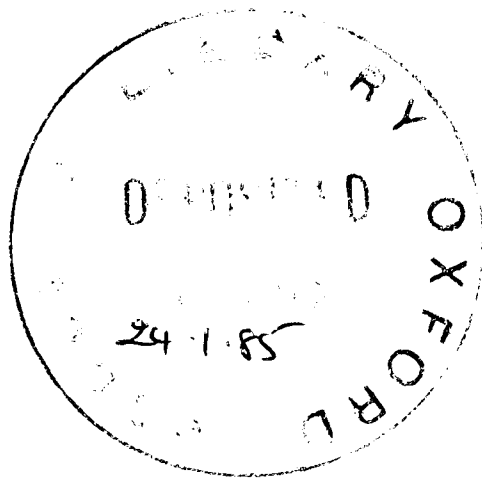


STRUCTURE-PROPERTY RELATIONS IN SUPERALLOY SINGLE CRYSTALS



Adrian Alan Hopgood,
St. Catherine's College,
Oxford.

A thesis submitted for the degree of Doctor of Philosophy in the
University of Oxford, Trinity Term, 1984.

STRUCTURE-PROPERTY RELATIONS IN SUPERALLOY SINGLE CRYSTALS

A.A. Hopgood,
St. Catherine's College,
University of Oxford.

D. Phil. Thesis.
Trinity Term, 1984

ABSTRACT

This research is concerned with a single crystal nickel-base superalloy which has been developed for application as a high pressure turbine blade material in jet aircraft engines. The microstructures and mechanical properties of superalloys, including the effects of heat-treatments, have been reviewed.

The effects of heat-treatments on the γ' precipitate distributions have been investigated. During ageing at 900 °C or 800 °C, the precipitates adopt an irregular, rounded and highly interconnected microstructure, indicative of precipitate coalescence, whilst at higher ageing temperatures a regular cuboidal precipitate morphology is formed. The kinetics of precipitate coarsening have been investigated, and slight deviations from the power-law predicted by a number of theoretical models were observed. These deviations have been discussed in terms of a progressive transition in the dominant coarsening mechanism.

Constant load creep tests were carried out, and although the tensile axis was nominally parallel to [001], the degree and direction of misorientation were found to be critical to the extent of the primary creep strain. Primary creep was shown to proceed by slip on a single $(\bar{1}11)[1\bar{1}2]$ system, until the activation of intersecting slip systems brings about the onset of the secondary creep stage. The extent of primary creep has been shown to be reduced by application of a final ageing treatment at 870 °C.

Precipitate shear by paired dislocations in intense slip bands occurs during high strain-rate deformation at both ambient temperature and at 750 °C. Application of a final ageing treatment at 870 °C was found to increase the 0.2% proof stress and to bring about the activation of an alternative mode of precipitate shear by dissociated dislocations. The 870 °C ageing treatment was shown to cause slight chemical changes at the γ/γ' interfaces, and these are believed to have caused the observed changes in mechanical properties.

ACKNOWLEDGEMENTS

Many people have helped me during the course of this research and I should like to thank them all. In particular I should like to express my thanks to the following:

Professor Sir P.B. Hirsch, F.R.S. and Professor J.W. Christian, F.R.S. for the provision of laboratory facilities.

The Science and Engineering Research Council and Rolls-Royce Limited for financial support.

My supervisor, Dr. J.W. Martin, for his guidance throughout the project.

Rolls-Royce Limited for the provision of materials and facilities.

All the members of the Metallurgical Research and Development Division at Rolls-Royce Limited in Derby, and most especially to Paul Spilling for his enthusiastic help and advice throughout this project. Also to the XRD group for carrying out the crystal orientation measurements.

Dr. G.D.W. Smith for allowing access to the atom probe and to all of the FIM group for their co-operation. In particular, to Geoff Worrall for his help and advice on the operation of the atom probe, the preparation of suitable specimens and the processing of the data.

The members of the laboratory workshop, the photographic unit, and the electronics workshop for their assistance.

My past and present colleagues in the JWM group, namely Ian Baker, Phil Bischler, John Blind, Andy Busby, Bill Clegg, Jeff Crompton, Lyndon Edwards and Mike Harrison for their help, encouragement and friendship over the past three years and especially to Bill Clegg for his many useful comments and suggestions concerning this thesis.

Finally to Suky Kaplan for her careful and patient typing of this thesis.

Adrian Hopgood

September 1984

PREFACE

This thesis is an account of research carried out in the Department of Metallurgy and Science of Materials at the University of Oxford between October 1981 and September 1984. The work reported is original, and is not substantially the same as any thesis submitted in this or any other university. Where the work of other authors has been included in the text, this has been acknowledged and its source given in an alphabetical list of references at the end of the thesis. Part of this work has been presented at the 8th European Congress on Electron Microscopy, Budapest, Hungary during August 1984.

CONTENTS

	Page
Abstract	i
Acknowledgements	ii
Preface	iii
Chapter 1. Microstructural and Mechanical Properties of Nickel-Base Superalloys.	1
1.1 Materials Requirements for Gas Turbines	1
1.2 The Microstructure of Superalloys	1
1.2.1 The Principal Phases	1
1.2.2 Precipitate Morphology	3
1.2.3 The Kinetics of Precipitate Coarsening	5
1.2.4 The Effects of Precipitate Volume Fraction on Coarsening Kinetics	8
1.2.5 The Effects of Precipitate Coalescence on Coarsening Kinetics	9
1.3 Deformation Mechanisms in Superalloys	11
1.3.1 Solid Solution Strengthening	11
1.3.2 Precipitation Strengthening	12
1.3.2.1 Coherency Hardening	13
1.3.2.2 Order Hardening	14
1.3.2.3 Other Precipitation Hardening Mechanisms	16
1.3.3 The Anomalous Temperature-Dependence of the Yield Stress of Superalloys	17
1.3.4 Precipitate Shearing Mechanisms	20
1.3.5 Dislocation Climb around Precipitates	22
1.4 Creep in Superalloys	25
1.4.1 The Stress Dependence of Creep	26
1.4.2 Dislocation Creep Mechanisms	28

1.4.2.1	Recovery-Controlled Models	29
1.4.2.2	Glide-Controlled Models	34
1.4.2.3	Other Dislocation Creep Mechanisms	34
1.4.3	The Effects of Hard Particles	35
1.4.4	The Concept of a Threshold Stress, σ_0	37
1.4.5	The Effects of Precipitate Morphology	39
1.4.6	The Early Onset of Tertiary Creep	42
1.4.7	Crystal Anisotropy Effects	44
1.5	Superalloy Development	48
1.5.1	Alloying Trends	48
1.5.2	Directional Solidification	49
1.5.3	Single Crystals	51
1.6	The Present Investigation	52
Chapter 2. Materials and Experimental Techniques		54
2.1	Materials	54
2.2	Heat-Treatments	54
2.3	Creep Testing	55
2.3.1	Specimens	55
2.3.2	Apparatus	56
2.3.3	Calibration	57
2.3.4	Testing Procedure	58
2.3.5	Crystal Orientation Measurements	59
2.4	High Strain-Rate Tests	60
2.4.1	Specimens	60
2.4.2	Room Temperature Compression Tests	61
2.4.3	Elevated Temperature Compression Tests	61
2.5	Optical Metallography	62

2.6	Scanning Electron Microscopy	62
2.7	Transmission Electron Microscopy	63
2.8	Field-Ion Microscopy and Time of Flight Atom Probe Microanalysis	65
2.8.1	Field-Ion Microscopy	65
2.8.2	Atom Probe Microanalysis	66
2.8.3	Application in the Present Study	67
2.8.4	Specimen Preparation	69
2.9	Precipitate Size Measurements	69
Chapter 3. Effects of Heat-Treatment on Microstructure:		
	Results and Discussion	72
3.1	Solution Heat-Treatments	72
3.2	Precipitate Morphology	73
3.3	Precipitate Size Distributions	77
3.4	Coarsening Kinetics	79
3.5	The Activation Energy for Precipitate Coarsening	86
Chapter 4. Creep Behaviour : Results and Discussion		
4.1	The Effects of Ageing at 1100 °C	88
4.2	Crystal Orientation Effects	89
4.3	The Effects of an Additional Ageing Treatment at 870 °C	92
4.4	Deformation Structures	96
4.4.1	Without 870 °C Ageing Treatment	96
4.4.2	With 870 °C Ageing Treatment	98
4.5	Microstructural and Microchemical Effects	99
4.6	Creep Fracture	106

Chapter 5. High Strain-Rate Deformation : Results and	
Discussion	109
5.1 Dependence of Yield Stress upon Heat-Treatment	109
5.2 Deformation Structures	110
5.3 Macroscopic Deformation	112
Chapter 6. Conclusions and Suggestions for Further Work	114
6.1 Conclusions	114
6.2 Suggestions for Further Work	116
Appendix	118
References	122
Glossary of Symbols	132

CHAPTER 1

MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF NICKEL-BASE SUPERALLOYS

1.1 Materials Requirements for Gas Turbines

The power and efficiency of gas turbine engines increase with the inlet gas temperature. Therefore the need has arisen for materials capable of maintaining good mechanical properties and corrosion resistance at elevated temperatures. To meet this demand a large range of alloys, known as superalloys, have been developed based on nickel, iron, cobalt and chromium systems. The work presented here is concerned with a single crystal nickel-base superalloy which has been developed by Rolls-Royce Limited for use as a high pressure turbine blade material in jet aircraft engines.

Typically the aerofoil section of a turbine blade experiences longitudinal stresses of 140 MPa, and temperatures of 650-980 °C, whilst the blade root is subjected to tensile stresses of 275-550 MPa, and temperatures of approximately 760 °C (Fawley, 1972). Under such conditions, resistance to creep deformation is a major design criterion. However, suitable materials must also exhibit resistance to high and low cycle fatigue, thermal fatigue, impact and corrosion.

1.2 The Microstructure of Superalloys

1.2.1 The Principal Phases

Pure nickel does not exhibit great creep resistance, since it possesses neither a high modulus of elasticity nor low diffusivity (Decker, 1969). However, owing to its nearly filled 3d electron orbital, nickel displays an exceptionally high tolerance for alloying

without phase instabilities occurring. By carefully controlling alloy additions, superalloys can be used at up to 80% of their absolute melting temperature. Those elements most commonly included in superalloy design are shown in table 1.1.

Corrosion resistance is enhanced by chromium and aluminium. Chromium forms Cr_2O_3 -rich protective scales having a low cation vacancy content, which restrict the diffusion rate of metallic elements outward and oxygen and sulphur inward. The formation of Al_2O_3 -rich scales has a similar effect.

Superalloys generally comprise two major phases, namely a face centred cubic austenitic matrix known as the γ phase and a precipitate phase known as γ' . γ' is an intermetallic phase having an ordered L1_2 structure which Corey and Lisowsky (1967) have shown to remain fully ordered up to temperatures approaching the melting temperature. The nominal composition of γ' is A_3B where A sites are occupied primarily by nickel atoms and B sites by aluminium atoms as shown in Figure 1.1. Aluminium may be partially substituted for by titanium and tantalum. The γ' phase is fully coherent with the γ matrix for precipitate sizes of up to typically 1 μm . Coherency between the two phases is maintained by tetragonal distortion of the atomic planes. The compatibility of the two crystal structures, together with a low mismatch (normally less than 1%) allows homogenous nucleation of γ' with low surface energy and long time stability.

Carbon and boron are often included in superalloys in order to precipitate carbides and borides. The most common carbides are MC and M_{23}C_6 (where M represents a metal), although M_6C and M_7C_3 are sometimes observed. M_{23}C_6 carbides tend to form at grain boundaries and it has been suggested by Decker and Sims (1972) that they can improve creep resistance by impairing grain boundary sliding. Boron

also segregates to grain boundaries to form borides which are thought to improve creep properties by retarding grain boundary diffusion (Holt and Wallace, 1976).

Owing to their nearly filled 3d orbital, nickel atoms are essentially incompressible. Consequently the formation of the γ' phase is energetically more favourable than other more complex phases where atomic size changes are necessary (Decker, 1969). However, a highly alloyed superalloy microstructure is in metastable equilibrium. Long term exposure to elevated temperatures allows migration of alloy elements which can result in phase changes taking place. The phase changes which are most harmful to mechanical properties are those which result in the precipitation of topologically close packed (t.c.p.) phases such as σ , χ , μ or Laves phases. These are intermetallic phases which, owing to their brittle nature and plate- or needle-like morphology, can facilitate the nucleation and growth of cracks (Ross, 1967). Furthermore they tend to deplete the superalloy matrix of vital solid solution strengthening elements. The formation of t.c.p. phases can be avoided by careful control of the alloying additions. A computer program known as PHACOMP has been developed by Woodyatt et al. (1966) to predict alloy stability from knowledge of the overall alloy composition.

1.2.2 Precipitate Morphology

In common with most systems containing inter-metallic precipitates in a metallic matrix, γ' precipitates in superalloys are prone to coarsening at elevated temperatures. Because the driving force for precipitate coarsening comes from the specific free energy of the precipitate/matrix interface, low growth rates demand that the γ/γ' interfaces be coherent and have a low lattice mismatch. Since both γ

and γ' can exist over a wide range of compositions, they have a range of possible lattice parameters. The γ/γ' misfit or mismatch parameter is defined as $\Delta a/a$, where Δa is the difference between the lattice parameters of the two phases and a is the lattice parameter of the matrix. Ricks et al (1983) have determined $\Delta a/a$ at ambient temperatures in a number of superalloys and their results are presented in table 1.2. By convention, a positive misfit indicates that the γ' precipitates have a larger lattice parameter than the matrix.

Table 1.2 also indicates the mean size of γ' at which deviations from a spherical morphology occur. Hagel and Beattie (1959a,b) have related the shape of γ' precipitates to the mismatch parameter ($\Delta a/a$) alone. They observed that γ' occurred as spheres at approximately 0-0.5% lattice mismatch, became cuboidal at mismatches around 0.5-1.0% and formed cells or plates at mismatches above approximately 1.0%. However, the size of the precipitates is also important in determining their morphology since the misfit displacement is proportional to size. Ardell and Nicholson (1966a) showed that on ageing a Ni-Al alloy at 750 °C the γ' precipitates formed initially as spheres, which during the coarsening process transformed to cubes aligned with their sides parallel to crystallographic {100} planes. Furthermore, the precipitates aligned with each other, forming rows of precipitates in $\langle 100 \rangle$ directions. Similar results have been observed in other superalloy systems by, for instance, Davies et al. (1980a) and Ricks et al. (1983).

As a result of the γ/γ' mismatch there is an energy associated with the coherency straining of the lattice, and this energy has a minimum for strain in the directions of lowest Young's modulus, namely $\langle 100 \rangle$. Consequently there is a low strain energy associated with γ/γ' interfaces lying on {100} planes. The precipitates are believed to

nucleate as spheres to minimise the particle surface area per unit volume. As they grow, the coherency strains increase and thus the reduction in strain energy made by maximising the {100} surfaces more than compensates for the increase in surface area per unit volume on changing from spheres to cubes. Ardell and Nicholson (1966a) further proposed that elastic interactions between cuboidal precipitates lead to alignment of precipitates with each other.

After long term exposure to elevated temperatures, deviations from the cuboidal morphology have been observed. Davies et al. (1980a) observed the formation of plates of γ' aligned along $\langle 100 \rangle$ directions whilst in a different series of superalloys Ricks et al. (1983) demonstrated the degeneration of the cuboidal morphology into faceted γ' dendrites.

1.2.3 The Kinetics of Precipitate Coarsening

Ostwald (1900) showed that when finely divided particles of mercuric oxide were suspended in a saturated solution, large particles tended to grow while small particles dissolved. This phenomenon, known as Ostwald ripening, is now known to occur in many systems where dispersed particles of a second phase exist in a saturated solution. Competitive growth of particles by this process arises from the higher solubility of small particles compared with larger ones, since they have a larger ratio of surface area to volume. The solubility is related to particle size by the Gibbs-Thompson equation (Martin and Doherty, 1976):

$$\frac{C(r)}{C(\infty)} = \exp \left(\frac{\gamma_{int} V_m}{k T r C_p} \right) \quad (1.1)$$

where $C(\infty)$ is the equilibrium molar concentration of the solute in the matrix, $C(r)$ is the solute concentration in the matrix at the curved interface with a precipitate of radius r , Ψ_{int} is the specific interfacial energy of the matrix/precipitate boundary, V_m is the molar volume of the precipitate, C_p is the mole fraction of solute in the precipitate, T is the absolute temperature and k is Boltzmann's constant.

Lifshitz and Slyozov (1961) and Wagner (1961) independently derived theoretical treatments of Ostwald ripening based on this equation. They showed that if an initially narrow Gaussian distribution of particle sizes is assumed, this relaxes to a steady distribution of sizes if plotted as a function of the reduced radius, $r^*=r/\bar{r}$, where r is the precipitate radius and $\bar{r}$ the mean radius. The predicted size distribution $h(r^*)$ is given by

$$h(r^*) = (r^*)^2 \left(\frac{3}{3+r^*} \right)^{7/3} \left(\frac{3/2}{3/2-r^*} \right)^{11/3} \exp\left(\frac{-r^*}{3/2-r^*} \right); \quad r^* < 3/2$$

(1.2)

$$h(r^*) = 0; \quad r^* > 3/2.$$

The distribution has an upper cut-off at $r^* = 1.5$, as shown in figure 1.2. When this steady distribution has been achieved, the coarsening rate is given by

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8D\Psi_{int}V_m^2C(\infty)t}{9RT}$$

(1.3)

or

$$\bar{r}^3 - \bar{r}_0^3 = K_3 t$$

(1.4)

where $\bar{r}_0$ is the value of $\bar{r}$ at time $t=0$, D is the diffusion coefficient

for the solute in the matrix and R is the molar gas constant.

This treatment assumed that the rate-controlling process for coarsening is the diffusion of solute atoms through the matrix. Wagner (1961) derived a further expression for the rate of coarsening where the rate-controlling step is the transfer of atoms across the particle/matrix interface. In this case

$$\bar{r}^2 - \bar{r}_0^2 = K_2 t. \quad (1.5)$$

Alternative treatments have dealt with the cases of diffusion along grain boundaries (Speight, 1968; Kirchner, 1971; Ardell, 1972a) and sub-boundaries (Ardell, 1972a) being rate-controlling. These treatments predict that

$$\bar{r}^4 - \bar{r}_0^4 = K_4 t \quad (\text{grain boundary diffusion controlled}) \quad (1.6)$$

and $\bar{r}^5 - \bar{r}_0^5 = K_5 t \quad (\text{sub-boundary diffusion controlled}). \quad (1.7)$

Ardell and Nicholson (1966b) investigated the coarsening of γ' in two nickel-aluminium alloys. They showed that the observed size distributions and coarsening rates were in good agreement with equations 1.2 and 1.4 respectively. This was considered surprising since the system examined violated several of the assumptions inherent in the theory of Lifshitz, Slyosov and Wagner (LSW). The LSW theory assumes that the dispersed phase is randomly distributed throughout the matrix and that its volume fraction is sufficiently small that the mean particle size is negligible compared with the interparticle spacing. The γ' precipitates were observed to form as cubes aligned in rows running parallel to $\langle 100 \rangle$ directions and thus the distribution was certainly not random. Furthermore, the volume fraction of precipitates

in one of the alloys was as high as approximately 20%.

1.2.4 The Effects of Precipitate Volume Fraction on Coarsening Kinetics

Ardell (1972b) proposed a modification to the LSW theory to take account of the effect of the volume fraction of the dispersed phase. The modification was based on the supposition that the diffusion field of an individual particle is localised and has a range related to the mean free path between the particle and its nearest neighbour. This treatment maintains the form of the coarsening rate equation 1.4, but the rate constant, K_3 , is modified by a numerical factor so that it becomes a sensitive function of the volume fraction (f). When f is set to zero the original LSW rate equation and size distributions are maintained. However, the predicted size distributions are very sensitive to slight deviations from zero volume fraction, as shown in figure 1.3.

In order to test the applicability of the modified theory, Chellman and Ardell (1974) examined the coarsening of γ' precipitates in a series of Ni-Al alloys containing volume fractions of γ' ranging from 9% to 60%. In complete disagreement with the modified theory, they found the coarsening behaviour to be independent of the γ' volume fraction, f . The coarsening rate equation (equation 1.4) was found to be obeyed with K_3 insensitive to f and the precipitate size distributions were in reasonable agreement with those originally proposed by Lifshitz and Slyosov (1961) and by Wagner (1961).

A further theoretical attempt at assessing the effects of volume fraction on the kinetics of Ostwald ripening has been proposed by Brailsford and Wynblatt (1979). In calculating the diffusion of solute to a growing particle or from a dissolving one, the influence of all

particles was considered simultaneously in an infinite domain. Once again, equation 1.4 was maintained, but in this model K_3 is much less sensitive to f than in Ardell's model. Similarly the predicted size distributions show only a slight sensitivity to f , as shown in figure 1.4. The authors compared the predictions of their model to the available published data, and concluded that the observed discrepancies could be due to scatter of the experimental data.

Tsumuraya and Miyata (1983) have considered the effects of both the volume fraction and the shape of precipitates. In particular they dealt with the case of a regular array of cuboidal precipitates, typical of the γ' distribution in superalloys. Equation 1.4 was again maintained with K_3 containing a numerical function of the precipitate volume fraction, and the predicted size distributions are shown in figure 1.5.

1.2.5 The Effects of Precipitate Coalescence on Coarsening Kinetics

The treatments of γ' coarsening presented above specifically excluded the possibility of precipitates encountering each other and coalescing. Davies et al. (1980a, b) have examined the morphology of high γ' volume fraction Ni-Co-Al alloys and have observed elongated and L-shaped precipitates. This represents clear evidence for precipitate coalescence, and the hypothesis is further supported by the observed broad distribution of precipitate sizes. The authors assumed that the precipitates grew in accordance with conventional Ostwald ripening theories, and that as the precipitate boundaries expanded outwards they occasionally encountered each other. The centre-to-centre distances between precipitates were specified as remaining constant throughout. When an encounter occurred, coalescence was assumed to take place by a rapid diffusion interaction.

This possibility had been outlined by Lifshitz and Slyosov (1961) in their original analysis of Ostwald ripening, but they did not fully develop this approach. Davies et al. (1980b) analyzed the effects that coalescence by encounter might have on the coarsening kinetics and found that the basic rate equation (1.4) was still maintained where K_3 includes a numerical function of γ' volume fraction (f). The predicted size distributions are shown in figure 1.6. As the volume fraction tends to zero, the size distribution tends towards that for the LSW theory, since the probability of encounters falls to zero. An assessment was made of the rate of coarsening and of the size distribution of γ' precipitates in these alloy systems and they were found to be in reasonable agreement with the theoretical predictions.

Whilst agreeing that precipitate coalescence had clearly taken place, Doherty (1982) disagreed with the interpretation of the physical processes involved. He pointed out that if the precipitates grow by arrival of solute from surrounding smaller precipitates, it seems unlikely for this solute to diffuse into the narrowing gap between the larger precipitates. To overcome this problem, Doherty suggested that the precipitates will actually attract each other and move together. The driving force for this attraction would be the removal of the elastically strained matrix lying between two coherent precipitates and thus the process would depend on the γ/γ' misfit parameter. The mechanism would require stress-directed diffusion of solute into the gap and nickel out to lower the total elastic energy. One appealing aspect of this hypothesis is that it explains how a regular array of aligned cuboidal precipitates can be maintained, compared with the conventional models where precipitate centre-to-centre distances remain fixed.

1.3 Deformation Mechanisms in Superalloys

1.3.1. Solid Solution Strengthening

Typical nickel-base superalloys contain substantial amounts of alloying additions in solid solution, which increase the strength of the γ matrix. This solid solution strengthening arises from differences in the atomic diameter, the electron vacancy number (N_v) and the elastic modulus, between the solute atom and nickel. Pelloux and Grant (1960) have suggested that atomic diameter oversize of solute atoms is related to hardening through the effects of lattice expansion. The effects of electron vacancy number on solid solution strengthening result, at least in part, from its influence on the stacking fault energy. The dependence of the stacking fault energy on specific alloy additions has been determined by Beeston et al. (1968) and by Beeston and France (1968), and is shown in figure 1.7 together with the effect on yield stress. The lowering of stacking fault energy by alloying elements tends to make cross-slip and climb more difficult in the γ matrix.

Decker (1969) has estimated the potency of various additions to a superalloy matrix as solid solution strengtheners based on considerations of atomic diameter and N_v . He concludes that aluminium, tungsten, molybdenum and chromium are most effective, whilst iron, titanium, cobalt and vanadium contribute little to the strength of the matrix. In the range of high temperature creep, γ strengthening is diffusion dependent so in this regime slowly diffusing elements like molybdenum and tungsten would be expected to be the most potent hardeners. Furthermore, Decker points out that the presence of molybdenum and tungsten has been shown to lower the effective diffusivity of titanium and chromium.

1.3.2. Precipitation Strengthening

The resistance to deformation of superalloys at both ambient and elevated temperatures can largely be attributed to the presence of coherent γ' precipitates, which act as obstacles to the passage of dislocations. There are three fundamental mechanisms by which dislocations can pass precipitates, namely precipitate shearing, looping between precipitates or climb around them. Since climb is a diffusion controlled mechanism, it only becomes important at elevated temperatures.

Above a certain critical diameter (d_c) dislocations can by-pass precipitates by forming Orowan loops. Assuming a random array of precipitates, this mode of deformation gives a shear yield stress (τ_{or}) of

$$\tau_{or} = \frac{0.81 G b \ln(d/r_i)}{2\pi(1-\nu)^{1/2}(L-d)} \quad (1.8a)$$

where d is the precipitate diameter in the slip plane, L is the planar centre-to-centre precipitate spacing, r_i is the inner dislocation cut-off radius, ν is Poisson's ratio, G is the shear modulus and b is the magnitude of the dislocation Burgers vector (Martin, 1980). A commonly used approximation for the shear yield stress when Orowan looping is occurring is

$$\tau_{or} \approx \frac{G b}{L} \quad (1.8b)$$

At precipitate diameters below d_c , particle shearing takes place, generally giving a shear yield stress (τ_y) of

$$\tau_y = C_1(f d)^{1/2} \quad (1.9)$$

where C_1 is a constant dependent on the hardening mechanism.

Mitchell (1966), has examined the change in hardness with increasing mean particle diameter in a Ni-Cr-Ti-Al alloy for constant volume fraction of γ' . He found that as the diameter was increased, the hardness initially increased, passed through a maximum and then diminished as shown in figure 1.8. The ascending portion of the curve was ascribed to dislocation shearing of precipitates and the descending portion to dislocation looping, the peak occurring at a mean diameter of approximately 20 nm.

Most modern superalloys contain a high volume fraction of γ' precipitates, typically up to about 70%. In these alloys the inter-precipitate spacing is necessarily small with respect to the precipitate size and consequently deformation by dislocation looping is rarely observed. Of the strengthening mechanisms involving γ' shearing the two most important are considered to be coherency hardening and order hardening (Chaturvedi et al., 1976).

1.3.2.1. Coherency Hardening

Coherency hardening arises from the coherency strain associated with precipitates. The coherency strains and the consequent effect on yield stress depend on the misfit parameter $\Delta a/a$ between the precipitate and matrix and on the precipitate size. The effect of various alloying additions on the coherency strains and on the hardness of Ni-Al alloys has been investigated by Decker and Mihalisin (1969) and is shown in figure 1.9. Gerold and Haberkorn (1966) have predicted the contribution to the critical resolved shear stress arising from coherency hardening, $\Delta\tau_y$, to be given by:

$$\Delta\tau_y = \beta_1 G(\Delta a/a)^{3/2} \left(\frac{r}{b}\right)^{1/2} f^{1/2} \quad (1.10)$$

where β_1 is a numerical constant equal to 3 for edge and 1 for screw dislocations, G is the shear modulus of the matrix and b is the magnitude of the dislocation Burgers vector.

1.3.2.2 Order Hardening

The ordered $L1_2$ structure of γ' is shown in Figure 1.10 before and after the passage of an $a/2\langle 110\rangle\{111\}$ dislocation, $\langle 110\rangle$ and $\{111\}$ being the close-packed directions and planes respectively. It can be seen that whilst the same positions in space are occupied in the latter case, atoms in the $\{111\}$ plane shown by broken lines no longer have the correct nearest neighbours. There is thus a planar defect known as an antiphase boundary or APB. Considering only nearest neighbour interactions, the characteristic energy per unit area, Ψ_{apb} , of an $a/2[110](111)$ APB has been calculated by Flinn (1960) as

$$\Psi_{apb} = \frac{2}{\sqrt{3}a^2} [E_{AB} - 1/2(E_{AA} + E_{BB})] \quad (1.11)$$

where E_{XY} is the bond energy between atoms X and Y . The creation of this energy acts as an obstacle to the passage of dislocations. Ham (1967) has shown that for a low precipitate volume fraction, the shear stress arising from this effect is given by

$$\Delta\tau = \frac{2\Psi_{apb}}{b} \left(\frac{rf}{\pi\Gamma}\right)^{1/2} \quad (1.12)$$

where Γ is the dislocation line tension.

However, a complication arises since the dislocations tend to travel in pairs, the second dislocation removing the APB created by the first. There are several examples of the occurrence of such paired dislocations in the literature (for instance, Merrick, 1964; Gleiter and Hornbogen, 1967/68; Brown and Ham, 1971; Beardmore et al., 1969; Reppich et al., 1982; Thompson and Brooks, 1982). Hüther and Reppich (1978) and Reppich (1982) have considered two modes of particle shearing by dislocation pairs, which they refer to as weak and strong coupling. Weak coupling occurs when the size and volume fraction of the dispersed phase are small. The spacing of the dislocation pair is greater than the mean precipitate diameter and so the dislocations do not lie in the same precipitate, as illustrated in fig. 1.11(a). This situation has been treated by Brown and Ham (1971), who showed that the yield stress was given by

$$\tau_y = \left(\frac{\Psi_{apb}}{2b} \right) \left[\left(\frac{4\Psi_{apb}rf}{\pi\Gamma} \right)^{1/2} - f \right] \quad \text{for} \quad \frac{\pi\Gamma f}{4\Psi_{apb}} < r < \frac{\Gamma}{\Psi_{apb}} \quad (1.13)$$

and

$$\tau_y = \left(\frac{\Psi_{apb}}{2b} \right) \left[\left(\frac{4f}{\pi} \right)^{1/2} - f \right] \quad \text{for} \quad r > \frac{\Gamma}{\Psi_{apb}} .$$

The strength of pair coupling increases with increasing particle size so that in the case of strong pair coupling both dislocations lie within the same precipitate as shown in fig. 1.11(b). An upper limit of the cutting stress in this case is given by approximately one half of the Orowan stress for a single dislocation (Reppich, 1975). A more rigorous treatment by Reppich (1982) for spherical precipitates sheared by this mechanism yields

$$\tau_y = \frac{1}{2} \frac{1.72}{2br} \frac{\Gamma f^{1/2} C_2}{C_2 \Gamma} \left(\frac{1.28 \Psi_{apb}}{C_2 \Gamma} \frac{2r}{-1} \right)^{1/2} \quad (1.14)$$

where C_2 is a constant of the order of unity. In this model, the peak strength is attributed to the transition from weak pair coupling to strong pair coupling, rather than from precipitate cutting to Orowan looping.

1.3.2.3 Other Precipitation Hardening Mechanisms

Other hardening mechanisms involving the shearing of coherent precipitates are surface hardening, stacking fault hardening and modulus hardening. Surface hardening arises from the energy needed to create additional precipitate/matrix interfacial area when a precipitate is sheared by dislocations. Harkness and Hren (1970) have estimated the magnitude of the increment to the shear yield stress resulting from surface hardening as

$$\Delta\tau_y = \frac{f^{1/2} r^2 \psi_{int}^{3/2}}{b^3} 30.4 \left[\frac{G b}{\pi} \ln \left(\frac{L}{r_i} \right) \right]^{-1/2} \quad (1.15)$$

Hirsch and Kelly (1965) suggested the possibility of stacking fault hardening arising from a strong interaction between dislocations and particles whose stacking fault energy is much lower than that of the matrix. In this case the separation of partial dislocations is greater in the precipitate than in the matrix, and there is a reduction in the energy per unit length of dislocation. Thus an additional shear stress ($\Delta\tau_y$) is required to drag the dissociated dislocation out of the precipitate and this is given by

$$\Delta\tau_y = \left(\frac{8}{\pi} \right)^{1/2} G \left(\frac{\Delta\psi_{sf}}{G b} \right)^{3/2} \left(\frac{r f}{b} \right)^{1/2} I_m \quad (1.16)$$

where $\Delta\psi_{sf}$ is the difference between the stacking fault energy of the precipitate and that of the matrix, and I_m is a complex function of r and the stacking fault energy of the precipitate (Kelly, 1973).

Similarly there will be a change in energy and thus a force associated with a dislocation interacting with a precipitate of different shear modulus from the matrix. Kelly (1973) quotes the shear stress ($\Delta\tau_y$) arising from modulus hardening as

$$\Delta\tau_y = \frac{\Delta G}{4\pi^2} \left(\frac{3\Delta G}{G b} \right)^{1/2} (0.8 - 0.143 \ln(r/b))^{3/2} r^{1/2} f^{1/2} \quad \text{for } r > 2b \quad (1.17)$$

where ΔG is the difference in shear modulus between matrix and precipitate and G is the shear modulus of the matrix.

1.3.3. The Anomalous Temperature-Dependence of the Yield Stress of Superalloys

Superalloys have been shown to exhibit a very low temperature sensitivity of yield stress and often a slightly increasing yield stress up to temperatures of approximately 700 °C. Beardmore et al. (1969) have assessed the temperature dependence of yield stress in a series of alloys containing differing volume fractions (0-100%) of the γ' phase and their results are shown in figure 1.12. The fairly constant value of yield stress (σ_y) with respect to temperature in the two-phase alloys can be ascribed to a balance between a drop in σ_y of the γ matrix and an anomalous increase in σ_y of the γ' phase (Davies and Stoloff, 1965). The high σ_y of low γ' volume fraction alloys at low temperatures was found to be due to the presence of hyperfine γ' precipitates in the matrix, which dissolve at higher temperatures.

Much work has been carried out on single phase γ' in order to understand the deformation characteristics of this phase. The temperature dependence of σ_y for γ' is particularly unusual in showing a progressive increase up to temperatures of approximately 700 °C and subsequently decreasing (see for example, Davies and Stoloff, 1965; Thornton et al., 1970; Umakoshi et al., 1984). Guard and Westbrook (1959) suggested that this behaviour could be due to strain ageing, whilst Flinn (1960) considered the contribution from thermally activated climb. Davies and Stoloff (1965) have pointed out that both of these processes are diffusion-controlled and therefore cannot explain the observed continuous increase in σ_y from 77 K (Davies and Stoloff, 1965; Lall et al., 1979).

An alternative explanation based on temperature-modified interactions between the lattice and dislocations has been proposed by Copley and Kear (1967). The authors measured the temperature dependence of the yield stress of single crystals of γ' with the stress axis parallel to $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ crystallographic directions. As shown in figure 1.13, the yield stresses show a similar temperature dependence for each orientation, but with the peak in the yield stress occurring at different temperatures. By considering the Schmid factors for slip on $\{111\}\langle 110 \rangle$ and $\{100\}\langle 110 \rangle$ systems, the authors were able to rationalise the differences between the crystals in terms of a transition from octahedral $\{111\}$ slip to cube slip with increasing temperature in $\langle 111 \rangle$ and $\langle 110 \rangle$ oriented crystals. This transition was not thought to occur in crystals with $\langle 100 \rangle$ orientation. An examination of surface slip steps was found to be consistent with the hypothesis. As a qualitative explanation of the temperature dependence of the yield stress, Copley and Kear suggested that lattice anisotropy changes with increasing temperature result in Schockley partials

becoming more constricted and therefore the dislocations are subject to an increasing friction stress. Beyond the σ_y peak it was suggested that disordering of the γ' lattice results in the partials becoming dissociated again. However, it has been shown by Corey and Lisowsky (1967) that γ' remains ordered up to at least 1250 °C.

Thornton et al. (1970) have measured the yield stress of γ' at selected plastic strains as low as 10^{-6} over a wide temperature range and their results are shown in figure 1.14. The characteristic flow stress peak is not shown at very low strains. Consequently it was concluded that dislocations become mobile at a constant stress irrespective of the testing temperature, which conflicts with models based upon changes in friction stress with temperature. The proposed explanation of the temperature dependence of the yield stress at higher strains was based upon the observation of slip on $\{100\}$ planes at elevated temperatures. It was suggested that the increase in flow stress with temperature occurred as a result of a progressive transition from a low temperature mode (mode I) to a high temperature mode (mode II) of deformation. In mode I, $\{111\}\langle 110 \rangle$ slip systems are active, with exhaustion hardening occurring whereby edge dislocations move out of the crystal, undergo mutual annihilation or adopt relatively immobile screw orientations by cross-slip onto $\{100\}$ planes. Cross-slip from $\{111\}$ to $\{100\}$ planes had been proposed as a favourable process by Kear and Wilsdorf (1962), due to the low APB energy on $\{100\}$ planes (Flinn, 1960).

In mode II both $\{111\}$ and $\{100\}$ slip systems are active, with hardening occurring due to interactions between the slip systems. It was suggested that beyond the σ_y peak, the flow process is dominated by recovery. The authors pointed out that in the case of $\langle 100 \rangle$ oriented crystals the resolved shear stress on $\{100\}$ planes is zero.

In this case they assumed that local inhomogeneities could cause sufficient dislocation movement on $\{100\}$ planes for interaction with dislocations on $\{111\}$ planes to take place. The limited movement of dislocations on $\{100\}$ planes in this situation was postulated as an explanation of the displacement of the yield stress peak in $\langle 100 \rangle$ oriented crystals compared with $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations.

A modification to the Thornton et al. model has been proposed by Takeuchi and Kuramoto (1973) and has been applied to experimental data by Lall et al. (1979). In this model it was suggested that below the σ_y peak interactions occur between primary dislocations on $\{111\}$ planes and sessile segments which have cross-slipped onto $\{100\}$ planes as a result of thermal activation. An increase in temperature would promote more cross-slip and therefore a higher flow stress. The decrease in the flow stress at high temperatures was attributed to macroscopic slip on $\{100\}$ planes. TEM studies by Staton-Bevan and Rawlings (1975) have confirmed that slip on $\{100\}$ planes only occurs beyond the σ_y peak, but as yet no direct observations of the mechanism of cross-slip have been made.

Recently a new type of defect, namely APB tubes, have been discovered in γ' by Chou et al. (1982). These tubes are formed by non-aligned jogs in superlattice dislocations and it has been speculatively suggested that they might account for the high strength of γ' at high temperatures.

1.3.4. Precipitate Shearing Mechanisms

Dislocations of the disordered matrix must be considered as partial dislocations in the γ' superlattice owing to the formation of APB. Three types of stacking faults exist in the $L1_2$ structure, namely:

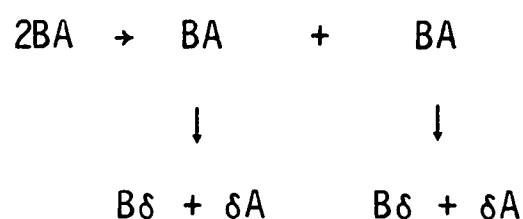
1. Superlattice (intrinsic or extrinsic) faults
2. Antiphase boundary faults
3. Complex faults.

Superlattice intrinsic (S-ISF) and superlattice extrinsic (S-ESF) stacking faults are produced by shear displacements of type $\{111\} \frac{a}{3} \langle 112 \rangle$, and APB faults are produced by $\{111\} \frac{a}{2} \langle 110 \rangle$ displacements. The energy of the latter is higher than for S-ISF or S-ESF faults, since some of the atoms in the APB have incorrect nearest neighbours. Complex faults (CF), which may be regarded as a superposition of APB and S-ISF faults, are related to the $L1_2$ structure by $\{111\} \frac{a}{6} \langle 112 \rangle$ shear displacements.

Combinations of these faults lead to several possible modes of dislocation-precipitate interactions. These possibilities have been considered in detail by Kear et al. (1970) and are outlined below.

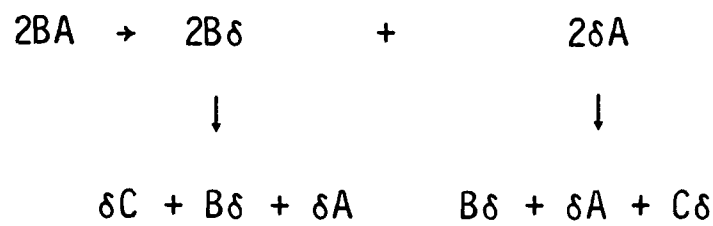
a $\langle 110 \rangle$ shear

If dissociation of paired $\frac{a}{2} \langle 110 \rangle$ dislocations into $\frac{a}{6} \langle 211 \rangle$ partials occurs, shear of γ' precipitates proceeds by the passage of two sets of dissociated dislocations. There are then four possible resultant configurations, as illustrated in figure 1.15. Using the notation of Frank (1951) and Thompson (1953), schemes (a) and (b) involve dissociations of the form



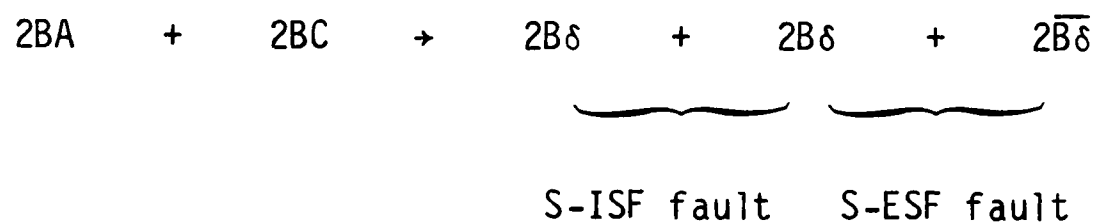
Schemes (c) and (d) are more complex, requiring the nucleation of dislocation loops at the γ/γ' interfaces in order to facilitate shear by partials linked by the associated S-ISF or S-ESF faults. Here the

dissociations are of the form



a $\langle 211 \rangle$ shear

The order of the $L1_2$ lattice can also be maintained by shear with a net Burgers vector of a $\langle 211 \rangle$. As in the ordinary fcc lattice, two total superlattice dislocations with Burgers vectors at 60° in $L1_2$ can react to form intrinsic/extrinsic fault pairs bounded by three partial dislocations having the same Burgers vector as follows:



The mechanism of precipitate shearing in this situation is illustrated in figure 1.16, showing two sets of partial dislocations shearing the precipitate separated by S-ISF and S-ESF faults. More detailed considerations by Kear et al. (1969a) of the exact dislocation structures in the precipitate require that small dislocation dipole displacements be obtained before glide of the paired partial dislocations can proceed and therefore this mode of deformation is only likely under high temperature, low strain-rate conditions.

1.3.5 Dislocation Climb around Precipitates

Dislocation climb is a diffusional process. Consequently by-pass of dislocations around precipitates by a climb mechanism is important

only at elevated temperatures. A commonly used climb model is that proposed by Brown and Ham (1971). They considered a dislocation surmounting a cuboidal particle of side length w , where the slip plane is AA'BB' as shown in figure 1.17(a). The additional line length created when the dislocation moves forward by a distance δx is $\sqrt{2}\delta x$. Thus assuming a line energy of $Gb^2/2$ and a particle spacing L , the flow stress is given by

$$\tau = \frac{G b}{2^{1/2} L} . \quad (1.18)$$

If the rate-controlling process for climb is then considered to be pipe diffusion with a diffusion coefficient D_p , then the strain rate is given by

$$\dot{\epsilon} = \frac{C_v D_p b^5 \rho}{w^2} \quad (1.19)$$

where C_v is the vacancy concentration in the neighbourhood of a climbing dislocation having a Burgers vector b , and ρ is the number of dislocations per unit volume.

If the particle in figure 1.17 is assumed to represent a $\{100\}$ aligned γ' precipitate, then the slip plane in this model is $\{110\}$. Since $\{110\}$ slip is not generally observed, it is more appropriate to consider a dislocation whose slip plane in the matrix is $\{111\}$, as shown in figure 1.17(b). In this case the additional line length created when the dislocation moves forward by a distance δx is $(2^{1/2}-1)\delta x$. Thus the flow stress is given by

$$\tau = \frac{(2^{1/2}-1)G b}{2L} \quad (1.20)$$

which is less than one third of the value predicted by equation 1.18. Similarly, adapting Brown and Ham's strain-rate calculations to this situation yields the following expression

$$\dot{\epsilon} = \frac{2\sqrt{6} C_v D_p b^5 \rho}{w^2} \quad (1.21)$$

As pointed out by Brown and Ham, these treatments are incomplete since they ignore the tendency of the dislocation to smooth itself out under the influence of its own line tension. Lagneborg (1973) has modified the Brown and Ham model to take account of this effect. He found that the maximum back stress $\tau_{\text{back}}^{\text{max}}$ was largely insensitive to changes in the particle diameter or spacing, but was proportional to the applied stress such that

$$\tau_{\text{back}}^{\text{max}} \approx 0.7\tau. \quad (1.22)$$

Brown (1982) has distinguished between two distinct mechanisms of climb around particles, namely local climb as in the Brown and Ham model, and general climb. For local climb most of the dislocation remains in the glide plane and a small segment surmounts the particle, whereas general climb involves climb of the whole dislocation segment between two particles. Less extra dislocation line length is created by general climb and thus the mechanism may proceed under the influence of a lower stress, derived by Brown (1982) as

$$\sigma = \frac{f^{3/2}}{2^{5/4}} \sigma_{\text{or}} \quad (1.23)$$

where σ_{or} is the stress required to form Orowan loops. However, local climb requires less mass transport and therefore may be more favourable on kinetic grounds.

Arzt and Ashby (1982) considered interactions between a single dislocation and an array of hard particles in its slip plane. They showed that for the dislocation to by-pass the obstacles by a mechanism involving local climb, the shear stress, τ , required was given by

$$\tau \approx 0.3 \frac{G b}{L} . \quad (1.24)$$

However, if instead climb is general, then the required shear stress falls to

$$\tau \approx 0.04 \frac{G b}{L} . \quad (1.25)$$

Alternative treatments of the climb process have been suggested by, for example, Shewfelt and Brown (1977), Stevens and Flewitt (1981a), Hausselt and Nix (1977) and Evans and Knowles (1980). These are based on a variety of assumed particle geometries and distributions and dislocation configurations.

1.4 Creep in Superalloys

Creep is a thermally activated time-dependent deformation process. To investigate creep properties a constant load or stress may be applied to a specimen and the strain recorded as a function of time. Bird et al. (1969) have identified several different types of creep curves resulting from such tests in a variety of metals and alloys, as illustrated in figure 1.18. Three distinct stages are often observed.

Directly on loading, the specimen may undergo an instantaneous strain followed by the primary or transient stage. The strain rate declines either throughout or towards the end of this region and reaches a constant value in the secondary or steady-state stage. In the tertiary stage the creep rate starts to accelerate and this leads to final fracture. The observation of a tertiary stage is normally attributed to the growth of cracks or cavities at grain boundaries or other crystal discontinuities.

In many engineering applications the steady-state creep rate $\dot{\epsilon}_s$, is used as a quantitative parameter for creep performance. However, the various stages of creep are not always distinctly defined, and superalloys often exhibit a continually accelerating creep strain-rate from the onset of secondary creep through to failure, as shown by, for example, Kear and Piarcey (1967), Stevens and Flewitt (1981a) and Dyson and McLean (1983). For this reason many authors use the minimum creep rate as a representative creep parameter.

1.4.1 The Stress Dependence of Creep

The relationship between $\dot{\epsilon}_s$ and the applied stress (σ) for a wide range of polycrystalline materials can be represented by the common curve shown in figure 1.19. Sherby and Burke (1967) identified the occurrence of three distinct regions. At low stresses $\dot{\epsilon}_s$ varies linearly with σ :

$$\dot{\epsilon}_s = K\sigma \quad (1.26)$$

where K is a constant. This regime may be due to diffusional creep, occurring by a diffusional flux of vacancies from transverse to longitudinal grain boundaries either by bulk diffusion through the grain, known as Nabarro-Herring creep, or by grain boundary diffusion

around the grains, known as Coble creep (Burton, 1977).

Over a wide intermediate stress range at sufficiently high temperatures, $\dot{\epsilon}_S$ can be represented by a power law function of stress, referred to as the Bailey-Norton equation (Bailey, 1930; Norton, 1929):

$$\dot{\epsilon}_S = K' \sigma^n. \quad (1.27)$$

Under these conditions deformation occurs by a combination of glide and climb of dislocations. Equation 1.27 can be generalised to account for differences between materials by normalising $\dot{\epsilon}_S$ and σ with respect to the volume diffusion coefficient (D) and shear modulus (G) of the alloys respectively. Thus Mukherjee et al. (1969) expressed the creep rate as

$$\frac{\dot{\epsilon}_S}{D} = K'' \frac{Gb}{kT} \left(\frac{\sigma}{G} \right)^n \quad (1.28)$$

At sufficiently high stresses ($\geq 10^{-3}G$) the power law representation of creep breaks down and an exponential dependence of $\dot{\epsilon}_S$ upon σ has been shown to provide an adequate fit to experimental data (Sherby and Burke, 1967):

$$\dot{\epsilon}_S = K''' \exp(B\sigma) \quad (1.29)$$

where B is a constant.

There is no generally accepted model of this behaviour, but Sherby and Burke (1967) considered the regime to involve dislocation climb under conditions where the vacancy concentration is greater than the thermal equilibrium.

Various empirical relationships have been proposed with the object of describing both the intermediate and high stress range in one expression. For this purpose Garofalo (1963) suggested the following expression:

$$\dot{\epsilon}_S = K''''(\sinh \beta_2 \sigma)^n \quad (1.30)$$

where β_2 is a constant. Similar expressions have been proposed by Weertman (1957) and by Barrett and Nix (1965).

1.4.2 Dislocation Creep Mechanisms

Ashby (1973) developed the approach of delineating conditions under which various deformation mechanisms are operative by means of deformation mechanism maps. Figure 1.20 shows two such maps for the cast nickel-base superalloy Mar-M200 having two different grain sizes, namely 0.1 mm and 10 mm. The range of operation of a typical turbine blade is indicated. It is seen that for the coarser-grained alloy diffusional creep is suppressed. Since the current work is concerned with single crystal superalloys, those creep phenomena which relate only to fine-grained materials or to grain boundary effects will not be considered and the discussion restricted to dislocation mechanisms in the crystal lattice.

Dislocation creep models generally assume the establishment of a three-dimensional dislocation network. At high temperatures recovery of the dislocation network is important and during the secondary stage a balance exists between the recovery rate and the work-hardening rate. Thus in a true steady-state condition, the dislocation density and the strain rate ($\dot{\epsilon}_S$) remain constant. The models fall into two categories, depending on whether the subprocesses of dislocation glide or of recovery of the dislocation structure are assumed to control the rate of deformation. The strain rate is generally assumed to be given by

$$\dot{\epsilon}_S \propto \rho b v \quad (1.31)$$

where ρ is the number of dislocations per unit volume and v is the mean dislocation velocity. The essential differences between many of the creep models lie in the assumed forms of ρ and v . The postulated dislocation structures are often similar in each case. Advocates of recovery-controlled models include Orowan (1946/47), Weertman (1957), McLean and Hale (1961) and Lagneborg (1969) whereas glide-controlled mechanisms have been proposed by, for example, Raymond and Dorn (1964), Barrett and Nix (1965) and Ansell and Weertman (1959).

Several models of dislocation creep, for instance those due to Stüvve (1965) and Lindroos and Miekko-Oja (1968), rely on the postulated establishment of subgrain boundaries to form a steady-state dislocation structure. The rate-limiting process of dislocation annihilation is assumed to occur by climb at or near sub-boundaries, while glide occurs within the subgrains. The dynamic dislocation interactions have been incorporated by Blum (1982) and by Blum and Portella (1983) into a 'knitting model'. The contribution to deformation arising from migration of the subgrain boundaries has been considered by Excel and Warrington (1972). However, Lupinc (1982) has pointed out that superalloys generally exhibit a fairly uniform dislocation distribution during creep and that subgrain structure rarely appears. Thus the applicability of models based on subgrain structure is limited.

1.4.2.1 Recovery-Controlled Models

The basis of recovery controlled models is the establishment of a dynamic equilibrium between strain-hardening and recovery during steady-state creep. The strain-rate in this situation was given by Orowan (1946/47) as

$$\dot{\epsilon}_s = \left(\frac{-\partial \sigma_i}{\partial t} \right) / \left(\frac{\partial \sigma_i}{\partial \epsilon} \right) = r'/h \quad (1.32)$$

where σ_i is the internal stress due to strain-hardening, r' is the rate of recovery and h is the strain-hardening coefficient. This expression has been verified experimentally in pure nickel by Mitra and McLean (1966).

Lagneborg's (1972a) model assumes the formation of a homogeneous three-dimensional dislocation network. According to this model, during steady-state creep some dislocation junctions will break as a result of thermal fluctuations, those links connected with the longest dislocations breaking most frequently. The released dislocations will then undergo glide until held up by the network. Thus a strain increment together with local strain hardening will occur. Simultaneously recovery of the dislocation network will be occurring, the driving force being provided by the line tension of the curved dislocation meshes. The recovery process tends to increase the average mesh size of the network, encouraging breakage of the dislocation links. Thus a dynamic equilibrium is established for which the strain rate is given by

$$\dot{\epsilon}_s = 2blm_d\Gamma\rho^2 \quad (1.33)$$

where l is the mean free path of dislocation motion and m_d is the mobility of climbing dislocations. Lagneborg considered the separation of the applied stress (σ) into an athermal (internal stress, σ_i) and a thermal component (effective stress, σ_e). A simple Bailey-Norton relation (equation 1.27) was only predicted under conditions of low stress and high temperature, when $\sigma_i \approx \sigma$. Under these conditions it was shown that

$$\dot{\epsilon}_s \approx 2b l m_d \Gamma \left(\frac{\sigma}{\beta_3 G b} \right)^4 \quad (1.34)$$

where β_3 is a constant of the order of unity.

The same model has been used by Lagneborg (1972b) to explain transient or primary creep behaviour. During this stage the dislocation network is considered to be developing. Some of the initially formed dislocation links would be able to break free under the influence of small thermal fluctuations and thus an initially high strain rate is predicted. As the easily activated links become depleted, they are replaced by links whose mean strength is greater, the network becomes progressively more dense and the mean glide path of the dislocations becomes shorter. Thus strain hardening processes dominate over recovery in this regime and the strain rate shows a progressive decline. However, since the driving force for recovery increases with dislocation density, a dynamic equilibrium is eventually achieved, corresponding to the onset of secondary creep. McLean (1966) presented a very similar view of the primary creep region and formulated the creep strain rate in terms of an Arrhenius equation:

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp \left(\frac{-bA^*(h\epsilon - r't)}{kT} \right) \quad (1.35)$$

where $\dot{\epsilon}_0$ is the initial strain-rate and A^* is the activation area.

Under the mechanism described above, the strain-rate would continuously decrease during the primary stage. However, some directionally solidified and single crystal superalloys have been shown by Webster and Pearcey (1967) and by Leverant and Kear (1970) to exhibit a sigmoidal type of creep curve over the primary stage, in

accordance with curve D in figure 1.18. This effect has also been observed in single crystals of germanium by Penning and De Wind (1959) and to a less noticable extent in a well-annealled polycrystalline Fe-Mo alloy by Maeda et al. (1974). After a period of negligible creep strain, known as the incubation period, the strain rate accelerates before entering the conventional primary creep stage of decelerating strain rate. This behaviour is generally attributed to an initial absence of mobile dislocations. Leverant and Kear (1970) showed that samples shock-loaded at room temperature prior to creep testing did not exhibit an incubation period. This was assumed to be the result of having introduced a high density of mobile dislocations. Incubation periods are particularly noticeable in single crystals since grain boundaries are potent dislocation sources.

The majority of dislocation creep models deal only with the secondary creep stage, where a steady-state dislocation structure is assumed. Weertman (1957) considered deformation occurring by glide of groups of dislocation loops emitted by fixed dislocation sources. The motion of these loops would be arrested by strong interactions with dislocation groups on neighbouring slip planes and dislocation pile-ups would result. Recovery was envisaged as occurring by the leading edge dislocations of the piled-up groups climbing towards each other and annihilating. This was treated as the rate-limiting process. Each annihilated dislocation loop would be replaced by a new one emitted from the sources, and the resultant strain rate would be given by

$$\dot{\epsilon}_S = \frac{\beta_4 D_S \sigma^{4.5}}{b^{1/2} N_d^{1/2} G^{3.5} kT} \quad (1.36)$$

where β_4 is a numerical constant of the order of 0.2, D_S is the self

diffusion coefficient, and N_d is the number of dislocation sources per unit volume. Several of the assumptions inherent in this approach have been questioned by Lagneborg (1972b), and in particular he points out that dislocation pile-ups have not been observed during secondary creep.

An alternative treatment of steady-state creep has been proposed by Gittus (1974) based on Friedel's (1964) equation which describes the rate at which a dislocation network will coarsen due to jog-controlled climb under the driving force of the line tension within the network:

$$\frac{\partial r_n}{\partial t} = \frac{DG b^3 C_j}{kT} r_n^{-1} \quad (1.37)$$

where r_n is the network size and C_j is the temperature-dependent jog concentration. Gittus assumed that the network size and hence the dislocation density ρ is determined by the applied stress, σ :

$$\sigma = \frac{\beta_5 G b}{r_n} = \beta_5 G b \rho^{1/2} \quad (1.38)$$

where β_5 is a constant having a theoretical value of $(2\pi)^{-1}$. Then assuming that the mean free glide path of dislocations is equal to the network spacing, Gittus derived that

$$\dot{\epsilon}_s = \frac{DC_j G b}{\beta_5^3 kT} \left(\frac{\sigma}{G} \right)^3. \quad (1.39)$$

In a similar model, Evans and Knowles (1979) have shown that, depending on whether the mean free dislocation glide path is assumed to be equal to the network spacing or to be constant, the stress exponent can be set to 3 or 4 respectively.

1.4.2.2. Glide-Controlled Models

Jogs on a screw dislocation have edge character. Thus if a screw dislocation glides under the influence of an external stress, these jogs must undergo climb in order to maintain their positions in the dislocation. Many authors have analysed thermally activated motion of jogged screw dislocations as a possible mechanism controlling plastic deformation. In particular this process has been discussed as the rate-controlling factor for high temperature steady-state creep by , for example, Raymond and Dorn (1964), Barrett and Nix (1965) and Hirsch and Warrington (1961). Barrett and Nix (1965) obtained the following expression for the steady-state creep rate:

$$\dot{\epsilon}_S = \beta_6 D_S \rho \sinh \left(\frac{\sigma b^2 L_j}{kT} \right) \quad (1.40)$$

where β_6 is a numerical constant having a value of ~ 20 and L_j is the distance between the jogs.

Weertman and Weertman (1965) have considered glide-controlled creep in solid solution alloys. Gliding dislocations were envisaged to drag along an impurity atmosphere whose motion is controlled by diffusion of the constituent foreign atoms. The steady-state creep rate resulting from this process was shown to be given by:

$$\dot{\epsilon}_S = \frac{B' 4\pi^2 \sigma^3}{G^2} \quad (1.41)$$

where B' is a temperature-dependent constant.

1.4.2.3 Other Dislocation Creep Mechanisms

Nabarro (1967) has proposed a creep mechanism based on a

dislocation network whose links are able to emit and absorb vacancies. Under the influence of an applied shear stress, τ , a flux of vacancies between source and sink links would bring about a steady climb motion of the dislocations. By considering deformation occurring by this climb motion alone, without accompanying glide, Nabarro showed that $\dot{\epsilon}_s$ would be proportional to τ^3 , assuming lattice diffusion of vacancies. The shear stress exponent was shown to increase to 5 at lower temperatures if pipe-diffusion along dislocation cores was assumed to predominate.

Under certain conditions, normally at temperatures approaching the melting point and at low stresses, the phenomenon known as Harper-Dorn creep has been observed (Harper and Dorn (1957)). In this regime the strain rate has been found to be directly proportional to the applied stress, as for diffusional creep. However, the Coble mode of diffusional creep would be precluded at very high temperatures, and the measured strain rates are up to three orders of magnitude higher than predicted by the Nabarro-Herring mechanism. Furthermore, the strain rates are insensitive to grain size, contrary to diffusional creep mechanisms. The reported observations and proposed mechanisms of Harper-Dorn creep have been reviewed by Yavari et al. (1982) and by Langdon and Yavari (1982). The proposed mechanisms include models based on the glide of jogged screw dislocations, the climb of isolated edge dislocations and the balance between creation and annihilation of gliding dislocations. However, as yet there is no entirely satisfactory explanation of the phenomenon.

1.4.3 The Effects of Hard Particles

Ansell and Weertman (1959) were among the first authors to

consider the effects of second phase particles on creep deformation. They assumed that at low stresses and high temperatures deformation occurs by climb of dislocations around particles, with the dislocations originating at Frank-Read sources. They derived an expression for steady-state creep rate such that

$$\dot{\epsilon}_S = \frac{\pi \tau b^3 D}{2kTd^2} \quad (1.42)$$

where d is the particle diameter in the slip plane. This expression was derived for a stress ranging from that required to activate Frank-Read sources up to the onset of Orowan looping. Thus

$$\frac{Gb}{L_{FR}} < \tau < \frac{Gb}{L}$$

where L is the particle spacing and L_{FR} is the length of a Frank-Read source.

At stresses greater than Gb/L , dislocations were considered to by-pass particles by bowing out and pinching-off loops around them. This would occur until the back-stress exerted by the loops prevented new dislocations from bowing. The rate-controlling process would then be the climb of the loops to the top of the particles resulting in their annihilation. The creep rate for this process was derived as

$$\dot{\epsilon}_S = \frac{2\pi\tau^4 L^2 D}{dG^3 kT} \quad (1.43)$$

Investigations of the steady-state creep of the γ' strengthened alloys M252 and Inconel 700 by Rowe and Freeman (1963) and of ThO_2 dispersion hardened nickel by Clauer and Wilcox (1966) showed that $\dot{\epsilon}_S \propto L^2/d$ in accordance with the above model. In the latter case

TEM observations were consistent with the hypothesis that the rate-controlling process was the climb of edge dislocations over the ThO₂ particles. However the stress exponent was observed to be an order of magnitude higher than predicted.

1.4.4 The Concept of a Threshold Stress, σ_0

As creep is a thermally activated process, the temperature dependence of the creep rate can be accounted for by means of an Arrhenius factor. Thus the Bailey-Norton relation (equation 1.27) may be rewritten:

$$\dot{\epsilon}_s = A\sigma^n \exp\left(\frac{-Q}{RT}\right) \quad (1.44)$$

where A is a constant. For pure metals and single phase alloys, $n \approx 4$ and $Q \approx Q_{SD}$, the activation energy for self-diffusion. However, for the more complex engineering alloys such as superalloys and particle-containing materials it has been observed that $n \gg 4$ and $Q \gg Q_{SD}$, especially at the higher strain rates. (See, for example, Clauer and Wilcox, 1966; Jienting et al., 1983; Howson et al., 1980a,b.) This problem has been rationalised by expressing equation 1.44 in terms of an effective stress (σ_e) rather than the applied stress (σ), where

$$\sigma_e = \sigma - \sigma_0 \quad (1.45)$$

Thus equation 1.44 can be re-written as

$$\dot{\epsilon}_s = A'(\sigma - \sigma_0)^n \exp(-Q/RT) \quad (1.46)$$

where $n \approx 4$ and $Q \approx Q_{SD}$ for all metals and alloys.

The threshold stress (σ_0) is not constant for a particular alloy, but has been reported to change with temperature (Williams and Wilshire, 1973) and stress (Evans and Harrison, 1979) as well as microstructure. Advocates of dislocation glide-controlled creep regard σ_0 as a long range elastic back or internal stress (Ahlquist and Nix, 1971), whereas proponents of recovery-controlled creep treat σ_0 as a friction or resisting stress (Parker and Wilshire, 1978). Stevens and Flewitt (1981a) suggest that although σ_0 acts in opposition to dislocation glide, it can be considered to affect the rate of recovery by altering the network size.

σ_0 may be regarded as a short range threshold required to overcome obstacles to dislocation motion. Thus it can be treated as the stress required to shear particles or to by-pass them by climb or by Orowan looping. As was shown in section 1.3.3, the predicted threshold stress for dislocation climb around precipitates varies greatly depending on which model is assumed. Ajaja et al. (1980) have treated contributions to σ_0 from precipitates (σ_p) and solid solution strengthening (σ_s) separately, such that

$$\sigma_0 = \sigma_p + \sigma_s \quad (1.47)$$

The authors assumed σ_s to be proportional to the effective stress in the matrix such that

$$\sigma_s = C_3(\sigma - \sigma_p) \quad (1.48)$$

where C_3 is a constant, and thus they were able to show that

$$\dot{\epsilon}_s = A'(1-C_3)^n(\sigma - \sigma_p)^n \exp\left(\frac{-Q}{RT}\right) \quad (1.49)$$

where A' is the constant from equation 1.46.

A number of different techniques have been devised for measuring σ_0 , although some controversy exists concerning their interpretation (see, for example, McLean, 1980; Gibeling and Nix, 1977). The techniques due to Ahlquist and Nix (1969) and Williams and Wilshire (1973) involve the introduction of decrements to the applied stress and observation of the resulting strain transients. An alternative method used by Knowles and Evans (1976) involved arresting the cross-head during a constant strain-rate test and noting the level to which the stress decayed.

Evans and Harrison (1976) have used a stress decrement technique to measure σ_0 for three types of nickel-base superalloys, for unalloyed Ni_3Al and a steel. They found that the data fitted a single empirical expression:

$$\dot{\epsilon}_s = B''[(\sigma - \sigma_0)/\sigma_{0.05}]^{3.5} \quad (1.50)$$

where B'' is a constant and $\sigma_{0.05}$ is the 0.05% proof stress at the appropriate temperature.

1.4.5 The Effects of Precipitate Morphology

Many modern superalloys contain large volume fractions (up to 70%) of the γ' phase. The effect of γ' volume fraction (f) on the creep resistance of some commercial superalloys is shown in figure 1.21. An increase in f from 14% to 60% can quadruple the stress required for a 100 hour life (Decker, 1969). For given superalloys containing specific γ' volume fractions, a variety of types of microstructure have been reported in the literature to provide optimum creep resistance. Many industrial heat-treatments are tailored to provide a duplex distribution of coarse and fine γ' precipitates (Decker and Sims,

1972). The fine precipitates provide an effective barrier to dislocation motion at temperatures below $\sim 800^{\circ}\text{C}$. At higher temperatures these precipitates begin to dissolve in the matrix, leaving the coarse dispersion of γ' as the major obstacle to deformation.

Recently the effects of two different heat treatments on $\langle 100 \rangle$ oriented single crystal superalloy CMSX-2 have been assessed by Caron and Khan (1983). The first treatment (T_1) produced irregularly shaped precipitates whose mean size varied from region to region between $0.25\text{ }\mu\text{m}$ and $0.36\text{ }\mu\text{m}$. The second treatment (T_2) produced a homogeneous structure of aligned cuboidal precipitates of mean size $0.45\text{ }\mu\text{m}$. The latter treatment was found to result in a two-fold improvement in creep lives over the former at both $760^{\circ}\text{C}/750\text{ MPa}$ and $1050^{\circ}\text{C}/120\text{ MPa}$, as shown in figure 1.22. The authors attributed differences in the primary creep deformation at 760°C to the formation of a heterogeneous dislocation structure in material containing the irregularly shaped precipitates. During secondary creep the dislocation structures were observed to be similar in each type of specimen, and the lower creep rate for specimens containing aligned cuboidal γ' was attributed to the higher stability of dislocation networks at the γ/γ' interfaces.

During creep testing at 1050°C the microstructures were unstable and directional coarsening of the precipitates was observed. This resulted in the formation of plates of γ' , known as rafts, running perpendicular to the stress axis. Such a microstructure has been observed in other superalloys and has been shown to be beneficial to the creep performance (Tien and Gamble, 1972; Pearson et al., 1981). The formation of these rafts is envisaged to inhibit mechanisms involving by-pass of γ' by dislocations. Thus deformation takes place predominantly by shearing of the rafts.

Pearson et al. (1981) pointed out that viscous slip processes in γ' tend to be slower than in the γ matrix due to the lower diffusivities in the ordered phase. They proposed that in a superalloy containing a rafted structure the creep rate is determined by the nucleation rate for dislocation sources at the γ/γ' interfaces, the slip distance in the γ' phase and the average dislocation velocity in the γ' . Furthermore, they pointed out that the effectiveness of the suppression of γ' by-passing mechanisms would depend on the degree of perfection of the rafted structure and would be greatest for rafts having a large aspect ratio (the ratio of length to thickness). This view was used by Caron and Khan to explain the enhanced creep performance at 1050 °C of specimens whose microstructure at the onset of creep testing consisted of regularly aligned γ' cuboids. They argued that such a microstructure allows the rapid formation of nearly perfect rafts, compared to the alternative irregular structure that they considered.

Tipler et al. (1981) investigated the effects of long-term ageing at 850 °C on the superalloy IN597. The treatments were shown to produce marked γ' coarsening and the resultant effects on creep properties were determined at 850 °C and 750 °C. It was shown that the treatments had very little effect on the creep performance at 850 °C, under stresses of 75 MPa and 130 MPa. Tests at 750 °C were carried out under stresses of 300 MPa and 450 MPa and here the creep rate for the over-aged specimens was found to have increased by a factor of ~ 50 and ~ 150 respectively compared with the standard heat-treated material. It is unclear whether the lower testing temperature or the higher applied stress was primarily responsible for the increase in microstructural sensitivity. Interpretation of the results is further complicated by the observed precipitation of the deleterious η phase

and coarsening of the grain structure during the long-term ageing treatments.

Dennison et al. (1978), Stevens and Flewitt (1979a,b; 1981b) and Burt et al. (1979) have demonstrated that the creep lives of several alloys can be increased by employing successive creep and re-heat treatments designed to maintain as far as possible the original precipitate dispersion throughout the creep test. However, such heat-treatments will also inevitably modify the dislocation structures formed during creep testing and in this way change the creep behaviour observed.

1.4.6 The Early Onset of Tertiary Creep

Many superalloys have been shown not to exhibit distinct steady-state and tertiary creep stages (see, for example, Kear and Piearcey, 1967; Stevens and Flewitt, 1981a; Dyson and McLean, 1983). Instead the creep rate tends to continually increase from the beginning of the secondary creep stage through to final failure. It is a widely held view that this phenomenon arises due to γ' coarsening during creep testing (see, for example, Stevens and Flewitt, 1981a; Burt et al., 1979; Williams and Cane, 1979). Stevens and Flewitt (1981a) have calculated the decrease in the precipitate contribution, σ_p , to the threshold stress, σ_0 , during creep by assuming LSW coarsening and using equation 1.49 with the stress exponent set to 3. Their experiments were carried out using the superalloy IN738 heat-treated to produce a duplex γ' distribution consisting of cuboids of width $\sim 1 \mu\text{m}$ and spheroids of diameter $\sim 90 \text{ nm}$. They considered that below a given stress, σ_p arose from a combination of the back stress due to dislocation bowing between γ' cuboids and dislocation climb over γ' spheroids. In all cases the values of σ_p calculated from their model

were lower than those calculated from the experimental results, although the authors considered the level of agreement to be reasonable. It was proposed that at higher stresses shear of precipitates would take place and that here σ_p would be independent of any coarsening process.

Nathal and Ebert (1983) have considered the effects of coarsening in the superalloy NASAIR100 after formation of a rafted structure. Specimens were tested at 1000 °C and 148 MPa, under which conditions γ' rafts were observed to form during the primary creep stage. The rafts thickened during creep testing, thus reducing their aspect ratio. In accordance with the model of Pearson et al. (1981), the mean slip distance for mobile dislocations would increase as the plates thicken. Thus it was proposed that this effect led to the progressive increase in creep rate and the early onset of tertiary creep.

The view that the accelerating secondary creep rate observed in superalloys is due to precipitate coarsening during testing has been disputed by Dyson and McLean (1983). On the basis of a coarsening-controlled creep model involving dislocation by-pass of precipitates by climb and by Orowan looping, Dyson and McLean derived the following relationship between strain rate and microstructure:

$$\dot{\epsilon} = C_5 \left[\sigma - C_6 - C_7 (\bar{r}_0^3 + C_8 t)^{-p/3} \right]^4 \quad (1.51)$$

where C_5 , C_6 , C_7 , C_8 and p are positive constants. They then proceeded to demonstrate that neither their own data nor those previously published show satisfactory quantitative agreement with this model. In particular equation 1.51 implies that if σ_0 is independent of σ then a plot of $(\dot{\epsilon}/\dot{\epsilon}_{\min})^{1/4}$ versus t at constant σ would be linear at small t with a gradient which would increase with decreasing σ_0 . Alternatively

if σ_0 is considered proportional to σ then all the data would fall on a common line. In contradiction to these two extreme cases it was found that the slope increased with increasing σ .

As the authors pointed out, the model assumes that the coarsening process is stress-independent, but they justified this by citing the work of Pearson et al. (1981) which showed stress-directed coarsening to reduce, rather than increase, the strain rate. Furthermore the authors demonstrated that inelastic strain is a more satisfactory parameter than time (and hence precipitate coarsening) in determining the acceleration of strain rate. Thus it was suggested that tertiary creep is produced by a strain-softening mechanism related to a progressive accumulation of dislocations, together with the more conventional ideas of cavitation and cracking prior to rupture.

Support for this view has subsequently been provided by Henderson and McLean (1983), who have investigated the creep behaviour of the superalloy IN738LC. By carrying out stress-drop tests to measure σ_0 , they showed that σ_0 decreased only slightly during testing and not sufficiently to explain the accelerating strain rate. In contrast, it was found that the kinetic dislocation recovery factors increased significantly during creep. TEM examination of interrupted tests showed the presence of dislocation networks at the γ/γ' interfaces and that the network spacing decreased with accumulating creep strain. It was thus proposed that the intensification of the interfacial dislocation network during creep testing affects the dislocation climb kinetics so as to cause the creep rate to increase.

1.4.7 Crystal Anisotropy Effects

The first attempt to assess the effects of orientation on the creep properties of single crystal superalloys was undertaken by Kear

and Pearcey (1967) using Mar-M200. They carried out tests at 760 °C, 871 °C and 982 °C and under loads corresponding to initial stresses of 690 MPa., 345 MPa. and 207 MPa. respectively. Crystals whose stress axis was close to $\langle 100 \rangle$ or $\langle 111 \rangle$ were shown to exhibit longer overall creep lives than those having stress axes lying elsewhere in the standard stereographic triangle. This was explained in terms of the activation of multiple $\{111\}$ -type slip systems in these orientations compared with single slip in other orientations, since interactions between dislocations gliding on intersecting slip systems is a potent source of work hardening. Similar trends in work hardening behaviour were observed in tensile tests in the temperature range 21 °C-760 °C, whilst at 980 °C the deformation was more isotropic. Likewise the anisotropy effects became less dramatic in the higher temperature creep tests and this was assumed to have resulted from the activation of multiple slip systems, including $\{100\}$ systems, in all orientations. Further tests showed that $\langle 110 \rangle$ oriented crystals exhibited the least creep resistance. $\langle 110 \rangle$ was considered to be an unstable multiple slip orientation which tends to degenerate into slip exclusively on one system.

A more detailed analysis of the slip systems involved during creep was carried out by Leverant and Kear (1970) who tested single crystals of Mar-M200 at 760 °C and at an initial stress of 690 MPa. All the crystals examined were oriented with the stress axis within 18 ° of $\langle 100 \rangle$, except for one crystal whose stress axis was closer to $\langle 011 \rangle$. It was shown that the amount of primary creep strain (ϵ_p) and the primary creep strain rate ($\dot{\epsilon}_p$) were dependent on the degree and direction of misorientation from $[001]$. In order of increasing ϵ_p and $\dot{\epsilon}_p$, the orientations were ranked thus:

- (i) On $[001]$ pole
- (ii) On $[001]$ - $[011]$ boundary of stereographic triangle
- (iii) Between $[001]$ - $[011]$ and $[001]$ - $[\bar{1}11]$ boundaries
- (iv) On $[001]$ - $[\bar{1}11]$ boundary.

All of the specimens falling into categories (iii) and (iv) showed primary creep strains in excess of 3%, some showing considerably higher strains. The orientation dependence of the extent and rate of primary creep could not be rationalised by consideration of the Schmid factors and multiplicity of slip for assumed $\{111\} \langle 110 \rangle$ slip systems. For instance, specimens on the $[001]$ - $[011]$ boundary showed a ϵ_p peak at about 10° from $[011]$, whereas the $(111)[\bar{1}01]$ Schmid factors show no such peak, as illustrated in the Schmid factor contour diagram in figure 1.23(a).

TEM investigations and lattice rotation measurements showed that primary creep deformation was taking place on the $(\bar{1}11)[1\bar{1}2]$ slip system. In the light of this discovery, the observed orientation dependencies were explained in terms of the Schmid factors and the multiplicity of slip for $\{111\} \langle 112 \rangle$ systems. Schmid factor contours for the most highly stressed $\{111\} \langle 112 \rangle$ systems are shown in figure 1.23(b). Primary creep was interpreted to proceed by single slip at a rate dependent on the Schmid factor until the crystal lattice had rotated sufficiently for activation of other slip systems to occur. Interactions between intersecting slip systems would then bring about the formation of a dislocation network and the onset of secondary creep. The lattice rotations which occur for $\{111\} \langle 112 \rangle$ and $\{111\} \langle 110 \rangle$ single slip systems are shown in figure 1.24. In the case of crystals oriented on the $[001]$ - $[011]$ boundary of the standard stereographic triangle, between $[001]$ and the orientation marked 'Y' in figure 1.24(b), duplex $\{111\} \langle 112 \rangle$ slip is activated immediately, giving rise to rapid

work hardening and low primary creep strains. Similarly for specimens accurately oriented on $[001]$, there is an equal resolved shear stress on four slip systems. A specimen oriented close to $[011]$ did not achieve the secondary creep stage, which is consistent with this model.

The primary creep deformation process was shown to proceed by shearing of the γ' precipitates by loosely coupled partial dislocations separated by intrinsic and extrinsic stacking faults, the net Burgers vector being a $\langle 112 \rangle$. It was suggested that the dissociations would be diffusion controlled since some rearrangements would be necessary at the γ/γ' interfaces. This hypothesis was used to explain why $\langle 110 \rangle$ -type shearing of γ' precipitates was observed at high strain rates even though the Schmid factor is lower than for the $\langle 112 \rangle$ system and the APB energy is higher than the $\langle 112 \rangle$ superlattice stacking fault energy. A later study by Leverant et al. (1973) concluded that the secondary creep stage proceeded by the activation of $\{111\}\langle 110 \rangle$ type slip systems.

Similar results to those outlined above have been obtained by Winstone (1981) and by McKay and Maier (1982). McKay and Maier have pointed out that under constant load those crystals which undergo large primary creep strains before becoming oriented for intersecting slip and thus the secondary creep stage would experience a high effective stress at the onset of secondary creep owing to the reduction in cross-sectional area. As a result, high minimum creep rates and low stress rupture lives would occur. On this basis a map was drawn up to indicate the relationship between orientation and stress rupture life, as shown in figure 1.25.

Leverant et al. (1973) have also examined the creep behaviour of single crystal Mar-M200 at a higher testing temperature (857°C) and under an initial stress of 414 MPa. Under these conditions a different

mode of creep deformation was observed, together with a different associated orientation dependence. All the specimens exhibited small primary creep strains ($< 0.5\%$), but the secondary creep rates $\dot{\epsilon}_s$ varied by an order of magnitude, depending on orientation. In order of increasing $\dot{\epsilon}_s$, the orientations were ranked thus:

- (i) On $[001]$ pole
- (ii) On $[001]$ - $[\bar{1}11]$ boundary of stereographic triangle
- (iii) Between $[001]$ - $[\bar{1}11]$ and $[001]$ - $[011]$ boundaries
- (iv) On $[001]$ - $[011]$ boundary.

TEM observations showed that γ' shearing was occurring by the passage of $a/2\langle 110 \rangle$ type dislocations during both the primary and secondary stages and that dislocation networks were formed, particularly at γ/γ' interfaces. The most favourable $\{111\}\langle 110 \rangle$ type slip systems predicted from the Schmid factor criterion were found to be operating, together with other slip systems of the same type, thus promoting rapid work hardening and low primary creep strains. Leverant et al. offered an explanation of the orientation dependence of $\dot{\epsilon}_s$ in terms of the stability of the dislocation networks formed during secondary creep. The slip systems operating in $[001]$ - $[\bar{1}11]$ oriented crystals were considered to favour junction reactions which stabilised the network, producing a hexagonal array. In $[001]$ - $[011]$ crystals the favoured Burgers vectors would make 90° angles with each other producing a square network with less stable junctions. Since further deformation involves extracting dislocations from these networks, the former is more creep resistant than the latter.

1.5 Superalloy Development

1.5.1 Alloying Trends

The first generation of superalloys to be used for turbine blades

were wrought alloys. As the demand for increased high temperature capability grew, the amount of aluminium and titanium, the γ' -forming elements, in the alloys was increased. This produced alloys containing higher volume fractions of γ' . The advantages of increasing the γ' volume fraction in terms of improved creep resistance have been pointed out above and are illustrated in figure 1.21.

The introduction of vacuum induction melting and refining during the 1950s represented a major breakthrough in the production of superalloys, since it prevents the oxidation of reactive elements such as aluminium and titanium. Thus further increases in the γ' volume fraction became permissible. Vacuum refining also removes some of the volatile trace elements such as bismuth, lead and tellurium which may be present in the raw materials. These trace elements have been shown to be detrimental to creep strength and ductility (Holt and Wallace, 1976).

However, additions of aluminium and titanium tended to decrease the solidus and liquidus temperatures whilst raising the γ' solution temperature. Thus the permissible hot working temperature range for the stronger alloys such as Nimonic 115 and Udimet 700 was reduced and they became difficult to forge into the shapes required. Furthermore, turbine blade designs were becoming more intricate, incorporating complex air cooling channels. These problems were overcome in the next generation of turbine blade materials, which were cast superalloys. Since forgeability was no longer a consideration, this allowed still greater freedom for alloying. Figure 1.26 illustrates the increase in temperature capability of available superalloys since 1940.

1.5.2 Directional Solidification

It had been observed that creep fracture and thermal fatigue

failure in superalloys were generally initiated by the formation of cracks at grain boundaries. Thus VerSnyder and Guard (1960) reasoned that by aligning the grain boundaries parallel to the principal stress direction, grain boundary fracture might be inhibited and ductility increased. Such grain structures can be produced by a directional solidification process. This process requires that the heat be removed from the casting in a unidirectional manner whilst maintaining a sufficiently positive temperature gradient ahead of the solid/liquid interface to prevent extraneous nucleation (VerSnyder, 1982). These conditions can be achieved by pouring superheated metal against a chilled surface while concurrently establishing a suitable temperature gradient along the axial length of the mould by the use of induction heating methods. A typical production process relying on a mould translation technique to enhance heat transfer is shown in figure 1.27(a).

Considerable advantages of directionally solidified superalloys over conventionally cast equiaxed structures have been reported both in creep (VerSnyder and Guard, 1960) and in thermal fatigue (Erikson et al., 1974). The improvements stem partly from the elimination of grain boundaries lying normal to the stress axis and also from the existence of a preferred crystallographic orientation, namely $\langle 100 \rangle$. The fast-growing $\langle 100 \rangle$ orientation dominates during unidirectional casting and aligns parallel to the direction of solidification. Wells (1967) has shown that this results in a 30%-40% reduction in elastic modulus along the growth direction. Thermal fatigue is thus improved since the material is more able to accommodate thermally induced strains elastically, and therefore offer greater resistance to failure by cumulative plastic strain. Superimposed on this effect is the improved resistance to intergranular crack initiation and propagation resulting from grain boundary alignment. Similarly under creep conditions the

formation of cracks is delayed and their propagation impaired resulting in a considerable improvement in ductility and the extension of the overall creep life to rupture.

1.5.3 Single Crystals

Further improvements in high temperature mechanical properties can be obtained by casting superalloys with all the grain boundaries eliminated, that is, as single crystals. Single crystals can be cast in a similar manner to directionally solidified alloys (VerSnyder, 1982). Two different techniques have been adopted. The first involves the use of a multiple turn constriction adjacent to the chill plate which permits only one grain to enter the airfoil portion of the mould, as shown in figure 1.27(b). As solidification proceeds, two to six grains enter the helix, or grain selector. Some grains are physically blocked from entering the helix and after one or two turns of the helix only one crystal survives. Alternatively a seed crystal may be placed at the bottom of the mould. This technique does not require a single crystal selector and has the advantage that it allows control of the crystal orientation in both longitudinal and transverse directions.

Whereas some evidence has been obtained for the formation of cracks at ledges in longitudinal grain boundaries in directionally solidified alloys (VerSnyder and Shank, 1970), the primary sites available for crack initiation in single crystals are microporosities, which are less effective sites than grain boundaries (Erickson et al., 1974). Furthermore, reductions in microporosity have been noted in directionally solidified and single crystal castings (McLean, 1983). A comparison, due to Kear and Pearcey (1967), of the creep properties of single crystal, directionally solidified and conventionally cast superalloys is shown in figure 1.28.

Although $\langle 111 \rangle$ oriented single crystals have been shown to offer the greatest resistance to creep deformation (McKay and Maier, 1982), industrial interest has centred on $\langle 100 \rangle$ oriented crystals as these show the best combination of creep and thermal fatigue properties and are also easier to manufacture. The stresses acting on turbine blades are not unidirectional, and so the improvement in transverse creep strength and ductility of single crystals over directionally solidified alloys is also important.

One of the greatest advantages of single crystal alloys results from the increased freedom for alloying. Conventionally cast and directionally solidified superalloys are essentially not heat-treatable as the incipient melting point of the highly segregated cast structure is below the solvus of the γ' phase. Many of the solid solution strengthening elements are segregated to eutectic phases which add little to the strength of the alloy. The current work concerns the single crystal superalloy SRR99, which has been developed by Rolls-Royce limited. Since the material contains no grain boundaries it has been possible to eliminate the elements hafnium, boron and zirconium which are conventionally added to superalloys as grain boundary strengtheners. The elimination of these elements has raised the incipient melting temperature by up to 100°C , thus making possible heat-treatments which will fully dissolve the γ' and homogenise the structure. The importance to creep properties of applying a homogenising heat-treatment is illustrated in figure 1.29.

1.6 The Present Investigation

The aims of the present investigation fall into two categories. Firstly it was intended that the effects of heat-treatments on the microstructure of single crystal SRR99 be assessed. Particular

emphasis was placed on characterising and interpreting changes which occur in the morphology and size distribution of the γ' precipitates at various temperatures.

Secondly tests were to be carried out to assess the effects of these heat-treatments on the mechanical properties of the alloy. Creep properties were of the greatest interest, but it was also decided to undertake some high strain-rate compression tests at both ambient and elevated temperatures for comparison. Since there exists such a diversity of postulated and observed deformation mechanisms, it was intended that an insight be obtained into the modes of deformation occurring in SRR99. An understanding of the relations between the deformation characteristics and the heat-treatment history and microstructure would be sought.

Table 1.1

A portion of the periodic table, showing those elements commonly included in nickel-base superalloys.

(After Decker, 1969).

Table 1.2

γ/γ' misfit parameters for some nickel-base superalloys.

(After Ricks et al., 1983).

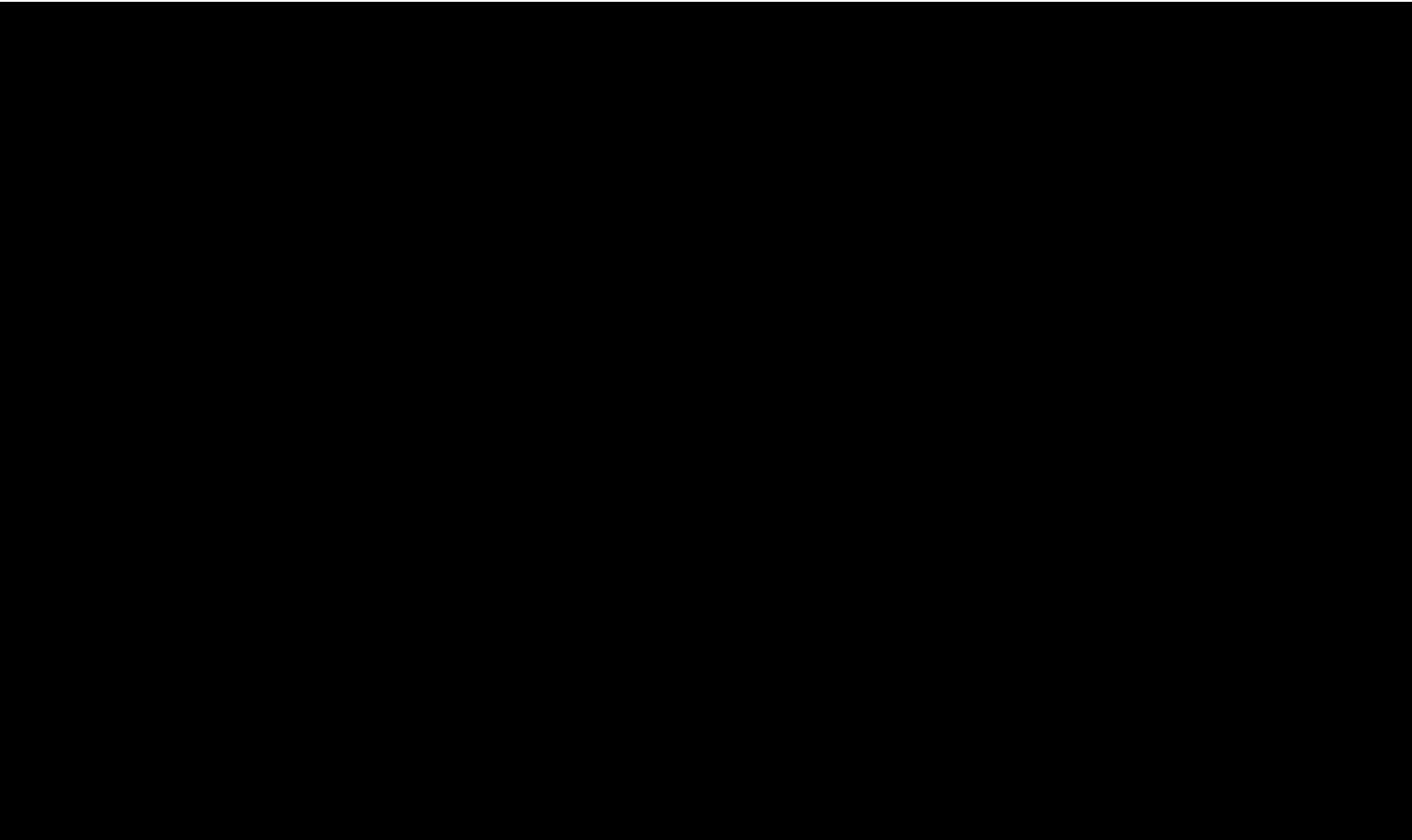
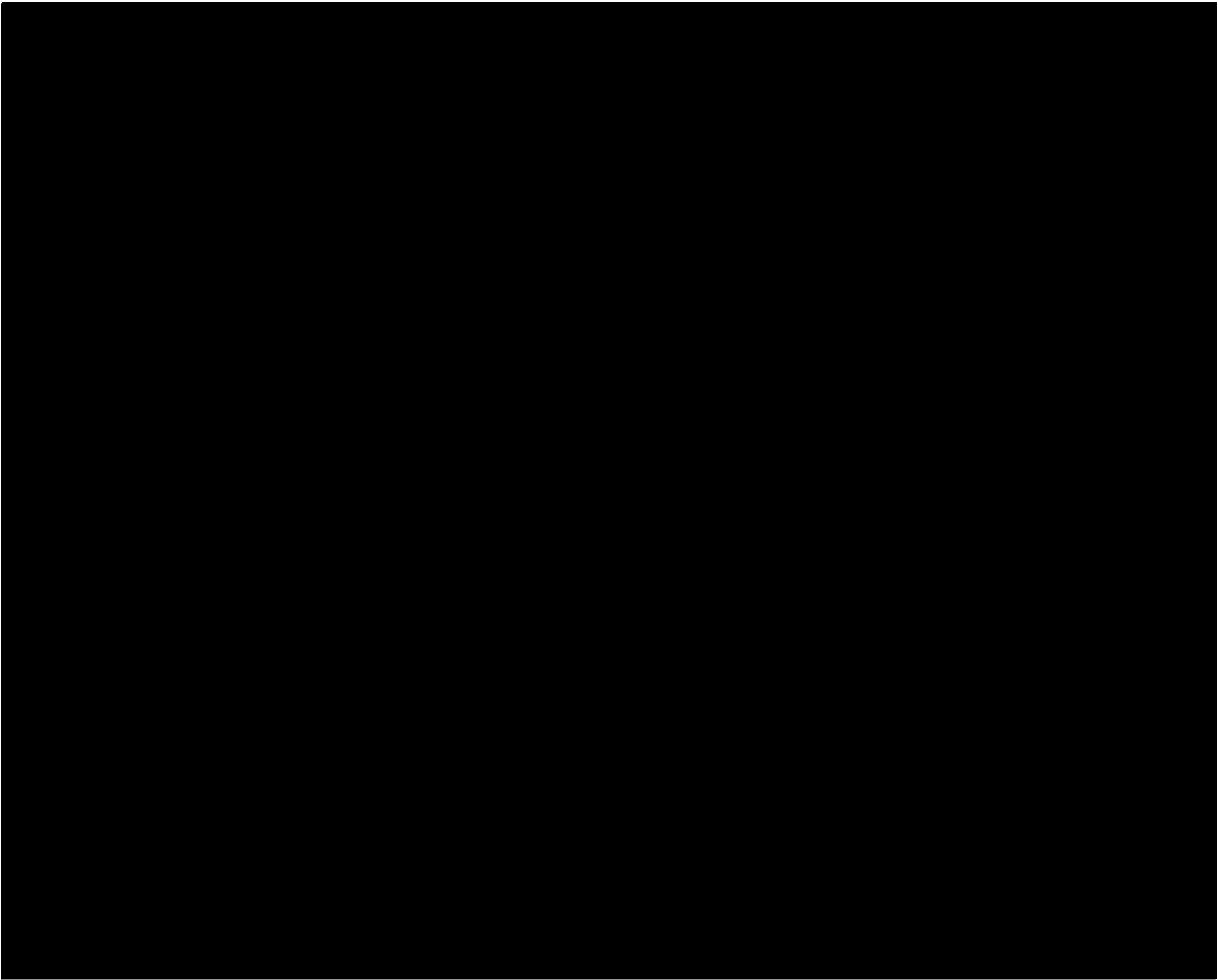
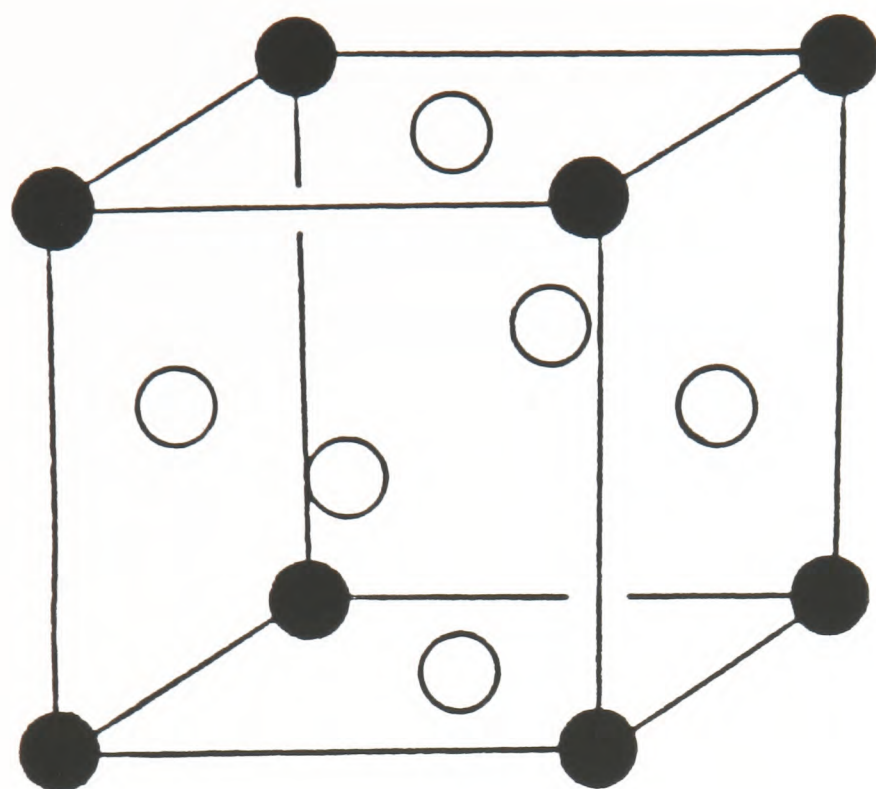


Figure 1.1

The $L1_2$ unit cell. In γ' , the A sites are occupied primarily by nickel atoms and B sites by aluminium or titanium atoms.

Figure 1.2

The relative precipitate size distribution predicted by the LSW theory.
(After Davies et al., 1980b.)



○ = A

● = B

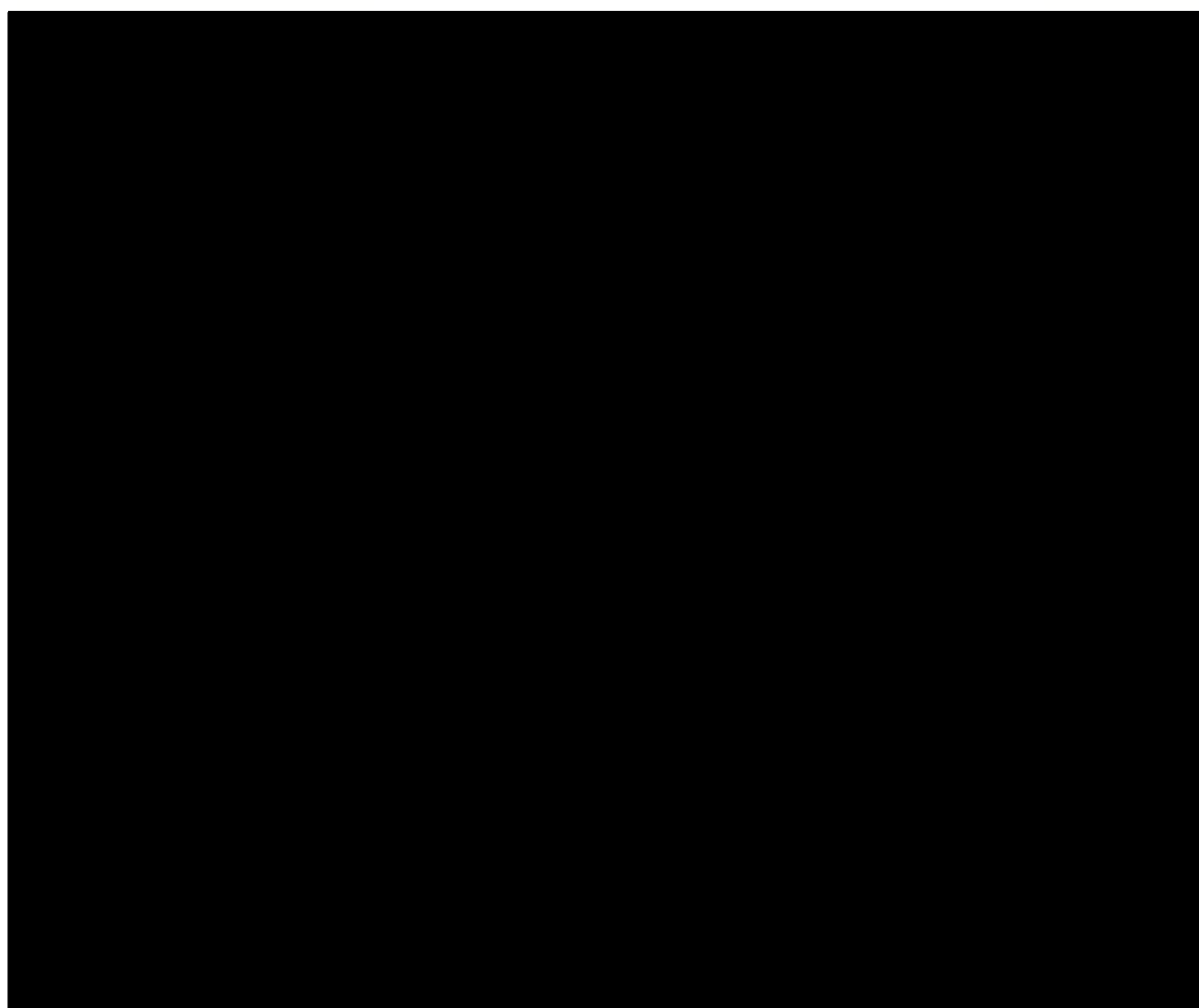


Figure 1.3

Relative precipitate size distributions as a function of volume fraction (f) predicted by the model of Ardell (1972b).

Figure 1.4

Relative precipitate size distributions as a function of volume fraction (f) predicted by the model of Brailsford and Wynblatt (1979).

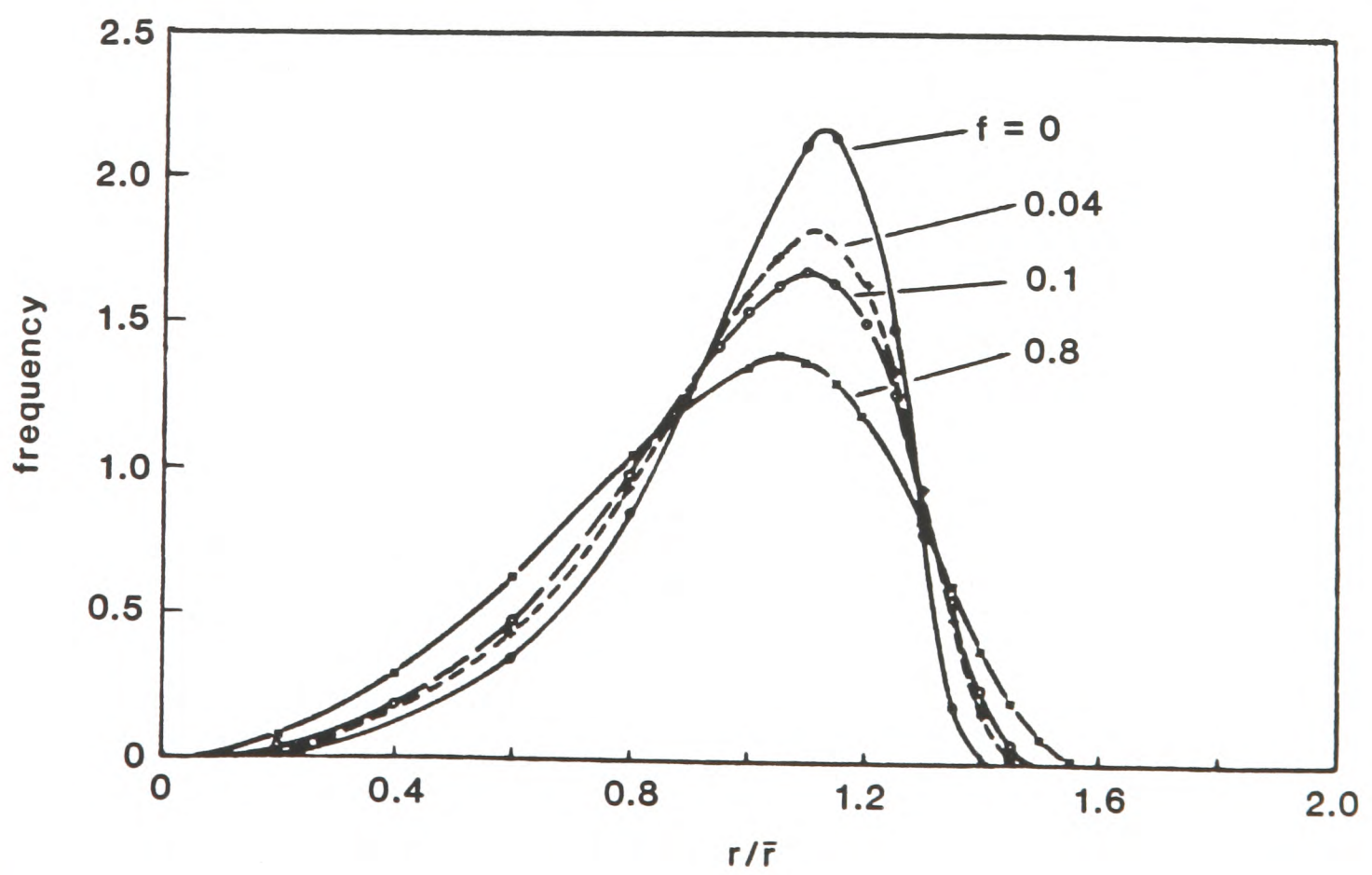
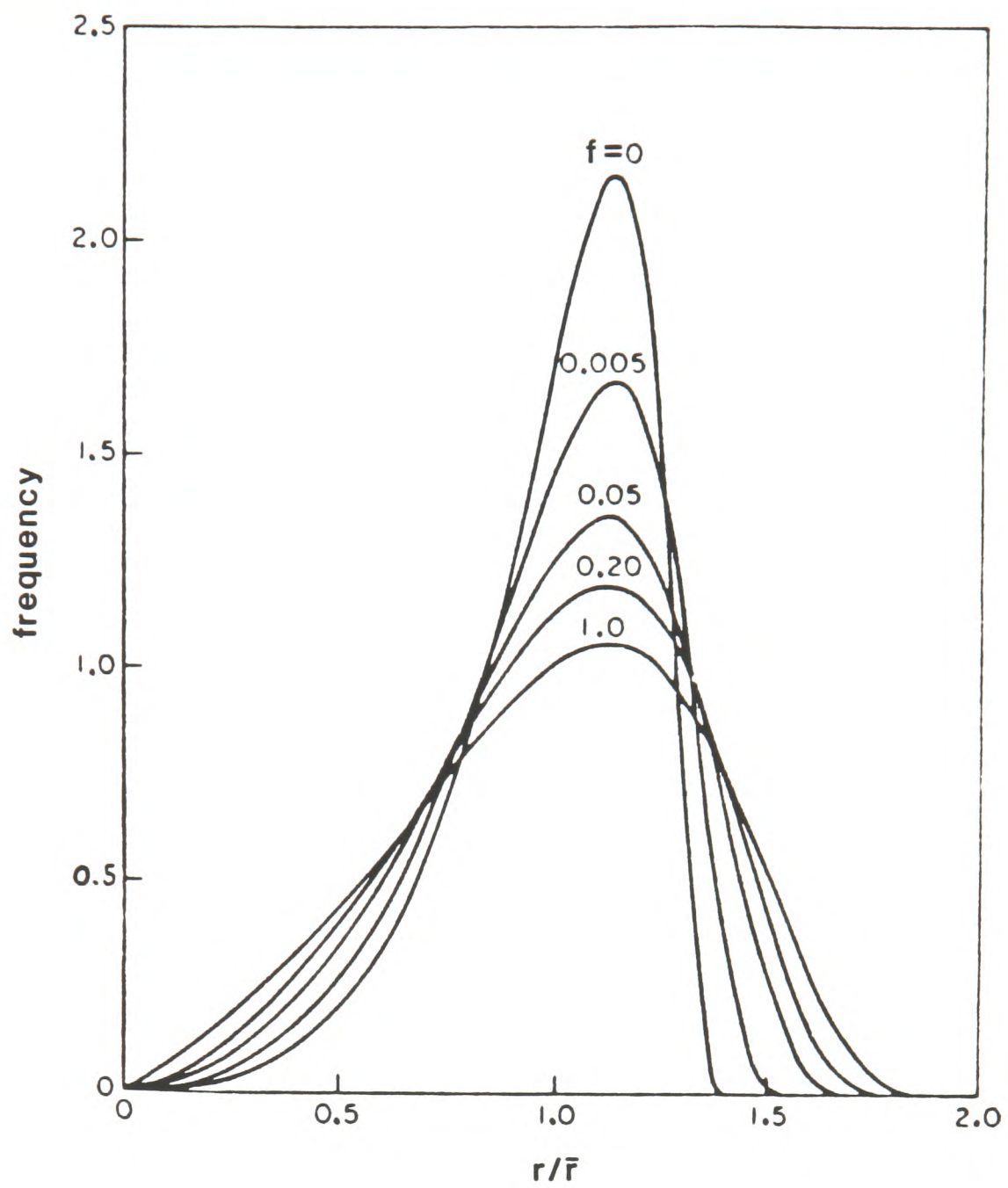


Figure 1.5

Relative precipitate size distributions as a function of volume fraction (f) predicted by the model of Tsumuraya and Miyata (1983) for cuboidal precipitates.

Figure 1.6

Relative precipitate size distributions as a function of volume fraction (f) predicted by the model of Davies et al. (1979b).

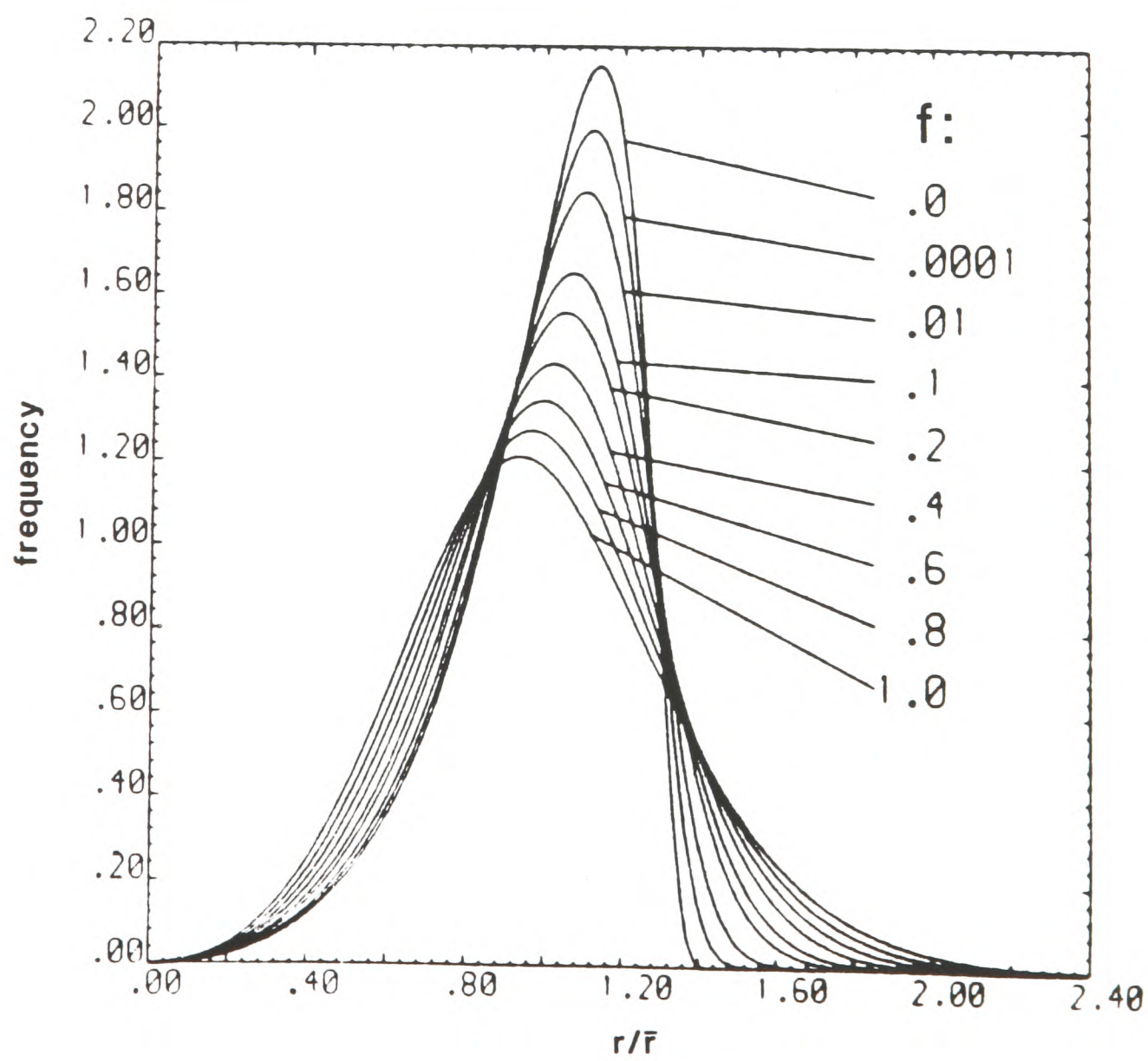
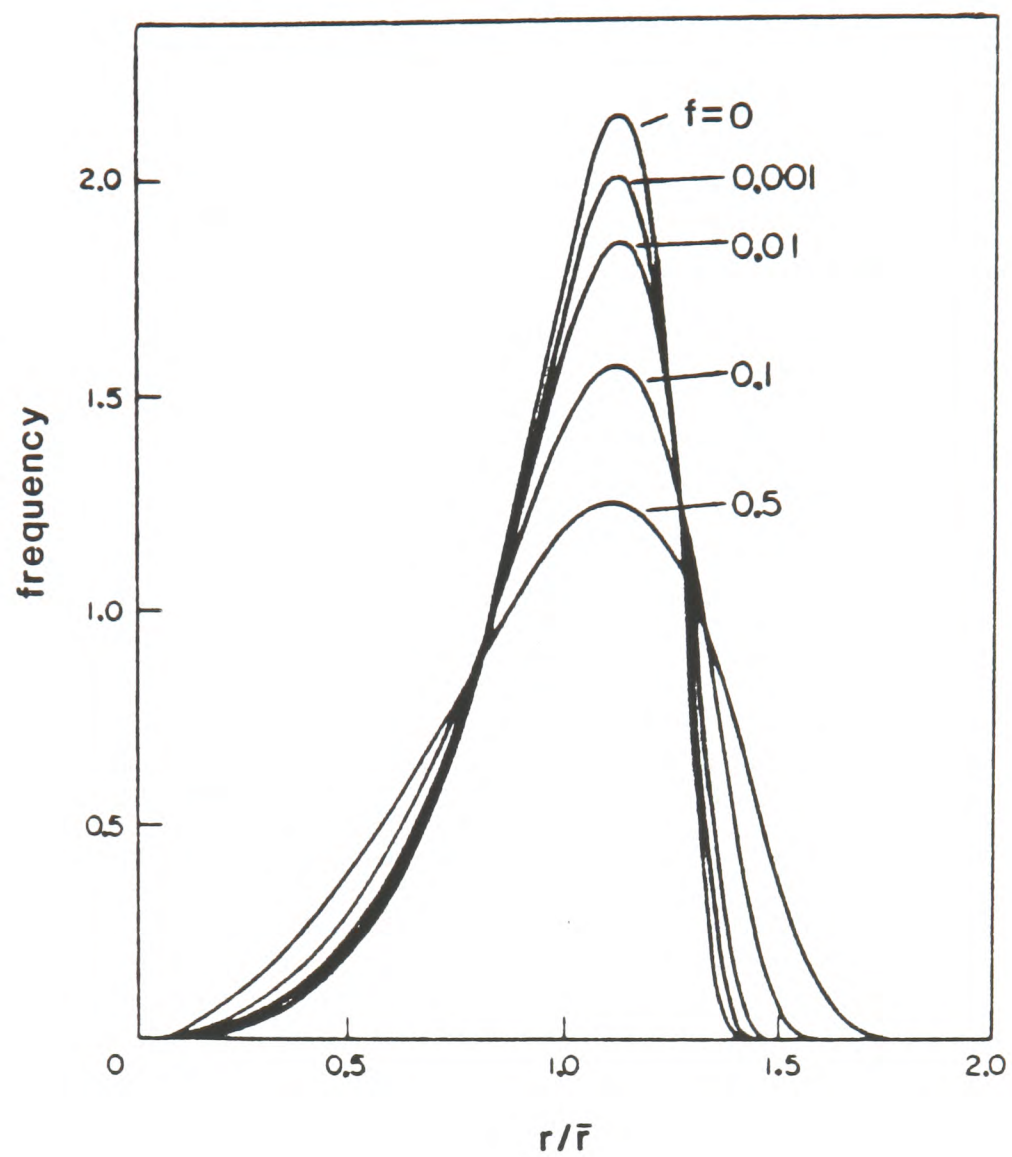


Figure 1.7

Effect of solute position in the periodic table and solute N_V on the stacking fault energy and the room temperature yield stress of nickel-base binary alloys.

(After Decker, 1969.)

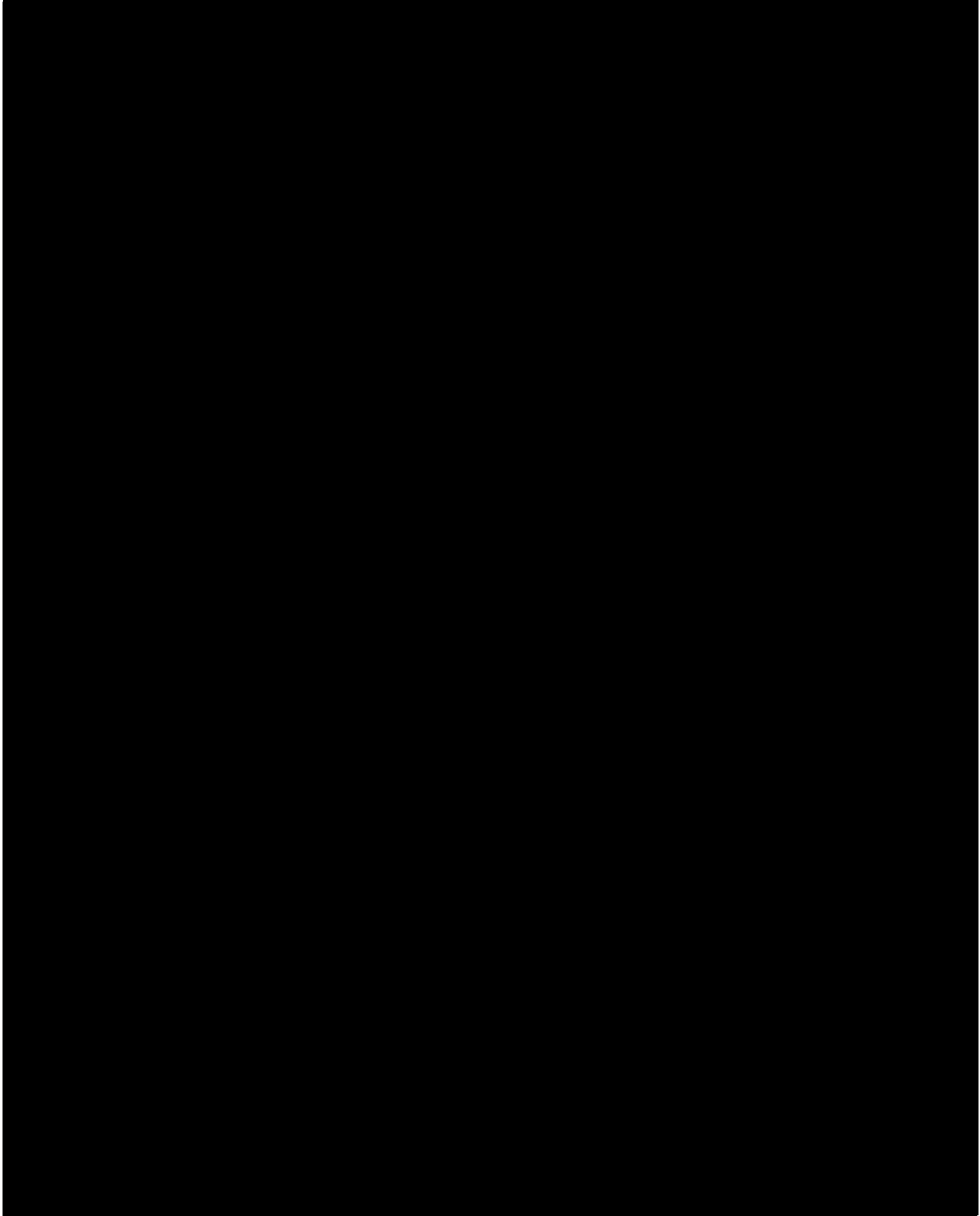


Figure 1.8

Relation between particle diameter and hardness for a nickel-base alloy with 22% Cr, 2.8% Ti, 3.1% Al.

(After Mitchell, 1966.)

Figure 1.9

Correlation of aged hardness with γ/γ' mismatch in nickel-aluminium-ternary element alloys.

(After Decker, 1969; adapted from Decker and Mihalisin, 1969.)

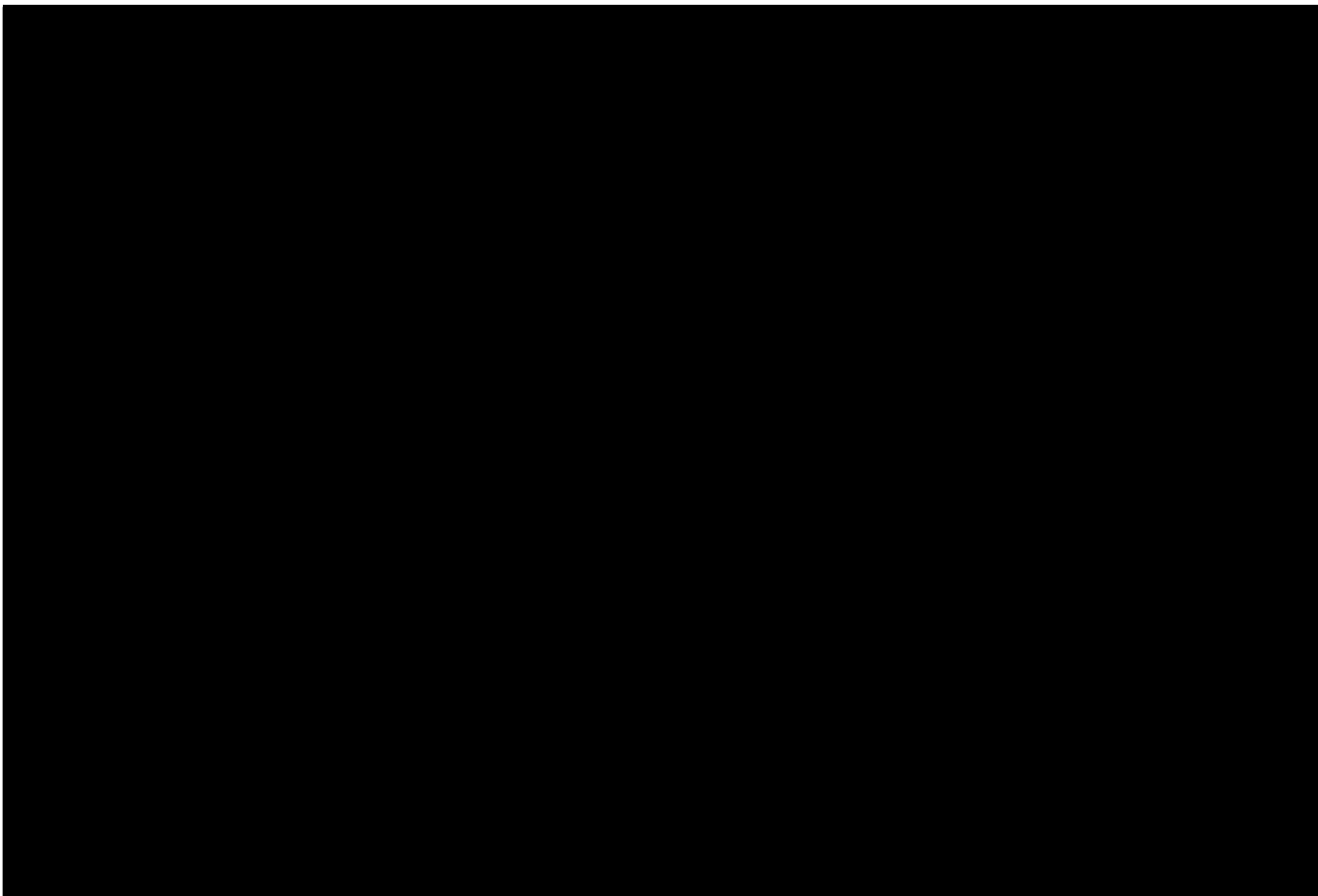
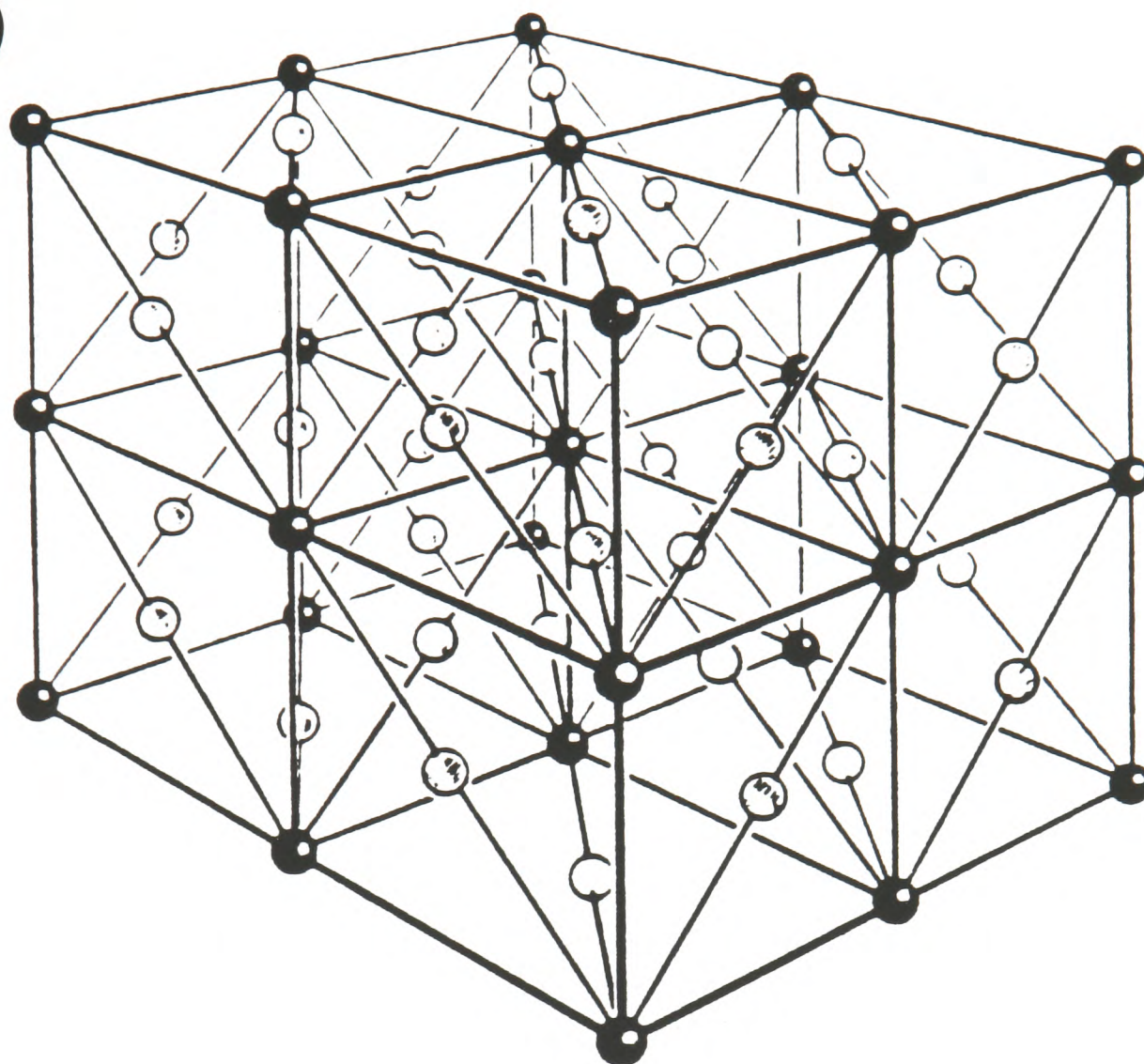


Figure 1.10

- (a) The ordered $L1_2$ structure of γ' .
 - (b) Antiphase boundary after passage of an $a/2 \{111\} \langle 100 \rangle$ dislocation.
- (After Flinn, 1960.)

(a)



(b)

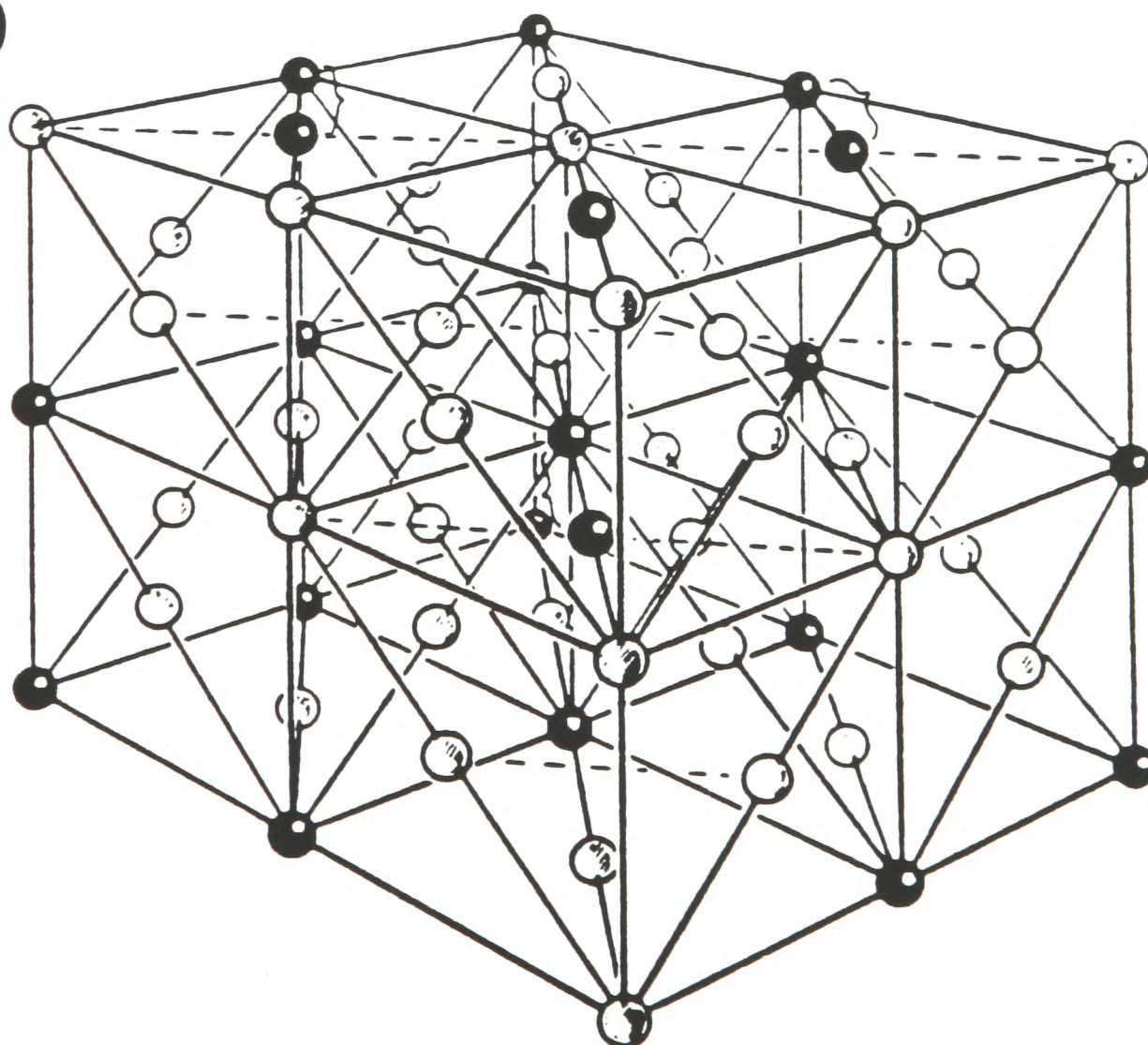


Figure 1.11

- (a) Precipitate shear by weakly coupled dislocations.
- (b) Precipitate shear by strongly coupled dislocations.
- (c) Dependence of the critical resolved shear stress (CRSS) upon particle size.

(After Hüther and Reppich, 1978.)

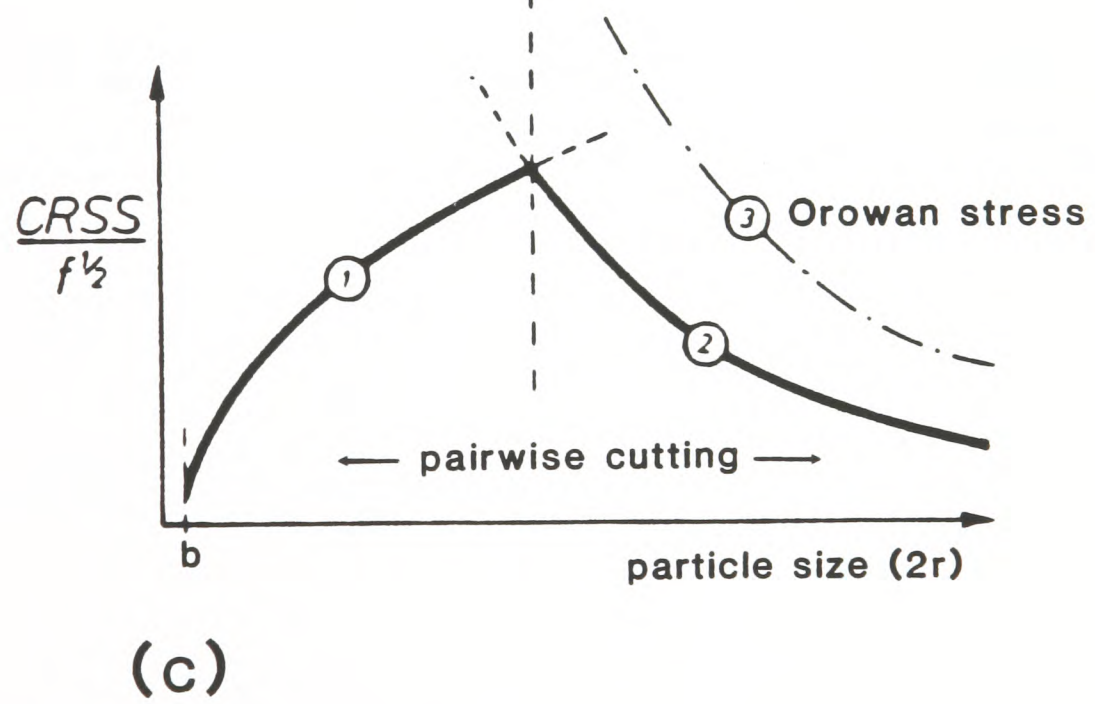
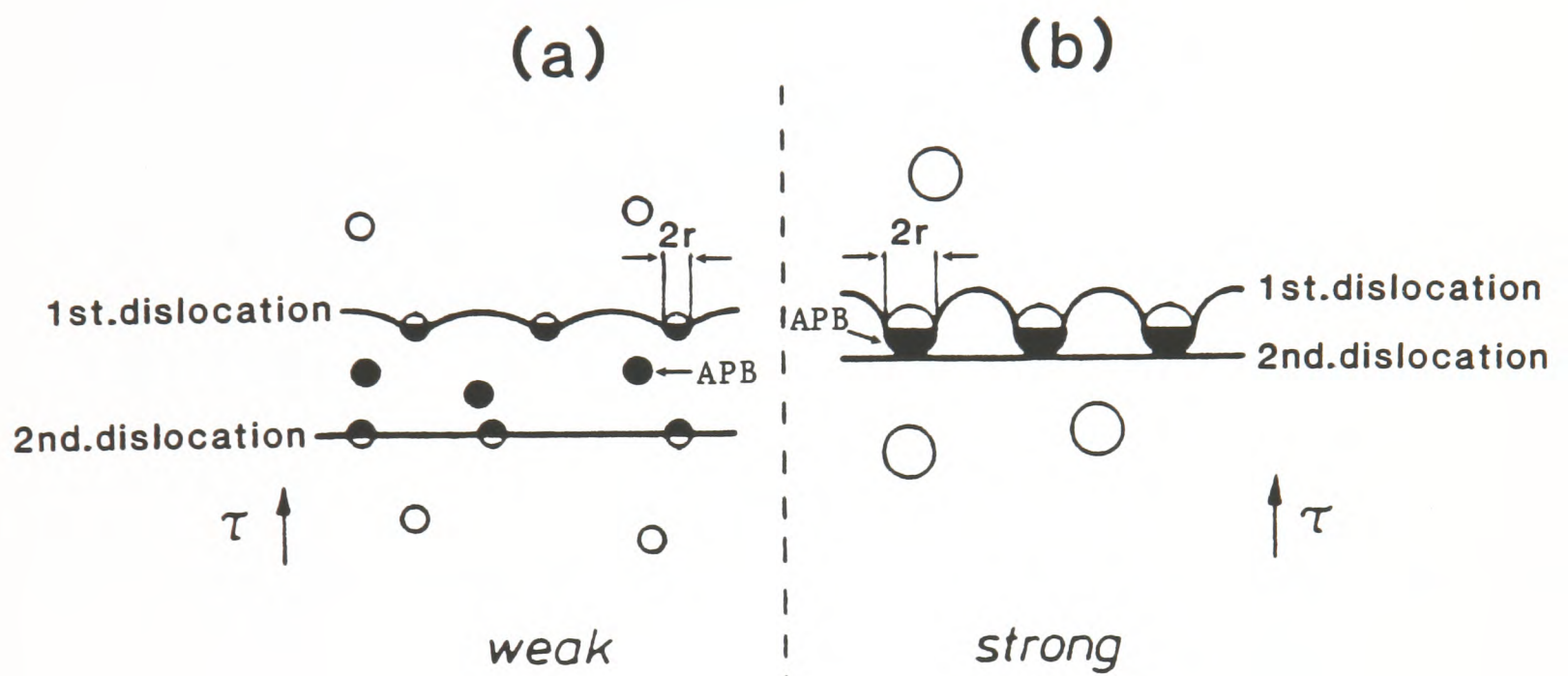
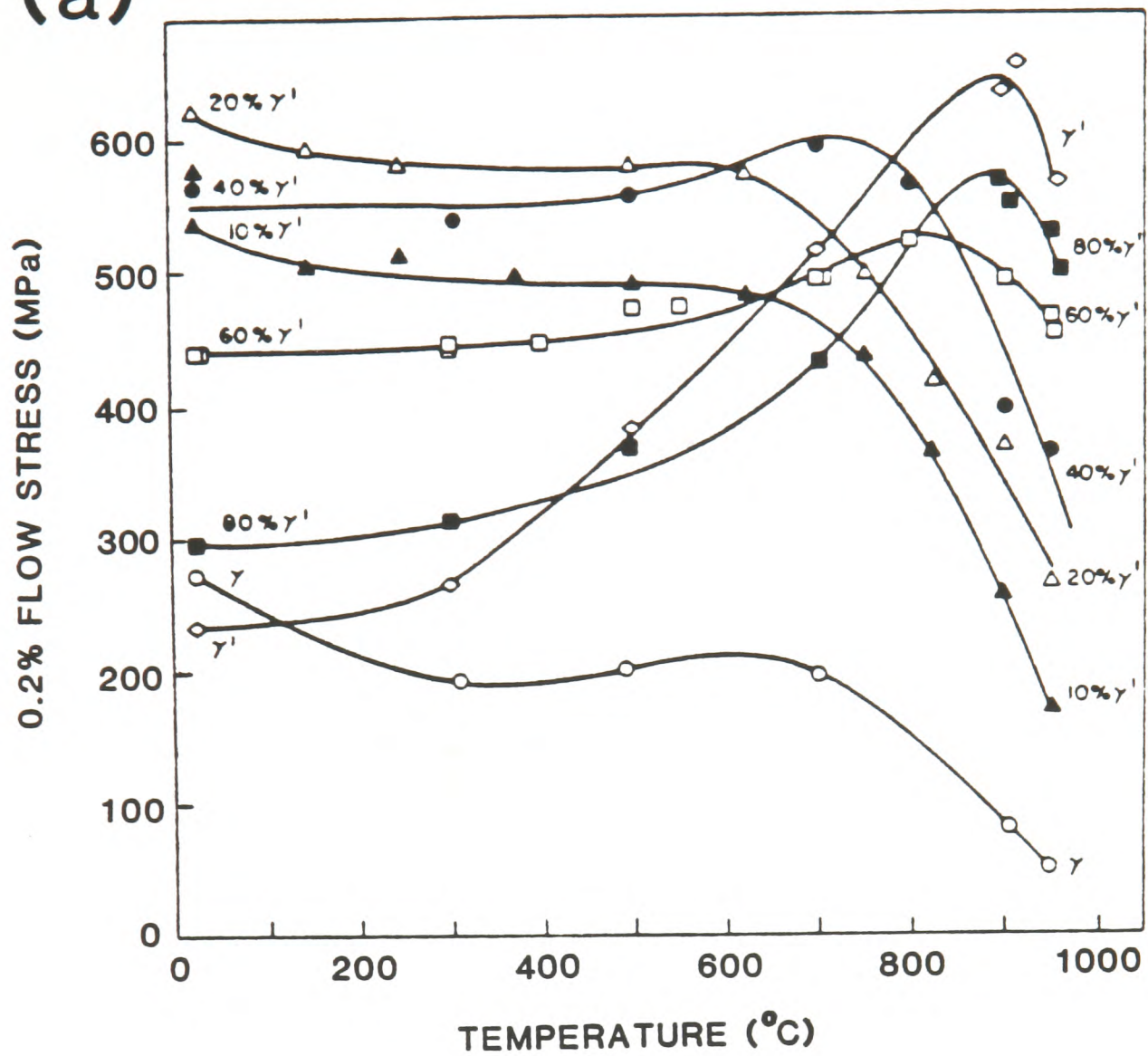


Figure 1.12

- (a) Temperature dependence of the 0.2% flow stress of alloys containing different volume fractions of γ' .
- (b) Schematic representation of the temperature dependence of flow stress.

(After Beardmore et al., 1969.)

(a)



(b)

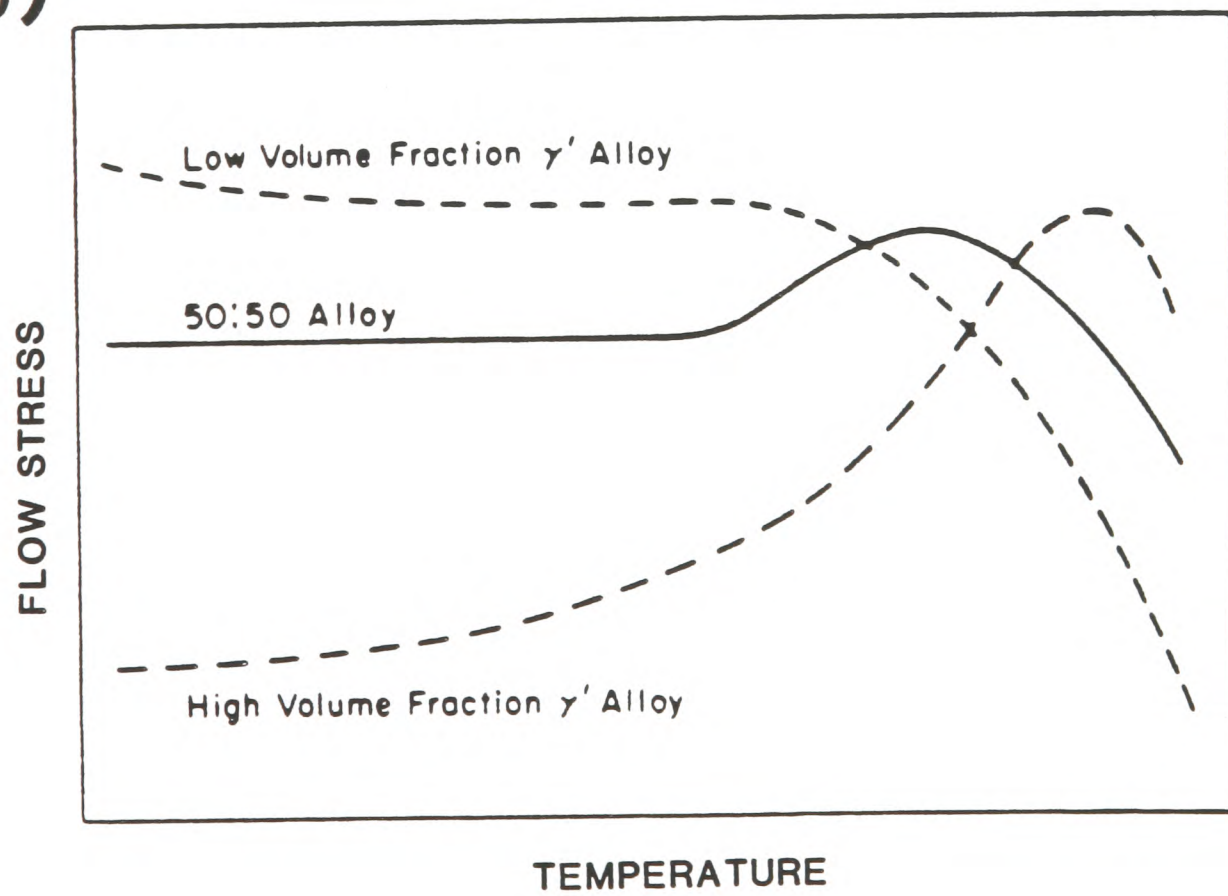


Figure 1.13

Dependence of compressive yield stress upon temperature for Ni_3Al crystals with $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ orientations.

(After Copley and Kear, 1967.)

Figure 1.14

Dependence of flow stress upon temperature at different levels of plastic strain in Ni_3Al .

(After Thornton et al., 1970.)

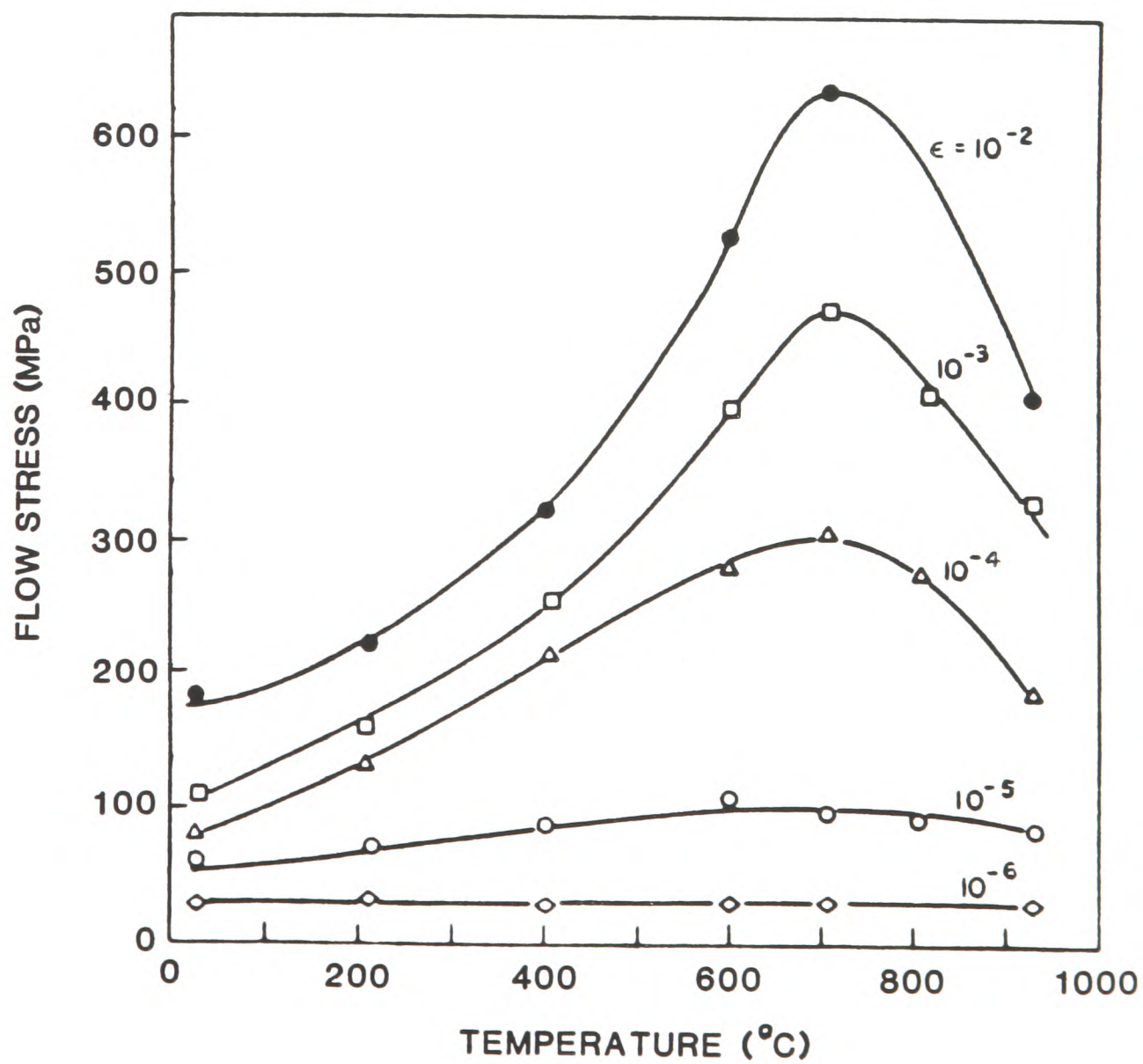
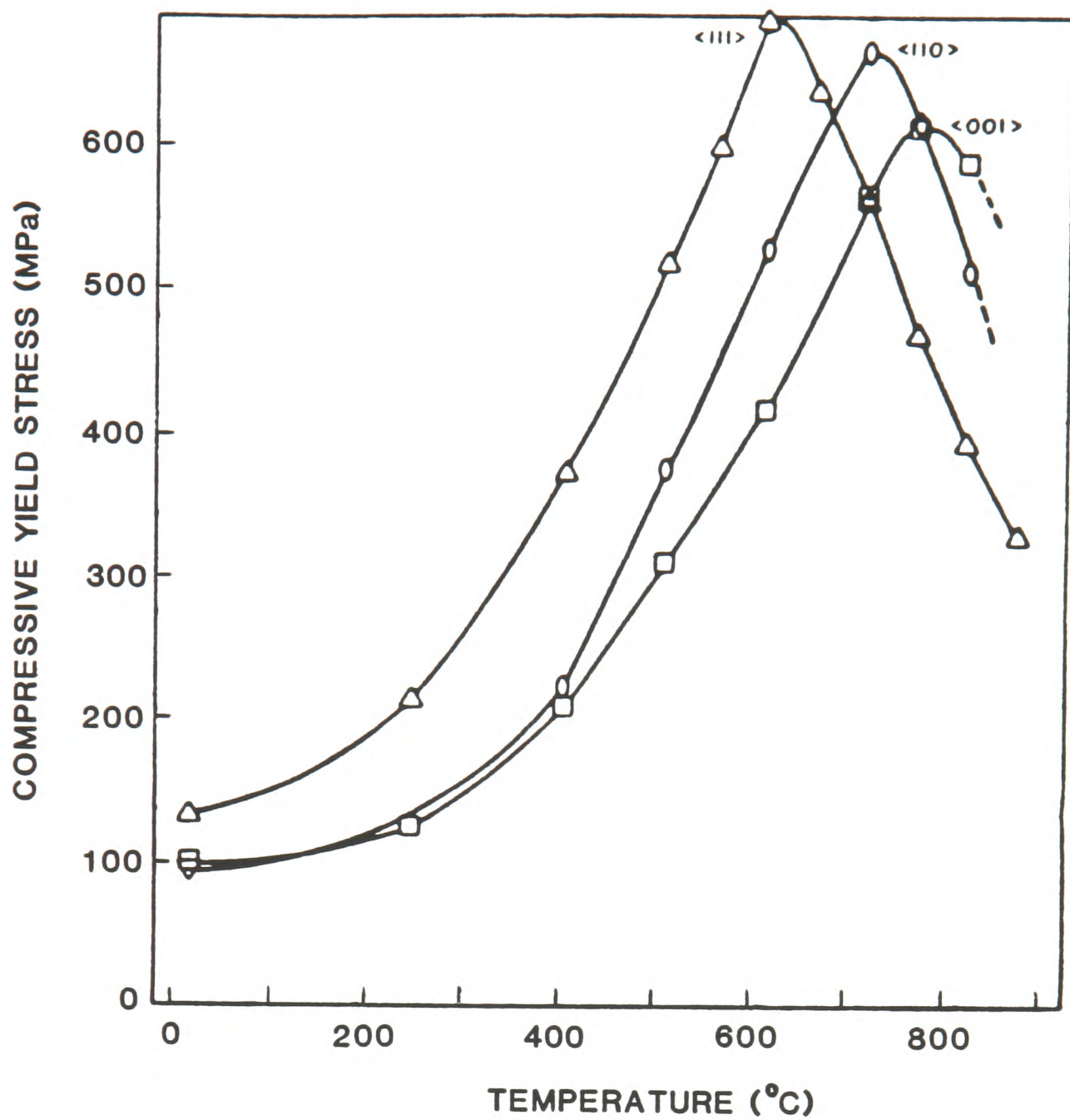


Figure 1.15

Proposed modes of precipitate shear by paired dislocations having a net Burgers vector of $a\langle 110 \rangle$.

(Adapted from Kear et al., 1969b and Kear et al., 1970.)

Figure 1.16

Proposed mode of precipitate shear by dislocations having a net Burgers vector of $a\langle 112 \rangle$. (After Kear et al., 1969b.)

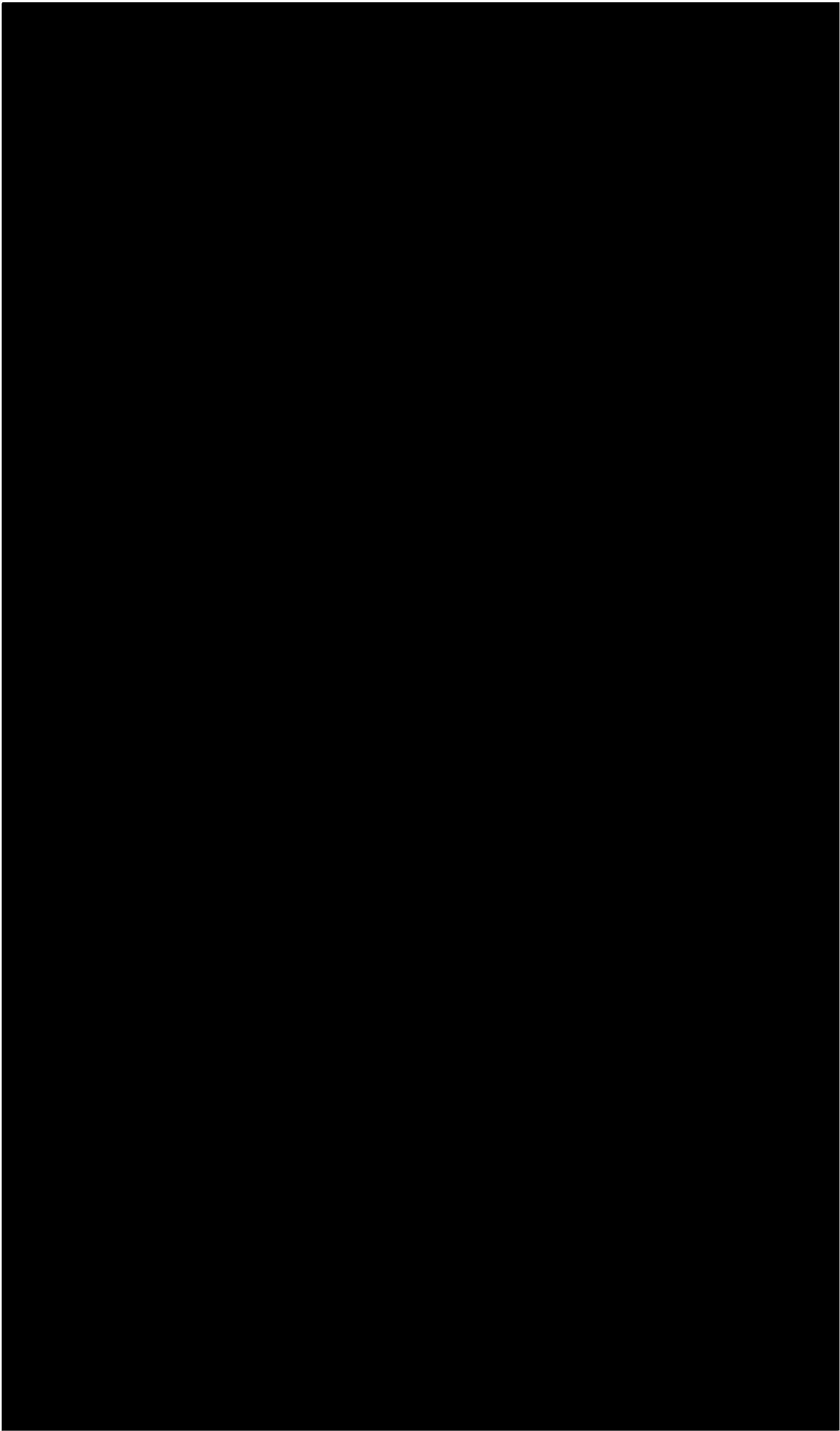


Figure 1.17

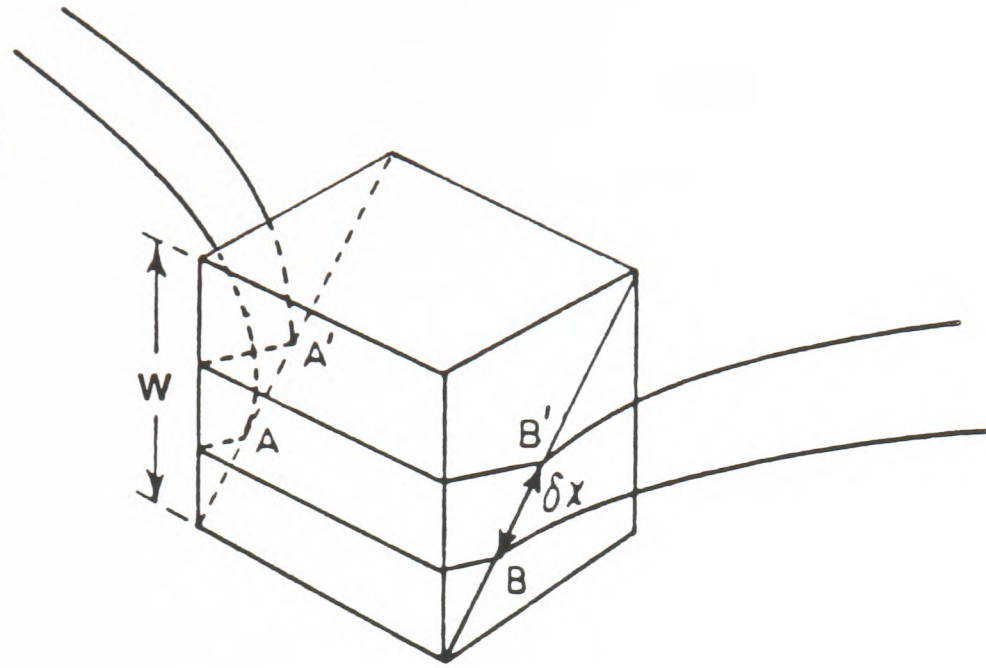
Dislocation encountering cubic obstacle.

- (a) The glide plane is the plane AA'BB'. If the obstacle is a γ' precipitate with sides parallel to $\{100\}$ then the glide plane is $\{110\}$.

(After Brown and Ham, 1971).

- (b) The glide plane is the plane AA'BB'. If the obstacle is a γ' precipitate with sides parallel to $\{100\}$ then the glide plane is $\{111\}$.

(a)



(b)

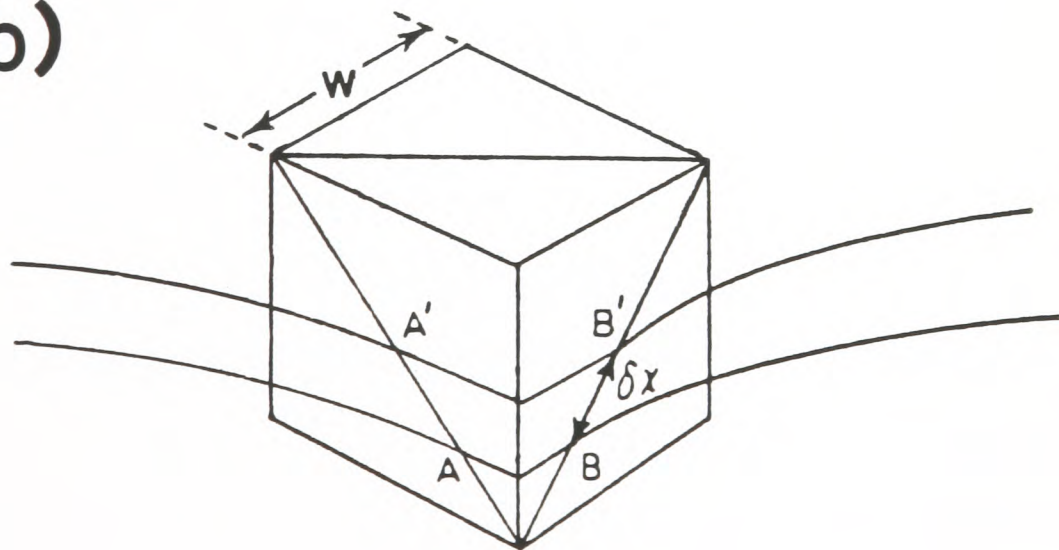


Figure 1.18

Typical types of creep curves.

(After Bird et al., 1969.)

Figure 1.19

Influence of stress on the diffusion-compensated steady-state creep rate in a typical pure polycrystalline metal.

(After Sherby and Burke, 1967).

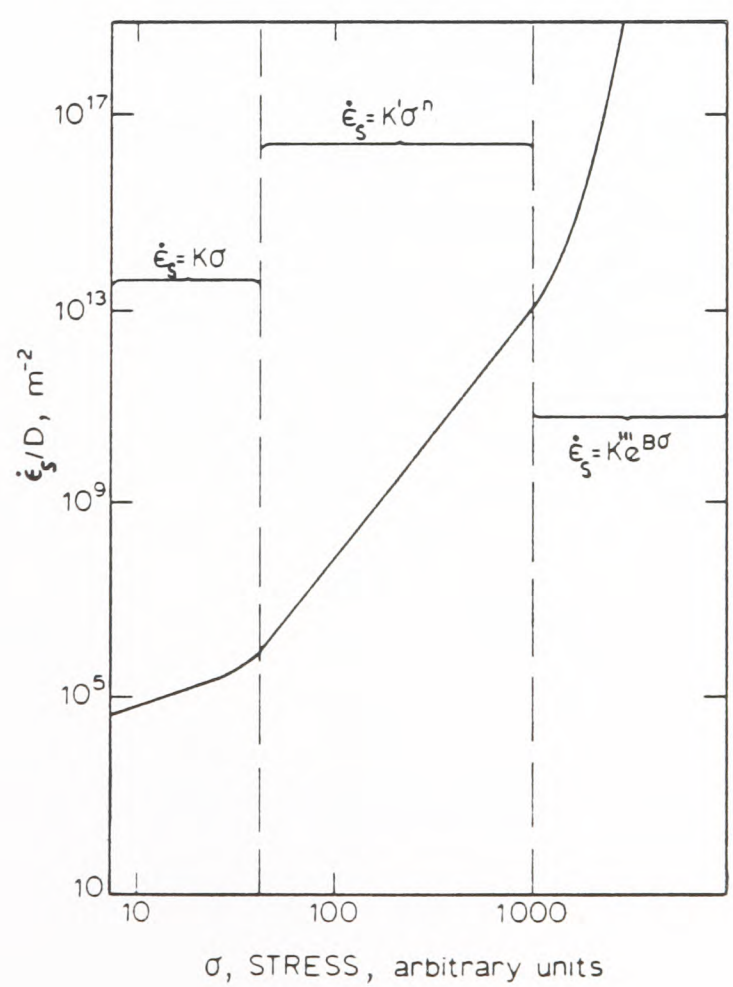
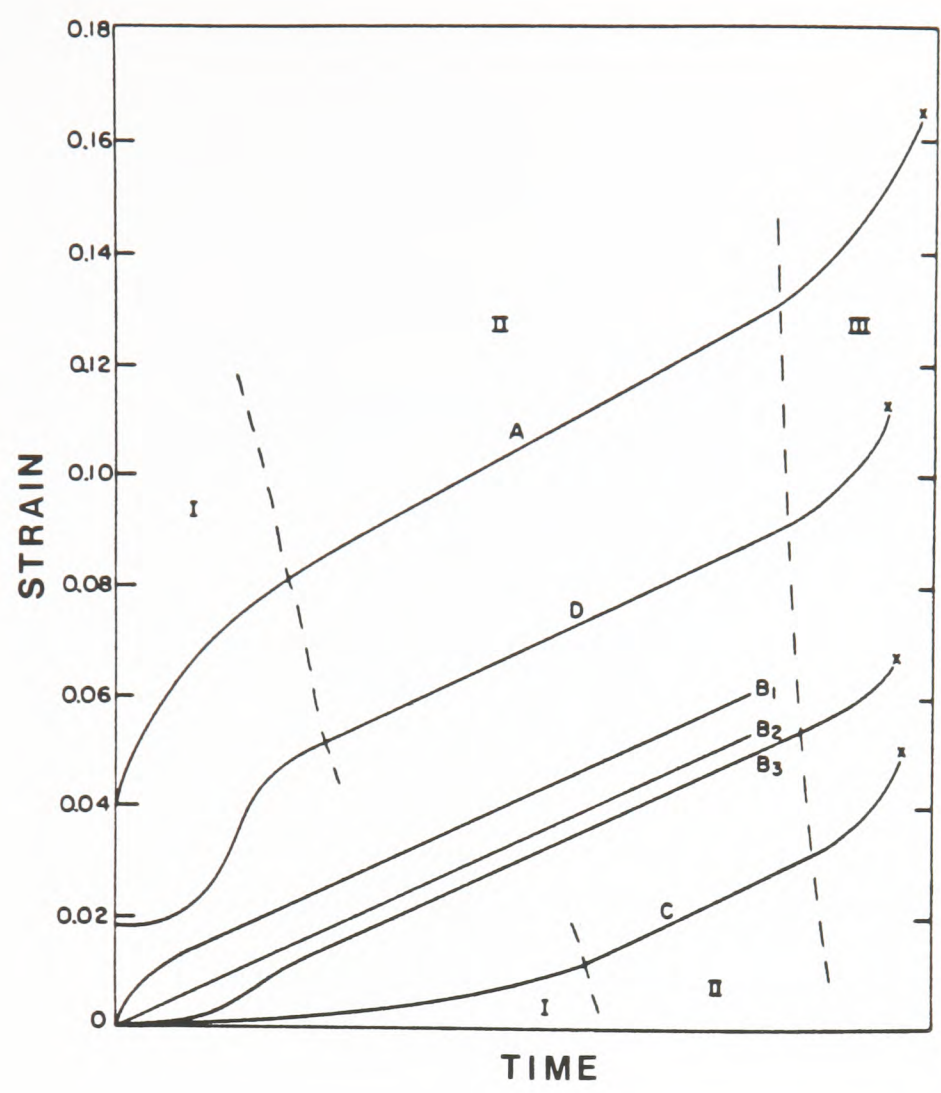


Figure 1.20

Deformation maps for conventionally-cast Mar-M200.

(a) Grain size = 100 μm .

(b) Grain size = 10 mm.

(After McLean, 1983; adapted from Ashby, 1973.)

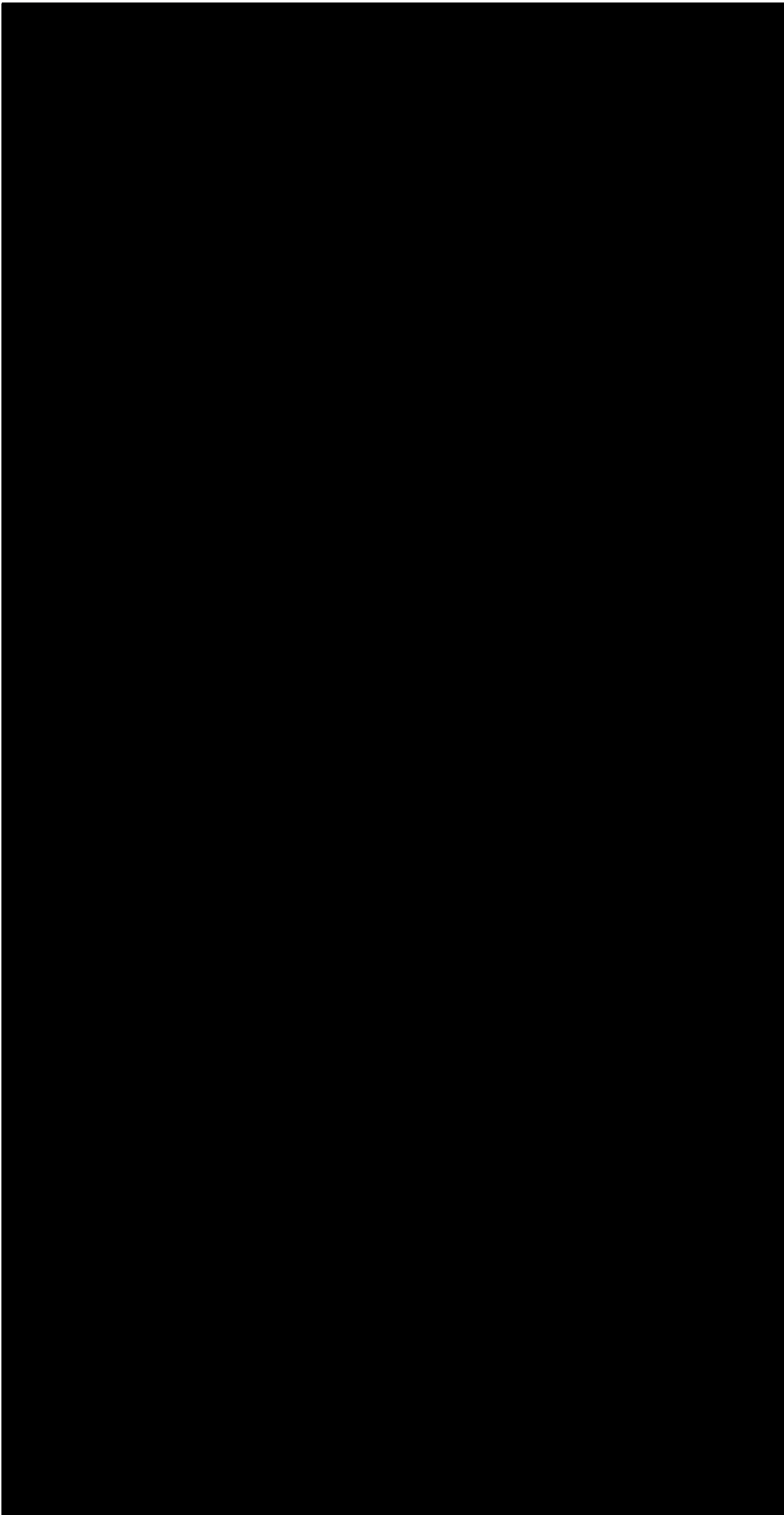


Figure 1.21

Effect of volume fraction of γ' on the creep rupture strength of superalloys.

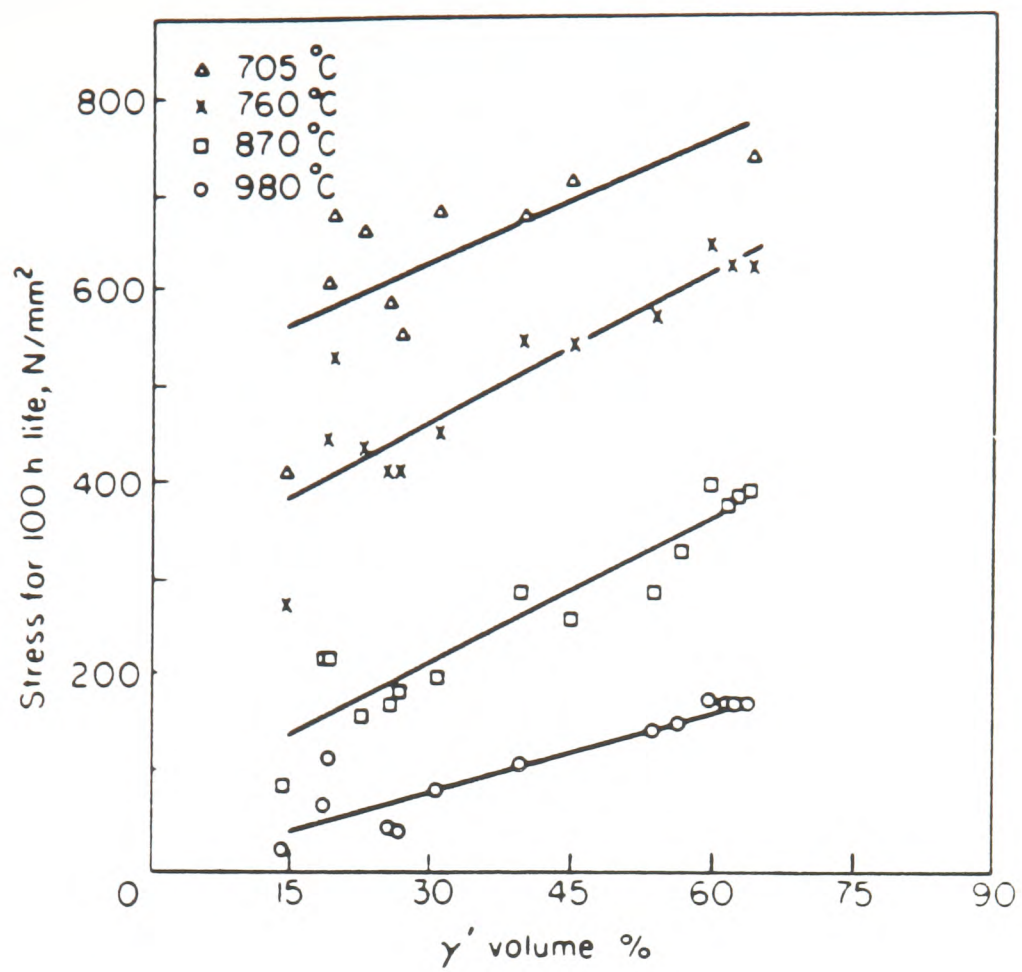
(After Decker, 1969.)

Figure 1.22

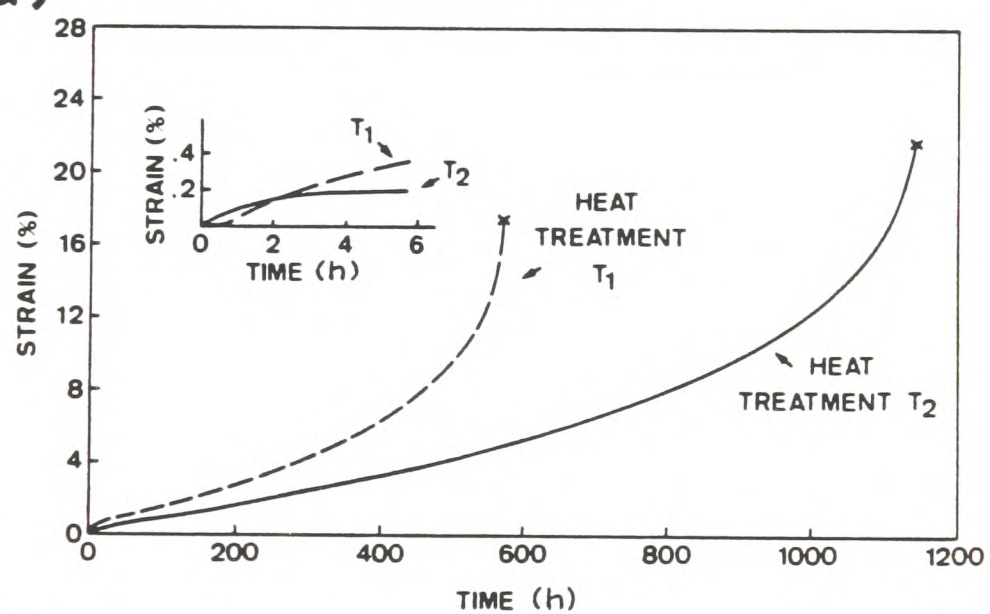
Creep curves for the single crystal nickel-base superalloy CMSX-2 in two different heat-treated conditions (T_1 = 30 minutes at 1315 °C, air cool, 5 hours at 950 °C, air cool, 48 hours at 850 °C; T_2 = 30 minutes at 1315 °C, air cool, 16 hours at 1050 °C, air cool, 48 hours at 850 °C).

- (a) Tested at 760 °C and 750 MPa.
- (b) Tested at 1050 °C and 120 MPa.

(After Caron and Khan, 1983.)



(a)



(b)

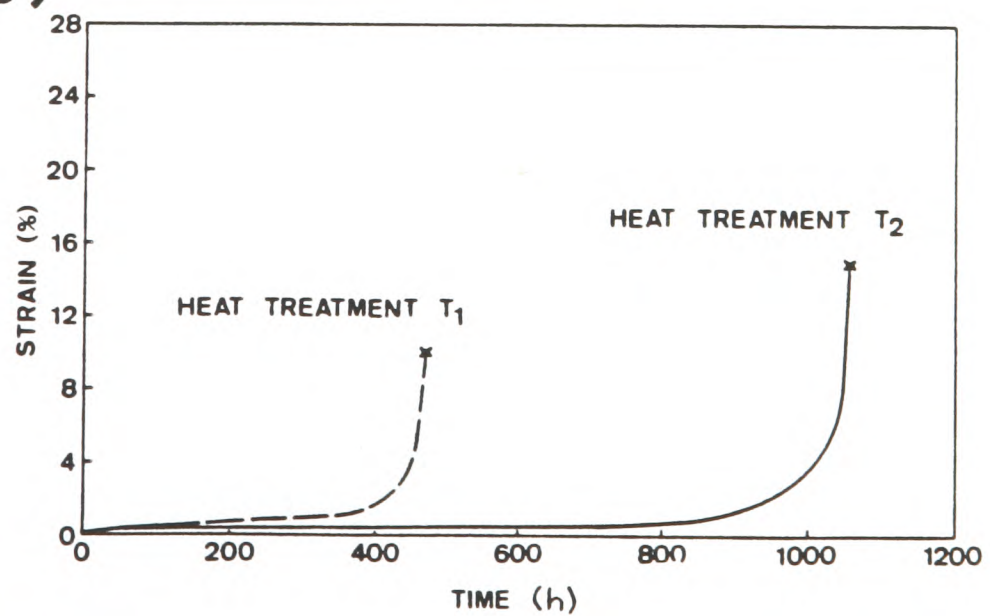


Figure 1.23

Schmid factor contours for the most highly stressed slip systems of type:

(a) $\{111\}\langle 110\rangle$

(b) $\{111\}\langle 112\rangle$.

(After McLean, 1983.)

Figure 1.24

Rotations of the tensile axis relative to the crystal lattice for

(a) $(111)[\bar{1}01]$ single slip

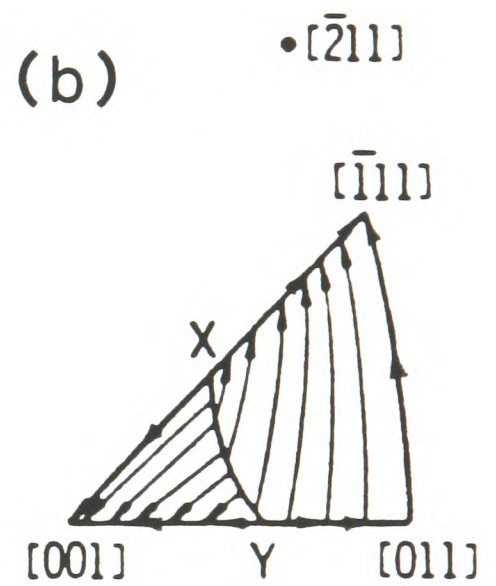
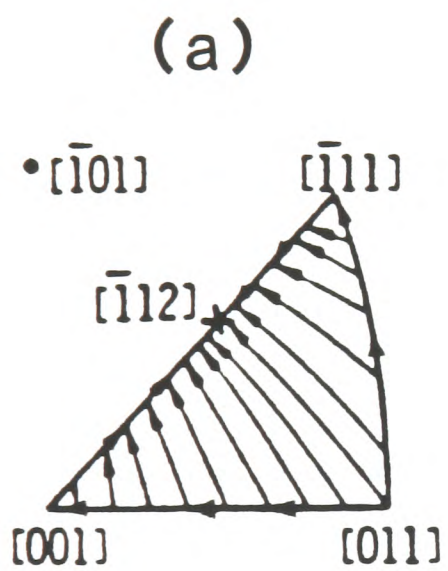
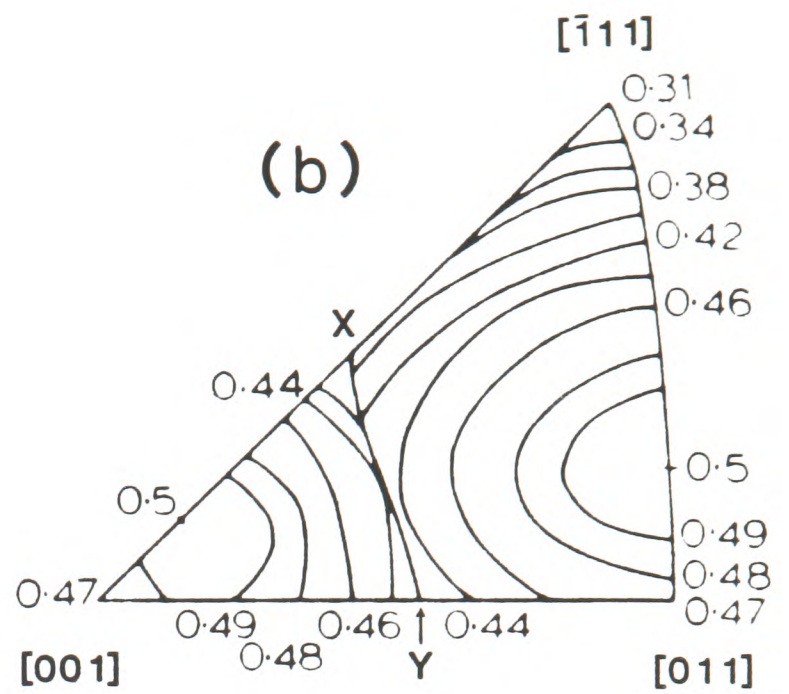
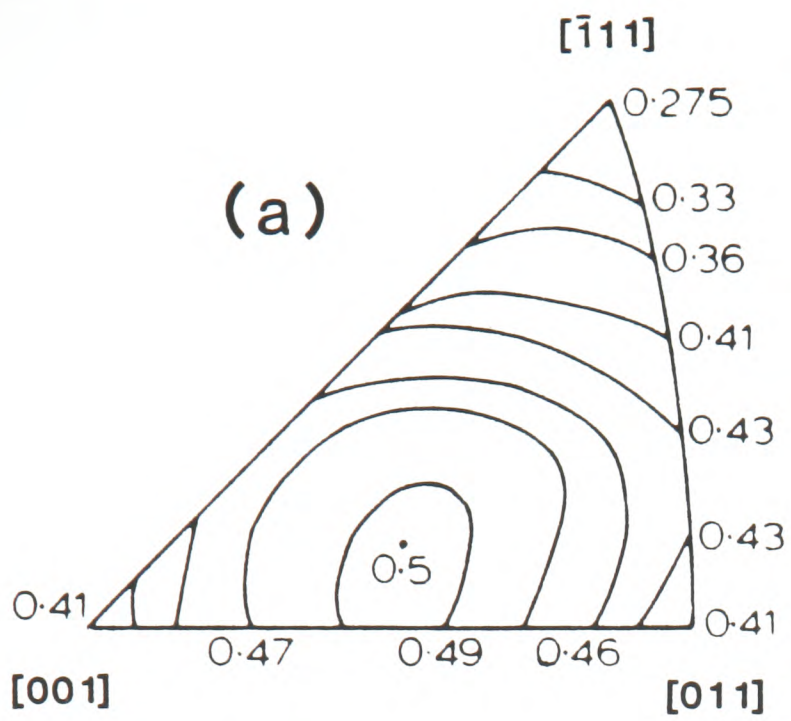
(b) $\{111\}\langle 112\rangle$ single slip.

(After McKay and Maier, 1982).

Figure 1.25

Variation in creep rupture lives of single crystals of Mar-M247 and Mar-M200 tested at 774 °C and 724 MPa.

(After McKay and Maier, 1982.)



• $[112]$

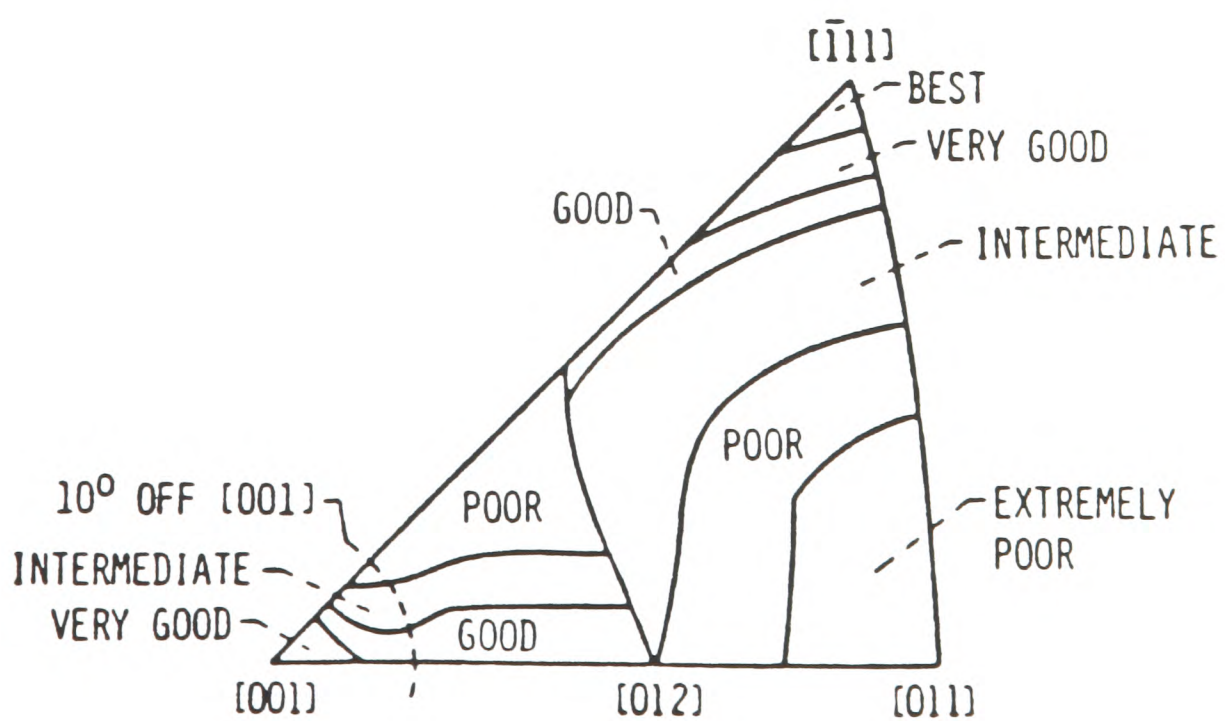


Figure 1.26

The temperature capability of turbine blade superalloys, based on a creep rupture life of 1000 hours at 150 MPa.

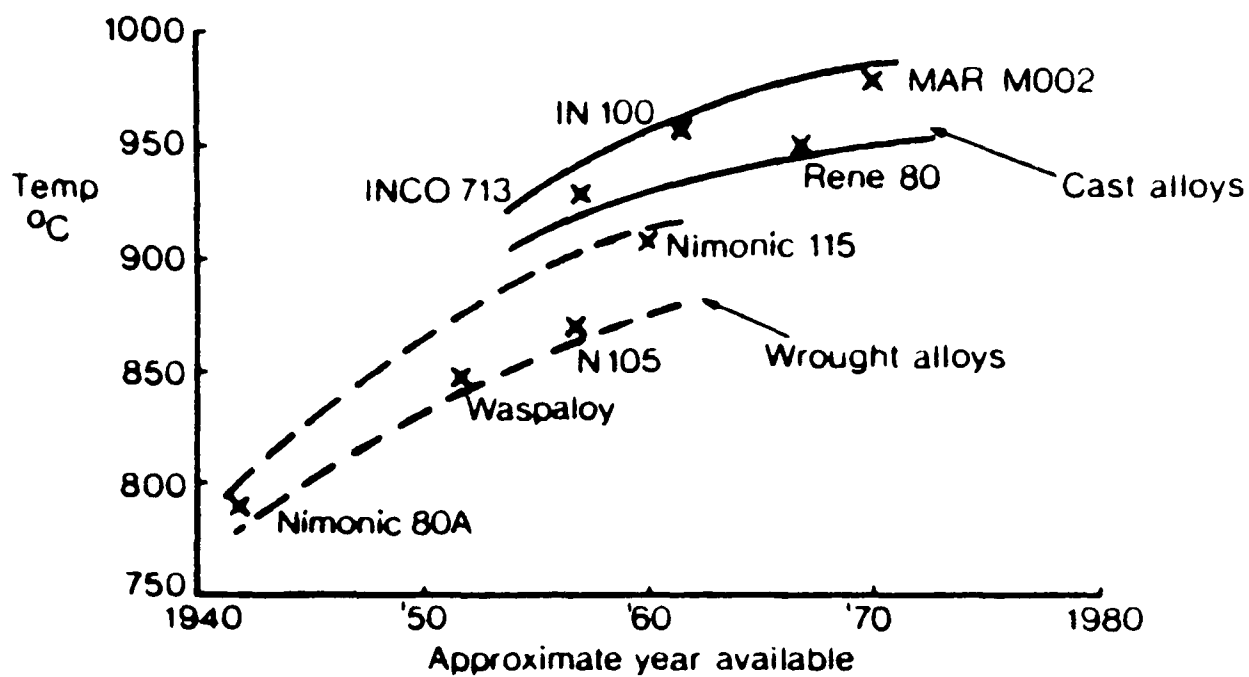
(After Meetham, 1982.)

Figure 1.27

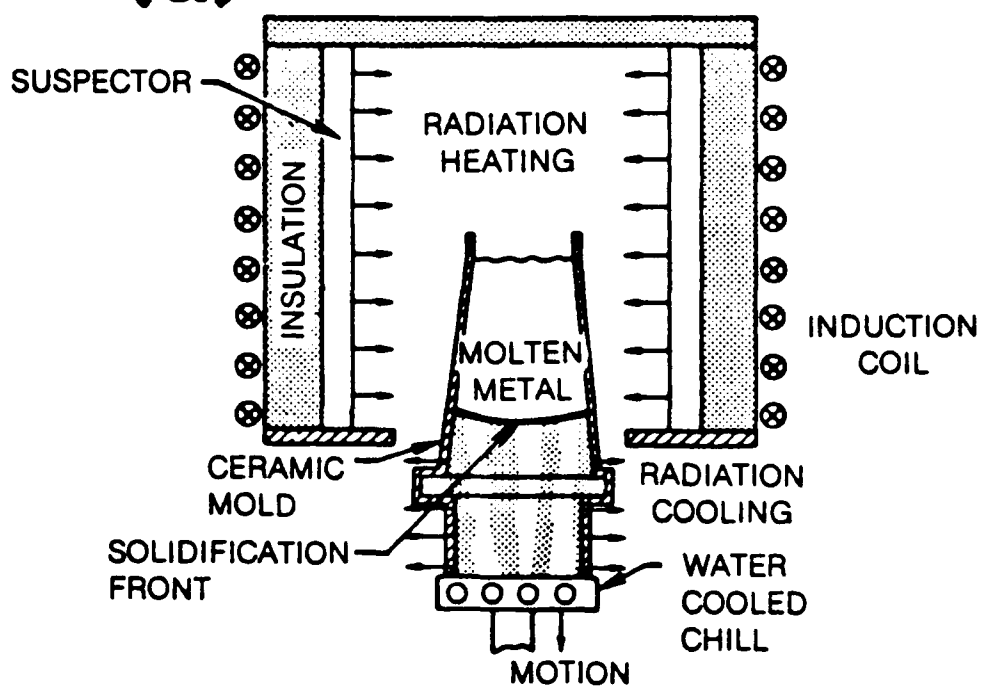
(a) Directional solidification casting.

(b) Single crystal casting.

(After VerSnyder, 1982.)



(a)



(b)

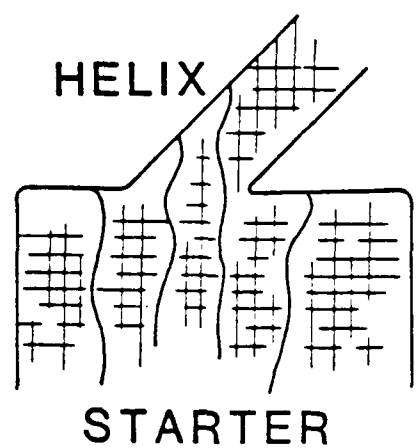
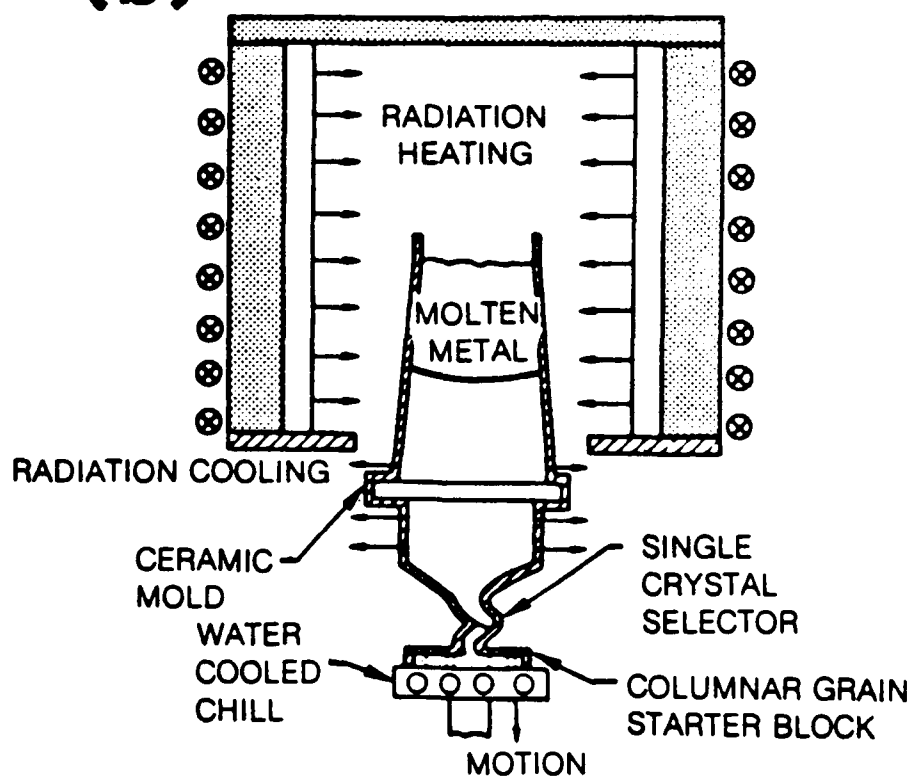


Figure 1.28

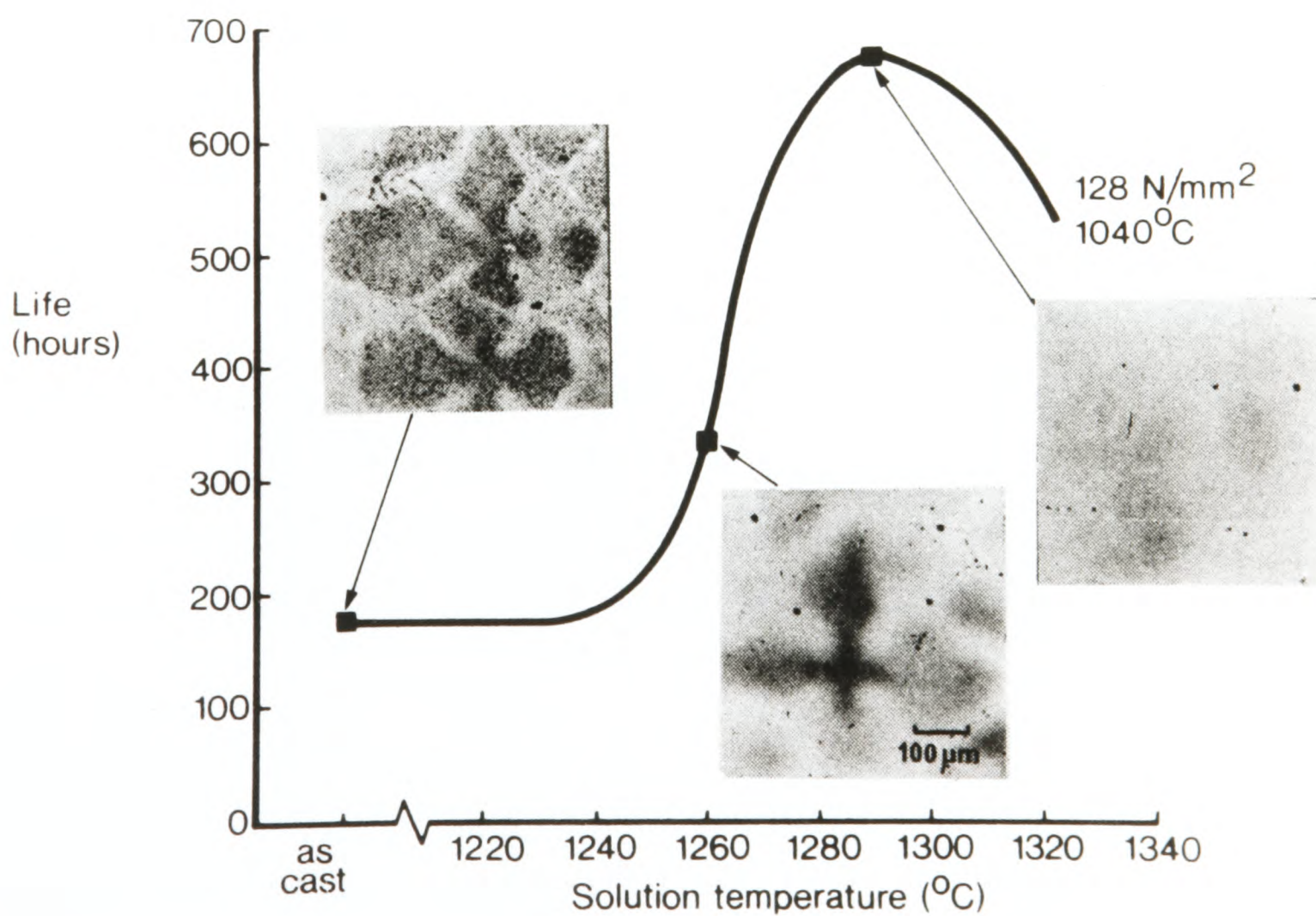
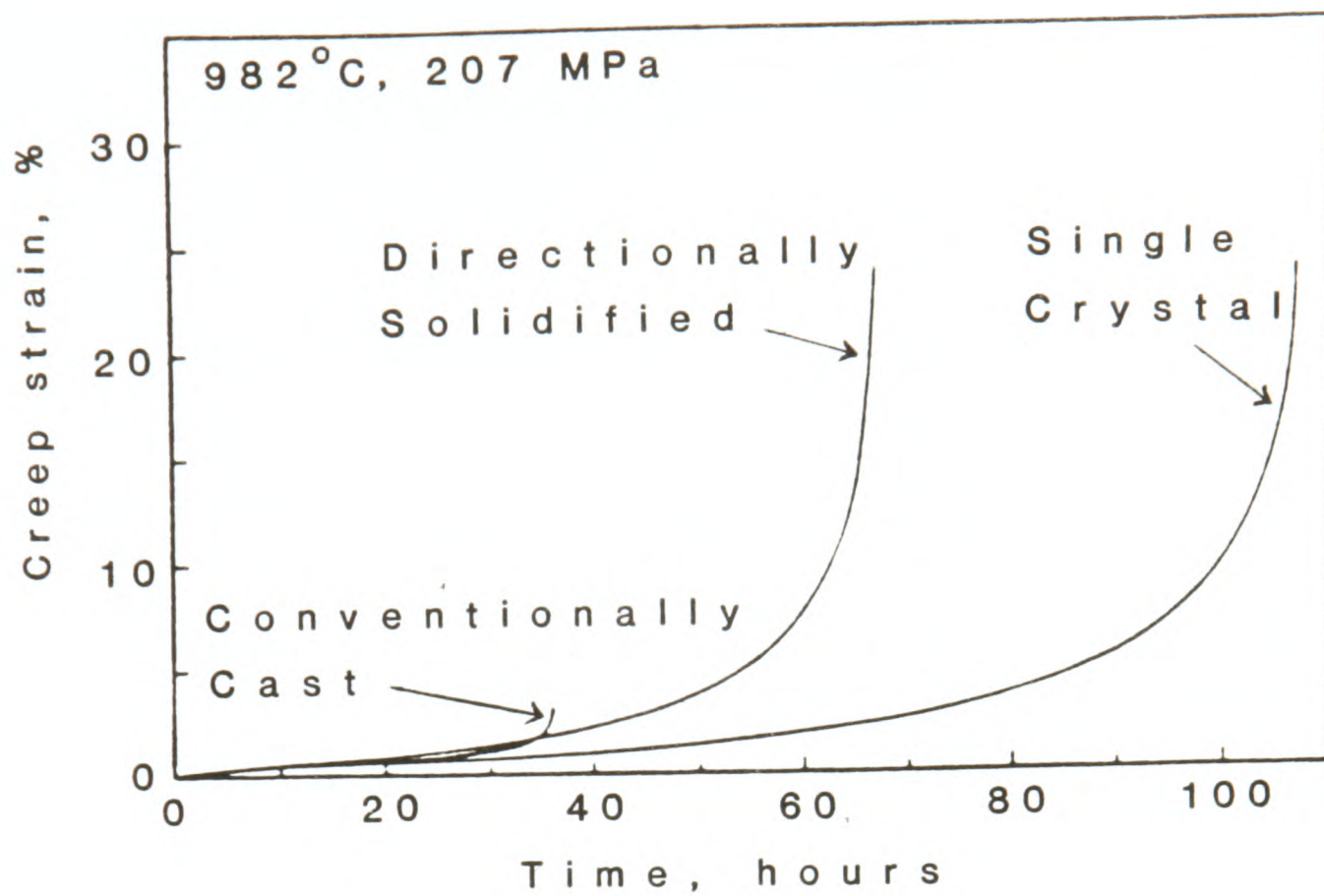
Comparison of the creep behaviour of conventionally cast, directionally solidified and single crystal forms of Mar-M200 tested at 980 °C and 207 MPa.

(After Kear and Pearcey, 1967.)

Figure 1.29

Effect of the solution heat-treatment temperature on the creep strength of a single crystal superalloy of similar composition to Mar-M002, tested at 1040 °C and 128 MPa.

(After Meetham, 1982.)



CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

Single crystals of SRR99 which had been grown by the helical single crystal selector technique described in Section 1.5.3 were provided by Rolls-Royce Limited. The mould was in the form of three tubes connected to a single helix. Thus crystals were grown in groups of three, where each was of length approximately 140 mm and diameter approximately 10 mm, as shown in figure 2.1(a). The crystal axes were aligned to within 10° of the [001] lattice direction, whilst the orientation in the plane normal to the growth direction was uncontrolled. The crystals were either supplied in this form or were machined to produce smaller specimens of length 25 mm and diameter 3.5 mm, as shown in figure 2.1(b). The latter were used in microstructural and microchemical investigations and to produce compression specimens. The larger crystals were cut in half and used to produce tensile creep specimens.

All the materials were supplied by Rolls-Royce Limited in a microstructurally as-cast condition, no heat-treatments being applied prior to supply. Two melts, namely RCL 170/6 and RCM 73/8, were used, these being chosen to be of closely similar composition. The compositions were measured by Rolls-Royce Limited and are listed in table 2.1, together with the nominal composition of SRR99.

2.2 Heat-Treatments

Heat-treatments were carried out using three furnaces. Two were platinum wound and were controlled by means of Eurotherm phase angle

controllers whilst the third had a Fecralloy winding and was controlled by a Eurotherm fast cycling controller. The Fecralloy wound furnace was used for the lower temperature heat-treatments. The temperature profile for each furnace was determined and subsequently heat-treatments were carried out by positioning the specimen at the plateau of the temperature profile. The temperature was monitored using a Pt/(Pt-13%Rh) thermocouple positioned alongside the specimen and was found to remain constant to within 2 °C of the nominal temperature.

Apart from during some preliminary investigations into the effects of solution heat-treatments, all specimens received a full solution heat-treatment of 4 hours at 1300 °C. The specimens were then either water quenched or directly transferred to a second furnace operating at a lower temperature for ageing. This procedure ensured that the ageing temperature was rapidly attained. By embedding a thermocouple in each type of specimen it was shown that the specimen temperature came within 20 °C of a typical ageing temperature of 1100 °C in less than 20 seconds from transfer between furnaces.

2.3 Creep Testing

2.3.1 Specimens

Tensile creep specimens were machined by Rolls-Royce Limited from heat-treated single crystals. These specimens had a gauge length of 20 mm and a circular cross-section whose diameter in the gauge length was 4 mm. The gauge length was terminated by ridges at each end onto which extensometers were clamped. The ends of the specimens were threaded with 24 UNF screw threads which fitted into grips on the testing rig. The full specifications of the specimens are given in figure 2.2.

2.3.2 Apparatus

Tests were carried out under constant load using a MAND creep testing rig, which is shown in figure 2.3. The load was applied by weights placed on a pan, which was connected to the specimen pull rods via a cantilever arrangement having a specimen load to applied weight ratio of 25:1. An automatic beam levelling device ensured that the loading lever remained in a horizontal position throughout the test, thus maintaining the 25:1 ratio. The specimen grips and the pull rods were made from Nimonic alloys.

To measure the specimen extension a set of extensometers were made from Inconel 600. These clamped onto the ridges at the extremes of the specimen gauge length. The location of the ridges with respect to the extensometer heads is shown in figure 2.4. Any extension occurring within the gauge length caused a relative movement between the extensometer heads and consequently between a pair of transducers and micrometer heads attached to the extensometers, as shown in figure 2.5. In this way deformation occurring within the gauge length was measured. Free unidirectional motion of the extensometers was ensured by a pair of polytetrafluoroethylene washers situated close to the extensometer base.

Automatic Systems Laboratories 'Super Linear Variable Capacitor' (SLVC) transducers, type 1071A, were used in conjunction with the manufacturer's standard model 22 conditioning units. The principles of operation of SLVC transducers have been reported by Wolfendale (1968). These devices offer a highly stable and accurate ($\pm 0.65 \mu\text{m}$ in this case) measure of displacement. The input voltage for the conditioning units was supplied by a DC power supply providing +15 V, 0 V and -15 V voltage levels. The power supply was connected to the mains via an Advance Volstat filter in order to eliminate any noise on the mains

supply. The conditioning units provided a DC output in the range 0-10 V, with a further 1 V overshoot available at each end of the range. The 0-10 V output corresponded linearly to 0-5 mm displacement of the transducer shaft. This output was recorded by means of a Normalair-Garrett 'Dynamco' model 6600 data-logger operating in its mid-range with ± 1 mV resolution. Readings from each of the conditioning units could be recorded at preset intervals of 1, 5, 10, 30 or 60 minutes and printed on a paper strip.

Heat was applied to the specimen by means of a three-zone nichrome wound furnace. Each zone was controlled by a Eurotherm fast cycling thyristor unit. The power output from each thyristor was adjusted to produce an even temperature profile throughout the hot zone to within 0.5°C . The specimen temperature was monitored by means of a thermocouple, which can be seen in figure 2.5, positioned alongside the specimen. The temperature remained constant at 750°C to within 1°C throughout the creep tests. The furnace was counterbalanced to enable it to be easily raised or lowered over the specimen and extensometer assembly.

2.3.3. Calibration

The data-logger was calibrated in accordance with the manufacturer's instructions against a 'PPM' DC voltage reference unit. Initial adjustments were made to the conditioning units in order to ensure that the transducers were operating in their linear region and that the nominal displacement-voltage correspondence was maintained. The procedure for achieving this is outlined below:

1. Connect yellow and red leads to conditioner. Disconnect the blue lead and short the inner wire to the outer shielding. Adjust the 'zero' potentiometer to produce -10 V output.

2. Reconnect the blue lead to the conditioning unit. Set the micrometer to produce an output of 0 V, then move the micrometer barrel and hence the transducer shaft by precisely 5 mm. Adjust the 'slope' potentiometer to produce an output of +10 V.
3. Repeat steps 1 and 2 until no further adjustment is required.

Prior to each test each transducer was calibrated by moving the micrometer barrel through a precise distance and noting the change in voltage. The results of these calibrations, which were always in very close agreement with the nominal displacement-voltage relationship, were used in calculating the strain within the specimen gauge length.

2.3.4 Testing Procedure

After setting up the specimen and extensometer assembly, the furnace was lowered such that the specimen was situated in the position corresponding to the centre of the hot zone. The ends of the furnace were then insulated using heat-resistant ceramic wool and the furnace was allowed to heat up. After the specimen had attained a temperature of 750 °C it was maintained at this temperature for 16 hours prior to testing in order to allow the system to stabilise.

After calibrating and re-zeroing the transducers, weights were placed on the loading pan, which at this stage was supported on plastic blocks. In order to produce a nominal stress of 800 MPa, a load of 402 N would be required on the pan. A further 3 N weight was required to balance the loading beam, giving a total weight of 405 N. The load was progressively applied over a period of approximately 5 minutes by driving the capstan motor such that the weights were gradually raised off their supports. Throughout the primary creep stage the data-logger was set to record the transducer outputs at 5-minute intervals. After the end of the primary stage, readings were taken every 30 minutes.

The specimen extension was taken to be the average of the displacements measured by each transducer.

Some tests were carried through until the specimen failed. A microswitch located beneath the weight pan caused the furnace to be switched off after failure of the specimen. This minimised oxidation of the fracture surfaces so that they could be more easily examined. Other tests were interrupted to allow examination of the dislocation structures. The tests were interrupted by cooling the specimen under load in order to avoid relaxation of the dislocation structure occurring. However, to avoid low temperature deformation being introduced on cooling as a result of contraction of the specimen cross-section or a drop in the yield stress, the load was reduced immediately prior to interruption of the test. The procedure that was adopted was to remove 105 N from the pan, then immediately raise the furnace and cool the specimen using a compressed air line. A further 100 N would then be removed from the pan.

2.3.5 Crystal Orientation Measurements

After testing, the specimens were sectioned transversely by cutting through the gauge length using a low speed diamond saw. A reference mark was spark-machined onto the side of the specimen and then the faces at each end were ground, mechanically polished and electropolished, as described in table 2.2. Using an x-ray Laue technique at both the screw-threaded end and at the other end, it was possible to measure the orientation of the specimen axis relative to the crystal lattice before and after creep deformation respectively.

The specimen was mounted in a brass block with flat perpendicular sides and was held in place in the block by a screw-threaded hole whose axis was parallel to the edges. All faces of the block were milled to

ensure correct alignment. The hole was positioned slightly off-centre, so that the x-ray beam avoided the centre-drill hole at the screw-threaded end. The specifications for the block are given in figure 2.6. The specimen was mounted such that the reference mark corresponded to a pointer on the block.

X-ray diffraction was carried out by Rolls-Royce Limited using the 'SCORPIO' real-time orientation measuring system. In this system the back-scattered x-rays are detected using a photodetector. The signal is then fed into a computer system which produces a simulated Laue pattern and interprets the crystal orientation. An orientation measurement would be taken from one end, then the block turned around and a measurement taken from the other end. In comparing the orientations allowance was made for the 180° rotation.

2.4 High Strain-Rate Tests

2.4.1 Specimens

The high strain-rate deformation of SRR99 was investigated by means of compression testing. Specimens were prepared from the 3.5 mm diameter rods described in section 2.1. After heat-treatment, the rods were centreless ground to a diameter of 3 mm. The ground surface was then polished with 3 μ m diamond paste, the final polish being applied in the direction parallel to the specimen axis. The specimen was then cut into lengths of just over 6mm using a low speed diamond saw. The ends were ground using 500 and 1200 grade silicon carbide paper and polished using 3 μ m diamond paste to produce specimens of length 6 mm. A specimen is illustrated in figure 2.7. The chosen dimensions have a height to diameter ratio of 2:1, in accordance with the recommendations of the American Society for the Testing of Materials (ASTM) for compression testing of strong materials (ASTM, 1983).

2.4.2 Room Temperature Compression Tests

Tests were carried out using an Instron testing machine, fitted with a 50 kN capacity load cell which was calibrated using standard weights. The specimens were compressed between two push rods fitted with hardened steel platens. No lubrication of the specimen/platen interface was used. Prior to testing, the platens were driven together to ensure that all screw joints were firmly bedded in. A nominal strain-rate of $1.4 \times 10^{-3} \text{s}^{-1}$ was employed, and the chart recorder was run at a speed of 20 cm per minute with a full scale deflection of 10 kN. Some tests were interrupted after 1%-5% plastic deformation to allow examination of the dislocation structures, whilst other specimens were deformed by up to 25%.

2.4.3 Elevated Temperature Compression Tests

The elevated temperature compression testing rig is shown in figure 2.8. The tests were carried out at 750 °C in a similar manner to room temperature tests and at the same nominal strain-rate. Nimonic push rods were screw-fitted to the existing rods, and the ends of the Nimonic were capped with hot-pressed silicon nitride. Silicon nitride was chosen since no metallic materials were available whose hardness at 750 °C exceeded that of the SRR99 specimens. A nichrome wound furnace was supported over the Nimonic rods such that a specimen situated between the silicon nitride platens would be located at the centre of the hot zone of the furnace. The furnace temperature was controlled using a Eurotherm fast cycling controller. Both ends of the furnace were insulated using heat-resistant ceramic wool and the temperature of the specimen was monitored by means of a thermocouple placed alongside it. To avoid any heat from the furnace reaching the load cell, which was situated at the top of the machine, a coil of circulating water

cooled the top Nimonic rod above its point of emergence from the furnace.

After calibration of the load cell, the furnace was allowed to attain the testing temperature. As for room temperature tests, the platens were driven together to ensure that all screw joints were firmly bedded together. The lower push rod was then withdrawn from the furnace, the specimen placed on the silicon nitride platen and the whole driven up into the furnace until positioned just below the top platen. Sufficient clearance was allowed for expansion of the push rods. The apparatus was allowed to stabilise for one hour before testing, which was then carried out in the same manner as the room temperature tests.

2.5 Optical Metallography

Specimens for optical metallographic examination were mounted in a bakelite resin and ground using wet silicon carbide paper, progressing from 200 grade through to 1200 grade. After grinding, the specimens were thoroughly washed, rinsed in ethanol and dried using a warm air drier. Mechanical polishing was carried out using Metallurgical Services Limited 'Metron' polishing cloth impregnated with 3 μ m diamond paste on a rotating wheel. The specimens were then washed once more and electroetched in an orthophosphoric acid solution by passing a platinum wire cathode over the specimen surface. Specimens were finally rinsed in water and in ethanol before drying using a warm air drier. This preparation procedure, including the electroetching conditions, is summarised in table 2.3.

2.6 Scanning Electron Microscopy

Most microstructural investigations by scanning electron

microscopy (SEM) were carried out using a JEOL JEM 100C scanning transmission electron microscope incorporating an EM-ASID-40 scanning attachment. The microscope was operated in the secondary electron image mode at an accelerating voltage of 100 kV. A small number of microstructural SEM studies were also carried out using a JEOL JSM35CF and a CAMECA CEMEBAX, the latter providing electron-probe microanalysis facilities. Fracture surfaces from specimens crept to failure were examined in a JEOL JSM35X microscope.

One of the JEOL JEM100C specimen holders required specimens in the form of flat 3mm diameter discs. To produce such specimens, 3.5 mm diameter cylinders were centreless ground to 3 mm and sliced into discs of thickness 0.35 mm using a low speed diamond wafering saw. A bulk holder was also available, for which specimens having maximum dimensions of 20 mm x 6 mm x 2 mm were mounted in a copper boat using silver dag. This holder was used when examining sections from crept specimens, the appropriate section being cut to suitable size using a spark erosion machine fitted with a wire slicing jig. Both types of specimen were ground on wet 1200 grade silicon carbide paper and mechanically polished as for optical metallographic specimens. They were then electropolished in a 2-butoxyethanol/perchloric acid/acetic acid solution according to the conditions in table 2.4., prior to being electroetched.

2.7 Transmission Electron Microscopy

Thin foils for transmission electron microscope (TEM) examination were produced from 3 mm diameter discs. The technique for producing these discs varied according to the type of specimen being examined. For the examination of undeformed material, 3.5 mm diameter rods were centreless ground to 3 mm and discs sliced off using a low speed

diamond wafering saw. Slicing by this technique has been shown by Wellner (1980) to introduce less damage into the material than cutting with either abrasive wheels or by spark erosion. For the examination of crept or compressed specimens, most slices were taken normal to the stress axis using the same technique. In the case of crept specimens this produced over-size discs, from which 3 mm discs were trepanned by spark erosion machining. For this purpose the discs were mounted on a brass block using Durofix glue impregnated with graphite so as to maintain an electrical contact and were cut using a thin-walled brass tube of internal diameter 3 mm as the cutting tool.

Some specimens were cut along other selected crystallographic planes. To achieve this, one end was firstly polished as described in section 2.3.5. The specimen was then mounted on a goniometer having tilting and rotation facilities, taking care to maintain an electrically conductive contact. A back reflection x-ray Laue photograph was taken from the polished end to establish the orientation of the specimen. The whole goniometer assembly was then transferred to a spark erosion machine and, using the goniometer, the specimen was oriented so that it could be sliced along the chosen crystallographic planes. Discs of diameter 3 mm were then trepanned out as described above.

Having obtained discs of diameter 3 mm, these were ground using wet 1200 grade silicon carbide paper to a thickness of 0.25 mm. They were then jet polished using a 10% solution of perchloric acid in ethanol with a Struers 'Tenupol' apparatus. The appropriate conditions for jet polishing are listed in table 2.5. The photocell was set such that the device switched off immediately after perforation of the specimen, and the resulting foil was then rinsed in three successive beakers of ethanol. TEM examination of the foil was carried out at

this stage, but almost invariably it was found that the area around the perforation was too thick to be imaged. This is possibly due to initial perforation occurring at pores in the material. The specimen would then be slowly electropolished in a 2-butoxyethanol/perchloric acid/acetic acid solution in accordance with the conditions listed in table 2.5. Successive TEM examination and electropolishing would then be carried out until a satisfactory foil had been produced. Often the foil would have perforated in several places by this stage.

TEM studies were carried out using both a high voltage electron microscope (HVEM) operating at 1 MV and a Philips EM300 microscope operating at 100 kV. The HVEM was capable of imaging thicker sections of a given foil. However, since no relaxation of the dislocation structures was observed in the thinner parts of the foils, it was concluded that dislocation structures could satisfactorily be investigated at an electron accelerating voltage of 100 kV. Consequently the majority of the TEM studies were carried out using the Philips EM300 microscope.

2.8 Field-Ion Microscopy and Time of Flight Atom Probe Microanalysis

2.8.1 Field-Ion Microscopy

The field-ion microscope (FIM) was invented by Müller (1951) as a device for providing atomic-scale microstructural resolution of metal surfaces. A FIM specimen takes the form of an ultra-sharp needle, typically having a tip radius of 10-100 nm and a cone angle of 3-4 °. The specimen is cryogenically cooled and held in a vacuum chamber containing a low pressure of inert gas. Neon or helium are commonly used at pressures in the range 10^{-4} - 10^{-6} torr. Application of a positive potential, V_0 , of up to 30 kV produces a high electric field of the order of 40 V/nm at the specimen tip. Gas atoms polarised under

the influence of the electric field are drawn towards the specimen where they become trapped in a narrow ionization zone. Electron tunnelling to the metal surface may occur, producing positive gas ions, which are repelled from the specimen towards a channel plate image intensifier and phosphor screen. This process, known as field-ionisation, is illustrated in figure 2.9.

Ionisation of the gas occurs preferentially in the regions of highest electric field. These regions coincide with areas on the specimen surface which are most sharply curved on an atomic scale, namely at the edges of atomic planes. Thus the image formed on the phosphor screen appears as a dot pattern representing the surface atomic structure at the tip of the specimen. The image approximates to a stereographic projection from the apex of the specimen.

2.8.2 Atom Probe Microanalysis

Müller et al. (1968) proposed that by combining a FIM with a mass spectrometer, atomic scale chemical as well as microstructural information would become available. The resultant device, known as an atom probe, is shown schematically in figure 2.10. An aperture or probe hole has been introduced into the channel plate, such that it has a diameter of 2-4 nm on the scale of the FIM image. Chemical analysis of a selected area of the image is obtained by firstly manipulating the specimen until the required portion of the image is over the probe hole. The image gas is removed, leaving a residual pressure of $\leq 10^{-9}$ torr. A series of high voltage pulses (V_p) having a duration of the order of 10 nanoseconds is then applied in addition to the standing voltage (V_0) such that ionization of metal atoms at the specimen tip occurs. These ions are accelerated away from the specimen, those from the selected area passing through the probe hole,

through a field-free time of flight tube to a single ion detector. The time (t) for an ion to travel the distance (d_{ap}) from the specimen to the detector is measured by a digital clock which starts upon application of the pulse and stops when an ion is detected. By equating the kinetic energy of the ion to its potential energy in an accelerating electric field, the mass to charge ratio (m/n_e) of the ion may be determined as

$$\frac{m}{n_e} = \frac{2et^2(V_0 + V_p)}{d_{ap}^2} \quad (2.1)$$

where n_e is the number of electronic charge units (e) of the ion. The ionic species can then be identified from knowledge of the preferred isotopes and charge states of the elements.

2.8.3 Application in the Present Study

The spatial resolution of the more common microanalytical techniques such as energy dispersive x-ray analysis is limited to the size of the electron interaction volume. Often this volume may impinge upon regions other than that which is intended. Such problems are avoided by the single ion detection afforded by the atom probe. The spatial resolution is typically less than 4 nm laterally and of the order of the atomic lattice spacing depthwise. Furthermore, the instrument offers equal sensitivity to all elements and freedom from contamination of the region being examined. Therefore the atom probe is suitable not only for obtaining reliable analyses from fine-scale microstructural features such as γ' precipitates and γ matrix, but also for studying phase interfaces (see, for example, Delargy and Smith, 1983; Blavette and Bostel, 1984).

The present studies were carried out using the Oxford time of

flight atom probe. Specimens were cooled to approximately 100 K by means of a cryostat containing liquid nitrogen and, whilst in the FIM mode, neon imaging gas was used. The power supplies and pulsing equipment were capable of producing standing voltages (V_0) and pulse voltages (V_p) of up to 30 kV and 5 kV respectively. The pulses were nominally rectangular with a duration of 20 ns and emitted ions were detected by a Johnston detector. Values of m/n_e were calculated on-line using a DEC pdp-11/10 microcomputer and times of flight were stored on paper tape to allow off-line analysis on an ICL 2988 mainframe computer.

Superalloys generally contain elements spanning a large range of atomic numbers (Z). In the case of SRR99 elements from carbon ($Z=6$) through to tungsten ($Z=74$) are present. Thus evaporation of atoms from the specimen tip may take place over a wide range of electric field strengths. To ensure that no elements would systematically escape detection, it was important that the standing DC potential (V_0) was kept below the evaporation potential of the most loosely bound atoms, whilst the total pulse amplitude (V_0+V_p) had to be sufficiently high to permit evaporation of the most tightly bound atoms. In accordance with the recommendations of Delargy (1981), a pulse fraction of 25% was chosen. Through the course of an experiment, V_0 and V_p were increased stepwise as the tip radius increased.

The preferred mass to charge ratios (m/n_e) for the elements present in SRR99 are shown in table 2.6. The ranges of experimentally determined m/n_e values, or m/n_e windows, which were allocated to each element are shown in table 2.7. At large values of m/n_e , the windows chosen are slightly displaced relative to the theoretical values as a result of a small deviation from linearity for the experimental m/n_e spectra.

2.8.4 Specimen Preparation

The starting material for the preparation of atom probe specimens was in the form of 3.5 mm diameter rods, as described in section 2.1. These were mounted vertically in a spark erosion machine and sliced longitudinally using a fine wire cutting jig. Several slices were made in each of two perpendicular directions, to produce bars having a square cross-section of width approximately 0.25 mm. These were then cut to a length of approximately 11 mm. The axes of bars produced in this manner were parallel to the [001] crystal growth direction.

The bars were electropolished in a 5 mm layer of a perchloric acid/glycerol/ethanol mixture floated on carbon tetrachloride. Polishing proceeded until a very narrow neck had formed in the centre, a gentle upward and downward motion being applied throughout. The specimen was then slowly electropolished in a solution of 2% perchloric acid in 2-butoxyethanol until the bottom section separated from the top, producing two potential atom probe specimens. The conditions for each stage of the electropolishing procedure are detailed in table 2.8. Finally the specimens were mounted in short nickel tubes, with the tip protruding.

2.9 Precipitate Size Measurements

In order to investigate γ' precipitate coarsening, measurements of precipitate sizes were required. Brøndsted and Tøft Sorenson (1978) have suggested the possibility of systematic differences occurring between particle size measurements made from SEM and TEM images. To check whether this was the case in the present studies, some samples were imaged by both SEM and TEM. In the latter case the precipitates were brought into strong contrast by a central aperture selected area

dark field technique, using an excited superlattice reflection. Measurements made using the technique outlined below from each type of image yielded mean values which were indistinguishable. Therefore, since SEM specimens could be produced more simply and efficiently, all measurements and analyses were made from SEM images.

The measurements were carried out using a Graphics Tablet attached to an Apple microcomputer via slot number 4. This device enables shapes which are traced out on the tablet with an electronic pen to be sent to the computer and recorded on the visual display unit screen. The pen detects a radio frequency signal which is sent along wires running beneath the tablet surface. By measuring the phase lag of the signal together with the relative amplitudes of pulses detected from the closest sections of the signal-carrying wires, the pen position is detected with a precision of 0.05 mm. The controlling software allows distances and areas which are traced out to be determined.

Photographs of the microstructures were enlarged to A4 size and secured in position on the tablet. The magnifications were chosen such that on this scale a typical γ' precipitate would have a width of approximately 30 mm. Since the magnifications of the photographs were known, the tablet could be calibrated. To do this the pen was placed at each end of the photograph, and the distance corresponding to the separation of these points on the specimen entered into the computer. All subsequent measurements were then scaled accordingly and measured in the chosen units.

The pen was used to draw around precipitates on the photograph and the computer then measured the area traced out, corresponding to the area of the precipitate. An image remained on the screen, ensuring that no precipitates could accidentally be traced out more than once. Unfortunately the commercially available software did not allow the

measured areas to be recorded. Instead they would be momentarily displayed and then lost. In order to overcome this problem, modifications were made to the main controlling program. Commands were written such that after making an area measurement, the value would be stored in an array. Upon completion of measurements from a photograph, the contents of the array were stored on a magnetic disc under a file name of the operator's choosing. The data were then transferred by means of an interfaced Apple microcomputer from the magnetic disc to a DEC VAX 11/780 minicomputer for further analysis.

Since the conventional controlling program exhausted the program memory available on the Apple, these additions to the program could only be achieved by erasing parts of the program. Thus it was decided to sacrifice the options relating to multi-coloured graphics. Since only a monochrome visual display unit was available, the elimination of this facility did not cause any concern. The modified controlling program is listed on microfiche at the end of this work.

Table 2.1

Composition of SRR99

(Figures supplied courtesy of Rolls-Royce Limited).

Element	Nominal		Melt no. RCL 170/6		Melt no. RCM 73/8	
	Atomic % Weight %		Atomic % Weight %		Atomic % Weight %	
Al	12.00	5.5	11.45	5.23	11.36	5.18
Ti	2.70	2.2	2.63	2.13	2.72	2.20
Cr	9.62	8.5	9.54	8.40	9.62	8.46
Co	5.00	5.0	5.18	5.17	5.09	5.07
Ta	0.91	2.8	0.84	2.57	0.86	2.63
W	3.04	9.5	3.14	9.78	3.08	9.57
C	0.074	0.015	0.094	0.019	0.069	0.014
Ni	Balance	Balance	Balance	Balance	Balance	Balance

Table 2.2

Preparation of specimens for x-ray Laue back-reflection.

- (i) Final grinding applied using 1200 grade silicon carbide paper.
- (ii) Mechanically polished with 3 μm diamond paste.
- (iii) Electropolished under the following conditions:
 - 10% perchloric acid, 45% acetic acid, 45% 2-butoxyethanol.
 - Approximately -20°C .
 - Large stainless steel mesh cathode.
 - Solution stirred continuously.
 - D.C. current density of 10 mA mm^{-2} .
 - Approximately 1.5 minutes.

Table 2.3

Preparation of specimens for optical metallographic examination.

- (i) Final grinding applied using 1200 grade silicon carbide paper.
- (ii) Mechanically polished with 3 μm diamond paste.
- (iii) Electro-etched under the following conditions:
 - 10% orthophosphoric acid in water.
 - Room temperature.
 - Platinum wire cathode.
 - 3 Volts D.C.
 - 1-2 seconds.

Table 2.4

SEM specimen preparation.

- (i) Ground using 1200 grade silicon carbide paper.
- (ii) Mechanically polished using 3 μm diamond paste.
- (iii) Electropolished under the following conditions:
 - 10% perchloric acid, 45% acetic acid, 45% 2-butoxyethanol.
 - Approximately -20°C .
 - Large stainless steel mesh cathode.
 - Stirring applied only for bulk specimens.
 - D.C. current density of 10 mA mm^{-2} .
 - Approximately 1.5 minutes.
- (iv) Electro-etched under the following conditions:
 - 10% orthophosphoric in water.
 - Room temperature.
 - Platinum wire cathode.
 - 3 Volts D.C.
 - 1-2 seconds.

Table 2.5

TEM specimen preparation

- (i) Discs ground to 0.25 mm thickness using 1200 grade silicon carbide paper.
- (ii) Jet-polished using Struers 'Tenupol' apparatus under the following conditions until perforation of the specimen occurs:
 - 10% perchloric acid in ethanol.
 - Approximately -20 °C.
 - Flow rate = 4.
 - 80 Volts D.C., open circuit (voltage drops slightly when jet-polishing commences).
- (iii) TEM examination.
- (iv) Successive electropolishing and TEM examination until a satisfactory foil is produced. Electropolishing conditions:
 - 10% perchloric acid, 45% acetic acid, 45% 2-butoxyethanol.
 - Approximately -20 °C.
 - Large stainless steel mesh cathode.
 - D.C. current density of 10 mA mm⁻².

Table 2.6

Preferred isotopes and charge states for ions of the elements present in SRR99.

(Adapted from Delargy, 1981).

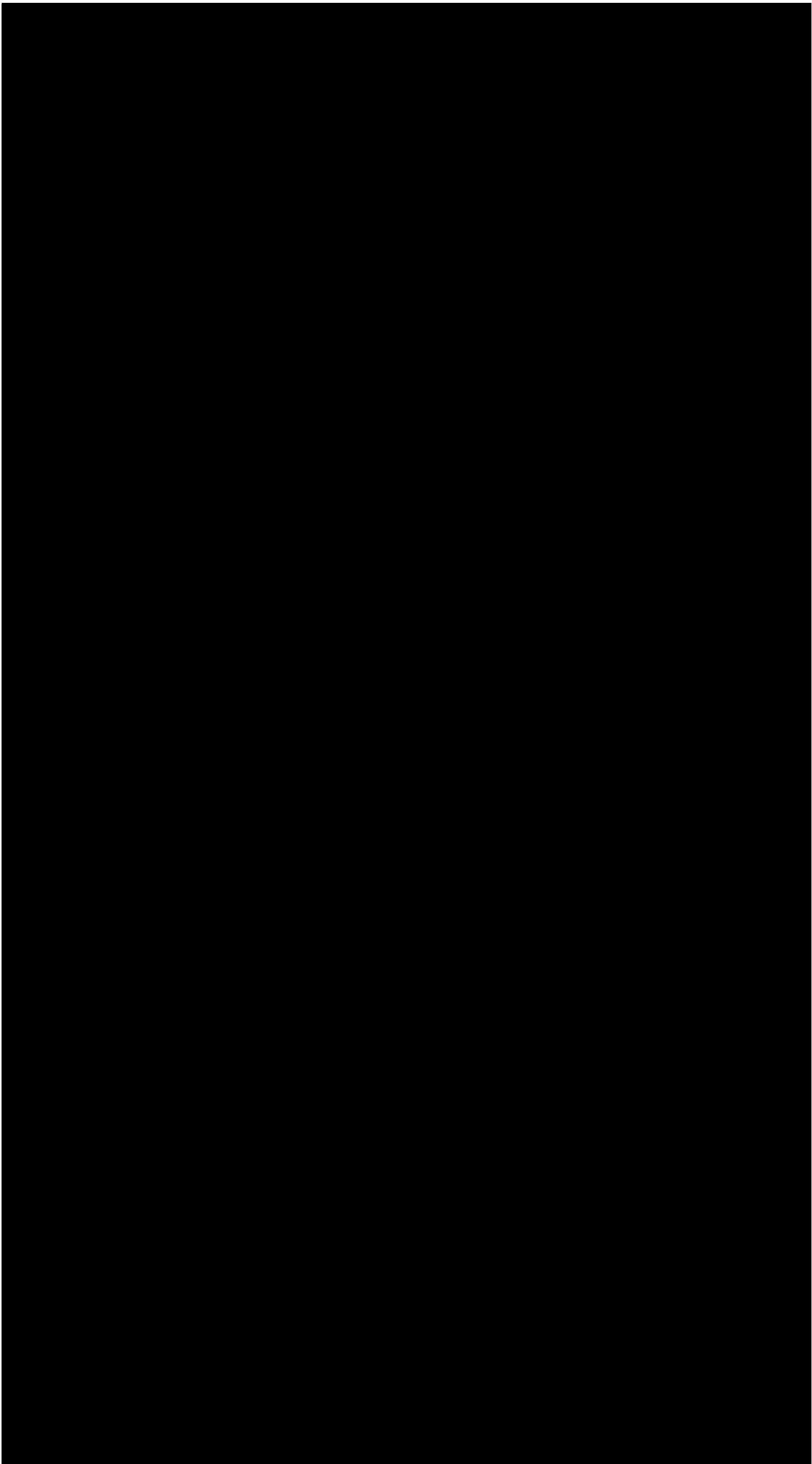


Table 2.7

Windowed m/n_e values used for identifying ions.

Element	m/n_e ratio (amu)
Al	8.45-9.75, 12.95-14.85
Ti	14.85-17.05, 22.25-25.00
Cr	25.00-28.20, 49.20-54.55
Co	29.40-29.60
Ta	45.00-45.40, 59.95-61.35, 89.95-92.75
W	45.40-47.00, 61.35-64.05, 92.75-96.05
C	5.45-6.55, 11.45-12.55
Ni	28.20-29.40, 29.60-36.00

Table 2.8

Preparation of FIM/atom probe specimens.

- (i) Bars having a square cross-section of width approximately 0.25 mm and length approximately 11 mm cut by spark erosion machining.
- (ii) Electropolished under the following conditions until a very narrow neck is formed:
 - 10% perchloric acid, 20% glycerol, 70% ethanol.
 - 5 mm layer floated on carbon tetrachloride.
 - Room temperature.
 - Gold foil cathode.
 - 22 volts D.C.
 - Gentle upward and downward motion applied throughout.
- (iii) Electropolished under the following conditions until bottom portion separates from the top:
 - 2% perchloric acid in 2-butoxyethanol.
 - Approximately -5 °C.
 - Gold foil cathode.
 - 25 volts D.C.

Figure 2.1

Single crystals of SRR99.

(a) As cast.

(b) Machined specimen of length 25 mm and diameter 3.5 mm.



(a)



(b)



Figure 2.2

Tensile creep testing specimen.

(Reproduced by kind permission of Rolls-Royce Limited.)

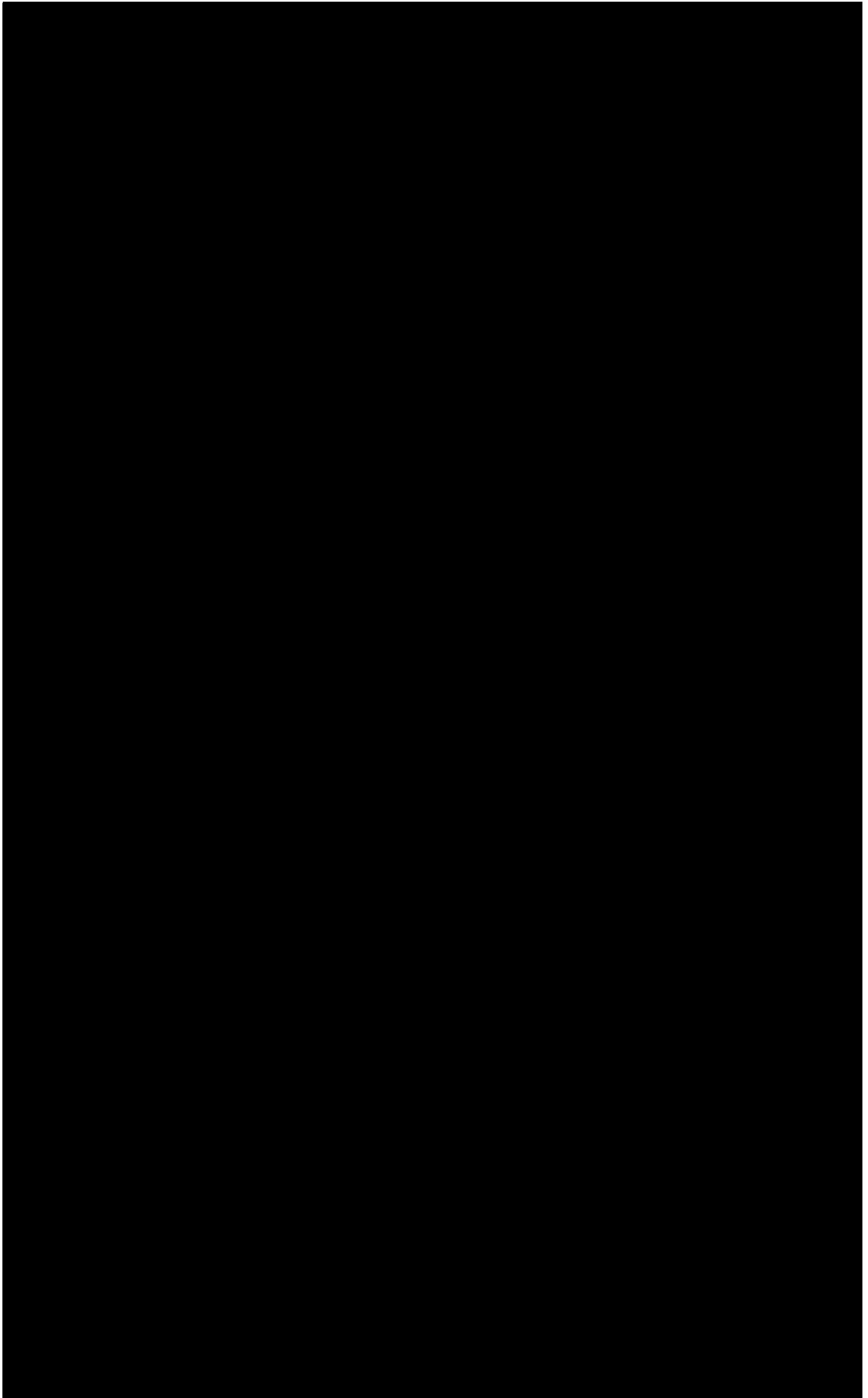


Figure 2.3

Creep testing rig.

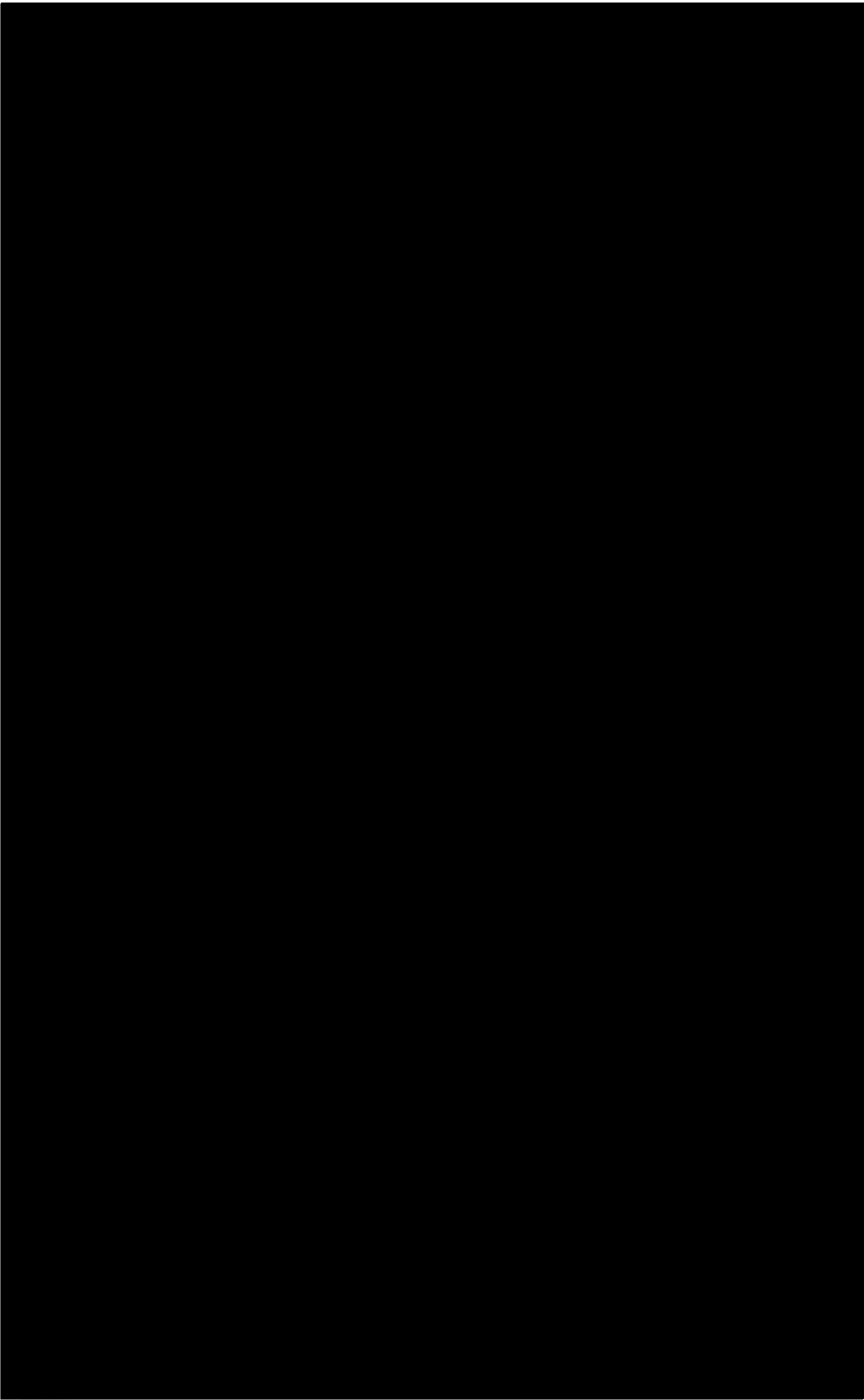


Figure 2.4

Showing the location of a creep specimen with respect to the extensometer heads, with the two front clamps removed.

Figure 2.5

Extensometer assembly on creep testing rig. (The furnace has been raised from its normal operating position in order to reveal the top part of the extensometers and the specimen grips.)

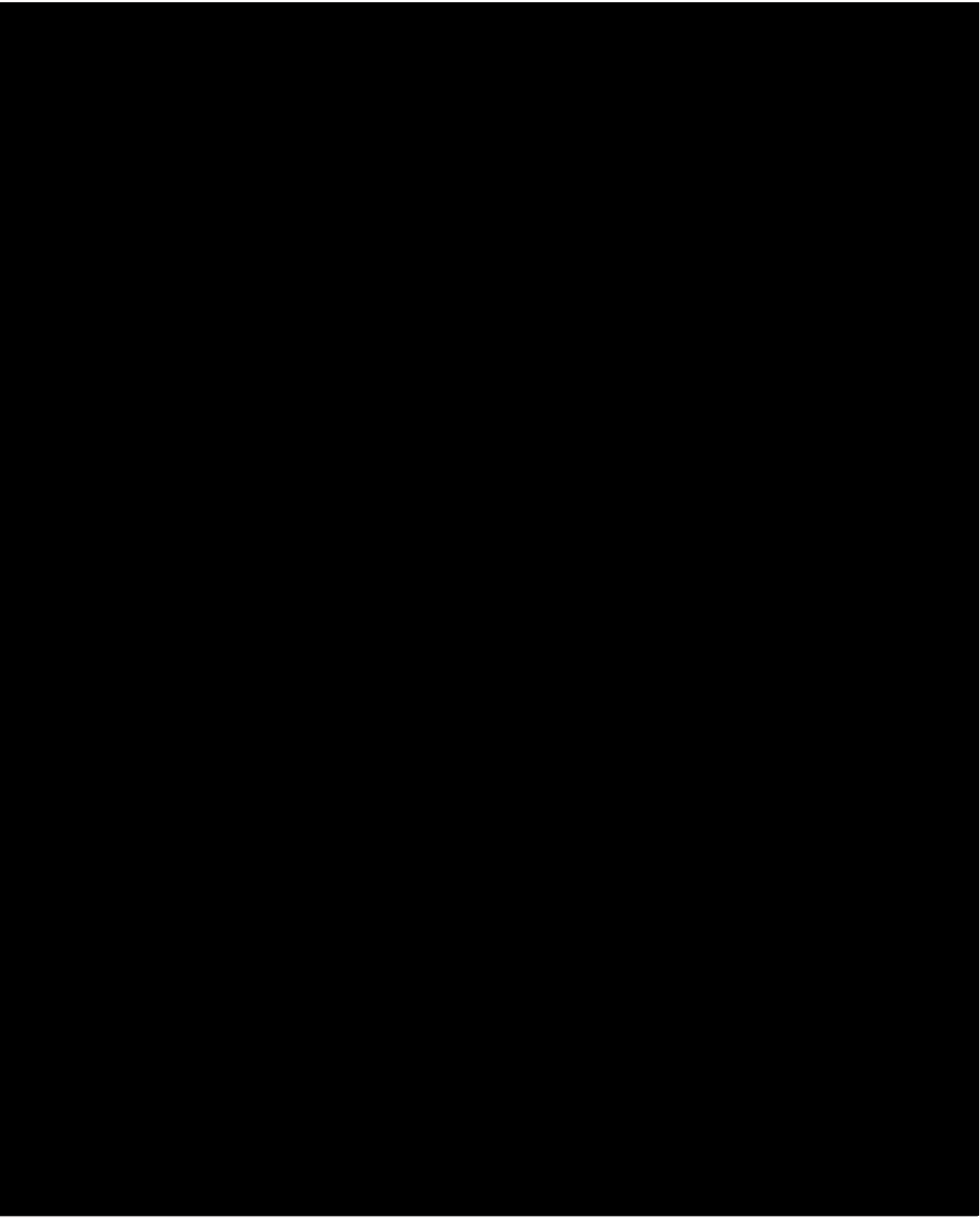
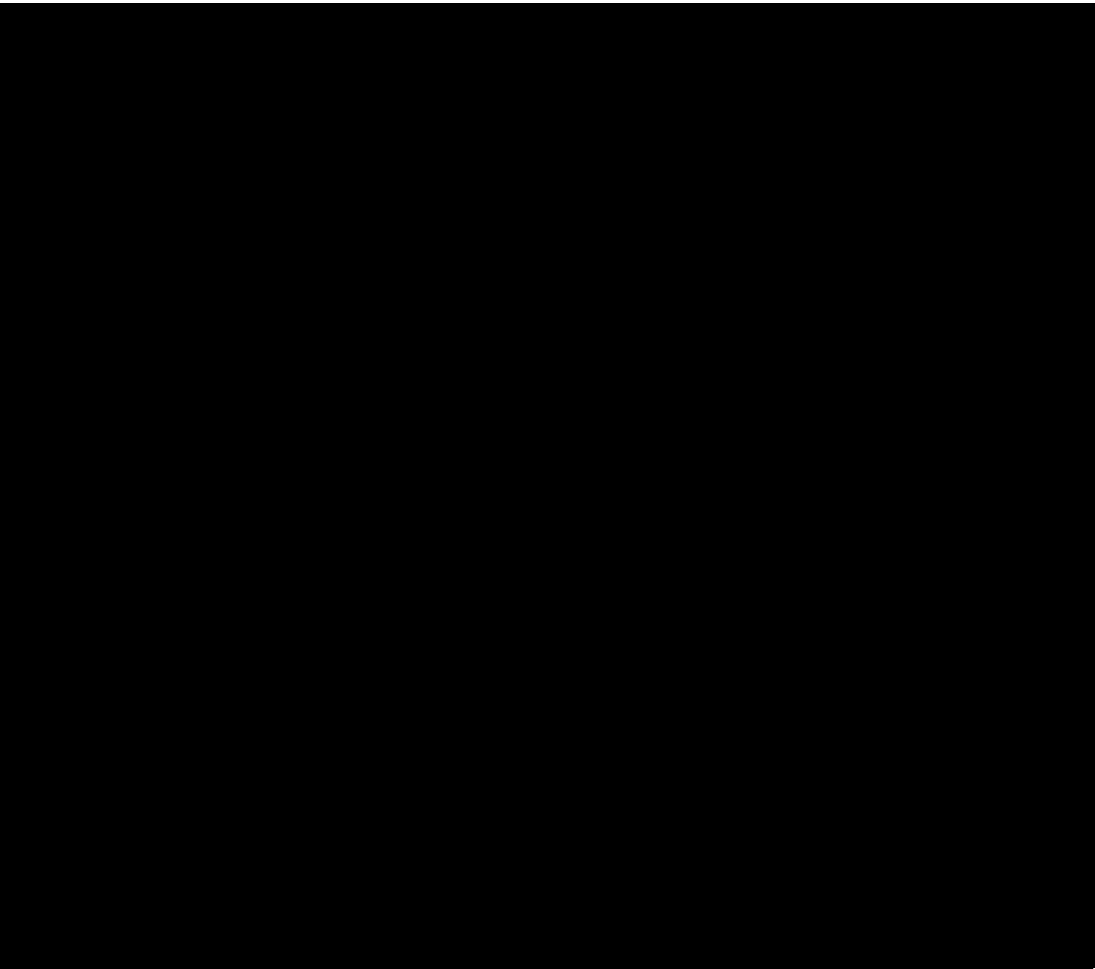


Figure 2.6

Brass block used for mounting crept specimens on the x-ray back-reflection apparatus.

Figure 2.7

Specimen type used for compression testing.

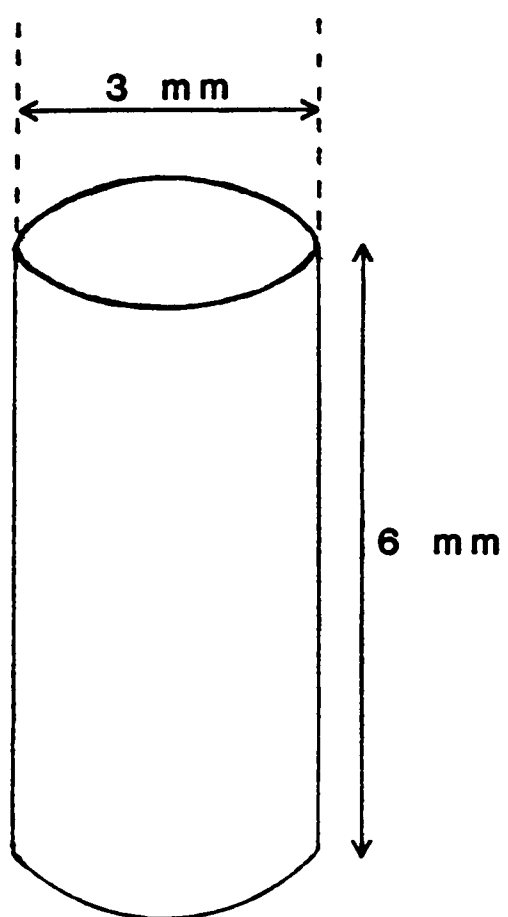
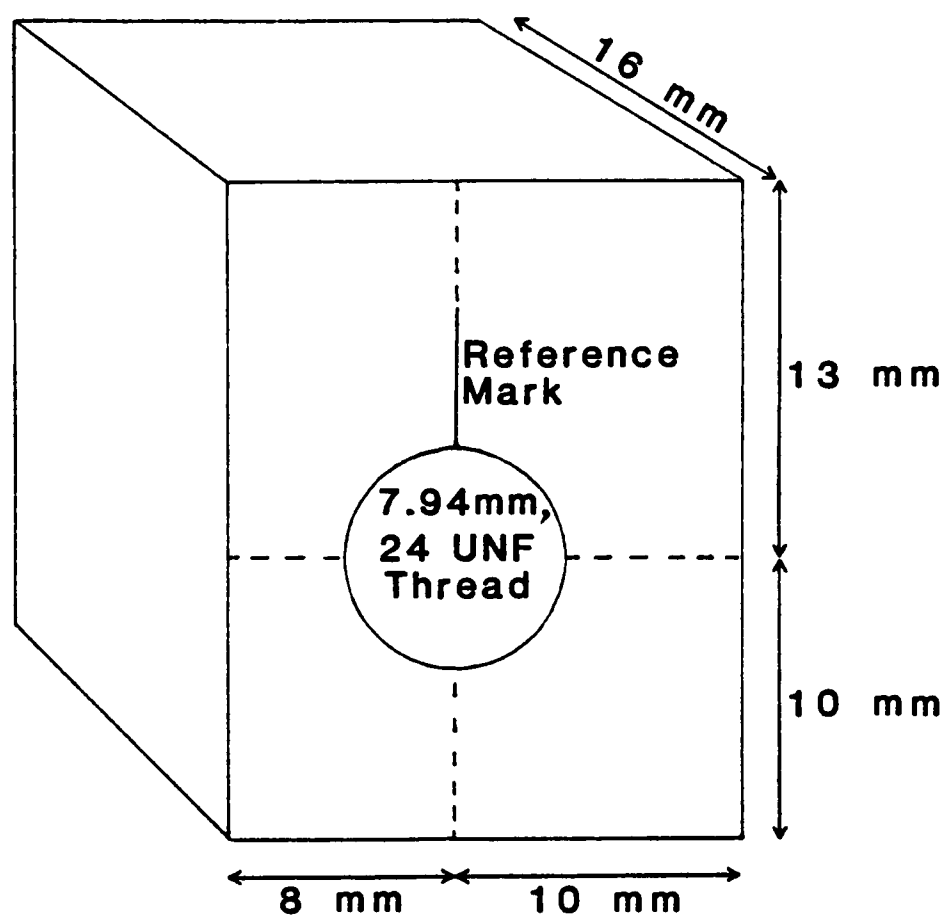


Figure 2.8

Elevated temperature compression testing apparatus.

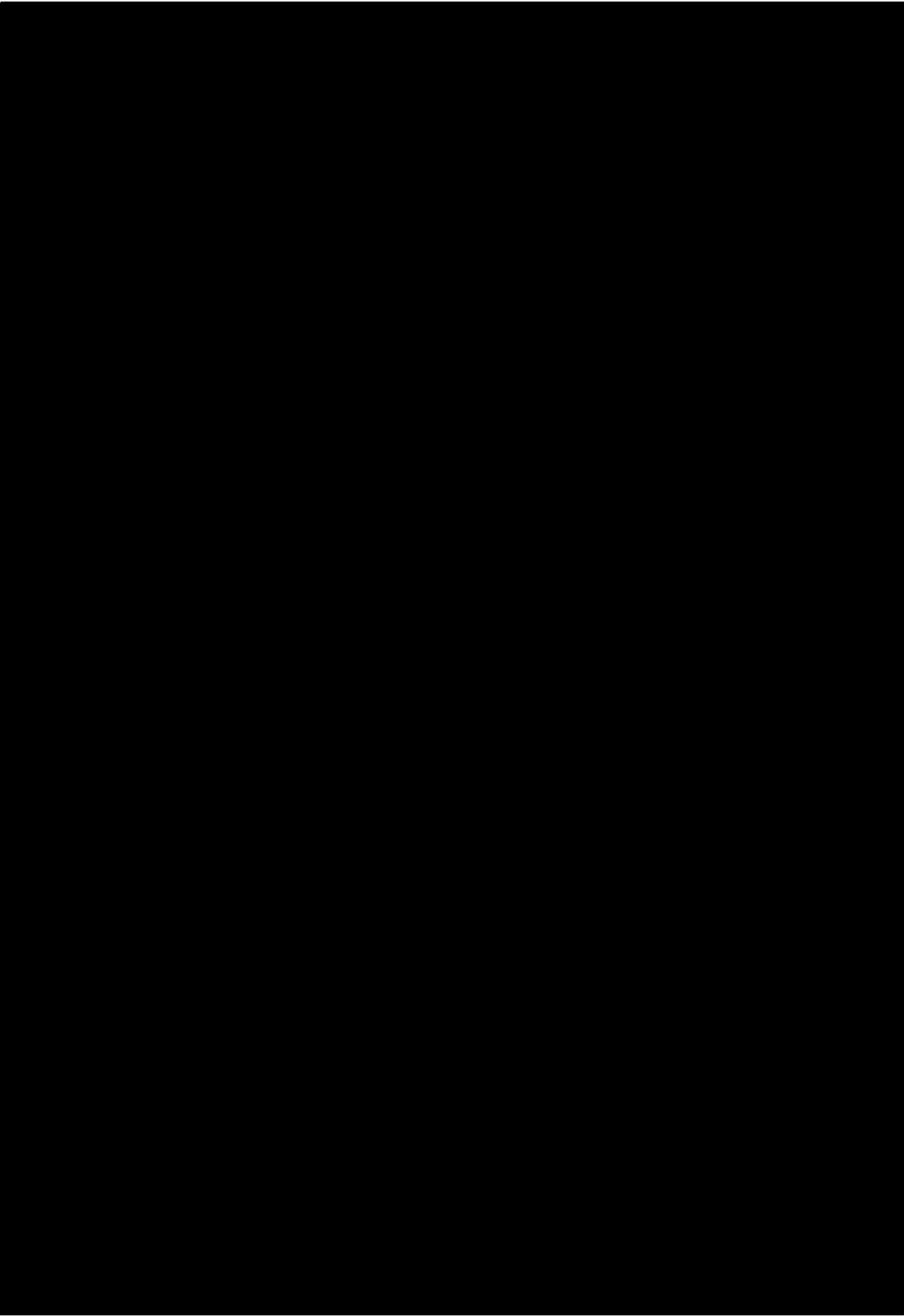


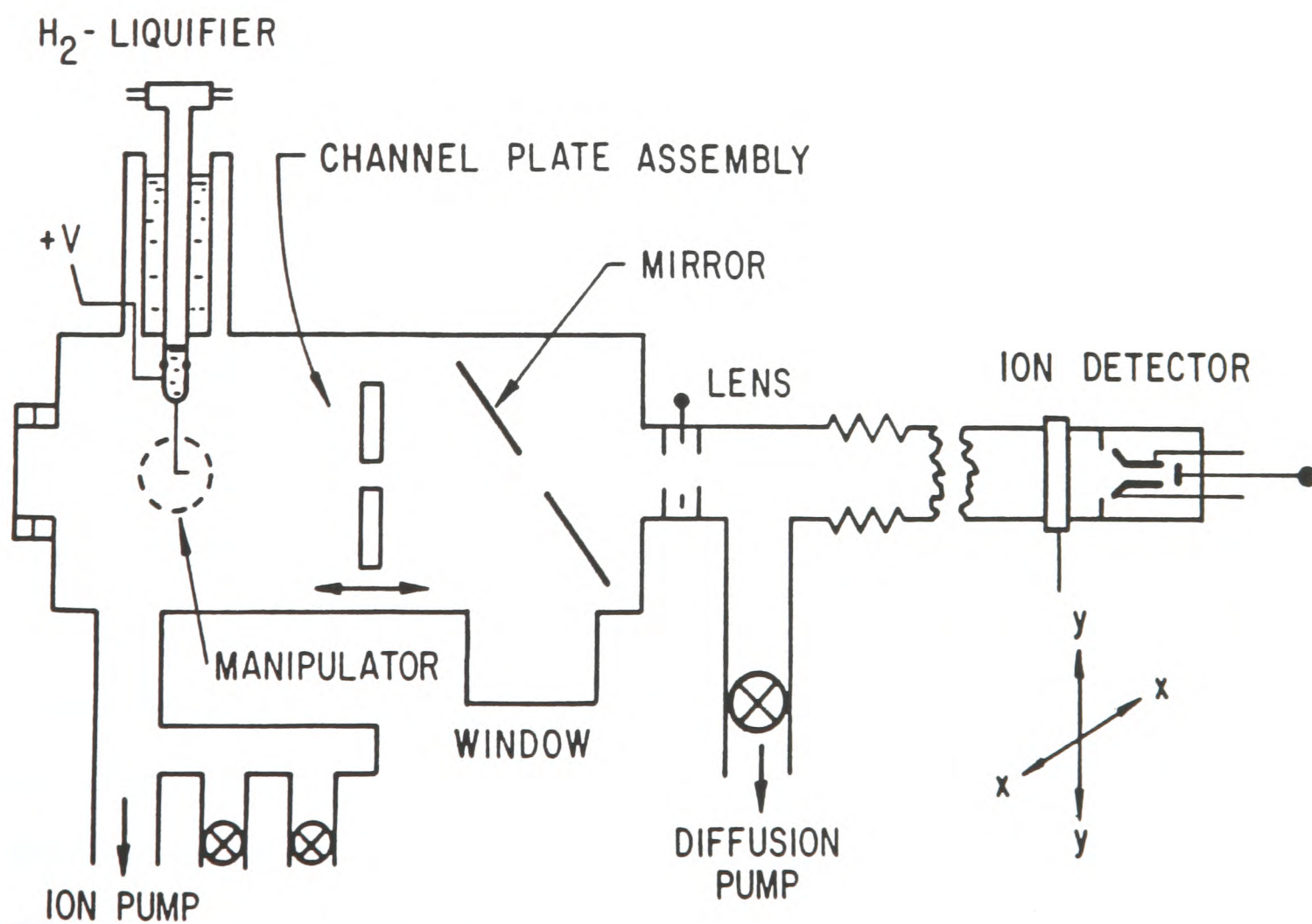
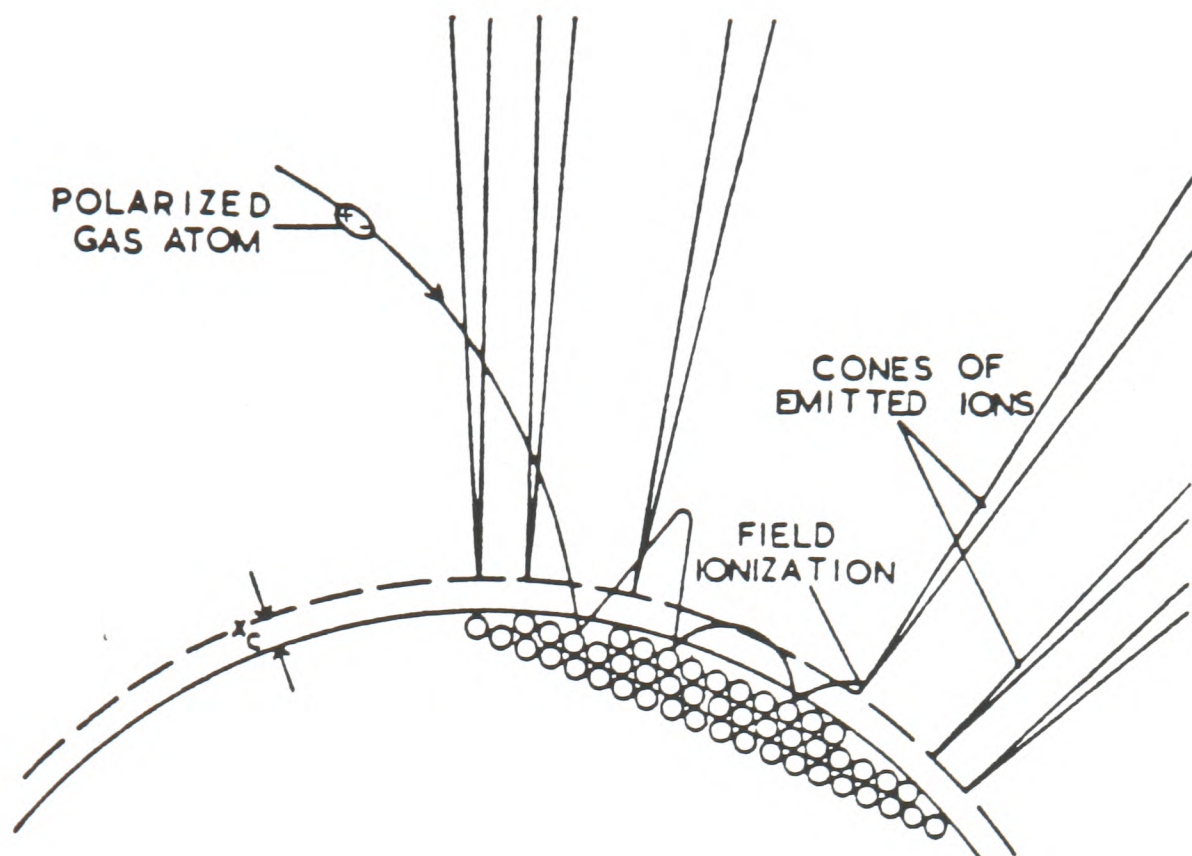
Figure 2.9

The image formation process in the field-ion microscope. Ionisation of the image gas occurs above the high field regions of the specimen tip.

(After Bowkett and Smith, 1970.)

Figure 2.10

Schematic representation of the time of flight atom probe.



ATOM PROBE

CHAPTER 3

EFFECTS OF HEAT-TREATMENT ON MICROSTRUCTURE: RESULTS AND DISCUSSION

3.1 Solution Heat-Treatments

Figure 3.1(a) shows an optical micrograph of SRR99 in the as-cast condition, sectioned in a plane perpendicular to the crystal growth direction. The as-cast material has a highly segregated dendritic structure, in common with other single crystal superalloys produced by a directional solidification technique, such as the CMSX range of superalloys (Harris et al., 1982; 1983). Tien and Gamble(1971) observed that the formation of such structures occurs when the ratio of alloy melting temperature range to liquid diffusion coefficient exceeds the ratio of thermal gradient to solidification rate.

The brightly imaging areas of figure 3.1(a) between the dendrites consist of eutectic γ' and γ . Figure 3.1(b) shows an SEM image of a eutectic region, where the presence of the two phases can be seen. Electron probe microanalysis revealed that the dispersed phase within the eutectic was rich in chromium but depleted in aluminium and titanium with respect to the rest of the eutectic. Since aluminium and titanium preferentially segregate to the γ' phase whilst chromium segregates to the γ phase, it was concluded that the eutectic consists primarily of γ' containing small inclusions of γ . By taking an electron probe scan across a region of eutectic, a map representing the intensity of the chromium K_{α} x-ray peak was built up and is shown in figure 3.1(c). The density of the dots characterises the concentration of chromium. It can be seen from figure 3.1(c) that the eutectic is depleted in chromium in comparison with the surrounding region, indicating that the eutectic consists predominantly of the γ' phase.

Typical γ' precipitate distributions close to the eutectic and within the dendrites are shown in figures 3.1(e) and 3.1(f) respectively. Close to the eutectic the precipitates have a ragged and irregular morphology, whereas the structure within the dendrites is more regular and the precipitates tend to occur as octahedrally diced cubes. Similar morphological inhomogeneities have been observed by Pearcey et al. (1967) and by Tien and Gamble (1971) in directionally solidified Mar-M200.

SRR99 was derived from SRR9, an alloy containing slightly lower concentrations of titanium and tantalum. Attwood (1981) has shown that in SRR9 a solution heat-treatment of 4 hours at 1300 °C fully dissolves the γ' and the γ/γ' eutectic whilst keeping chemical segregation to an acceptably low level and avoiding the occurrence of incipient melting. In the present studies the effects on the structure of as-cast SRR99 brought about by heat-treating for 4 hours at 1250 °C, 1280 °C and 1300 °C were investigated and are shown in the optical micrographs presented in figure 3.2. As the heat-treatment temperature is raised, the structure becomes increasingly homogeneous. After a treatment of 4 hours at 1300 °C complete dissolution of the structure, including the γ/γ' eutectic has taken place. The faint contrast across the dendrites is indicative of slight residual chemical segregation and the dark spots represent pores in the material. A solution heat-treatment of 4 hours at 1300 °C was employed throughout the remainder of the present studies in order to homogenise the microstructure.

3.2 Precipitate Morphology

The microstructure of SRR99 was investigated after applying a solution heat-treatment, followed by ageing at either 1200 °C, 1100 °C, 1000 °C, 900 °C or 800 °C, and then finally water quenching. Sections

were taken normal to the [001] crystal growth direction and examined by SEM. Figures 3.3-3.7 show the microstructures after ageing for increasing lengths of time at each temperature. The microstructure of an unaged specimen is also shown, this specimen having been solution heat-treated and then directly water-quenched. Even in such specimens, where the γ' phase has precipitated out of solid solution with a mean size of approximately 0.1 μm , some tendency for the precipitates to adopt a cuboidal rather than spherical morphology can be seen. Upon ageing at 1100 °C or 1000 °C the precipitates grow and in so doing become cuboidal and aligned with each other, as shown in figures 3.4 and 3.5. Some crystals were examined by TEM and the precipitates imaged using a centred aperture selected area dark field technique with an excited superlattice reflection. Together with a knowledge of the diffraction conditions, this showed that the sides of the cuboidal precipitates lay on {100} crystallographic planes. Typical TEM images obtained by this technique, which brings the precipitates into strong contrast, are shown in figure 3.8.

The formation of aligned cuboidal precipitates having sides parallel to {100} planes has been observed in other superalloy systems by, for instance, Ardell and Nicholson (1966a, b) and Davies et al. (1980a). This morphology can be explained by the arguments outlined in section 1.2.2, namely that the precipitates nucleate as spheres since the energy reduction brought about by minimising their surface area per unit volume exceeds the decrease in strain energy caused by alignment with {100} planes, and that while growing they become cuboidal as this balance is reversed. If the alignment of the cuboidal precipitates with each other is assumed to result from elastic interactions between precipitates, as suggested by Ardell and Nicholson (1966a), then it may be expected that such interactions would be particularly strong in

alloys containing high volume fractions of γ' , such as SRR99. The occasional occurrence of elongated and L-shaped precipitates which can be seen in figures 3.4, 3.5 and 3.8 is indicative of precipitate coalescence taking place. Such an effect has previously been reported by Davies et al. (1980a,b).

The microstructures that are produced by ageing at 900 °C are shown in figure 3.6. Comparison with figures 3.4 and 3.5 shows that the microstructures have a very different appearance from those produced by ageing at 1100 °C or 1000 °C. Precipitates of a comparable size do not have the characteristic cuboidal morphology of those formed at the higher temperatures. Instead the precipitates are irregularly shaped and their surfaces tend to be rounded. This can clearly be seen in the higher magnification image shown in figure 3.9.

Although there still appears to be some tendency for alignment of the interfaces with $\{100\}$ planes, the effect is much less pronounced after ageing at 900 °C than in material aged at 1100 °C or 1000 °C. Thus the minimisation of coherency strain energy by alignment with $\{100\}$ planes no longer predominates over the minimisation of surface area per unit volume of precipitate. Such a change can be brought about by a loss of coherency between the precipitates and the matrix. Interfacial dislocations reduce the long-range elastic strain fields around the precipitates and increase the interfacial energy. Alternatively the magnitude of the γ/γ' mismatch may be lower at 900 °C than at 1100 °C, presumably due to the two phases having different temperature coefficients of expansion. The latter explanation appears the most likely for the currently observed changes in morphology, since these were observed in precipitates of similar size. Loss of coherency would only be expected in large precipitates.

The irregular shapes of the precipitates formed at 900 °C appear

to have arisen largely through coalescence. Courtney (1977a) has distinguished between two types of morphology, referred to as isolated and skeletal. Skeletal or connected structures, similar to those formed at 900 °C, were considered to form by coalescence when the time required to fuse the particles into one was greater than the time between contacts. When this balance was reversed, the formation of a structure consisting of isolated particles was predicted.

Investigations were also undertaken into the effects of ageing at 800 °C and 1200 °C. The microstructure of SRR99 after ageing at 800 °C is shown in figure 3.7. No significant changes from the unaged material can be observed except in the specimen which received a long-term age for 1180 hours. In this case irregular rounded precipitates were produced, similar to those formed at 900 °C.

The effect of ageing at 1200 °C is shown in figure 3.3. After ageing for 3 hours the precipitate morphology has become irregular and plate-like structures, or rafts, of γ' have formed. There is also a large volume fraction of fine precipitates lying between the primary precipitates. It is thought that this is a result of large quantities of γ' -forming elements remaining in solid solution at 1200 °C and being precipitated as a fine dispersion of γ' upon quenching. The formation of a rafted γ' structure has been observed after ageing SRR99 at 1150 °C (Roome, 1982), and after long-term ageing at 800 °C of a Ni-Co-Al alloy (Davies et al., 1980a). In the present study, rafts were also found to be appearing after ageing for 72 hours at 1100 °C. Roome (1982) has suggested that the onset of rafting is associated with a loss of coherency between precipitates and the matrix. This view would explain the tendency for the primary distribution of precipitates to spheroidise, since the misfit displacement between the matrix and precipitates would be accommodated by interfacial dislocations.

However, it is likely that the rafts are partially coherent, since they show a tendency for alignment parallel to $\{100\}$ planes. Tensile stress annealing (see, for example, Tien and Copley, 1971a,b; Tien and Gamble, 1972; Pineau, 1976) and high temperature creep testing (see, for example, Caron and Khan, 1983; Pearson et al., 1981) have been found to promote the formation of rafts along planes perpendicular to the $\langle 100 \rangle$ stress axis. In this case the coherency strain energy associated with precipitate/matrix interfaces lying parallel to the stress axis is increased, thus favouring growth in perpendicular directions.

3.3 Precipitate Size Distributions

Precipitate size measurements were made from the microstructures produced by ageing at 1100 °C, 1000 °C, 900 °C and 800 °C. Owing to the formation of rafts and the occurrence of a secondary dispersion of precipitates after ageing at 1200 °C, no size analyses were attempted for this ageing temperature. The technique described in section 2.9 produced values for areas of precipitates on (001) sections. The linear precipitate dimension, w , was taken to be the square root of this area. In the case of a cubic precipitate, w corresponds to the side length of the cube. For spherical precipitates, assuming that the maximum cross-sectional area is taken, w is equal to $\pi^{1/2}r$ where r is the precipitate radius.

It was found that with the exception of the specimen aged for 1180 hours, precipitate coarsening at 800 °C was negligible. The size distributions obtained for ageing temperatures of 1100 °C, 1000 °C and 900 °C after increasing ageing times are shown in figures 3.10, 3.11 and 3.12 respectively. A minimum population of 100 precipitates was measured to produce each histogram. The histograms have been normalised with respect to the total population such that the total of

the frequencies for each division is equal to unity.

Assuming the experimentally determined value for the mean size, $\bar{w}$, theoretical distributions, $g(w)$, predicted by the LSW theory for precipitate coarsening were determined and are shown for comparison. These were calculated using the formula

$$g(w) = 0.02 \frac{4}{9} \frac{h(w^*)}{\bar{w}} \quad (3.1)$$

where $\bar{w}$ is the mean value of w , w^* is the reduced size, $w/\bar{w}$, and $h(w^*)$ is the LSW distribution function, defined in equation 1.2, with respect to w^* . The area between the abscissa and the function $h(w^*)$ is given by

$$\int_0^{\infty} h(w^*) dw^* = 9/4, \quad (3.2)$$

whilst the area under the experimentally determined histograms is equal to the range of each division, namely $0.02 \mu\text{m}$. Thus the factors of $4/9$ and 0.02 appearing in equation 3.1 arise in order to normalise the LSW distributions with respect to the experimental ones. Since the theoretical distributions shown were derived from equation 3.1 using experimental values of $\bar{w}$, they serve only as a comparison of the shape of the distributions, and do not represent the predictions of the LSW theory for the rate of coarsening.

After short ageing times there is good correspondence between the shapes of the experimental distributions and those predicted by the LSW theory at each temperature. After longer ageing times the experimental distributions become broader than the theoretical distributions. Whereas the LSW theory predicts a sharp cut-off at the right-hand side of the distribution function, the experimental

distributions show a diffuse right-hand edge after the longer ageing times. In particular, some precipitates have sizes greater than $1.5 \bar{w}$, which is not permitted by the LSW theory. Similar deviations have been observed by Calderon and Fine (1984), Ya-fang Han et al. (1982), Ardell (1970) and Ardell and Nicholson (1966b).

In contrast, Rastogi and Ardell (1971) found that the size distributions of γ' in Ni-Si alloys showed reasonable agreement with the LSW theory for intermediate ageing times, but not at shorter times. This effect was attributed to the need for a finite time to elapse before a steady-state distribution was attained. The authors suggested that reported variations in the upper cut-off size were related to the γ/γ' misfit parameter, $\Delta a/a$, although they did not offer an explanation as to how this might arise.

A broadening of the right-hand edge of the size distribution function has been predicted by those theories of Ostwald ripening which include modifications to take account of precipitate volume fraction (Ardell, 1972; Brailsford and Wynblatt, 1979; Tsumoraya and Miyata, 1983), as shown in figures 1.3, 1.4 and 1.5. Davies et al. (1980b) have pointed out that coalescence of precipitates would have a similar effect on the observed distributions. Their theoretical distributions, which allow for the possibility of growing precipitates meeting each other and coalescing, are shown in figure 1.6.

3.4 Coarsening Kinetics

From the experimentally determined values of the size (w) of the γ' precipitates, mean values ($\bar{w}$) were calculated for each distribution. It was found that $\bar{w}$ was independent of the field of view for a given specimen, which indicates the effectiveness of the homogenising solution heat-treatment. All of the theories for the kinetics of

precipitate coarsening presented in section 1.2 predict that $\bar{w}$ should change with time (t) whilst ageing according to

$$\bar{w}^n - \bar{w}_0^n = K_n t. \quad (3.3)$$

In order to determine the best-fitting values of the constants, n and K_n , a least squares technique was employed. Since the values of t considered increased non-linearly, it was inappropriate to apply such a technique directly to equation 3.3 as this would result in an unbalanced statistical weighting of the experimental points. To overcome this problem, a logarithmic form of equation 3.3 was taken, such that

$$\log_{10}(\bar{w}^n - \bar{w}_0^n) = \log_{10} K_n + \log_{10} t. \quad (3.4)$$

The values of $\log_{10} t$ were approximately evenly spaced. Values of n and K_n were then calculated using an iterative computer procedure such that the function

$$\sum_{i=1}^q [\log_{10}(\bar{w}_i^n - \bar{w}_0^n) - \log_{10} K_n - \log_{10} t_i]^2 \quad (3.5)$$

was minimised with respect to n and K_n , where q is the number of experimental points for each temperature. A value of 0.10007 μm , which was the mean precipitate size measured from an unaged specimen, was substituted for $\bar{w}_0$. Using the values of n and K_n calculated in this manner, the variation of $(\bar{w}^n - \bar{w}_0^n)$ against time at 900 °C, 1000 °C and 1100 °C was plotted on logarithmic axes as shown in figure 3.13. Each graph takes the form of a straight line of gradient unity, in accordance with equation 3.4, and the rate constant (K_n) is given by

the intercept on the ordinate axis. The calculated values of n for each ageing temperature are indicated. The scatter of the data is greatest at 900 °C. This is thought to be due to the irregular morphology of the precipitates formed at this temperature, which caused difficulties in assigning sizes to individual precipitates.

It can be seen that the values of the exponent n are greater than 3, the value predicted by the LSW model for lattice diffusion-controlled Ostwald ripening. Furthermore the value of n tends to increase as the ageing temperature is lowered. In figures 3.14-3.16 the data are re-plotted on similar axes but with the exponent n set to 3. For clarity the data for each temperature are plotted separately. The broken lines indicate the best straight line fit to the data with the gradient unconstrained, whilst the solid lines indicate the best fit when the gradient is constrained to equal unity, yielding a different rate constant, K_3 , where

$$\bar{w}^3 - \bar{w}_0^3 = K_3 t. \quad (3.6)$$

It can be seen that at 1100 °C and at 1000 °C the data fall on a line whose gradient is less than unity. This confirms that there is a slight deviation from a power law with $n=3$ and that this deviation lies outside of the experimentally determined errors in $\bar{w}$ and $\bar{w}_0$. Although the calculated value of n was highest at 900 °C, the scatter of the data was considerably greater than at 1100 °C or 1000 °C and so the apparent deviation from $n=3$ must be treated with caution in this case. The error bars shown in figures 3.13-3.16 were derived by combination of the errors in $\bar{w}$ and $\bar{w}_0$, each of which was calculated as $\sigma_{sd}/N_p^{1/2}$ where σ_{sd} is the standard deviation of measured sizes in a population of N_p precipitates. By plotting figures 3.14-3.16 with different

values substituted for $\bar{w}_0$, the observed trends were unchanged. This indicates that the deviation from $n=3$ cannot be explained in terms of unforeseen errors in the measured value of $\bar{w}_0$.

In most of the previous studies of precipitate coarsening, the data have been presented as plots of $\bar{w}^3$ versus time (see, for example, Chellman and Ardell, 1974; Ardell and Nicholson, 1966b; Davies et al., 1980a; Rastogi and Ardell, 1971; Ya-Fang Han et al., 1982; Calderon and Fine, 1984) or $\bar{w}$ versus $(\text{time})^{1/3}$ (see, for example, Hornbogen and Roth, 1967; Vittori, 1981; Ardell, 1970; Gröhlich et al., 1982). When plotted in this manner the data have generally fallen on a straight line, and therefore agreement with equation 3.6 has been reported. However, Perry and Smallman (1972) have pointed out that the same data can show an approximately equal fit to a straight line when plotted as $\bar{w}^2$, $\bar{w}^3$ or $\bar{w}^4$ against time. For this reason, experimental deviations in the value of the exponent n would largely have gone unnoticed. McLean (1984) has analysed some previously published coarsening data and shown that a power law with an exponent of 3 describes the data more accurately than with an exponent of 2. However, he did not consider the possibility of a higher exponent than 3.

Since equation 3.3 cannot be rearranged in such a way that substitution of experimental data gives a unique value for n , Perry and Smallman (1972) recommended that an iterative technique be used, and this approach has been adopted in the present study. It may also be significant that those authors who have chosen to plot $\bar{w}$ versus $(\text{time})^{1/3}$ have implicitly assumed that $\bar{w}_0$ can be approximated to zero, as only then can equation 3.6 be suitably rearranged. Such an approximation would be invalid in SRR99, since upon rapid quenching from 1300 °C, γ' precipitates having a mean size of approximately 0.1 μm form from the solid solution.

As shown in equations 1.6 and 1.7, exponents of 4 and 5 are predicted for the cases where diffusion along grain boundaries or sub-boundaries are the rate-controlling processes for Ostwald ripening. However, it seems unlikely that these models are applicable in the case of SRR99, which is a single crystal material having a low grown-in dislocation density. The models of Ostwald ripening which have been modified to take account of the finite volume fraction of the dispersed phase (Ardell, 1972; Brailsford and Wynblatt, 1979; Tsumuraya and Miyata, 1983) predict a similar exponential dependence of the mean particle size upon time to the original LSW theory, that is, with n equal to 3.

Equation 3.3 may be re-written as

$$(\bar{w}^n - \bar{w}_0^n)^{1/n} = (K_n t)^{1/n} \quad (3.7)$$

Thus dimensionally $\bar{w}$ scales as $t^{1/n}$. If K_n is no longer treated as a constant but is allowed to vary with time, this would have a significant effect on the apparent value of n . For instance, if K_n showed a weak time dependence such that $K_n^{1/n} \propto t^{-1/12}$, then a real value of $n=3$ would be observed as $n=4$. Thus the observed deviations from $n=3$ could be accounted for by very slight decreases in the rate constant.

There are a number of considerations which can be taken into account in treating this effect. Firstly, if the measurements of precipitate sizes from SEM images were larger than the true value by a constant amount, then this would have a greater proportional effect for smaller precipitate sizes than for larger sizes. However, this seems an unlikely explanation since, as was pointed out in section 2.9, mean size measurements taken from SEM images and from dark-field TEM images

were found to be indistinguishable.

Although several models have been considered which predict a value for n of 3, different values of the rate constant, K_3 , were predicted. The materials parameters upon which K_3 was predicted to depend are the diffusion coefficient of solute atoms in the matrix (D), the equilibrium solute concentration ($C(\infty)$), the interfacial free energy (Ψ_{int}), and in all but the original LSW theory, the volume fraction of precipitates (f). It seems unlikely that any of these parameters would decrease during coarsening at a given temperature. However, if one mechanism were to progressively displace another having a higher rate constant, then a value of n which was apparently greater than 3 could be observed. The two processes would probably have to be interdependent, otherwise the faster process would predominate.

As mentioned in section 3.2, there is evidence from examination of the micrographs that coalescence of precipitates constitutes at least part of the coarsening mechanism. This is consistent with the broadening of the size distributions compared with the theoretical LSW distributions which was observed after the longer ageing times. The standard power law with $n=3$ was produced by Davies et al. (1980b) in their treatment of Ostwald ripening where encounters and subsequent coalescence of growing precipitates were taken into account. As pointed out in section 1.2.5, Doherty (1982) disagreed with this interpretation of precipitate coalescence. In his proposed model, precipitates would move together and coalesce, but unfortunately Doherty did not offer a theoretical treatment of the kinetics of his proposed mechanism. Several authors have assessed the kinetics of sintering of particles in a liquid matrix through migration and coalescence (see, for example, Courtney, 1977a,b; Takajo et al., 1984). However, in these treatments the diffusive migration of the

particles arose from a form of Brownian motion. This approach therefore seems unrealistic when considering coherent precipitates in a solid matrix.

According to Doherty (1982), the driving force for the attraction between coherent precipitates would be the removal of the elastically strained matrix between them. Using Mott and Nabarro's (1940) formulation for the stress field around a spherical inclusion, an analysis of the kinetics of this coarsening mechanism is presented in the appendix, where it is shown that

$$\bar{w}^2 - \bar{w}_0^2 \propto t. \quad (3.8)$$

The rate limiting process in this derivation was assumed to be the diffusive migration of precipitates towards each other. As in Davies et al.'s (1980b) model, the time taken for coalescence to take place once precipitates had encountered each other was assumed to be negligibly small in comparison to the time between encounters.

Since this model predicts a value of $n=2$, the model would appear to be inconsistent with the present results. However, several simplifying assumptions have been made to render the problem more tractable. In particular, the time taken for an individual coalescence event to occur was calculated by considering the migration of two isolated particles towards each other. The strain field associated with other precipitates would tend to slow this process, since although the energy associated with the strained matrix between the migrating precipitates would be reduced by the migration process, an increase in the interacting strain fields from other neighbouring precipitates would occur. Indeed the process could only be initiated by local perturbations in the structure, such that some precipitates were not

equidistant from their neighbours. Similarly the initiation of conventional Ostwald ripening requires that precipitates of various sizes are present.

3.5 The Activation Energy for Precipitate Coarsening

Stevens and Flewitt (1979a) have considered the terms in the rate constant for Ostwald ripening (equation 1.3) to be constant with respect to temperature except for the diffusion coefficient (D), equilibrium solute concentration ($C(\infty)$) and the absolute temperature (T) itself. Since Van der Molen et al. (1971) had shown that the composition of the γ' phase does not change significantly during ageing or with temperature, and assuming a constant volume fraction of γ' , Stevens and Flewitt approximated $C(\infty)$ to a constant with respect to time and temperature. Examination of the data of Ardell and Nicholson (1966b) for $C(\infty)$ shows this approximation to be reasonable. The diffusion coefficient D has a temperature dependence given by

$$D = D_0 \exp(-Q/RT) \quad (3.9)$$

where Q is the activation energy. Therefore a plot of $\ln(K_3T)$ versus $1/T$, where K_3 is the rate constant when $n=3$, should form a straight line of slope $-Q/R$. Such a plot for the present results is shown in figure 3.17.

The activation energy derived by this method was 242 kJ mol^{-1} . This may be compared with values of 280 kJ mol^{-1} for the self-diffusion of nickel, or of 270 kJ mol^{-1} and 257 kJ mol^{-1} respectively for the diffusion of the γ' -forming elements, aluminium and titanium, in nickel (Swalin and Martin, 1956). Good agreement between the experimentally determined values and the established diffusional activation energies

has been reported in other superalloy systems by Stevens and Flewitt (1979a) and by Van der Molen et al. (1971).

An Arrhenius plot of the type shown in figure 3.17 is only valid in the case where the same mechanism is occurring at each temperature. The pronounced changes in precipitate morphology observed over the temperature range considered suggest that this may not have been the case in the present studies. This view is also supported by the observed changes in the best-fitting values for the size exponent, n . Furthermore, the data deviated from $n=3$ at each temperature considered, and yet in order to calculate K_3 , a value for n of 3 had to be assumed. In the light of these limitations, the level of agreement between the experimentally determined activation energy and the established values can be considered reasonable.

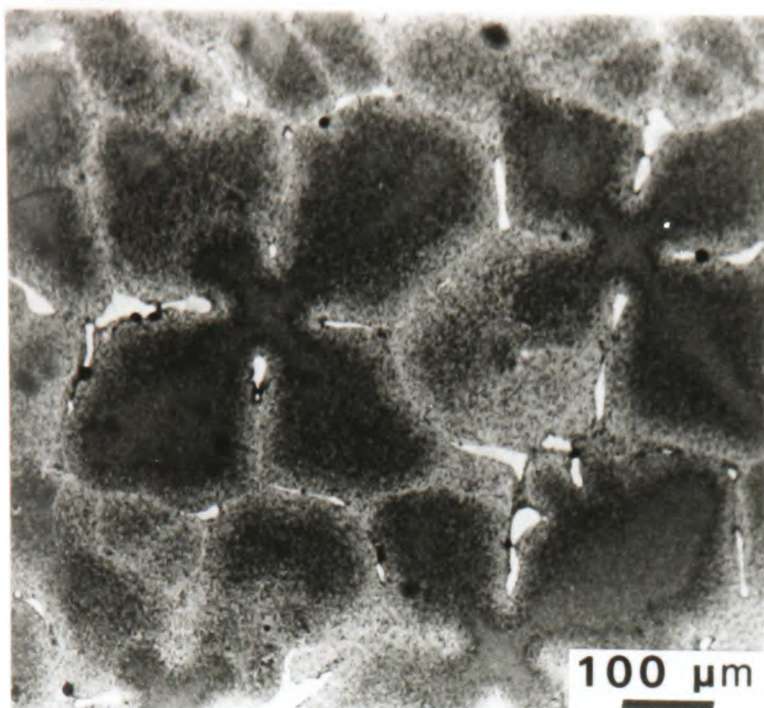
Figure 3.1

THE AS-CAST STRUCTURE OF SRR99

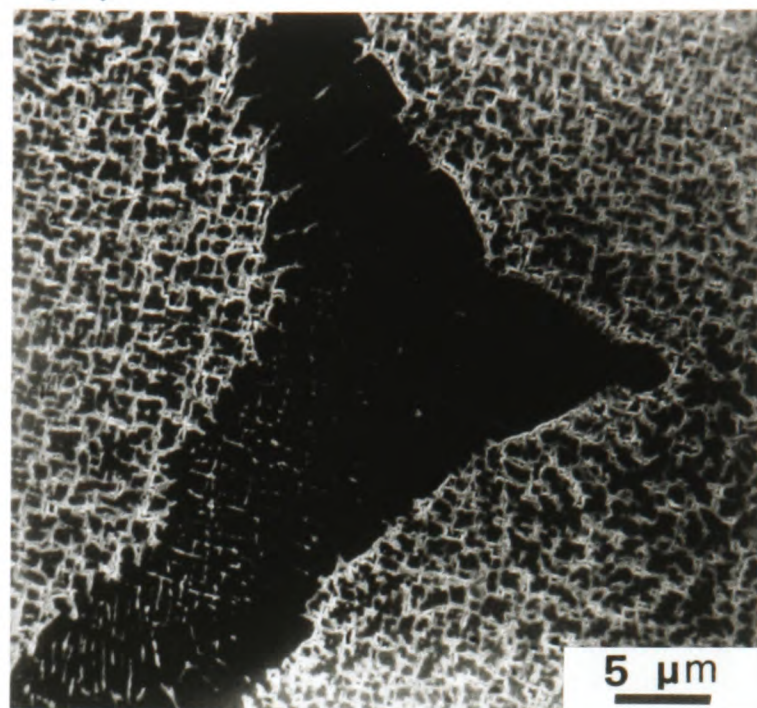
Sections taken normal to the [001] crystal growth direction

- (a) Optical micrograph.
- (b) SEM micrograph of a eutectic region.
- (c) Chromium K_{α} x-ray dot map from an electron probe scan across a eutectic region.
- (d) Schematic representation of the shape of the eutectic region in (c).
- (e) SEM micrograph showing the γ' precipitate morphology close to a eutectic region.
- (f) SEM micrograph showing the γ' precipitate morphology within the dendrites.

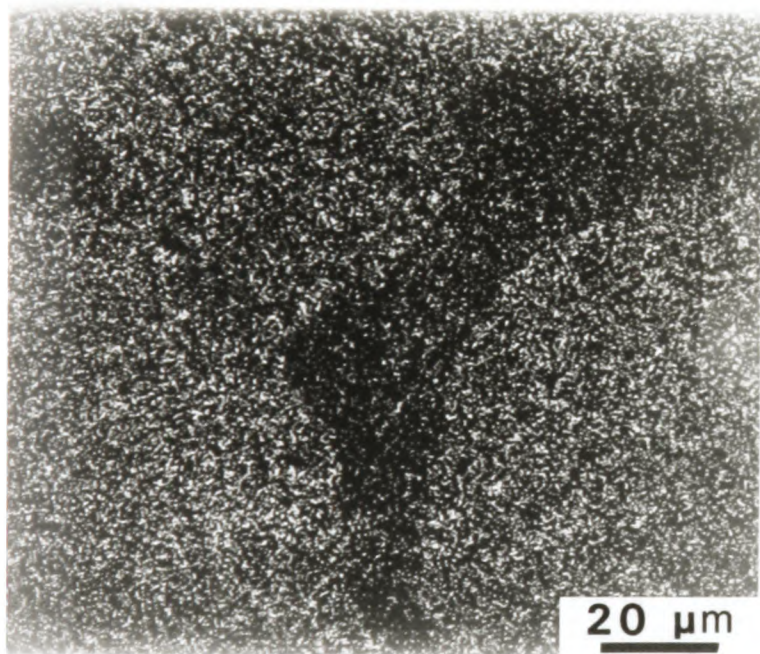
(a)



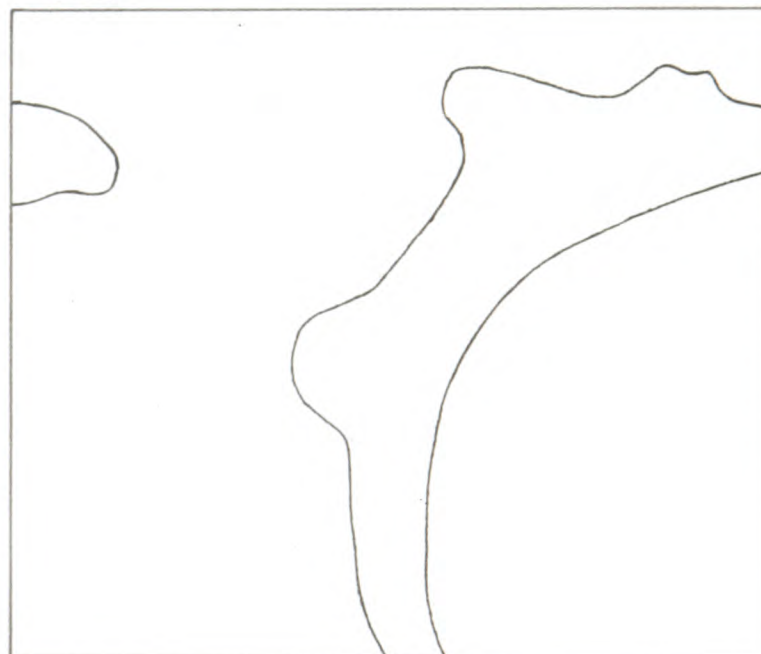
(b)



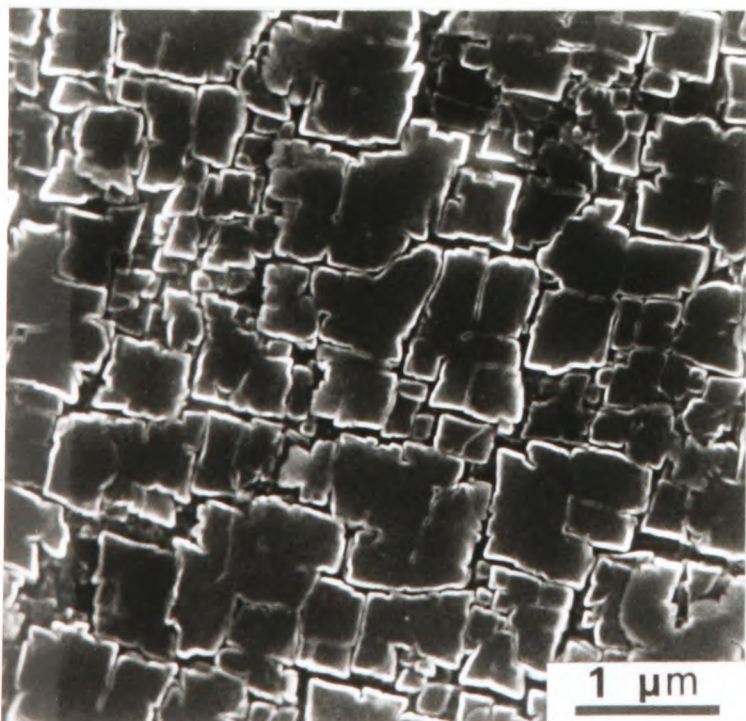
(c)



(d)



(e)



(f)

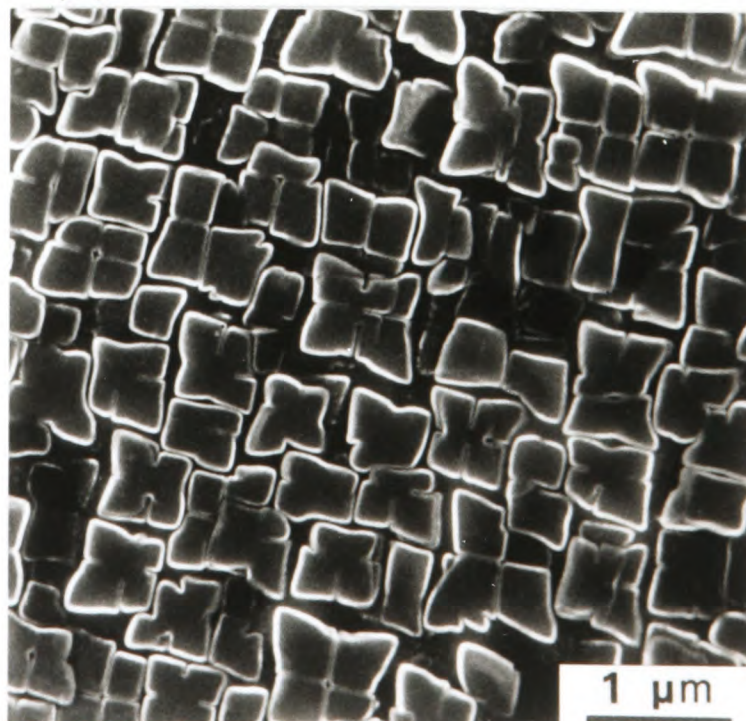


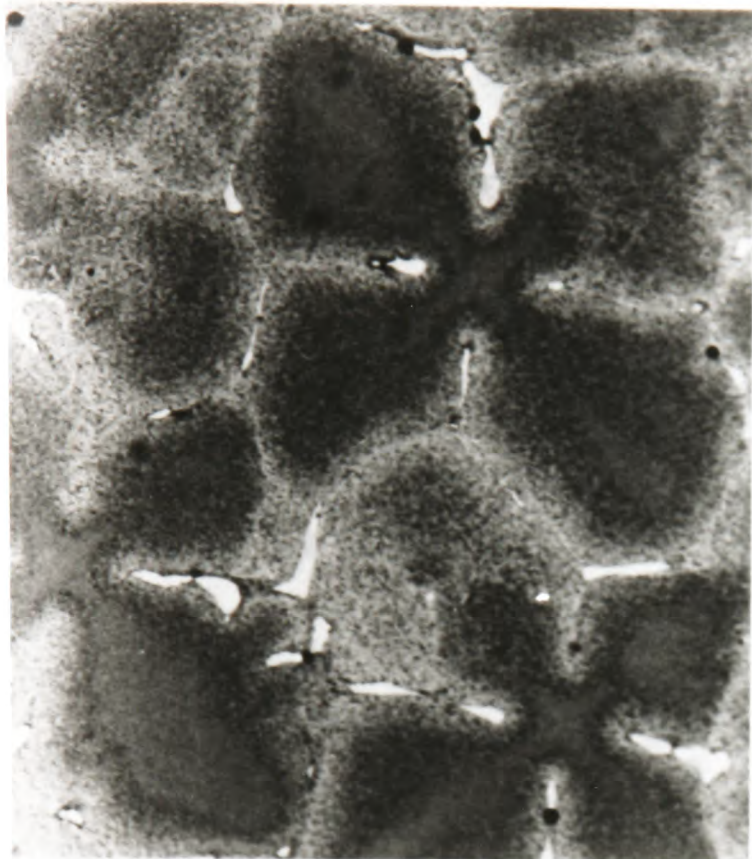
Figure 3.2

Optical micrographs showing the effects of solution heat-treatment temperature on the structure of SRR99

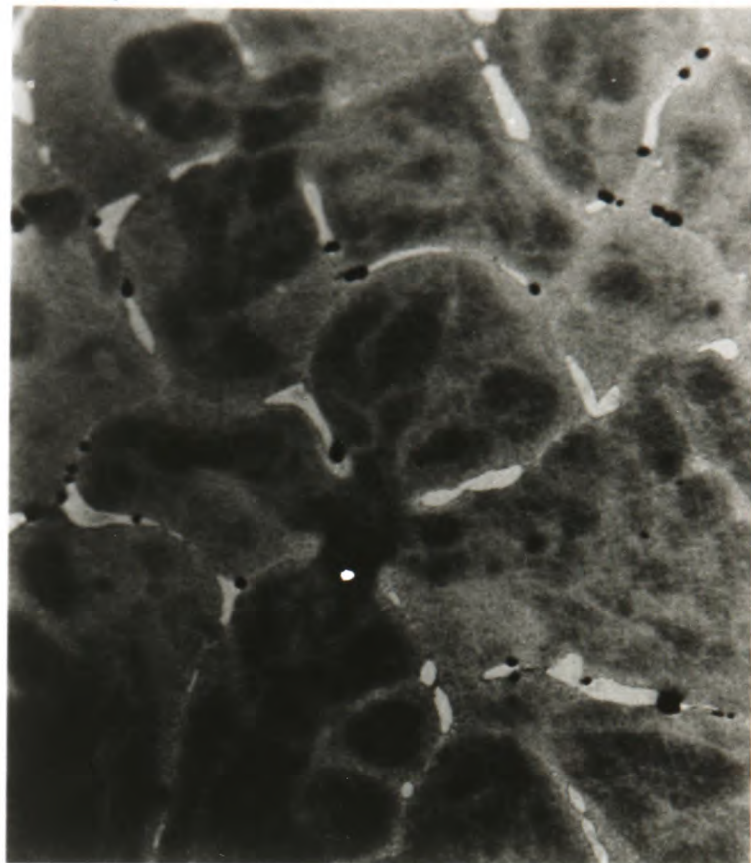
Sections taken normal to the [001] crystal growth direction.

- (a) As cast.
- (b) 4 hours at 1250 °C.
- (c) 4 hours at 1280 °C.
- (d) 4 hours at 1300 °C.

(a)



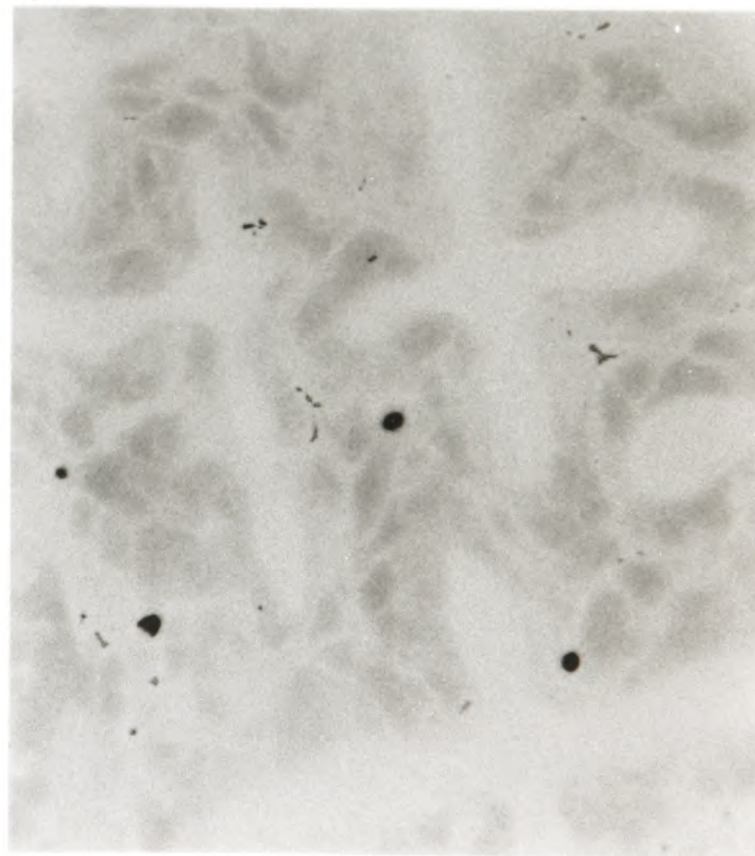
(b)



(c)



(d)

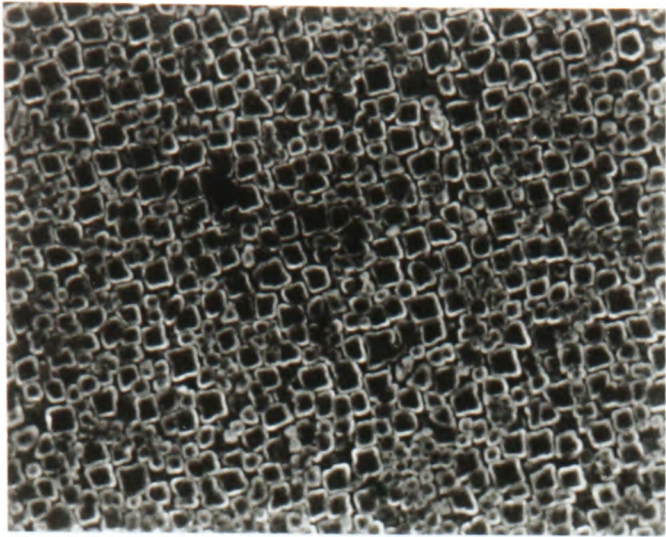


200 μm

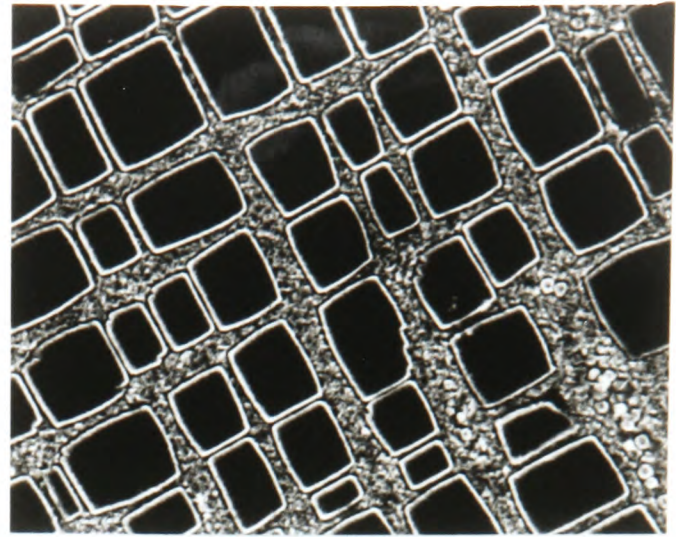
Figure 3.3

The microstructure of SRR99 after ageing at 1200 °C. Specimens were solution heat-treated for 4 hours at 1300 °C, aged for the times shown at 1200 °C and water quenched.

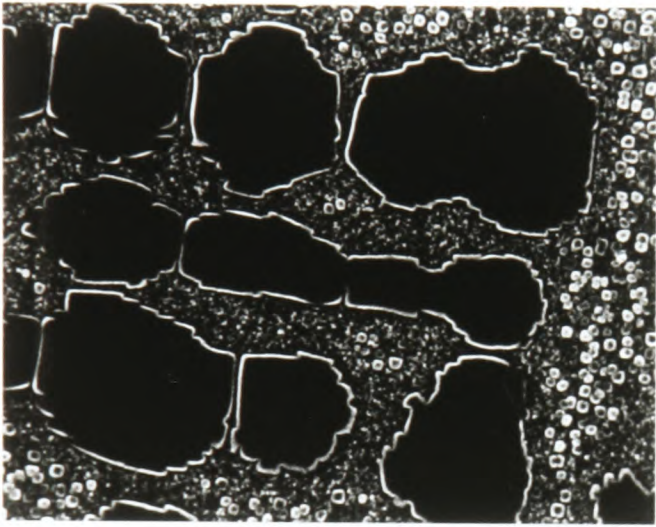
Sections taken normal to the [001] crystal growth direction. (SEM micrographs.)



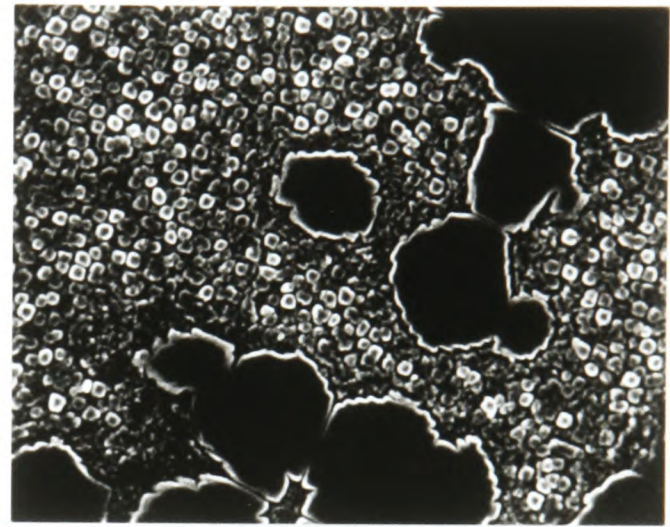
Unaged



0.167 Hours

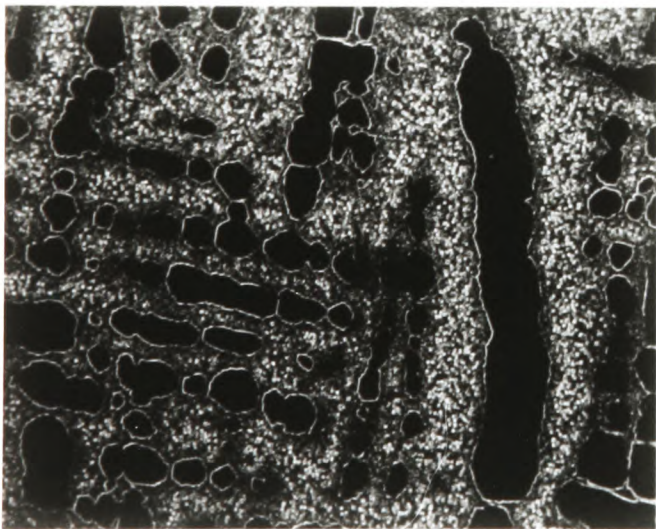


3 Hours

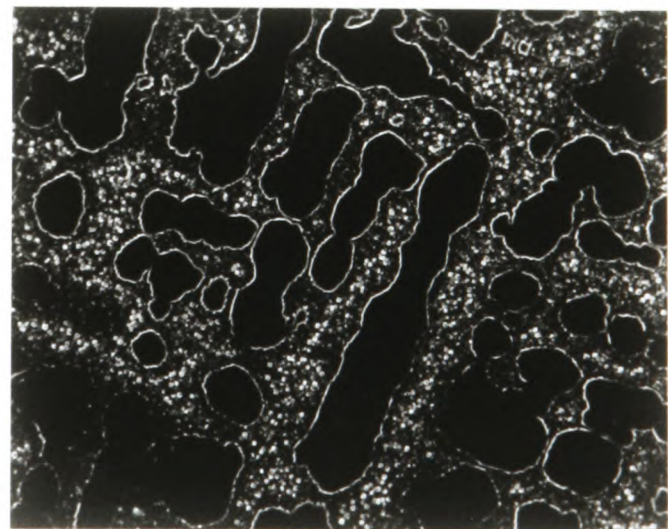


18 Hours

1 μm



3 Hours



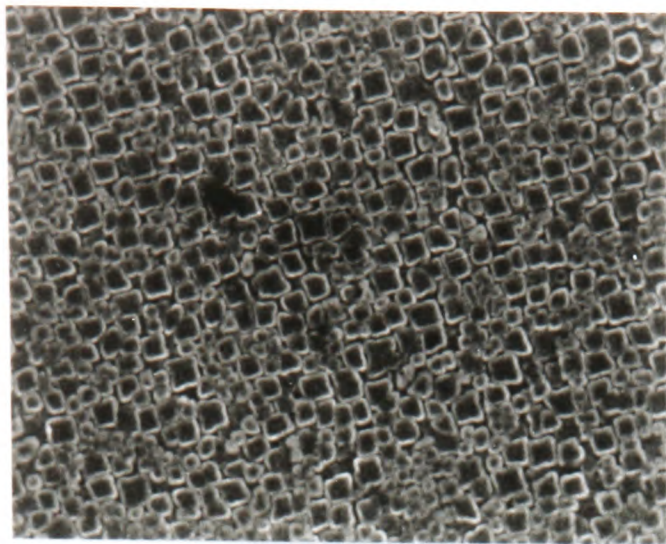
18 Hours

5 μm

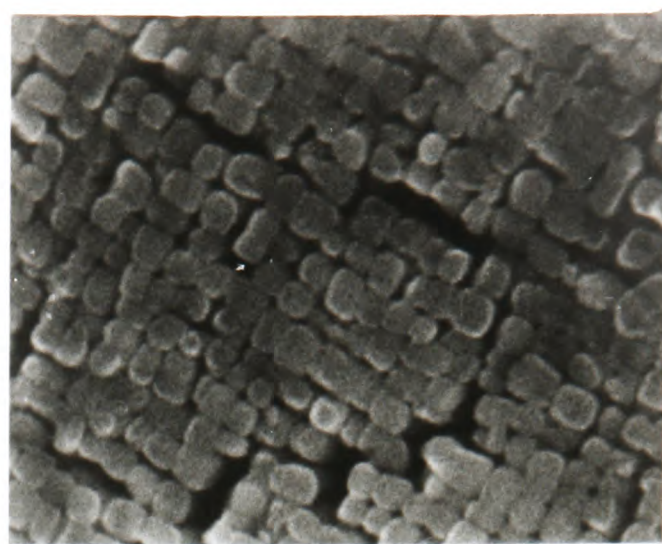
Figure 3.4

The microstructure of SRR99 after ageing at 1100 °C. Specimens were solution heat-treated for 4 hours at 1300 °C, aged for the times shown at 1100 °C and water quenched.

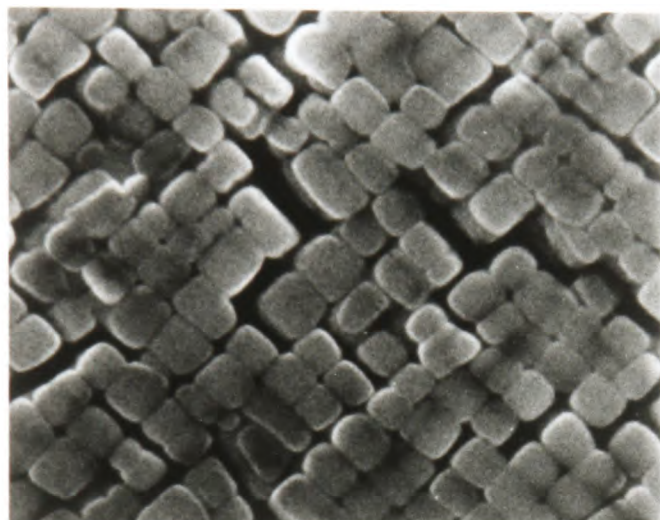
Sections taken normal to the [001] crystal growth direction. (SEM micrographs.)



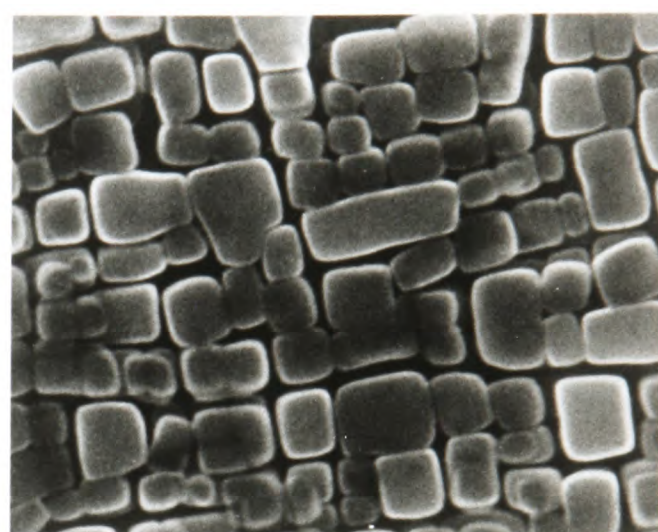
Unaged



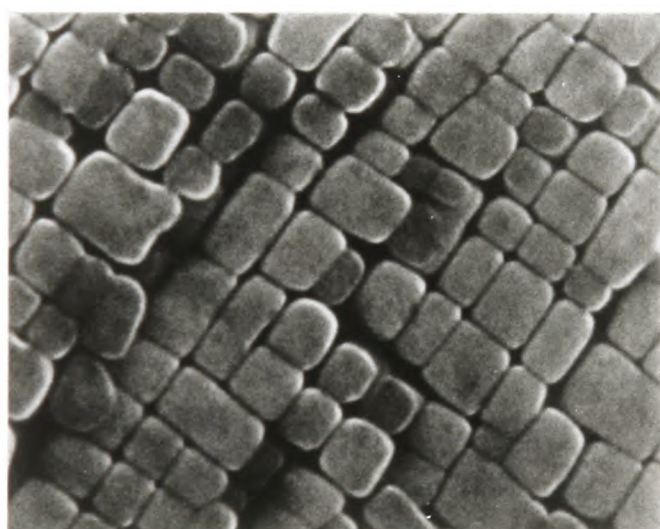
0.167 Hours



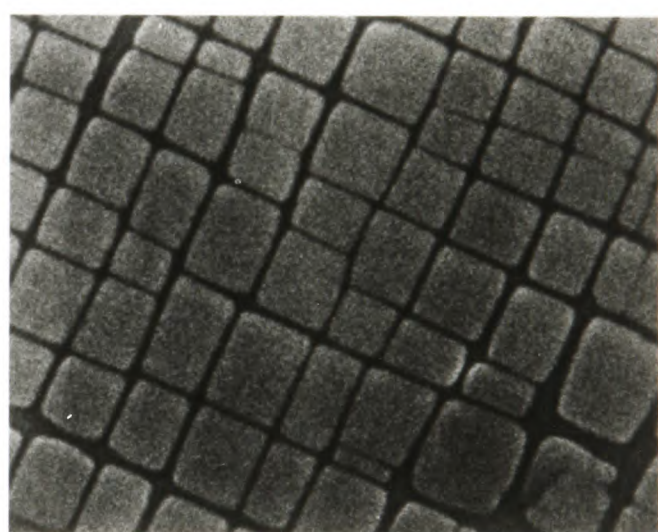
0.5 Hours



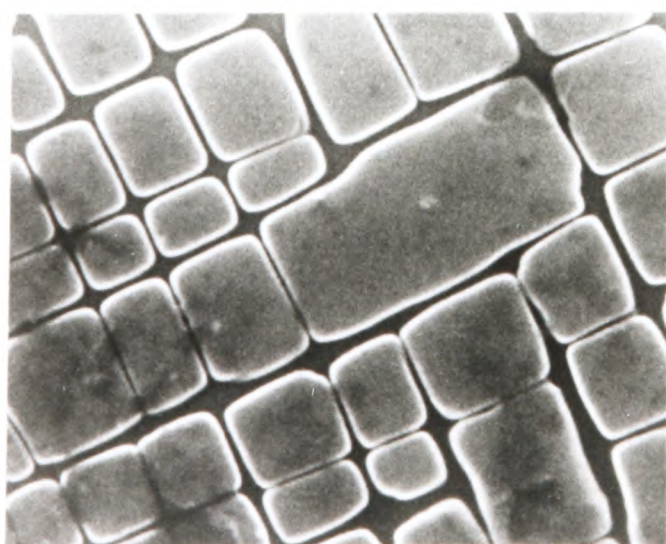
1 Hour



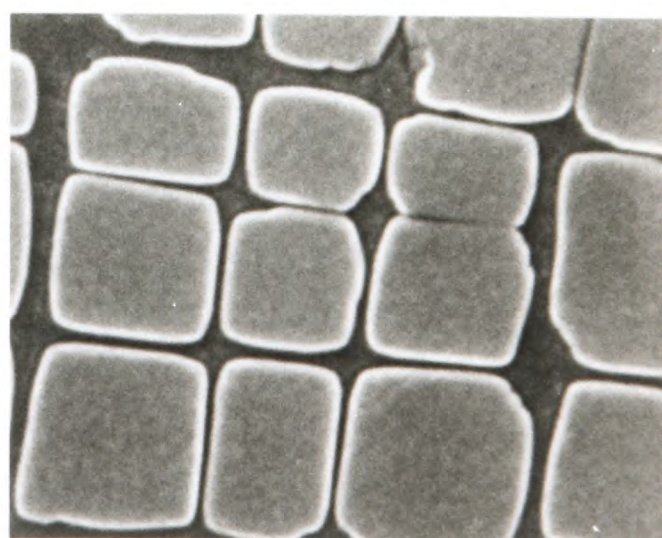
1.5 Hours



4 Hours



11 Hours



72 Hours

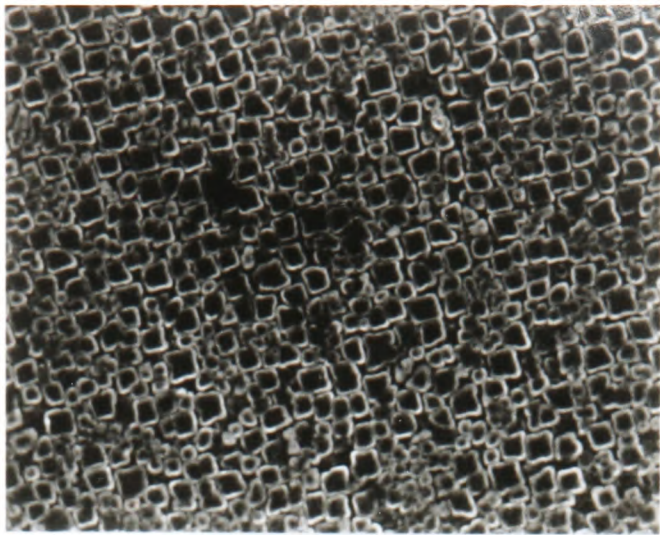
1 μm



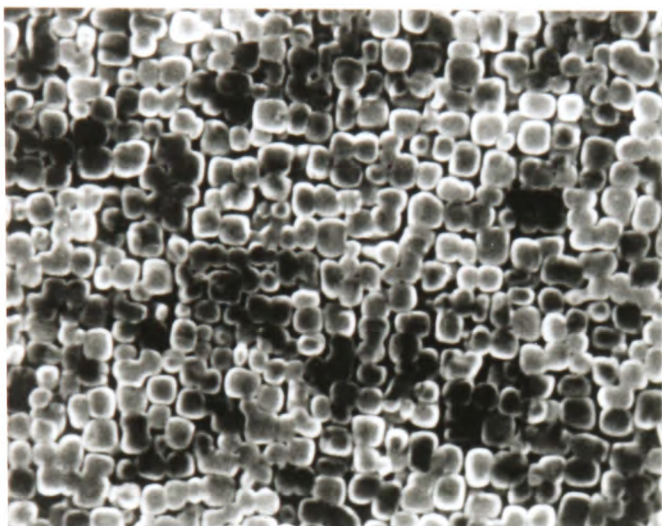
Figure 3.5

The microstructure of SRR99 after ageing at 1000 °C. Specimens were solution heat-treated for 4 hours at 1300 °C, aged for the times shown at 1000 °C and water quenched.

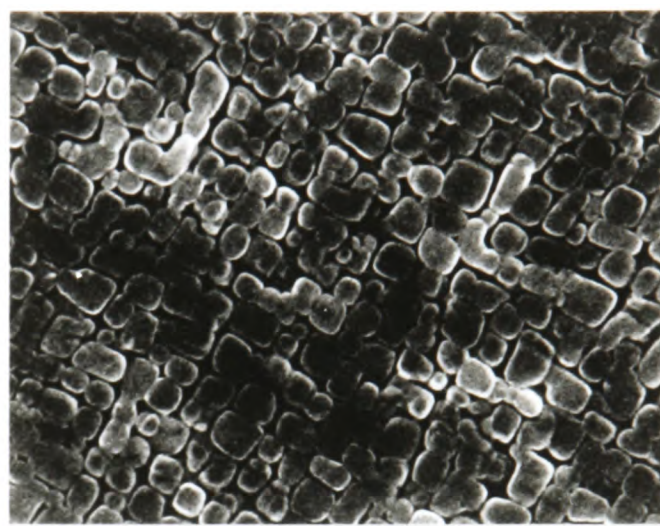
Sections taken normal to the [001] crystal growth direction. (SEM micrographs.)



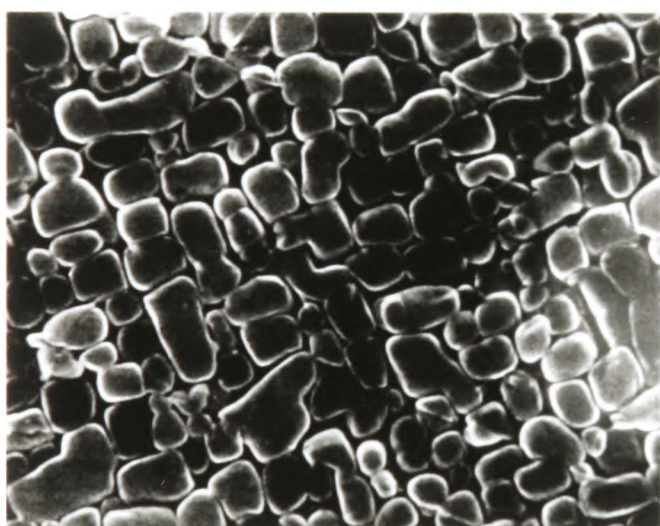
Unaged



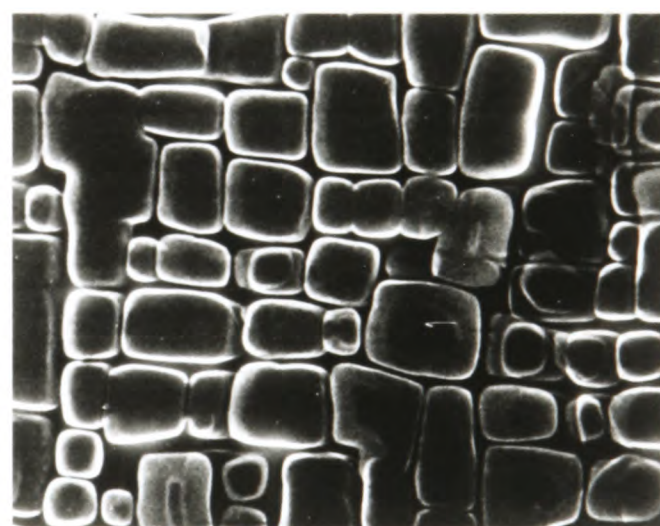
0.167 Hours



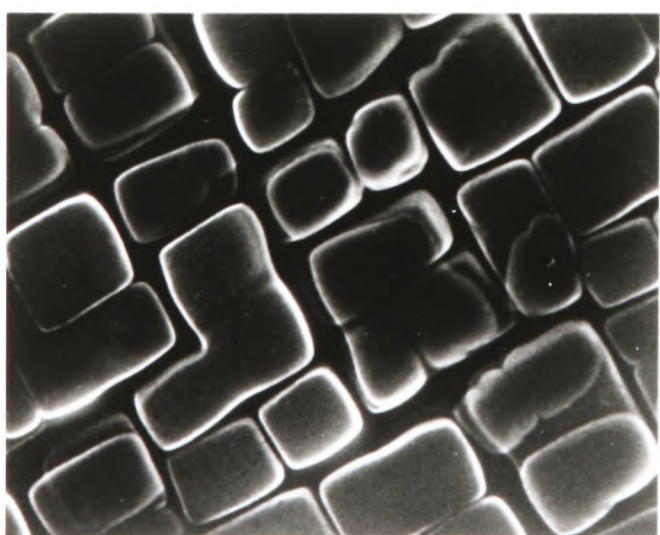
1 Hour



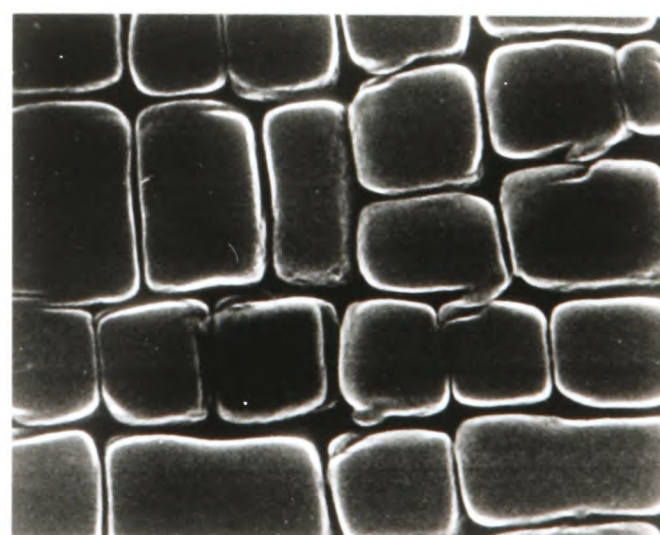
3 Hours



25 Hours



144 Hours



187 Hours

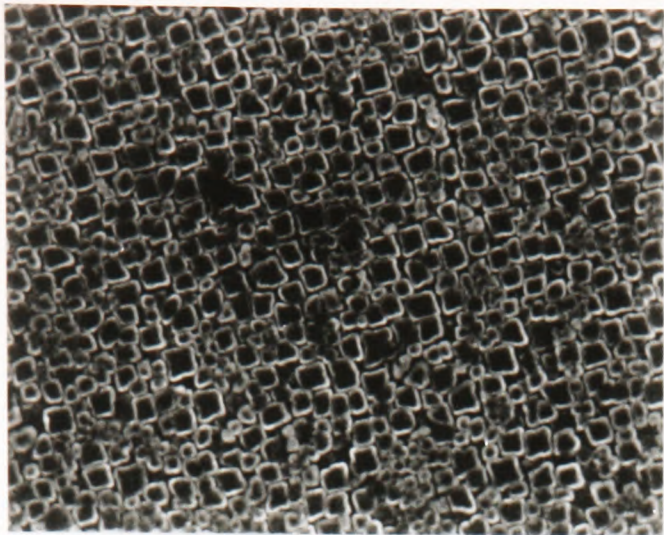
1 μm



Figure 3.6

The microstructure of SRR99 after ageing at 900 °C. Specimens were solution heat-treated for 4 hours at 1300 °C, aged for the times shown at 900 °C and water quenched.

Sections taken normal to the [001] crystal growth direction. (SEM micrographs.)



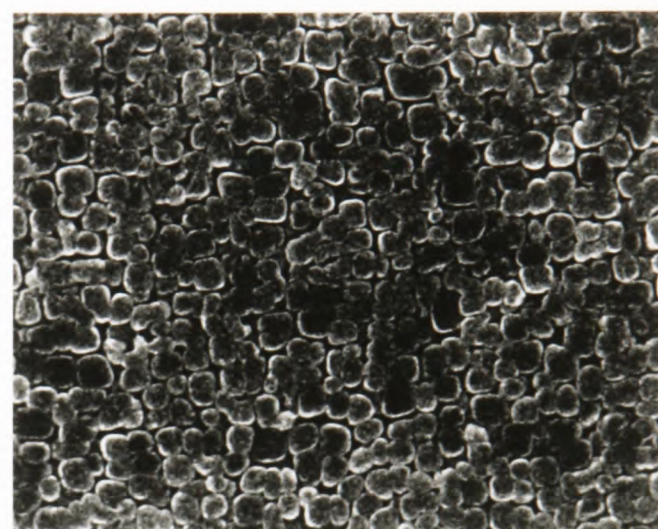
Unaged



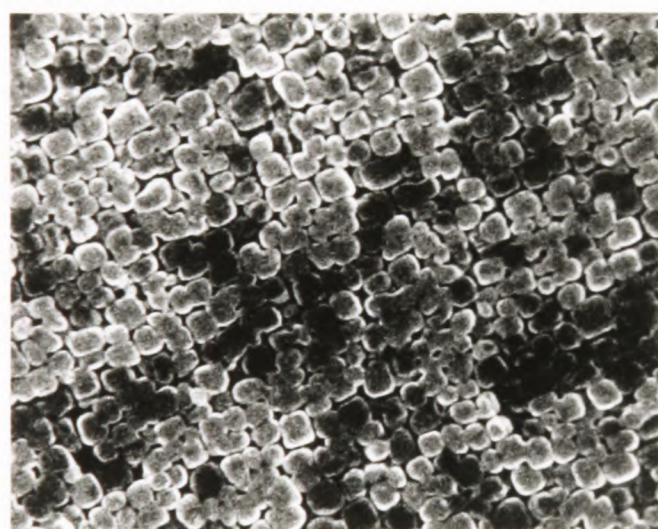
0.5 Hours



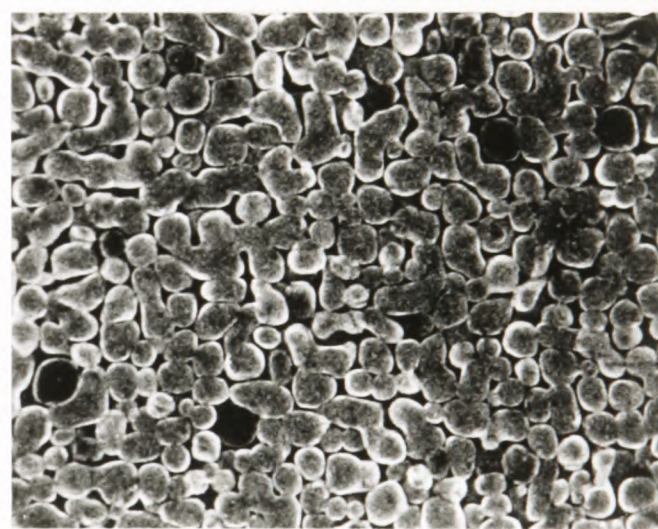
1 Hour



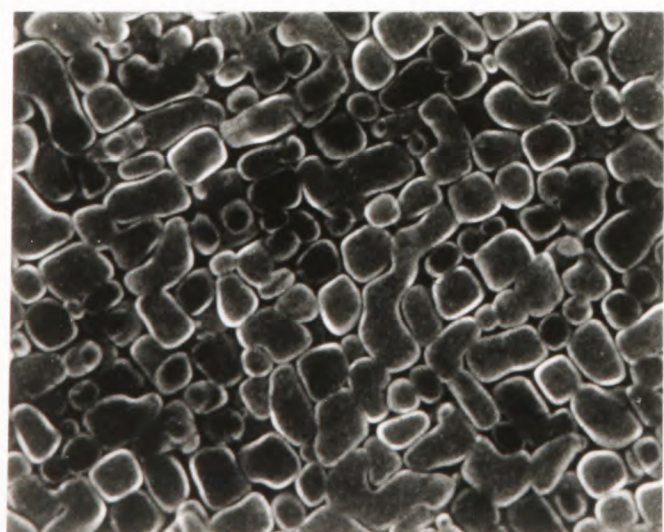
2 Hours



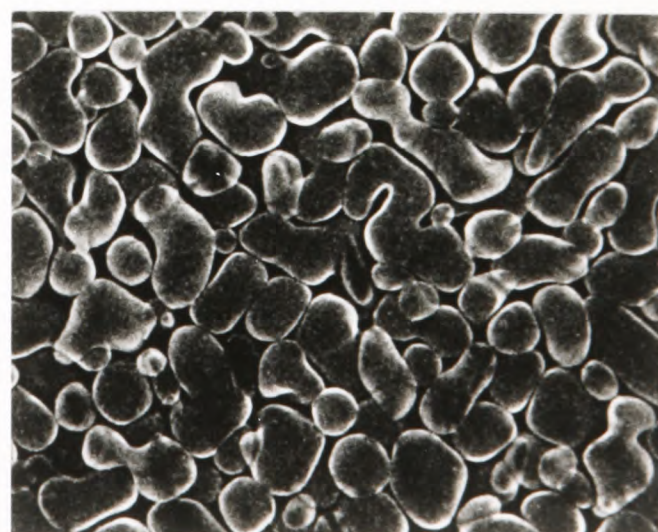
2.33 Hours



16 Hours



70 Hours



96 Hours

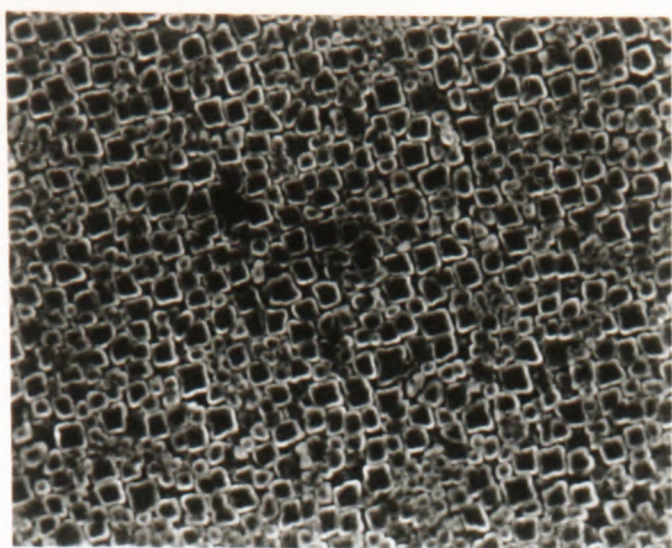
1 μm



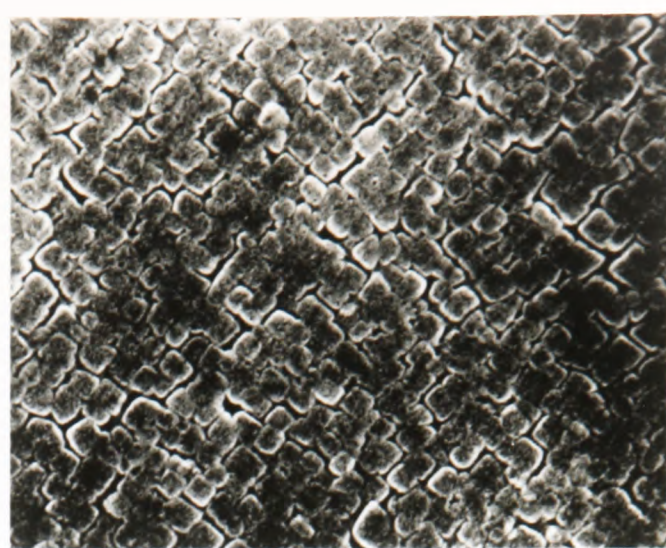
Figure 3.7

The microstructure of SRR99 after ageing at 800 °C. Specimens were solution heat-treated for 4 hours at 1300 °C, aged for the times shown at 800 °C and water quenched.

Sections taken normal to the [001] crystal growth direction. (SEM micrographs.)



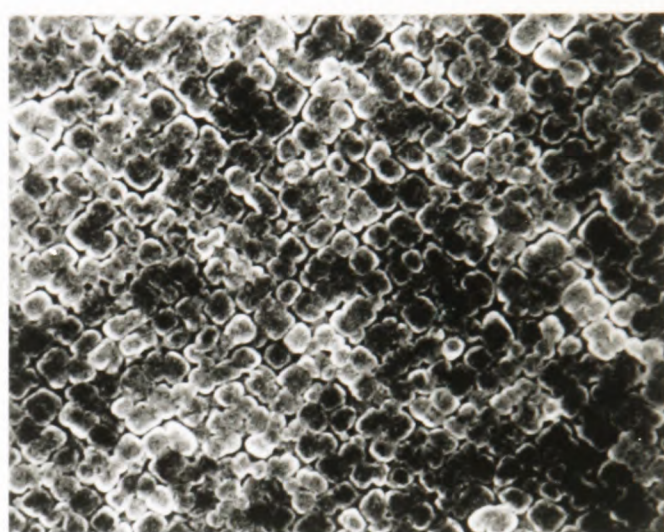
Unaged



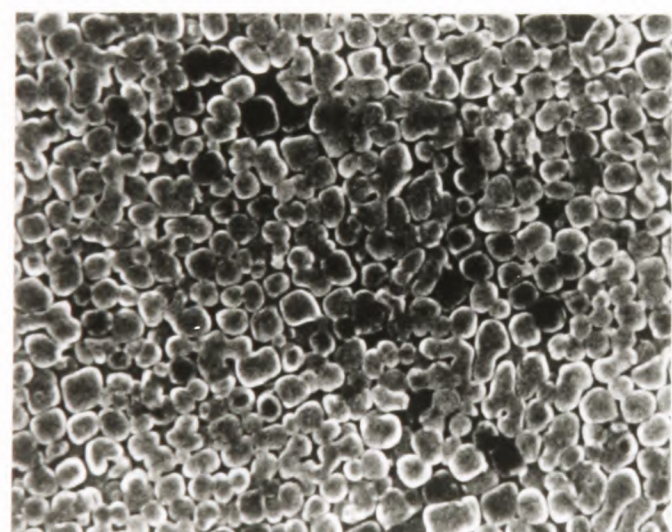
1.25 Hours



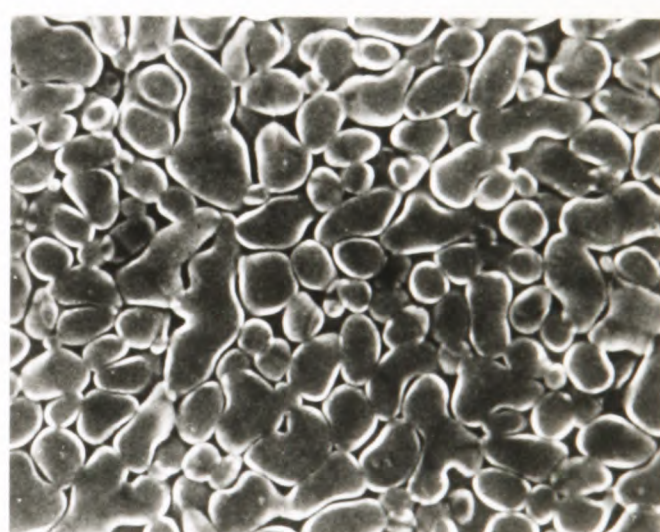
4 Hours



16 Hours



144 Hours



1180 Hours

1 μm



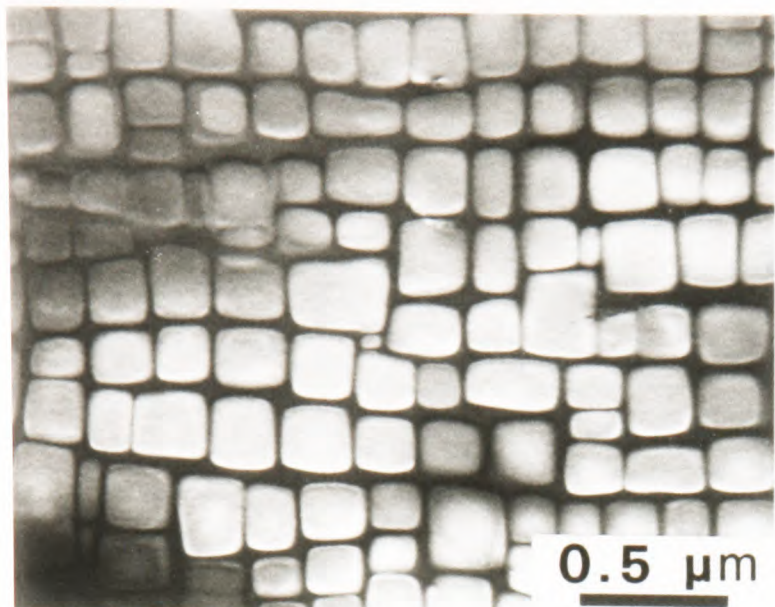
Figure 3.8

- (a) Microstructure of SRR99 after ageing for 30 minutes at 1100 °C.
Foil normal parallel to the [001] crystal growth direction.
(Central aperture selected area dark field TEM image using a {100}-type superlattice reflection).
- (b) Microstructure of SRR99 after ageing for 1 hour at 1100 °C.
Foil normal parallel to the [001] crystal growth direction.
(Central aperture selected area dark field TEM image using a {300}-type superlattice reflection.)
- (c) Diffraction pattern close to the [001] pole, showing excited superlattice reflections.

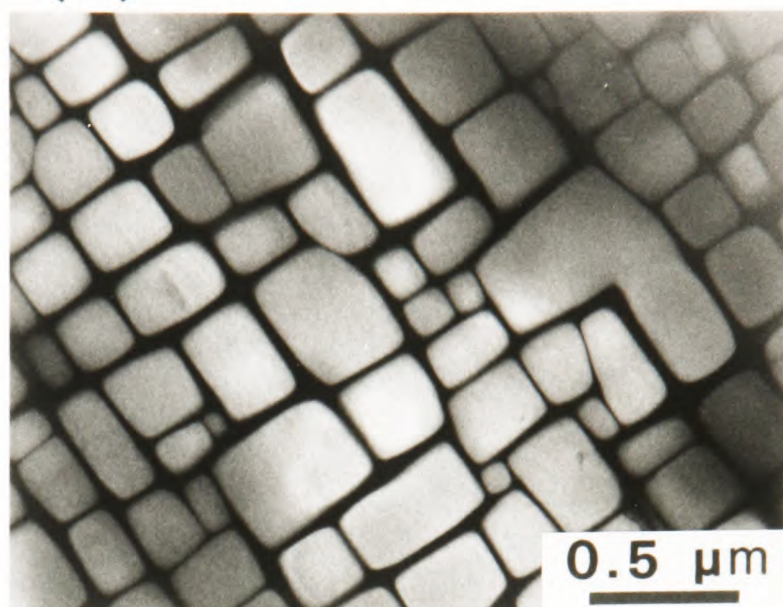
Figure 3.9

Microstructure of SRR99 after ageing for 96 hours at 900 °C. Section taken normal to the [001] crystal growth direction. (SEM micrograph).

(a)



(b)



(c)

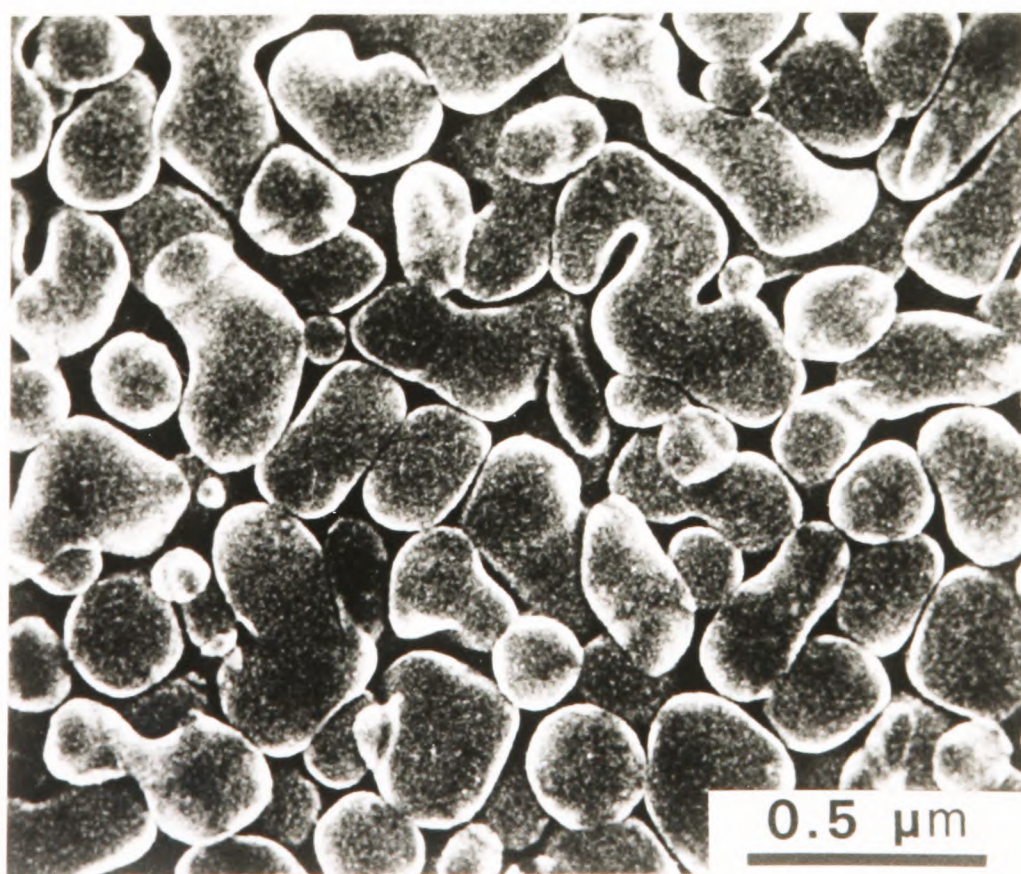
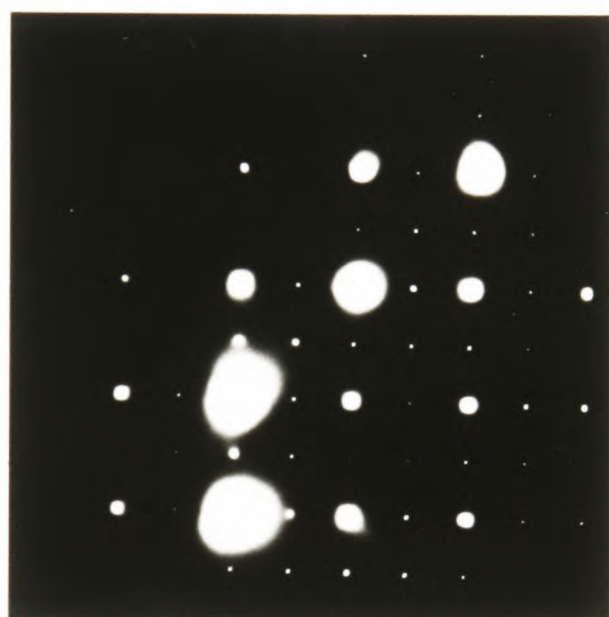


Figure 3.10

γ' precipitate size distribution produced by ageing at 1100 °C for the times indicated. Distributions predicted by the LSW theory for a mean precipitate size equal to the experimental value are also shown.

PRECIPITATE COARSENING AT 1100°C

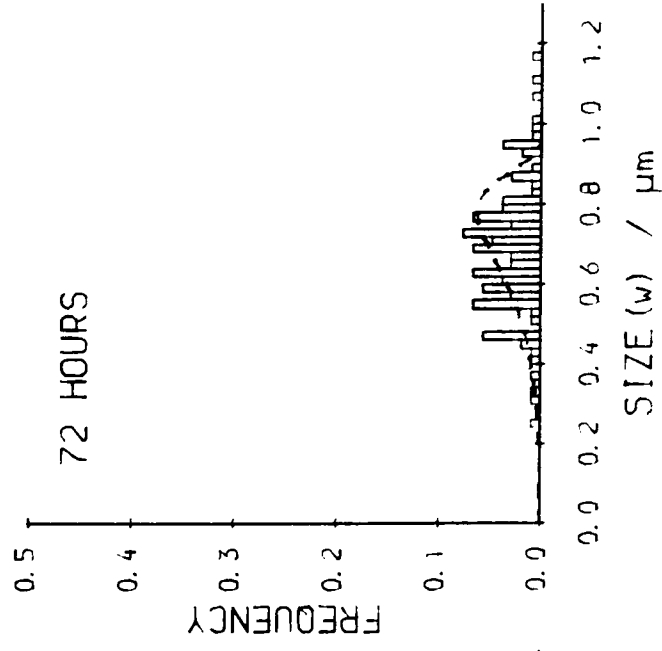
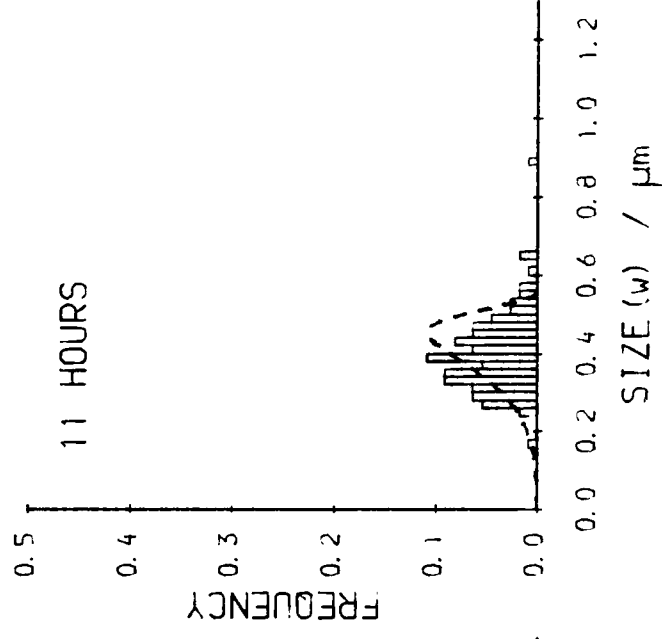
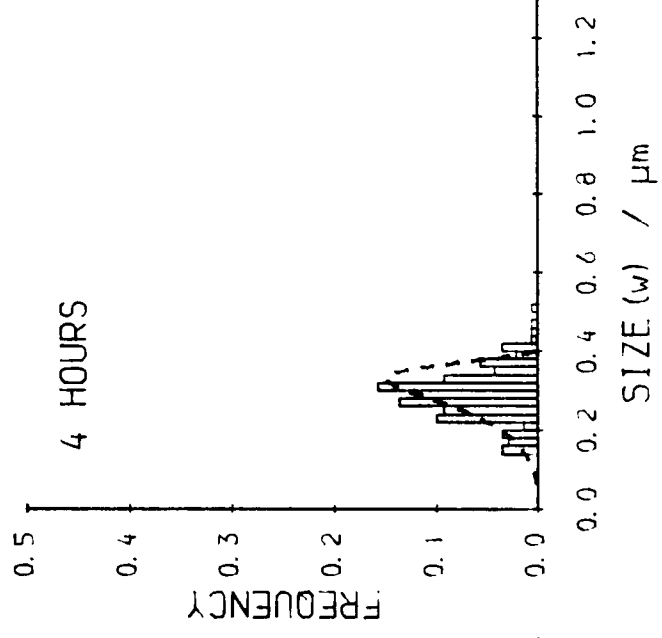
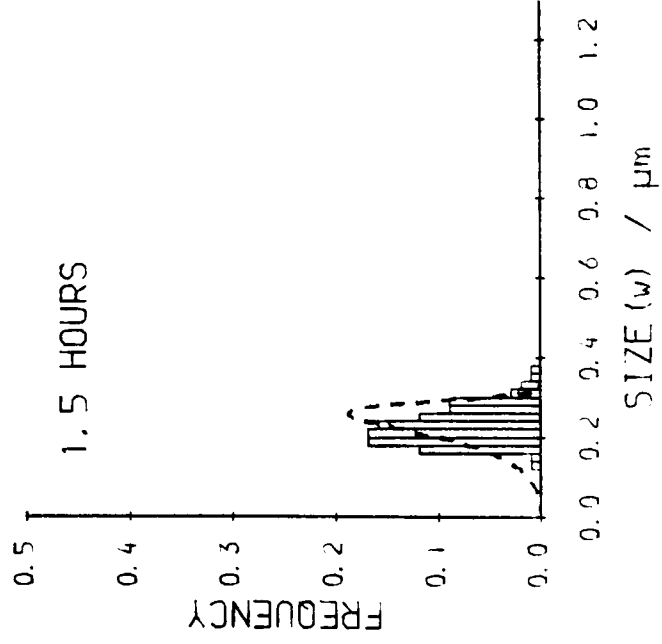
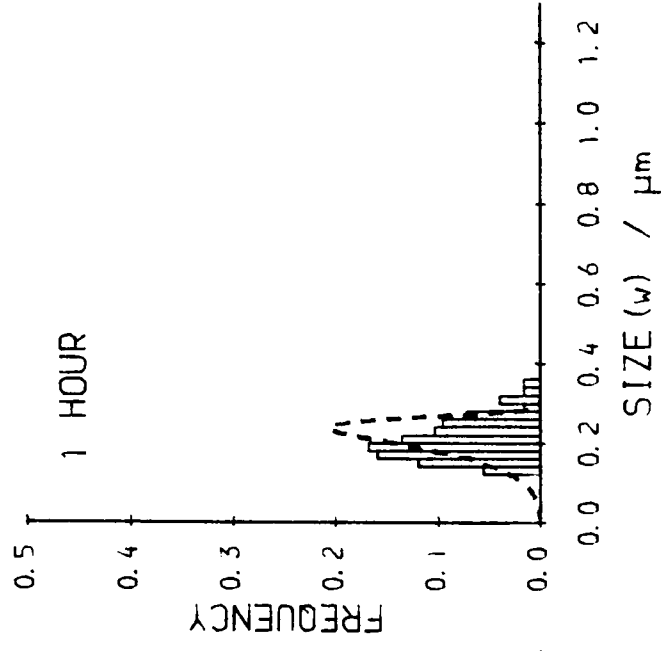
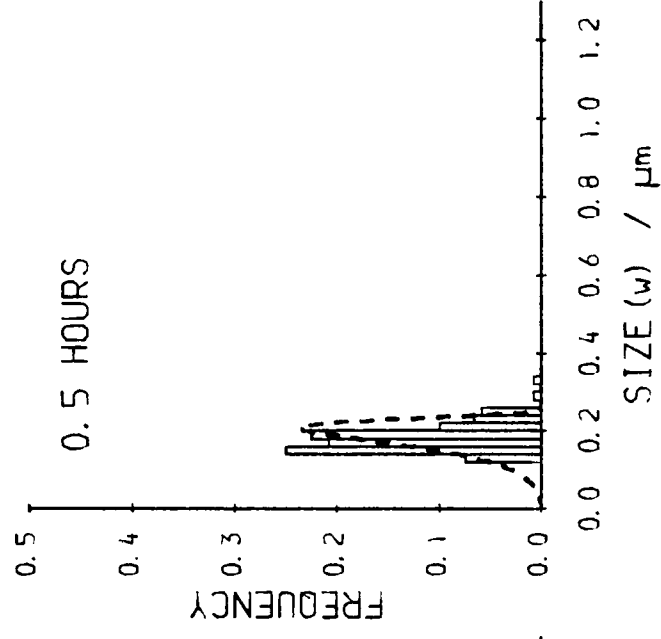
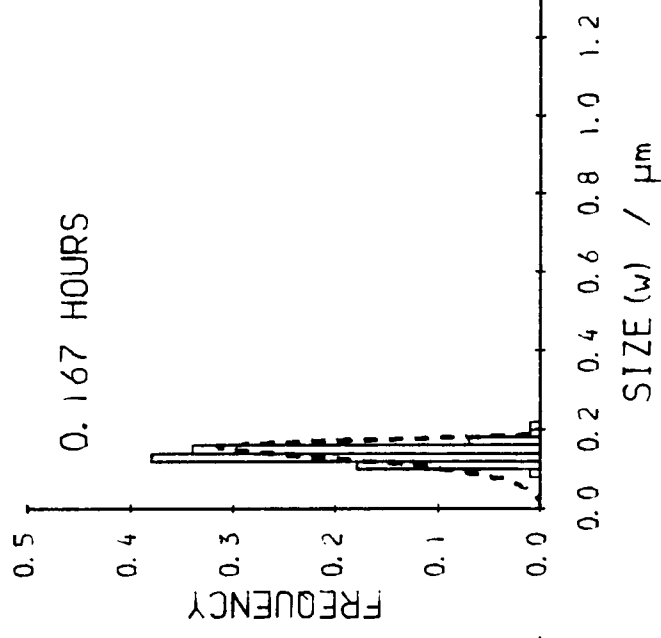
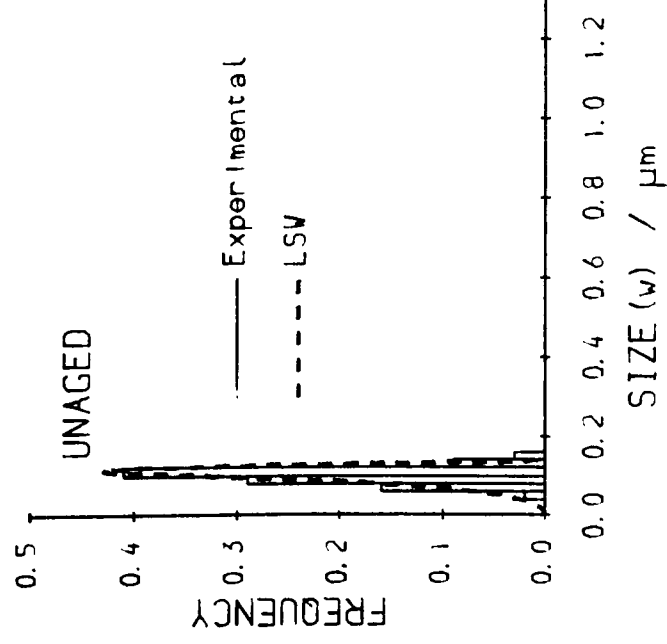


Figure 3.11

γ' precipitate size distribution produced by ageing at 1000 °C for the times indicated. Distributions predicted by the LSW theory for a mean precipitate size equal to the experimental value are also shown.

PRECIPITATE COARSENING AT 1000°C

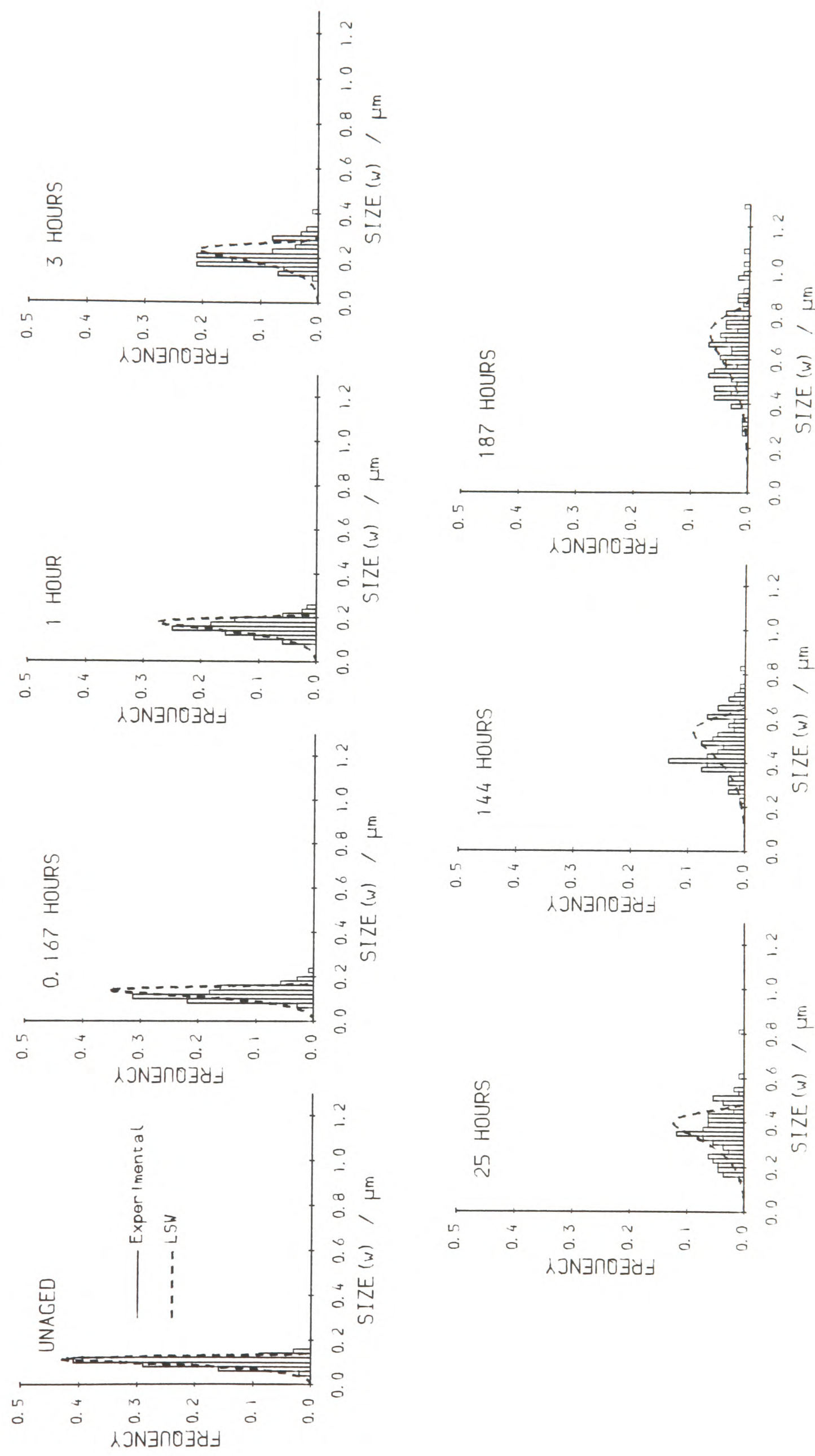


Figure 3.12

γ' precipitate size distribution produced by ageing at 900 °C for the times indicated. Distributions predicted by the LSW theory for a mean precipitate size equal to the experimental value are also shown.

PRECIPITATE COARSENING AT 900°C

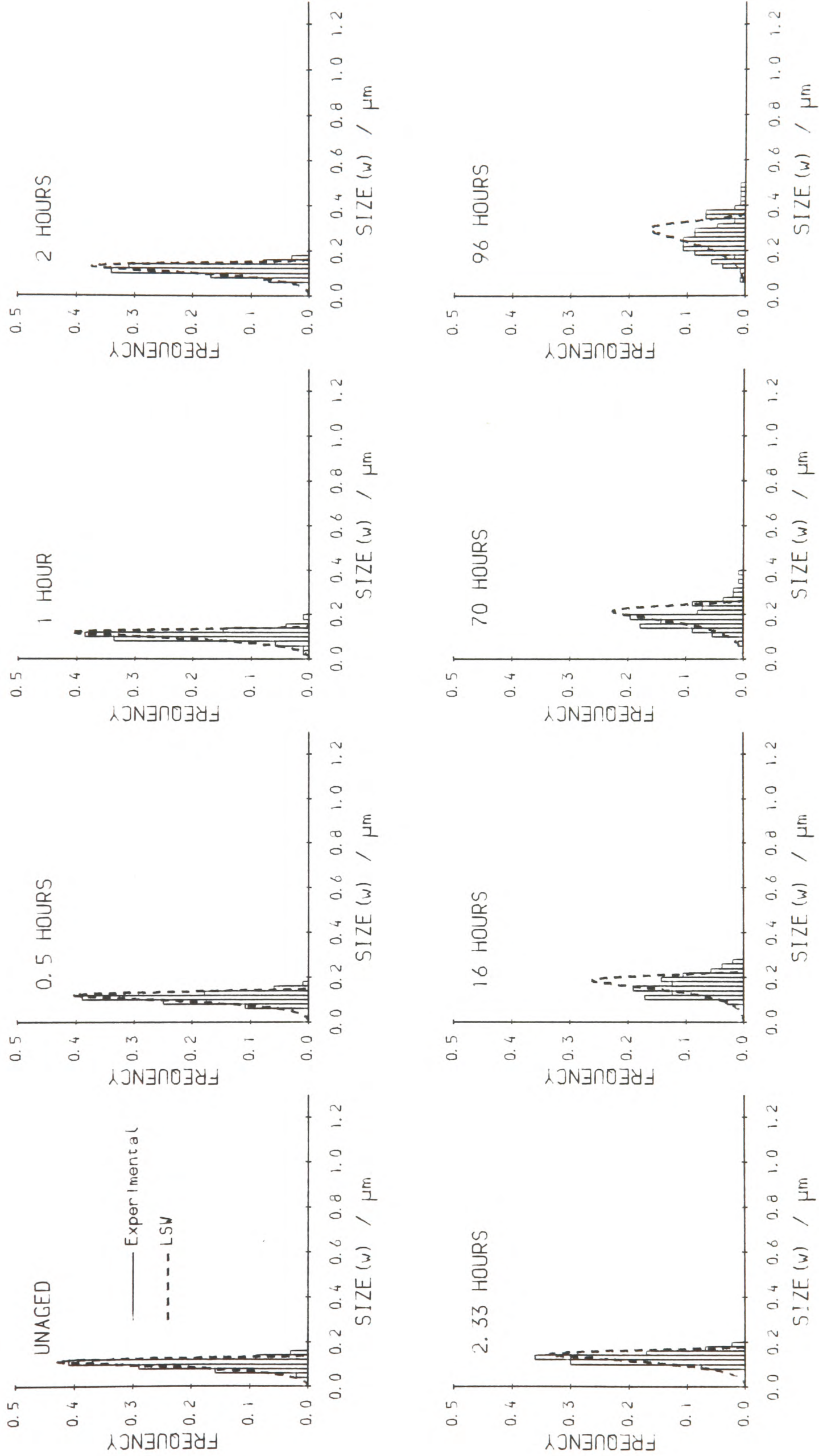


Figure 3.13

Plots of $(\bar{w}^n - \bar{w}_0^n)$ versus time (t), using the best-fitting values of n. The line shown has a gradient of unity, indicating the best fit to the equation $\log_{10}(\bar{w}^n - \bar{w}_0^n) = \log_{10}K_n + \log_{10}t$.

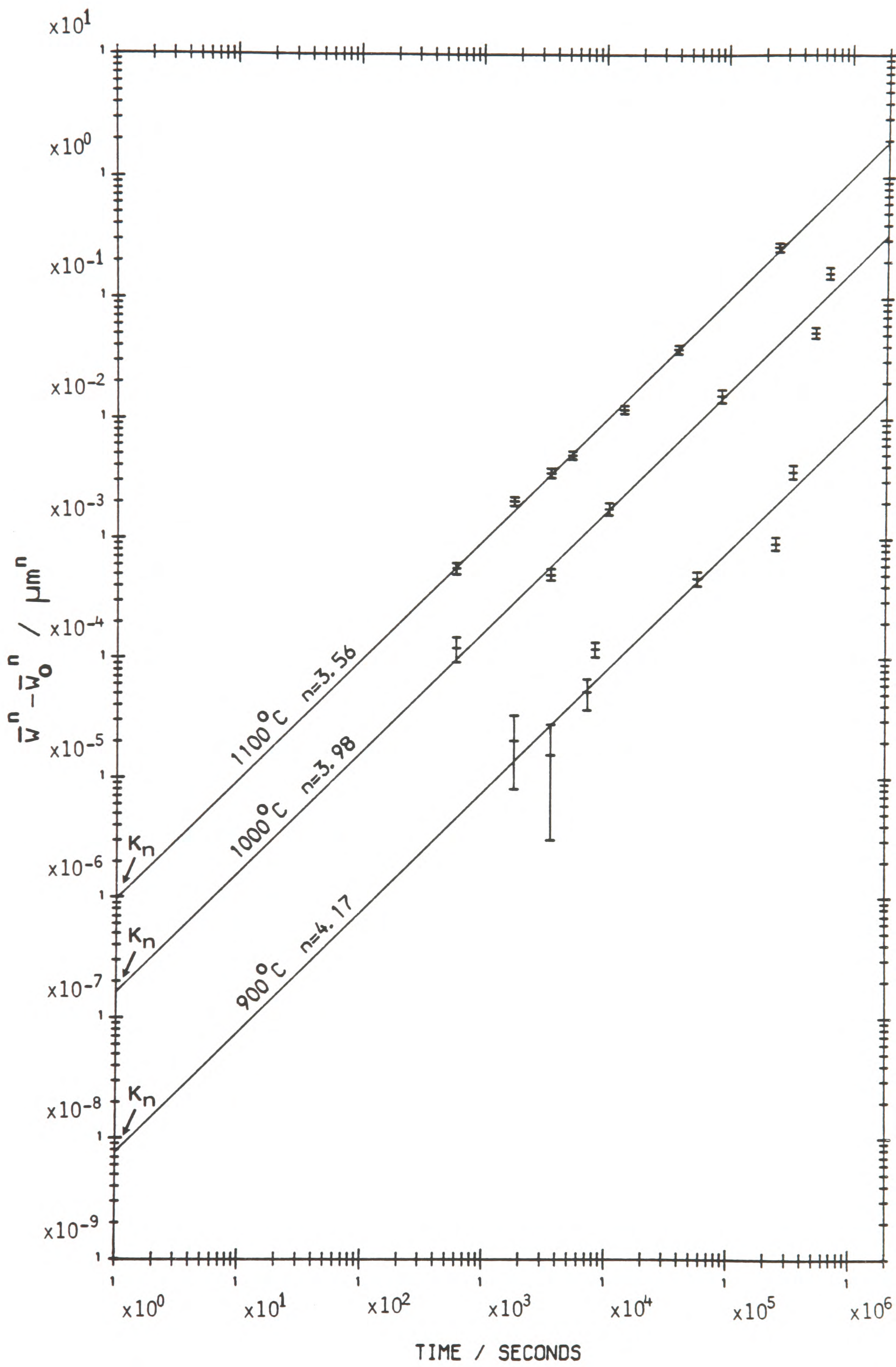


Figure 3.14

Plot of $(\bar{w}^3 - \bar{w}_0^3)$ versus time (t) for an ageing temperature of 1100 °C. The solid line shows the best fit to the data with the gradient equal to unity, whilst the broken line shows the best fit with the gradient unconstrained.

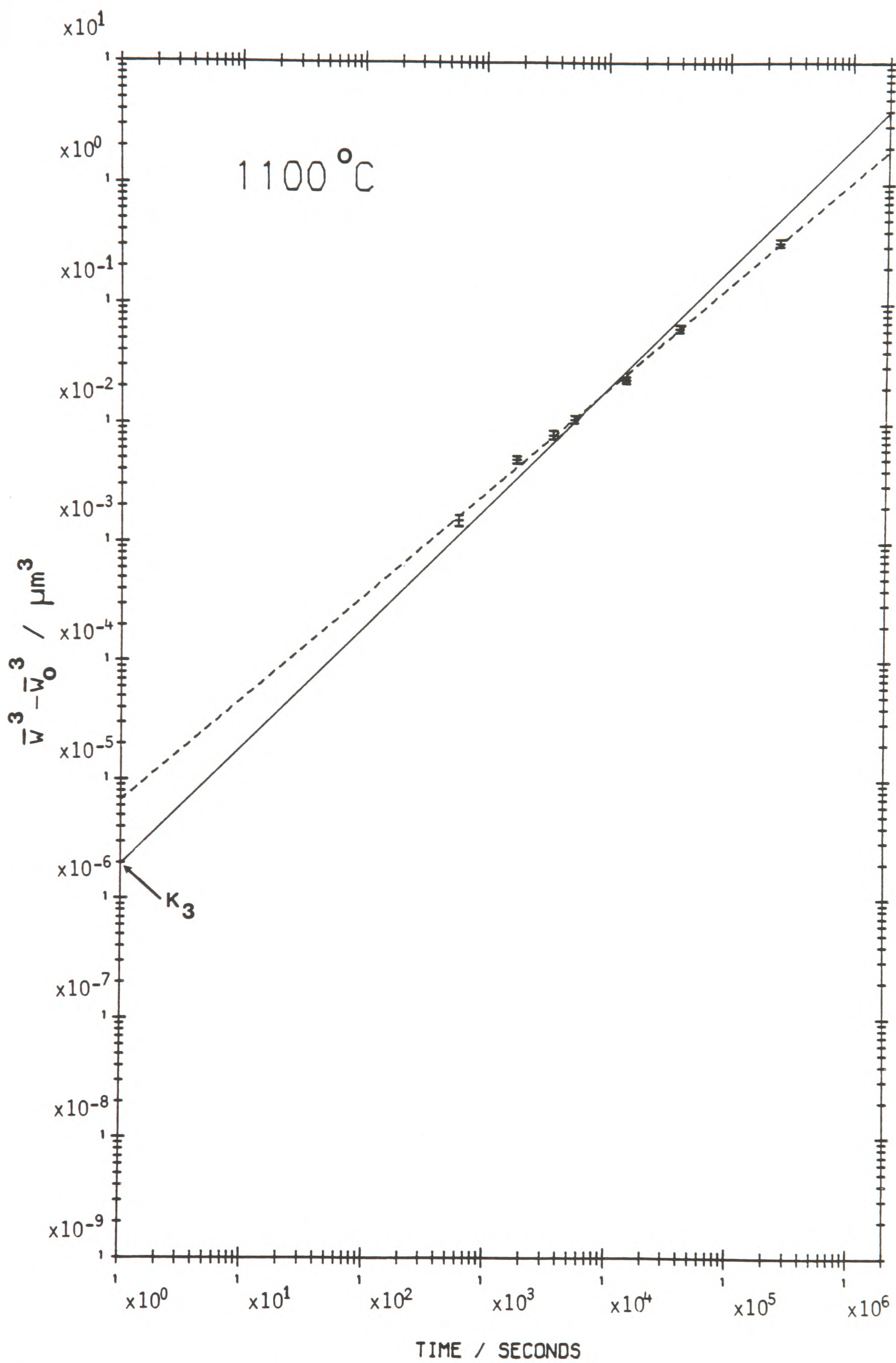


Figure 3.15

Plot of $(\bar{w}^3 - \bar{w}_0^3)$ versus time (t) for an ageing temperature of 1000°C . The solid line shows the best fit to the data with the gradient equal to unity, whilst the broken line shows the best fit with the gradient unconstrained.

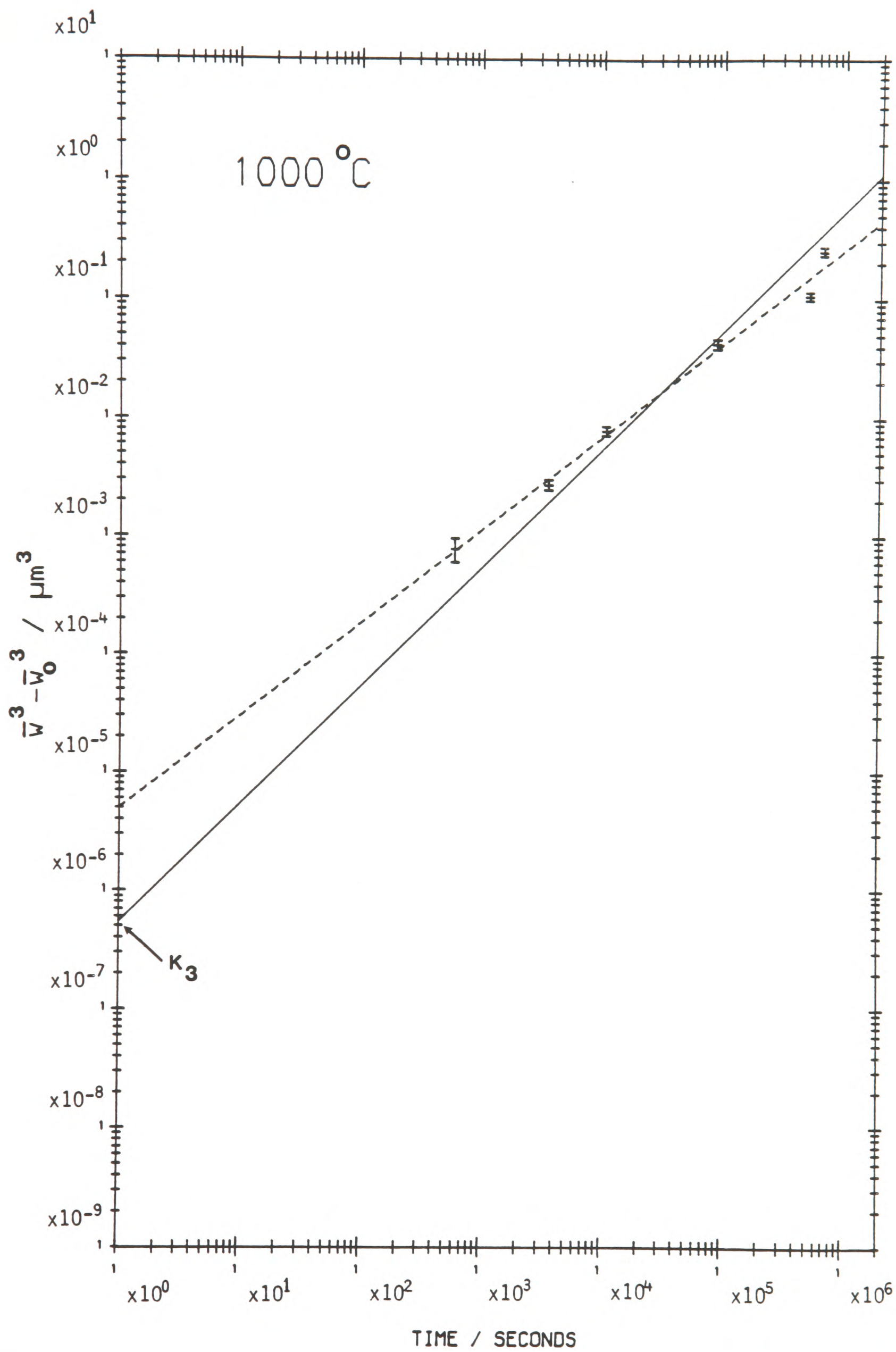


Figure 3.16

Plot of $(\bar{w}^3 - \bar{w}_0^3)$ versus time (t) for an ageing temperature of 900°C . The solid line shows the best fit to the data with the gradient equal to unity, whilst the broken line shows the best fit with the gradient unconstrained.

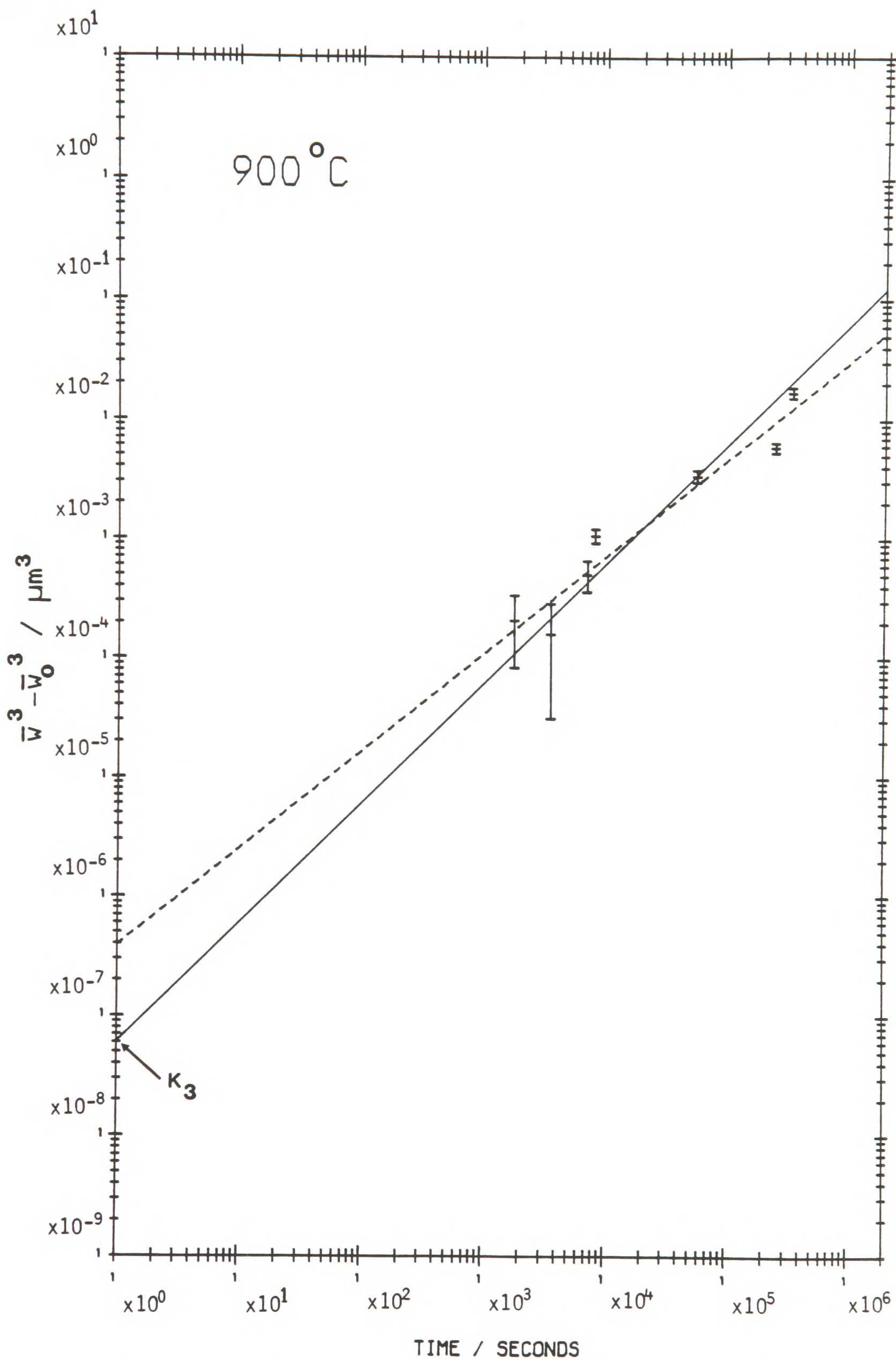
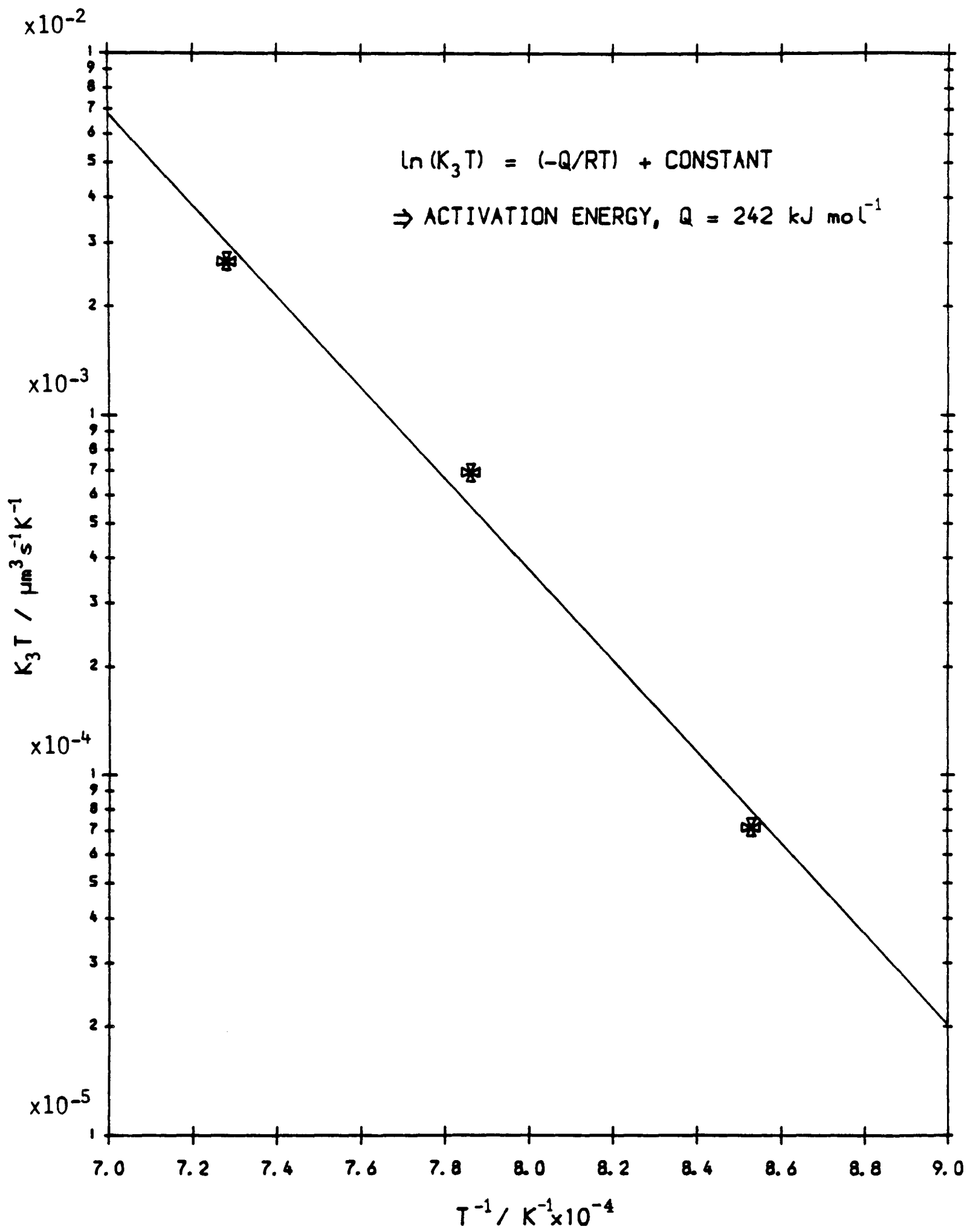


Figure 3.17

Arrhenius plot of K_3T versus $1/T$.

(Least squares fit.)



CHAPTER 4

CREEP BEHAVIOUR: RESULTS AND DISCUSSION

4.1 The Effects of Ageing at 1100 °C

Initial investigations into the creep behaviour of SRR99 were concerned with the effects of ageing at 1100 °C. This ageing temperature was chosen because the resulting precipitate microstructures had been thoroughly assessed, as reported in chapter 3, and also because such treatments are of industrial importance. The Rolls-Royce production process for single crystal turbine blades includes the forming of local brazed joints, and also the diffusion of aluminium through the blade surface to form an aluminium-rich coating for enhanced corrosion resistance. Both of these processes can be carried out at 1100 °C.

Prior to machining into test specimens, crystals were solution heat-treated for 4 hours at 1300 °C and then aged for different lengths of time at 1100 °C before finally being water quenched. Some others were water quenched directly from the solution heat-treatment temperature. Since the specimens were held at the testing temperature of 750 °C for 16 hours prior to applying the load, this should also be regarded as part of the heat-treatment. All of the creep tests were carried out under constant load corresponding to an engineering stress of 800 MPa.

Curves of strain versus time for specimens aged for 0, 10, and 60 minutes at 1100 °C are presented in figures 4.1, 4.2, and 4.3 respectively. The strain (ϵ) was calculated as

$$\epsilon = \ln \left(\frac{\Delta l}{l_0} + 1 \right) \quad (4.1)$$

where Δl is the extension within the gauge length and l_0 is the initial gauge length. Therefore ϵ represents the true strain assuming that the deformation is evenly distributed throughout the gauge length. The initial strain (ϵ_0) upon loading is included for each specimen. Several tests were carried out on material aged for 10 minutes and 60 minutes, some of which were interrupted prior to failure. It can be seen from the strain versus time curves that the creep performance varies greatly for specimens which have received identical heat-treatments and that the strain occurring during the primary stage is particularly variable. The total primary creep strain (ϵ_p) may be defined by the method of Leverant and Kear (1970), which is illustrated in figure 4.4. As an example of the variations in primary creep behaviour, values for ϵ_p of 8.5% and 2.8% were exhibited by crystals E and H respectively, both of which received an age of 1 hour at 1100 °C. In the presence of such variable behaviour, the effects of the precipitate microstructure could not be deduced from these results alone.

4.2 Crystal Orientation Effects

Although all of the specimens tested were nominally oriented with the stress axis parallel to the [001] crystallographic direction, it was decided that the crystal orientations should be checked to determine whether these could account for the observed variations in creep performance. Orientation measurements were taken from both the screw-threaded portion of the specimens and from within the gauge length, corresponding to the crystal orientations before and after

deformation respectively. These were then plotted using measured values of the angles θ and ϕ , which are defined in figure 4.5. The orientations of the specimen axes with respect to a standard stereographic triangle are shown in figure 4.6. The chosen triangle has as its vertices the $[001]$, $[011]$, and $[\bar{1}11]$ poles, in accordance with the convention used by Roome (1981), Winstone (1981) and McKay and Maier (1982).

Rotations of the crystal lattice have taken place as a result of creep testing, and these are apparent in figure 4.6 as movements of the specimen axes with respect to the crystal lattice. During tensile plastic deformation on a single slip system, the slip direction rotates towards the tensile axis. At the same time, the originally circular cross-section of a crystal becomes oval as the crystal lengthens. Such a change in cross-sectional shape was clearly visible in those specimens which underwent large primary creep strains. The extent of the primary creep stage can be rationalised in terms of the activation of a single $(\bar{1}11) [1\bar{1}2]$ slip system. Considering for instance crystal A, which exhibited a large primary creep strain of 9.3%, it can be seen from figure 4.6 that the crystal axis has apparently rotated towards the $[1\bar{1}2]$ pole. Its final orientation may be considered sufficiently close to $[001]$ for the activation of other slip systems.

All four $\{111\} \langle 112 \rangle$ slip systems are equally stressed in a crystal exactly oriented on the $[001]$ pole. Similarly two such systems are equally stressed in a crystal oriented along the $[001]$ - $[011]$ boundary of the stereographic triangle, provided that the deviation from $[001]$ is not so great that the axis lies beyond the point marked 'Y' in figure 1.23(b). Interactions between dislocations on different slip systems slow the deformation process and this is generally interpreted as leading to the onset of the secondary creep stage, as

discussed in section 1.4.7. Therefore crystals which were interrupted during the secondary creep stage or which were tested until failure can be considered to have initially rotated towards $[1\bar{1}2]$ and then either maintained a constant orientation close to the $[001]$ pole or to have moved towards $[001]$ in a direction parallel to the $[001]$ - $[011]$ boundary.

The primary creep strain observed depends on the angle through which the crystal axis has to rotate before becoming sufficiently close to either the $[001]$ pole or to the $[001]$ - $[011]$ boundary for activation of a multiplicity of slip systems. McKay and Maier (1982) have pointed out that crystals which have to rotate through the greatest angles, and which therefore exhibit the largest primary creep strains, will be under the greatest stress at the onset of secondary creep when tested under a constant load due to the reduction in the cross-sectional area. This is consistent with the observation that those crystals which underwent large primary creep strains generally exhibited the highest strain rates during the secondary creep stage.

The true stress (σ) on a specimen which has undergone an engineering strain of ϵ_{eng} is given by

$$\sigma = \frac{F}{A_0} (\epsilon_{\text{eng}} + 1) \quad (4.2)$$

where F is the applied load and A_0 is the initial cross-sectional area of the specimen. The true strain (ϵ) and the engineering strain (ϵ_{eng}) resulting from single slip are related to the lattice rotation by

$$\epsilon = \ln \left(\frac{\sin \chi_0}{\sin \chi_1} \right) \quad (4.3)$$

and

$$\epsilon_{\text{eng}} = \frac{\sin x_0}{\sin x_1} - 1 \quad (4.4)$$

where x_0 and x_1 are the angles between the tensile axis and the slip direction before and after slip respectively. The angle between $[001]$ and $[1\bar{1}2]$ is approximately 35° . Application of equations 4.3 and 4.4 shows that for a $[1\bar{1}2]$ slip direction and a tensile axis close to $[001]$, a strain of 1% gives rise to a lattice rotation of less than 0.5° . Although the orientations shown in figure 4.6 have been determined with sufficient accuracy to demonstrate the directions in which the crystals have rotated, there are inevitable errors in the measurements resulting from the mechanical alignment of the specimens with the x-ray beam. This limitation prevented reliable quantitative relations being obtained between the measured rotation and the extent of plastic deformation.

In the case of crystal G a further error in the lattice rotation measurement could have arisen through the possible introduction of low temperature deformation upon cooling. Whereas in all of the other interrupted tests the load was reduced prior to cooling, as described in section 2.3.4, this procedure was not carried out for crystal G. For this crystal the test was interrupted during the secondary creep stage by cooling under the full load. It therefore seems likely that the specimen underwent some low temperature deformation as a result of either a contraction of the specimen cross-section or a drop in the yield stress upon cooling.

4.3 The Effects of an Additional Ageing Treatment at 870°C

Similar relations between the crystal orientation and the observed

primary creep strain to those reported above have previously been reported in single crystals of Mar-M200 tested at 760 °C and 695 MPa (Leverant and Kear, 1970), Mar-M002 tested under the same conditions (Winstone, 1981; Roome, 1981) and Mar-M247 tested at 774 °C and 724 MPa (McKay and Maier, 1982). However, the present studies are apparently unique in their sensitivity to the magnitude and direction of misorientation from [001]. All the crystals had their tensile axes oriented to within 10° of [001]. In the previous studies the observed primary creep strains did not exceed 6% for specimens whose axes were oriented as close as this to [001], even for those crystals having the least favourable direction of misorientation, namely on the [001]-[$\bar{1}11$] boundary of the stereographic triangle. The currently observed primary creep strains of up to 10% are also in excess of those previously observed by Rolls-Royce Limited in SRR99 tested under identical conditions (Spilling, 1983). Such large primary creep strains are clearly unacceptable for engineering applications. Furthermore, under a constant load, large primary creep strains result in a higher value of the true stress during the secondary stage and consequently a reduced overall life to rupture.

It was noted that the standard Rolls-Royce procedure for the preparation of single crystal superalloys included an age for 16 hours at 870 °C followed by an air cool as the final stage of any heat-treatments. It was therefore decided that the effects of such an ageing treatment on the creep properties would be examined. Specimens were initially solution heat-treated, aged at 1100 °C and water quenched as before. They were then aged for 16 hours at 870 °C and air cooled, prior to machining into tensile creep specimens.

The creep curves obtained for such specimens are presented in figures 4.7 and 4.8 and the orientation measurements are shown in

figure 4.9. It would appear from these tests that the 870 °C ageing treatment has been beneficial to the creep performance. However, this could not be stated with certainty at this stage, since the low primary creep strains could have arisen as a result of the crystals being favourably oriented for the early activation of multiple slip systems.

In order to ascertain unambiguously the effects of the 870 °C ageing treatment it was necessary to compare specimens having an identical initial orientation. This could accurately be achieved by cutting in half the rod-shaped crystals described in section 2.1, and applying a different heat-treatment to each half. Three pairs of specimens were prepared in this way and heat-treated as follows:

Crystal 1	{	Crystal 1a: Solution treated, 1 hour at 1100 °C, water quenched, 16 hours at 870 °C, air cooled. Crystal 1b: Solution treated, 1 hour at 1100 °C, water quenched.
-----------	---	--

Crystal 2	{	Crystal 2a: Solution treated, water quenched, 16 hours at 870 °C, air cooled. Crystal 2b: Solution treated, water quenched.
-----------	---	--

Crystal 3	{	Crystal 3a: Solution treated, 1 hour at 1100 °C, water quenched, 16 hours at 870 °C, air cooled. Crystal 3b: Solution treated, water quenched, 16 hours at 870 °C, air cooled.
-----------	---	---

Each specimen was tested to failure, and the strain-time curves obtained are presented in figures 4.10, 4.11 and 4.12. The improvements in the creep behaviour which have been introduced by

ageing at 870 °C are clearly demonstrated. In the case of crystals 1a and 1b, both of which were previously aged for 1 hour at 1100 °C, the application of the 870 °C ageing treatment has reduced the observed primary creep strain from 7.4% to 1.6%. The minimum creep rate was also reduced and the stress-rupture life was increased by more than 150%.

Similar beneficial effects resulting from ageing at 870 °C were observed in crystal 2, where the 1100 °C age was omitted. Although crystal 2a, which received a 16 hour age at 870 °C, showed a reduced primary creep strain and an enhanced life to failure in comparison with crystal 2b, it may be noted that neither exhibited a particularly satisfactory resistance to creep deformation. The tests on the specimens prepared from crystal 3 confirmed that the creep performance is improved by including an age of 1 hour at 1100 °C in the heat-treatment procedure. Both crystals 3a and 3b were aged for 16 hours at 870 °C as the final stage of the heat-treatment. The primary creep strain and the minimum creep rate were reduced and the overall life increased for the specimen which received an initial age for 1 hour at 1100 °C.

The orientation measurements from each of the paired crystals are presented in figure 4.13. The accuracy with which the angle ϕ can be determined becomes greatly reduced when the tensile axis is close to the [001] pole, and it is believed that this may be responsible for the apparent anomalies in some of the orientation measurements.

Furthermore, some of the crystals were found to be loosely fitting in their mounting on the x-ray apparatus. It is therefore believed that the initial orientations were closely similar for each crystal in a given pair, although this is not apparent from the measured orientations. The creep test data and orientation measurements from

all of the specimens tested in the present study are summarised in table 4.1.

4.4 Deformation Structures

TEM studies were carried out to identify the deformation mechanisms occurring during creep testing. All of the specimens examined had been aged for 1 hour at 1100 °C prior to testing. Some had also received an age of 16 hours at 870 °C, which was shown above to have a critical effect on the creep behaviour.

4.4.1 Without 870 °C Ageing Treatment

Figure 4.14 shows the deformation structure observed in a foil taken from crystal J, which had been aged at 1100 °C but not at 870 °C. The test was interrupted after 4% primary creep strain. At this stage the strain-time relation was approximately linear, the specimen showing no indication of moving into the secondary creep stage. The foil was prepared from a disc cut parallel to (110) planes.

It can be seen from figure 4.14(a) that the deformation structure is characterised by stacking faults lying parallel to each other and perpendicular to the plane of the foil. By tilting the foil to a {111} pole, the interference fringes which are characteristic of stacking faults were observed, as shown in figure 4.14(c). Since the apparent width of the stacking faults is minimised when imaged with a [110] beam direction, it can be deduced that the faults lie perpendicular to the (110) plane of the foil. Comparison with the associated diffraction patterns was consistent with these stacking faults lying on ($\bar{1}11$) crystallographic planes. Since the tensile axis rotates towards $[1\bar{1}2]$ during testing, it was concluded that primary creep deformation was taking place through the passage of

dissociated dislocations on $(\bar{1}11)$ planes and with a net Burgers vector parallel to $[1\bar{1}2]$. The deformation was observed to be homogeneously distributed throughout the examinable portion of the foil, and as can be seen from figure 4.14(b), the dislocations appear to be dissociated only within the γ' precipitates.

Figure 4.15 shows the deformation structure observed in crystal K, which was interrupted at the end of the primary creep stage. The transition to secondary creep was occurring at this point, after 2.3% creep strain. The specimen did not receive an 870 °C age and was in the same heat-treated condition as crystal J. The observed primary creep strain was lower in crystal K than in crystal J, presumably through crystal K being more favourably oriented for the activation of multiple slip systems. The normal to the foil lay parallel to the stress axis of the crystal. Slight inhomogeneity of the density of the dislocation structure was observed. Stacking faults have occurred on intersecting slip planes, which is consistent with the onset of secondary creep, and dislocation tangles appear to be forming.

The deformation structure observed in crystal F after termination of creep testing during the secondary stage is presented in figure 4.16. The crystal had undergone a total creep strain of 5.6% when the test was interrupted. The specimen contains a dense homogeneous network of dislocations. There are still occasional stacking faults occurring within the γ' precipitates, but these would no longer appear to represent the dominant deformation mechanism.

Similar dislocation structures have been identified in the secondary creep of single crystals of Mar-M200 by Leverant et al. (1973), who concluded that precipitate shear was taking place by the passage of $a/2\langle 110 \rangle$ dislocations. It also seems likely that dislocation climb around precipitates forms part of the deformation

mechanism. The formation of a three-dimensional dislocation network during secondary creep represented the basis for several of the models of dislocation creep reviewed in section 1.4.2, where the establishment of a dynamic equilibrium between work-hardening and recovery was assumed.

4.4.2 With 870 °C Ageing Treatment

The dislocation and stacking fault configurations were examined in crystal N, which was aged for both 1 hour at 1100 °C and 16 hours at 870 °C prior to testing. None of the specimens which received this combination of ageing treatments exhibited large primary creep strains. Therefore direct comparison with the deformation structures found within crystal J, which was interrupted after 4% primary creep strain, was not possible. The testing of crystal N was terminated after 0.7% primary creep strain. The deformation structure observed is shown in figure 4.17, where the plane of the foil is normal to the stress axis of the crystal. The structure shows very similar features to those exhibited by crystal K, which did not receive the 870 °C age and which was interrupted at the end of the primary creep stage. Again some inhomogeneity of the density of the dislocation structure was observed. The observation of stacking faults on intersecting slip planes is indicative of the rapid work-hardening and consequent low primary creep strains observed in specimens having this particular heat-treatment history. As in crystal K, dislocation tangles appear to be forming and frequent dark patches from which dislocations are emanating can be seen. The higher magnification image shown in figure 4.17(b) suggests that these features comprise dense bundles of dislocations.

Figure 4.18 shows the deformation structure observed in crystal M

after termination of creep testing during the secondary stage after 2.2% creep strain. Like crystal N, this specimen had been aged for both 1 hour at 1100 °C and 16 hours at 870 °C prior to testing. The deformation structure closely resembles that observed in crystal F, which was also interrupted during the secondary stage but which did not receive the 870 °C ageing treatment. Again a dense homogeneous dislocation network has formed, with only occasional occurrence of stacking faults within γ' precipitates.

To summarise, the mechanisms of deformation occurring during both primary creep and secondary creep are apparently unchanged by applying a final age for 16 hours at 870 °C prior to testing. Large primary creep strains have been observed in specimens which had not received the 870 °C treatment, and this is believed to be due to extensive deformation on a single $(\bar{1}11)[1\bar{1}2]$ slip system. The activation of multiple slip systems, and consequently the onset of secondary creep, occurs after less accumulated strain in material which has received the 870 °C ageing treatment.

4.5 Microstructural and Microchemical Effects

The creep resistance of SRR99 has been shown to be enhanced by application of a two-stage ageing treatment comprising 1 hour at 1100 °C and 16 hours at 870 °C. The effects of ageing for one hour at 1100 °C can be rationalised in terms of the coarser microstructure produced. The larger precipitates might be expected to act as more effective obstacles to the passage of dislocations by precipitate shearing or climb.

The TEM investigation reported in the previous section revealed that the deformation mechanisms occurring during creep testing are unchanged by the application of a final age for 16 hours at 870 °C.

However, by applying different heat-treatments to two halves of the same crystal it has been unambiguously demonstrated that the observed primary creep strain is dramatically reduced by the 870 °C ageing treatment. Therefore the secondary creep stage begins after less accumulated strain. The secondary creep rate was also reduced, but this could have arisen through the lower stress at the onset of the secondary creep stage, owing to the diminished contraction of the specimen cross-section.

Investigations were undertaken to determine the effect of a final ageing treatment at 870 °C on the microstructure of SRR99. In figures 4.19(a) and (c) the microstructure of a specimen aged at 1100 °C only is compared to that of one aged at both 1100 °C and 870 °C. The microstructures show no apparent difference. However, examination after testing of specimens which had not been aged at 870 °C revealed the presence of a secondary dispersion of γ' precipitates, as shown in figure 4.19(b). These were not observed in specimens which had received an 870 °C age, as shown in figure 4.19(d).

In order to ascertain whether these precipitates were formed independently of an applied stress, some specimens were aged at the testing temperature of 750 °C. This treatment was carried out under conditions identical to those encountered by creep specimens prior to testing. The specimens were allowed to heat up to 750 °C in the furnace used for creep tests and were maintained at this temperature for 16 hours before being air cooled. A secondary distribution of precipitates was found to have formed in the specimen which had been aged at 1100 °C, but not in the specimen which had been aged at both 1100 °C and 870 °C. Since all creep specimens were maintained at the testing temperature of 750 °C for 16 hours prior to applying the load, these microstructural changes would have occurred before testing began.

Those specimens containing secondary precipitates exhibited higher primary creep strains than those containing a single dispersion of precipitates. This was regarded as surprising, since the presence of secondary precipitates is normally considered to improve the resistance to deformation. However, the secondary precipitates could enhance deformation on a single slip system. Assuming that these precipitates are sheared by dislocations, the passage of further dislocations along the same planes would be made easier (Hornbogen and Zum Gahr, 1975). For this reason such crystals might undergo greater deformation before the activation of intersecting slip systems and the subsequent onset of secondary creep.

It was decided that the relations between the microchemistry of SRR99 and the applied heat-treatments would be investigated in order to determine whether these could account for the dependence of the creep behaviour on the ageing history. A time of flight atom probe was used for this purpose. Some atom probe specimens were prepared from a crystal which had been solution treated and then aged for 1 hour at 1100 °C prior to water quenching, whilst others were prepared from a crystal which had received the same heat-treatment followed by an age for 16 hours at 870 °C and then air cooled. Some further specimens were prepared from a crystal aged for only 10 minutes at 1100 °C and water quenched, in order to examine any microstructural changes which might be occurring during the 1100 °C age. Each of the heat-treated crystals originated from the same large crystal, whose Rolls-Royce identification number was DP2270, produced from melt number RCM 73/8.

A typical atom probe specimen is shown in figure 4.20, imaged by TEM using a dark-field technique with an excited superlattice reflection, thus highlighting the γ' precipitates. The precipitates are cuboidal with sides parallel to $\{100\}$ planes. Since the specimens

were prepared with their axes parallel to the [001] crystal growth direction, the sides of the precipitates lie parallel and perpendicular to the specimen axes. With the atom probe operating in the FIM mode, the specimen could be tilted inside the instrument to align the [001] pole with the probe hole in the channel plate. As probing proceeded, layers of atoms were progressively removed, so that upon reaching a γ/γ' phase boundary this was penetrated in a direction normal to the plane of the interface. In practice probing proceeded with the specimens oriented such that the probe hole lay a few degrees away from the [001] pole. This was because probing on a major crystallographic pole causes atoms to be detected in intense bursts, corresponding to the removal of the last atoms in a given atomic layer, and can lead to unreliable quantitative results.

By calculating the mass to electronic charge ratio (m/n_e) for individual ions removed from atomic layers in both the γ and γ' phases, spectra of m/n_e values were built up from specimens in each heat-treated condition. These spectra are shown in figures 4.21-4.23. Using the m/n_e windows for each element present in SRR99, defined in table 2.7, it was possible to obtain an accurate chemical composition for both phases in each specimen. These results are presented in tables 4.2-4.4. The calculated concentrations of cobalt may be unreliable, since the m/n_e peak for cobalt falls between two closely spaced peaks for nickel isotopes, which led to some overlapping of the calculated m/n_e values.

It was of particular interest to compare the specimen aged for 1 hour at 1100 °C with that aged for both 1 hour at 1100 °C and 16 hours at 870 °C. It can be seen from tables 4.2 and 4.3 that the chemical compositions of the γ' phase are closely similar in each case. However, there is a difference in the γ phase. In the specimen

through which analyses were carried out. Where both phases can be seen in the same micrograph, the γ' phase is the more brightly imaging. All of the interfaces were probed through in a direction approximately normal to the plane of the phase boundary, except for interface 2 where probing was slightly oblique to the interfacial plane.

The chemical composition profiles for each interface are presented in figures 4.25-4.29. Here the data have been smoothed by a moving arithmetic mean process. The composition was calculated at 50-ion intervals, each composition being based on a population of 400 ions comprising the previous 200 ions and the following 200 ions. In this manner local fluctuations are smoothed out and the trends in composition across the interfaces can be clearly seen. Most striking is the fall in the level of aluminium on moving from γ' into γ , together with an increase in the chromium level. Titanium, another γ' -forming element, also shows a noticeable depletion upon crossing from γ' into γ .

In figures 4.30-4.34 the composition profiles for the same interfaces are shown again, this time using a ladder diagram. This is a means of representing the sequential nature of the detection of individual ions without introducing either smoothing of the data or grouping into blocks of ions. Chromium ions are represented by horizontal lines, whilst aluminium and titanium ions are represented by vertical lines. The γ phase is therefore identified as the approximately horizontal portion of the diagram and the γ' phase as the approximately vertical portion, with the interfacial region lying between. The presence of other elements is also indicated, with the exception of the base element, nickel.

The apparent increase in the sharpness of interface 1 in comparison with the others can largely be explained in terms of the

lower ionising voltage employed. The magnification of a FIM image decreases with increasing ionising voltage. Therefore a given number of detected ions corresponds to a greater thickness of material when the applied voltage is lower. In addition, the number of atomic plane edges lying within the probed region is diminished at lower voltages. The apparent difference in sharpness between interfaces 2 and 3 is somewhat anomalous. Interface 3 appears considerably more diffuse than 2, and yet the applied voltage was only slightly greater. Furthermore, interface 2 was probed at an oblique angle, which would be expected to increase its apparent diffuseness.

The general characteristics of the analysed interfaces appear to be very similar in most respects. However, in the specimen which was aged at 870 °C there is a large concentration of chromium close to the interface in the γ phase. In an unsmoothed block of 50 ions the chromium level reached 42 atomic % at this point. Further away from the interface the chromium level within the γ phase settled to a steady value of approximately 24 atomic %. There is some evidence of chromium enhancement close to the interface in the other specimens, but it is not so pronounced as in the specimen aged at 870 °C.

The enhancement of chromium levels close to γ/γ' interfaces has been reported by Delargy (1983) in a series of experimental superalloys. Furthermore, close examination of the composition profiles reported by Blavette and Bostel (1984) reveals a similar chromium enhancement in the single crystal superalloy CMSX-2. In the latter studies the alloy had received a heat-treatment which had previously been demonstrated to enhance creep performance (Caron and Khan, 1983). This is a particularly interesting observation since in the present studies chromium enhancement close to the phase boundary was most pronounced in the specimen which was aged at 870 °C. This

heat-treatment was shown in section 4.3 to reduce the observed primary creep strain and to promote an increased life to rupture.

Decker (1969) considers chromium to be a potent solid solution strengthening element. On this basis a build-up of chromium close to a γ/γ' interface could inhibit shearing of the precipitates by dislocations.

Strutt et al. (1976) have proposed that segregation of carbon or boron or of heavy elements such as tungsten and tantalum to γ/γ' interfaces may act to increase the activation energy for creep. Time of flight atom probe studies in the superalloy IN939 (Delargy and Smith, 1983) revealed little or no segregation of minor elements to γ/γ' interfaces. However, investigations by Delargy (1983) into the phase compositions of the Rolls-Royce single crystal superalloy SRR39 did show some signs of tungsten enhancement at the γ/γ' phase boundary, with a depleted zone on either side.

In the current studies no statistically significant segregation to phase boundaries of tungsten or tantalum was observed. Occasional small clusters of these elements were observed throughout the composition profiles, without any clear preference for interfacial regions. Since very little carbon was detected in any of the specimens, it may be significant that a cluster of carbon atoms was detected close to an interface, namely interface 3. However, the other interface (interface 2) analysed in the same specimen exhibited no such segregation.

4.6 Creep Fracture

The fracture surfaces from failed specimens were examined by SEM. Similar features were observed in each case. Figure 4.35 shows the fracture surface from crystal E which was aged for 1 hour at 1100 °C

prior to testing, whilst in figure 4.36 the fracture surface from crystal L is presented, this specimen having been aged for both 1 hour at 1100 °C and 16 hours at 870 °C. The fracture surfaces are characterised by square facets surrounding rounded, often circular, holes. These facets appear to be lying on (001) planes perpendicular to the stress axis and are linked by highly crystallographically oriented surfaces.

Similar features have been observed in SRR9 tested at 760 °C and under an engineering stress of 730 MPa (Twigg, 1981). Twigg concluded that the square-shaped facets were caused by microcrack growth around gas pores in the material. In the absence of grain boundaries, eutectic regions, brittle phases or areas where incipient melting during heat-treatment had occurred, gas pores represent the most effective sites available for the initiation of cracks. Although carbides can also act as crack initiation sites, very few carbides are observed in SRR99. The surfaces between the cracks are consistent with final creep rupture occurring by shear failure along {111} planes.

In order to gain a further insight into the fracture mechanism, a longitudinal section beneath the fracture surface of crystal E was examined. The section was taken along a {100} plane, the orientation of the crystal having been determined from an x-ray Laue image taken at the opposite end of the specimen from the fracture surface. Optical examination revealed the occurrence of cracking around pores, as shown in figure 4.37(a). Close examination of cracks at individual pores was carried out by SEM. Figure 4.37(b) shows a crack growing at either side of a typical pore, whilst in figure 4.37(c) a higher magnification view of the right hand crack tip is shown. From this micrograph it can clearly be seen that a sharp crack is propagating by cleavage of individual γ' precipitates. The crack tip shown here was not an

isolated example, the same mechanism being observed at the other cracks which were examined.

This mode of crack propagation during creep contrasts with crack growth under the high strain-rate conditions encountered during fatigue testing. Crompton (1983) has shown that in the fatigue of single crystals of Mar-M002 at 600 °C and at a cyclic loading frequency of 10 Hz, cracks preferentially propagate in the matrix along (001) planes.

Table 4.1

SUMMARY OF CREEP TEST RESULTS

Crystal	Heat-Treatment* (WQ = water quench; AC = air cool)	
A	Unaged (WQ from 1300 °C)	
B	}	Aged for 10 minutes at 1100 °C, WQ
C		
D		
E		
F	}	Aged for 1 hour at 1100 °C, WQ
G		
H		
I		
J		
K		
L	}	Aged for 1 hour at 1100 °C, WQ, 16 hours 870 °C, AC
M		
N		
1a	Aged for 1 hour at 1100 °C, WQ, 16 hours 870 °C, AC	
1b	Aged for 1 hour at 1100 °C, WQ	
2a	WQ from 1300 °C, aged for 16 hours at 870 °C, AC	
2b	Unaged (WQ from 1300 °C)	
3a	Aged for 1 hour at 1100 °C, WQ, 16 hours 870 °C, AC	
3b	WQ from 1300 °C, aged for 16 hours at 870 °C, AC	

*All crystals initially solution treated for 4 hours at 1300 °C.

Table 4.1 continued

SUMMARY OF CREEP TEST RESULTS CONTINUED

Crystal	F/I ¹	Rupture Life (hours)	Total Creep Strain (%)	Primary Creep Strain (%)	Minimum Creep Rate (s ⁻¹)	Measured Orientations (Degrees (°))			
						undeformed		deformed	
						θ	φ	θ	φ
A	F	145	16.9	9.3	8.2x10 ⁻⁸	6.0	36.7	1.0	6.9
B	F	136	19.0	10.3	1.1x10 ⁻⁷	6.8	27.6	3.1	19.1
C	I	-	5.5	4.8	3.1x10 ⁻⁸	3.7	5.2	1.6	0.7
D	I	-	3.8	-	-	4.2	24.5	2.4	26.4
E	F	104	16.8	8.5	1.4x10 ⁻⁷	9.1	33.6	3.3	13.0
F	I	-	5.6	4.6	4.0x10 ⁻⁸	2.1	40.5	0.8	33.4
G	I	-	4.1	3.6	2.9x10 ⁻⁸	7.2	12.1	4.4	13.0
H	I	-	3.5	2.8	3.2x10 ⁻⁸	1.2	20.0	0.9	9.1
I	I	-	2.3	-	-	2.2	4.3	1.7	0.9
J	I	-	4.0	-	-	8.2	35.8	-	-
K	I	-	2.3	-	-	1.3	1.2	0.1	29.8
L	F	569	10.2	1.2	2.6x10 ⁻⁸	3.5	44.4	2.2	32.1
M	I	-	2.2	1.1	3.0x10 ⁻⁸	5.7	28.5	4.6	33.5
N	I	-	0.7	-	-	7.5	12.3	6.6	8.6
1a	F	313	8.8	1.6	4.5x10 ⁻⁸	6.2	27.5	4.2	11.7
1b	F	116	13.1	7.4	9.9x10 ⁻⁸	5.3	7.7	1.9	33.7
2a	F	113	13.0	3.8	1.3x10 ⁻⁷	3.0	15.3	2.5	17.0
2b	F	85	16.0	9.4	1.6x10 ⁻⁷	8.3	6.2	3.0	42.0
3a	F	343	7.2	0.7	2.8x10 ⁻⁸	2.3	26.4	2.0	16.9
3b	F	234	10.7	2.0	5.5x10 ⁻⁸	1.5	31.5	0.9	39.5

¹Failed or interrupted.

Table 4.2

Phase composition for SRR99 from time of flight atom probe microanalysis.

Ageing treatment: 1 hour at 1100 °C, 16 hours at 870 °C.

Element	Gamma - Prime		Gamma	
	(Ion total = 8672)		(Ion total = 2002)	
	Atomic %	Weight %	Atomic %	Weight %
Al	17.75	8.34	4.07	1.84
Ti	4.69	3.91	0.65	0.52
Cr	3.69	3.34	23.81	20.73
Co	5.06	5.19	6.93	6.84
Ta	1.74	5.48	0.55	1.67
W	2.37	7.58	2.71	8.35
C	0.012	0.0024	0.251	0.0505
Ni	64.71	66.16	61.02	59.99

Table 4.3

Phase composition for SRR99 from time of flight atom probe microanalysis.

Ageing treatment: 1 hour at 1100 °C only

Element	Gamma - Prime		Gamma	
	(Ion total = 9329)		(Ion total = 9617)	
	Atomic %	Weight %	Atomic %	Weight %
Al	17.92	8.46	5.78	2.61
Ti	4.95	4.15	1.08	0.87
Cr	4.03	3.67	22.55	19.61
Co	5.48	5.65	6.97	6.87
Ta	1.75	5.54	0.91	2.76
W	2.21	7.12	2.79	8.58
C	0.022	0.0045	0.157	0.0316
Ni	63.65	65.41	59.77	58.68

Table 4.4

Phase composition for SRR99 from time of flight atom probe
microanalysis.

Ageing treatment: 10 minutes at 1100 °C only

Element	Gamma - Prime		Gamma	
	(Ion total = 24310)		(Ion total = 1656)	
	Atomic %	Weight %	Atomic %	Weight %
Al	16.41	7.68	5.46	2.40
Ti	5.27	4.38	0.85	0.66
Cr	4.24	3.82	21.83	18.50
Co	4.74	4.84	5.64	5.42
Ta	1.89	5.94	1.09	3.22
W	2.16	6.88	3.70	11.08
C	0.058	0.0121	0.061	0.0119
Ni	65.24	66.44	61.37	58.71

Figure 4.1

Creep curve for crystal A.

This crystal was water quenched from the solution heat-treatment temperature of 1300 °C.

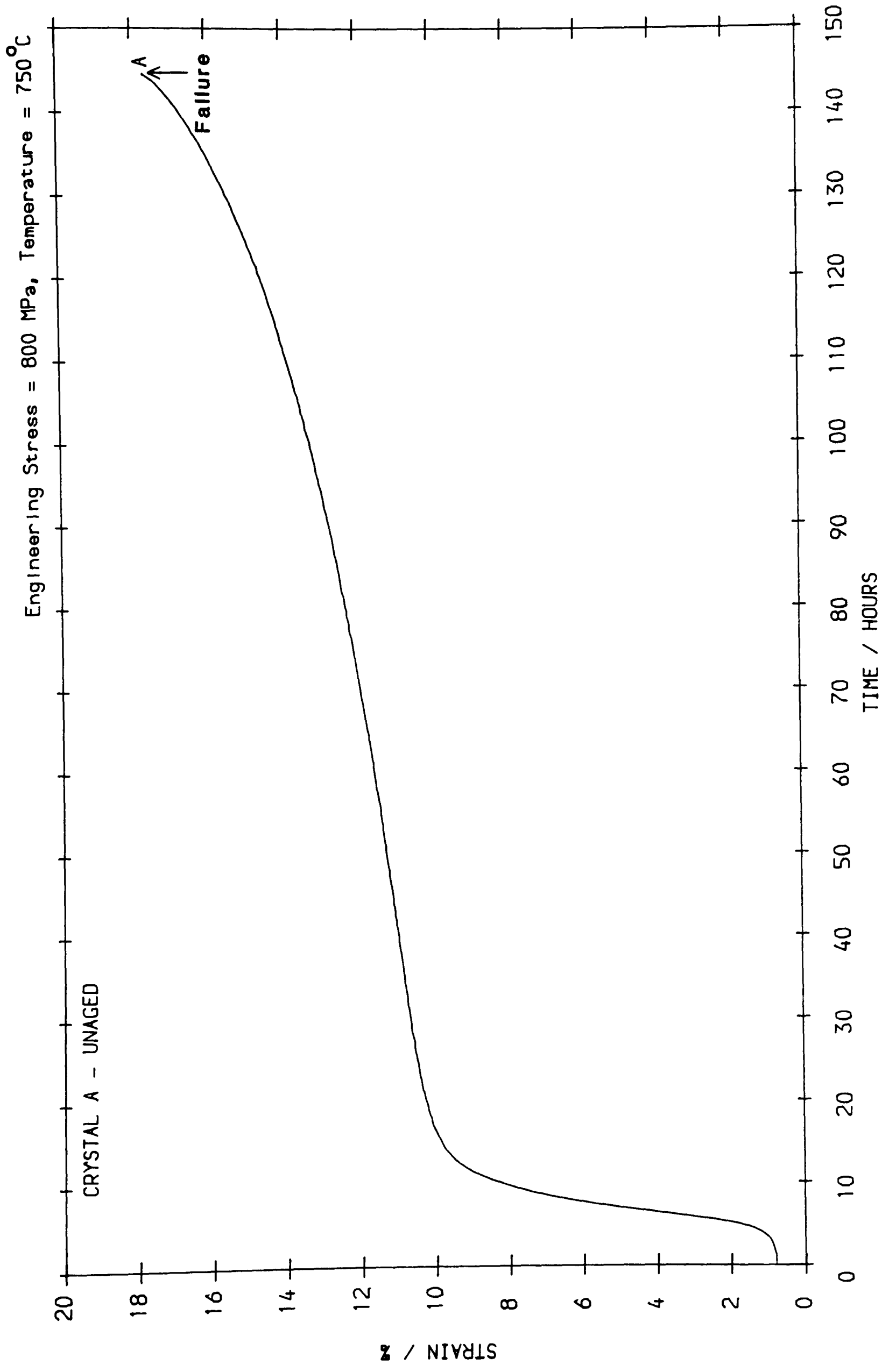


Figure 4.2

Creep curves for crystals B-D.

These crystals were aged for 10 minutes at 1100 °C. (Crystal B tested to failure, crystals C and D interrupted.)

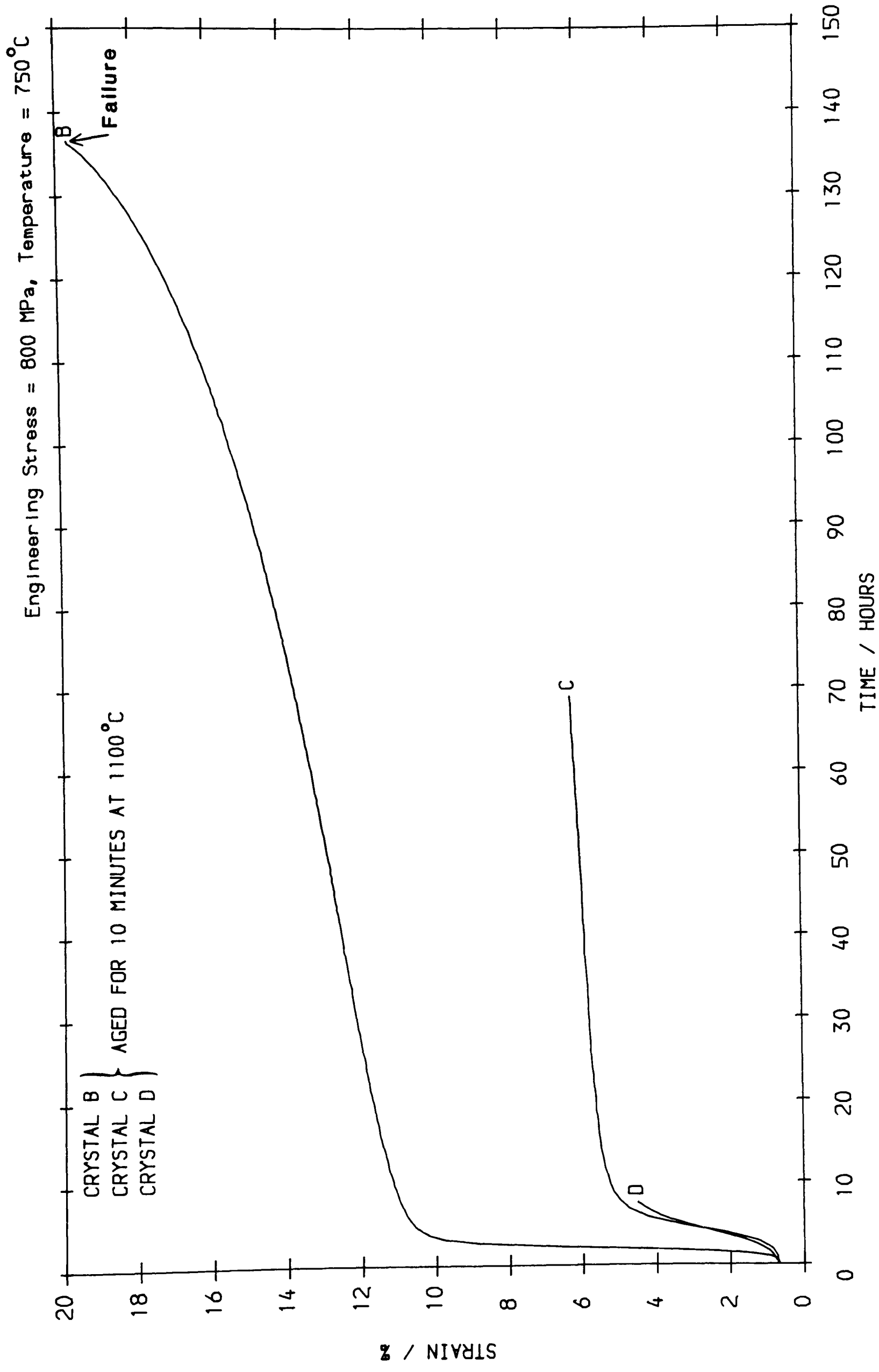


Figure 4.3

Creep curves for crystals E-K.

These crystals were aged for 1 hour at 1100 °C. (Crystal E tested to failure, others interrupted.)

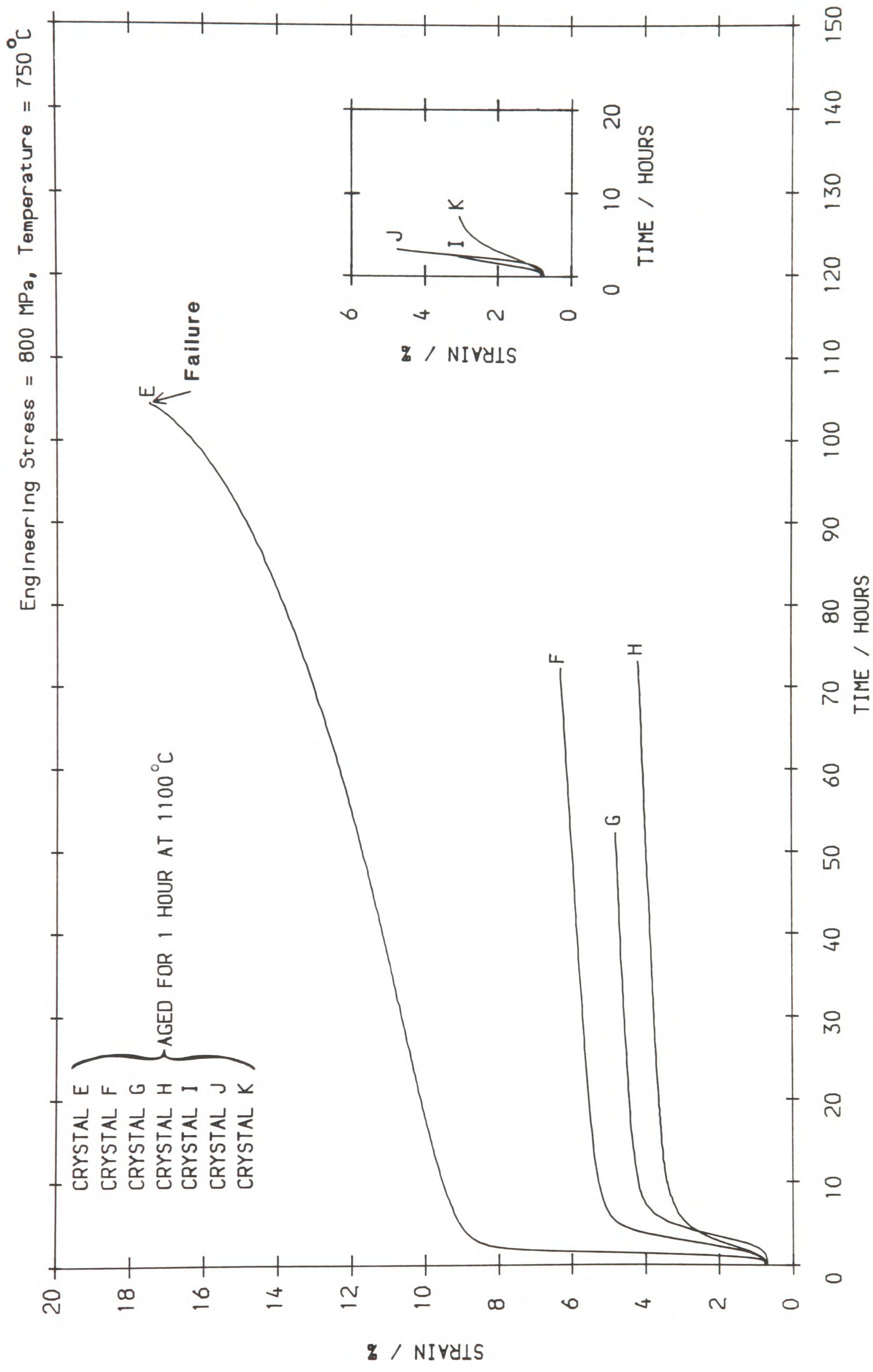


Figure 4.4

Definition of primary creep strain (ϵ_p) using the method of Leverant and Kear (1970).

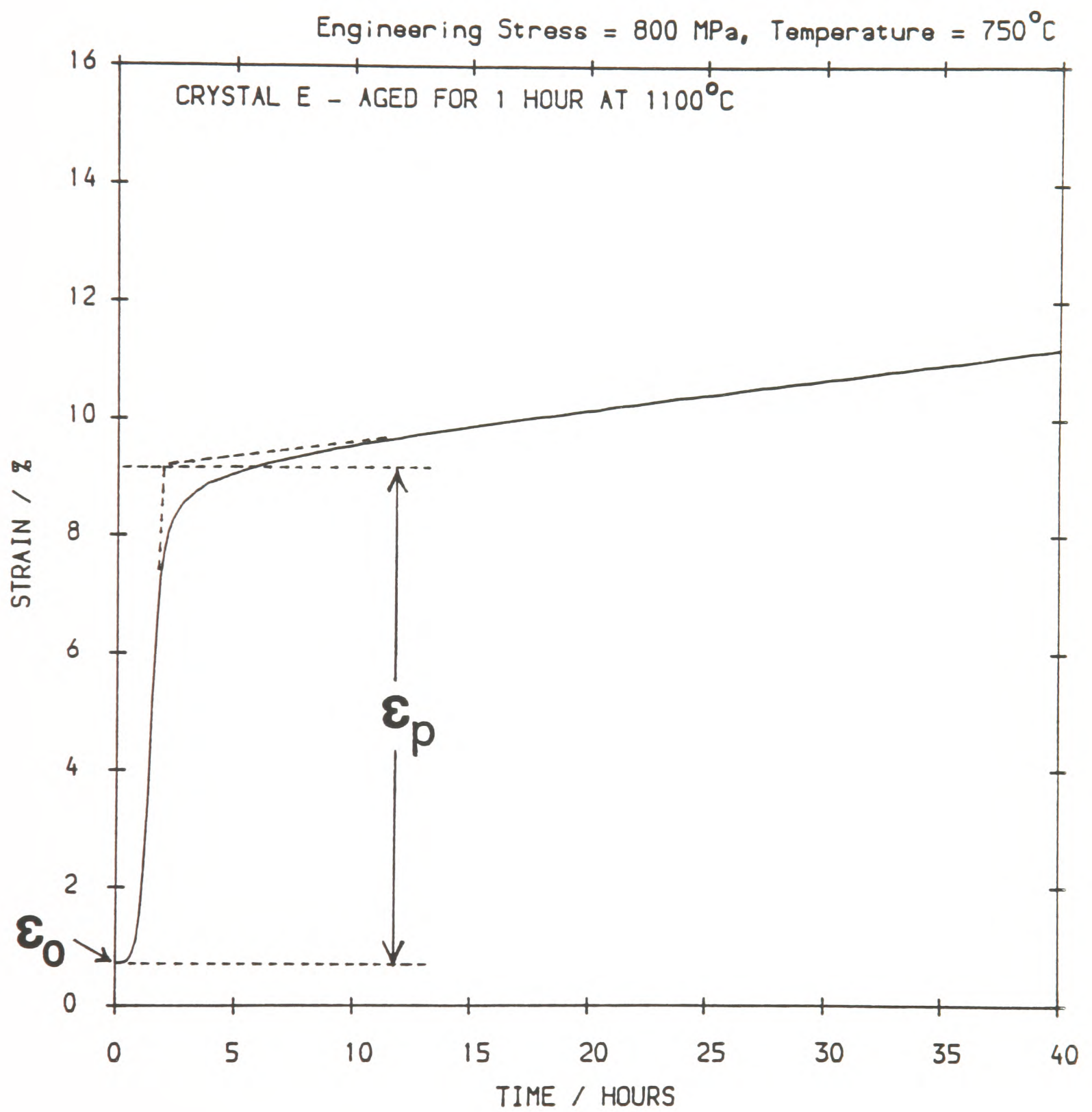


Figure 4.5

Definition of the orientation parameters θ and ϕ describing the orientation of the tensile axis relative to the cubic crystallography.

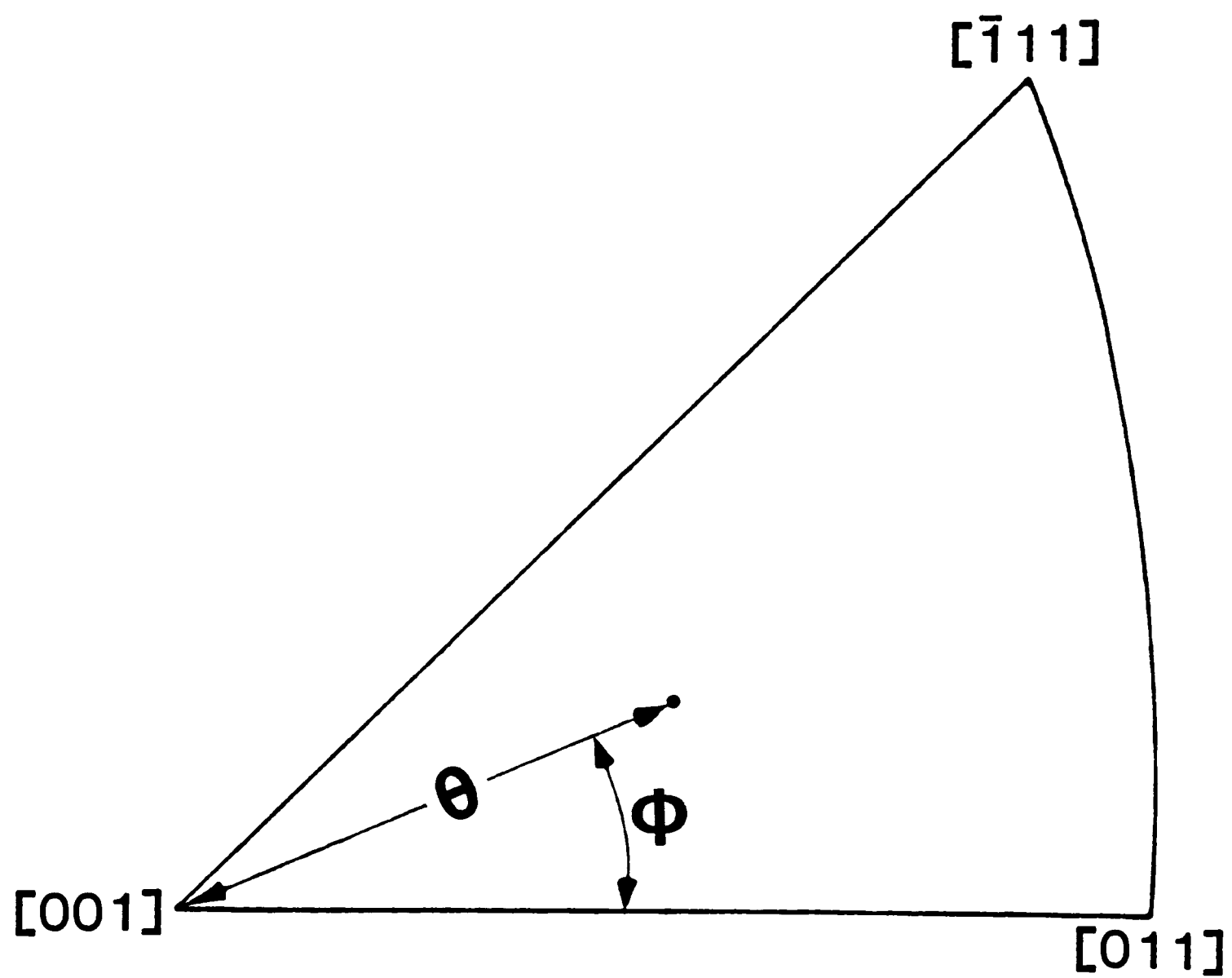


Figure 4.6

Lattice rotation measurements for crystals A-K.

(No post-deformation orientation available for crystal J.)

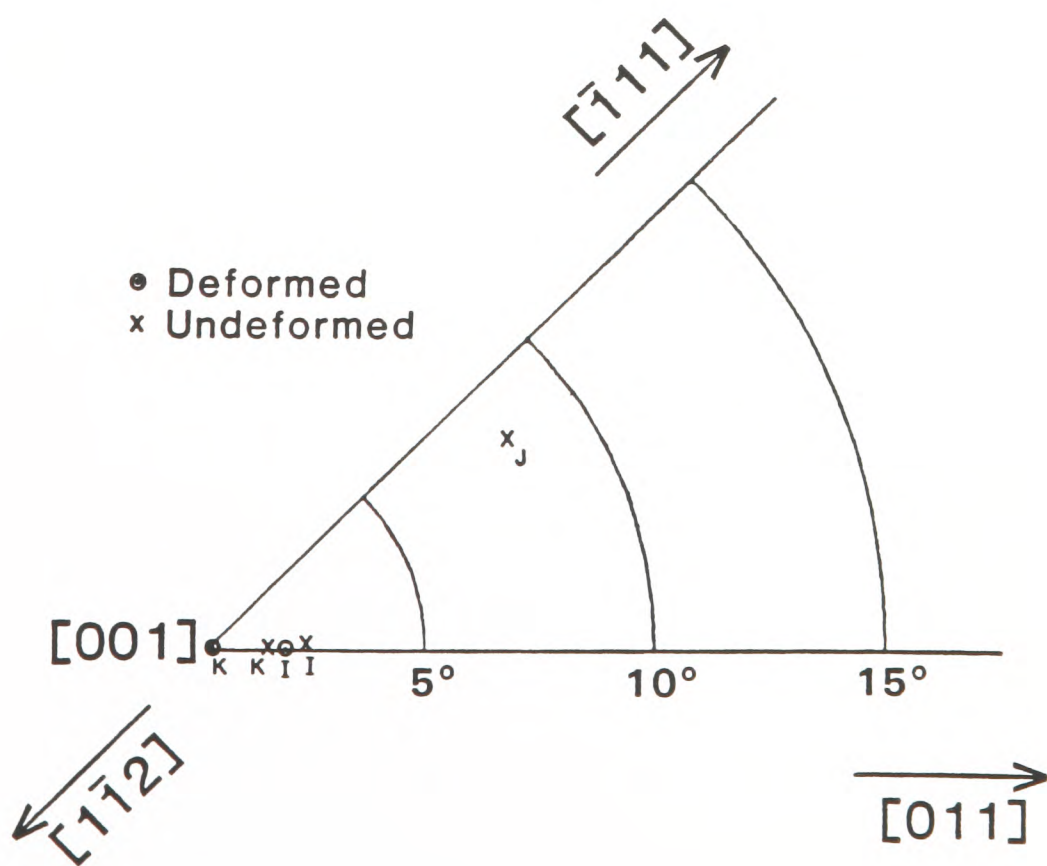
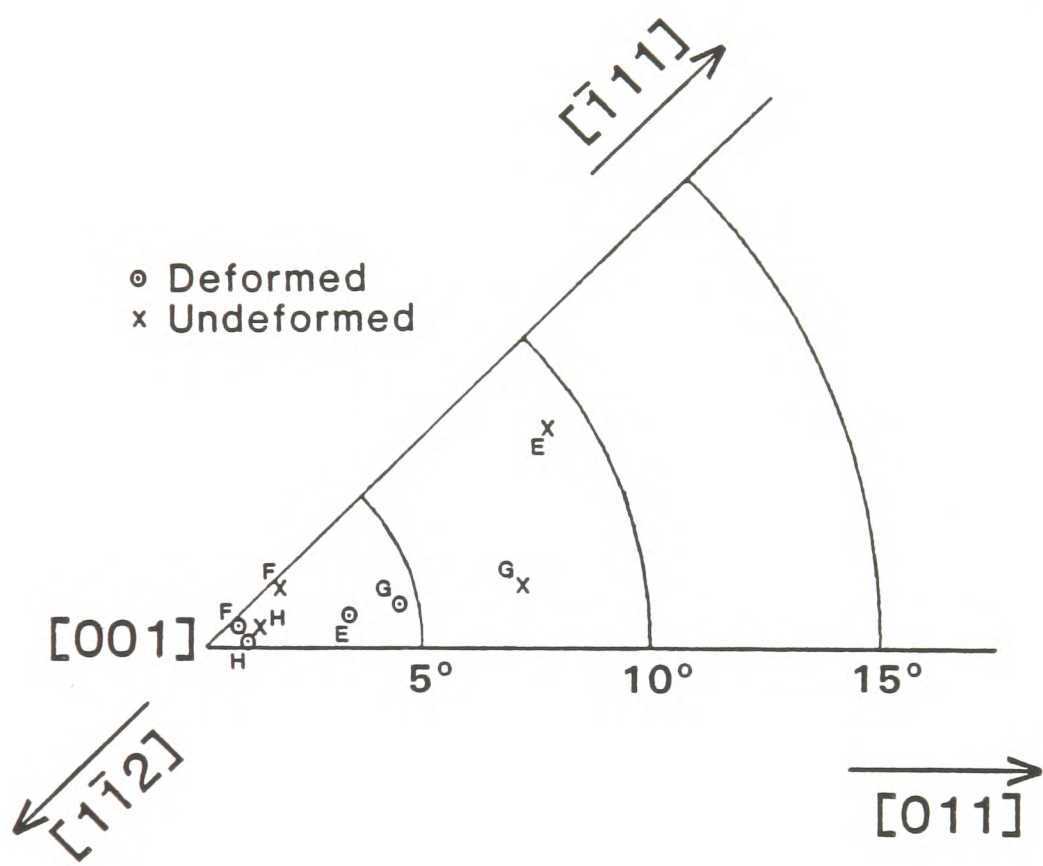
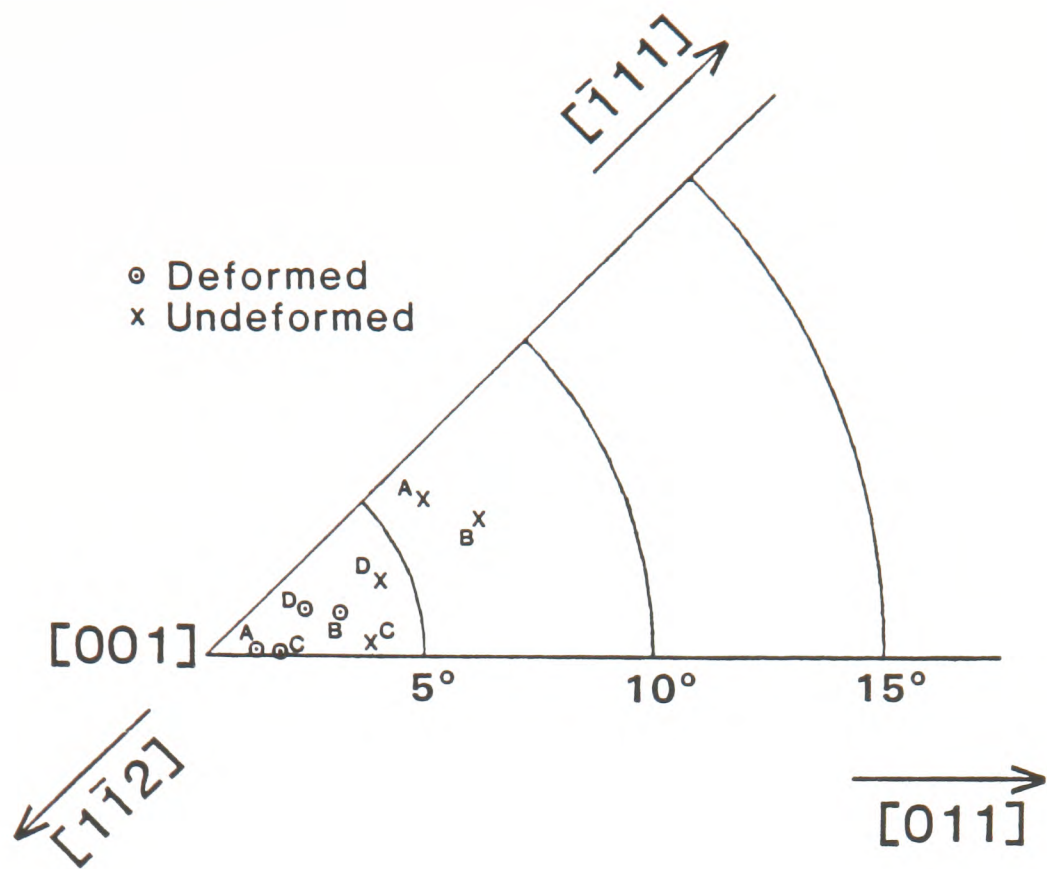


Figure 4.7

Creep curves for crystals L-N.

These crystals were aged for 1 hour at 1100 °C and 16 hours at 870 °C.

(Crystal L tested to failure, others interrupted. The full creep curve for crystal L is shown in figure 4.8.)

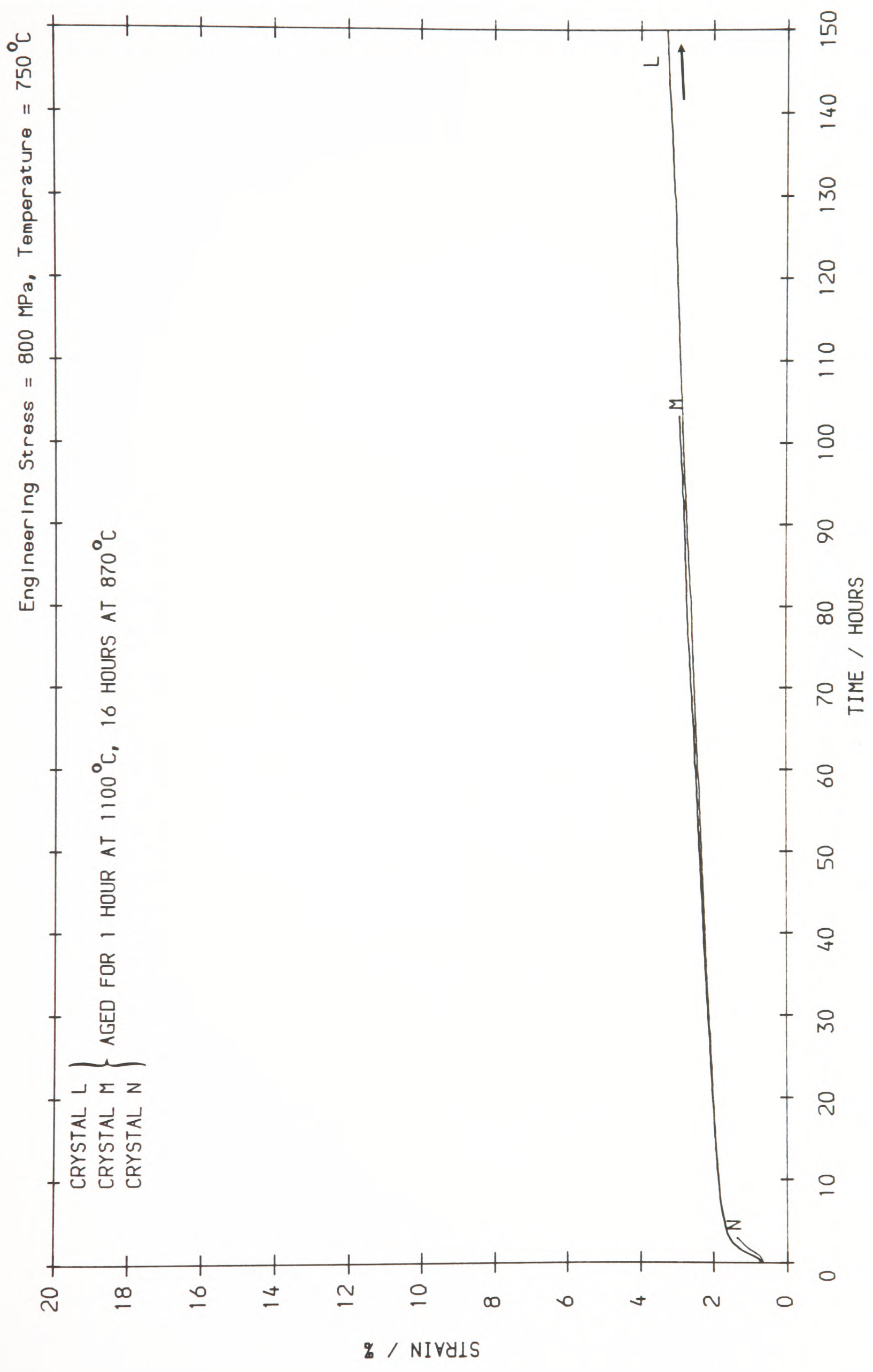


Figure 4.8

The full creep curve to failure for crystal L.

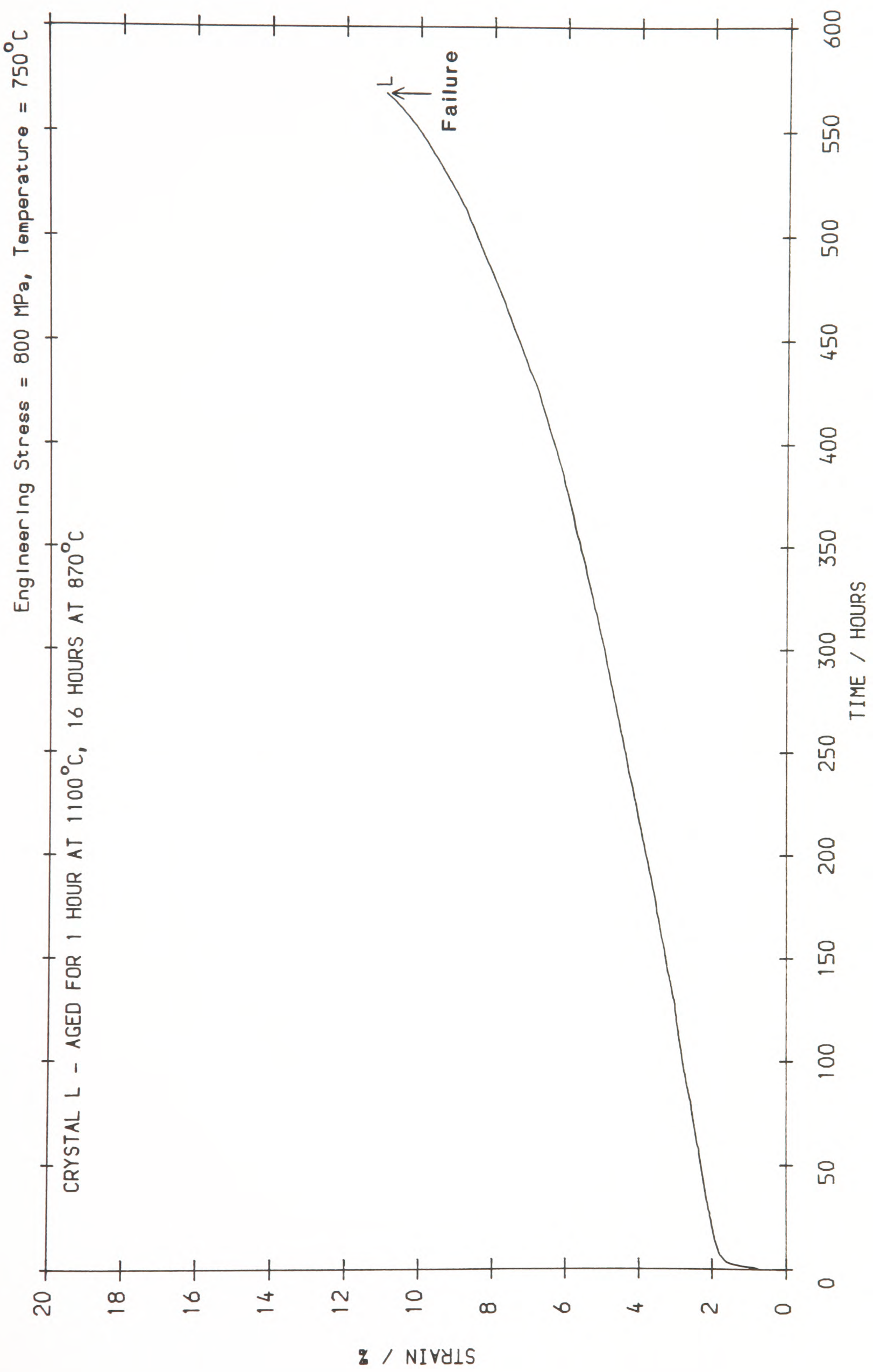


Figure 4.9

Lattice rotation measurements for crystals L-N

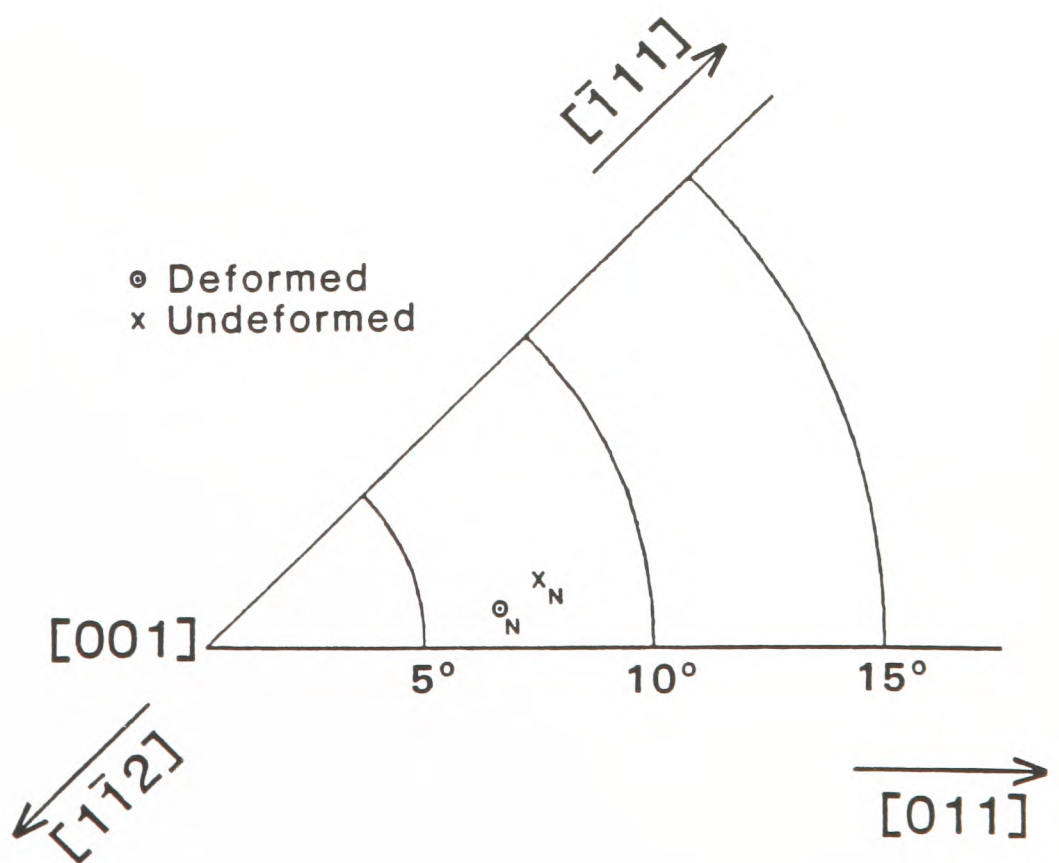
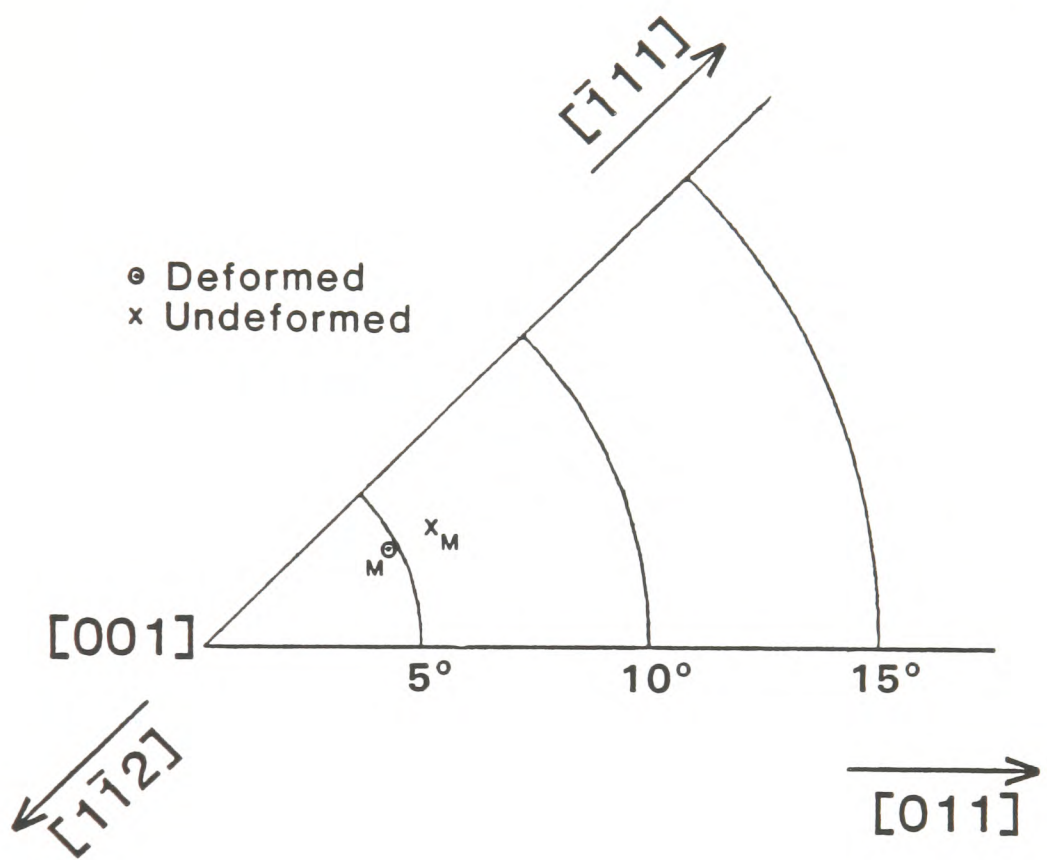
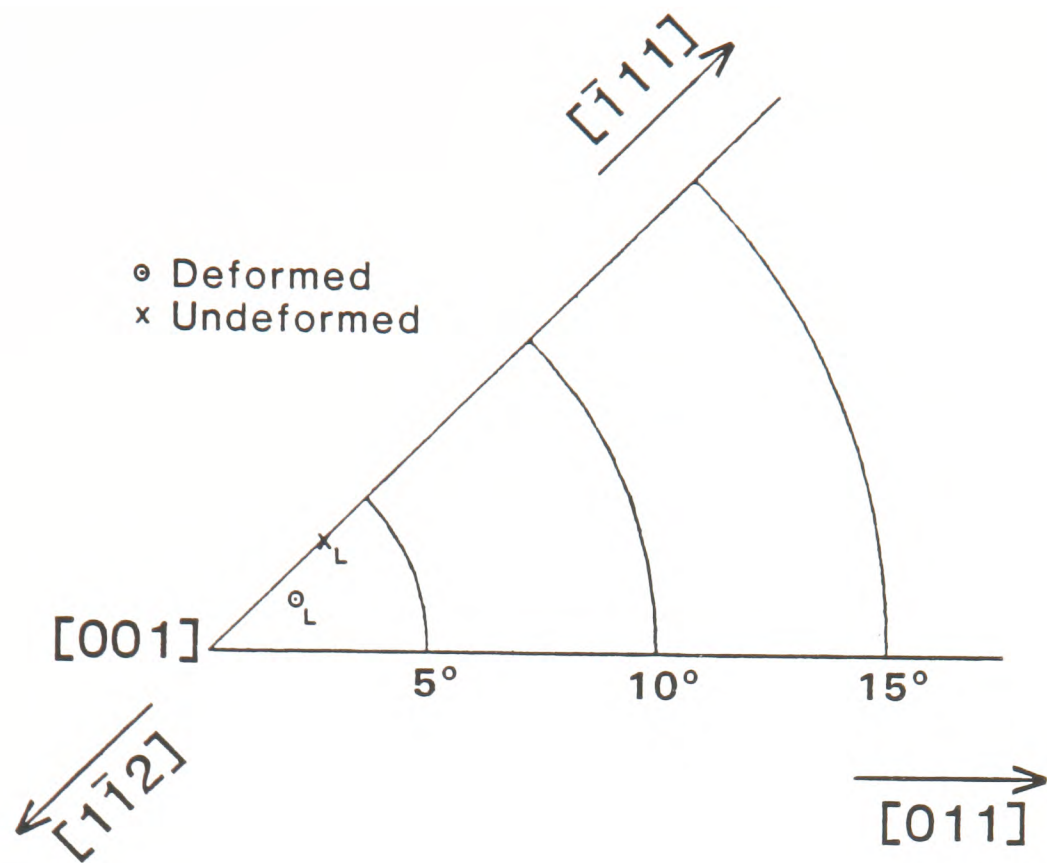


Figure 4.10

Creep curves for crystals 1a and 1b.

Both crystals were cut from the same rod-shaped crystal.

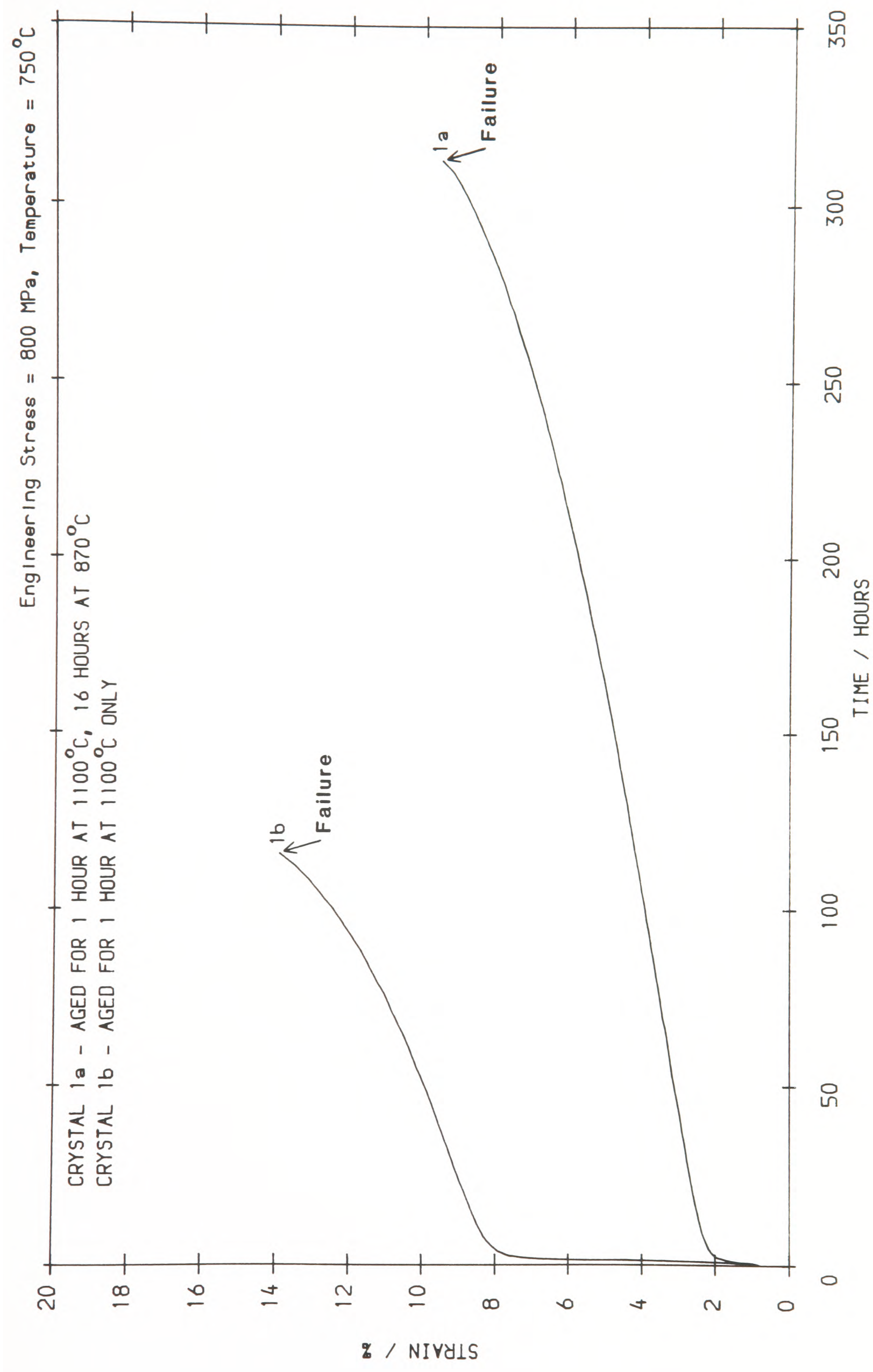


Figure 4.11

Creep curves for crystals 2a and 2b.

Both crystals were cut from the same rod-shaped crystal.

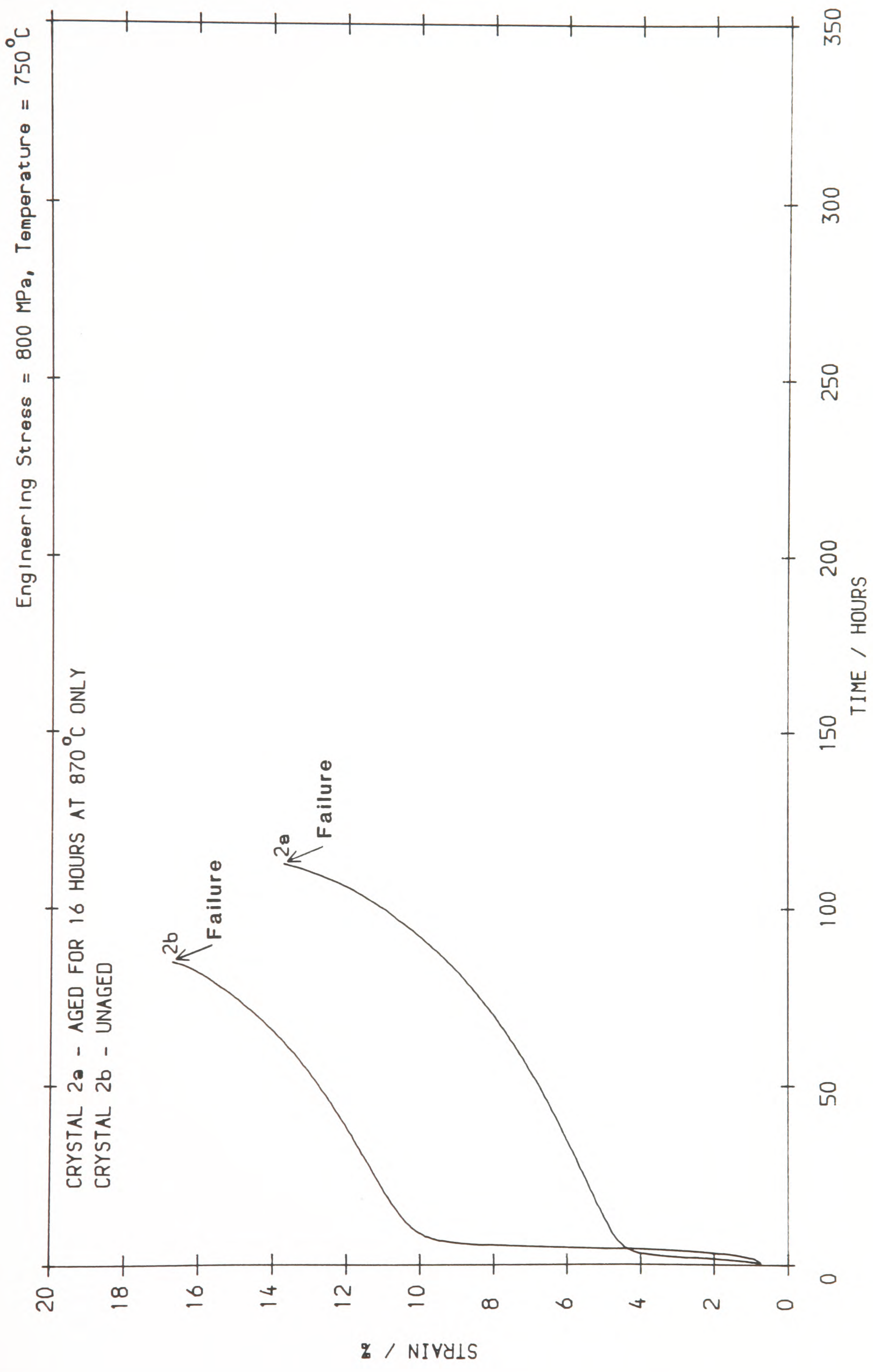


Figure 4.12

Creep curves for crystals 3a and 3b.

Both crystals were cut from the same rod-shaped crystal.

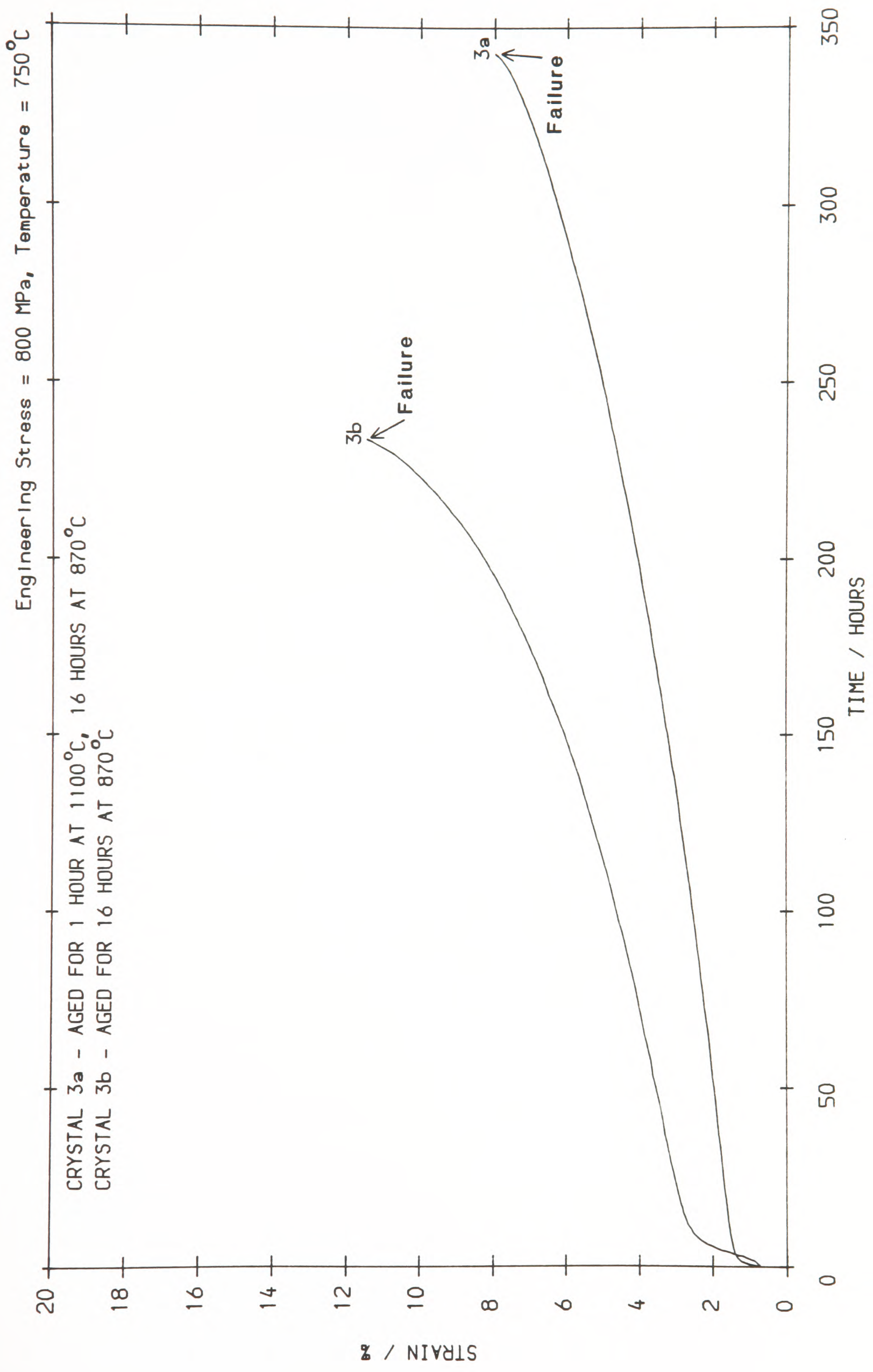


Figure 4.13

Lattice rotation measurements for crystals 1a, 1b, 2a, 2b, 3a and 3b.

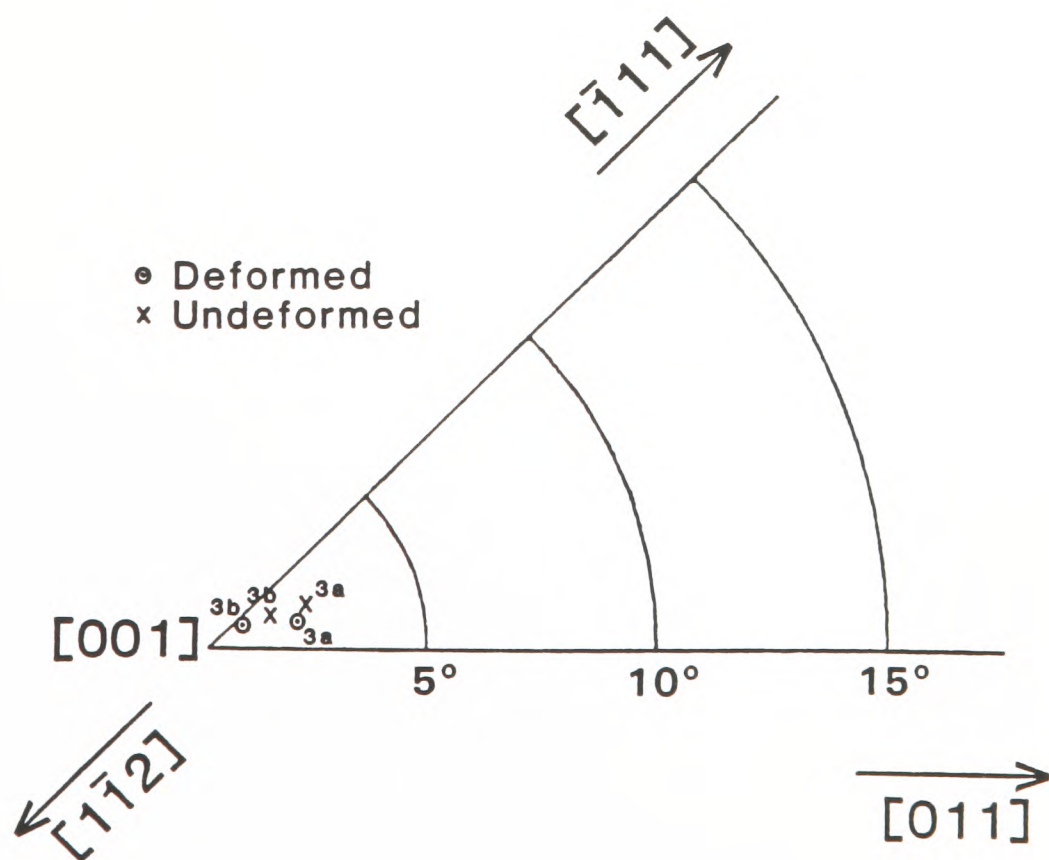
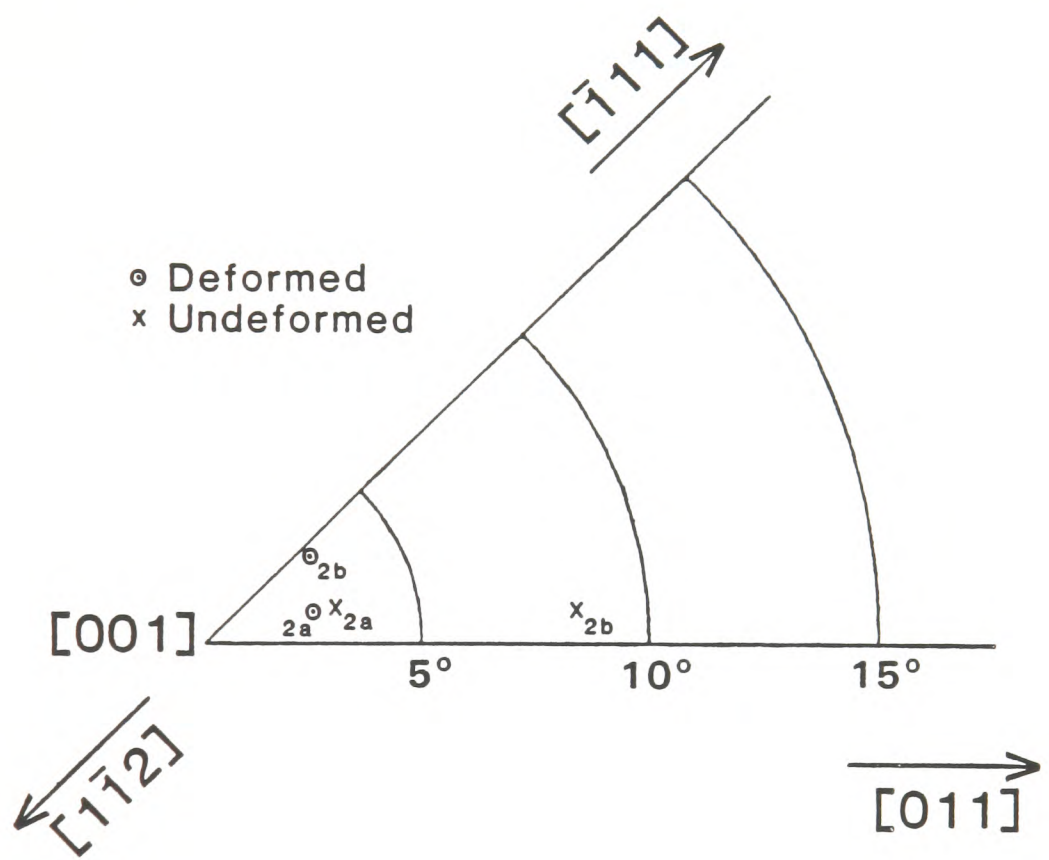
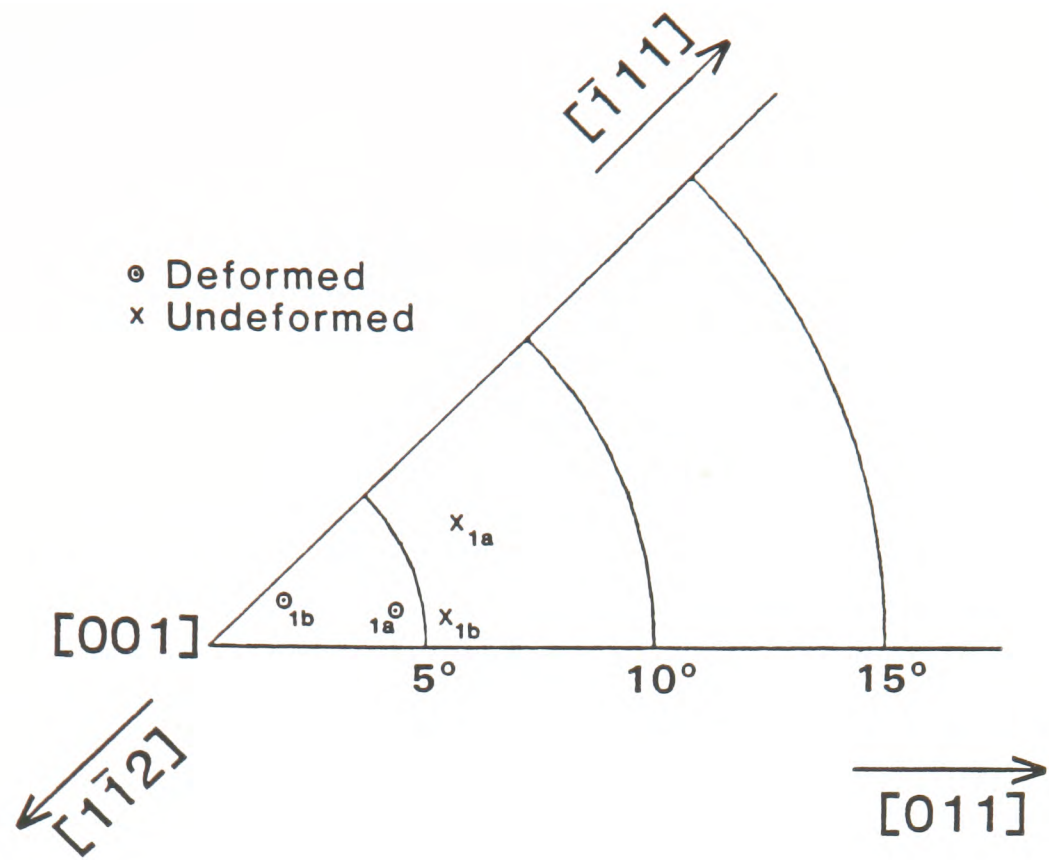


Figure 4.14

Deformation structure occurring during primary creep.

Foil prepared from crystal J (aged for 1 hour at 1100 °C), interrupted after 4.0% primary creep strain.

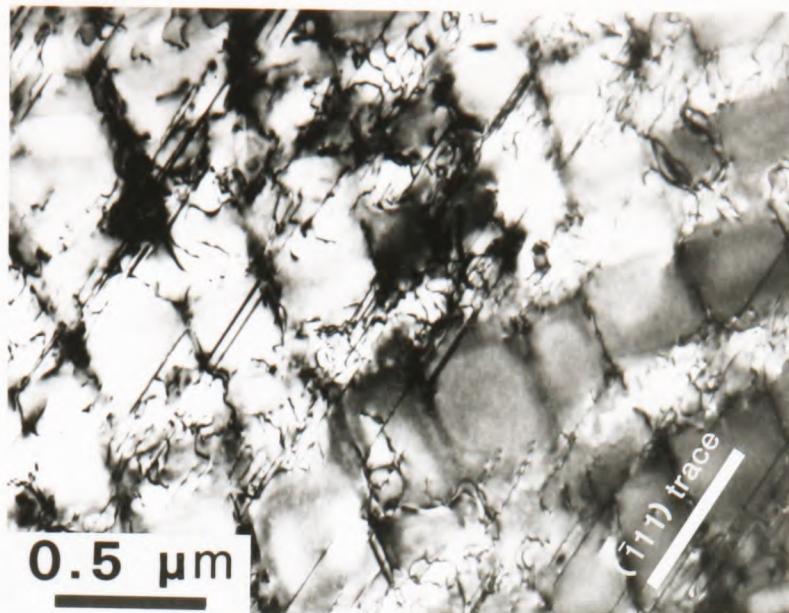
Bright field TEM images.

(a) Electron beam $\approx$ parallel to $[110]$ foil normal.

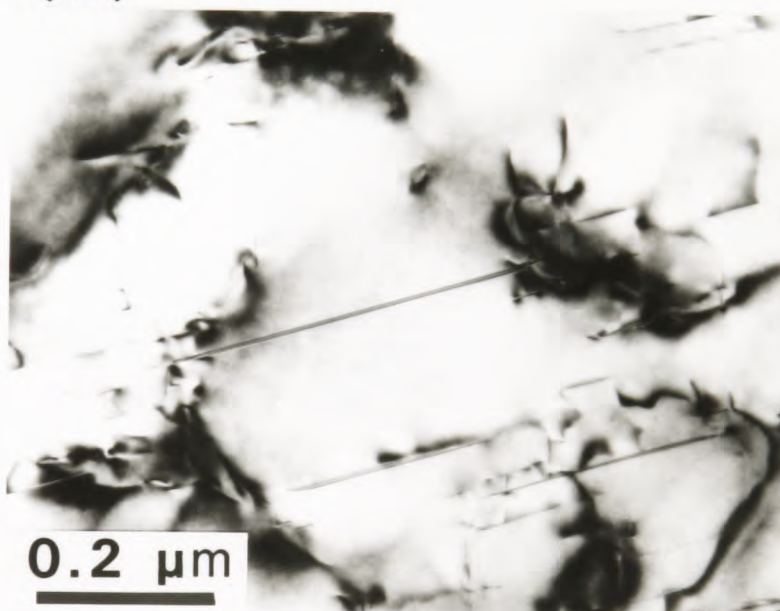
(b) Electron beam $\approx$ parallel to $[110]$ foil normal.

(c) Foil tilted to a $\{111\}$ pole.

(a)



(b)



(c)

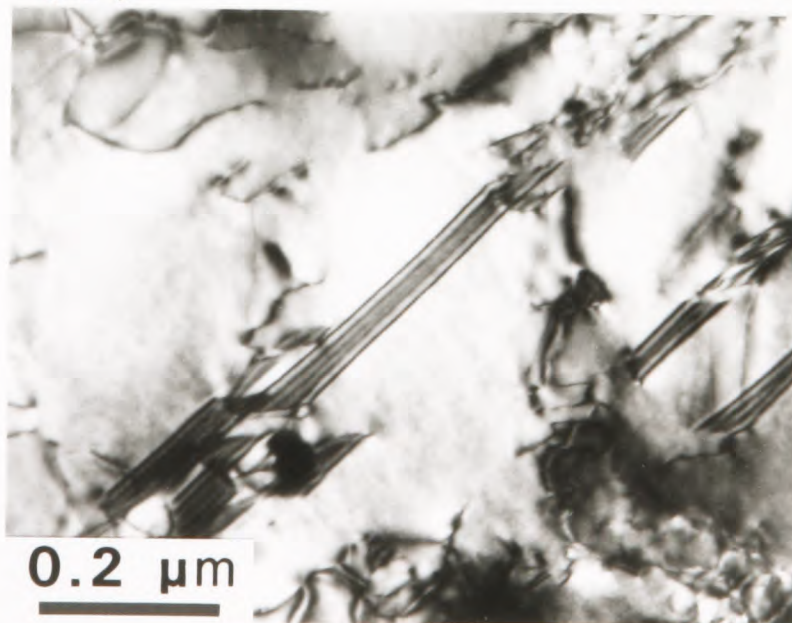


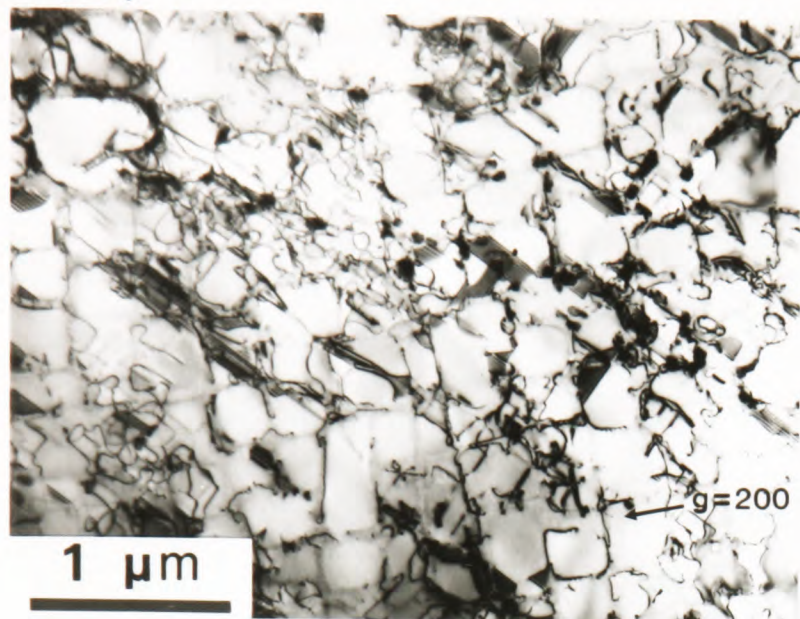
Figure 4.15

Deformation structure occurring at the end of the primary creep stage.
Foil prepared from crystal K (aged for 1 hour at 1100 °C), interrupted
after 2.3% creep strain.
Bright field TEM images. Foil normal parallel to [001] stress axis.

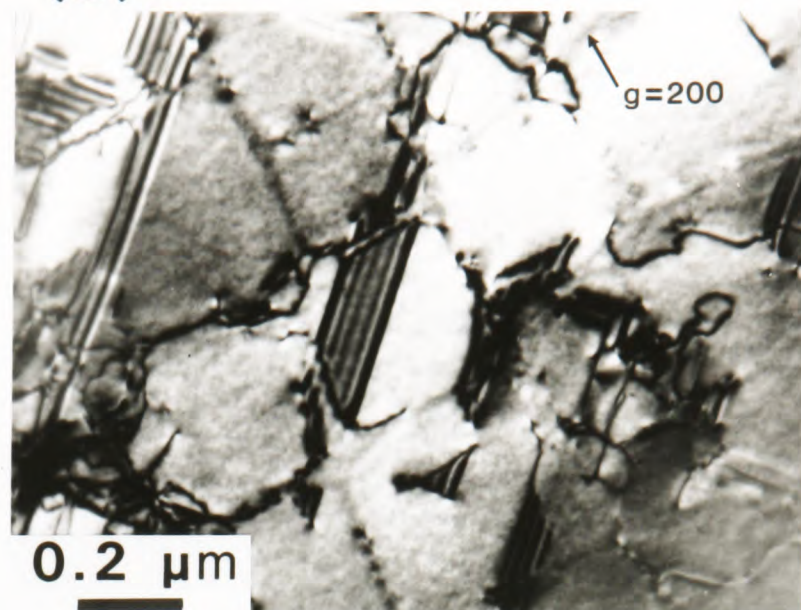
Figure 4.16

Deformation structure occurring during secondary creep.
Foil prepared from crystal F (aged for 1 hour at 1100 °C), interrupted
after 5.6% total creep strain.
Bright field TEM images. Foil normal parallel to [001] stress axis.

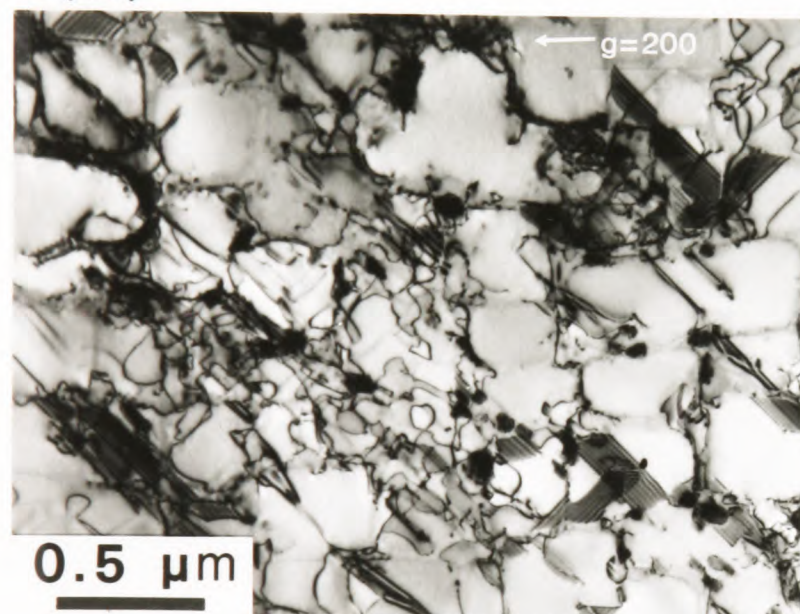
(a)



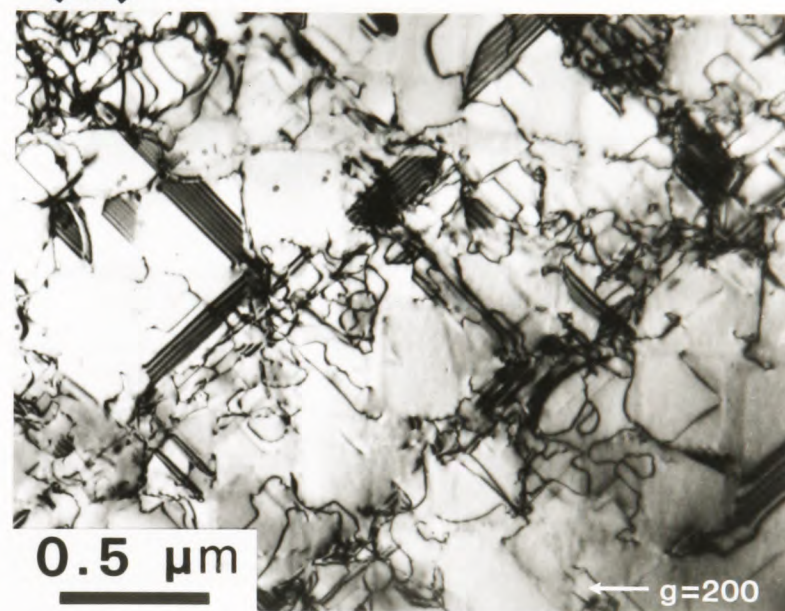
(b)



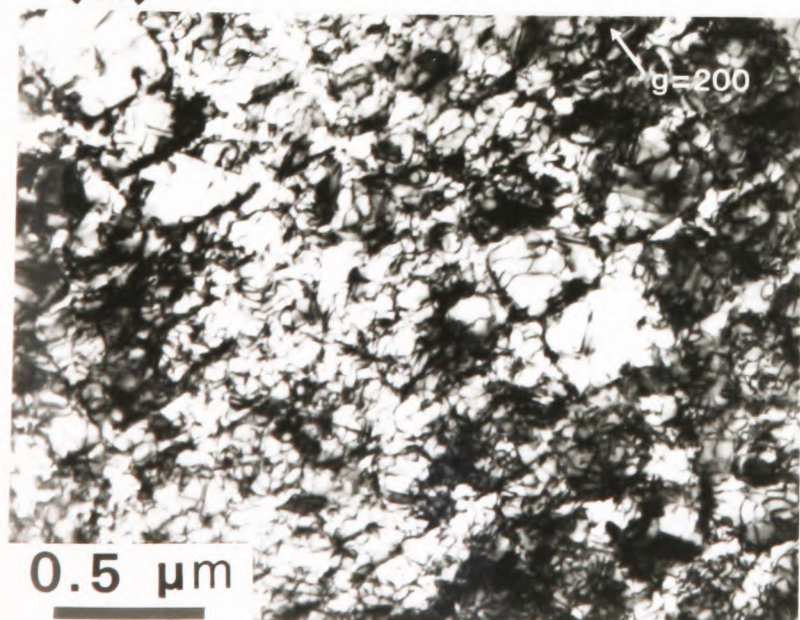
(c)



(d)



(a)



(b)

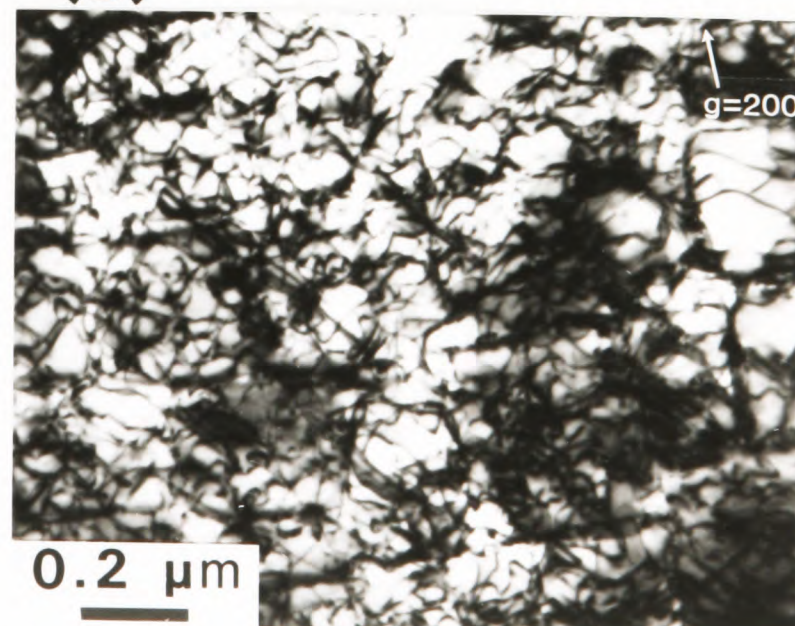


Figure 4.17

Deformation structure occurring during primary creep.

Foil prepared from crystal N (aged for 1 hour at 1100 °C and 16 hours at 870 °C), interrupted after 0.7% primary creep strain.

Bright field TEM images. Foil normal parallel to [001] stress axis.

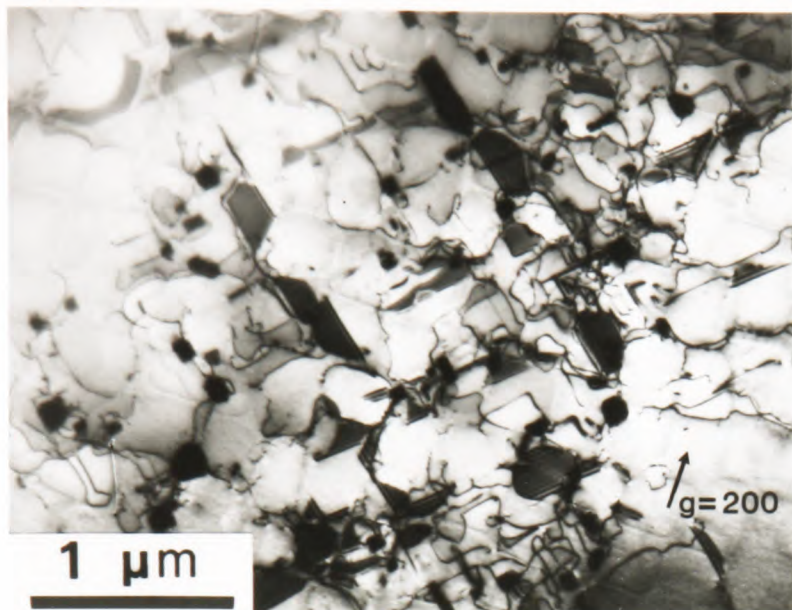
Figure 4.18

Deformation structure occurring during secondary creep.

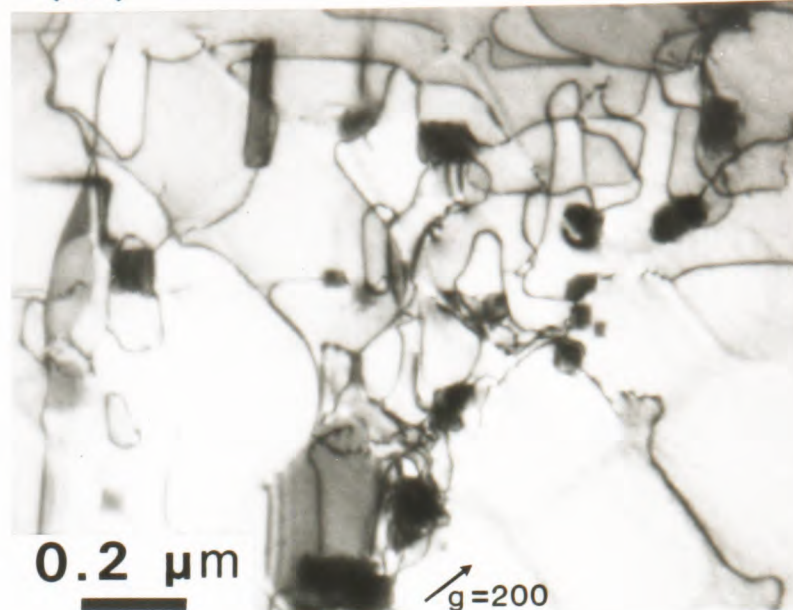
Foil prepared from crystal M (aged for 1 hour at 1100 °C and 16 hours at 870 °C), interrupted after 2.2% total creep strain.

Bright field TEM images. Foil normal parallel to [001] stress axis.

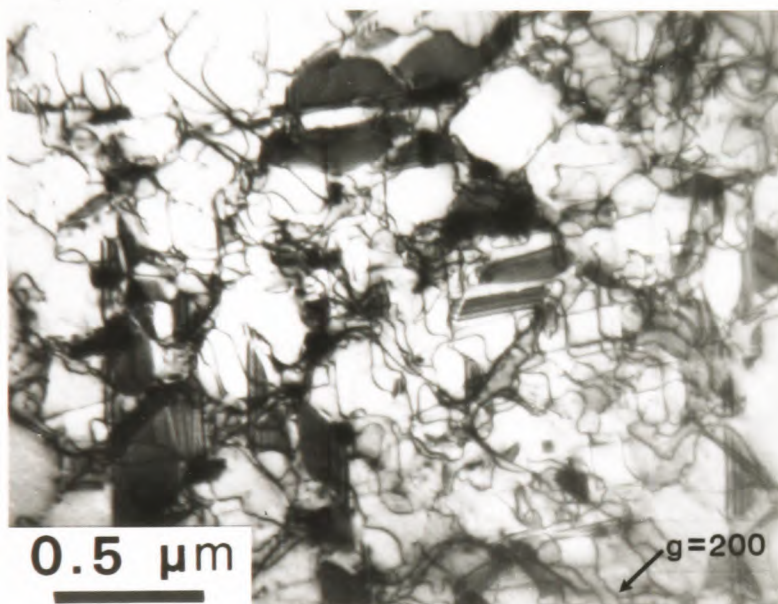
(a)



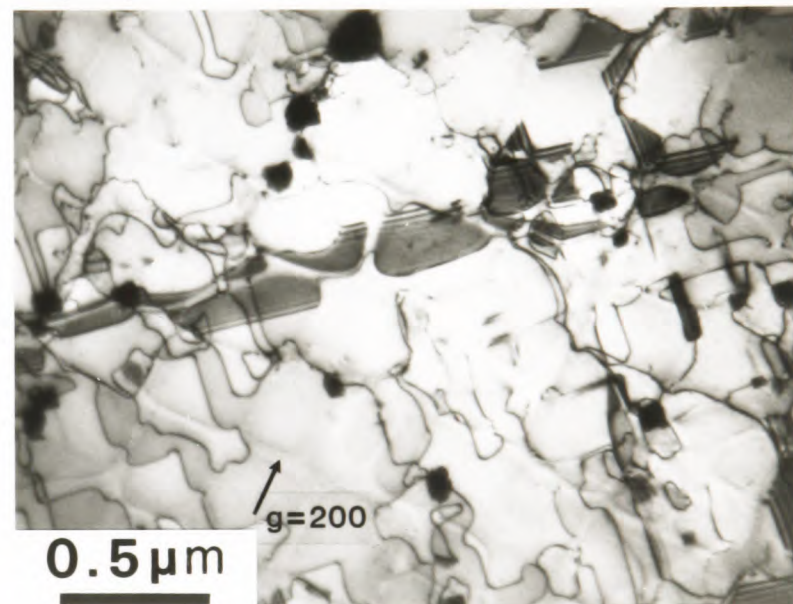
(b)



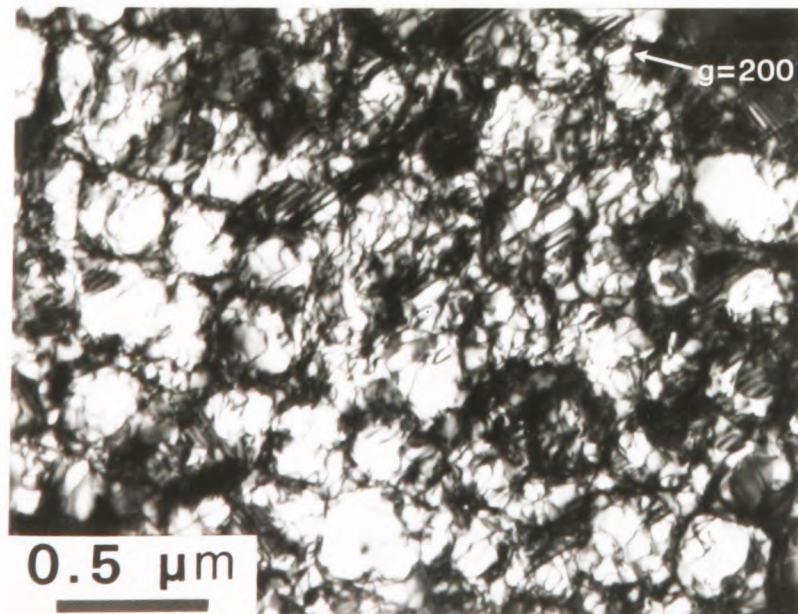
(c)



(d)



(a)



(b)

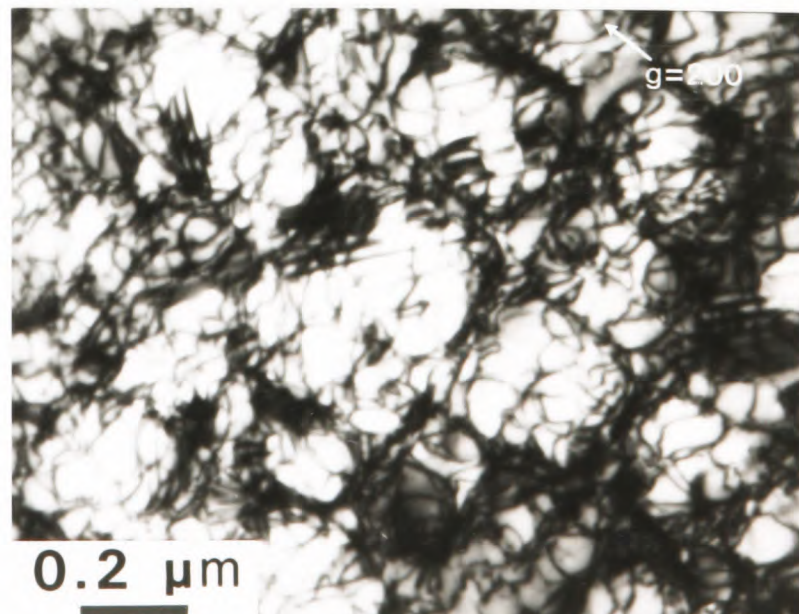


Figure 4.19

Dark field TEM images produced using a {300} superlattice reflection.

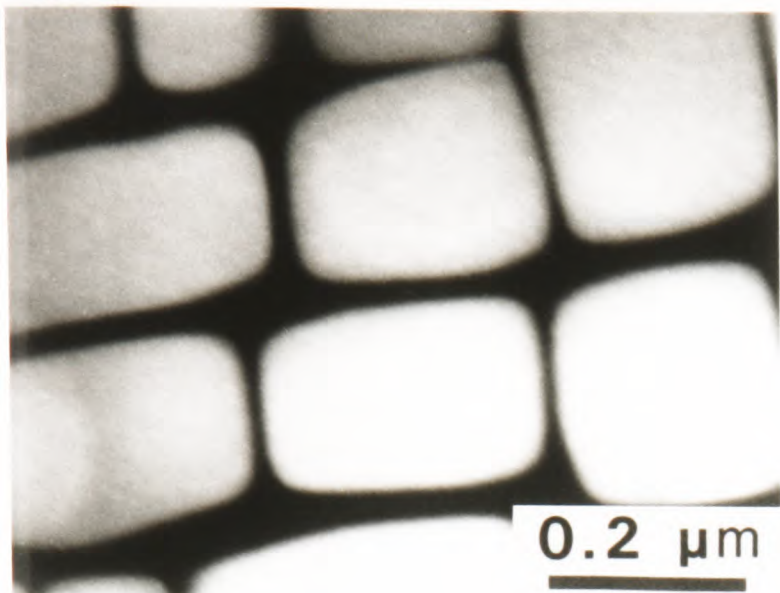
- (a) Before testing
 - (b) After testing
 - (c) Before testing
 - (d) After testing
- } Aged for 1 hour at 1100 °C
- } Aged for 1 hour at 1100 °C
and 16 hours at 870 °C

Figure 4.20

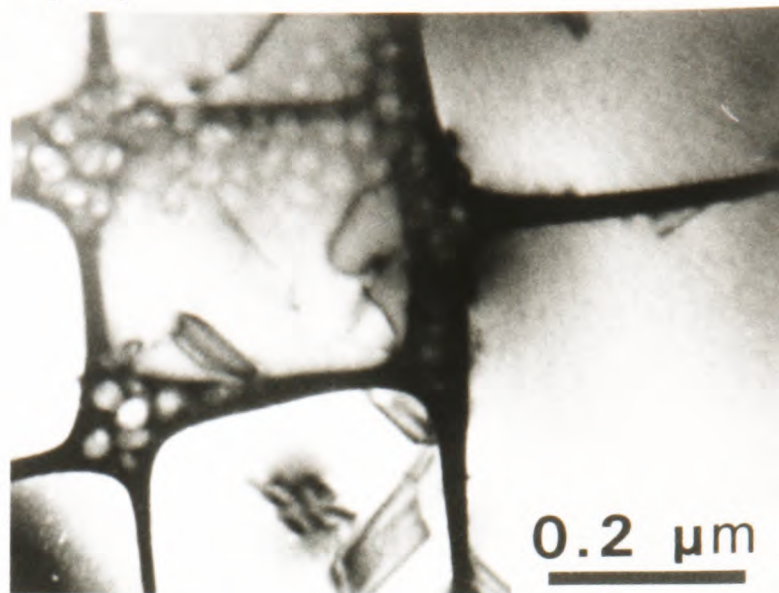
A typical FIM/atom probe specimen.

(Dark field TEM image produced using a {300} superlattice reflection.)

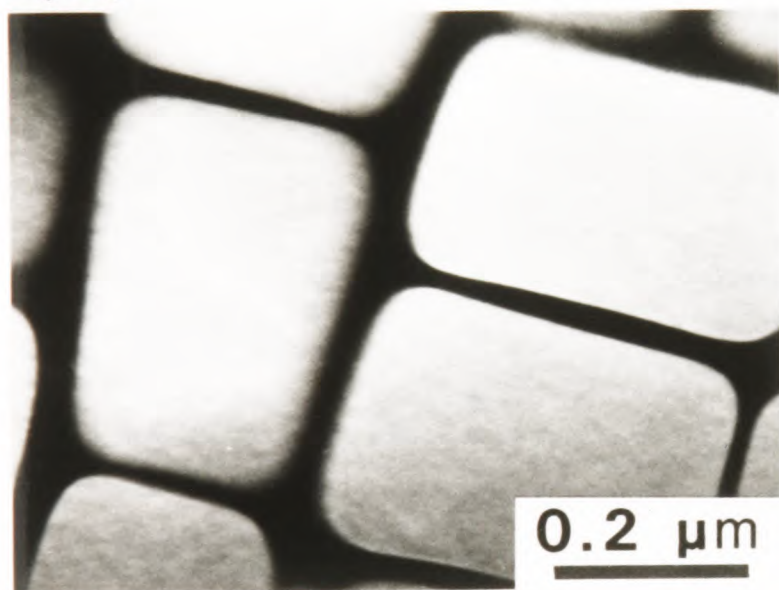
(a)



(b)



(c)



(d)

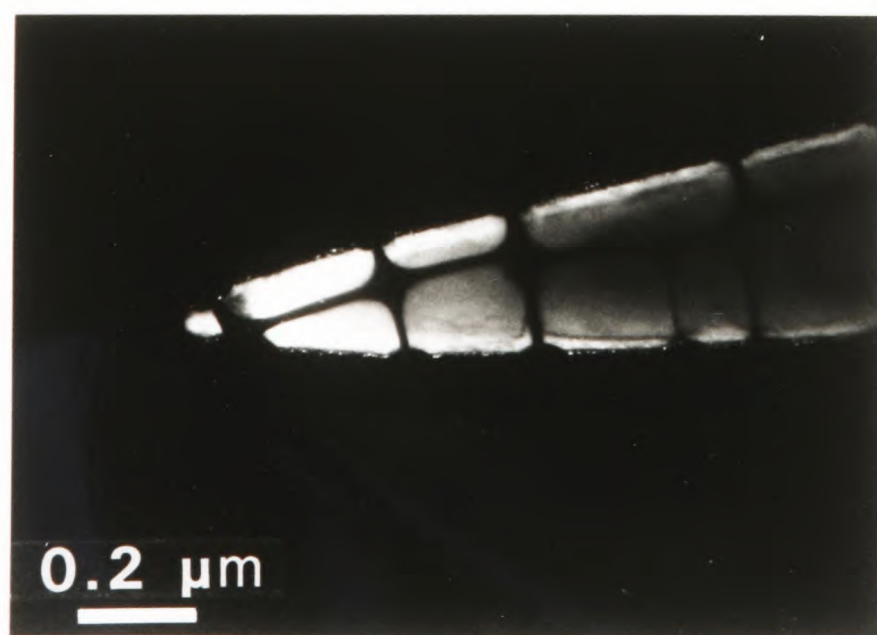
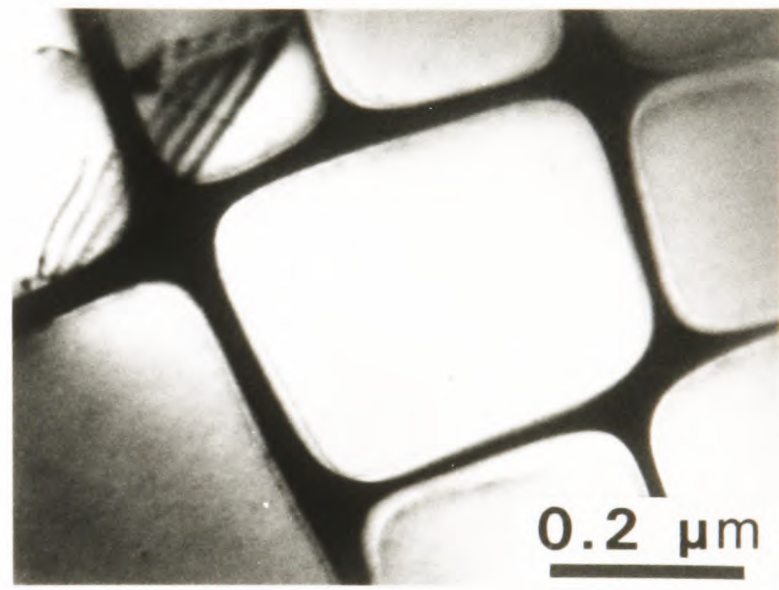


Figure 4.21(a)

m/n_e spectrum for the γ' phase.

Specimen aged for 1 hour at 1100 °C and 16 hours at 870 °C.

GAMMA-PRIME: SOLN, 1HR. 1100°C, 16HR. 870°C

COMBINED MASS SPECTRUM

8672 IONS

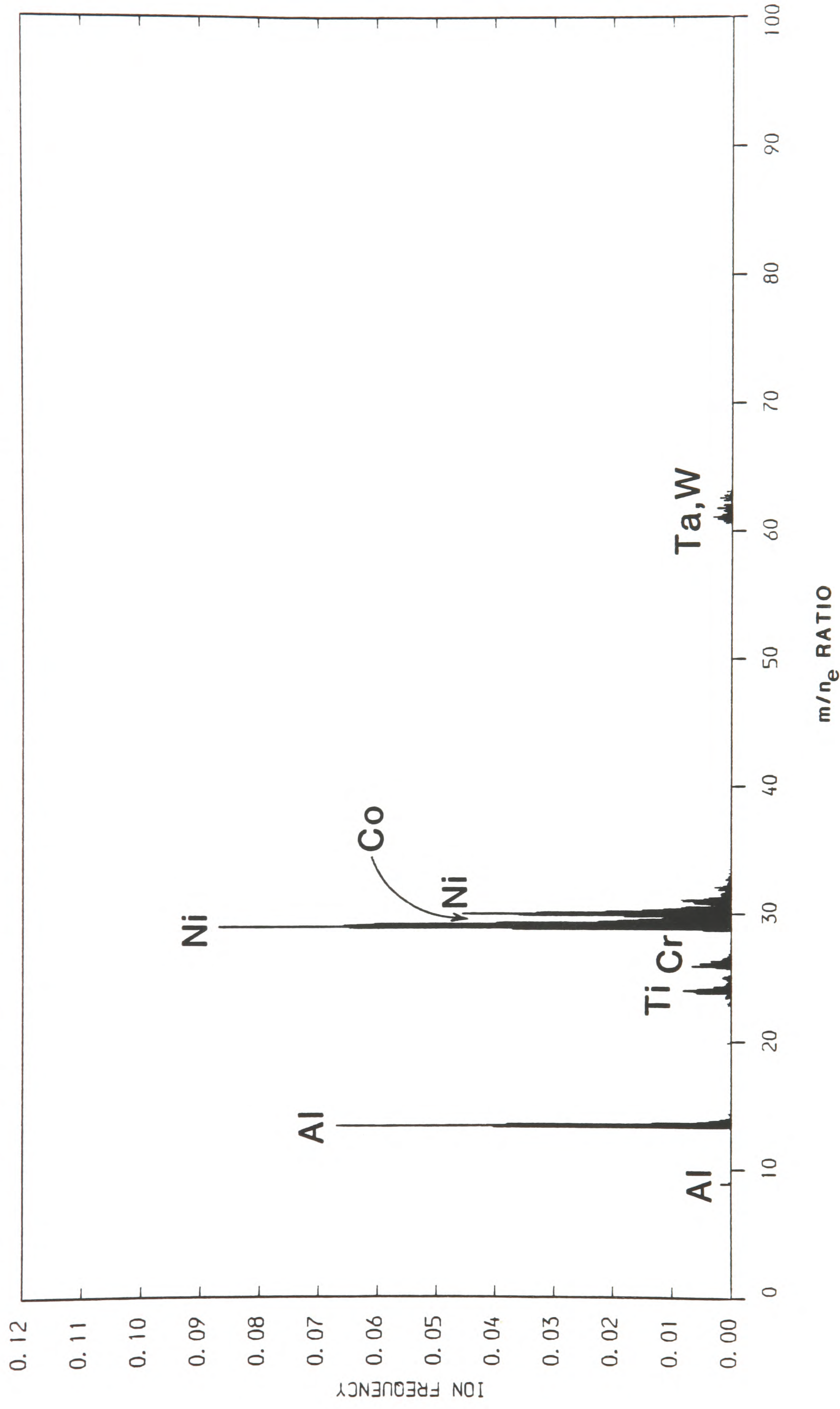


Figure 4.21(b)

m/n_e spectrum for the γ phase.

Specimen aged for 1 hour at 1100 °C and 16 hours at 870 °C.

GAMMA: SOLN, 1HR, 1100°C, 16HR, 870°C

COMBINED MASS SPECTRUM

2002 IONS

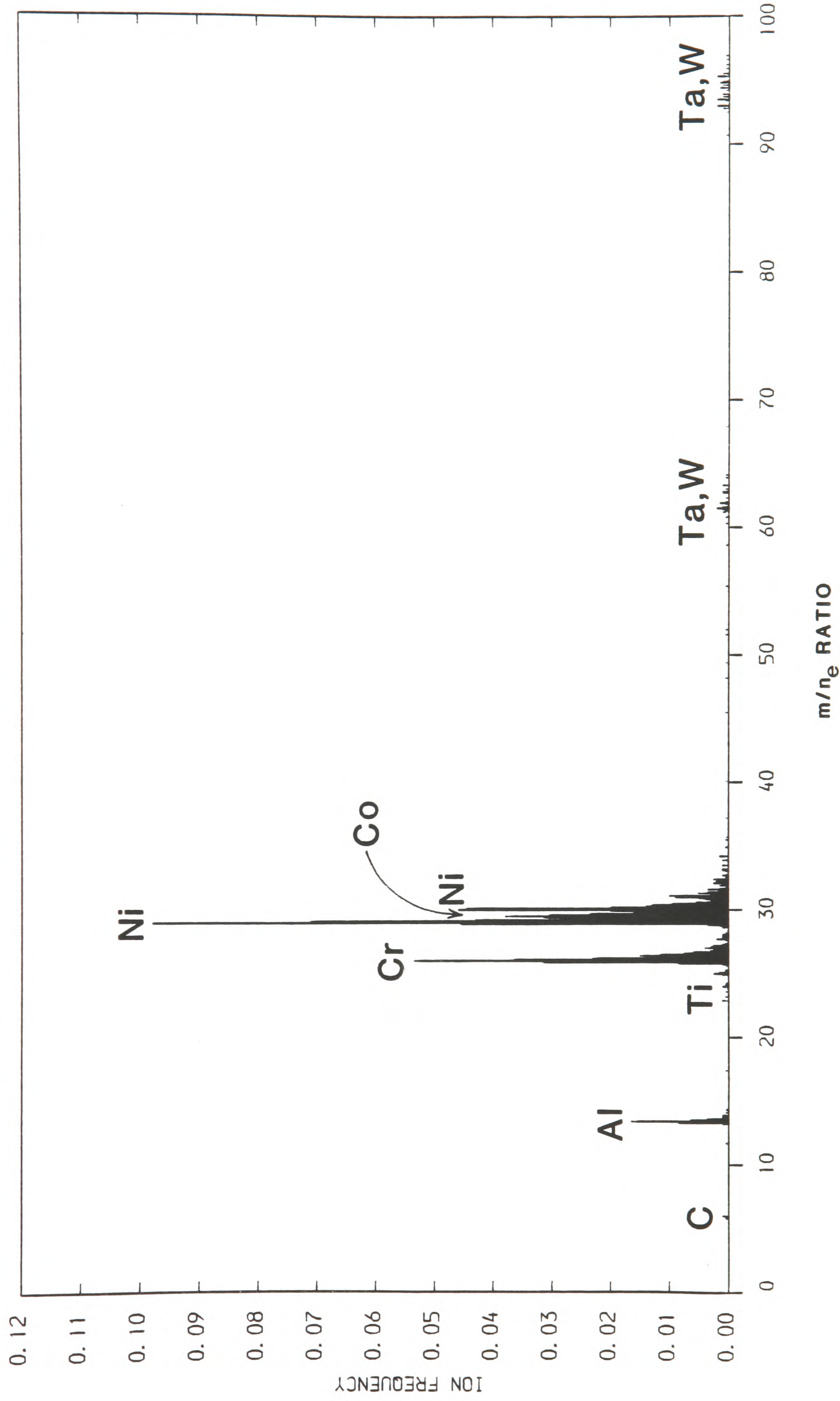


Figure 4.22(a)

m/n_e spectrum for the γ' phase.

Specimen aged for 1 hour at 1100 °C.

GAMMA-PRIME: SOLN, 1HR. 1100°C ONLY

COMBINED MASS SPECTRUM

9329 IONS

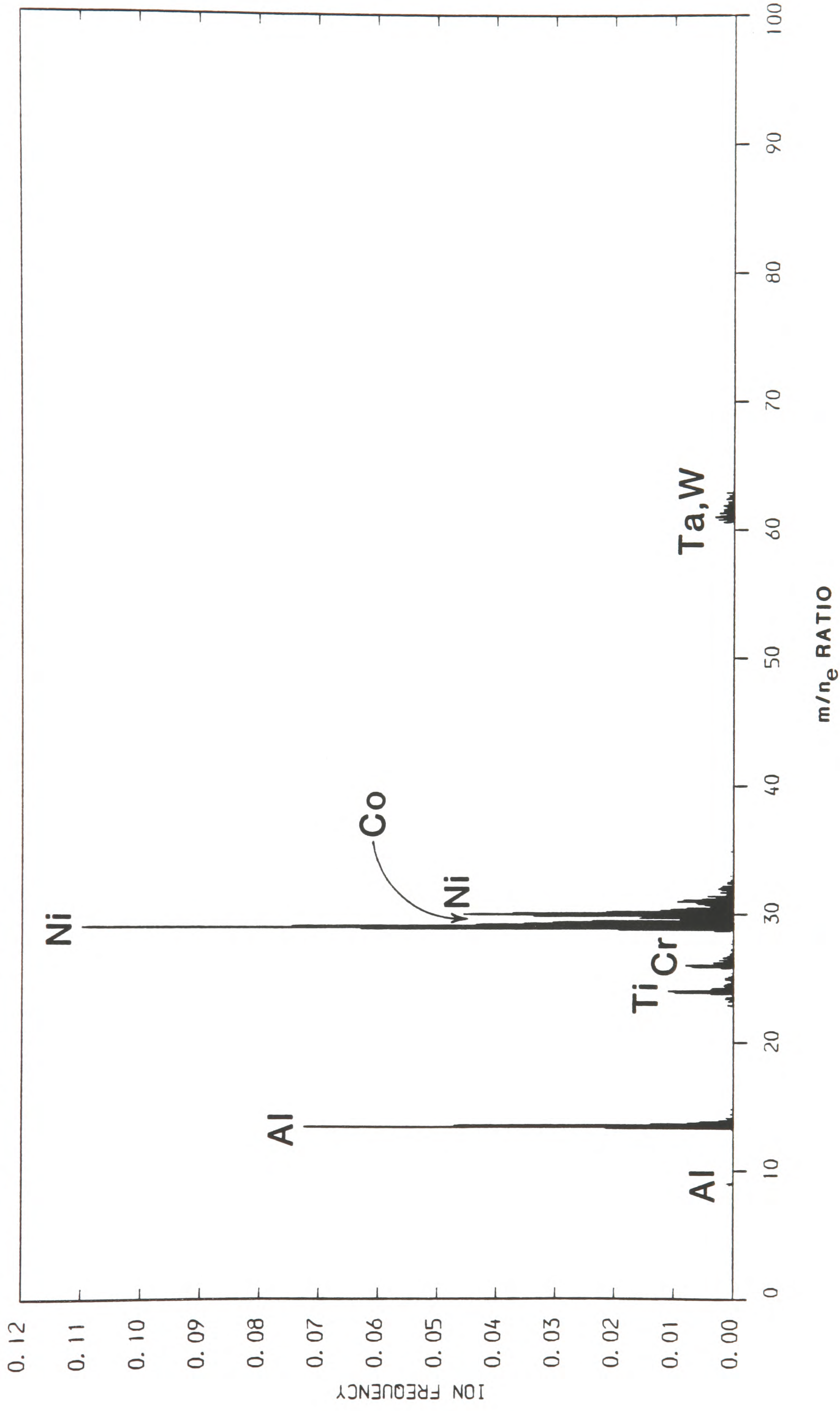


Figure 4.22(b)

m/n_e spectrum for the γ phase.

Specimen aged for 1 hour at 1100 °C.

GAMMA: SOLN, 1HR. 1100°C ONLY

COMBINED MASS SPECTRUM

9617 IONS

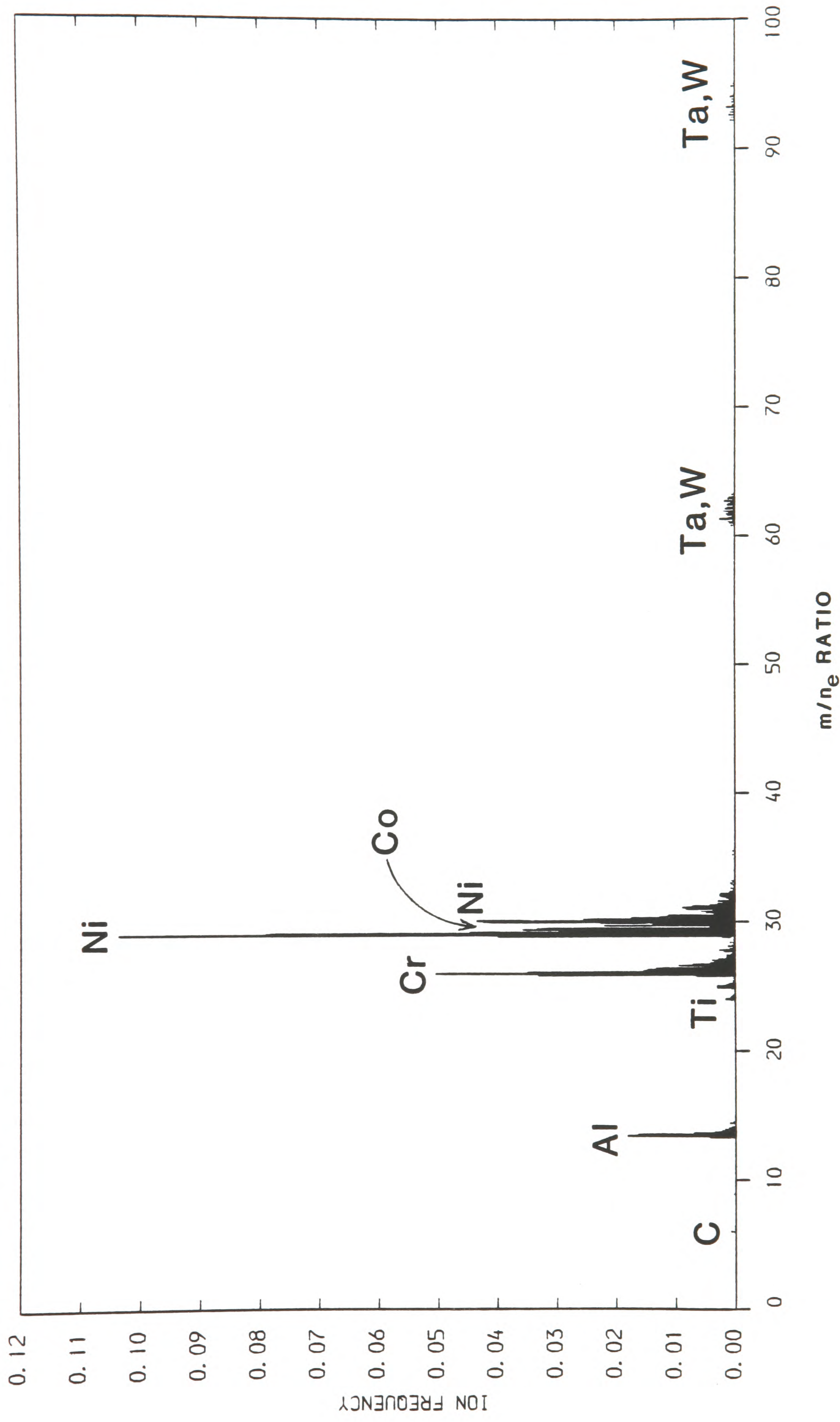


Figure 4.23(a)

m/n_e spectrum for the γ' phase.

Specimen aged for 10 minutes at 1100 °C.

GAMMA-PRIME: SOLN, 10 MINS, 1100°C

COMBINED MASS SPECTRUM

24310 IONS

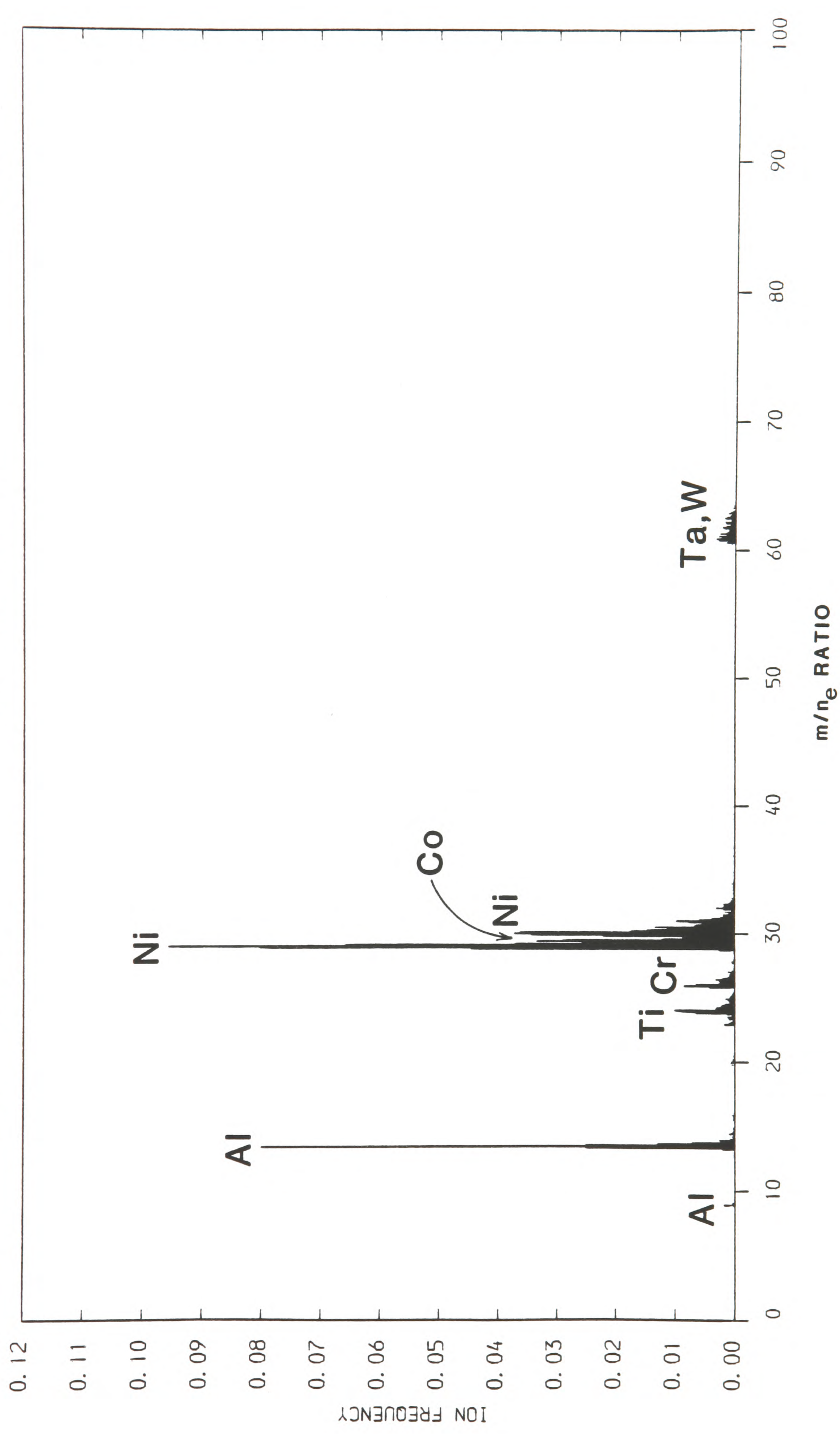


Figure 4.23(b)

m/n_e spectrum for the γ phase.

Specimen aged for 10 minutes at 1100 °C.

GAMMA: SOLN, 10 MINS. 1100°C

COMBINED MASS SPECTRUM

1656 IONS

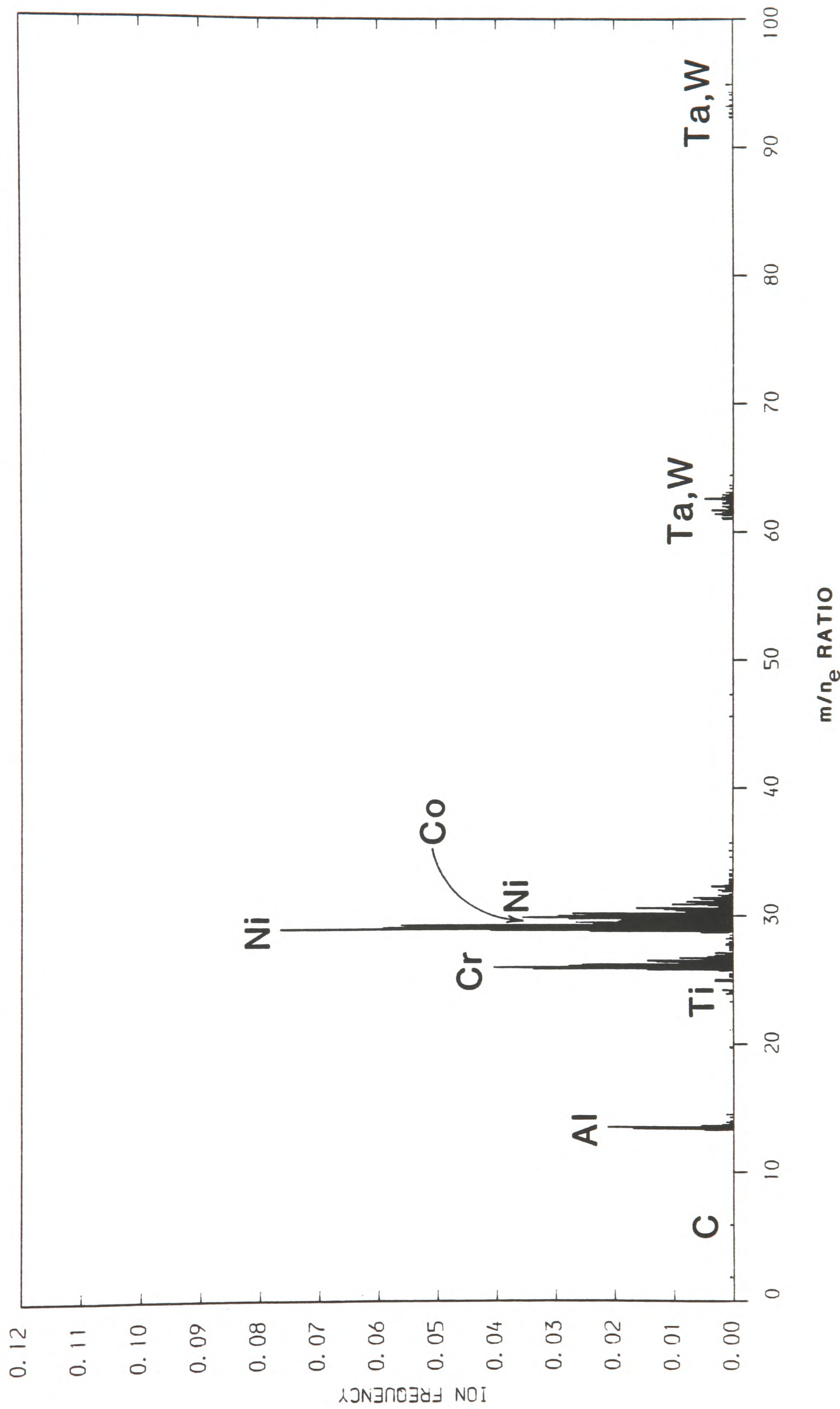
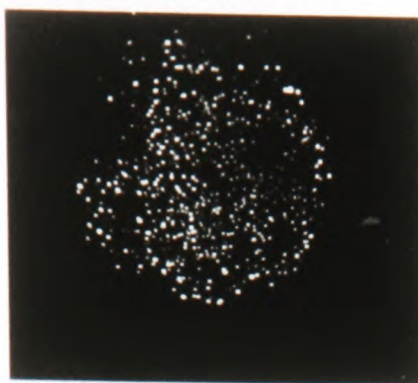


Figure 4.24

Field evaporation sequence through five phase interfaces.

Interface 1: $\gamma' \rightarrow \gamma$	- Aged for 1 hour at 1100 °C, 16 hours at 870 °C.
Interface 2: $\gamma' \rightarrow \gamma$	- Aged for 1 hour at 1100 °C.
Interface 3: $\gamma \rightarrow \gamma'$	
Interface 4: $\gamma' \rightarrow \gamma$	- Aged for 10 minutes at 1100 °C.
Interface 5: $\gamma \rightarrow \gamma'$	

Interface 1:



9.40 kV
Analysing γ'

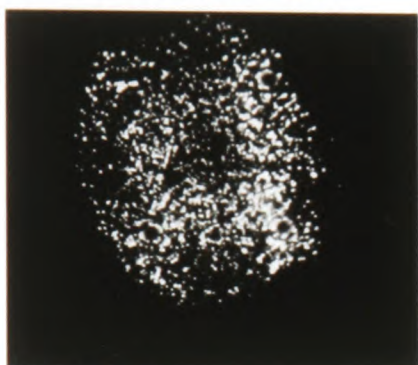


9.73 kV
Analysing γ

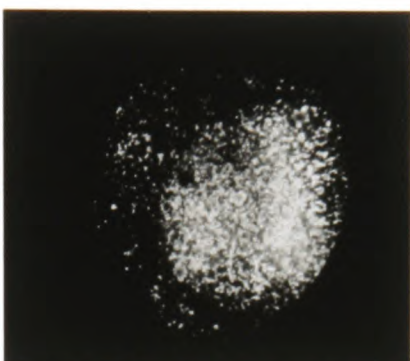


12.50 kV
Analysing γ

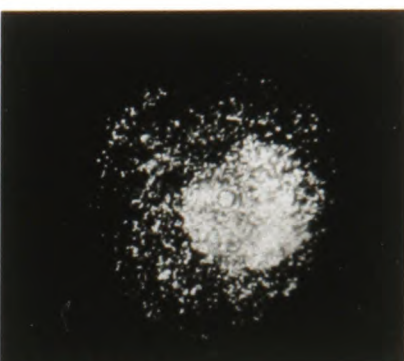
Interface 2:



12.55 kV
Analysing γ'

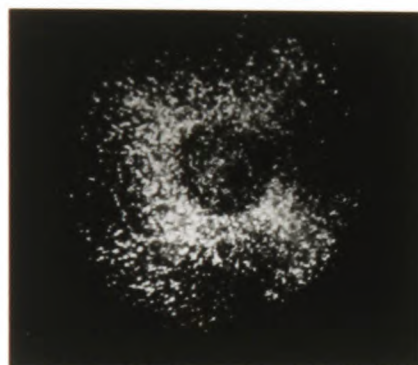


14.75 kV (Specimen tilted)
Analysing γ'

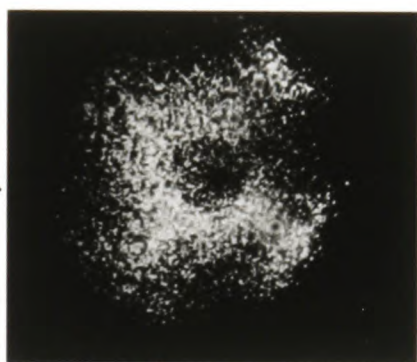


15.25 kV
Analysing γ

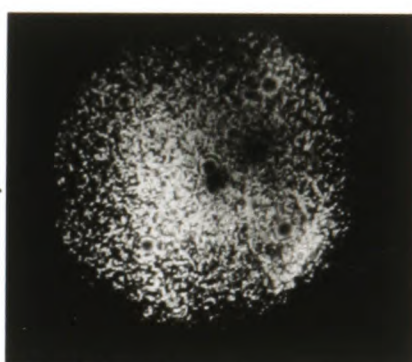
Interface 3:



17.50 kV
Analysing γ

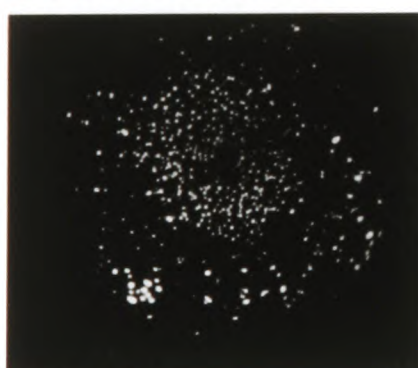


17.75 kV
Analysing γ



18.60 kV
Analysing γ'

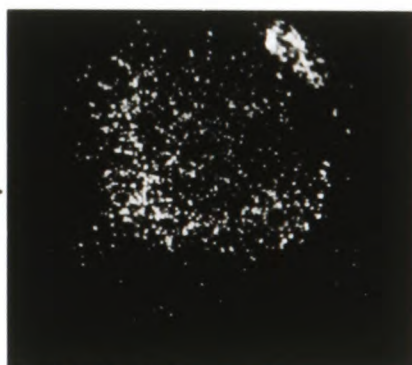
Interface 4:



8.91 kV
Analysing γ'

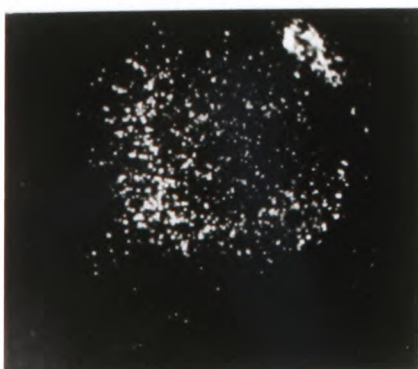


10.00 kV
Analysing γ'

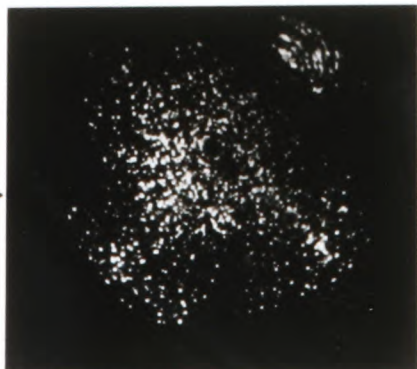


10.80 kV
Analysing γ

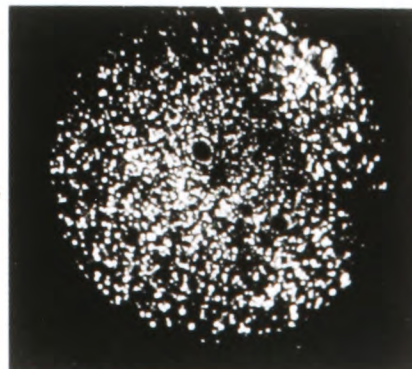
Interface 5:



10.80 kV
Analysing γ



11.25 kV
Analysing γ'



12.75 kV
Analysing γ'

Figure 4.25

Composition profile through interface 1.

$\gamma' \rightarrow \gamma$.

Aged for 1 hour at 1100 °C, 16 hours at 870 °C.

Compositions calculated from 8 sets of 50 ions.

At the interface, $V_0 = 8.50$ kV and $V_p = 2.13$ kV.

INTERFACE 1 AGED 1 HOUR 1100°C, 16 HOURS 870°C IROUND= 8 NISSET= 50 4255 IONS

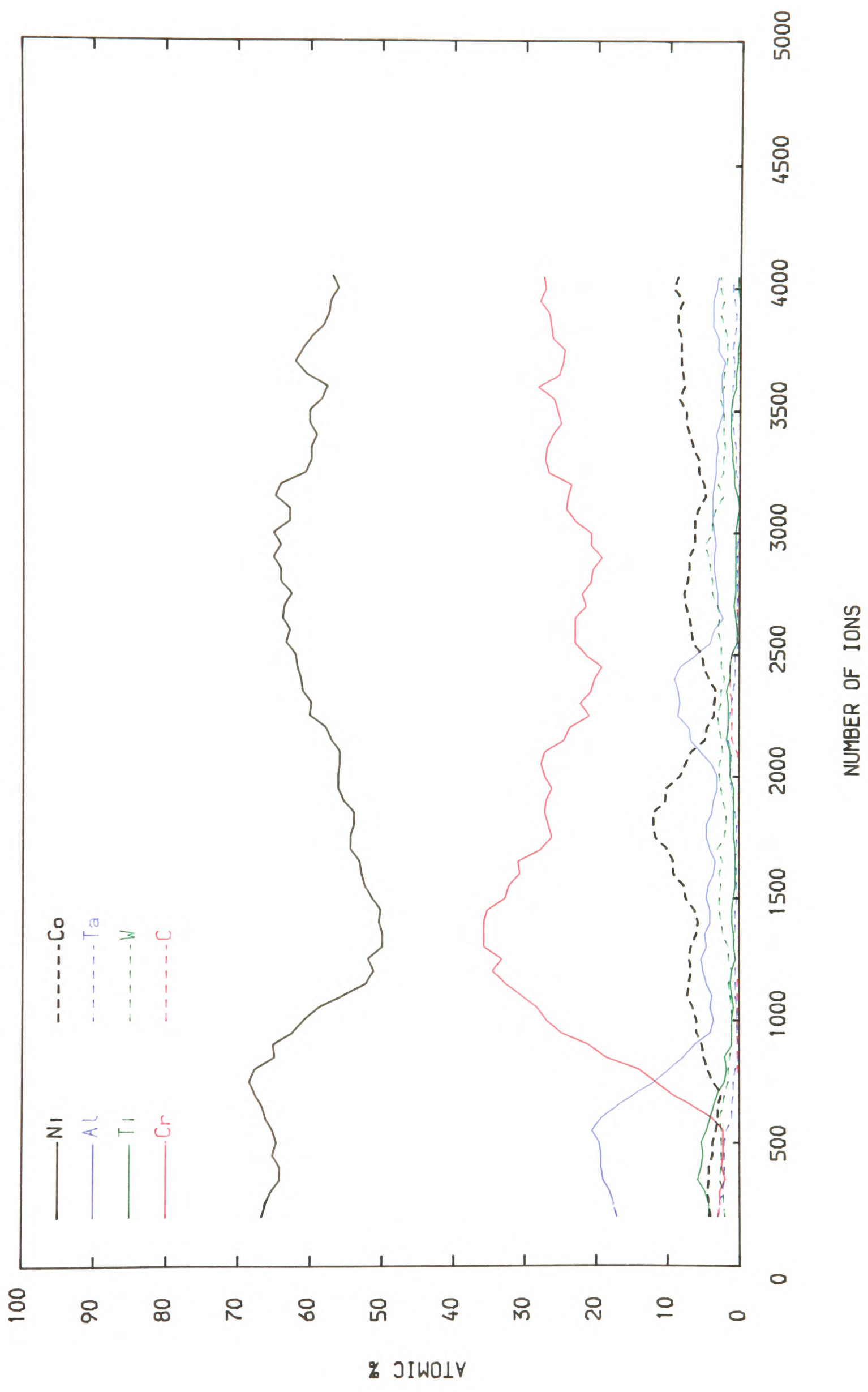


Figure 4.26

Composition profile through interface 2.

$\gamma' \rightarrow \gamma$.

Aged for 1 hour at 1100 °C.

Compositions calculated from 8 sets of 50 ions.

At the interface, $V_0 = 15.25$ kV and $V_p = 3.81$ kV.

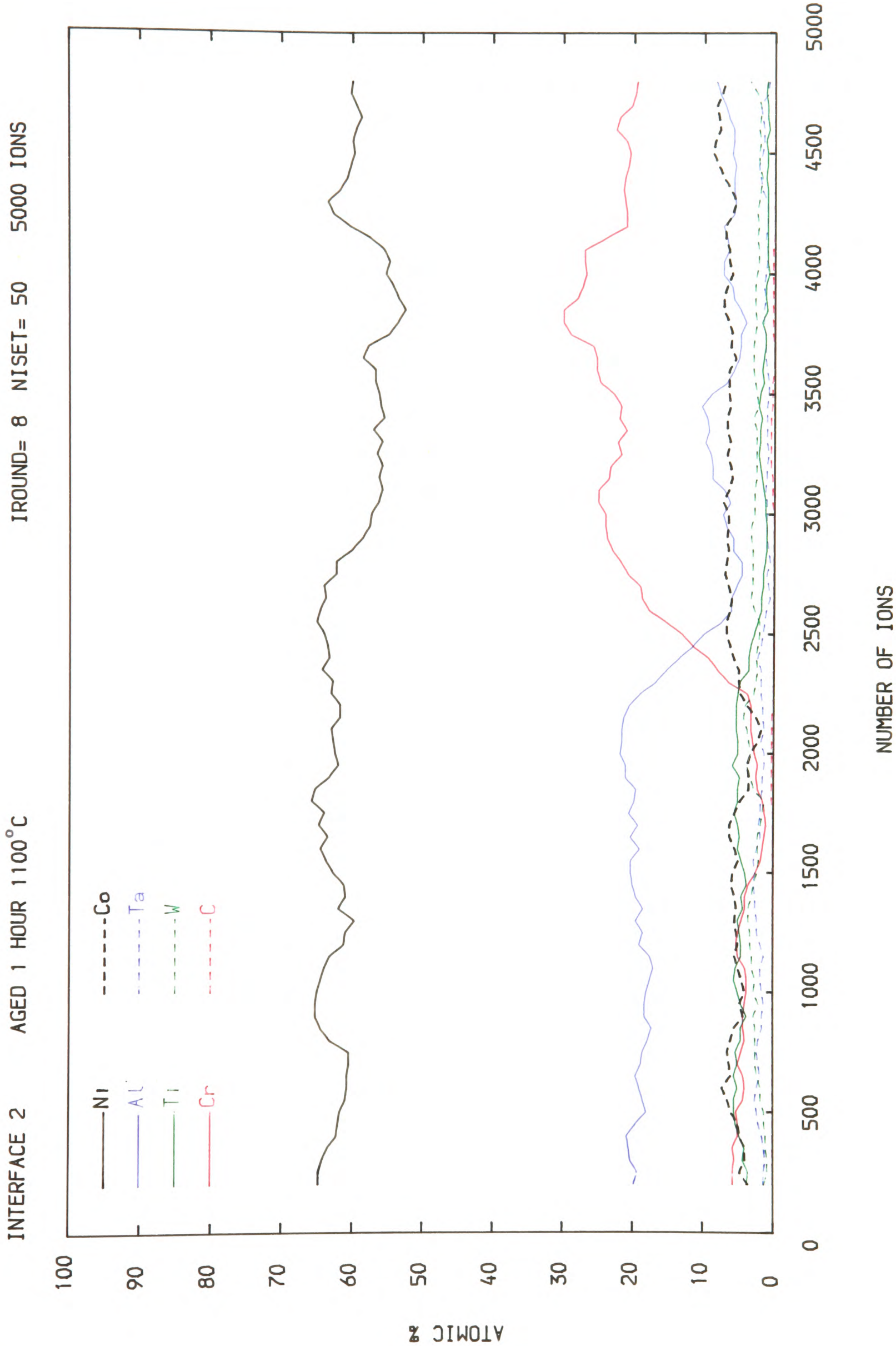


Figure 4.27

Composition profile through interface 3.

$\gamma \rightarrow \gamma'$.

Aged for 1 hour at 1100 °C.

Compositions calculated from 8 sets of 50 ions.

At the interface, $V_0 = 16.75$ kV and $V_p = 4.19$ kV.

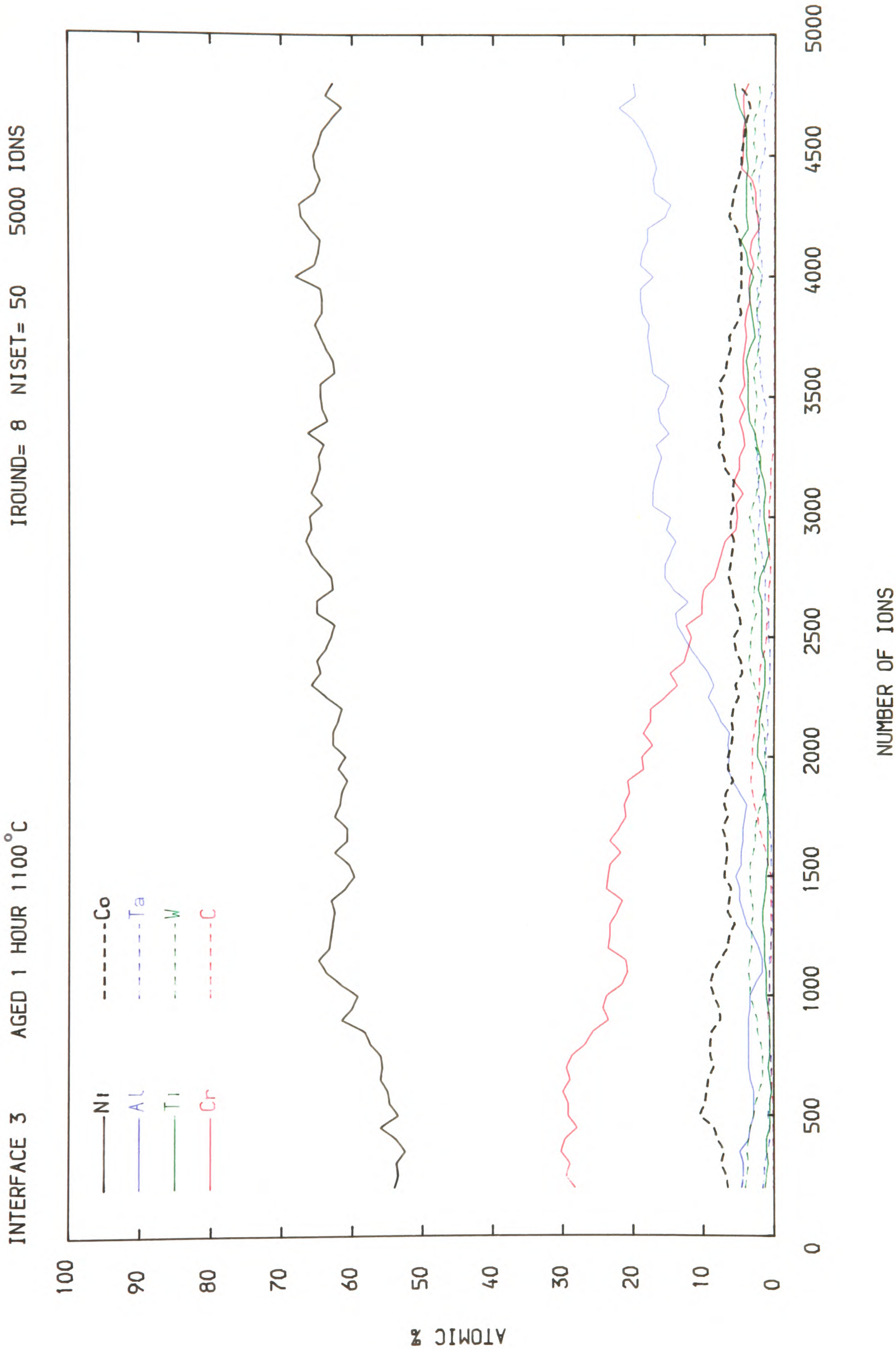


Figure 4.28

Composition profile through interface 4.

$\gamma' \rightarrow \gamma$.

Aged for 10 minutes at 1100 °C.

Compositions calculated from 8 sets of 50 ions.

At the interface, $V_0 = 10.00$ kV and $V_p = 2.50$ kV.

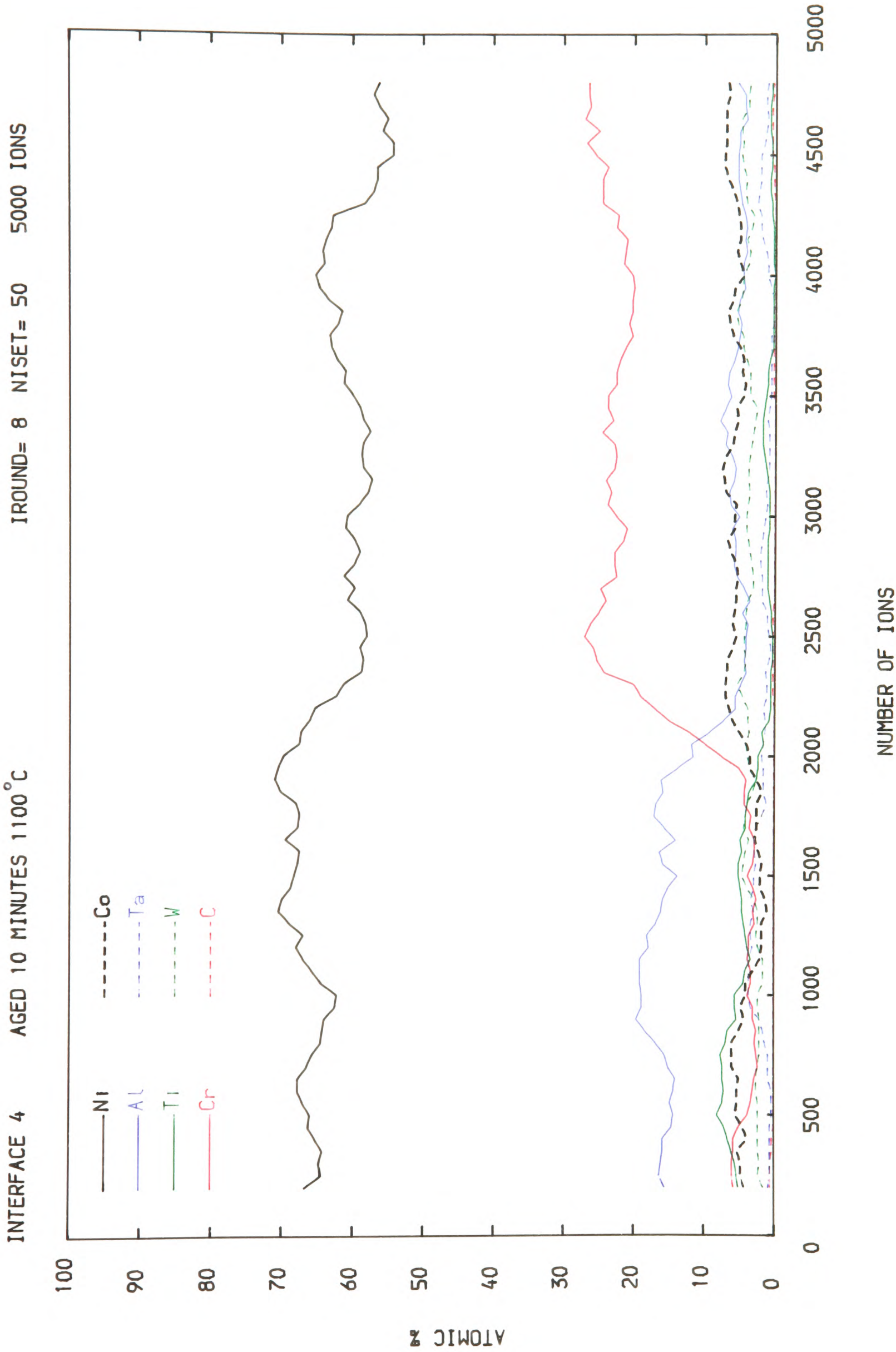


Figure 4.29

Composition profile through interface 5.

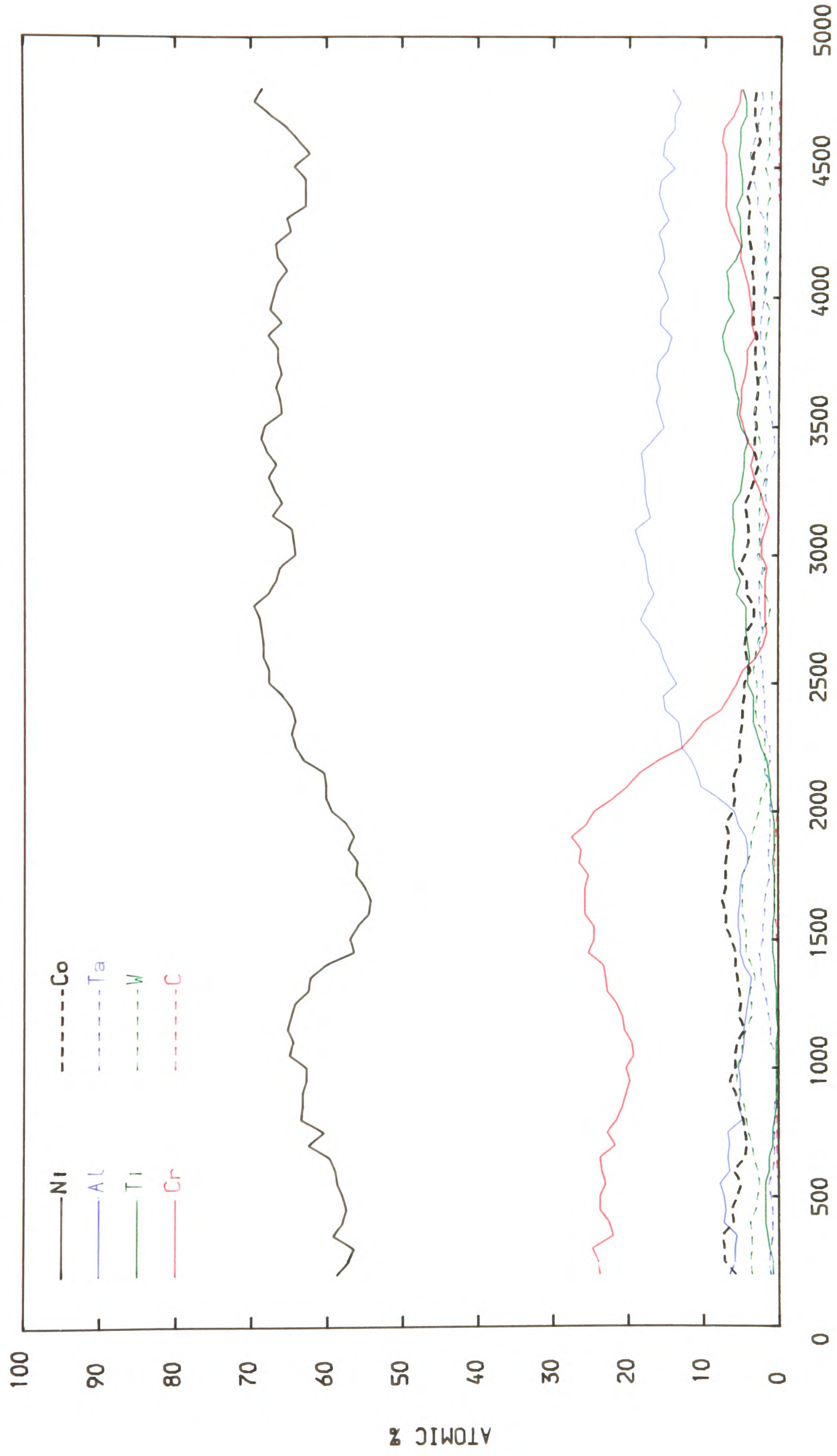
$\gamma \rightarrow \gamma'$.

Aged for 10 minutes at 1100 °C.

Compositions calculated from 8 sets of 50 ions.

At the interface, $V_0 = 10.75$ kV and $V_p = 2.69$ kV.

INTERFACE 5 AGED 10 MINUTES 1100°C IROUND= 8 NISSET= 50 5000 IONS



NUMBER OF IONS

Figure 4.30

Ladder diagram for interface 1.

$\gamma' \rightarrow \gamma$.

Aged for 1 hour at 1100 °C, 16 hours at 870 °C.

At the interface, $V_0 = 8.50$ kV and $V_p = 2.13$ kV.

INTERFACE 1 AGED 1 HOUR 1100°C, 16 HOURS 870°C

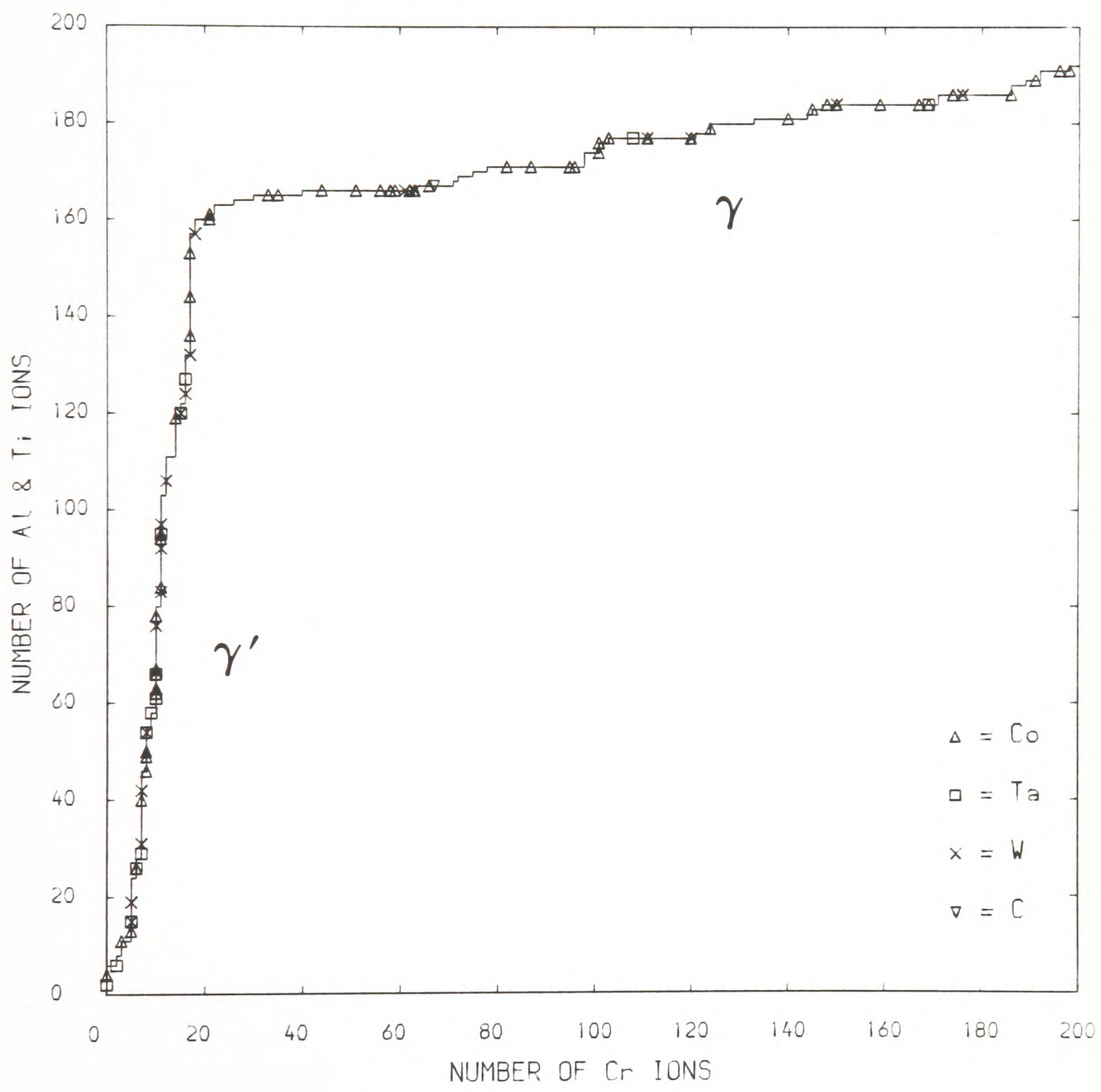


Figure 4.31

Ladder diagram for interface 2.

$\gamma' \rightarrow \gamma$.

Aged for 1 hour at 1100 °C.

At the interface, $V_0 = 15.25$ kV and $V_p = 3.81$ kV.

INTERFACE 2

AGED 1 HOUR 1100°C

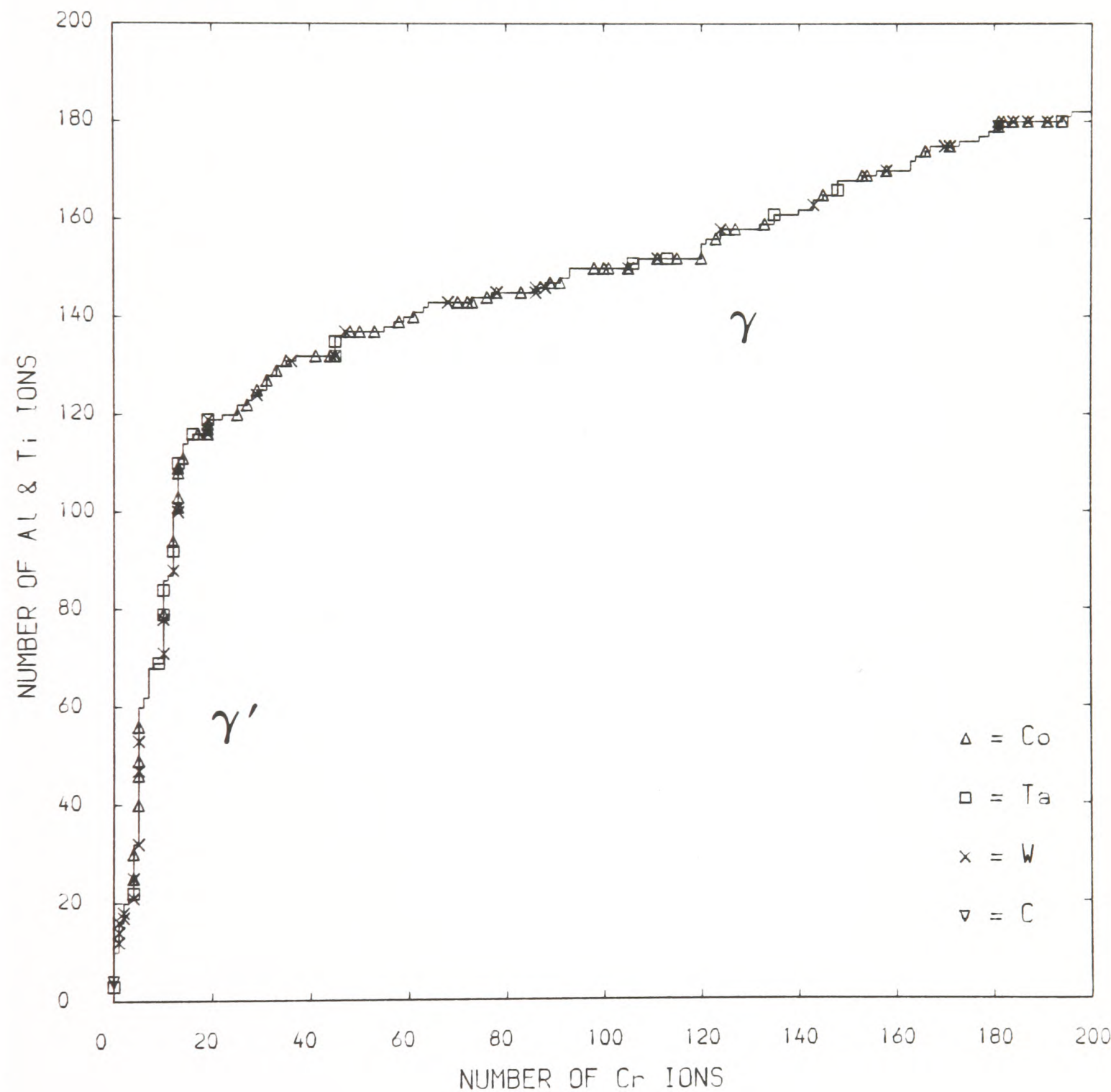


Figure 4.32

Ladder diagram for interface 3.

$\gamma \rightarrow \gamma'$.

Aged for 1 hour at 1100 °C.

At the interface, $V_0 = 16.75$ kV and $V_p = 4.19$ kV.

INTERFACE 3

AGED 1 HOUR 1100°C

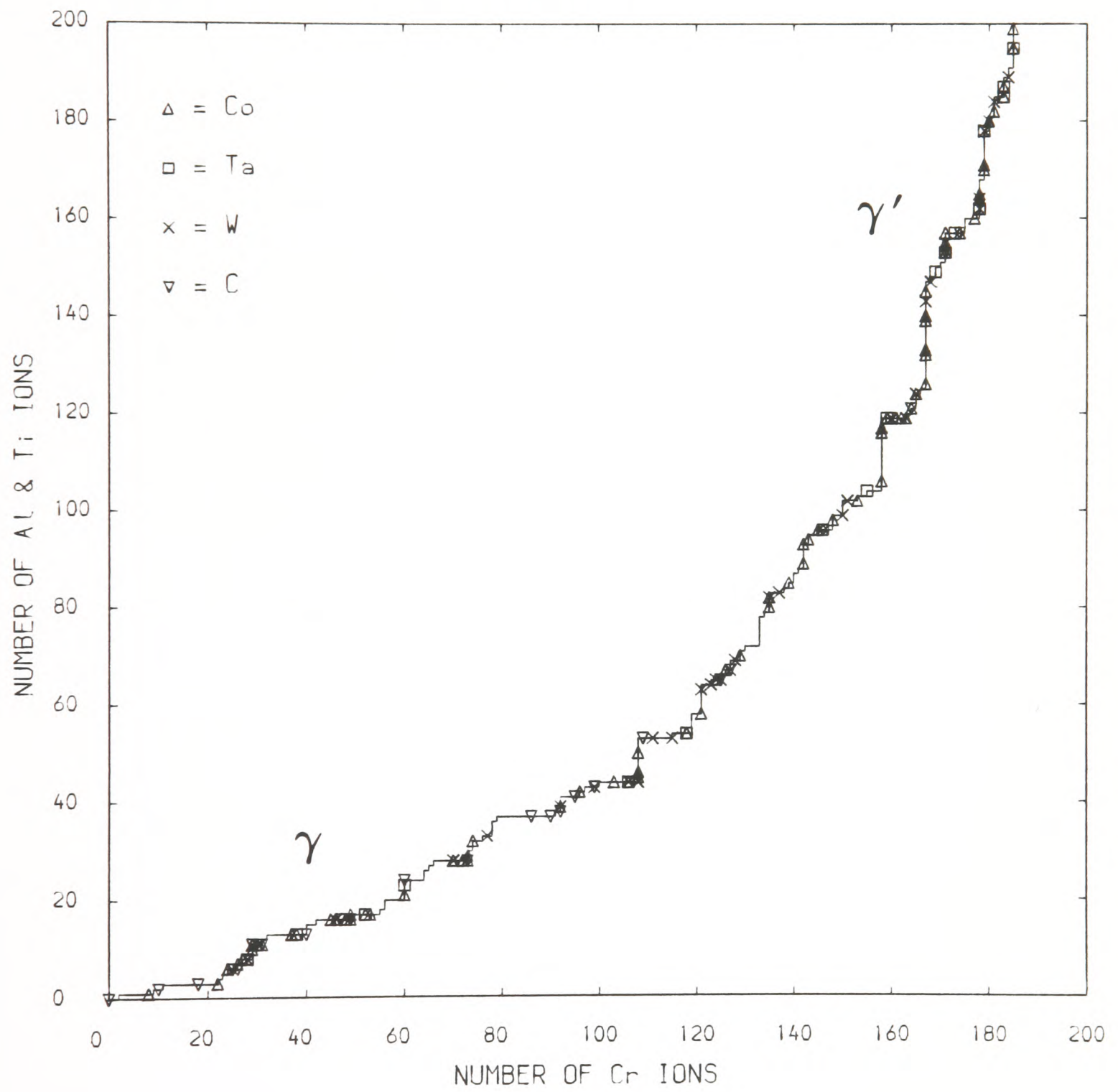


Figure 4.33

Ladder diagram for interface 4.

$\gamma' \rightarrow \gamma$.

Aged for 10 minutes at 1100 °C.

At the interface, $V_0 = 10.00$ kV and $V_p = 2.50$ kV.

INTERFACE 4

AGED 10 MINUTES 1100°C

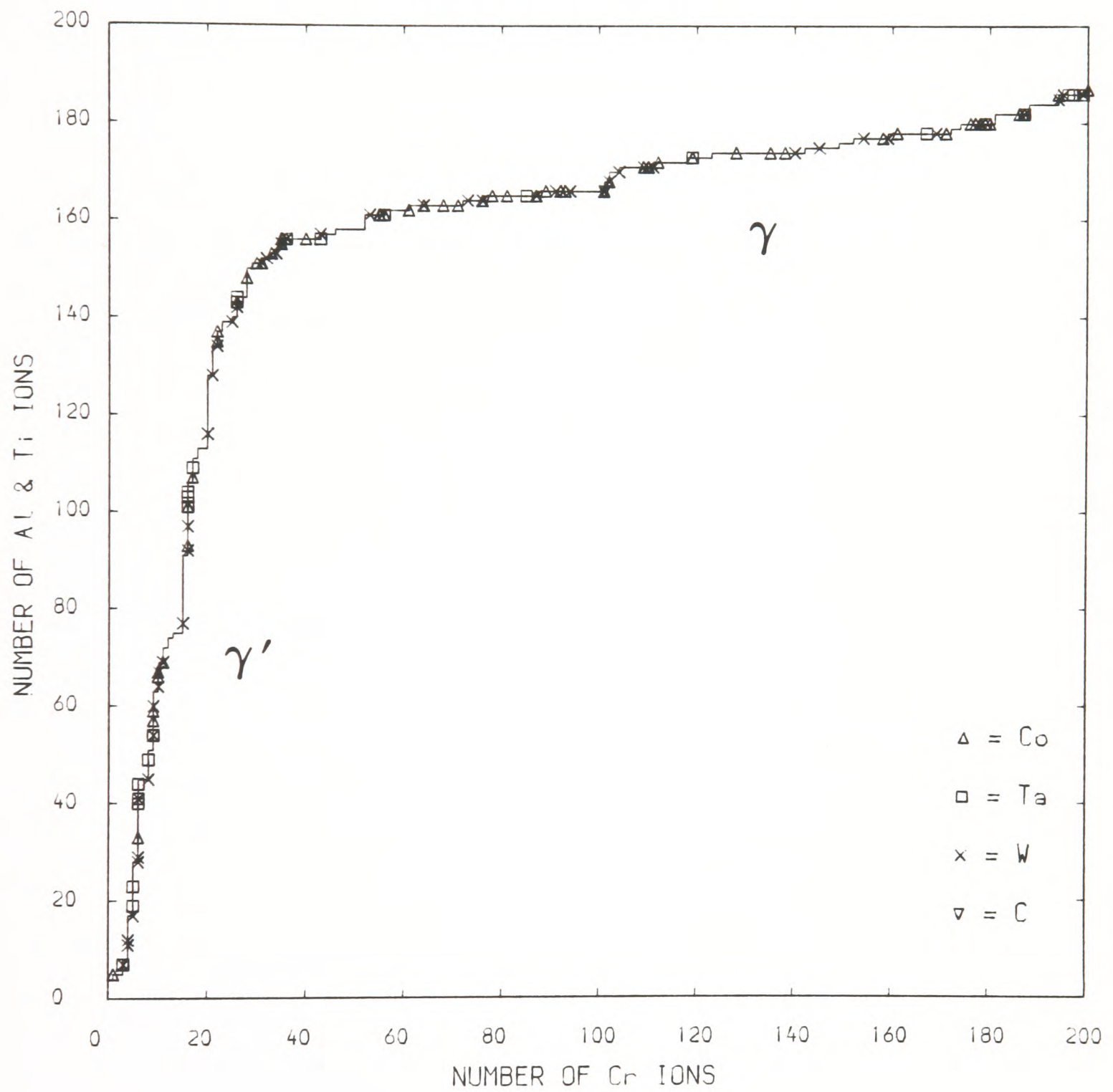


Figure 4.34

Ladder diagram for interface 5.

$\gamma \rightarrow \gamma'$.

Aged for 10 minutes at 1100 °C.

At the interface, $V_0 = 10.75$ kV and $V_p = 2.69$ kV.

INTERFACE 5

AGED 10 MINUTES 1100°C

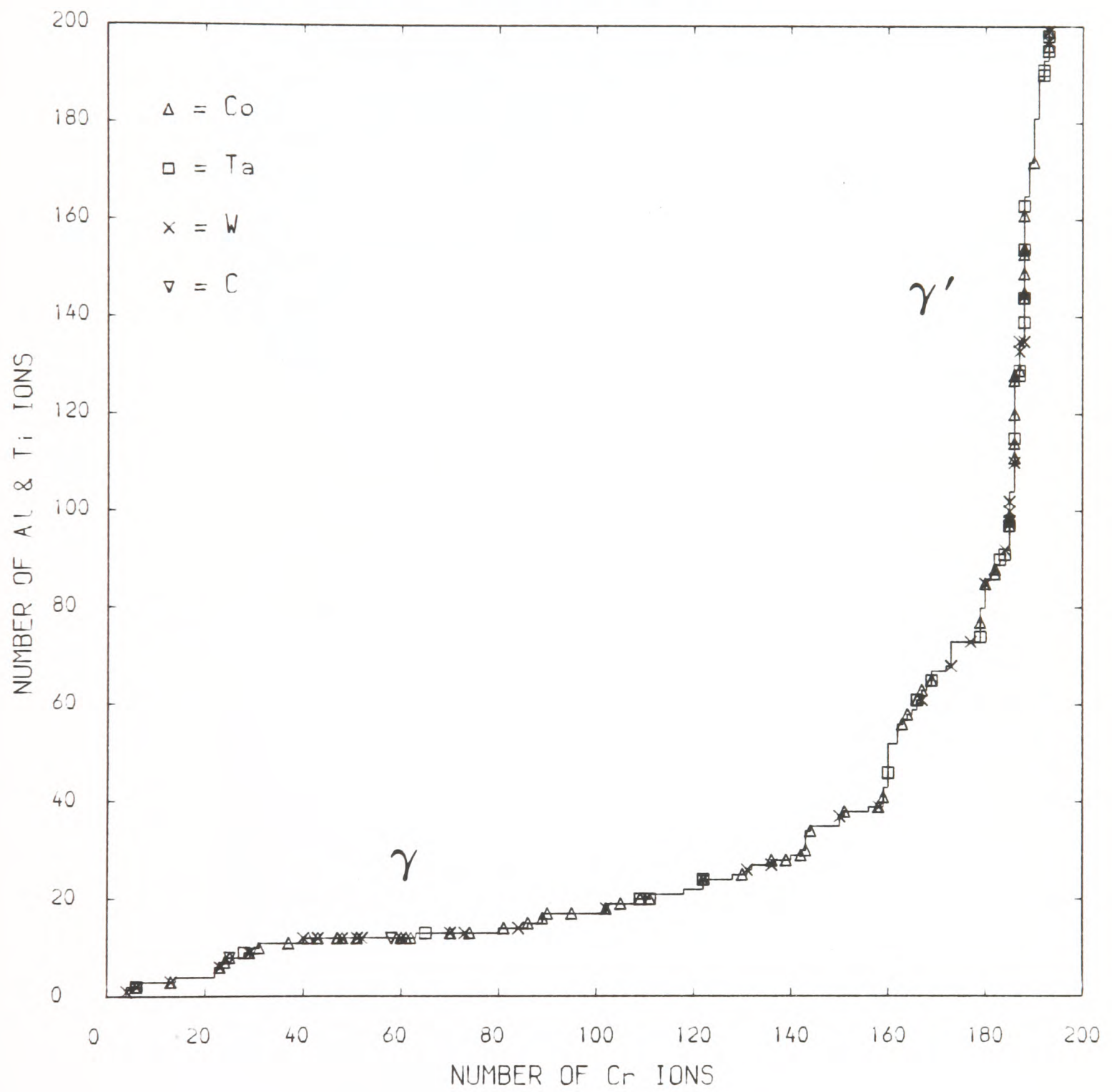
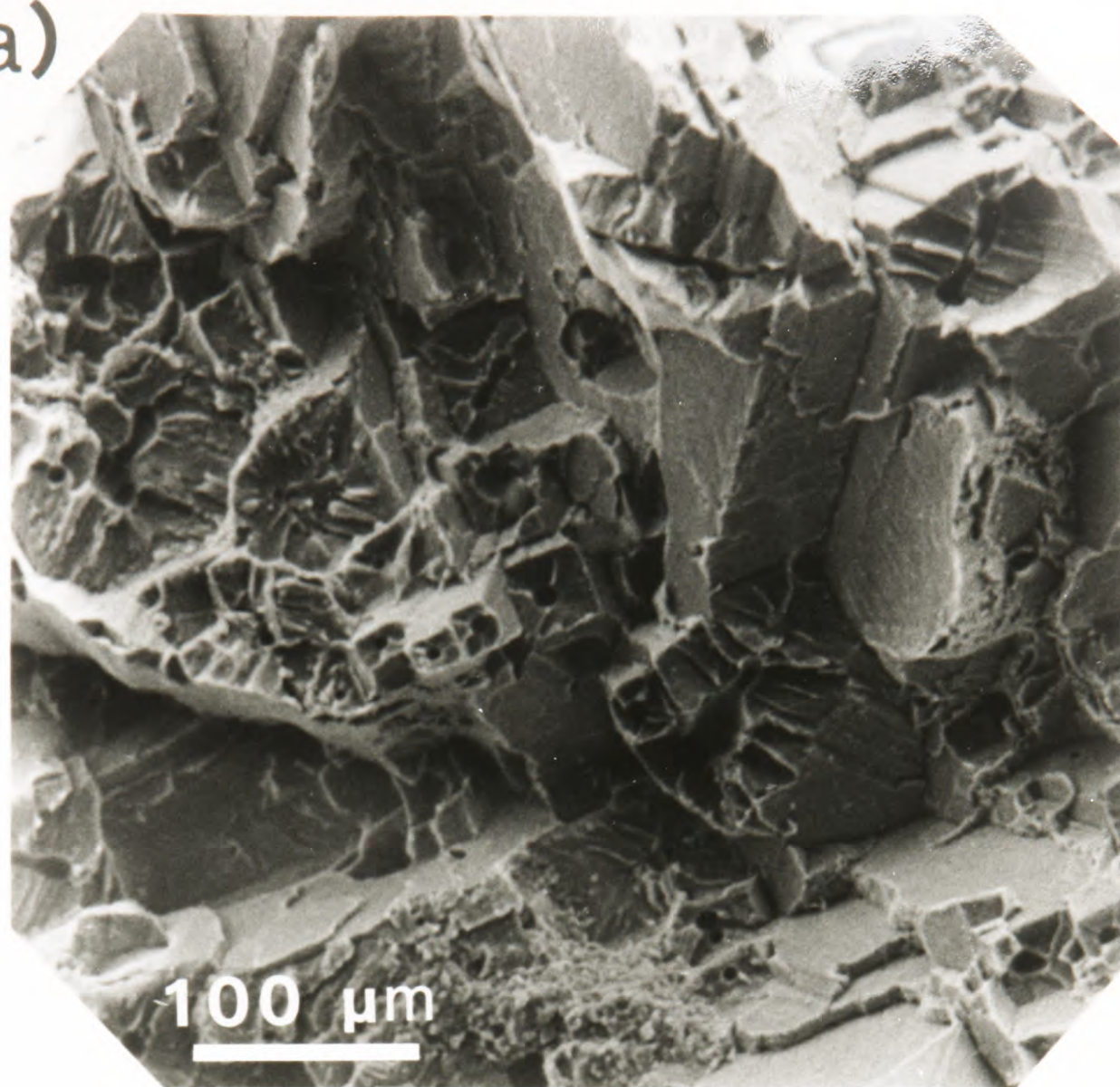


Figure 4.35

Fracture surface from crystal E, crept to failure.
(Crystal aged for 1 hour at 1100 °C.)
SEM micrographs.

(a)



(b)

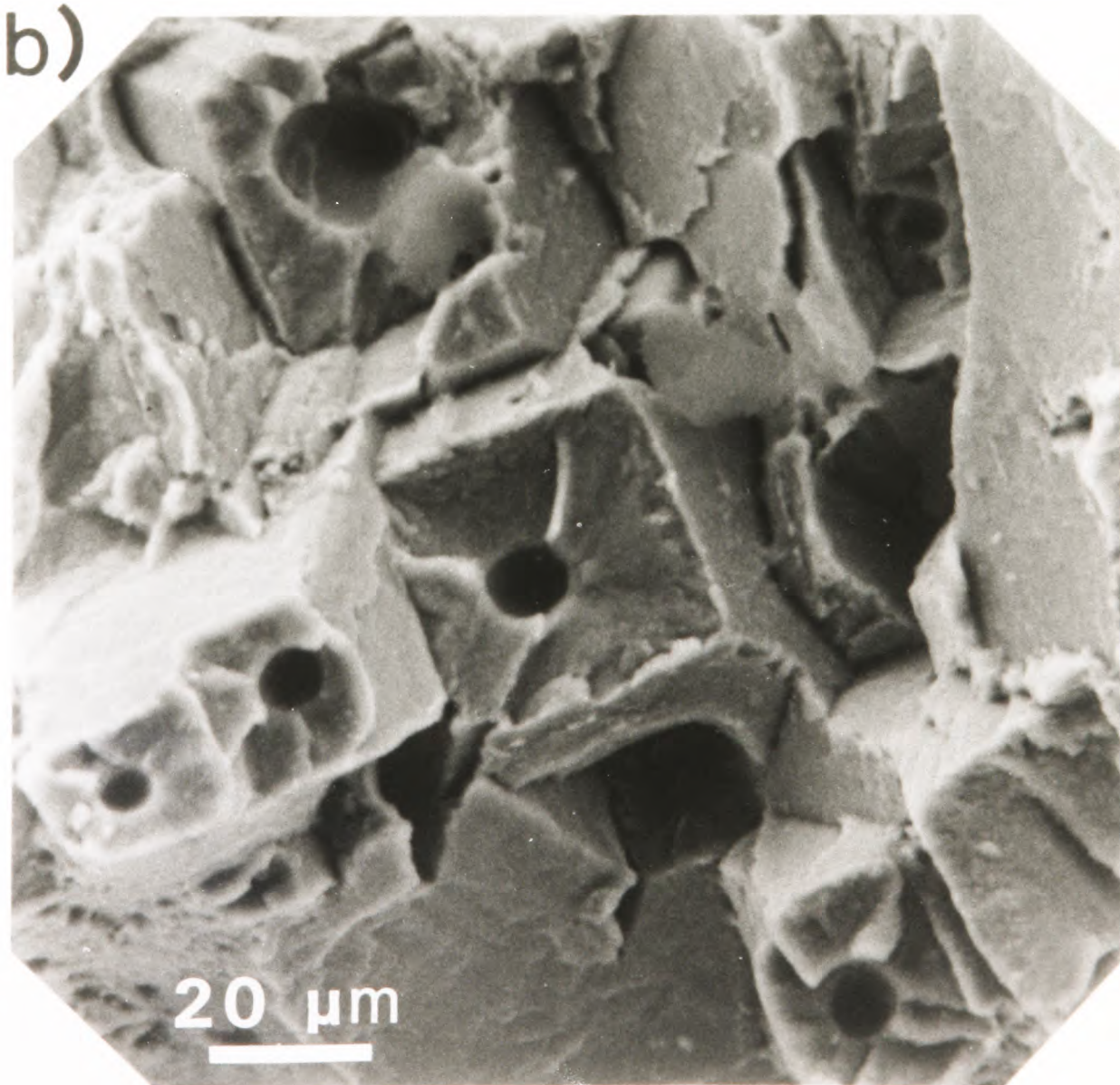


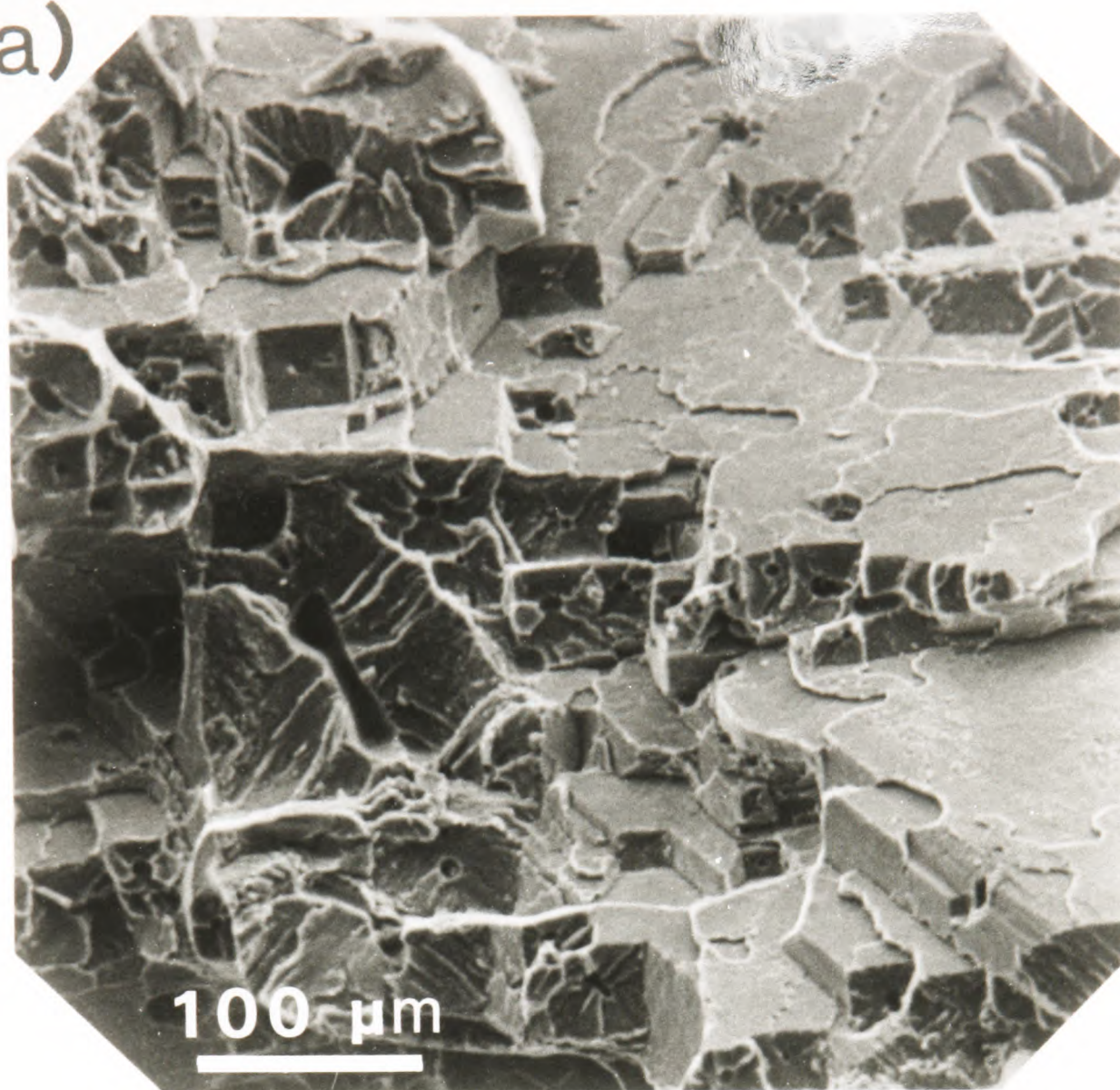
Figure 4.36

Fracture surface from crystal L, crept to failure.

(Crystal aged for 1 hour at 1100 °C, 16 hours at 870 °C.)

SEM micrographs.

(a)



(b)

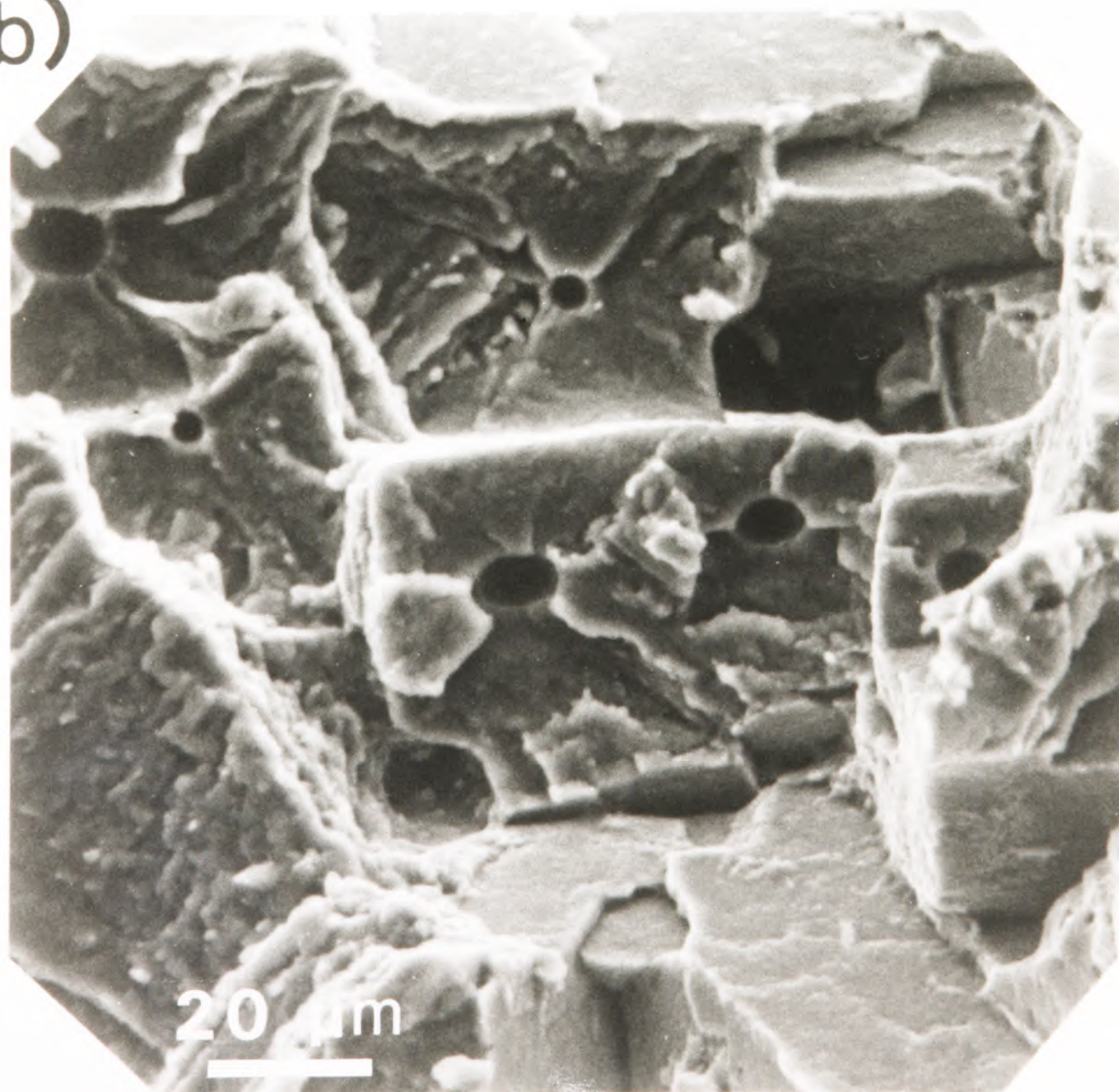


Figure 4.37

{100} longitudinal section beneath the fracture surface of crystal E
(aged for 1 hour at 1100 °C).

[001] stress axis: σ 

(a) Optical micrograph.

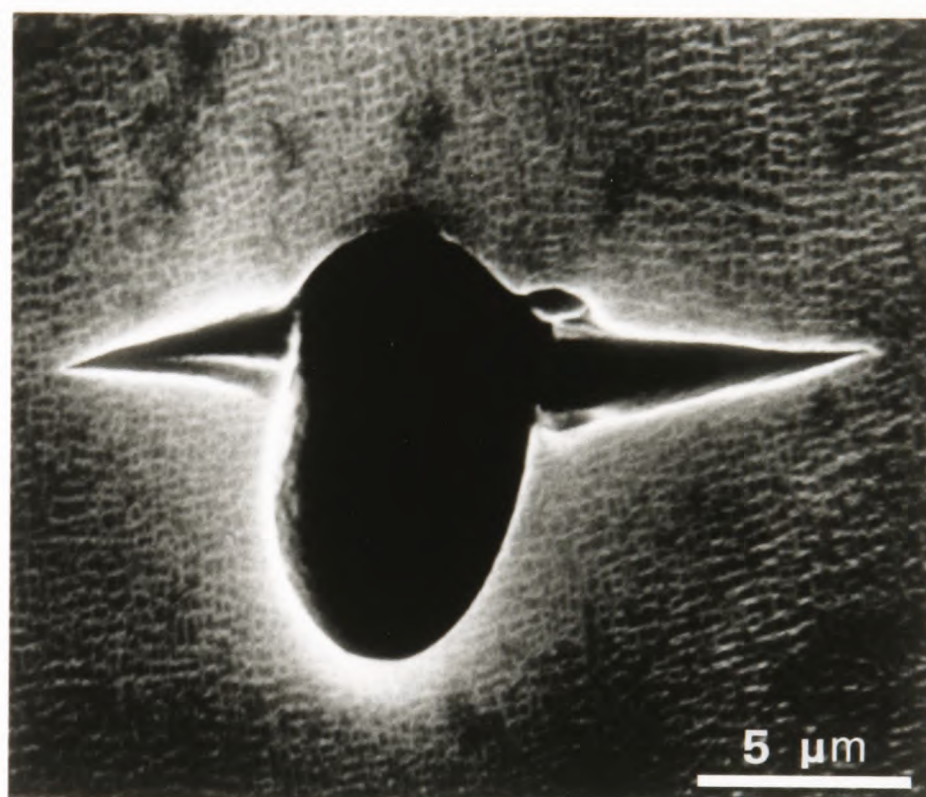
(b) SEM micrograph.

(c) SEM micrograph of right-hand crack in (b).

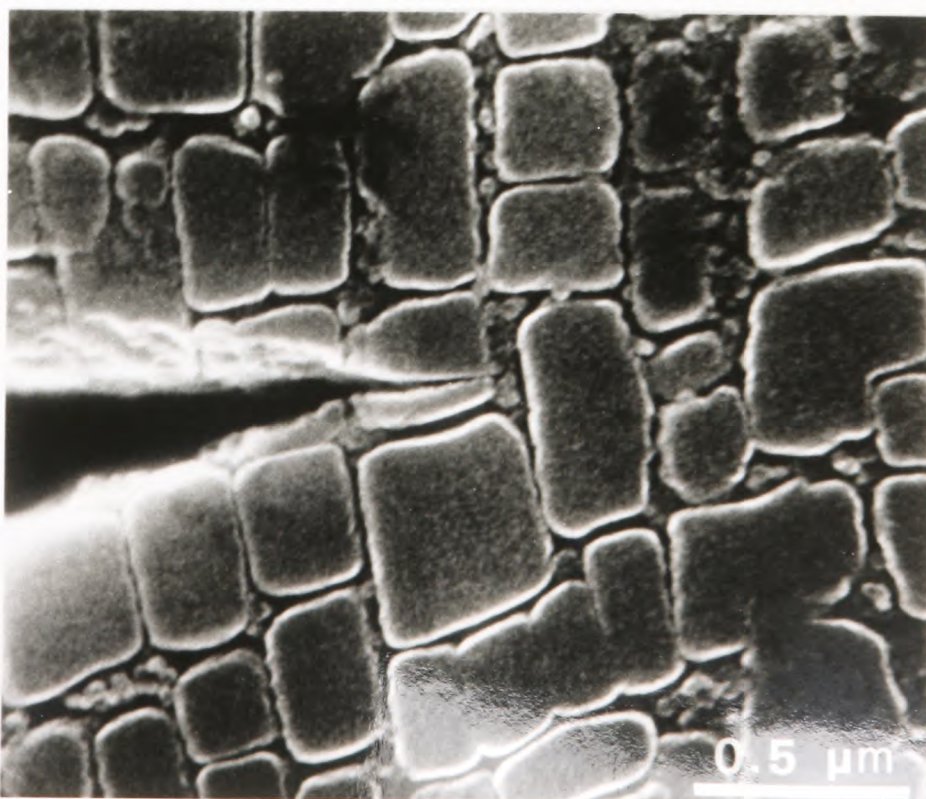
(a)



(b)



(c)



CHAPTER 5

HIGH STRAIN-RATE DEFORMATION : RESULTS AND DISCUSSION

5.1 Dependence of Yield Stress upon Heat-Treatment

Compression tests were carried out at room temperature and at 750 °C on specimens which had been aged for various lengths of time at 1100 °C and water quenched. Some of the specimens had subsequently been aged for 16 hours at 870 °C and then air cooled. A constant cross-head speed corresponding to an engineering strain-rate of $1.4 \times 10^{-3} \text{s}^{-1}$ was employed. Values for the 0.2% proof stress versus ageing time at 1100 °C are plotted in figures 5.1 and 5.2. It can be seen from these graphs that there is considerable scatter of the values obtained. It is thought that this might be due partly to crystallographic orientation variations between specimens and partly to the nature of the compression test, which is very sensitive to the alignment of both the specimen and the apparatus.

As a result of this scatter, interpretation of the results presented in figures 5.1 and 5.2 must be treated with caution. However, some trends are nevertheless apparent. The 0.2% proof stress, which can be treated as an approximation to the yield stress, appears to decline with the duration of ageing at 1100 °C. Furthermore, for a given ageing time at 1100 °C the proof stress is raised upon application of an age of 16 hours at 870 °C.

The application of the various heat-treatments has generally brought about only slight changes in the observed proof stress, and values obtained at room temperature and at 750 °C are similar. A low sensitivity of yield stress to temperature has previously been observed in other superalloy systems by, for example, Beardmore et al. (1969).

The fairly constant or slightly increasing value of the yield stress with respect to temperature has been ascribed to a balance between a drop in the yield stress of the γ matrix and an increase in that of the γ' precipitates, as discussed in section 1.3.3.

5.2 Deformation Structures

TEM studies were carried out on plastically deformed specimens in order to investigate the operative deformation mechanisms. The dislocation structures observed at room temperature and at 750 °C are shown in the micrographs presented in figures 5.3-5.7. In every specimen the deformation was found to occur inhomogeneously in intense slip bands which apparently lie on $\{111\}$ planes. Within the slip bands the dislocations can be seen to be occurring in closely constricted pairs inside the γ' precipitates. These structures are indicative of γ' shearing by $a/2\langle 110 \rangle$ dislocations separated by a band of APB. Mechanisms involving precipitate shear tend to promote inhomogeneous structures since the passage of each dislocation reduces the effectiveness of the precipitates as obstacles to deformation in the operative slip plane (Hornbogen and Zum Gahr, 1975).

The strengthening mechanisms arising from dispersed precipitates have been reviewed in section 1.3.2. The treatment by Reppich (1982) dealt with the shearing of ordered precipitates by strongly coupled dislocations. In this treatment both dislocations of a superlattice pair were in the same precipitate, as is clearly the case in the present studies. The yield stress calculated from considerations of order hardening in this regime was given by

$$\tau_y = \frac{1}{2} \frac{1.72}{2br} \frac{rf^{1/2}C_2}{C_2\Gamma} \left(\frac{1.28 \Psi_{apb}}{C_2\Gamma} \frac{2r}{-1} \right)^{1/2}. \quad (5.1)$$

The yield stress is therefore predicted by this model to decrease with increasing precipitate size. This is consistent with the apparent fall in the 0.2% proof stress with ageing time in the present studies. The alternative treatments of strengthening involving precipitate shear that were considered in section 1.3.2 predicted the yield stress to be proportional to the square root of the particle size. However, the analysis due to Reppich (1982) may be the more appropriate since pairs of dislocations occur within the same precipitate. A decreasing yield stress with increasing particle size is often attributed to the process of Orowan looping between precipitates by dislocations. Such a process is unlikely to occur in alloys such as SRR99 which contain large volume fractions of γ' so that the inter-precipitate spacing is small with respect to the precipitate size. However, at large precipitate sizes it is possible that dislocations could exhibit slight bowing prior to precipitate shearing. Viewed on $\{111\}$ planes, cuboidal precipitates appear as triangles. Bowing of a dislocation around the vertex of a precipitate would tend to assist its entry into the precipitate. This mechanism would therefore provide the basis for an alternative explanation of the fall in the yield stress with increasing particle size.

In figures 5.5 and 5.7, which show the dislocation structures in specimens previously aged for 16 hours at 870 °C, the presence of stacking faults can be seen in addition to the paired dislocations. These are occurring both in specimens tested at room temperature and in those tested at 750 °C. Rae (1983) has observed extensive stacking faults in undeformed SRR99 which was solution treated and aged for 16 hours at 870 °C. However, she did not observe any stacking faults in undeformed material which received an intermediate age at 1100 °C. To check for the possibility of the stacking faults seen in figures 5.5

and 5.7 having occurred prior to deformation, some undeformed material having received the same heat-treatment was examined by TEM. As no stacking faults could be found, it was concluded that the faults observed in the strained material were produced during the deformation process. The activation of an alternative deformation mechanism involving precipitate shear by partial dislocations could have become favoured in specimens aged at 870 °C as a result of chemical changes at the γ/γ' interfaces, as discussed in section 4.5. The observed differences in the proof stress may be related to such changes.

5.3 Macroscopic Deformation

After large plastic strains had been incurred, many crystals, irrespective of their heat-treatment, underwent extensive deformation on a single slip plane. In the specimens tested at room temperature this caused large macroscopic displacements on a single plane. This can be seen in figure 5.8(a), which shows a specimen after 25% plastic strain. The plane of the macroscopic offset lies at approximately 55 ° to the [001] stress axis and is therefore almost certainly a {111} plane. The local work-softening associated with precipitate shear had presumably become so great on a specific plane that all further deformation was confined to the same plane.

During testing at 750 °C many specimens underwent compressive fracture. Figure 5.8(b) shows a specimen which failed after 17% plastic strain. The failure is clearly crystallographically oriented and apparently lies along a {111} plane. Copley and Kear (1967) observed that the anomalous increase in the yield stress of γ' is accompanied by a reduction in ductility. The minimum ductility was found to occur at the peak in the yield stress, suggesting that the two phenomena are closely related. Pearcey et al. (1967) found a similar

correlation in directionally solidified Mar-M200. The present observation of the reduced ductility of SRR99 at 750 °C, bringing about compressive failure, is probably a result of these changing properties of the γ' phase with temperature.

Figure 5.1

0.2% proof stress at room temperature versus ageing time at 1100 °C.

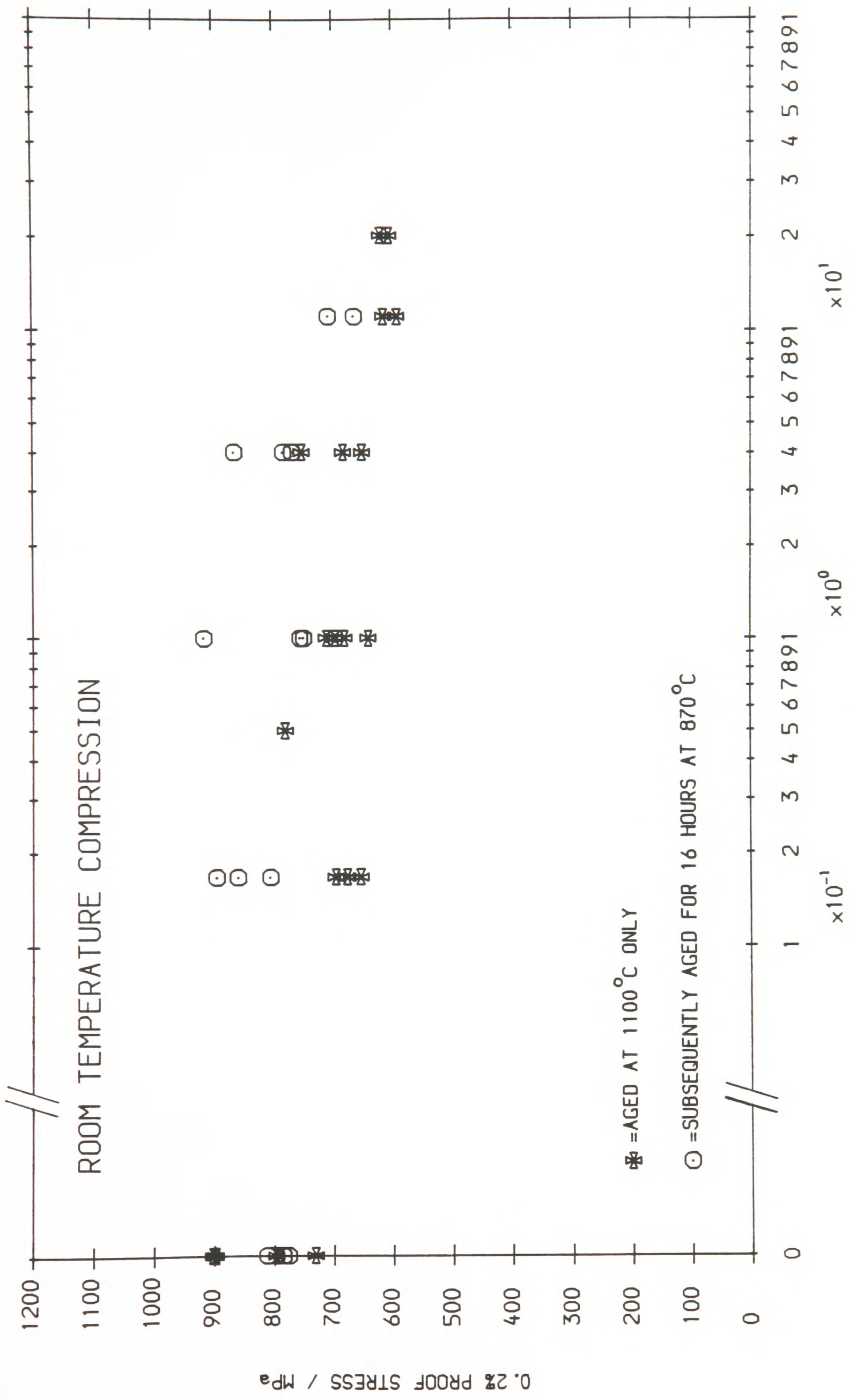
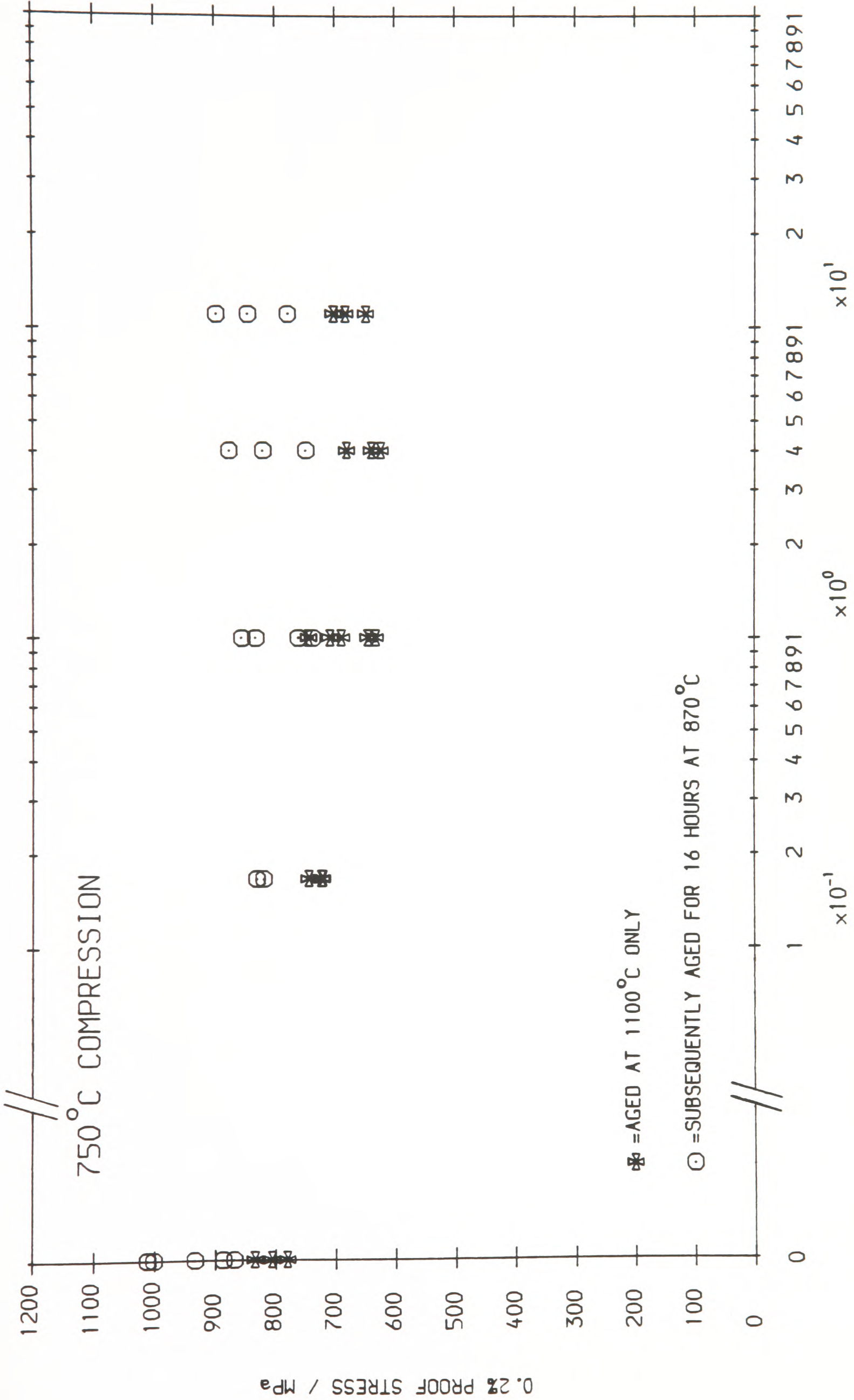


Figure 5.2

0.2% proof stress at 750 °C versus ageing time at 1100 °C.



DEFORMATION AT ROOM TEMPERATURE

Figure 5.3

Crystal aged for 30 minutes at 1100 °C.

2.2% plastic strain at room temperature.

Bright field 1 MeV HVEM micrographs.

(a) Electron beam $\approx$ parallel to $\langle 110 \rangle$ foil normal.

(b) Foil tilted to a $\{111\}$ pole. Slip traces parallel to $\langle 110 \rangle$ directions.

Figure 5.4

Crystal aged for 1 hour at 1100 °C.

4.3% plastic strain at room temperature.

Bright field TEM micrographs.

Foil normal parallel to $[001]$ stress axis.

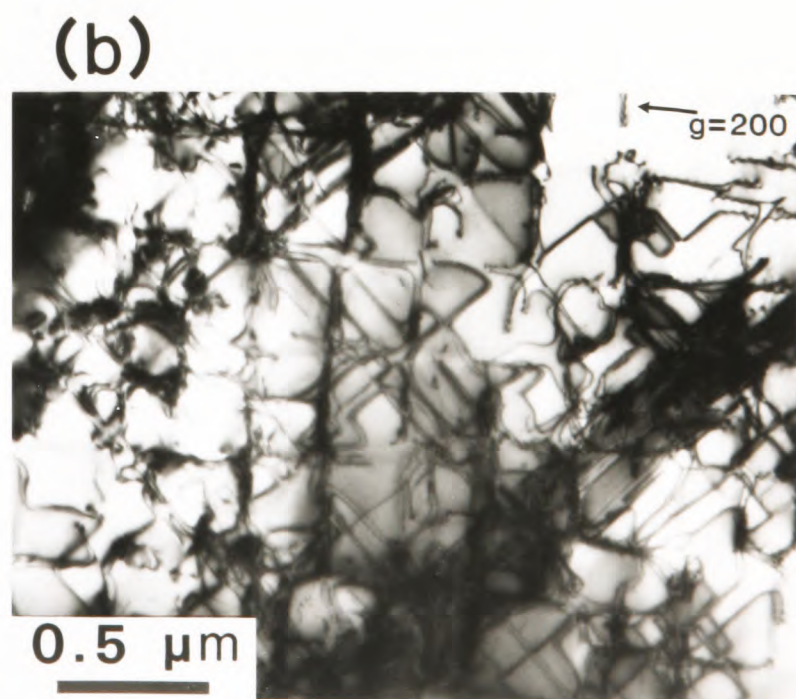
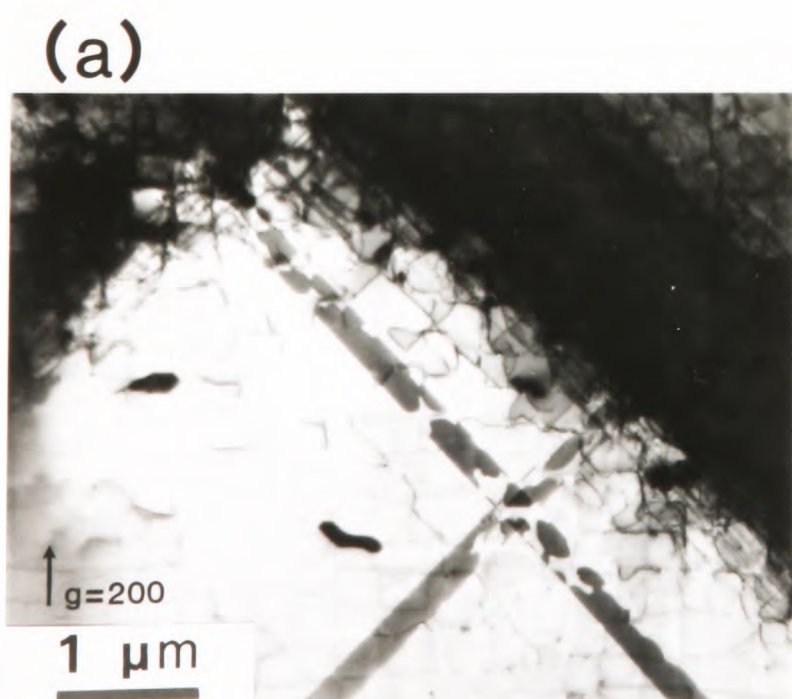
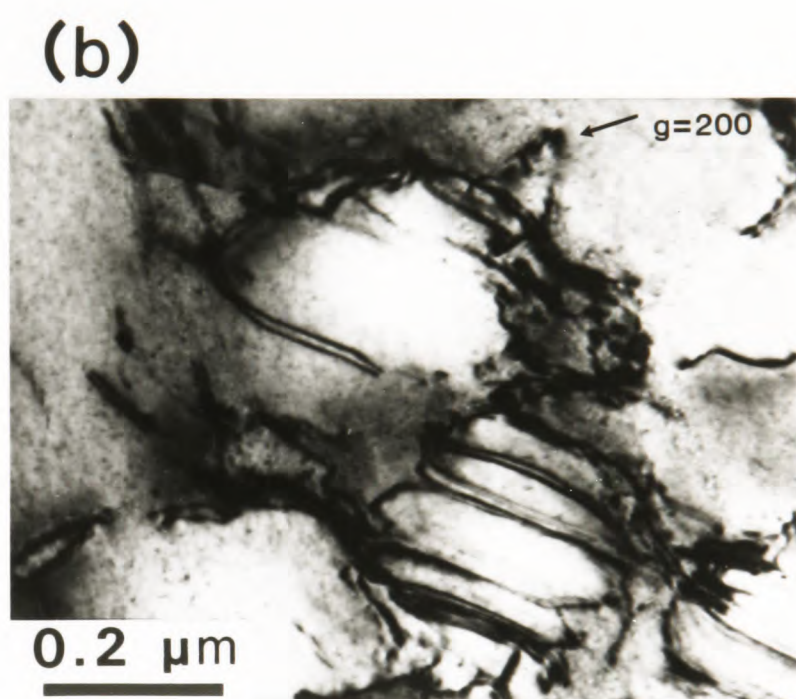
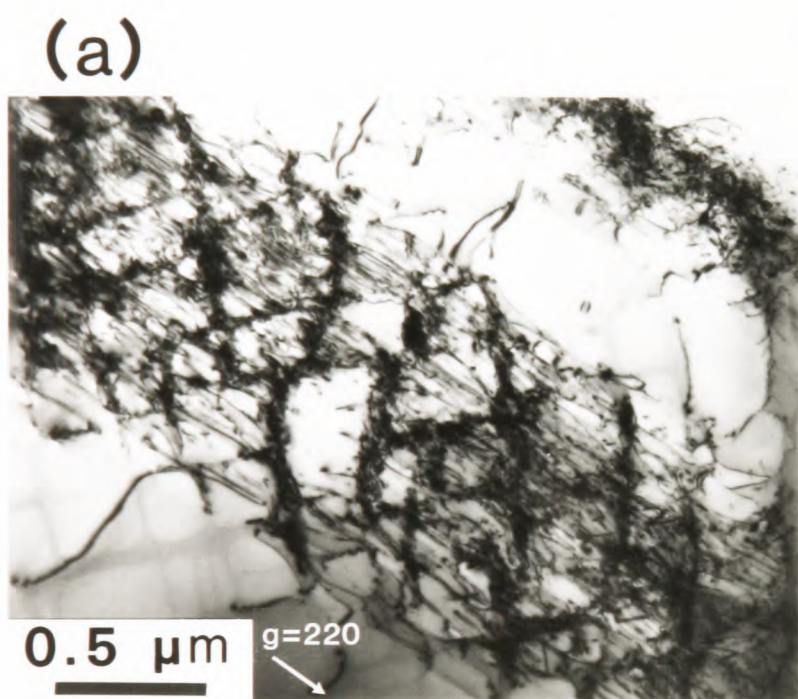
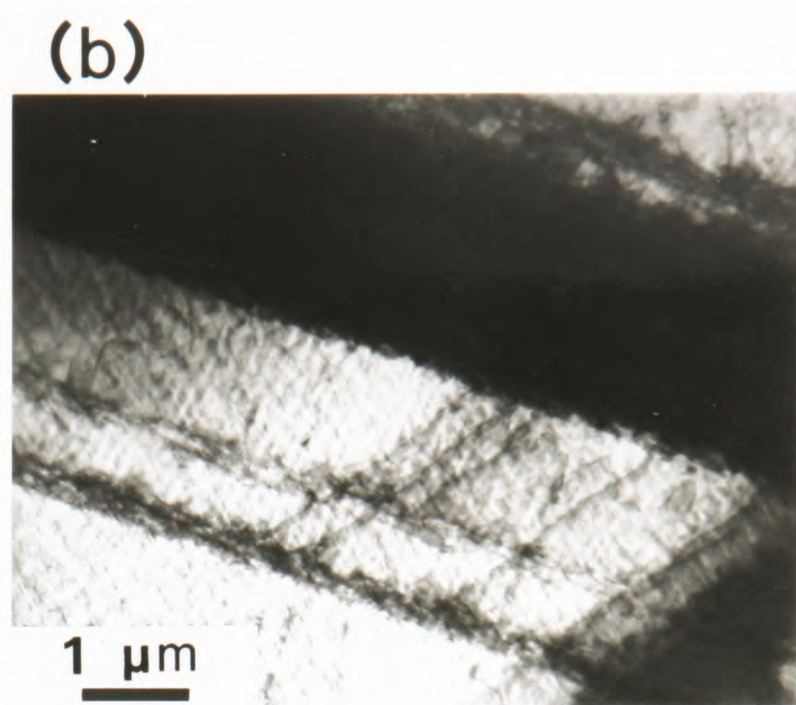
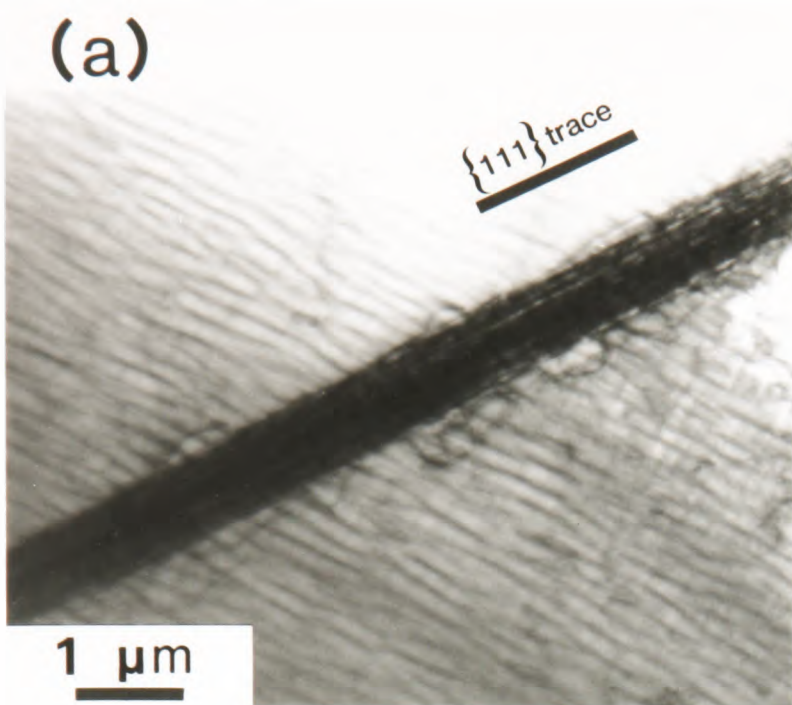
Figure 5.5

Crystal aged for 1 hour at 1100 °C and 16 hours at 870 °C.

4.5% plastic strain at room temperature.

Bright field TEM micrographs.

Foil normal parallel to $[001]$ stress axis.



DEFORMATION AT 750 °C

Figure 5.6

Crystal aged for 1 hour at 1100 °C.

4.4% plastic strain at 750 °C.

Bright field TEM micrographs.

Foil normal parallel to [001] stress axis.

Figure 5.7

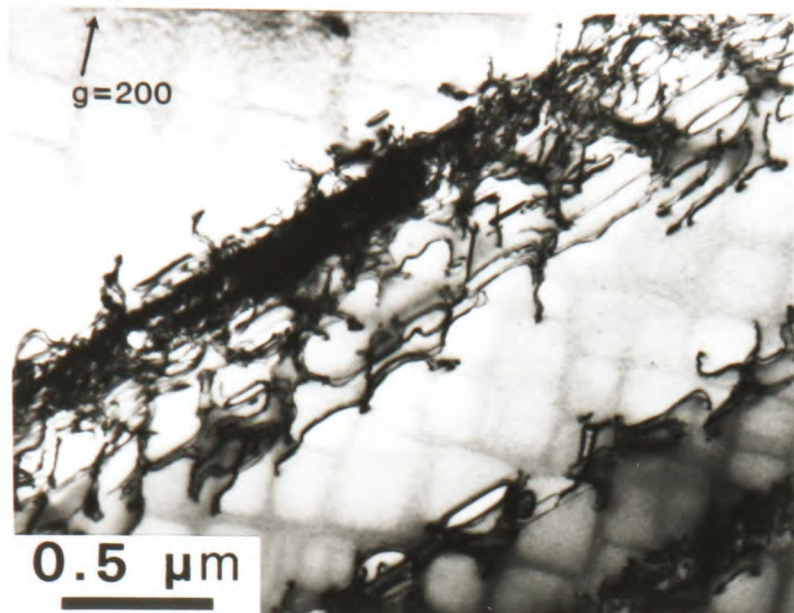
Crystal aged for 1 hour at 1100 °C and 16 hours at 870 °C.

4.3% plastic strain at 750 °C.

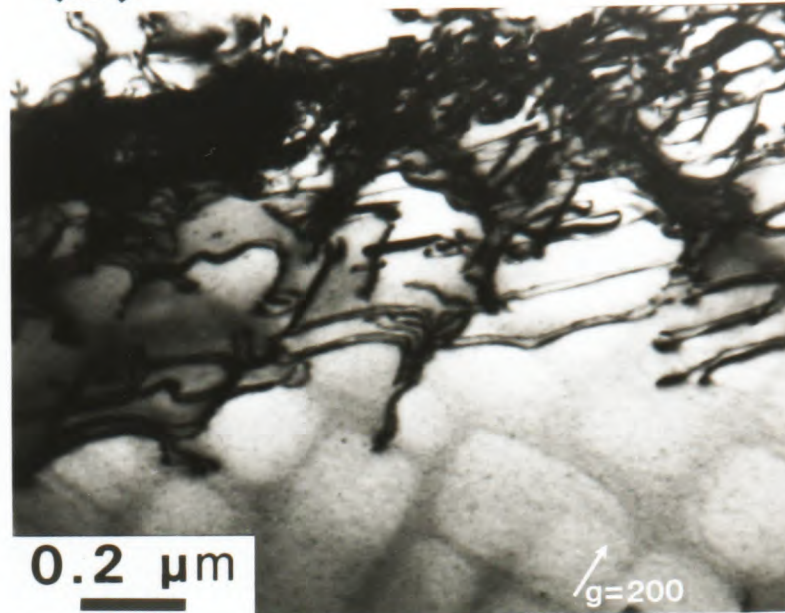
Bright field TEM micrographs except for (c), which is a dark field image using a {300} superlattice reflection.

Foil normal parallel to [001] stress axis.

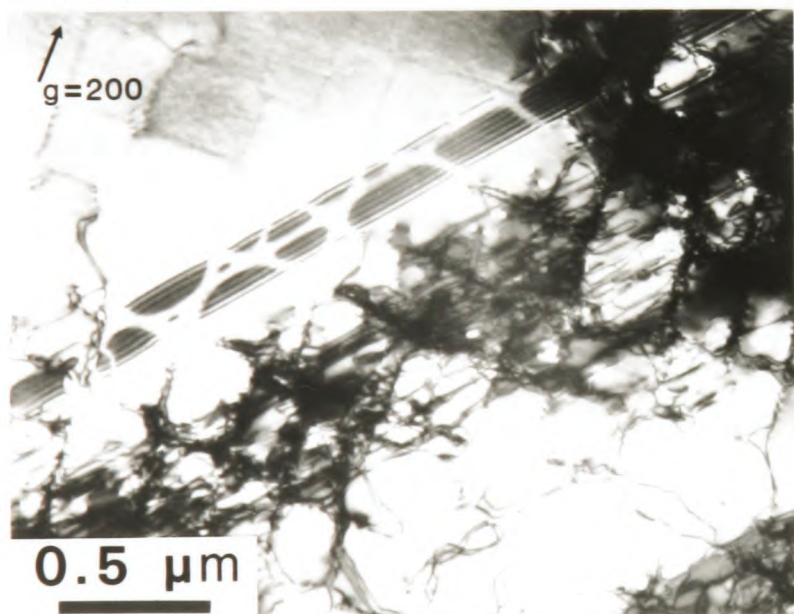
(a)



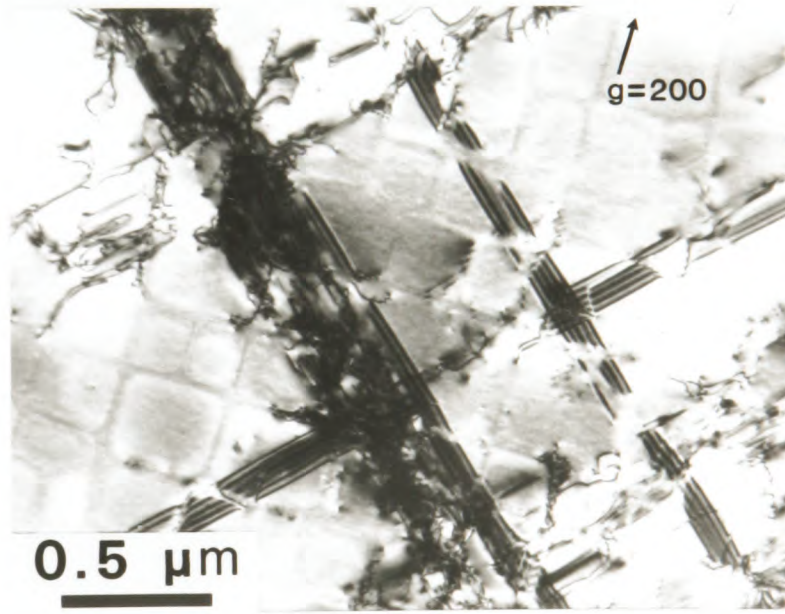
(b)



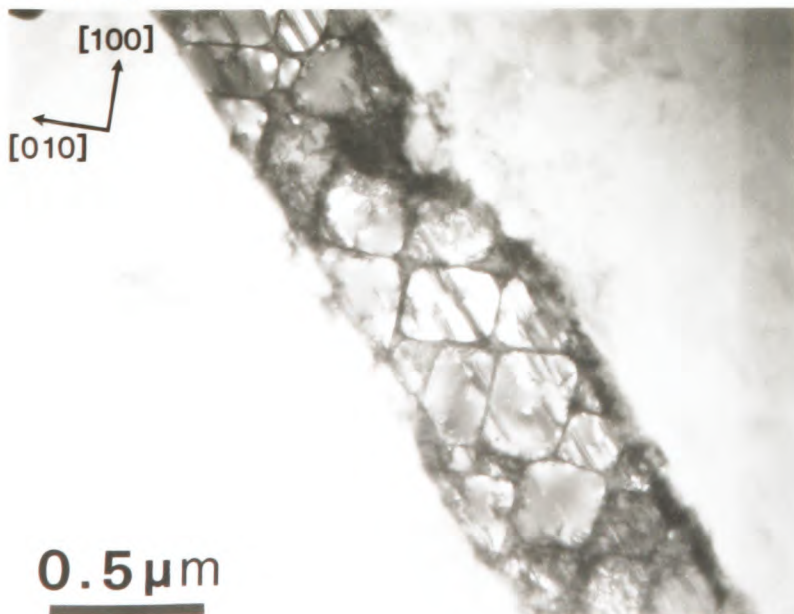
(a)



(b)



(c)



(d)

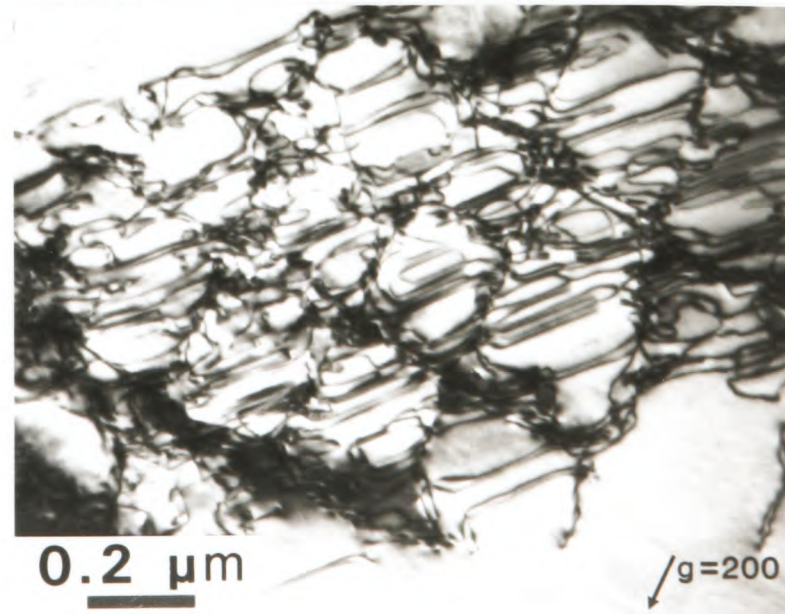


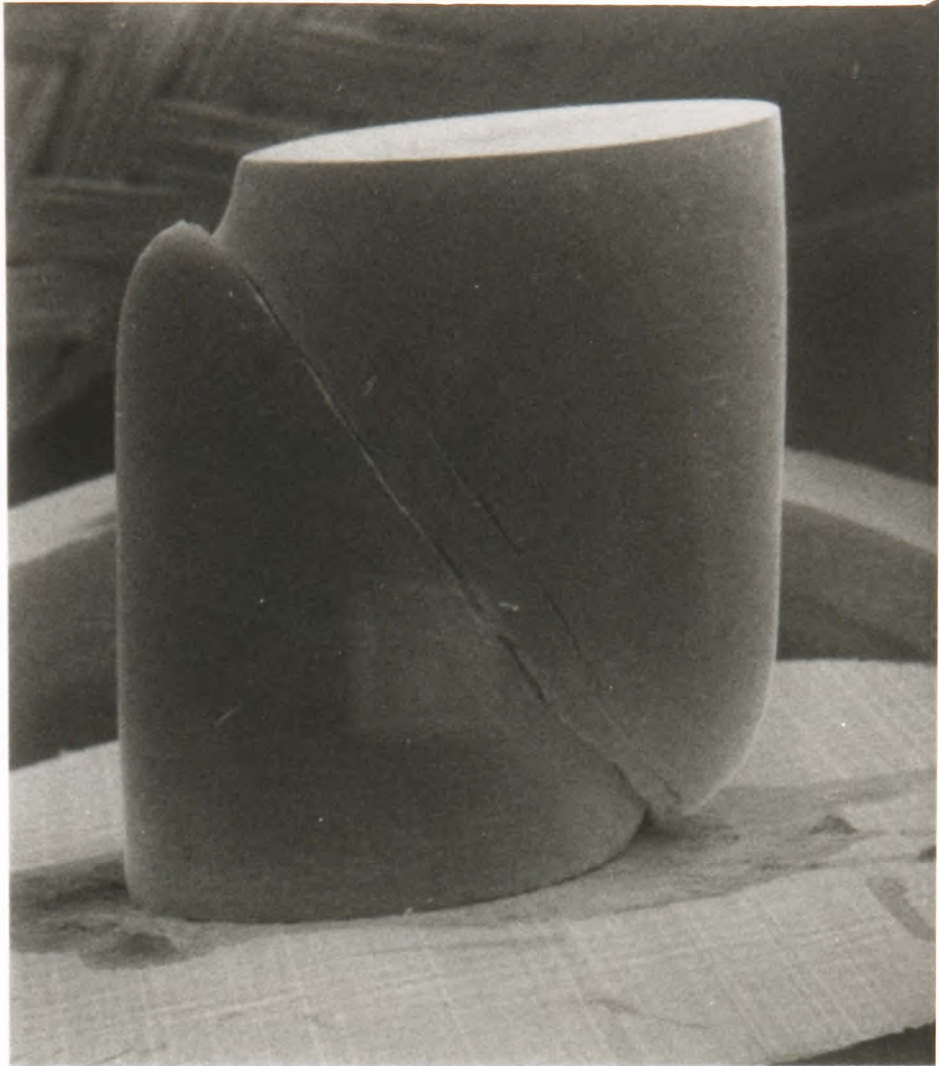
Figure 5.8

(a) Large macroscopic offset in a specimen deformed by 25% plastic strain at room temperature.

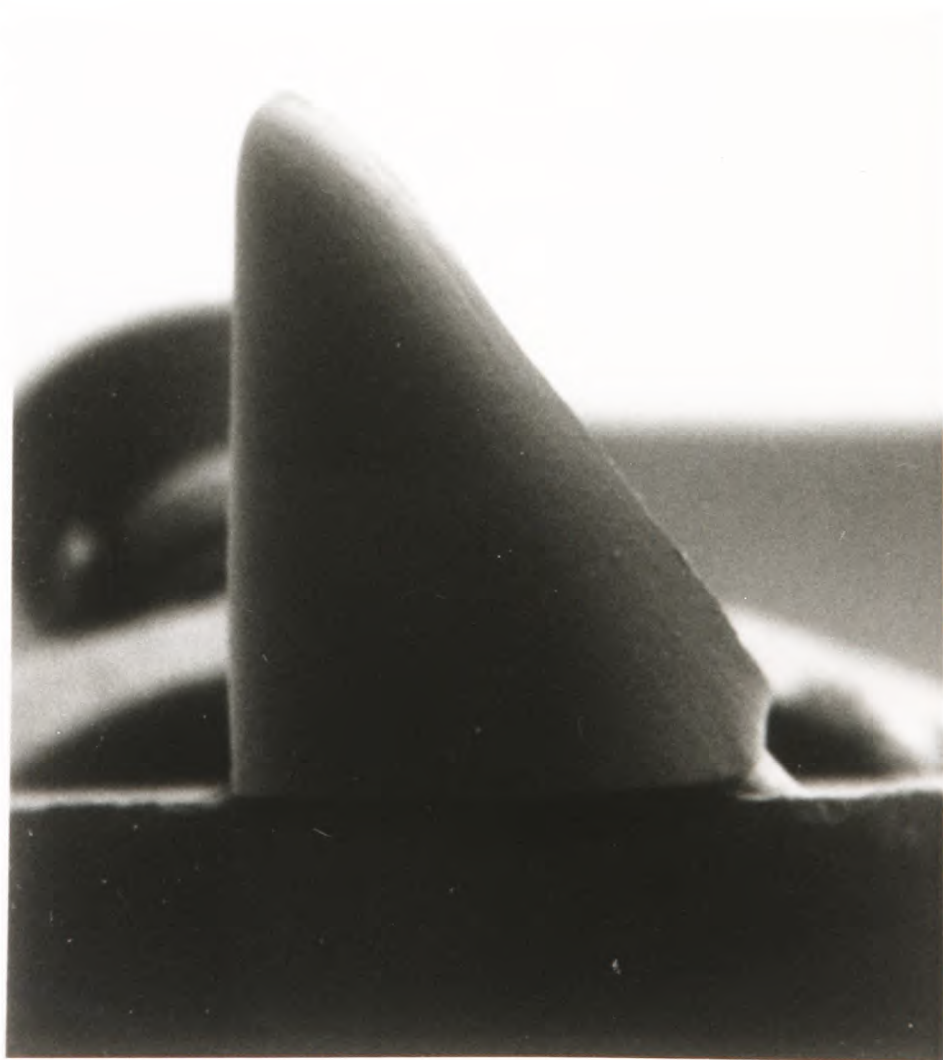
(b) Compressive failure in a specimen deformed by 17% plastic strain at 750 °C.

((a) and (b) are both SEM images.)

(a)



(b)



CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusions

The effects of heat-treatments on the microstructural and mechanical properties of SRR99 have been investigated. A solution heat-treatment of 4 hours at 1300 °C has been shown to be suitable for the homogenisation of the microstructure. During subsequent ageing at 900 °C or long-term ageing at 800 °C, rounded precipitates form. These are highly interconnected, indicative of precipitate coalescence having occurred. Upon ageing at 1000 °C, 1100 °C or 1200 °C, isolated cuboidal precipitates form. At 1200 °C, these rapidly degenerate into a rafted structure. It is thought that the occurrence of cuboidal precipitates at the higher ageing temperatures is due to an increase in the magnitude of the γ/γ' misfit parameter and that rafting is associated with a loss of coherency.

The mean precipitate size during ageing at 1100 °C, 1000 °C and 900 °C varies with time in accordance with a power-law whose size exponent is in each case greater than 3, the value theoretically predicted by a number of coarsening models. It is considered that this deviation from the theoretical value could have arisen through a slight decrease in the rate constant during ageing, due to a progressive transition in the dominant coarsening mechanism.

The activation energy for the coarsening process was calculated by means of an Arrhenius plot, assuming a size exponent of 3. Larger size exponents than 3 were observed in practice, and comparison of the microstructures suggested that the coarsening mechanism was not the same at each ageing temperature. In spite of these limitations, the

Arrhenius plot yielded an activation energy of 242 kJ mol^{-1} for the coarsening process, which is comparable with the established activation energies for the self-diffusion of nickel and for the diffusion of aluminium or titanium in nickel.

The creep behaviour of SRR99 was investigated at 750°C and under an engineering stress of 800 MPa. After either a solution heat-treatment alone or a solution heat-treatment followed by an age at 1100°C , the primary creep strain is very sensitive to crystal orientation. Lattice rotation measurements, together with TEM studies, showed that primary creep deformation takes place on a single $(\bar{1}11)[1\bar{1}2]$ system and involves the shear of γ' precipitates by dissociated dislocations. Those crystals which require the greatest lattice rotations before the activation of intersecting slip systems exhibit the largest primary creep strains. The activation of intersecting slip systems reduces the strain-rate and leads to the onset of secondary creep. Dense dislocation networks form during the secondary creep stage, with only occasional dissociation into partial dislocations.

Of the heat-treatments considered, a two-stage treatment involving an age for 1 hour at 1100°C followed by a 16 hour age at 870°C leads to the greatest resistance to creep deformation. The extent of the primary creep strain is reduced by applying the final ageing treatment of 16 hours at 870°C . The deformation mechanisms are unchanged, but the onset of the secondary creep stage occurs after a smaller accumulated strain. Atom probe studies have demonstrated that a build-up of chromium in the γ matrix close to γ/γ' interfaces occurs during ageing at 870°C . It is believed that this inhibits the shearing of the precipitates by dislocations.

Tertiary creep has been shown to occur by the growth of cracks

emanating from gas pores in the material. These cracks propagate through the γ' precipitates along (001) planes. Final failure is believed to occur by $\{111\}$ shear between the cracks.

High strain-rate tests showed that the yield stress of SRR99 is similar at room temperature and at 750 °C. The yield stress appears to decrease with ageing time at 1100 °C, and is increased upon application of a final age of 16 hours at 870 °C. Deformation occurs inhomogeneously and the precipitates are sheared by paired dislocations. The decrease in yield stress with ageing time at 1100 °C is believed to be due to the coarsening of the precipitates, which according to Reppich (1982) results in a reduction in their resistance to shear by closely spaced pairs of dislocations. Deformation of specimens which have received a final age of 16 hours at 870 °C involves the shear of precipitates by partial dislocations as well as by paired dislocations. It is thought that this is due to the same γ/γ' interfacial chemical changes which brought about the enhanced creep performance.

6.2 Suggestions for Further Work

It has been shown in the present work that the creep performance of SRR99 at 750 °C and under an engineering stress of 800 MPa is enhanced by the application of a two-stage heat-treatment of 1 hour at 1100 °C and 16 hours at 870 °C. Leverant et al. (1973) have shown that, in single crystals of Mar-M200, raising the testing temperature to 857 °C brought about a change in the primary creep deformation mechanism from a $\{111\}\langle 112 \rangle$ mode of shear to a $\{111\}\langle 110 \rangle$ mode. It is suggested that SRR99 crystals be tested under different conditions in order to ascertain whether such changes in mechanism occur and whether the same combination of heat-treatments provides the greatest

resistance to creep deformation.

The possibility of obtaining further improvements in creep performance by applying different combinations of heat-treatments may be investigated. For instance, it has been demonstrated that ageing at 900 °C produces an irregular, rounded and highly interconnected precipitate microstructure. The mechanical properties of material having such a microstructure might be expected to be considerably different from those of the more regular structures investigated in the present work. However, the mechanisms involved might be difficult to interpret.

APPENDIX

Coarsening by Particle Migration and Coalescence

An assessment is presented below of the kinetics of particle coarsening which would arise through the migration of particles towards each other and their subsequent coalescence. Doherty (1982) has proposed that such a mechanism might describe the coarsening of γ' precipitates in nickel-base superalloys containing large volume fractions of γ' . The driving force for the migration of the precipitates was suggested to be the removal of the elastically strained matrix lying between the precipitates. In the following treatment the rate-controlling process is considered to be the migration of the precipitates towards each other. The time taken for coalescence to occur once precipitates have encountered each other is assumed to be negligible.

Using Brown et al.'s (1968) adaptation of the formulation due to Mott and Nabarro (1940), the normal stress (σ) outside a misfitting spherical particle of radius r at a distance z from the centre of the particle is given by

$$\sigma = \frac{4G\epsilon^*r^3}{z^3} \quad (A.1)$$

where G is the shear modulus of the matrix and ϵ^* is a strain parameter for the particle. ϵ^* is defined as

$$\epsilon^* = \frac{3\kappa (\Delta a/a)}{3\kappa + 2E/(1 + \nu)} \quad (A.2)$$

where $\Delta a/a$ is the misfit parameter, κ is the bulk modulus of the

particle and E and ν are respectively Young's modulus and Poisson's ratio of the matrix. If $\nu = 1/3$ and the moduli of the matrix and of the precipitates are similar, then

$$\epsilon^* \approx \frac{2}{3} \Delta a/a. \quad (A.3)$$

Equation A.1 may be approximated to the case of a cubic precipitate of width w by substituting $w/2$ for r . Assuming that the strain energy per unit volume (U) is given by

$$U = \frac{\sigma^2}{2E}, \quad (A.4)$$

then

$$U = \frac{G^2 \epsilon^{*2} w^6}{8Ez^6}. \quad (A.5)$$

The strain field between two isolated cubic particles, whose initial centre-to-centre spacing is L may be considered, as shown in figure A.1.

As the two particles migrate towards each other, the line QQ' moves in the direction of increasing x , from its initial position where $x = 0$. The relation between z and x is given by

$$z = L/2 - x. \quad (A.6)$$

The motion of the precipitate is considered to be brought about by a flux of atoms from face A to face B. This flux may be expressed as

$$J = -C_a m_a \frac{dU}{dx} \quad (A.7)$$

or

$$J = \frac{-3C_a m_a G^2 \epsilon^2 w^6}{4E(L/2-x)^7} \quad (A.8)$$

where J is the number of atoms crossing unit area in unit time, C_a is the concentration of migrating atoms and m_a is their mobility.

The distance (δx) moved by interface B in time δt is given by

$$\delta x = J \Omega \delta t \quad (A.9)$$

where Ω is the atomic volume. Therefore the interface velocity, v_{int} is given by

$$v_{int} = J \Omega . \quad (A.10)$$

The time (t_c) taken for the particles to coalesce is

$$t_c = \int_0^{(L/2-w/2)} \frac{dx}{v_{int}}, \quad (A.11)$$

which upon substitution from equations A.8 and A.10 yields

$$t_c = \frac{E((L/2)^8 - (w/2)^8)}{6C_a m_a G^2 \epsilon^2 \Omega w^6} . \quad (A.12)$$

Assuming that the volume fraction (f) of particles is constant, then

$$L/2 = f^{-1/3} w/2 \quad (A.13)$$

and therefore

$$t_c = \frac{(f^{-8/3} - 1) E w^2}{1536 C_a m_a G^2 \epsilon^{*2} \Omega} . \quad (A.14)$$

Upon coalescing, the size of the new particle is greater than that of the two constituent particles by a factor of $2^{1/3}$. In a distribution having a mean size of $\bar{w}$, the rate of increase of $\bar{w}$ is therefore given by

$$\frac{d\bar{w}}{dt} = \frac{\bar{w}(2^{1/3} - 1)}{t_c} . \quad (A.15)$$

Assuming that the size of the two migrating particles treated above is the mean size of the whole distribution, then substitution for t_c from equation A.14 yields

$$\int_{\bar{w}_0}^{\bar{w}} \bar{w} d\bar{w} = \int_0^t \frac{1536 C_a m_a G^2 \epsilon^{*2} \Omega (2^{1/3} - 1) dt}{(f^{-8/3} - 1) E} \quad (A.16)$$

where $\bar{w}_0$ is mean particle size at time $t = 0$. Upon integrating, this expression yields

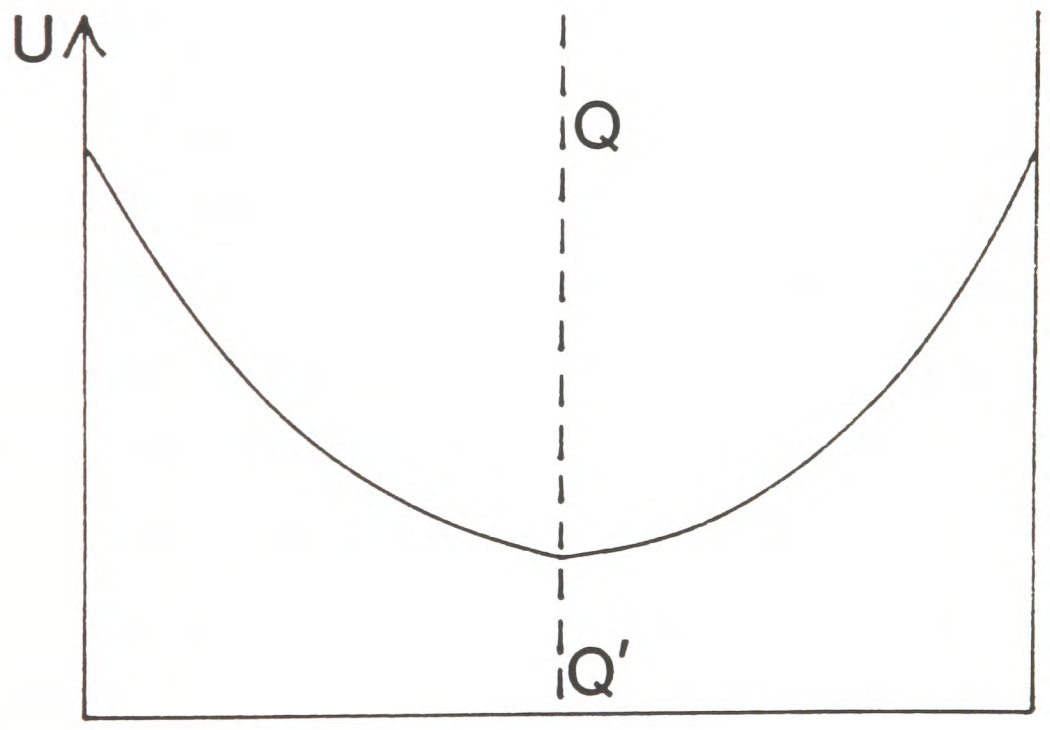
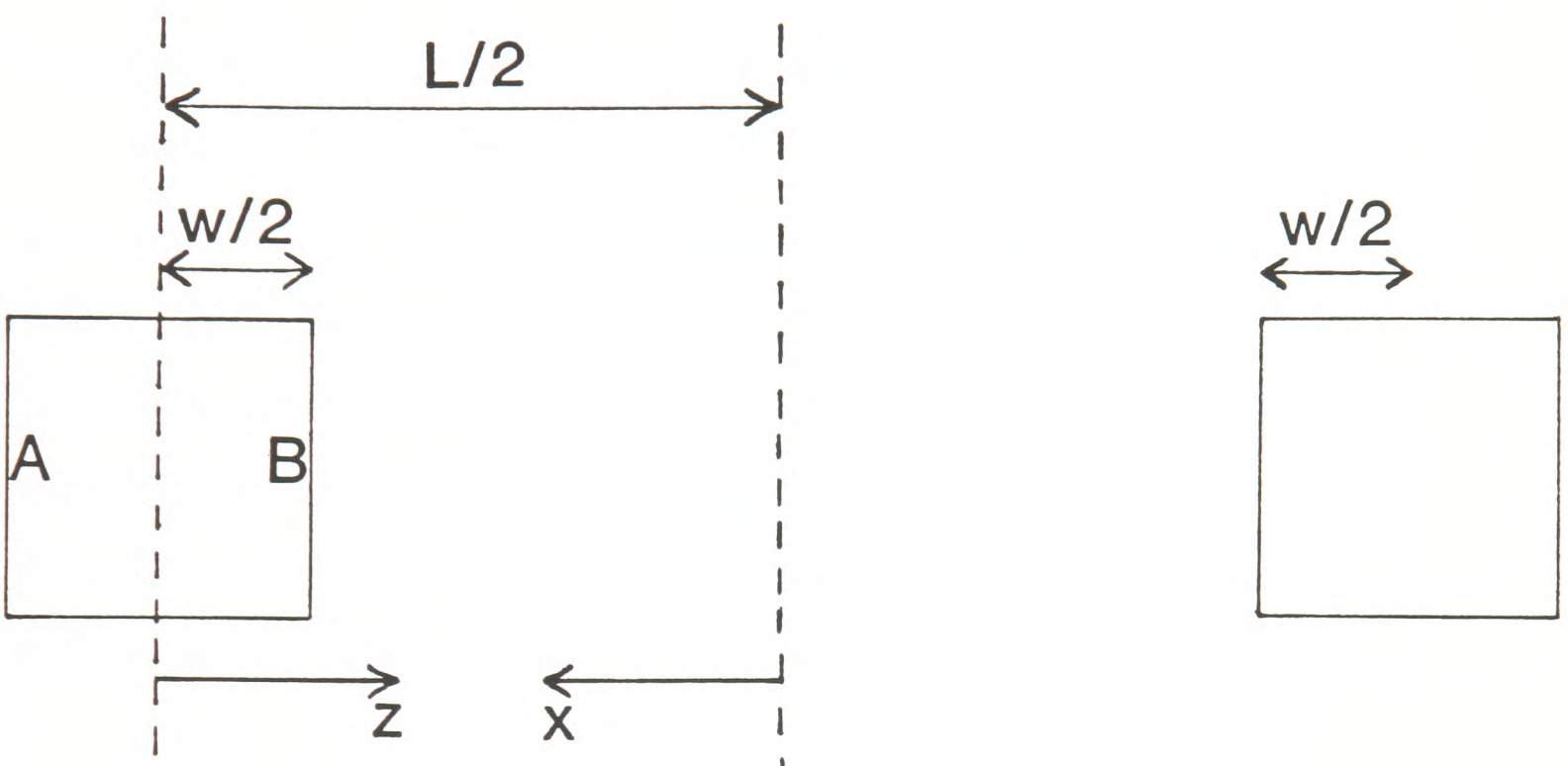
$$\bar{w}^2 - \bar{w}_0^2 = \frac{1536 C_a m_a G^2 \epsilon^{*2} \Omega (2^{1/3} - 1) t}{E(f^{-8/3} - 1)} \quad (A.17)$$

$$\text{or } \bar{w}^2 - \bar{w}_0^2 \propto t . \quad (A.18)$$

Thus the precipitate size is predicted by this model to increase in accordance with a power-law having a size exponent (n) of 2.

Figure A.1

Assumed form for the strain energy between two coherent precipitates.



REFERENCES

- Ahlquist, C.N. and Nix, W.D. (1969), Scripta Met., 3, 679.
- Ahlquist, C.N. and Nix, W.D. (1971), Acta Met., 19, 373.
- Ajaja, O., Howsen, T.E., Purushothaman, S. and Tien, J.K. (1980), Mat. Sci. Eng., 44, 165.
- American Society for the Testing of Materials (1983), Annual Book of ASTM Standards, 03.01, 140.
- Ansell, G.S. and Weertman, J. (1959), Trans. AIME, 215, 838.
- Ardell, A.J. (1970), Met. Trans., 1, 525.
- Ardell, A.J. (1972a), Acta Met., 20, 601.
- Ardell, A.J. (1972b), Acta Met., 20, 61.
- Ardell, A.J. and Nicholson, R.B. (1966a), Acta Met., 14, 1295.
- Ardell, A.J. and Nicholson, R.B. (1966b), J. Phys. Chem. Sol., 27, 1793.
- Arzt, E., and Ashby, M.F. (1982), Scripta Met., 16, 1285.
- Ashby, M.F. (1973), Proc. 3rd Int. Conf. on the Strength of Metals and Alloys, Cambridge, England, vol.2, p.8.
- Attwood, M., (1981), "Effect of Solution Treatments on the Metallography of Single Crystal Alloys", Rolls-Royce Internal Report No. CML 24341.
- Bailey, R.W. (1930), Engineering, 129, 265.
- Barratt, C.R. and Nix, W.D. (1965), Acta Met., 13, 1247.
- Beardmore, P., Davies, R.G. and Johnston, T.L. (1969), Trans. AIME, 245, 1537.
- Beeston, B.E.P., Dillamore, I.L. and Smallman R.E. (1968), Met. Sci. J., 2, 12.
- Beeston, B.E.P. and France, L.K. (1968), J. Inst. Metals, 96, 105.
- Bird, J.E., Mukherjee, A.K. and Dorn, J.F. (1969), Proc. Int. Conf. on Quantitative Relation Between Properties and Microstructure,

- Haifa, Israel, p.255.
- Blavette, D. and Bostel, A. (1984), *Acta Met.*, 32, 811.
- Blum, W. (1982), *Scripta Met.*, 16, 1353.
- Blum, W. and Portella, P.D. (1983), *Proc. 4th Risø International Symposium on Metallurgy and Materials Science*, ed. Bilde-Sørensen, H.B., Hansen, N., Horsewell, A., Leffers, T. and Lilholt, H., Risø National Laboratory, Roskilde, Denmark, p.161.
- Bowkett, K.M. and Smith, D.A. (1970), "Field-Ion Microscopy", North Holland Publishing Co.
- Brailsford, A.D. and Wynblatt, P. (1979), *Acta Met.*, 27, 489.
- Brøndsted, P. and Tøft Sørensen, O. (1978), *J. Mat. Sci.*, 13, 1224.
- Brown, L.M. (1982), *Proc. 3rd Risø International Symposium on Metallurgy and Materials Science*, ed. Lilholt, H. and Talreja, R., Risø National Laboratory, Roskilde, Denmark, p.1.
- Brown, L.M. and Ham, R.K. (1971) in "Strengthening Methods in Crystals", ed. Kelly, A and Nicholson, R.B., Elsevier Publishing Co., p.12.
- Brown, L.M., Woolhouse, G.R. and Valdré, U. (1968), *Phil. Mag.*, 17, 781.
- Burt, H., Dennison, J.P. and Wilshire, B. (1979), *Met. Sci.*, 13, 295.
- Burton, B. (1977), "Diffusional Creep of Polycrystalline Materials", Trans. Tech. Publications.
- Calderon, H. and Fine, M.E. (1984), *Mat. Sci. Eng.*, 63, 197.
- Caron, P. and Khan, T. (1983), *Mat. Sci. Eng.*, 61, 173.
- Chaturvedi, M.C., Lloyd, D.J. and Chung, D.W. (1976), *Met. Sci.*, 10, 373.
- Chellman, D.J. and Ardell, A.J. (1974), *Acta Met.*, 22, 577.
- Chou, C.T., Hirsch, P.B., McLean, M. and Hondros, E.D. (1982), *Nature*, 300, 621.

- Clauer, A.H. and Wilcox, B.A. (1966), Trans. AIME, 236, 570.
- Copley, S.M. and Kear, B.H. (1967), Trans. AIME, 239, 977.
- Corey, C.L. and Lisowsky, B. (1967), Trans. AIME, 239, 239.
- Courtney, T.H. (1977a), Met. Trans., 8A, 679.
- Courtney, T.H. (1977b), Met. Trans., 8A, 685.
- Crompton, J.S. (1983), D. Phil. Thesis, Oxford University.
- Davies, C.K.L., Nash, P. and Stevens, R.N. (1980a), J. Mat. Sci., 15, 1521.
- Davies, C.K.L., Nash, P. and Stevens, R.N. (1980b), Acta Met., 28, 179.
- Davies, R.G. and Stoloff, N.S. (1965), Trans. AIME, 233, 714.
- Decker, R.F. (1969), Proc. Symposium on Steel Strengthening Mechanisms, Zurich, Switzerland, Climax Molybdenum Co., p.147.
- Decker, R.F. and Mihalisin, J.R. (1969), Trans. ASM, 62, 481.
- Decker, R.F. and Sims, C.T. (1972), in "The Superalloys", ed. Sims, C.T. and Hagel, W.C., Wiley, p.33.
- Delargy, K.M. (1981), D. Phil. Thesis, Oxford University.
- Delargy, K.M. (1983), Rolls-Royce/Universities Meeting, Rolls-Royce Internal Report No. CML 25400.
- Delargy, K.M. and Smith, G.D.W. (1983), Met. Trans., 14a, 1771.
- Dennison, J.P., Holmes, P.D. and Wilshire, B. (1978), Mat. Sci. Eng., 33, 35.
- Doherty, R.D. (1982), Met. Sci., 16, 1.
- Dyson, B.F. and McLean, M. (1983), Acta Met., 31, 17.
- Erickson, J.S., Sullivan, C.P. and VerSnyder, F.L. (1974) in "High Temperature Materials in Gas Turbines", ed. Sahm, P.R. and Speidel, M.O., Elsevier Publishing Co., p.315.
- Evans, H.E. and Knowles, G. (1979), Proc. 5th Int. Conf. on the Strength of Metals and Alloys, Aachen, W. Germany, vol.1, p.301.
- Evans, H.E. and Knowles, G. (1980), Met. Sci., 14, 262.

- Evans, W.J. and Harrison, G.F. (1976), *Met. Sci.*, 10, 307.
- Evans, W.J. and Harrison, G.F. (1979), *Met. Sci.*, 13, 641.
- Exell, S.F. and Warrington, D.H. (1972), *Phil. Mag.*, 26, 1121.
- Fawley, R.W. (1972) in "The Superalloys", ed. Sims, C.T. and Hagel, W.C., Wiley, p.3.
- Flinn, P.A. (1960), *Trans. AIME*, 218, 145.
- Frank, F.C. (1951), *Phil. Mag.*, 42, 809.
- Friedel, J. (1964), "Dislocations", Pergamon Press, Oxford, p.239.
- Garofalo, F. (1963), *Trans. AIME*, 227, 351.
- Gerold, V. and Haberkorn, H. (1966), *Phys. Stat. Sol.*, 16, 675.
- Gibeling, J.C. and Nix, W.D. (1977), *Met. Sci.*, 11, 453.
- Gittus, J.H. (1974), *Acta Met.*, 22, 789.
- Gleiter, H. and Hornbogen, E. (1967/68), *Mat. Sci. Eng.*, 2, 285.
- Gröhllich, M., Haasen, P. and Frommeyer, G. (1982), *Scripta Met.*, 16, 367.
- Guard, R.W. and Westbrook, J.H. (1959), *Trans. AIME*, 215, 807.
- Hagel, W.C. and Beattie, H.J. (1959a), *Trans. AIME*, 215, 967.
- Hagel, W.C. and Beattie, H.J. (1959b) in "Precipitation Processes in Steels", Iron and Steel Inst. Special Report No. 64, p.98.
- Ham, R.K. (1967), *Proc. 1st Int. Conf. on the Strength of Metals and Alloys*, Tokyo, Japan, p.52.
- Harkness, S.D. and Hren, J.J. (1970), *Met. Trans.*, 1, 43.
- Harper, J. and Dorn, J.E. (1957), *Acta Met.*, 30, 881.
- Harris, K., Erickson, G.L. and Schwer, R.E. (1982), TMS-AIME High Temperature Alloys Committee Session, St. Louis, Missouri, U.S.A.
- Harris, K., Erickson, G.L. and Schwer, R.E. (1983), TMS-AIME High Temperature Alloys Committee Session, Philadelphia, Pennsylvania, U.S.A.
- Hausseilt, J.H. and Nix, W.D. (1977), *Acta Met.*, 25, 1491.

- Henderson, P.J. and McLean, M. (1983), *Acta Met.*, 31, 1203.
- Hirsch, P.B. and Kelly, A. (1965), *Phil. Mag.*, 12, 881.
- Hirsch, P.B. and Warrington, D. (1961), *Phil. Mag.*, 6, 735.
- Holt, R.T. and Wallace, W. (1976), *Int. Met. Rev.*, 21, 1.
- Hornbogen, E. and Roth, M. (1967), *Z. Metallk.*, 58, 842.
- Hornbogen, E. and Zum Gahr, K.H. (1975), *Metallography*, 8, 181.
- Howson, T.E., Mervyn, D.A. and Tien, J.K. (1980a), *Met. Trans.*, 11A, 1609.
- Howson, T.E., Stulga, J.E. and Tien, J.K. (1980b), *Met. Trans.*, 11A, 1599.
- Hüther, W. and Reppich, B. (1978), *Z. Metallk.*, 69, 628.
- Jianting, G., Ranucci, D., Picco, E. and Strocchi, P.M. (1983), *Met. Trans.*, 14A, 2329.
- Kear, B.H., Giamei, A.F., Leverant, G.R. and Oblak, J.M. (1969a), *Scripta Met.*, 3, 455.
- Kear, B.H., Leverant, G.R. and Oblak, J.M. (1969b), *Trans. ASM*, 62, 639.
- Kear, B.H. and Pearcey, B.J. (1967), *Trans. AIME*, 239, 1209.
- Kear, B.H., Oblak, J.M. and Giamei, A.F. (1970), *Met. Trans.*, 1, 2477.
- Kear, B.H. and Wilsdorf, H.G.F. (1962), *Trans. AIME*, 224, 382.
- Kelly, P.M. (1973), *Int. Met. Rev.*, 18, 31.
- Kirchner, H.O.K. (1971), *Met. Trans.*, 2, 2861.
- Knowles, G. and Evans, H.E. (1976), *Met. Sci.*, 10, 357.
- Lagneborg, R. (1969), *Met. Sci. J.*, 3, 161.
- Lagneborg, R. (1972a), *Met. Sci. J.*, 6, 127.
- Lagneborg, R. (1972b), *Int. Met. Rev.*, 17, 130.
- Lagneborg, R. (1973), *Scripta Met.*, 7, 605.
- Lall, C., Chin, S. and Pope, D.P. (1979), *Met. Trans.*, 10A, 1323.
- Langdon, T.G. and Yavari, P. (1982), *Acta Met.*, 30, 881.

- Leverant, G.R. and Kear, B.H. (1970), Met. Trans, 1, 491.
- Leverant, G.R., Kear, B.H. and Oblak, J.M. (1973), Met. Trans., 4, 355.
- Lifshitz, I.M. and Slyosov, V.V. (1961), J. Phys. Chem, Sol., 19, 35.
- Lindroos, V.K. and Miekko-Oja, H.M. (1968), Phil. Mag., 17, 119.
- Lupinc, V. (1982) in "High Temperature Alloys for Gas Turbines", ed.
Brunetaud, R., Coutsouradis, D., Gibbons, T.B., Lindblom, Y.,
Meadowcroft, D.B. and Stickler, R., Reidel Publ. Co., p.395.
- McKay, R.A. and Maier, R.D. (1982), Met. Trans., 13A, 1747.
- McLean, D. (1966), Rep. Prog. Physics, 29, 1.
- McLean, D. (1984), Met. Sci., 18, 249.
- McLean, D. and Hale, K.F. (1961) in "Structural Processes in Creep",
The Iron and Steel Institute, p.19.
- McLean, M. (1980), Proc. R. Soc. Lond., A371, 279.
- McLean, M. (1983), "Directionally Solidified Materials for High
Temperature Service", The Metals Society, London.
- Maeda, M., Oikawa, H. and Karashima, S. (1974), Scripta Met., 8, 183.
- Martin, J.W. (1980), "Micromechanisms in Particle-Hardened Alloys",
Cambridge University Press.
- Martin, J.W. and Doherty, R.D. (1976), "Stability of Microstructure in
Metallic Systems", Cambridge University Press.
- Meetham, G.W. (1982), The Metallurgist and Materials Technologist, 14,
387.
- Merrick, H.F. (1964), Proc. 3rd European Regional Conf. on Electron
Microscopy, Prague, Czechoslovakia, vol.A, p.171.
- Mitchell, W.I. (1966), Z. Metallk., 57, 586.
- Mitra, S.K. and McLean, D. (1966), Proc. R. Soc. Lond., A295, 288.
- Mott, N.F. and Nabarro, F.R.N. (1940), Proc. Phys. Soc., 52, 86.
- Mukherjee, A.K., Bird, J.E. and Dorn, J.E. (1969), Trans. ASM, 62, 155.
- Müller, E.W. (1951), Z. Phys, 131, 136.
- Müller, E.W., Panitz, J.A. and McLane, S.B. (1968), Rev. Sci. Instrum.,

39, 526.

Nabarro, F.R.N. (1967), Phil. Mag., 16, 231.

Nathal, M.V. and Ebert, L.J. (1983), Scripta Met., 17, 1151.

Norton, F.H. (1929), "The Creep of Steel at High Temperature",
McGraw-Hill.

Orowan, E. (1946/47), J. West Scotland Iron and Steel Inst., 54, 45.

Ostwald, W. (1900), Z. Phys. Chem., 34, 495.

Parker, J.D. and Wilshire, B. (1978), Met. Sci., 12, 453.

Pelloux, R.M.N. and Grant, N.J. (1960), Trans. AIME, 218, 232.

Penning, P. and De Wind, G. (1959), Physica, 25, 765.

Pearson, D.D., Kear, B.H. and Lemkey, F.D. (1981) in "Creep and
Fracture of Engineering Materials and Structures", ed. Wilshire,
B. and Owen, D.R.J., Pineridge Press, p.213.

Perry, B. and Smallman, R.E. (1972), Scripta Met., 6, 149.

Piearcey, B.J., Kear, B.H. and Smashey, R.W. (1967), Trans. ASM, 60,
635.

Pineau, A. (1976), Acta Met., 24, 559.

Rae, C.M.F. (1983), Rolls-Royce/Universities Meeting, Rolls-Royce
Internal Report No. CML 25400.

Rastogi, P.K. and Ardell, A.J. (1971), Acta Met., 19, 321.

Raymond, L. and Dorn, J.E. (1964), Trans. AIME, 230, 560.

Reppich, B. (1975), Acta Met., 23, 1055.

Reppich, B. (1982), Acta Met., 30, 87.

Reppich, B., Schepp, P. and Wehner, G. (1982), Acta Met., 30, 95.

Ricks, R.A., Porter, A.J. and Ecob, R.C. (1983), Acta Met., 31, 43.

Roome, R.G. (1981), "The Effect of an Ageing Treatment on the Creep
Behaviour of MM002 Single Crystal", Rolls-Royce Internal Report
No. CML 23865.

Roome, R.G. (1982), "The Effect of Nominal Composition Variations on

- the Creep Behaviour of Single Crystal Alloys derived from MM002",
Rolls-Royce Internal Report No. MEG 0645.
- Ross, E.W. (1967), J. Met., 19, December 1967, 12.
- Rowe, J.P. and Freeman, J.W. (1963), Joint Int. Conf. on Creep,
Inst. Mech. Eng., London, vol.1, p.65.
- Sherby, O.D. and Burke, P.M. (1967), Prog. Mat. Sci., 13, 325.
- Shewfelt, R.S.W. and Brown, L.M. (1977), Phil. Mag., 35, 945.
- Speight, M.V. (1968), Acta Met., 16, 133.
- Spilling, P. (1983), Private Communication.
- Staton-Bevan, A.E. and Rawlings, R.D. (1975), Phil. Mag., 32, 787.
- Stevens, R.A. and Flewitt, P.E.J. (1979a), Mat. Sci. Eng., 37, 237.
- Stevens, R.A. and Flewitt, P.E.J. (1979b), Proc. 5th Int. Conf. on
the Strength of Metals and Alloys, Aachen, W. Germany, vol.1,
p.439.
- Stevens, R.A. and Flewitt, P.E.J. (1981a), Acta Met., 29, 867.
- Stevens, R.A. and Flewitt, P.E.J. (1981b), Mat. Sci. Eng., 50, 271.
- Strutt, P.R., Khobaib, M., Polvani, R.S. and Kear, B.H. (1976),
Proc. 4th Int. Conf. on the Strength of Metals and Alloys,
Nancy, France, vol.1, p.314.
- Stüvve, H.P. (1965), Acta Met., 13, 1337.
- Takeuchi, S. and Kuramoto, E. (1973), Acta Met., 21, 415.
- Thompson, A.W. and Brooks, J.A. (1982), Acta Met., 30, 2197.
- Thompson, N. (1953), Proc. Phys. Soc., 66B, 481.
- Thornton, P.H., Davies, R.G. and Johnston, T.L. (1970), Met. Trans.,
1, 207.
- Tien, J.K. and Copley, S.M. (1971a), Met. Trans., 2, 215.
- Tien, J.K. and Copley, S.M. (1971b), Met. Trans., 2, 543.
- Tien, J.K. and Gamble, R.P. (1971), Mat. Sci. Eng., 8, 152.
- Tien, J.K. and Gamble, R.P. (1972), Met. Trans., 3, 2157.

- Tipler, H.R., Varma, R.K. and Loveday, M.S. (1981), Res Mechanica, 3, 141.
- Tsumuraya, K. and Miyata, Y. (1983), Acta Met., 31, 437.
- Twigg, E.S. (1981), "Fractographic Examination of Stress Rupture Test pieces in Single Crystal SRR9 Material", Rolls-Royce Internal Report No. CML 24635.
- Umakoshi, Y., Pope, D.P. and Vitek, V. (1984), Acta Met., 32, 449.
- Van der Molen, E.H., Oblak, J.M. and Kriege, O.H. (1971), Met. Trans., 2, 1627.
- VerSnyder, F.L. (1982) in "High Temperature Alloys for Gas Turbines", ed. Brunetaud, R., Coutsouradis, D., Gibbons, T.B., Lindblom, Y., Meadowcroft, D.B. and Stickler, R., Reidel Publ. Co., p.1.
- VerSnyder, F.L. and Guard, R.W. (1960), Trans. ASM, 52, 485.
- VerSnyder, F.L. and Shank, M.E. (1970), Mat. Sci. Eng., 6, 213.
- Vittori, M. (1981), J. Mat. Sci., 16, 3461.
- Wagner, C. (1961), Z. Electrochem., 65, 581.
- Webster, G.A. and Pearcey, B.J. (1967), Met. Sci. J., 1, 97.
- Weertman, J. (1957), J. Appl. Physics, 28, 362.
- Weertman, J. and Weertman, J.R. (1965) in "Physical Metallurgy", ed. Cahn, R.W., North-Holland Publ. Co., p.793.
- Wellner, P. (1980), Praktische Metallographie, 17, 525.
- Wells, C.H. (1967), Trans. ASM, 60, 270.
- Williams, K.R. and Cane, B.J. (1979), Mat. Sci. Eng., 38, 199.
- Williams, K.R. and Wilshire, B. (1973), Met. Sci. J., 7, 176.
- Winstone, M.R. (1981), "The Effects of Orientation on the Properties of Single Crystals of the Nickel Superalloy Mar-M002", NGTE Memorandum M81017.
- Wolfendale, P.C.F. (1968), J. Sci. Instrum., 1, 817.

Woodyatt, L.R., Sims, C.T. and Beattie, H.R. (1966), Trans. AIME,
236, 519.

Ya-Fang Han, Deb, P. and Chaturvedi, M.C. (1982), Met. Sci., 16, 555.

Yavari, P., Miller, D.A. and Langdon, T.G. (1982), Acta Met., 30, 871.

GLOSSARY OF SYMBOLS

A, A'	Constants
A^*	Activation area
A_0	Initial cross-sectional area of specimen
APB	Antiphase boundary
a	Lattice parameter
$\Delta a/a$	γ/γ' misfit parameter
B, B', B''	Constants
b	Magnitude of Burgers vector
$C_1, C_2, C_3, C_4, C_5, C_6, C_7$	Constants
$C(r)$	Molar solute concentration in matrix at interface with precipitate of radius r
$C(\infty)$	Equilibrium molar solute concentration in matrix
C_a	Concentration of migrating atoms
C_p	Molar fraction of solute in precipitate
C_v	Vacancy concentration
CF	Complex fault
CRSS	Critical resolved shear stress
D	Diffusion coefficient
D_s	Self-diffusion coefficient
D_p	Pipe diffusion coefficient
D_0	Pre-exponential term for diffusion coefficient
d	Particle diameter in the slip plane
d_c	Critical particle diameter for the onset of Orowan looping
d_{ap}	Ion flight distance in the atom probe

E	Young's modulus
E_{XY}	Bond energy between atoms X and Y
e	Charge of an electron
F	Applied load
f	Precipitate volume fraction
G	Shear modulus
ΔG	Difference in shear modulus between matrix and precipitate
g	Diffraction vector
$g(w)$	LSW precipitate size distribution function, normalised with respect to the experimental distribution
$h(r^*), h(w^*)$	LSW precipitate size distribution function
h	Strain-hardening coefficient
I_m	Complex function of r and Ψ_{sf}
J	Number of atoms crossing unit area in unit time
K, K', K'', K''', K''''	Constants
K_n, K_2, K_3, K_4, K_5	Rate constants for precipitate coarsening where the size exponent is $n, 2, 3, 4, 5$ respectively
k	Boltzmann's constant
L	Planar centre-to-centre particle spacing
L_{FR}	Length of Frank-Read source
L_j	Separation of jogs
l	Mean free path of dislocation motion
l_0	Initial length of specimen
Δl	Increase in length of specimen

m	Mass of ion
m/n_e	Mass to charge ratio of ion
m_a	Mobility of migrating atoms
m_d	Mobility of climbing dislocations
N_d	Number of dislocation sources per unit volume
N_p	Number of precipitates measured in an experimental size distribution
N_v	Electron vacancy number.
n	Stress exponent or precipitate size exponent
n_e	Number of electronic charge units on an ion
p	Constant
q	Number of different ageing times at a given temperature
Q	Activation energy
Q_{SD}	Activation energy for self-diffusion
R	Molar gas constant
r	Precipitate radius
$\bar{r}$	Mean precipitate radius
$\bar{r}_0$	Mean precipitate radius at time $t = 0$
r^*	Reduced precipitate radius, $r/\bar{r}$
r_i	Inner dislocation cut-off radius
r_n	Dislocation network spacing
r'	Rate of recovery
S -ISF	Superlattice intrinsic stacking fault
S -ESF	Superlattice extrinsic stacking fault
T	Absolute temperature
T_m	Absolute melting temperature
t	Elapsed time

t_c	Time for particles to migrate and coalesce
U	Strain energy per unit volume
V_m	Molar volume of precipitate
V_0	Standing voltage
V_p	Pulse voltage
v	Mean dislocation velocity
v_{int}	Velocity of migrating particle/matrix interface
w	Square root of measured precipitate area, equal to side length for cubic precipitate.
$\bar{w}$	Mean value of w
$\bar{w}_0$	Value of $\bar{w}$ at time $t = 0$
w^*	Reduced precipitate size, $w/\bar{w}$
x	Distance
z	Distance
Z	Atomic number
$\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6$	Constants
Γ	Dislocation line tension
ϵ	True strain
ϵ_{eng}	Engineering strain
ϵ_0	Instantaneous strain
ϵ_p	Primary creep strain
$\dot{\epsilon}$	Strain-rate
$\dot{\epsilon}_0$	Initial strain-rate
$\dot{\epsilon}_p$	Primary creep strain-rate
$\dot{\epsilon}_s$	Steady state creep strain-rate
$\dot{\epsilon}_{min}$	Minimum strain-rate
ϵ^*	Strain parameter (defined in equation A.2)

θ	Angular orientation parameter for tensile axis (defined in figure 4.5)
κ	Bulk modulus
ν	Poisson's ratio
ρ	Number of dislocations per unit volume
σ	True stress
σ_{eng}	Engineering stress
σ_e	Effective stress
σ_i	Internal stress
σ_0	Threshold stress
σ_{or}	Orowan stress
σ_p	Contribution to σ_0 from precipitates
σ_s	Contribution to σ_0 from solute
σ_{sd}	Standard deviation
σ_y	Yield stress
$\Delta\sigma_y$	Increment to yield stress
$\sigma_{0.05}$	0.05% proof stress
$\sigma_{0.2}$	0.2% proof stress
τ	Shear stress
τ_{or}	Orowan shear stress
τ_{back}^{max}	Maximum back shear stress
τ_y	Shear yield stress
$\Delta\tau_y$	Increment to shear yield stress
ϕ	Angular orientation parameter for tensile axis (defined in figure 4.5)
χ_0	Angle between tensile axis and slip direction before deformation
χ_1	Angle between tensile axis and slip direction after deformation

Ψ_{apb}	Antiphase boundary energy per unit area
Ψ_{int}	Interfacial energy per unit area
Ψ_{sf}	Stacking fault energy
$\Delta\Psi_{\text{sf}}$	Difference in stacking fault energy between precipitate and matrix
Ω	Atomic volume