of oxidized GBs on stainless steel*

Parallel to further studies on Alloy 600, it would be useful to compare the fracture behaviour and to better understand the influence of Cr availability on oxide and potential void formation. It might moreover be interesting to carry out a study on oxidized deformation bands, as often seen on cold-worked stainless steel.

9. *Microcantilever fracture tests at reactor operating temperature*

As modern Nanoindentation systems provide a high temperature function it would be very interesting to test cantilevers on the same GB at different temperatures. Differences concerning tests performed at room temperature, as performed in this study, and reactor-operating temperatures could be revealed.

10. *The combination of the presented cohesive zone models with a crystal plasticity UMAT subroutine*

Combining cohesive zone models with a crystal plasticity formulation, as the one used in the context of this thesis, is highly desirable to obtain an even better prediction and quantification of the beam response, as minor plasticity before the onset of failure can't be captured accurately with cohesive zones alone.

11. FEA based on a full 3D representation of the tested cantilever volume (real microstructure)

As a next step in achieving even more realistic results, besides thriving for a successful combination of the cohesive surface approach with the crystal plasticity formulation developed by Dunne *et al.* ^[180], the final step could be to use the 3D tomography data of tested microcantilevers. This could be achieved by using conventional 3D FIB-SEM or its adaption, presented in this thesis (see section 3.3.3.2), to preserve a TEM sample by lifting out whole cantilevers to built an even more realistic 3D mesh of the cantilever's microstructure. The success might however depend on the possibility to change and optimize the mesh, which is automatically generated by the FEI Avizo 9.0 3D reconstruction software.

11 APPENDIX

APPENDIX A: DETERMINATION OF MISORIENTATION ANGLES BASED ON EULER ANGLES

The following script can be used to transform Euler angles into the respective rotation matrices R_{G1} and R_{G2} of the 2 grains enclosed in a typical cantilever. It then determines the misorientation angle $\gamma = \arccos(\text{Trace}(M_{G1G2}) - 1)/2$ based on the misorientation matrix of grain 1 and grain 2 ($M_{G1G2} = R_{G1} * R_{G2}^{-1}$), considering all 24 symmetry operators in a cubic system. For further information about the maths underlying the script, please refer to reference [213].

```
% Created by Judith Dohr (version 09.05.2016)
% FROM EULER ANGLES TO MISORIENTATION
%Calculation of rotation matrices from euler angles of 2 grains
(g1 and g2) for the determination of the misorientation matrix and
Misorientation Angle

% STEP1: Converting Euler Angles from Degrees to Radians

% Grain 1 (g1)
g1_phi_1 = deg2rad(319)
g1_phi = deg2rad(44)
g1_phi_2 = deg2rad(67)

% STEP2: Definition of rotations for g1 in matrix form (sample
reference to crystal reference frame). Rotation around z,x_new and
z_new axis (Bunge notation)
z_new_g1 = [cos(g1_phi_2) sin(g1_phi_2) 0; -sin(g1_phi_2)
cos(g1_phi_2) 0; 0 0 1]
x_new_g1 = [1 0 0; 0 cos(g1_phi) sin(g1_phi); 0 -sin(g1_phi)
cos(g1_phi)]
z_g1 = [cos(g1_phi_1) sin(g1_phi_1) 0; -sin(g1_phi_1) cos(g1_phi_1) 0;
0 0 1]

% STEP3: Definition of rotation matrix R for g1
r_g1 = z_new_g1 * x_new_g1 * z_g1
```

CHAPTER 11 Appendix

```
%Repeat for 2nd grain

% Grain 2 (g2)
g2_phi_1 = deg2rad(244)
g2_phi = deg2rad(26)
g2_phi_2 = deg2rad(76)

% Definition of rotations for g2 in matrix form (sample reference
to crystal reference frame). Rotation around z,x_new and z_new axis
(Bunge notation)
z_new_g2 = [cos(g2_phi_2) sin(g2_phi_2) 0; -sin(g2_phi_2)
cos(g2_phi_2) 0; 0 0 1]
x_new_g2 = [1 0 0; 0 cos(g2_phi) sin(g2_phi); 0 -sin(g2_phi)
cos(g2_phi)]
z_g2 = [cos(g2_phi_1) sin(g2_phi_1) 0; -sin(g2_phi_1) cos(g2_phi_1) 0;
0 0 1]
% Definition of rotation matrix R for g2
r_g2 = z_new_g2 * x_new_g2 * z_g2

% Calculation of the Misorientation matrix between the two grains (g1
and g2)

% Misorientation Matrix M_delta_g of r_g1 and r_g2
M_delta_g = r_g1 * inv(r_g2)

% 24 symmetry operators for cubic systems
ops = [1 0 0; 0 1 0; 0 0 1];
ops(:,2) = [0 0 -1; 0 -1 0; -1 0 0];
ops(:,3) = [0 0 -1; 0 1 0; 1 0 0];
ops(:,4) = [-1 0 0; 0 1 0; 0 0 -1];
ops(:,5) = [0 0 1; 0 1 0; -1 0 0];
ops(:,6) = [1 0 0; 0 0 -1; 0 1 0];
ops(:,7) = [1 0 0; 0 -1 0; 0 0 -1];
ops(:,8) = [1 0 0; 0 0 1; 0 -1 0];
ops(:,9) = [0 -1 0; 1 0 0; 0 0 1];
ops(:,10) = [-1 0 0; 0 -1 0; 0 0 1];
ops(:,11) = [0 1 0; -1 0 0; 0 0 1];
ops(:,12) = [0 0 1; 1 0 0; 0 1 0];
ops(:,13) = [0 1 0; 0 0 1; 1 0 0];
ops(:,14) = [0 0 -1; -1 0 0; 0 1 0];
ops(:,15) = [0 -1 0; 0 0 1; -1 0 0];
ops(:,16) = [0 1 0; 0 0 -1; -1 0 0];
ops(:,17) = [0 0 -1; 1 0 0; 0 -1 0];
ops(:,18) = [0 0 1; -1 0 0; 0 -1 0];
ops(:,19) = [0 -1 0; 0 0 -1; 1 0 0];
ops(:,20) = [0 1 0; 1 0 0; 0 0 -1];
ops(:,21) = [-1 0 0; 0 0 1; 0 1 0];
ops(:,22) = [0 0 1; 0 -1 0; 1 0 0];
ops(:,23) = [0 -1 0; -1 0 0; 0 0 -1];
ops(:,24) = [-1 0 0; 0 0 -1; 0 -1 0];

% Determination of number of operators (e.g. 24 for cubic system)
number_of_elements = size(ops); %(3,3,24)
number_of_elements = number_of_elements(3); %24

% Application of 24 symmetry operators to M_delta_g
ops_result = zeros(3,3,number_of_elements);
for i = 1:number_of_elements
    s_i = ops(:,i);
    ops_result(:,i) = s_i * M_delta_g;
end
```

CHAPTER 11 Appendix

```
% Calculate misorientation angle gamma for all 24 misorientation
matrices
gamma_result = zeros(number_of_elements);
for i = 1:number_of_elements
    matrix = ops_result(:, :, i);
    gamma = acos((trace(matrix)-1) / 2);
    gamma_result(i) = gamma;
end

% Find minimum Gamma --> Misorientation angle
minimum = min(gamma_result)

% Transform gamma from radiant to degree
gamma_degrees = radtodeg(minimum)
```

APPENDIX B: SOME MORE RELEVANT DEFINITIONS

Constructing a rotation matrix based on Euler angles (Bunge notation), as also implemented in the Matlab script in APPENDIX B.

$$\begin{aligned}
 & \mathbf{R}_{Z''}(\varphi_2) \mathbf{R}_{X'}(\Phi) \mathbf{R}_Z(\varphi_1) = \\
 & \begin{pmatrix} \cos \varphi_2 & \sin \varphi_2 & 0 \\ -\sin \varphi_2 & \cos \varphi_2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \Phi & \sin \Phi \\ 0 & -\sin \Phi & \cos \Phi \end{pmatrix} \begin{pmatrix} \cos \varphi_1 & \sin \varphi_1 & 0 \\ -\sin \varphi_1 & \cos \varphi_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 & = \begin{pmatrix} \cos \varphi_1 \cos \varphi_2 - \sin \varphi_1 \sin \varphi_2 \cos \Phi & \sin \varphi_1 \cos \varphi_2 + \cos \varphi_1 \sin \varphi_2 \cos \Phi & \sin \varphi_2 \sin \Phi \\ -\cos \varphi_1 \sin \varphi_2 - \sin \varphi_1 \cos \varphi_2 \cos \Phi & -\sin \varphi_1 \sin \varphi_2 + \cos \varphi_1 \cos \varphi_2 \cos \Phi & -\cos \varphi_2 \sin \Phi \\ \sin \varphi_1 \sin \Phi & -\cos \varphi_1 \sin \Phi & \cos \Phi \end{pmatrix}
 \end{aligned}$$

Definition of the global elastic stiffness matrix

$$D = T_\sigma C T_\sigma^T$$

The rotation matrix T_σ is thereby defined as

$$T_\sigma = \begin{pmatrix} R_{11}^2 & R_{12}^2 & R_{13}^2 & 2R_{11}R_{12} & 2R_{11}R_{13} & 2R_{12}R_{13} \\ R_{21}^2 & R_{22}^2 & R_{23}^2 & 2R_{21}R_{22} & 2R_{21}R_{23} & 2R_{22}R_{23} \\ R_{31}^2 & R_{32}^2 & R_{33}^2 & 2R_{31}R_{32} & 2R_{31}R_{33} & 2R_{32}R_{33} \\ R_{11}R_{21} & R_{12}R_{22} & R_{13}R_{23} & R_{11}R_{22} + R_{21}R_{12} & R_{11}R_{23} + R_{21}R_{13} & R_{12}R_{23} + R_{22}R_{13} \\ R_{11}R_{31} & R_{12}R_{32} & R_{13}R_{33} & R_{11}R_{32} + R_{12}R_{31} & R_{11}R_{33} + R_{13}R_{31} & R_{12}R_{33} + R_{13}R_{32} \\ R_{21}R_{31} & R_{22}R_{32} & R_{23}R_{33} & R_{21}R_{32} + R_{22}R_{31} & R_{21}R_{33} + R_{23}R_{31} & R_{23}R_{32} + R_{22}R_{33} \end{pmatrix}$$

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