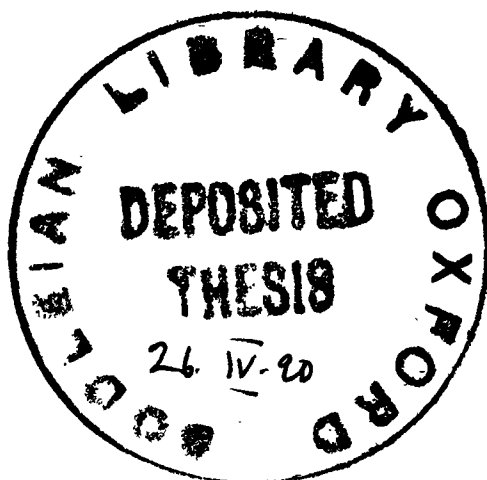


THE STRESS CORROSION OF A SENSITISED STAINLESS STEEL

A study of the effect of low frequency cyclic loading on the process of stress assisted corrosion in "sensitised" 20% Cr, 25% Ni, 0.7% Nb stainless steel, whilst in HNO_3 solution.

Thesis submitted for the degree of Doctor of Philosophy in the University of Oxford.



Trinity Term 1989.

C.J.Moss
Linacre College, Oxford.

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THE STRESS CORROSION OF A SENSITISED STAINLESS STEEL

Abstract

C.J.Moss

Linacre College, Oxford University

The following work divides into two parts:

- a: a study of the effect of stress on the inter-granular stress assisted corrosion attack of sensitised 20% Cr, 25% Ni, 0.7% Nb in HNO_3 environments. This problem was suggested by the C.E.G.B. and relates to the potential corrosion problems of AGR fuel cladding during storage after use. The aim of this work was therefore to determine how metallurgical condition, test potential and mechanical test variables affect corrosion behaviour. Low frequency cyclic loading offers a way to investigate the stress corrosion of systems at realistic stress levels and strain rates found in practice.
- b: an investigation into the effect of a low frequency cyclic stress on the process of stress assisted corrosion. The aim of this work was to gain information on the effect of stress cycling on the process of stress assisted corrosion attack.

Tensile specimens were subjected to static loads both alone and with superimposed low frequency (10^{-4} to 10^{-2} Hz) saw-tooth stress cycles. Cycling was carried out potentiostatically in HNO_3 environments, at below yield stress levels and ambient temperatures. Different frequencies, cyclic amplitudes and levels of background tensile stress were used. Irrespective of loading conditions the optimum potential for accelerated stress assisted corrosion attack was found to be -200mV (SCE).

The results of tests showed that test potential, cycle frequency, cycle amplitude and level of background stress strongly affect rates of attack. Grain boundary penetration rates were found to increase as frequency decreased and as peak stress and stress amplitude increased. Different kinetics of penetration were seen for cyclic and static loading. Increase of penetration depth with time for cyclic loading experiments was found to vary with $(\text{time})^{0.5}$ whilst that for static loading experiments increases linearly with time.

A number of reasons are discussed to explain the difference in observations between cyclic and static penetration rates. Such reasons included the difficulty of ion transport down narrow paths, blunting of the penetration front, the possibility of local strain

induced martensite transformation leading to hydrogen embrittlement and plastic strain enhanced dissolution resulting during cyclic loading.

The anomalous effects observed during cyclic loading (such as "strain softening") were examined for tensile specimens cycled under a range of mechanical conditions. It was found that the extent of plastic strain increased for higher stress and larger cycle amplitudes.

The process of thermal sensitisation of 20 wt% Cr, 25 wt% Ni, 0.7 wt% Nb stainless steel in three different material starting conditions (bar, "reworked bar" and tube) was investigated. Both Cr depletion and impurity segregation are discussed as mechanisms of sensitisation. An attempt was made to correlate response in chemical and electrochemical tests with both microanalytical (STEM/EDX) observations on the shape of Cr depletion profiles and with analytical modelling. The collector plate model was found to describe AEM measured Cr depletion profiles well.

PREFACE AND ACKNOWLEDGEMENTS

The work described in this thesis was carried out by the author in the Department of Metallurgy and the Science of Materials, University of Oxford, between the dates of October 1983 and September 1986.

No Part of this thesis has been submitted for a degree at this or at any other university. The work of others has been freely drawn on, and where this is so reference is made in the text.

A small part of the work in chapter 4 forms the basis of a paper presented (by J.M.Sykes and C.J.Moss) at a symposium on Radiation Induced Sensitisation of Stainless Steels, held at Berkeley Nuclear Laboratories, September 1986.

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INTRODUCTION

Fe/Cr/Ni alloys are extensively used in industry because of their ability to withstand highly corrosive conditions. However under certain conditions they can fail by the conjoint action of stress and corrosion at stress levels well below those necessary for mechanical failure. Sudden catastrophic failure of engineering structures resulting from stress corrosion cracking (SCC) or stress assisted corrosion attack must be avoided.

1.1. Objectives of work

The major goal of this study was to examine the effect of imposed low frequency cyclic stress on the stress assisted corrosion attack of 20% Cr, 25% Ni, 0.7% Nb stainless steel, when it is in a specific microstructural condition. The practical motivation underlying the work arises from a need to understand potential corrosion problems that may occur in Advanced Gas Cooled Reactor (AGR) fuel cladding, resulting from a change in microstructure during long term reactor exposure.

1.2. Structure of thesis.

The introduction aims to outline why the problem dealt with in this thesis is important and to place the work in context.

Existing theories and mechanisms of stress assisted corrosion attack are reviewed in chapter 2, and evidence that low frequency stress cycling accelerates SCC is discussed.

To understand the relationship between intergranular attack (IGA) and SCC it is also necessary to understand the local microstructural change that leads to enhanced local corrosion (sensitisation). An explanation of such phenomena requires an understanding of the precipitation of the phases causing the effect. The process and modelling of sensitisation, and the metallurgy of 20%Cr, 25% Ni 0.7% Nb are discussed in chapter 3.

Chapter 4 discusses experimental techniques used to assess the extent of sensitisation, and presents the results of such tests for a range of different heat treatments of the materials used in this study.

Chapter 5 describes microanalysis of grain boundary regions carried out by analytical electron microscopy (AEM). Data from modelling the local changes in composition with time at ageing temperature are compared to microstructural and microanalytical observations. A correlation with experimental measurements of sensitisation is attempted.

Chapter 6 describes the method used for examining the effect of an

imposed low frequency cyclic stress on stress assisted corrosion attack behaviour and presents the results of such tests on sensitised AGR can material.

Chapter 7 discusses the effect of the imposed cyclic stress system on the mechanical response of the alloy and the importance of this response to enhancement of stress assisted corrosion attack.

Chapter 8 draws all observations together and provides an overall summary of this work and suggests recommendations for further work.

1.3. Background to the study

1.3.1. Clad requirements

A fuel element in the current Advanced Gas Cooled Reactor (AGR) consists of a bundle of 36 pins; 8 such elements are suspended from a common tie bar to form a stringer. The stringer remains in the reactor for times up to 3 years. Fuel pins comprise of stacks of one meter long fuel elements containing enriched UO_2 pellets. Stainless steel cladding separates the CO/CO_2 gas coolant from the enriched UO_2 fuel pellets. The main duty of the cladding alloy is to isolate radioactive products from the gas coolant and therefore it must remain leak tight throughout its dwell time in the reactor. Integrity must be maintained in order that fission products are not released into the primary coolant circuit. Thus the clad must be compatible with the fuel, fission products and the coolant at service temperatures, and its mechanical properties must be sufficient to prevent failure during steady state and transient reactor operating conditions. A further requirement is that the clad must have sufficient strength and corrosion resistance to remain intact during fuel handling and storage operations. The material designed for AGR fuel cladding is a Nb stabilised, 20 wt % Cr, 25 wt % Ni austenitic stainless steel.

Long term exposure to the reactor environment (where temperatures range from 300 to 600°C and cans are exposed to irradiation doses of 10^{24} displacements per atom) results in intergranular precipitation of M_{23}C_6 and Ni_3Si together with solute segregation [1]. Precipitation and segregation result in a change in local composition at grain boundaries from the matrix composition. The resulting sensitised regions at grain boundaries may have markedly impaired corrosion resistance to the environments that the can will meet at later stages [2].

1.3.2. The integrity of cladding

Interest in the integrity of the fuel cladding arises from the following observations.

1. At commercial AGR's spent fuel is discharged from the reactor directly into cooling ponds containing water dosed with 1250 ppm boron (added as boric acid, neutralised with NaOH). Originally it was intended that the fuel should spend about 120 days in the cooling pond in order to permit the dissipation of decay heat prior to transportation to Windscale for reprocessing; in practice longer storage times may be necessary.
2. After pond storage fuel pins may be stored in "caves". Although the air in the caves is of low humidity (<30% RH) monolayer condensation and droplet formation (resulting from capillary radius condensation) may occur on the surface of the clad. Because the pins are highly radioactive, radiolysis of air may produce oxides of N_2 . Therefore condensation and corrosive ion (NO_3^-) formation may occur [3], in cracks or pores in corrosion products. Fuel pins have been shown to experience IGA in damp electrochemical environments [4]. Radiation is known to move the potential of the material to regions where IGSCC occurs [5].
3. AGR fuel temperatures during full power operation vary with can position but can be of the order of 700°C. The pins may experience peak systematic temperatures of 750°C with random hot spots of up to 850°C, during exposure to moist CO_2 at 40 ATM [6]. Slow straining of the fuel cladding may result. When reactor power is reduced strain reversal may then take place in the clad by mechanical interaction between fuel and fuel cladding as a result of differential thermal contraction. Therefore, the cladding may experience a combination of creep and fatigue cycling at a variety of temperatures in an irradiation environment. The fuel cladding after use will therefore have undergone a complex stress/strain history before storage, and will contain residual stress.

Therefore the need for more characterisation of the intergranular corrosion of AGR fuel cladding in HNO_3 environments, when a stress is present became apparent.

1.3.3. SCC and stress assisted corrosion attack

SCC is a phenomenon which is seen where, in the presence of corrosion or stress alone, no failure would be expected. Normally ductile

alloys can display apparently brittle behaviour and can fail at much reduced stress intensity levels. Under cyclic loading conditions, cracking can occur in many material/environment combinations that will not promote attack. It has been observed [7,8] that cyclic loading is very potent for inducing SCC, and indeed SCC may be seen at peak stresses well below those required for SCC during static stress cracking.

The imposed stress system may greatly affect the rate of attack; however in the systems found in practice the conditions of stress are complex and may not be fully known. SCC test methods are required that give a correct understanding of susceptibility to SCC. Many existing methods of assessing SCC susceptibility use either static stress levels that are above the yield stress, or constant strain rate (CSR) methods, where the yield stress is rapidly exceeded. The advantage of the CSR test as compared with constant load or constant strain testing is the improved reproducibility by a better control and registration of significant SCC parameters such as strain rate [9,10]. The CSR method indicates relatively quickly the susceptibility of a material to SCC in a particular environment. Static tests at the stresses found in the system in question are often slow to show cracking, and the use of a pre-cracked specimen to overcome initiation times may be unrepresentative of the practical situation.

Low frequency cyclic loading offers the chance of studying SCC initiation and propagation at below yield stress levels whilst keeping strain rate as an important variable. However little work has been carried out on the phenomena of the enhancement of environmentally assisted attack or crack growth, under cyclic stress.

This work combines two elements:

1. To gain further knowledge of the stress assisted corrosion attack and SCC of sensitised 20% Cr, 25% Ni, 0.7% Nb stainless steel.
2. To extend the previous work of low frequency cyclic stress on SCC and stress assisted corrosion attack.

It was therefore decided to investigate the SCC of sensitised 20% Cr, 25% Ni, 0.7% Nb stainless steel, in HNO_3 environments. The stress system chosen imposed low frequency cyclic loading at below yield stress levels.

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CHAPTER 2

STRESS CORROSION CRACKING

The aim of this chapter is to describe the fundamental ideas and underlying mechanisms of stress corrosion cracking (SCC), and the exacerbating role of a low frequency dynamic stress on SCC.

The terms SCC and environmentally assisted crack growth refer to the synergistic effect of stress and a corrosive environment. Damage is much more severe than that resulting from either parameter alone and causes macroscopically observed cracking, which may lead to failure. Environmentally assisted attack covers a broad spectrum of failure mechanisms ranging from corrosion fatigue to SCC and hydrogen embrittlement. These forms of attack are related and much work has been done to provide knowledge of observed effects.

Under the action of SCC, normally ductile alloys such as austenitic stainless steels show embrittled behaviour, and high strength alloys fail at much reduced stress intensities, well below those necessary for fast fracture in the absence of environmental influence. Virtually all alloys are susceptible to some form of SCC when specific conditions exist. The most important variables are microstructure, stress state, environmental composition and electrode potential. Although most engineering materials operate outside the narrow regimes of intolerance random failures still occur. Despite satisfactory general corrosive behaviour, SCC of stainless steels is a major problem. A study by Dupont, carried out in 1968, revealed that one quarter of all their material failures (both mechanical and corrosive) was due to SCC. This data is shown in Table 1 [1].

Although the list of chemically distinct environments that cause SCC in a given alloy is continually being extended, the concept that specific environment/alloy combinations are susceptible to SCC still remains. A list of combinations classically regarded as leading to SCC are listed in Table 2 [2]. The list may be extended to embrace a much wider range of bulk failure environments. Furthermore, under cyclic loading conditions (corrosion fatigue) environment assisted attack can occur in many materials which would not promote SCC.

2.1. Mechanisms and the phenomenon of SCC.

It is not possible to produce a single unified theory of SCC and different mechanisms are applicable to different cases. Any proposed mechanism must explain why the characteristic geometry of a crack is developed and retained.

The presence of a large number of variables influencing SCC and the difficulty of explaining why SCC proceeds along a narrow path, has given rise to a number of different mechanistic theories for different systems. It is now the opinion of most researchers that SCC is a generic term and that no single mechanism can account for all the situations where SCC occurs.

The process of failure due to SCC may be split into two parts.

1. Initiation.
2. Propagation.

The initiation period refers to the time before cracks are detectable; propagation refers to the period during which cracks are lengthening.

2.1.1. Initiation.

Initiation is preceded by localised damage of the protective passive film. The time to initiation is a measure of resistance of an alloy to SCC. Table 3 summarises the principal mechanisms of crack initiation. Initiation sites divide into pre-existing and those developed in service. Within each group the initiating feature may exert a localised mechanical influence or have a chemical influence associated with the concentration of ionic species or the development of acidity.

It has been postulated [3] that the following properties influence initiation:

1. The resistance of the metal in its active state to general corrosion.
2. The chemical immunity of the passive film at the metal surface.
3. The kinetics of film formation.
4. The physical and mechanical properties of the film eg, ductility.

5. The structure of the metal (inhomogeneity, grain size, inclusions)

Microstructural change leading to SCC is especially insidious because it is not associated with deviation in environment or materials specification problems, but because change occurs during service.

Cracks can often initiate at second phase inclusions and precipitates.

Inclusions and precipitates may have three effects:

1. In stagnant solutions chemical attack on the inclusion/precipitate or depleted zone may alter the solution chemistry.
2. Removal of a favourably orientated inclusion may leave a stress concentrating flaw and generate a pit-like environment, (stress raisers on a plain surface will be preferred sites for initiation)
3. The second phase may alter the rate of formation of the passive film locally over such microstructural features.

An example of the influence of the role of inclusions is given by Parker [4], who demonstrated that crack initiation could be controlled by the presence of non-metallic inclusions, and attributed the presence of fractures in segregated regions of turbine discs, when testing in high purity steam and the unusual occurrence of TGSCC in ferritic alloys to the presence of inclusions. He suggested that pits do not act as stress raisers (such that the stress concentration effect exceeds that necessary for fracture), but through causing local changes in potential and concentration.

2.2. Crack Propagation.

The models of SCC propagation can be divided into two main classes:

1. Those which consider that crack propagation proceeds by anodic dissolution at the crack tip and
2. Those which consider that crack propagation is predominantly mechanical.

These were considered by Parkins [3] as mechanisms at the extremes of a spectrum of SCC mechanisms. As the spectrum is traversed a picture of SCC is gained where emphasis shifts from the mechanical properties of the alloy as the important factor, with corrosion playing only a minor part, to one in which the metal of the crack is removed by dissolution, and only marginally assisted by stress.

Parkins listed the following mechanisms for SCC propagation.

1. Strain generated active paths
2. Pre-existing active paths
3. Adsorbed species at the crack front (including hydrogen embrittlement mechanisms)

These mechanisms are now outlined.

If the microstructure is such that the alloy has a continuous path of segregant or precipitate at grain boundaries, then intergranular attack (IGA) along pre-existing paths may be activated by stress. This implies that in these systems, the grain boundary is a preferred region for attack owing to chemical heterogeneity or precipitation of a second phase. These effects may be rationalized in relation to the effects on the nature and distribution of sites for localised corrosion. The grain boundaries will be electrochemically and mechanically different to the matrix by virtue of its structure and altered composition. The precipitate, or associated precipitate denuded zone, or segregant may act as the anode or as an efficient cathode in a local cell and cause local dissolution. The ensuing corrosion acts under stress to open up a crack. Where pre-existing paths do not exist, strain may initiate attack by rupturing the protective film and allowing dissolution at emerging slip systems. Such forms of attack follow strain generated paths and are usually transgranular. The final mechanism listed is brittle fracture, which may be facilitated by either the adsorption of aggressive species or the formation of brittle phases at the crack tip.

Fig. 1 shows a montage prepared by Staehle [7] showing the large number of processes that may influence SCC propagation. As shown, these processes may include metal dissolution, film rupture, slip, change in local solution composition, electrochemical reduction, dislocation/crack interactions, grain boundary precipitation, adsorption reactions at the crack tip, etc and many others.

2.2.1. Dissolution models.

SCC may occur in alloys which are otherwise highly resistant to overall corrosion in the same environment; indeed, it is usually a requirement that this is so. The high rate of the anodic process at the crack tip can only be understood in terms of differences in electrochemical behaviour between the unaffected regions and the anodic crack tip. Early SCC models to explain this were dominated by physical metallurgy considerations, with corrosion rarely being considered, until the ideas of Dix [5] where crack growth proceeded by metal dissolution along susceptible pre-existing paths. The concept maintains that the deforming film-free metal at the crack tip is

anodic with respect to the non-deforming walls of the crack. The surface away from the crack tip must be able to contribute to SCC by being the cathode of the corrosion couple.

The average crack velocity reflects the periods of time the crack is both active and inactive. If the material at the crack tip were to remain active and if growth were determined by dissolution when the metal surface is active, the crack growth from Faradaic considerations of the amount of material removed may be expressed by:

$$1. \quad V = \frac{IM}{ZFp}$$

V = crack velocity

I = anodic current density seen from bare, active surfaces

M = atomic weight of the metal of valency Z

p = density

F = The Faraday constant (9.65×10^4 Coulombs)

This represents the limiting bound for crack velocity when dissolution is the rate determining process. Faradaic rates describe some systems well [13,33,34]; fig. 2 was produced by Parkins [6]. The line shown is that determined from equation 1; the crack growth rates are shown for a number of systems, and good correlation is seen between theory and experiment. It is now realised [13,33,34] that a reasonable correlation between crack propagation and dissolution rate can only be obtained if the current (I in equation 1) corresponds to the measured current of the bare metallic surface exposed to the environment in the absence of a protective film.

Several models based on the anodic dissolution concept exist and only the major ideas are discussed here. Models may be represented by consideration of stress assisted dissolution, strain assisted dissolution, the bare crack tip concept and the periodic film rupture models.

2.2.1.1. Mechano-chemical mechanisms

Many authors [8 to 14] suggest that because the advancing crack tip is yielding, the metal at the crack tip is electrochemically active and dissolves rapidly. Hoar and West [15,16] concluded that this was due to an increase in the number of surface atoms available to react as slip planes or dislocations emerge at the surface. They suggested that yield-assisted dissolution was a conjoint mechanical/chemical phenomena and did not result from the consecutive action of processes. Hoar [17] was able to correlate current densities to crack propagation rates and concluded that crack propagation took place because metal at

the yielding advancing edge was kept electrochemically active by rapid straining and could dissolve many times faster than the passive sides.

2.3.1.2. Film Rupture model.

The slip dissolution model has the most support of any single SCC model and such a model has been correlated to SCC results for a variety of systems. The importance of dissolution processes resulting after film rupture was first suggested by Champion and Logan [18]. More recent authors include Parkins, Doig, Green, Pugh, Staehle, Scully and many others [19-34].

This model is based on the mechanical difference between the underlying ductile metal and the less ductile passive film. The metal remains passive until the protective film is ruptured by plastic deformation, which is caused by the transfer of strain from the base metal to the film. After rupture, active dissolution may take place on film-free areas. A suitable combination of strain rate and solution chemistry is required to propagate the initiating defect, in order to prevent it developing into a pit or repassivating too quickly.

The main features of such a model are shown schematically in fig. 3. This illustrates the relationship between the current-time transient (that resulting from film rupture), and the amount of material dissolved for a given slip event.

If the passive film forms rapidly SCC does not occur. If passivation is too slow, lateral dissolution is favoured and a wide shallow pit forms. A balance between dissolution and passivation is required, so that the geometry of the dissolved regions corresponds to a crack-like geometry and the crack does not develop into a pit or passivate too quickly.

Crack propagation occurs by a discontinuous cycle of passivation and film rupture. Stress activates dissolution either by oxide film rupture (to expose bare metal on a slip plane by emergence of dislocations) or at a pre-existing path. Anodic attack then occurs at a rate determined by Faraday's law. The rate decreases as the film forms and passivation occurs. The net result is metal loss to a certain depth of penetration each cycle of crack increment.

Precipitate-free or alloy depleted zones may lead to IGSCC by this mechanism because they differ from the matrix both mechanically and electrochemically [32].

Scully [33,34] suggested that the crack tip was continuously active, but the current varied in a periodic manner. He suggested that the main requirement for SCC is the delay in repassivation time during

which a certain coulombic charge flows. The strain rate and repassivation rate are in a state of imbalance. Fig. 4 shows the requirement that sufficient charge $[Q_{min}]$ passes before the strain rate falls. The model predicts that higher stresses at the crack tip produce higher initial creep rates and consequently times spent at higher current densities will be longer. The rate controlling process may, therefore, be the rate of film growth over the crack tip and the frequency with which the film is disrupted to reinitiate crack growth. Evidence of this process is given by many authors [21 to 31].

Coplanarity of slip favours SCC because stress produces a discrete break in the passive film. Coarse slip involves the formation of a small number of active long glide planes. For thin films and coarse slip, the slip steps produced by dislocations emerging at the surface can be larger than the passive film thickness, dislocations pile up at the surface until concentration of stress is sufficient to crack the oxide and expose bare metal. Potential is a critical parameter for the preferential activation of slip steps as crack initiation sites as it controls film thickness and repassivation rate [35]. Swann [36] attempted to relate SFE (stacking fault energy, which changes with Ni content in stainless steels) with the mode and rate of crack path, as the slip mode changes from wavy line to planar slip and the steel becomes more susceptible to SCC. Swann and Pickering [37] and Bubar and Vermilyea [38,39] suggested that if the oxide film were sufficiently plastic, a larger discrete slip step would be required for SCC.

2.2.2. Mechanical models.

Some systems show crack advance which is more rapid than would be seen if controlled by anodic dissolution alone. The high rate of crack propagation in such systems is therefore an objection to an electrochemical mechanism [40,41].

Alternative models to explain fast crack propagation are based on mechanical properties of the film and material at the crack tip. The models describing rapid crack propagation are adsorption, hydrogen embrittlement, brittle film and tunnelling models.

2.2.2.1. The adsorption model.

Uhlig [42] proposed that a critical potential existed for SCC in particular environment/metal systems and that at this potential ions chemisorbed preferentially on to emergent defects at the crack tip. Surface active species interact with strained bonds to cause a reduction in bond strength, and reduce the surface energy term. This reduction of surface energy reduces the energy for the crack to

progress, indicated by eg. Petch [43] or Stroh [44] relationships. McMahon and Vitek [45] suggested that strain energy and chemical energy was adsorbed in bond stretching and breaking and in dislocation emission, and that grain boundary fracture was related directly to grain boundary structure and bonding environment. Uhlig [46] maintained that the reduction in metal bond strength occurred in a similar way to that which causes liquid metal embrittlement. Bergen [47] has observed that Cl^- ions migrate to areas of maximum stress (where defect sites were available) by using radiotracer techniques. It is accepted that ions adsorb on the most stressed region of the metal in the region where fracture occurs [51,52]. Coleman et al [48], Poulson et al [49] and Long and Lockington [50] proposed that changes in interstitial concentration at grain boundaries during heat treatment aided chemisorption and therefore changed SCC susceptibility. Jones [53], suggested that adsorption of vacancies, generated by dissolution at the crack tip (rather than the corrosive species) reduces the local stress necessary for crack propagation. The use of an adsorption-induced cleavage model to describe SCC is less popular than other models as susceptible alloys are usually ductile and crack blunting would be expected around the crack tip. The crack tip would then not be sharp enough to cause cleavage.

2.2.2.2. Hydrogen embrittlement.

Although hydrogen embrittlement (HE) is usually considered to be a phenomenon distinct from SCC, a minority view exists that all SCC is the result of embrittlement by hydrogen. Corrosion reactions may create a hydrogen atmosphere on the metal surface, which may be equivalent to a partial pressure of many thousand atmospheres. Because of this high concentration the metal may become supersaturated with hydrogen.

The interaction of adsorbed hydrogen with the stress field will result in accelerated crack initiation and propagation. The process of hydrogen adsorption is shown schematically in fig. 5, where HE is sustained at the propagating crack tip. Hydrogen is produced continuously by local corrosion processes inside the initial crevice. The mechanisms by which atomic hydrogen is believed to facilitate fracture are:

1. Formation of a brittle hydride phase [54]
2. Development of high pressure within internal voids and microcracks [55,56]
3. Dislocation pinning [57,58,59]
4. Surface energy reduction [60,61]

5. Lattice decohesion [62]

Chemical factors that influence HE include an increase in hydrogen ion concentration (low pH), promotion of hydrogen evolution by applied cathodic potential, or testing in hydrogen releasing environments.

Several authors [eg 63,64,65,66] consider that strain induced martensite formation along the path of crack propagation is necessary for HE and SCC of austenitic steels. According to this theory the crack propagates through martensite, or along the martensite/austenite interface with greater ease than if propagating through the austenite. Furthermore hydrogen diffusion rates through bcc martensite are more rapid than through fcc austenite. However, in 20% Cr, 25% Ni, X% Nb martensite formation is unlikely because of the stability of the alloy.

Early authors believed that a common criterion for distinguishing SCC from HE was the effect of anodic and cathodic polarisation on cracking behaviour and time to failure. This is shown schematically in fig.

6. The external polarisation should affect the growth rate of the propagating SCC crack as follows. If the time to failure is increased by anodic stimulation, and decreased by a cathodic current the mechanism of crack propagation under free potential conditions involves dissolution. Alternatively where cracking is stimulated by the application of a cathodic current, the mechanism of cracking involves HE because cathodic polarisation leads to increased hydrogen input and a reduced time to failure. Interpretation of such experiments may not be straight-forward and evolution of hydrogen during crack propagation does not unequivocally demonstrate that HE occurs.

2.2.2.3. Brittle Film model.

A mechanism has been proposed to explain the SCC of brasses and bronzes, by which a tarnishing brittle film protects the underlying metal until film rupture occurs as a result of mechanical strain. The crack in the film may extend into the metal [67]. Sieradzki and Newman [68] extended ideas to explain SCC in ductile materials. They suggested that short range cleavage of ductile materials is possible provided that the thin surface film responsible for crack initiation has certain properties. The important parameters determining the effectiveness of films in initiating cleavage include the film-substrate misfit, the strength of the bonding across the film-substrate interface, the film thickness and the film ductility. They described suitable combinations of such parameters that lead to

microcleavage as determined by the state of coherency of the interface and the fracture toughness of the substrate. They examined oxidised (or de-alloyed) brass and stainless steels and suggested that an inherently ductile film could be responsible for the nucleation of a cleavage crack which would then propagate for a macroscopically significant distance into the underlying metal. Pugh [69] recently reviewed the present understanding of TGSCC in terms of the discontinuous cleavage of surface films.

2.2.2.4. Tunnelling.

This mechanism was originally suggested by Neilsen [70] to explain fracture surface observations on the transgranular SCC of stainless steels in $MgCl_2$ solutions. Evidence suggests that crack propagation occurs by dissolution tunnels progressing along favoured crystallographic directions ahead of the crack tip, followed by subsequent tearing of the remaining metal ligaments in between such tunnels. Further experiments [71,72,73] have suggested that the existence of tunnels is not a general requirement and that they are associated, though not critical SCC phenomena.

2.3. The Role of Mechanical Parameters.

2.4.1. Fracture Mechanics and SCC.

In many structures cracks can initiate rapidly at stress concentrations or pre-existing defects. The introduction of an aggressive environment during testing results in a crack growth rate greater than that seen in an inert environment. The advent of crack growth testing and characterisation in terms of stress intensity (K) has allowed crack growth behaviour in the laboratory to be investigated and extended to consider structural integrity. Fracture mechanics concepts, despite the increasing popularity of use for prediction of properties in high strength materials have not been extensively applied to austenitic stainless steels. This is because of the large plastic zone size observed in stainless steels (which introduces the requirement of large test pieces) and the tendency of cracks to branch (which makes calculation of K difficult). In a number of alloys, a definite limiting value of K_{Ic} is found, below which a fracture toughness specimen appears to last indefinitely; this is shown schematically in fig. 8. However, it is clear that if a definite K_{Isc} limit exists, resistance to SCC can be guaranteed by ensuring that service stresses do not produce values of K greater than K_{Isc} . If no K_{Isc} limit exists, or if it is so small that service stresses would have to be held at an unrealistic level,

design against SCC must rely on the quality assurance that crack growth rates in service are so slow that the cracks can be detected and eliminated during periodic inspection. A threshold stress may be envisaged where creep exhaustion following loading is fast enough for repeated film rupture, and thus the critical strain rate necessary for SCC is not exceeded. The effect of factors influencing K_{ISCC} , such as the plastic zone size, crack opening, dislocation cell structure and their effect on K_{ISCC} have been considered by Barsom and Tompkins [74].

West [75] suggested that a Griffith energy balance approach to fracture could be modified to consider the release of chemical energy by corrosion processes and film rupture. If the strain energy released by the advancing crack is greater than the work needed to form fracture surfaces then the crack is self propagating. The energy consumed in creating a new surface equals the sum of the change in chemical energy and that in achieving plastic deformation can be equated to the change in the stored energy.

Energy balance equation suggested by West [75]:-

Surface Energy Change	+	Plastic Work Done	=	Change in Internal Stored Energy	+	Electrochemical Chemical Energy Released
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West showed that an equation could be derived from fracture mechanics and electrochemical considerations to consider the threshold stress susceptibility to SCC:

$$2. \quad K_{ISCC} = [K_I \cdot (P - K_I^2 n)]^{0.5}$$

K_{ISCC} = threshold intensity for stress corrosion cracking

P = an plastic work term

K_I = stress intensity

n = the anodic overpotential.

Variables are dependent on each other, n for example is a function of the chemical conditions in the crack, such as pH, anion activity, metal composition and electrode potential. In a later paper [76] West utilised this energy balance approach to demonstrate that toughness is sensitive to surface energy even when extensive plasticity develops. He assumed the chemical energy release rate to be concentrated at the tip, and that the reduction in critical stress intensity was attributable to changes in free energy caused by the

environment.

2.3.2. Crack Path in SCC.

Both transgranular (TG) and intergranular (IG) SCC occurs in iron based alloys.

Examples of Fe based SCC systems exhibiting TGSCC are:

1. Austenitic Stainless Steels in acid chloride media
2. Low strength ferritic steels in acidic or phosphate media
3. Plain C steels in CO₂ saturated solutions

Examples of IGSCC include:

1. C steels in caustic, nitrate, acetate and carbonate/bicarbonate
2. Low alloy steels in oxygenated water
3. Tempered martensitic steels in chloride solutions.

Different regions of potential exist for IG and TG cracking when there is a difference in composition between the matrix and grain boundaries, this arises from differences in the polarisation behaviour between regions. Referring to fig. 8, if specimen potential is at B, TGSCC can be expected because the grain boundary area is in a passive condition. If, however, the potential is at A, IGSCC results. TGSCC occurs at potentials where the grain boundary is in a region of stable and rapidly developed passivity. IGSCC occurs when departure from the bulk composition renders the grain boundary less readily passivated.

The type of SCC that occurs depends critically on a combination of microstructure, applied stress levels and strain rates, environmental factors and temperature. The crack path in many alloys may change from IG to TG or vice versa, if stress, environmental composition or electrode potential are altered. An explanation for stress induced transition is that an increased contribution from ductile tearing of undissolved ligaments occurs as the crack tip strain rate increases [77]. However, the kinetics of repassivation and cathodic reaction play an important part. For example, Okada et al [78] noted that the crack path for sensitised 304 stainless steel in boiling MgCl₂ changed from TG to IG on the addition of inhibitors or slight cathodic protection. Scully [79] suggested that crack path transitions are consistent with changes in repassivation rate R. The interface between TG and IG SCC is determined by the relative kinetics of the two processes. A high R value favours IGSCC and a low value favours TGSCC in, for example, austenitic stainless steels resulting from minor environment changes at the crack tip. Variations in electrode

potential may change the mode of cracking and the cracking rate eg 304 stainless steel held at yield stress in boiling 70 % NaOH shows TG behaviour at low potentials and IG at high potentials [80]. This potential dependence of crack morphology relates to the electrochemical difference between the bulk material and the grain boundary. Reviews of IGSCC of sensitised stainless steels are given by Cragolino and MacDonald [81] and by Smialowska and Cragolino [82].

2.3.3. Stress and Strain rates in SCC

The role of stress in causing SCC has been extensively studied.

Swann [83] suggested that:

1. Stress prevents stifling of a corrosion produced crevice by opening it to fresh solution.
2. Stress causes plastic deformation which localises both the anodic and cathodic processes.
3. Stress provides a local concentration of elastic energy which allows the crack to propagate in a brittle manner.

In the SCC of many alloys both the stress level and stress mode (whether static or dynamic) are found to be important. For a number of different systems of alloy and environment the observation has been made that SCC growth is sometimes determined by the plastic strain rate at the crack tip. There are numerous publications [84 to 95] indicating that critical strain rates exist (where certain strain rates are required) to cause SCC. Fig. 9 illustrates the way in which a metal may fail under different strain rates when in a SCC environment that allows passive film formation. At high strain rates rapid mechanical fracture may result without influence from the corrosive medium. At low strain rates crack nuclei may heal by passivation as there is no mechanical activation (eg the extent of film rupture is insufficient for crack formation). SCC occurs at intermediate strain rates depending on the kinetics of the particular system. Outside the critical strain rate regime either pitting (low strain rates) or ductile fracture (high strain rates) occurs. Figs. 10a and b show the importance of both potential and strain rate in SCC. The value of potential will control the electrochemical factors of repassivation and dissolution. Two cases are shown:- fig. 10a shows the situation where passivation may occur; fig. 10b shows the situation where passivation does not occur. According to Scully [33,34] if the potential is too high pitting occurs for both cases. If passivation may occur, the regime of SCC depends on the balance between strain rate and repassivation rate.

Repassivation depends on factors such as pH, viscosity, inhibitor concentration and aggressive ion concentration. If repassivation does not occur SCC is seen over a much broader potential and strain rate regime.

For evaluation of SCC likelihood in service and establishing tests that have some bearing on practical situations it is necessary to know how the strain rates found in service vary and to consider the mechanical conditions of strain rate and stress level. Necessary information about the influence of strain rate may be obtained by slow strain rate testing. However, in this method, specimens are not cracked at low stress levels corresponding to design or working stress. It is not possible to extend constant strain rate tests to rates faster than about 10^{-5}s^{-1} because ductile fracture occurs in a relatively short time and little time is available for corrosion reactions to have much of a part in failure.

If cyclic loading or low frequency cyclic loading is used, where the maximum load is limited, the influence of stress level can be systematically investigated without rapid mechanical fracture, yet at the same time achieving high strain or loading rates. Cyclic loading tests allow investigation of plastic and elastic strain rates because cyclic loading can sustain creep rates for much longer periods of time than if the same stress were applied statically [86,87]. By this means the critical strain rate for SCC may be achieved at below yield stress levels.

Furthermore, cyclic loading may be more representative of material in service. Even under apparently constant stress, components suffer repeatedly from slow dynamic strain as a result of stress variation produced by fluctuations of temperature or pressure. Such cyclic variations lead to small alternating stresses. Under cyclic stress conditions, environment assisted crack growth can occur in many materials at stress levels where SCC would otherwise not be seen.

Such effects have been seen in line pipe steels [88,89] and steels in nuclear reactor environments [90] and in low carbon steels in Cowper stoves [91]. Parkins and Greenwell [92] working on mild steel in $\text{HCO}_3^-/\text{CO}_3^{2-}$ and Parkins and Fessler [93] working on bronze in sea water, concluded that essentially the same phenomenon was seen in both cycling and constant strain rate tests, because the fractographic characteristics for tests with a common strain rate produced by both means was the same. Parkins and Greenwell found that a cyclic component with a frequency of 11 Hz did not influence K_{ISCC} , though at 0.19 Hz, a small cyclic component lowered K_{ISCC} to half of its static value. Large cyclic components caused a transition to TGSCC. They suggested that cyclic stresses speeded up initiation. Their data is

shown in fig. 11 in the form of a modified Goodman diagram. The limiting stress intensity and frequency conditions within which IGA occurs as a function of frequency.

Fig. 11a shows that for $K_{min} > 22.6 \text{ MN/m}^{3/2}$ IGSCC was observed under cyclic conditions, the interface between the two modes of failure (TGSCC and IGSCC) being dependent on ΔK and K_{min} up to $30 \text{ MN/m}^{3/2}$.

At 11 Hz the rate of IGSCC decreased with increasing ΔK , shown on fig. 11a. At 0.19 Hz (shown in fig. 11b) the behaviour was similar to that observed at 11 Hz, but ΔK_i was higher at 0.19 Hz than for 11 Hz. Furthermore, K_{ISCC} for initiation was reduced to $10 \text{ MN/m}^{3/2}$. The rate of crack growth was independent of ΔK for $K < K_{ISCC}$, but increased with $K > K_{ISCC}$.

Wendler Kalsch [94] working on low alloy steels in $2M \text{ (NH}_4)_2\text{CO}_3$ at 70°C showed that the threshold stress for SCC was considerably reduced when low frequency loading was used. She pointed out that the most important factor was the method of loading rather than the deformation rates that occur during loading.

Mendoza [95] working on line pipe steel in $\text{HCO}_3^-/\text{CO}_3^{2-}$ at 70°C saw IGSCC at stresses for specimens where the peak stress during cycling was as low as 65% of the yield stress. The growth rate of such cracks was seen to increase if the frequency decreased, and if the mean stress or cyclic amplitude increased. The threshold stress was found to be independent of the cyclic amplitude and frequency.

Proposed explanations [94,95] for the enhancement of SCC resulting from cyclic loading are that localised plastic deformation during cyclic loading causes disruption of the otherwise protective film and promotes electrochemical activity. It was suggested [94,95] that during dynamic loading, frequency and amplitude influence the rate of crack growth because they determine the strain rate response of the material and the time spent within a critical strain rate range if the strain rate varies.

2.3.4. The interface between cyclic SCC and corrosion fatigue.

Brief mention is made below to illustrate the interface between SCC (where cyclic loading maybe involved) and corrosion fatigue (CF).

The boundary between SCC and CF is not well defined and as frequency is increased there is a gradual transition from SCC to CF to pure fatigue. A schematic diagram of the interface between SCC and CF is shown in fig. 12. The regions of the two different types of environmentally assisted attack are represented. In true corrosion fatigue, the conjoint action of fatigue cycling and environment is responsible for enhanced rates of crack growth and occurs throughout the range of stress intensity, as shown in fig. 12a. Stress corrosion fatigue occurs where the stress intensity exceeds the

threshold for SCC, K_{ISCC} , this is shown by fig. 12b. Stress corrosion fatigue is a result of SCC and CF. Fig. 12c shows the combination of CF and stress corrosion fatigue. Fig. 12d shows the region where cyclic stress corrosion may be represented on a fatigue type representation of crack growth rate. The environmental contribution is only present when K_{max} exceeds K_{ISCC} . K_{ISCC} implies that at some critical potential and applied stress the pit extends as a crevice or crack by dissolution aided by stress, until the crack is long enough to satisfy the K_{Ic} criterion and fast fracture ensues.

To apply such criteria, the rate of growth of the plastic zone should be comparable with the rate of crack growth and the size of the plastic zone should be small compared with the length of the crack.

If such criteria apply it should be possible to relate the K_{ISCC} to the stress dependence of the creep properties of materials providing the limiting strain rate for cracking is known. There is evidence that a true threshold stress does not exist, and that K_{ISCC} should be described as a value below which the rate of cracking in a certain environment is small [98].

Several models for prediction of crack growth rates during corrosion fatigue (CF) exist in the literature.

Wei and Landes [96] suggested that the mechanical and environmental contributions to crack extension could be summed algebraically.

Proposals for the superposition of SCC crack growth rates upon inert fatigue crack propagation rates are based on two observations:

1. The similarity of fracture surfaces between those resulting from fatigue and those produced by static loading in the same environment.
2. Fatigue crack growth in an aggressive environment shows a marked sensitivity to frequency.

Thus given a sustained loading curve of da/dt vs K_{max} in the environment, and a base line fatigue curve of da/dN vs K_{max} the fatigue curve in the environment can be estimated as

$$3. \quad \frac{da}{dN_c} = \frac{da}{dN_{air}} + \frac{da}{dt_{SCC}} k.(t)dt$$

$k.(t)$ = a function describing the fatigue cycle load wave form over the time period t .

a = crack length

N = number of cycles

Wei and Landes [96] found good agreement for high strength steels in hydrogen and humid air at low R values. A difficulty with such an

expression is that the environmental conditions under which corrosion fatigue occurs are much more extensive than for SCC and that initiation time is not considered and no account is made of environmental conditions within the crack. The reference environmental term forms only a base line. This term was replaced by Austin and Walker [97], who developed the process competition model, which suggests the mechanisms of crack extension by SCC and fatigue mechanics are different and therefore competitive in CF.

Prater et al [99] working on sensitised 304 stainless steel in water at 95°C concluded that although crack growth under monotonic loading may be negligible, environmentally controlled crack propagation is significant when the specimen is subjected to high mean stress levels and low amplitude cycles. Prediction of crack growth rate was possible when the cycle time was of the order of hours.

The role of low frequency stress on the process of SCC initiation and propagation is relatively unexplored. This work aims to gain information on the effect of stress cycling on the mechanisms of SCC in a sensitised stainless steel.

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Table 1
Metal Failure Frequency (1968 to 1969) (after [1] 1970)
313 cases, Corrosion 56.9%, Mechanical 43.1%

Corrosion Failures	
Form	Percent
General	31.5
SCC	21.6
Corrosion Fatigue	1.8
Pitting	15.7
Intergranular	10.2
Erosion Corrosion	7.4
Cavitation	1.1
Fretting	0.5
Crevice	1.8
De(metal)ification	1.1
Two-metal	0.0

Table 2
Classical SCC systems (after [18] 1965)

Alloy	Damaging environment
Mild steel, low strength ferritic	OH^- , NO_3^- , CN^- , PO_4^{2-}
Austenitic stainless steels	Cl^- , OH^- , H_2O
High strength steels	H_2 , H_2O , CN^- , Cl^-
Cu base	NH_4^+ , moist NH_3 vapours
Al base	Cl^-
Ti base	Cl^- , HNO_3
Ni base	OH^-

Table 3
Classification of SCC initiation

Influence	Pre-existing	Developed in service
Mechanical	1. Laps, seams	1. Pits, crevices
	2. Hammer marks, stamp marks	2. 'Oxide fingers'
	3. Storage corrosion	3. Brittle oxide, inward growing
	4. Hard spots (heat treatment or from (2))	4. Brittle oxide as site for anodic attack
	5. Machining residual stresses	5. Fretting damage
	6. Pickling damage	
Chemical	1. Non-metallic inclusions in stagnant solutions	1. Pits and crevices
	2. Grain boundary segregates	2. Contamination
	3. Contaminants	3. Selective leaching from alloy (de-alloying)
	4. Crevice corrosion	
H-Damage mechanism	1. Non-metallic inclusions	1. Hydrogen blisters
	2. Grain boundary segregates	2. Anodic depolarisation (pits/crevices)
	3. Hard spots	

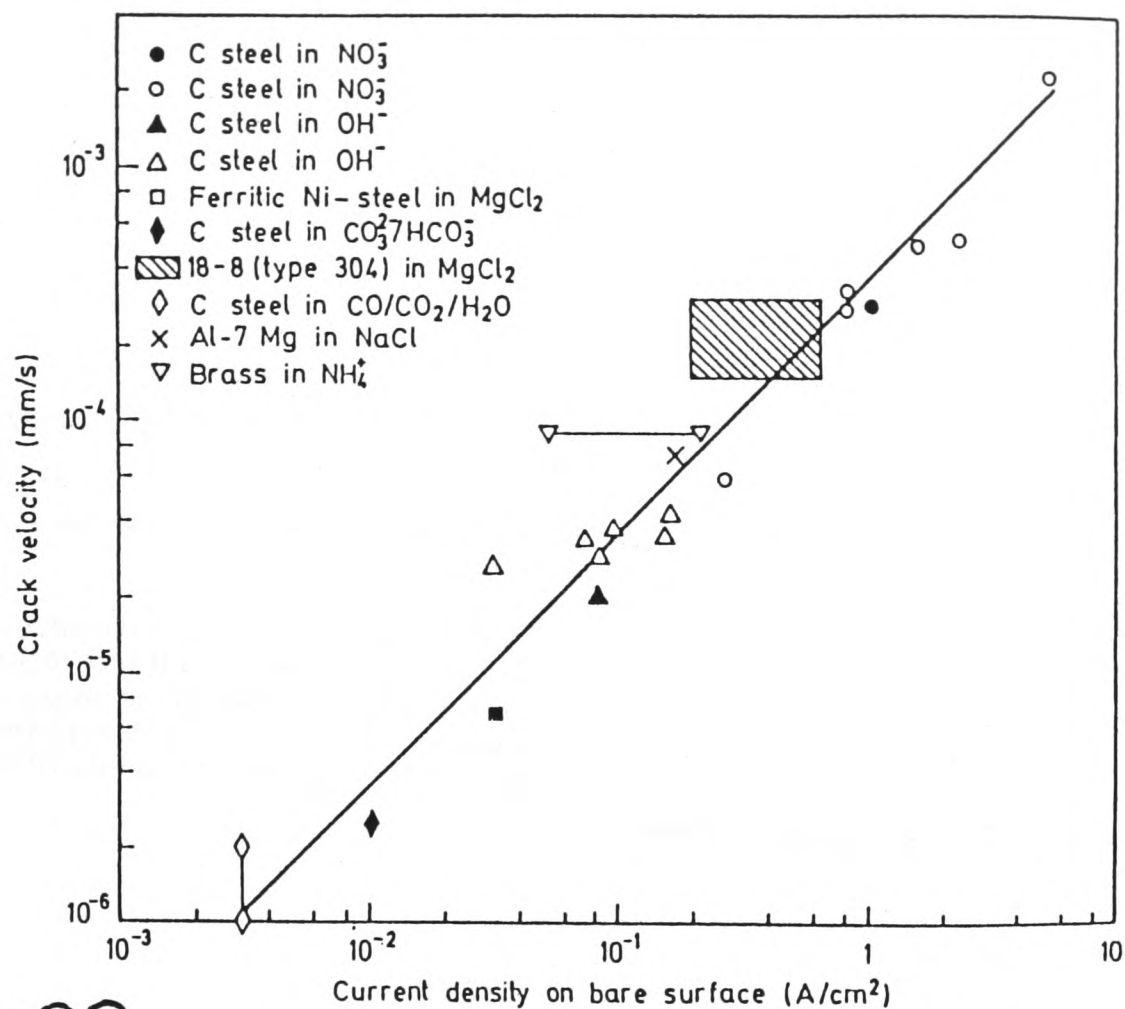


FIG 2.2 Observed crack velocities and current densities associated with 'bare' surfaces.
ref Parkins (17)

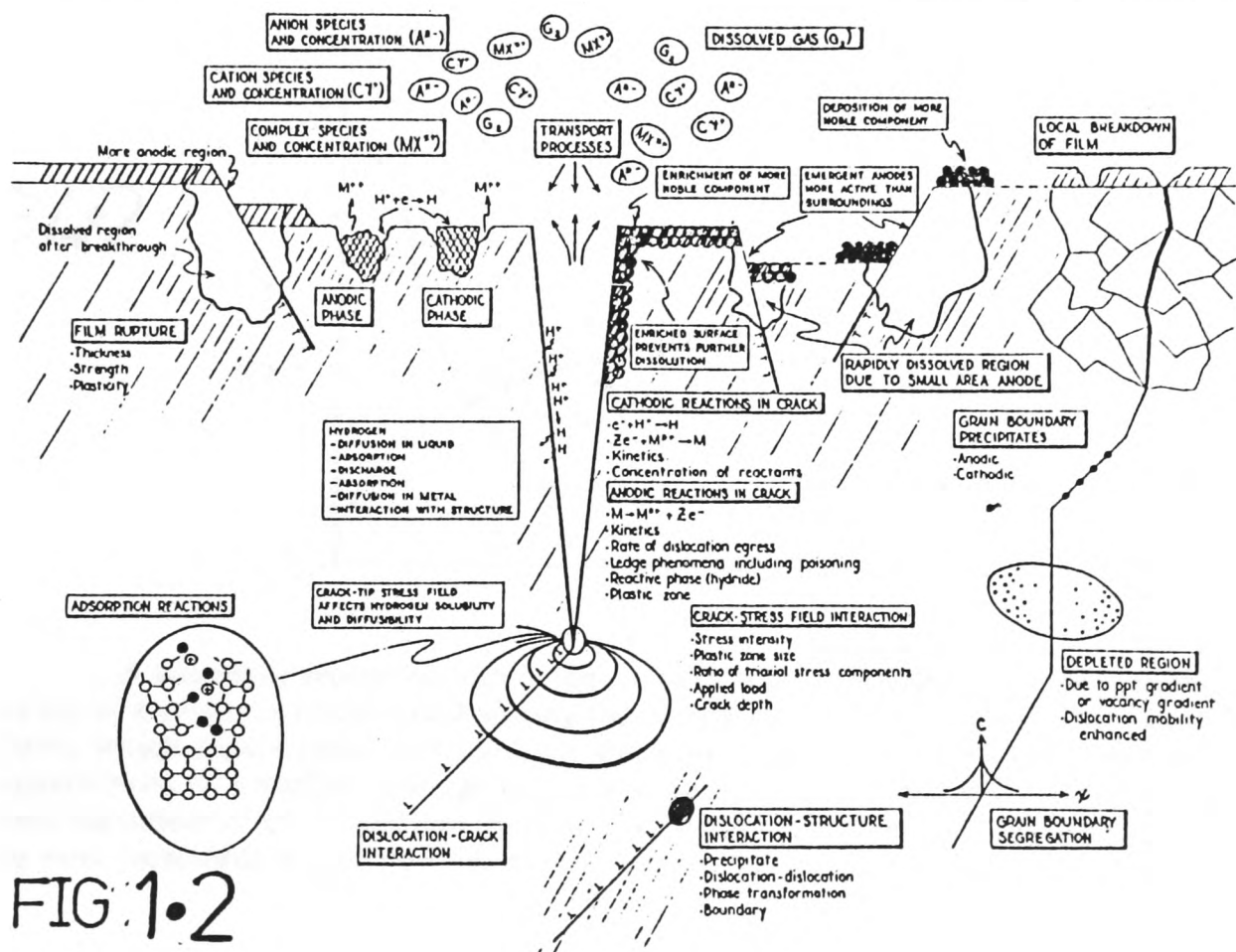
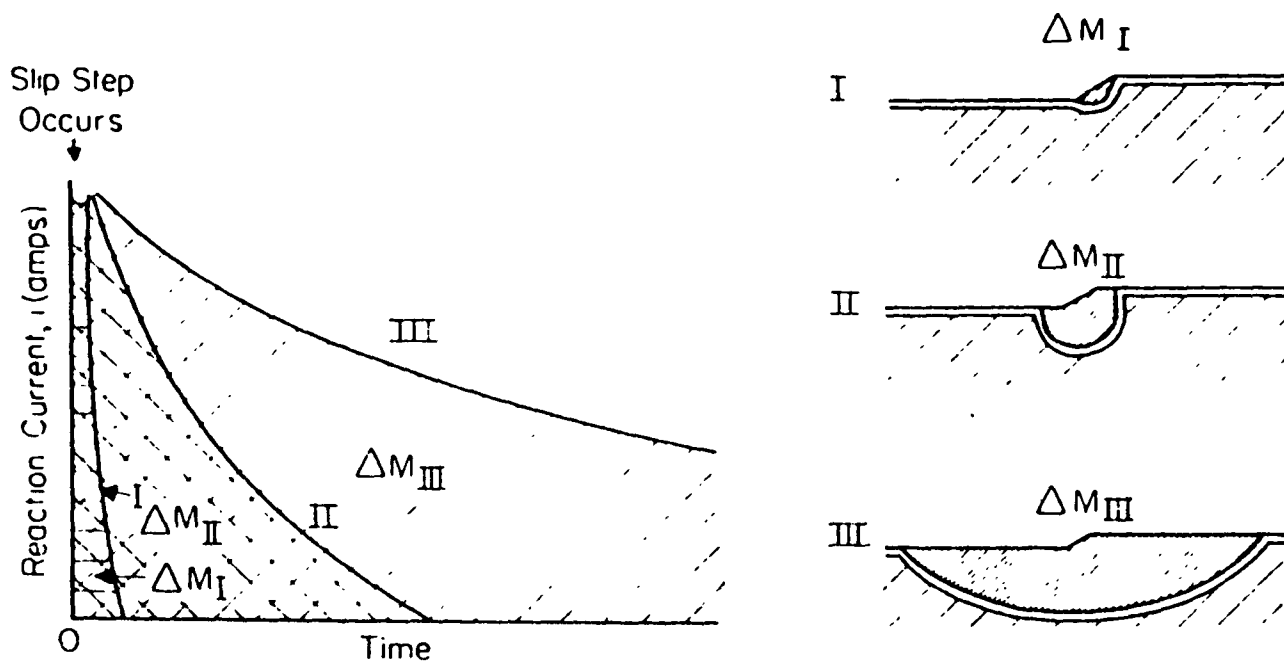


FIG 1.2

Schematic of the variables that influence SCC.
ref Staehle (7)



Schematic figure illustrating the relationship between the current time transient and the amount of material dissolved for a given slip step event.

Case I corresponds to immediate repassivation

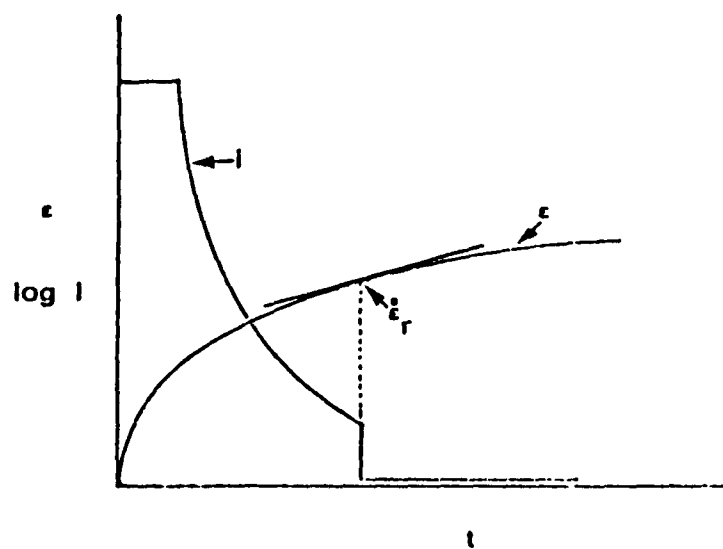
Case II corresponds to an intermediate situation favoring stress corrosion cracking

Case III corresponds to extensive or non-restricted lateral dissolution

FIG 3.2.

Ref Staehle (7)

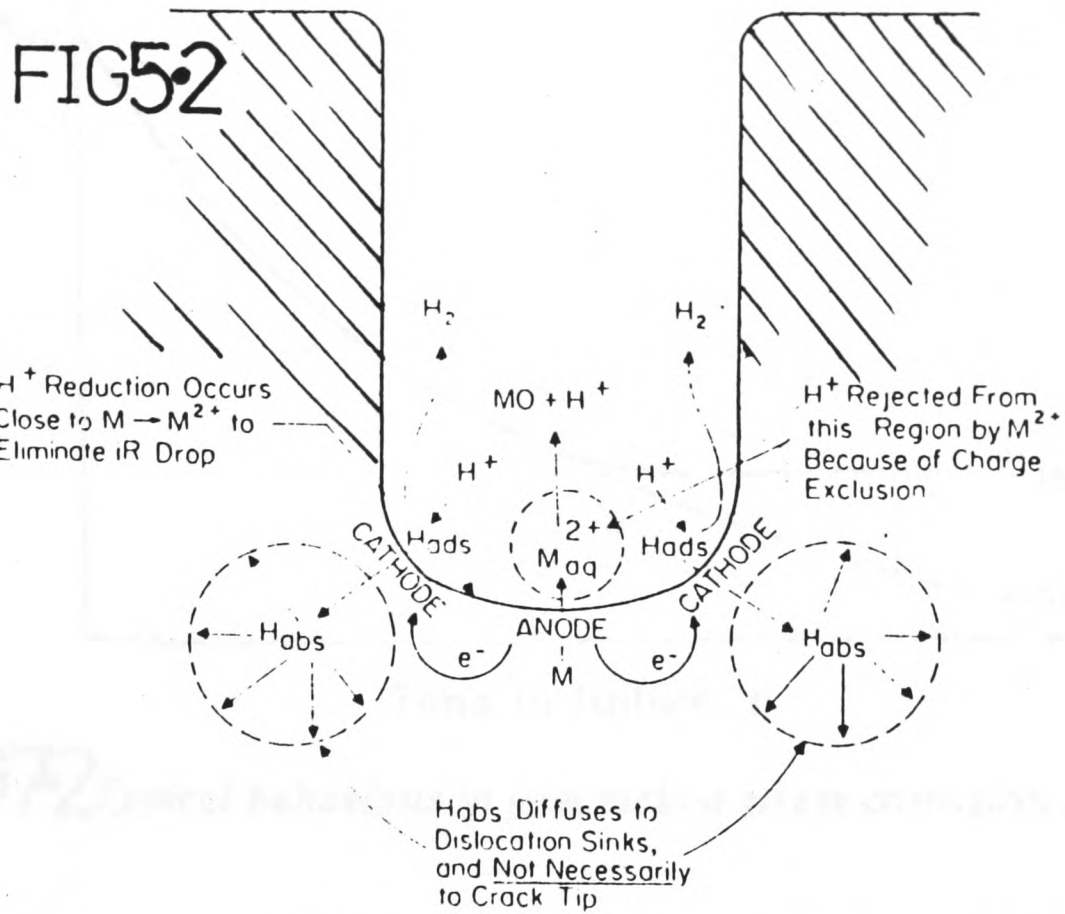
FIG 4.2



A schematic representation of the changes in creep strain and anodic current at the tip of a stress corrosion crack during the progress of an increment of crack growth during which repassivation occurs. This will only be possible in environments where repassivation of a surface undergoing a creep strain-rate is possible. This will occur at some maximum value, i_r , and will result in a rapid fall in current. Since this occurs before the next increment is initiated insufficient charge has passed (Q_{min}) crack arrest will occur.

Ref Scully (30)

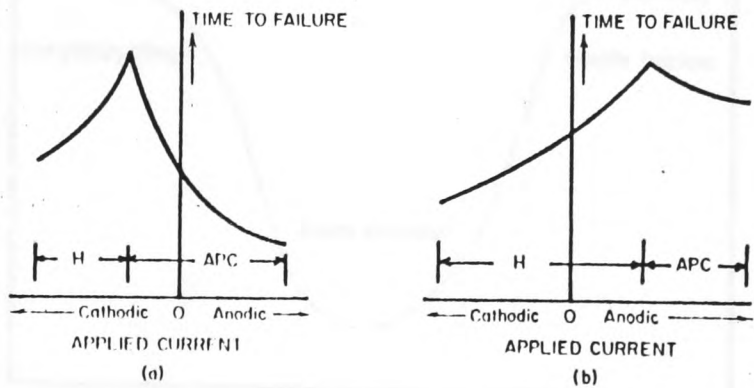
SOLUTION



Schematic figure illustrating the solution chemistry associated with the $H^+ \rightarrow H_{ads}$ reduction reaction during stress corrosion crack propagation, and the subsequent behavior of the adsorbed hydrogen.

Ref (60)

FIG 6.2



The effects of applied anodic or cathodic currents upon the time to failure of alloys undergoing hydrogen embrittlement and active path stress corrosion

Ref (63)

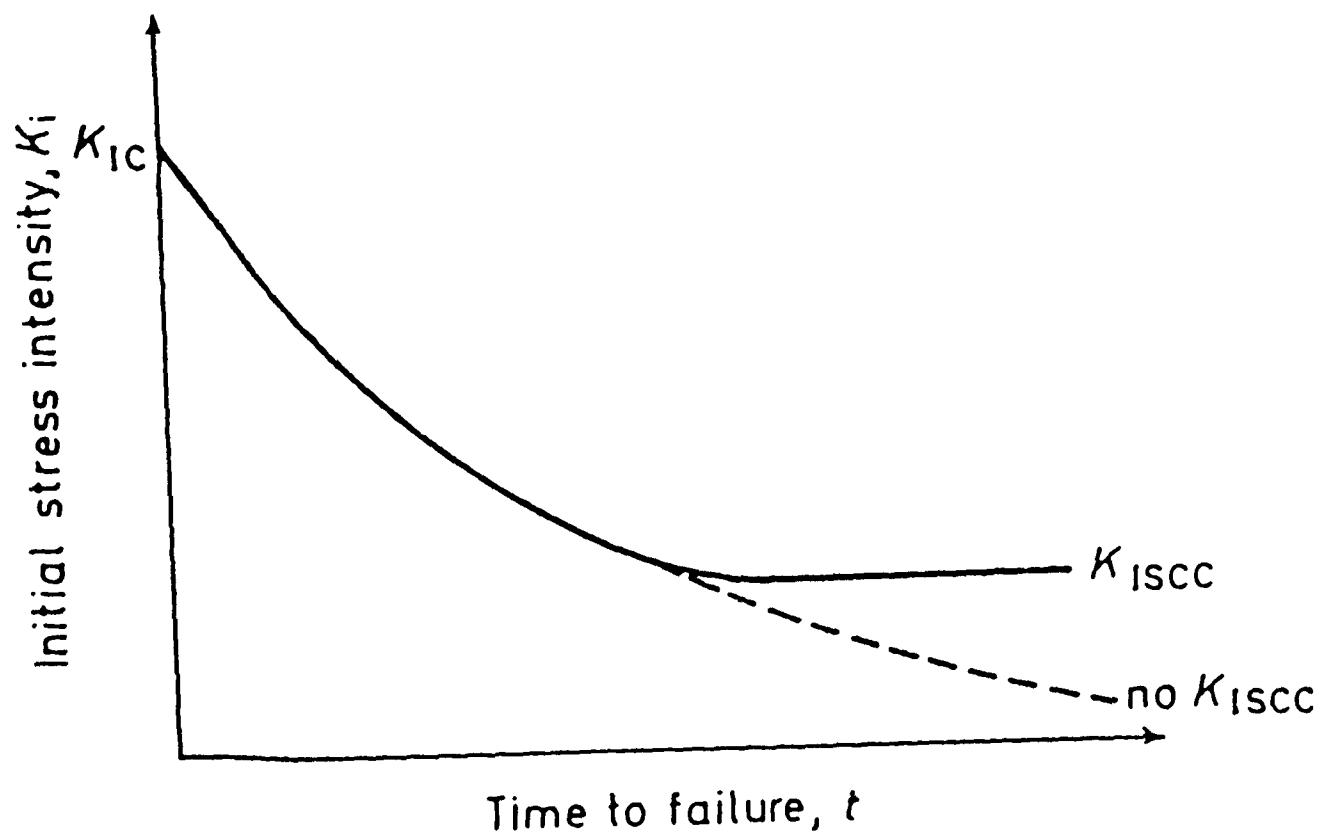
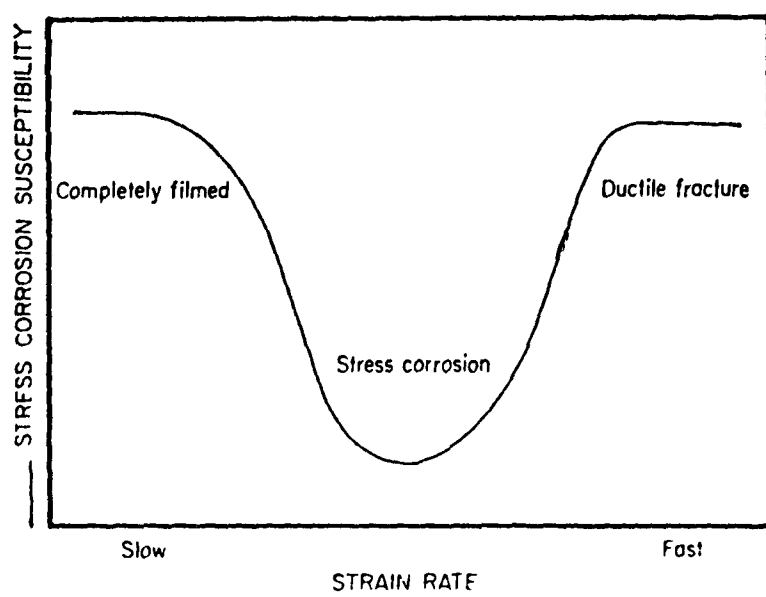


FIG 7.2 Typical behaviour in precracked stress-corrosion tests

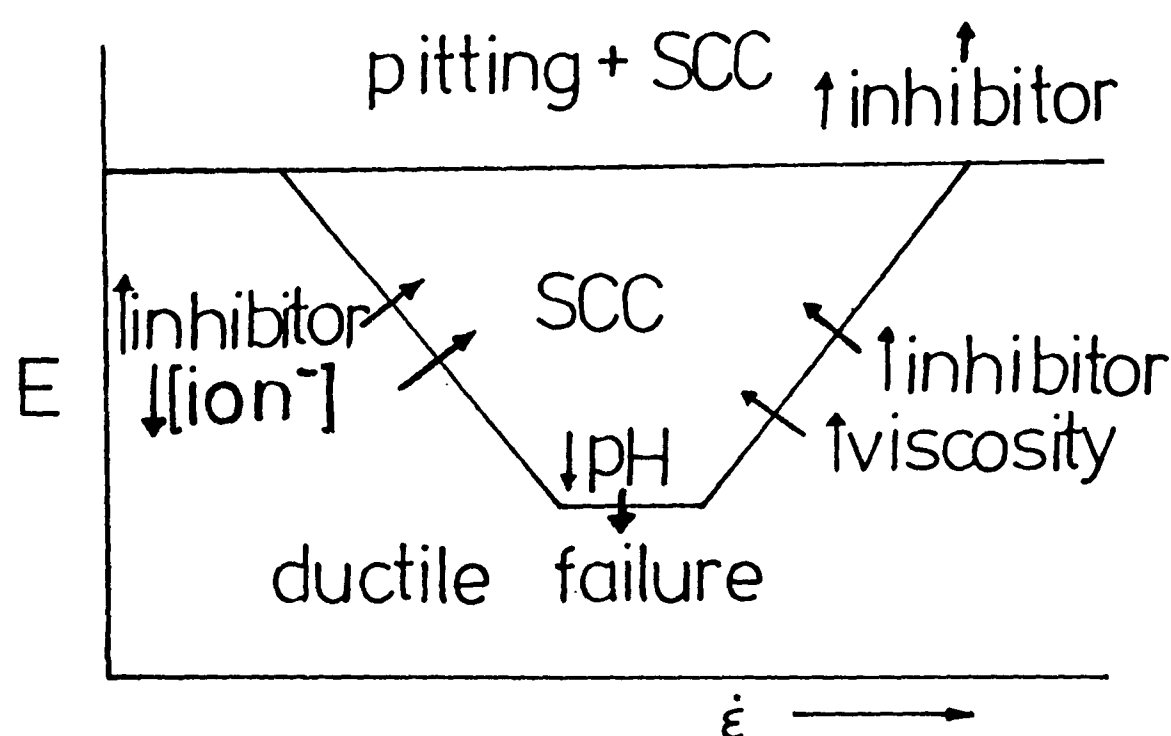


Schematic illustration of the effect of strain rate upon stress corrosion crack propagation in a filming environment

FIG 9.2

Ref (84)

a PASSIVATION POSSIBLE



b PASSIVITY DOES NOT OCCUR

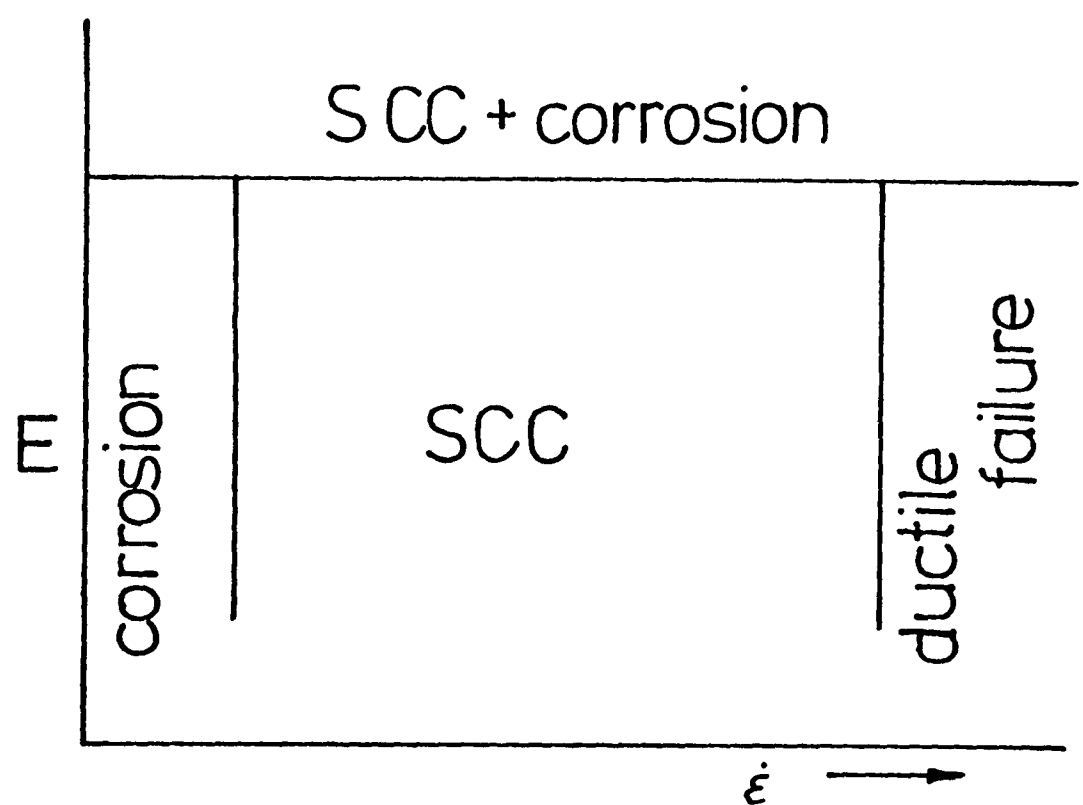
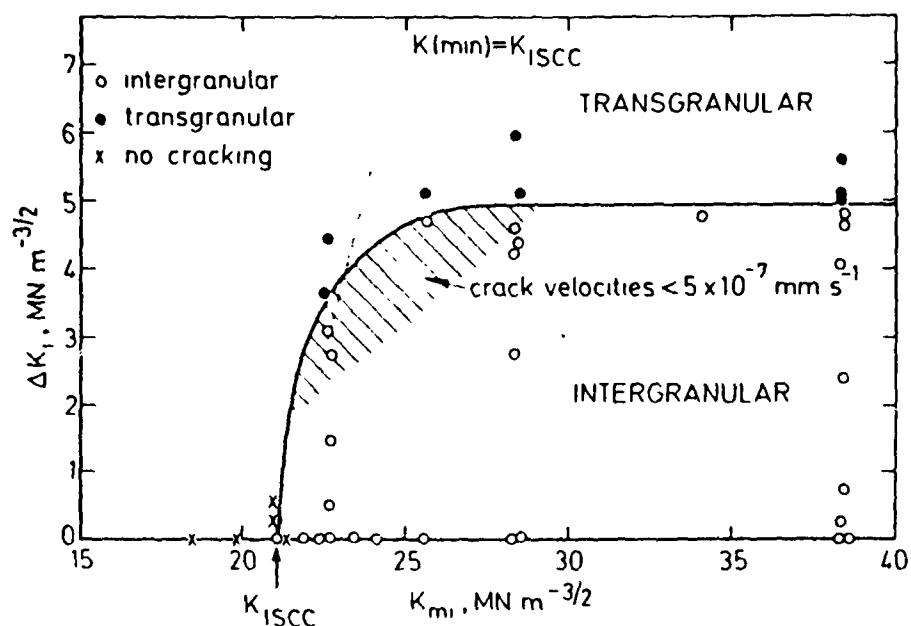


FIG10-2

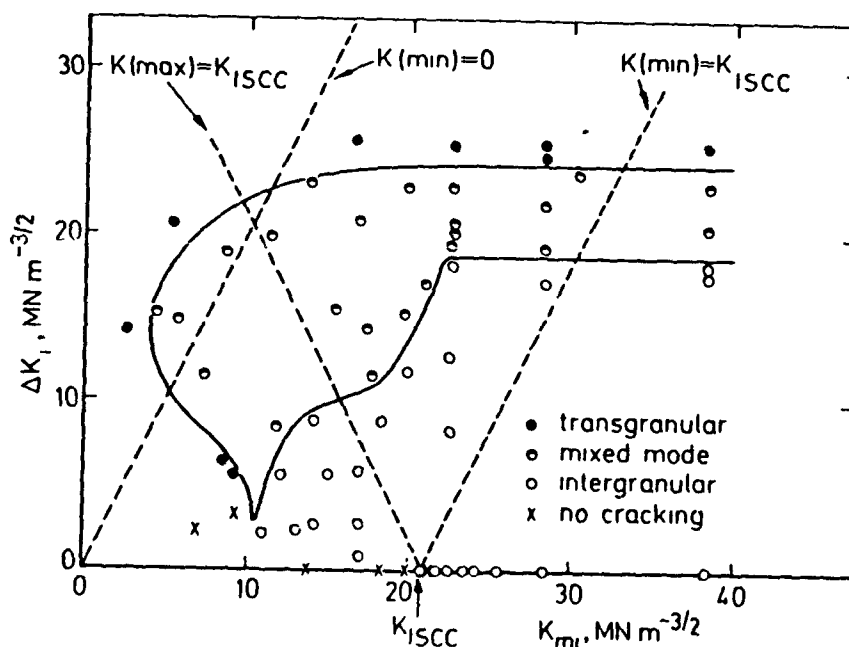
Schematic of the influence of strain rate on the potential regions where SCC occurs

a



Modified Goodman diagram indicating loading parameters for which inter- and trans-granular cracking were observed in mild steel immersed in CO_3/HCO_3 solution at -650 mV (s.c.e.) , 75°C , 11 Hz , $R > 0$.

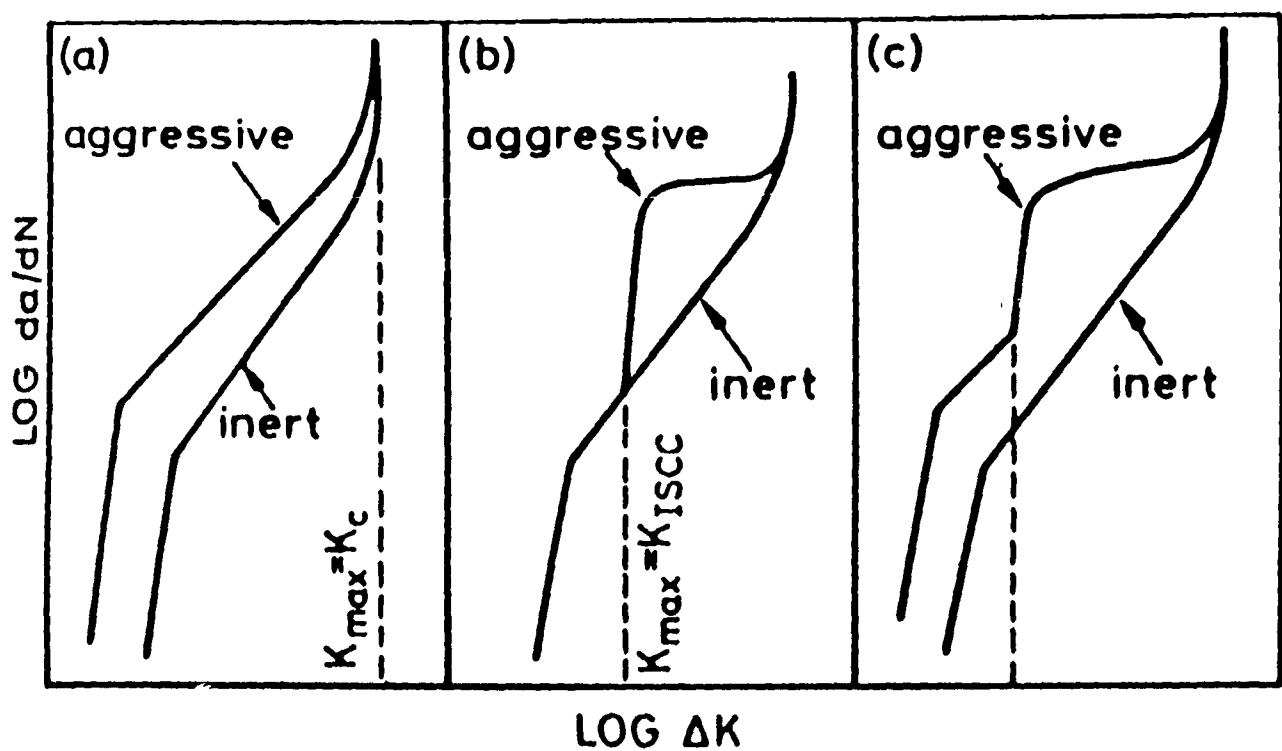
b



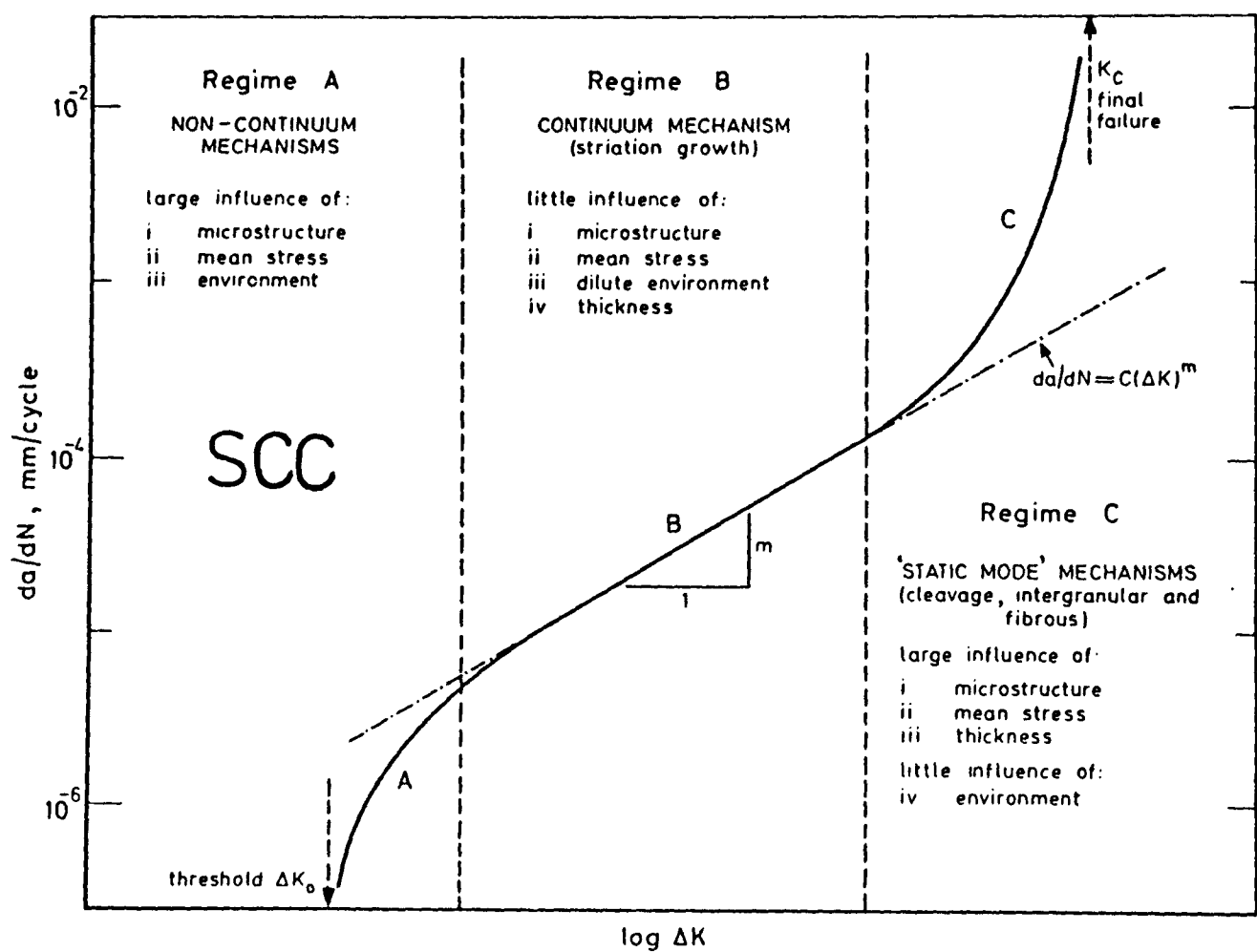
Modified Goodman diagram indicating loading parameters for which intergranular, mixed-mode, and transgranular cracking were observed in mild steel immersed in CO_3/HCO_3 solution at -650 mV (s.c.e.) , 75°C , 0.19 Hz , $R > 0$.

Data from Parkins and Greenwell (92) showing the effect of mechanical test variables on SCC.

FIG 11.2



Basic types of corrosion fatigue crack growth behaviour: (a) true corrosion fatigue; (b) stress corrosion fatigue; (c) s.c.f. and t.c.f. combined. [100]



Primary fracture mechanisms in steels associated with sigmoidal variation of fatigue crack propagation rate (da/dN) with alternating stress intensity (ΔK).

The interface between Stress Corrosion Cracking and Corrosion Fatigue. [101]

FIG 12.2

SENSITISATION

The phenomenon of sensitisation in stainless steels concerns the increased susceptibility to intergranular corrosion (IGA), resulting from microstructural change. Sensitisation results from either slow cooling from a solution anneal or from reheating in the temperature range 500-800°C. This occurrence of IGA is in contrast to the usual excellent corrosion resistance seen if the steel is rapidly quenched from the solution anneal temperature. If the material remains for sufficient time in the "critical temperature" regime (where sensitisation occurs) or is heated to a higher temperature, resistance to IGA is renewed and healing is said to have taken place.

The purpose of this chapter is to:

1. Review the mechanisms of sensitisation
2. Discuss the metallurgy of 20% Cr, 25% Ni, 0.7 % Nb in relation to sensitisation
3. Describe the development of a model for the prediction of sensitisation and for correlation with macroscopic corrosion results and microanalytical measurements.

Several explanations have been proposed to explain sensitisation and are critically reviewed by Wilson [1], Cowan and Gordon [2], Hanninen [3], Cowan and Tedmon [4]. The three most widely accepted theories, explaining the electrochemical activity associated with the chemical, electrochemical and mechanical properties of the grain boundary/matrix interface are:

1. Variation in grain boundary chemistry.
Local variations of chemical composition at grain boundaries due to alloy element depletion and impurity segregation may change the nature of passivation over such areas, therefore grain boundaries will be less passive because the film is less protective.
2. Local strain.
Incoherency strains resulting from precipitate/matrix lattice mismatch at the carbide matrix interface lead to preferential attack. The extent of attack depends on the amount of precipitation and size of the precipitates.

3. Microcell theory.

Dissolution of grain boundaries may be due to the formation of local cells through the formation of a second phase. The precipitates or segregating elements may act as either the cathode or anode with respect to the matrix.

After sensitisation there are four regions of microstructure which show different electrochemical responses. These are the matrix, the Cr depleted zone, the continuous or semi-continuous network of carbides and the segregation layer at the grain boundary [5].

IGA is found to occur at two distinct regions of electrochemical potential [6]. The depletion of Cr at grain boundaries in the alloy where Cr rich carbides form is directly responsible for the loss of IGA resistance for general low potential conditions [7] found in plant. However at higher potentials it is found that Degree of Sensitisation (DOS) does not arise solely through Cr depletion and minor impurities play a part in the heat to heat variability of IGA, as described in references [71 to 75].

3.1. Strain Theory

The early theories explaining IGA were based on the shape of carbide particles and the accompanying strain. Such theories arose because it was noted that the attack of grain boundaries in sensitised steels was not always uniform, and occurred preferentially on one side of the carbide/austenite interface [5,8]. Crystallographic and strain reasons were proposed to explain this [9,10]. Passivation of boundaries may not occur because of associated strain [11]. The strain theory suggests that attack occurs at high energy precipitate interfaces, irrespective of the presence of denuded zones or grain boundary segregants. The strain theory is now less popular because it is unable to explain why attack ceases as ageing progresses, although an orientation relationship is maintained throughout ageing and because substantially more evidence has been reported for both the chromium depletion theory and for the effect of grain boundary segregants.

3.2. The Chromium Depletion Theory

The theory, originally proposed by Bain, Aborn and Rutherford [12], attributes sensitisation to compositional change resulting from the precipitation of Cr rich carbides (eg $M_{23}C_6$) at grain boundaries. As the carbides grow, C (which diffuses rapidly relative to Cr) is always available to enter growing carbides. Cr however must be drawn from a volume of material adjacent to the growing carbide and along the grain boundary adjacent to the carbide. The formation of such

carbides requires diffusion of Cr to the grain boundary and thus causes concomitant depletion of Cr in regions adjacent to the grain boundary. Consequently the grain boundary region and surrounding matrix are depleted of Cr to well below the bulk value, as the bulk diffusion of Cr from the matrix to the depleted grain boundary is too slow to permit replenishment. As diffusion along the grain boundaries is rapid, the grain boundaries act as collector plates to which Cr diffuses from the matrix and along which Cr flows to the growing carbides. Aaron and Aaronson [13,14] proposed the collector plate model for grain boundary growth, based on an early model by Zener [15]. The basis for the model is shown in Fig. 1. Carbide growth is therefore controlled by volume diffusion to the grain boundary and by grain boundary diffusion to the precipitate. At low temperatures, volume diffusion is rate controlling. The model suggests that as the carbides grow, the depleted region will persist in the grain boundary plane and a Cr concentration gradient will be established between the depleted boundary and the undepleted bulk material. As Cr is a key element in the corrosion resistance, this Cr depletion leads to a susceptibility to IGA if the Cr level falls below a level required to form a protective passive film. The collector plate model has been shown to predict the growth of grain boundary carbides well [16].

Sensitisation occurs in a temperature region where carbides are thermodynamically stable and where there is disparity between the matrix and grain boundary diffusion rates. At higher temperatures (typically greater than 650°C), although precipitates form, depletion is insufficient to allow IGA because of 2 reasons:

1. The solubility of the Cr rich carbide is too high to lower the concentration of Cr sufficiently, and
2. Rapid matrix diffusion allows the Cr level to be brought above a level necessary to avoid attack.

At lower temperatures, because carbide growth kinetics are controlled by matrix diffusion as a means of mass transport and because of the low solubility of carbides, enough Cr depletion may occur for sensitisation to result. However at low temperatures (<500°C) because diffusion rates are slow, long times are required for the nucleation of carbides and consequently long times to sensitisation are required.

3.2.1. Evidence for the Cr depletion theory.

Much evidence, both direct and indirect, shows the involvement of Cr depletion in the process of sensitisation.

The electrochemical behaviour of material with the same composition as grain boundary material has been studied by examining the effect of Cr content on the anodic dissolution behaviour. Simulated grain boundary materials have been studied by Osozawa and Engell [17,19] Vermilyea and Indig [18], Cowan and Tedmon [3], Truman [20] and Baumel and Buhler [21]. Such experiments show that as the Cr concentration is reduced the maximum observed active current increase. It is evident that the dissolution rate of Cr depleted areas will be much higher than that of the matrix which remains essentially passive. It may be concluded that in sensitised materials grain boundaries play a dominant part in the observed electrochemistry. Examples of the data of Ozowawa and Engell are shown in Fig. 2.4 and 34.4.

Depleted areas have been spatially resolved directly by STEM/EDX, (Scanning Transmission Electron Microscopy with Energy Dispersive X-ray Spectrometry) by a number of researchers. Chapter 5 discusses the method used to carry this out. Early microprobe instruments having a spatial resolution of 10^{-4} cm were unable to detect such regions because of the narrow width of Cr depleted zones. However, even present state-of-the-art AEM with the capability of obtaining compositional information from areas as small as 10^{-7} cm is hard pressed to obtain totally accurate profiles. Atom probe and Field Ion Microscopy studies have been carried out [22,23] on sensitised stainless steels and have shown that Cr concentration on the grain boundary is much less than the matrix concentration and can fall to very low concentrations (as low as 3 at% [22]).

Further support for the Cr depletion mechanism comes from the work of Younger [5] and Cihal and Kasova [24], who characterised carbide morphology in sensitised 304 stainless steels and found that susceptibility to IGA should not be related to particles of any particular shape or quantity of precipitates, but rather with the distribution of carbides which give rise to continuous Cr depletion. This conclusion is in agreement with other authors [25 to 31] who showed that carbides may form discretely or continuously, and a form of attack (either patchy or continuous) results depending on the extent of depletion.

Poznansky and Duquette [32] correlated the transition from TGSCC to IGSCC with the nucleation of carbides and the depletion of Cr along grain boundaries where precipitation took place. Again an important observation was made that the degree of sensitisation was not correlated to the quantity of precipitated carbide, but rather with the extent of the formation of continuous films of Cr depletion.

The depletion theory is also supported by the examination of corrosion around precipitates in TEM thin foils, in solutions known to cause active dissolution of materials with reduced Cr content [26,33]. The precipitates themselves remain unattacked, whilst attack occurs along

the grain boundary and at the precipitate interface.

Depletion is also caused by surface oxidation where Cr rich oxide films form. Depletion occurs by the diffusion of Cr along grain boundaries to the surface oxide film via a collector plate mechanism as described above [34,35].

Although the Cr depletion theory explains many corrosion and SCC experiments it is unable to explain:

1. Attack at higher/transpassive potentials where even unsensitised material is attacked [36,37].
2. Why attack is seen even in material solution annealed at high temperatures (where all the carbides dissolve, and the temperature is high enough for rapid Cr diffusion) [82,83].
3. Why IGA may be seen in materials where no evidence of precipitation is found [79].

Further theories have been suggested to explain such phenomena, the most often proposed is segregation, which is now discussed.

3.3.Segregation.

The segregation of alloying elements and impurities (namely Si, S and P) to the grain boundary has both a pronounced effect on mechanical properties and the electrochemical behaviour of the grain boundary [38,39,40]. Impurities may affect IGA in two ways:

1. Accelerate corrosion and passivation processes, by affecting the dissolution and repassivation rates and affecting the cathodic reaction [42,43]
2. Affect the C/Cr equilibrium and change the kinetics and thermodynamics of precipitation [44].

According to Lea and Hondros [45] the harmfulness of a particular impurity depends on

1. Bulk level
2. Segregation thermodynamics and kinetics
3. Ability to promote electrochemical change at the grain boundary.

Segregation may result from either equilibrium or non-equilibrium effects:-

a. Equilibrium segregation results when grain boundaries are enriched with both impurity substitutional and interstitial atoms at higher temperatures when such atoms are mobile and able to move to

such energetically favourable positions. On moving to lower temperatures, diffusion is retarded and impurity levels cannot drop. The grain boundaries are then inhomogeneous with respect to the matrix [46]. Briant [46] suggested that the kinetics of grain boundary segregation of P were rapid and the equilibrium value was reached in a few hours at 650°C.

b. Non-equilibrium effects result during irradiation when a vacancy or solute flux to the grain boundary carries impurities rapidly to vacancy sinks. Non-equilibrium effects may be annealed out during low temperature annealing [47].

3.3.1. Evidence of segregation.

The earliest evidence of segregation was from Aust [46,48] who showed significant grain boundary hardening in 304 stainless steel due to the non-equilibrium segregation associated with the trapping of solutes by vacancies moving towards the grain boundary.

Temper embrittlement effects are well documented [49,50] and are now known to be the result of segregation. However, there has been little published work on the effects of impurity segregation in austenitic stainless steels [46].

One of the first observations of the electrochemical effects of segregation was by Armijo [51] who measured the polarisation behaviour of grain faces and grain boundary in both an impure steel and a high purity steel [14Ni,14Cr] by lacquering either the grain boundaries or grain faces. The maximum dissolution rate for grain boundaries was over an order of magnitude higher than that of the matrix. Armijo then showed that polarisation curves could be represented as the sum of matrix and grain boundary components.

By correlation of alloy additions and electrochemistry Flis [52] concluded that the active path for IGA and SCC resulted from substitutional element segregation. However, Lea and Hondros [45] found interstitial elements were the main contributors to IGA.

Desestret et al [55] and Aust et al [53] studied the effect of small levels of Si addition on the electrochemical response of high purity stainless steels at oxidising potentials. Both papers attributed attack in $\text{HNO}_3/\text{CrVI}^+$ tests to the segregation of Si to grain boundaries, because high purity alloys showed no IGA.

Direct observation of segregation has been made using atom probe techniques or Auger Electron Spectroscopy (AES) [54]. Joshi and Stein [56] reported that S, N, P and Si segregate to grain boundaries and the extent of segregation controls the rate of grain boundary corrosion during Huey tests (exposure to boiling HNO_3). Andreoni et al [57] found evidence of P segregation to grain boundaries in 304

stainless steel. Sputtering experiments [58,59,60] have shown that segregation extends over only a few atom layers, if not less, and may be at a level of sub-monolayer coverage.

3.3.2.Co-segregation

Co-segregation of impurities and alloy elements enhances the potency of attack over that seen from either segregation or Cr depletion alone [63,64].

Mechanisms of co-segregation are complex and where both Cr depletion and segregation are seen together a dramatic increase in corrosion rate in Huey tests is seen [63]. After long ageing times the amount of P segregation decreases because of the onset of healing [64] because the increased Cr concentration at the boundary lowers the solubility of P. Briant [71,72] directly related AES measurements of segregation [73,74,75] to increased corrosion rates in HNO₃ and Strauss tests. Briant suggested that segregants had little effect on tests carried out at low potential (such as Strauss tests), though at higher potentials second phases containing impurity elements, and P segregation cause accelerated corrosion in Huey tests. The effect also depended on the extent of Cr depletion; the presence of Cr depletion lead to additional attack, to a greater extent than where just segregation was seen. Briant et al [65,66,67] have, by experimenting on both commercial and high purity stainless steels, shown that elements such as Mo and Ni enhance IGA in P doped steels. Viswanathan [68] found P co-segregation with Ni. Other authors [69,70] suggested that P segregation was reduced by the presence of Mo, because of the effect of Mo on carbide formation. Danyluh et al [76] suggested that reaction of P with Cr occurs at temperatures greater than 650°C. In contrast, S segregation, together with Cr enhancement has been seen by Lumnsen et al [77]. Briant [61] and Erhart et al [62] suggested that segregants may compete for available location sites. An example is found in the co-segregation of P and N; P segregation is more sluggish, though the driving force for segregation is greater, and therefore P displaces N as time progresses. Was et al [78,79] using AES found the presence of grain boundary carbides did not affect the kinetics of P segregation and found no evidence of Cr/P co-segregation, however Banerjee [44] showed by X ray diffraction and microanalysis that P dissolves substitutionally in the carbide.

The effect of high temperature heat treatment on the rate of IGA for commercial alloys in a HNO₃/CrVI+ test solution is shown Fig. 2 [52]. The resulting corrosion resistance of the grain boundary is strongly dependent on prior heat treatment [80,81]. Heat treatments at 800°C result in the formation of large carbides which dissolve harmful

impurities, and remove them from grain boundaries thereby renewing resistance to IGA. The maximum corrosion rate is seen after solution anneals of 1050°C due to solute segregation [81,82,83]. After annealing at higher temperatures, impurities are homogeneously dissolved in the lattice and no difference is seen in the corrosion rates of the matrix and grain boundary [83].

Although a correlation between IGA and segregation has been established, the mechanisms by which impurity elements locally accelerate corrosion are debatable. For the case of P segregation, Grabke et al [84] suggested that P prevents a passive layer forming. Vermilyea and Tedmon [83] suggested that the oxidation of Cr^{3+} to Cr^{6+} at oxidising potentials of those found in a Huey test requires the transport of electrons through the oxide film. Impurities segregated at grain boundaries may locally increase the conductivity of the oxide thereby facilitating oxidation and corrosion at grain boundaries. Okada et al [85,86] suggested that impurities may affect the cathodic reaction and thereby affect the rate of anodic dissolution. Latanision [87] found that impurities may act as recombination poisons and affect the evolution of hydrogen.

AEM measurements of the concentration of segregants along grain boundaries often show wide variation in the same material [57 to 62]. Briant [88] analysed a number of sources of the variability of segregation from boundary to boundary and concluded that the major source was grain boundary structure. Bennett [89] suggested that the mis-orientation across boundaries determined whether boundaries were weak or strong impurity atom traps, depending on the bonding that formed between the segregant and metal atoms. Such mechanisms explain the variability in the extent of attack from boundary to boundary during chemical tests.

3.4. Reactor sensitisation

The aim of this section is to put into context the choice of material heat treatment chosen for the SCC experiments described later. During use in the reactor the 20% Cr, 25% Ni, 0.7% Nb fuel cladding may become sensitised, in that the structure becomes susceptible to IGA and may suffer attack during subsequent storage of the fuel elements after use. As the cladding is a stabilised alloy, sensitisation is unexpected, particularly in view of the careful processing route prior to service.

The aim of the project was to investigate material in the sensitised condition, ie where grain boundaries were depleted in Cr due to the formation of Cr-rich carbides. Material used for SCC experiments

(described in chapter 6) was thermally sensitised, on the basis that results may be related to reactor sensitised material if sensitisation results from the same mechanism, namely Cr depletion along grain boundaries. In the reactor, sensitisation is caused by other mechanisms besides the formation of Cr-rich carbides and subsequent depletion of Cr at grain boundaries. Depending on the temperature during irradiation, sensitisation is either seen as a through-wall or as a surface only phenomenon, as different mechanisms operate at different temperatures. The main mechanisms of in-reactor sensitisation are now outlined. In the reactor, heat is extracted by passing a pressurised gas coolant (CO/CO₂) rapidly over the clad. The first two mechanisms are surface phenomena, resulting from clad/coolant interaction.

1. Carburisation of the clad.

Interaction of the clad and coolant gas can result in C deposition on the surface of the fuel pins and subsequent precipitation of M₂₃C₆ [90]. Such deposition occurs at the metal/oxide interface, and the C produced diffuses into the metal. Microprobe work on irradiated pins [91,92] has showed that the surfaces are higher in C content than the mid-wall by a factor of 2 to 3. C deposition is a complex function of coolant composition, temperature, fuel and pin condition and time.

2. Surface Oxidation

The coolant gas may cause both oxidation and carburisation of the clad. Evidence of oxidation <650°C is scarce, therefore the mechanism only occurs at local hot spots. Diffusion data for 20% Cr, 25% Ni, 0.7% Nb demonstrate that grain boundary diffusion is the main mode of Cr transport <750°C (discussed in section 3.9.2). Thus grain boundary Cr depletion could result from low temperature oxidation of the surface. Indeed the Strauss test response for materials aged at temperature in Ar, or in oxidising environments is different [93], and such results are described in Appendix 4.

3. M₂₃C₆ precipitation from residual carbon in the alloy

Carbon may remain in solution after the 930°C process anneal. The extent of this depends on NbC/Nb/C equilibrium considerations [94] (discussed in section 5.11). Excess C in solid solution may result in through-wall sensitisation as Cr rich carbides may precipitate throughout the structure during reactor exposure, with associated local Cr depletion.

Material near the welded end caps may contain higher levels of dissolved C due to the welding temperature cycle as Nb(CN) particles can dissolve. Sensitisation may result on subsequent ageing. The process of reactor sensitisation has been modelled by Norris [95].

3.5. The metallurgy of 20% Cr, 25% Ni, 0.7% Nb stainless steel fuel cladding.

The degree of sensitisation that results during heat treatment depends on microstructural characteristics such as grain size, plastic deformation, the presence of carbides, composition etc [3]. It is therefore important to understand the microstructural condition of material both before and after the sensitising heat treatment as this controls corrosion properties and response during IGA or SCC. Evidence of the relationship between M₂₃C₆ precipitation and sensitisation is shown in that characteristic TTS curves (Time at a particular Temperature necessary to cause Sensitisation) coincide with the low temperature branch of TTP (Time/Temperature/Precipitation) curves for M₂₃C₆, however the incidence of IGA disappears before the upper temperature stability limit of M₂₃C₆ is approached [96,97].

The initial structure of 20% Cr, 25% Ni, 0.7% Nb bar used for fuel cladding manufacture is a totally austenitic alloy with a grain size of about 50 μ m, with randomly dispersed Nb(CN) precipitates throughout the structure. Stabilization of the primary grain structure and of the composition (to avoid further precipitation during long term reactor exposure) requires the presence of fine Nb(CN) precipitates and a uniform grain size. During processing, secondary recrystallisation is controlled by both the volume fraction of Nb(CN) and the particle size. Recrystallisation commences after an incubation time which is determined by Nb(CN) coarsening to a critical size. The alloy is processed to ensure an optimum distribution and fraction of precipitates. Similarly, to prevent sensitisation (areas depleted in Cr) M₂₃C₆ formation is discouraged by control of the Nb:C ratio (referred to as stabilisation). Both the use of a low temperature process anneal (930°C) and alloy composition control ensure that most C and N is locked up in the form of Nb carbonitrides. Nb is present in excess of the stoichiometric ratio Nb(CN), ie

$$\text{Nb:C+N} > 8:1 \text{ wt\%}.$$

To control recrystallization and to precipitate out Nb(CN) the production route listed in table 1 is used [98].

Table 1.	Production Route for AGR fuel cladding
1.	Anneal thick wall tube 1025°C, 5 min
2.	Cold draw 25%
3.	Machine ribs on.
4.	Load pellets and weld end caps on
5.	Hydraulically pressurise onto fuel
6.	Anneal 930°C 1 hr

The result is thin wall tube 15mm in diameter and approximately 300 μ m

in thickness. The average grain size is 12 μm , and little residual cold work remains. The final processed material contains a bi-modal dispersion of Nb(CN) (0.1-0.5 μm and 1.5-5 μm diameter) within the grains and both Nb(CN) and M_6C at the grain boundaries. The high dislocation density induced by the final sizing cold draw is not fully removed by the final 930°C anneal, ie the structure is partially recovered rather than fully recrystallised.

The 930°C anneal improves corrosion resistance as it is a stabilising anneal and further stable Nb(CN) precipitates form. At this temperature the solubility of C in equilibrium with stabilising carbides is not greater than the equilibrium solubility with M_{23}C_6 .

A simple approach for the prediction of precipitation phases was suggested by Knowles [99] which considers the degree to which matrix Cr is stabilised by the addition of Nb, the stronger carbide forming element. He suggested that if the alloy composition has a stabilisation ratio of Nb:C less than 7.7:1 (hypo-stoichiometric) M_{23}C_6 and Nb(CN) will form on ageing, while alloys with hyper-stoichiometric ratios will form NbC and M_6C because excess Nb is present to lock up free C in the form of Nb(CN).

Alloys with Nb:C+N greater than 23:1 form Fe_2Nb on ageing.

3.6. Precipitation on ageing 20% Cr, 25% Ni, 0.7% Nb stainless steel.

The following section discusses information reported in the literature on the precipitation reactions of 20% Cr, 25% Ni, 0.7% Nb. The development of microstructure in 20% Cr, 25% Ni, 0.7% Nb is complex, however sensitisation is seen only where extensive M_{23}C_6 precipitation leads to Cr depletion. The other precipitates that form ie G phase, Nb(CN) and sigma phase, do not directly affect response in corrosion tests though their precipitation and decomposition reactions may indirectly affect M_{23}C_6 formation.

Considerable information exists on the microstructural changes that occur during the ageing of 20% Cr, 25% Ni, 0.7% Nb in a variety of conditions resulting from prior solution and mechanical treatments. A number of microstructural studies of 20% Cr, 25% Ni, 0.7% Nb have been carried out dating from 1965 when this alloy was suggested as a candidate for AGR fuel can material [100]. Most of these studies are reviewed by Knowles [101]. Further microstructural study together with analytical work was carried out by Powell [102]. The precipitation reactions in 20% Cr, 25% Ni, 0.7% Nb at elevated temperature are complex; reference to binary or ternary phase diagrams does not give much information on the nature of precipitation and microstructures resulting during thermomechanical heat treatment are well away from equilibrium conditions. Thermodynamic equilibrium is not approached even after long term ageing. Examples of the long stability of

stainless steels are given by the work of Lai and Wickens [103,103a] and Minami et al [104] showed precipitation in 304 stainless steel to be continuing even after 10 years.

Time/Temperature/Precipitation reactions are described by fig 3 [102]. As may be seen, both intergranular and intragranular precipitation of G phase, $M_{23}C_6$, sigma phase and Nb(CN) occurs during ageing.

Fig 4 collects data from several workers [100,101,102,106,108] and shows the temperature ranges of formation of commonly occurring precipitate phases in 20% Cr, 25% Ni, 0.7% Nb.

3.6.1. G phase.

From fig 3, it is seen that the first phase to form on ageing between 500 and 900°C is G phase. This occurs when residual Nb(CN) on grain boundaries transform to G phase. Increased ageing time allows more G phase formation; the nose of the TTP curve occurs at 800°C. It is only recently that this phase was identified in thermally aged 20% Cr, 25% Ni, 0.7% Nb [102]; previously precipitates had been identified as M_6C and G phase was believed to be only irradiation induced at irradiation temperature >440°C. G phase [105,106] has a composition of $Nb_{0.6}Ni_{1.6}Si_{0.7}$ and a FCC structure of lattice parameter 11.2 Å. The formation of G phase in 20% Cr, 25% Ni, 0.7% Nb has been discussed by Ecob, Lobb and Kohler [106] and Powell [102].

3.6.2. $M_{23}C_6$, G phase and Sigma phase reactions

As the Nb(CN) to G phase reaction involves the transformation of a carbide to a silicide, C and N are released into solution. This increase of C in solution allows $M_{23}C_6$ to form in the previously stabilised structure and consequently $M_{23}C_6$ precipitates are usually found around G phase particles. Where no excess C is in solution after solution annealing the decomposition of Nb(CN) to G phase is the way of forming $M_{23}C_6$. As Ni and Si are consumed during the growth of G phase, the local composition may become Cr rich and change the stability of the austenite matrix; local matrix regions may become locally impoverished of Ni and de-stabilise the matrix austenite even further and promote sigma formation.

Thus it may be seen from fig 3 that two Cr rich phases form, $M_{23}C_6$ and sigma phase; both may result in local Cr depletion. However, $M_{23}C_6$ formation has the major influence on corrosion properties, as it is the only Cr-rich phase to form at temperatures where significant depletion can occur and matrix diffusion is slow.

Microanalysis [122] showed $M_{23}C_6$ to be a Cr rich phase containing small amounts of Nb, Ti and Fe. Decasa [122] found the Cr/Fe ratio to be characteristic of the tempering time and temperature. As either

the ageing time or temperature increases Cr replaces Fe in the lattice.

Sigma Phase has been mentioned as a candidate for inducing sensitisation. Cihal and Jezek [123] found that the resistance to grain boundary corrosion was impaired by sigma phase and suggested the cause to be Cr depletion. However, although sigma phase is Cr-rich [102] (48%Cr,42%Fe,8.5%Ni,1.5%Si), it is unlikely to lead to sensitisation, because precipitation of this phase occurs at temperatures at which matrix diffusion prevents the formation of zones of Cr depletion sufficient to lead to sensitisation.

3.6.3. Observations on $M_{23}C_6$ precipitation in 20% Cr, 25% Ni, 0.7% Nb stainless steel

The precipitation of $M_{23}C_6$ carbides in stainless steels has been widely studied by many investigators [8,108,109,110,111,112]. The observations of the early investigations may be summarised as follows. Carbides nucleate within the plane of the grain boundary and grow as dendrites within the plane of the boundary and not into the matrix [8,108,109,113]. Stickler et al [110], maintained that carbide shape was a function of the degree of registry of the lattice planes on either side of the carbide, ie morphologies are a function of the type of boundary in which precipitation occurred. On ageing for longer times or higher ageing temperatures compact idiomorphic forms result. Lewis and Hattersley [114] and Shingal and Martin [115] observed that $M_{23}C_6$ grew by discontinuous precipitation having (111) habit planes and in parallel orientation with one of the matrix grains comprising the grain boundary. Adamson [116] made similar observations, in that $M_{23}C_6$ had a parallel orientation relationship with the austenite matrix irrespective of its nucleation site, and that the morphology of growth had (111) interface planes. Dislocations in the grain boundary act as nucleation sites for $M_{23}C_6$ precipitates and the nucleation process involves the development of (111) growth facets. Both Lewis and Hattersley [114] and Beckett and Clark [117] calculated that good matching occurred across (111) planes in [110] directions in the precipitate and matrix lattices. They showed that the mismatch on (111) planes was just over 1% and thus low energy interfaces formed on such planes. One specific mechanism of carbide nucleation and growth has been postulated by Shingal and Martin [115,118] which incorporates elements of the cellular precipitation mechanism proposed by Tu and Turnbull [119]. They envisaged nucleation to occur on a (111) boundary plane, with the axis of the thin lath precipitate parallel to [110]. Thus any grain boundary which has a [110] direction lying in the plane of the boundary for a distance at least comparable with the nucleus size is likely to provide a favourable site for $M_{23}C_6$ nucleation. One lath/matrix interface would have low energy because

it was a coherent boundary; the other interface would have high energy because it was incoherent. As the carbide grows, it grows preferentially into the grain corresponding to the high energy interface in order to maximise the amount of low energy interface surrounding the particle, and the boundary moves. A further precipitation mechanism proposed by Filimonov [120] suggests that grain boundary movement is due to dislocation density differences on either side of the grain boundary. Dis-equilibrium in vacancy concentration allows dislocations to climb towards the boundaries forming different densities of networks either side of the boundary, and boundary migration occurs to decrease the free energy of the system. Work by Fournelle and Clark [121] has shown that a chemical driving force may also be present after the initial precipitate nucleation boundary movement takes place, leaving a solute-depleted region behind the moving boundary; the driving force for migration is derived from the difference in chemical free energy between the solute rich matrix and the solute-depleted region and causes the boundary to move in the direction of the undepleted matrix.

3.6.4. The effect of cold work and grain size on sensitisation and precipitation.

The amount of cold work and grain size are important parameters in determining sensitisation. Cold work can be beneficial in preventing sensitisation because slip bands and dislocations act as preferential sites for carbide nucleation and precipitation is spread over a wider area, resulting in a reduced concentration of Cr carbides at grain boundaries and therefore a reduced extent of Cr depletion [124,125]. Compared to the solution treated and aged samples, carbide particles are present in the cold worked and aged samples in far smaller particle sizes [126]. Cold work also causes lattice defects which both increase the formation of nuclei inside the grain and speed up the diffusion of solutes, so that equalisation of Cr concentration is more rapidly achieved [97].

Work examining the effect of dislocation density on the grain boundary precipitation of 20% Cr, 25% Ni, X% Nb has been previously carried out; Adamson [116] noted that low levels of strain subsequently affected precipitation on ageing. A greater precipitation density was seen as a result. It was suggested that dislocations act as sites for nucleation. The effect has been observed in other stainless steels [97,126]. Spuriell et al [127] examined the effect of pre-treatment on the microstructural stability of 316 stainless steel, assessing the variables of grain size, solution treatment, degree of cold work and initial precipitate distribution. They noted large variations in phase stability, so that cold work accelerated precipitation and that precipitation occurred at lower temperatures.

The grains in stabilised steels may coarsen if the stabilising carbides dissolve or if they are not well dispersed. Variation of grain size may lead to change in precipitation kinetics and therefore the process of sensitisation. As grains grow, the surface area of grain boundaries is reduced and an interrupted network of carbides may be able to form on subsequent ageing. A larger grain size means that a smaller grain boundary area will be available for the precipitation of $M_{23}C_6$, and thus depletion and consequently sensitisation may be more severe.

3.6.5. The effect of irradiation on precipitation

Irradiation has a dramatic effect on precipitation and a more complex and diverse microstructure results [128,128a]. Precipitation is more copious than seen in unirradiated materials aged at the same temperature. The microstructure seen depends on irradiation dose, temperature and prior thermomechanical treatment. An increased concentration of point defects formed by radiation damage accelerates diffusion and thus the precipitation reactions of the formation of intermetallics and carbides are governed by substitutional diffusion. Irradiation gives rise to non-equilibrium solute segregation effects. Large fluxes of point defects (vacancies and interstitials) are set up by irradiation. Their migration to sinks occurs by a series of interchanges with lattice atoms en route. The frequency of interchange depends on the constituent atom involved, with the result that relative fluxes of major constituent atoms are set up. Local element concentrations can build up as a result of diffusion of solute atoms against or with the flow of point defects. Irradiation can give rise to Cr-depleted zones without the formation of Cr rich precipitates. The elements known to segregate most strongly are the undersized solutes such as Si and Ni:- Si because of its strong binding with defects; Ni because it is a slow diffusing substitutional element and remains at sinks. The high solubility of Ni in austenite ensures that Ni segregation does not induce precipitation. However the solubility of Si in austenite is more restricted and Si-rich phases form at defect sinks.

3.7. Observations on precipitation in 20% Cr, 25% Ni, 0.7% Nb stainless steel

The precipitation of $M_{23}C_6$ in 20% Cr, 25% Ni, 0.7% Nb was examined for ageing temperatures between 550 and 750°C.

Specimens were made by initially solution treating thin strips of AGR fuel cladding tube (20% Cr, 25% Ni, 0.7% Nb) in an argon atmosphere and then ageing in either an argon or evacuated atmosphere. Two

solution heat treatments were used:- 1050 or 1150'C, and a variety of ageing temperatures between 550 and 750'C for times between 1 and 500 hrs were used. 3mm discs were punched or spark machined from the strip. Discs were then ground to 80 um thickness and 1200 grit finish. Thin foils were prepared from such discs by jet polishing using a Fishioni unit at 118V in a 2% HClO₄, 0.5% HNO₃ butoxyethanol mixture cooled to -25'C. TEM examination was carried out on both a Philips model EM300, and on a JEOL model 100B electron microscopes, both operating at 100 kV.

Fig. 5a and b show examples of the microstructures for material solution annealed at 1050'C for 30 min and aged for 500 hrs at 550'C. Both micrographs illustrate the complex nature of precipitation. Fig. 5a shows the transformation of Nb(CN) to G phase, the Nb(CN) particles do not display an orientation relationship with the matrix because they are formed during cooling of the melt. The reaction liberates C into solution for M₂₃C₆ formation. The unmarked precipitates proved too small for selected area diffraction pattern analysis. Fig. 5b shows a different grain boundary in the same material as Fig. 5a. Both G phase and M₂₃C₆ are co-precipitating on a grain boundary.

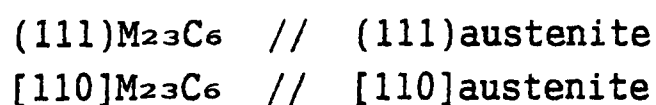
Fig. 6 shows a foil made from tube material aged for 500 hrs at 550'C. It is observed that M₂₃C₆ nucleates at discrete sites (intrinsic dislocations) along the high angle boundaries. These particles were identified by electron diffraction (shown Fig. 6) and X-ray micro analysis. The atomic composition of M₂₃C₆ in 20% Cr, 25% Ni, 0.7% Nb was estimated by EDX as Cr₁₇Fe₆C₆ and is listed below:

composition of M₂₃C₆ precipitates after heat treatment of 1050'C 30 min, followed by 550'C for 500 hrs.

M₂₃ = Cr: 16.94 parts, Fe: 5.56 parts, Nb: 0.5 parts.

Precipitates were found to possess a parallel orientation with one of the austenite grains forming the high angle boundary. The lattice spacing (measured by diffraction) of the matrix was 3.6 Å and of the precipitate 10.6 Å.

The observed relationship between matrix and precipitate (shown by the diffraction pattern in Fig. 6) was determined as:



Individual precipitates are seen to be tetrahedral in shape and the trace of edges found to be [110]. The outward form of the carbide was

found to be coherent with (111) lattice planes of the matrix, presumably in order to minimise the strain energy and interfacial area. The effect of grain boundary misorientation is shown in that the density of precipitation varies from grain boundary to grain boundary. High angle boundaries allow greater diffusion rates and exhibit the necessary orientation relationships to encourage nucleation and growth and thus allow precipitation where precipitation would not be seen along low angle boundaries such as twin boundaries [113,114,115]. The position of the grain boundary (along which precipitation has occurred) is shown by grain boundary fringes, the "wavy", non-parallel fringes indicate that the boundary has moved during precipitation. Local distortion of the grain boundary occurs to preserve the boundary plane as the growing plane for the growing precipitates. Preferential etching occurring during foil preparation is seen at a grain boundary in Fig. 6. The grain boundary acts as a solute sink and allows a short circuit diffusion path for Cr-rich precipitation on nearby boundaries.

Precipitates at triple points are larger and extend along the grain boundaries. Massive $M_{23}C_6$ precipitates at triple points were in parallel orientation with one constituent austenite grain and the regions along grain boundary adjacent to triple points are denuded of precipitates. Small precipitates are seen on matrix dislocations.

Fig. 7a shows material aged at 550°C for 780 hrs. Precipitation has occurred, but only on grain boundaries with a favourable habit plane and orientation. Intrinsic grain boundary dislocations are clearly visible. The unstable nature of $M_{23}C_6$ in this material is shown in Fig. 7b for a material annealed at 1050°C and aged for 130 hrs at 650°C. $M_{23}C_6$ particles are redissolving (as evidenced by the concave matrix precipitate interface) and Nb(CN) particles form on the grain boundary presumably as C concentration increases as $M_{23}C_6$ dissolves. After longer times of ageing precipitates are large and small in number. This results because particles coarsen by the growth of one large particle at the expense of smaller ones by diffusion along grain boundaries. This is energetically favourable as the interface area between the precipitate and matrix is reduced. The first particles to nucleate on energetically favourable defects grow faster and are less likely to redissolve. Fig. 7c shows material annealed at 1050°C and aged for 230 hrs at 650°C. Precipitation has occurred widely on matrix dislocations throughout the material.

Fig. 8a shows large sigma phase precipitates in material aged for 130 hrs at 750°C after a 1150°C anneal. Precipitates are seen to grow into both grains and maintain a characteristic growth morphology in the grain they grow into. Fig. 8b shows $M_{23}C_6$ in the same material, precipitates have edges parallel to the [110] trace directions.

Fig. 8c and 8d show material aged at 650°C for 48 hrs after a 1050°C anneal. Fig. 8c shows that as precipitates grow, dislocations may be punched out from around, due to the mismatch of lattice spacing of $M_{23}C_6$ compared with matrix austenite. Nb(CN) is observed to precipitate on such interfacial dislocations after long ageing times. Fig. 8d shows strain contrast around a large precipitate, and that the strain associated with such large precipitates may be considerable.

3.8. Modelling sensitisation.

In order to have a quantitative understanding of the process of sensitisation, it is important to understand the variation of Cr concentration at grain boundaries as a function of $M_{23}C_6$ precipitation characteristics ie time, temperature, and grain boundary orientation. The nature of corrosion may then be understood in terms of Cr depletion below levels necessary for the formation of a protective passive film. If the Cr level in the boundary at some point falls below a critical concentration (the Cr concentration marking the level between active and passive behaviour, usually assumed to be 12 wt%) but not at others then a patchy type of IGA results. However, if the entire boundary is depleted below this level, IGA may be seen continuously along the boundary. As an aid to prediction of the extent of Cr depletion quantitative models have been formulated. Such models aim to provide analytical solutions of Cr concentrations at a grain boundary and give a useful insight into the process of sensitisation by the prediction of ageing times and temperatures for sensitisation and de-sensitisation. Such calculations indicate that a Cr concentration gradient will exist normal to the grain boundary, and that the widths of depletion would have been impossible to measure on the microanalytical instruments until recently, because of the narrowness of the zones. Because of the difficulty in resolving such zones most reported profiles are for high temperature [700°C+] and for long aging times. The purpose of this section is to outline an approach for the prediction of the extent of Cr depletion. Two of the earliest models one by Stawstrom and Hillert [129], the other by Tedmon et al [130], will be described and contrasted.

3.8.1. Calculation of the extent of Cr depletion.

Earlier models suggested different controlling mechanisms for the processes of sensitisation and healing, eg Shvartz and Kristal [131] suggested C diffusion controlled sensitisation and Cr diffusion controlled healing. Baumel et al [132] suggested Cr grain boundary diffusion for sensitisation and volume diffusion for healing. However such mechanisms may be discounted as it was noted by Stickler

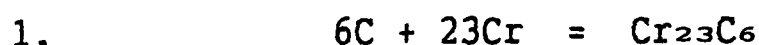
and Vinkler [26,27] that carbides may grow at the same time as healing, therefore only one diffusion mechanism applies to both healing and sensitisation.

The starting point for estimation of the extent of Cr depletion in the grain boundary network is to estimate Cr content at the carbide/grain boundary interface. To evaluate the Cr content at the $M_{23}C_6$ interface the following assumptions are made [13,14]

1. Uniform C activity exists throughout the material. The justification for this is that as the diffusion coefficient of C is several orders greater than that of Cr [134] the C activity is virtually uniform throughout the lattice over the relevant time scale. C activity does not change locally at the carbide/matrix interface [133,135].
2. The Cr diffusion coefficient in the carbide is high enough to keep the Cr concentration homogeneous throughout the carbide.
3. During Cr diffusion and carbide formation, the shift of the carbide/austenite interface and the variation of composition at the interface does not change ie the ratio of Cr to C atoms remains constant in the proportions found in the carbide.
4. Only the formation of intergranular carbides leads to Cr depletion.

It is assumed that local Cr/ $Cr_{23}C_6$ /C equilibrium is reached at the grain boundary and that the Cr concentration is thermodynamically controlled by this equilibrium. The Cr concentration at the matrix/carbide interface is calculated assuming local thermodynamic equilibrium between alloy, carbon and carbide.

For the reaction



the equilibrium constant K is calculated by:-

$$2. \quad K = \frac{1}{([Cr]\gamma_{Cr})^{23} \cdot ([C]\gamma_C)^6}$$

where unit activity is assumed for the carbide.

[Cr] or [C] = Cr or C concentration (mole fractions) in equilibrium with the carbide. γ_{Cr} γ_C = activity coefficient of Cr or C.

Data for the free energy of formation of $Cr_{23}C_6$ are available in the literature and hence K may be calculated. In order to determine [Cr] it is necessary to know the activity coefficients for C and Cr. As local equilibrium exists between the carbide and the austenite interface, the situation is defined uniquely by the C activity at that

moment. Microanalysis has shown that the composition of $M_{23}C_6$ is not $Cr_{23}C_6$ [122], and that Fe replaces Cr in the carbide. Therefore the equilibrium constant may be written as



4.
$$K = \frac{1}{([Cr] \gamma_{Cr})^{17} \cdot ([Fe] \gamma_{Fe})^6 \cdot ([C] \gamma_C)^6}$$

Comparing equations 2 and 4 it may be seen that the composition of the carbide has an important effect on C activity and thus the Cr concentration at the carbide interface. The equilibrium Cr concentration will depend on the value of the equilibrium constant K, which increases sharply with temperature, and will decrease for higher activities of C in solid solution.

An example of the effects of Cr content on the activity coefficient of C is shown for a steel containing 10 wt% Ni in Fig. 9. It can be seen that the C activity decreases as the Cr content rises. Fig. 10 shows that C activity increases as Ni content increases. Elements such as Ni, which raise the activity coefficient for C will lower the equilibrium level of C concentration necessary for sensitisation. Therefore, for a high Ni content steel the high C activity results in a lower Cr concentration necessary to maintain equilibrium with C, with the result that sensitisation occurs more readily.

A diagram of the Cr/ $Cr_{23}C_6$ /C equilibrium for 304 stainless steel is shown in Fig. 11, taken from ref [130]. The curves represent the Cr composition at a grain boundary in equilibrium with the carbide as a function of C content for a given temperature. The C concentration in the matrix in equilibrium with the carbide decreases with decreasing temperature. This curve is a plot of grain boundary Cr concentration in equilibrium with bulk C content. From this, the required concentration of C in solid solution (in equilibrium with $Cr_{23}C_6$) may be calculated to produce a Cr level less than the critical level. An example; taking 12 wt% Cr as the minimum quantity required to form a protective passive film, it is seen that if the alloy 304 stainless steel contains more than 0.03 wt% C it becomes sensitised by heating at 600°C. The effect of reducing ageing temperature is to reduce the C concentration required for a given equilibrium Cr concentration, and consequently sensitisation is predicted to occur at lower concentrations of C in solid solution.

3.8.2. Early models

Of the early models, Stawstrom and Hillert [129] assume that the Cr

diffusion rate determines precipitation, and over-ageing to immunity (self healing) occurs as Cr diffuses in from the matrix to the depleted zones. The model by Tedmon, Vermilyea and Rosolowski [130], emphasised the thermodynamic aspects of precipitation and describes the Cr/Cr₂₃C₆/C equilibrium at grain boundaries.

Stawstrom and Hillert [129] use unpublished thermodynamic expressions by Nishizawa on the solubility of M₂₃C₆ in austenite in the ternary Fe-Cr-C system, to obtain values for the activities of C. These values are corrected for the Ni and Cr content of the system.

Tedmon et al [130] used a more general approach by producing an equilibrium equation involving the mole fractions of dissolved C and Cr, and then employed the data of Richardson [137] to calculate activity coefficients corrected for temperature, Ni and Cr content.

Other alloying elements change the activities of C and Cr. The fact that information on the relationship between activities and concentration in steels of C, N, Cr, Ni and the resultant effect on the thermodynamic variables, is sparse makes an approach considering activity coefficients difficult. Tedmon et al [130] used a thermodynamic method proposed by Wagner [138] to calculate the effects of Cr content on the activity coefficient of C in austenite. Tedmon et al [130] then estimated the Cr activity coefficient from corrosion rates of 304 stainless steel heat treated at 600°C and exposed to a Strauss test, and from further samples exposed to 65% HNO₃ at 25°C.

Rates of boundary penetration were compared with the dissolution rates of a series of experimental alloys of varying Cr concentration and composition Fe+10% Ni. An estimate of Cr grain boundary concentration was then substituted into the equilibrium expression to provide values of Cr activity as a function of Cr concentration. Tedmon et al then used thermodynamic analysis to produce quantitative Cr/Cr₂₃C₆/C equilibrium diagrams for several austenitic stainless steels knowing the activities of C and Cr and calculating the Cr level at grain boundaries.

It is well established that if a sensitised steel is held at the sensitisation temperature long enough it will gradually become less susceptible to IGA with time. As the carbide film grows and the C content of the austenite decreases the C activity decreases and this will in turn allow the Cr content of the depleted zone to increase, maintaining thermodynamic equilibrium. Eventually the Cr concentration at the boundary will reach a safe level when IGA ceases. This process is known as self healing, and can take place during carbide precipitation.

Early models provide Cr and C solubility curves for Fe-Ni-Cr alloys but do not consider the effect that the metallurgical characteristics

of the steel (such as minor element composition and grain size) can have on the IGA susceptibility. An example is given in that Rollason (TTP) curves are displaced to higher temperatures and longer ageing times by Mo additions. Resistance to sensitisation is found to be improved. This is due to a reduction in the activity of C and the formation of complex carbides (eg. $(\text{CrFeMo})_{23}\text{C}_6$). The effect of alloying elements in stainless steels on the activities of C and Cr has been reviewed by Natesan and Kassner [133] and Wada et al [136].

3.8.3. Cr concentration Profile

At the temperature of interest the rate of grain boundary Cr diffusion is orders of magnitude faster than bulk diffusion, so that Cr transport to carbides will take place along grain boundary networks via a collector plate mechanism. To examine the Cr profile (concentration with distance from carbide particle or grain boundary) it is necessary to examine the variation of Cr concentration with time and distance from the carbide, ie the kinetics of diffusion-controlled growth. Several theoretical papers have been published on the growth of precipitates by diffusion in ternary systems [139,140,141]. These treatments, however, are restricted to the case of an isolated particle in an infinite matrix and where the interface compositions remain constant during growth. In the case of Cr depletion different rates of diffusion in the matrix and along the grain boundary complicate the situation.

Both Stawstrom and Hillert [129] and Tedmon et al [130] went on to calculate concentration gradients around grain boundary carbides. Stawstrom and Hillert treat diffusion as a one-dimensional problem, and assume that rapid grain boundary diffusion allows equilibrium to be established between particles along the entire grain boundary area of the material. They assume that the rate controlling step is diffusion of elements to the boundary, thus concentration along the grain boundary may be assumed uniform, and the grain boundary is regarded as a collector plate for the carbide/matrix interface. They further assume that a continuous carbide film of even thickness forms, and that the limiting diffusion is normal to the grain boundary only. They then followed the progress of the reaction by following the C concentration in the interior of the austenite grains and described the Cr concentration at the carbide interface.

Tedmon et al [130] calculated concentration gradients both along the grain boundary between carbides and away from the grain boundary by using an analysis developed by Aaron and Aaronson [13,14]. Such models may be used to provide a quantitative indication of the duration of IGA susceptibility by considering the time when the Cr concentration is below the critical level.

Stawstrom and Hillert [129] tackled the problem of predicting self

healing times. The calculated ageing time that raises the Cr content above the 12 wt% level was found to agree well with the experimental time that made the steel corrosion resistant (in Strauss tests) again. The healing time may be calculated using the determined C activity coefficient to calculate the time for a level of Cr depletion to be achieved. Using the values of 12 wt% and a zone 20nm wide led to correlation of the predicted times and the ageing times that led to little attack in a Strauss test. Tedmon [130] made observations on thin foils of samples heat treated at different temperatures and for different times and then exposed them to boiling Strauss solution. The foils in which grain boundaries were attacked correlated with theoretical predictions as to which would be unsensitised, sensitised, and healed.

To consider the change of Cr concentration with time, Fick's second law may be solved as a function of distance from a boundary. For each time considered the total Cr lost from the matrix is calculated and hence the quantity of C taken out of the solution by $M_{23}C_6$ adjusted and the diffusion equation solved again. Solutions to this differential equation have been approached in various ways. Numerical [142,143,144,145] and analytical [146] together with finite element modelling [89] have been used. Skyrme and Norbury [147] studied the kinetics of $M_{23}C_6$ growth in 316 stainless steel and reported C/Cr/ $M_{23}C_6$ equilibrium equations which did not involve activity coefficients. All methods have been correlated to experimental results. Bennett [146] was able to predict profiles over transient periods where profiles around carbides overlap. He incorporated grain boundary orientation and structure parameters into modelling and was able to calculate values of diffusion coefficients from precipitate spacings and Cr profiles.

Theoretically predicted times to sensitisation agree reasonably with experimental observations for sensitisation [129,130], but not for the healing process. Comparison of TTS curves theoretically and experimentally generated is shown in Fig. 12. An example of data and theoretical comparison is given in Fig. 12a. In comparison, Fig. 12b shows sensitisation data for the same material, gathered by Scott [147a]. Comparison shows that calculation is reasonably successful in predicting the process of sensitisation at higher temperatures (>600°C), but not for lower temperatures. This is because models assume that a carbide film forms at the grain boundary at time zero and do not consider the kinetics of nucleation or the microstructural condition of the steel when calculating sensitisation time. However, the nucleation time may be significant, and depends on microstructural features such as the grain size. At higher temperatures, the time required for the formation of a carbide film is small compared to sensitisation and desensitisation times, but becomes so large at low temperatures that it controls sensitisation times.

3.8.4. Low temperature sensitisation

Sensitisation at low temperatures is dominated by the time required for precipitation of carbides. The models apply to fully solution annealed rather than mill-annealed materials, which may already contain carbides which enhance further precipitation and consequent sensitisation during operation.

For example, sensitisation may be induced during low temperature ageing if precipitation is initially started at higher temperatures. eg. prior ageing for 1hr at 700°C will reduce the initial sensitisation time at 550°C from 500 hrs to 15 hrs, because the initiation time is much reduced [148]. Hanninen [148] suggested that changes in the mechanism of growth at low temperatures could also lead to prolonged time to sensitisation.

It is well known that after welding, during cooling the heat-affected zone (HAZ) is only in the temperature regime for the nucleation of Cr rich carbides at grain boundaries for a short time. Initially the degree of sensitisation is insufficient to result in severe attack. However, if the welded component operates well below the temperature for normal sensitisation, the previously nucleated carbides grow, while the low temperature (less than 400°C) prevents further nucleation and greatly impedes Cr diffusion. Thus after extended periods of time (10 years), low temperature sensitisation (LTS) increases the probability that IGSCC may occur [149,150]. An example of LTS data for 304 stainless steel is shown in Fig. 13. Values of LTS times are found to vary with ageing time and considerable discrepancy for the same material is found between authors. Continuous cooling has been observed to cause more severe sensitisation than predicted from isothermal data [151,152].

3.9. Prediction in 20% Cr, 25% Ni, 0.7% Nb stainless steel.

An attempt was made to predict sensitisation in the test material as a function of temperature and time. Comparison with data on the sensitisation of other steels can only be approximate because of the presence of Nb which forms Nb(CN) precipitates. Furthermore, increasing the Ni content of a steel increases the activity of C. On a qualitative basis any model of sensitisation for 20% Cr, 25% Ni, X% Nb stabilised steel would be expected to predict:

1. Increase in sensitisation with increase in alloy C level (for a fixed Nb content)
2. Decrease in sensitisation with increase in Nb content (for a fixed C content)
3. Increase in sensitisation for an increase in solution anneal temperature (at fixed C and Nb content).

3.9.1. A Computer Model

The model used to gain an insight into the shape of Cr depletion profiles generated in 20% Cr, 25% Ni, 0.7% Nb stainless steel will be outlined, in preparation for comparison with corrosion data and measured STEM profiles in chapter 5. This model (SAROC) was developed by Norris [95]. SAROC aims to quantify the kinetics of Cr depletion by the formation of Cr-rich carbides. The model addresses the following:

1. The amount of C available for precipitation, after the final stage anneal, by the dissolution of stabilising carbide NbC.
2. The equilibrium Cr concentration at the $M_{23}C_6$ /matrix interface after ageing for a length of time at a set temperature.
3. The disparity in the rates of lattice diffusion and grain boundary diffusion, and the Cr concentration profile that results perpendicular to the grain boundary.
4. calculation of the quantity of C remaining at each time step of precipitation and therefore the amount remaining for further precipitation.

3.9.1.1. Amount of C in solution.

$M_{23}C_6$ formation requires C to be available in solution. This may occur for two reasons in 20% Cr, 25% Ni, 0.7% Nb.

1. G phase formation.
2. NbC dissolution.

G Phase.

As previously explained, $M_{23}C_6$ precipitates are often closely associated with G phase and co-precipitation of the two phases is seen. As G phase transforms from Nb(CN), there is local enhancement of C and N in the region of G phase. This is sufficient to enable the local C concentration to become high enough for $M_{23}C_6$ precipitation. However, once the C and N from G phase transformation have been used, the Nb/C+N ratio may be restored to a value greater than 7.7 (the critical value determined by stoichiometry) and no further $M_{23}C_6$ precipitates.

Nb dissolution.

To stabilise the steel Nb is added as it forms carbides more readily than Cr, thus locking up all C in solution. Such stabilising alloying elements lower the solubility of C in solid solution, thereby reducing C activity for further carbides to form. To liberate C, the steel must be heated to above the temperature of stability of NbC.

NbC is not entirely insoluble, but dissolves at considerably higher temperature than $M_{23}C_6$ [153].

The concentration of C prior to precipitation of $M_{23}C_6$ can be estimated by assuming that in the final solution treatment the reaction $Nb + C = NbC$ reaches its thermodynamic equilibrium. The solubility product for the reaction (assuming unit activity for NbC) is given by:-

$$5. \quad K = [Nb].[C]$$

Fig. 14 shows the data of Deighton [153], the concentration of C as functions of Nb concentration and temperature. Deighton empirically showed that NbC solubility is given by

$$6. \quad \log_{10} C = 8.326 - \frac{8358}{T}$$

where T = solution temperature

C = concentration in ppm

Assuming that in the final solution treatment the formation of NbC reaches thermodynamic equilibrium and using solubility data of Deighton [153], shown in Fig. 14, the amount of C left in solution may be calculated using equations 5 and 6. This quantity is the amount of C available for the precipitation of Cr-rich carbides. Therefore the initial Nb to C ratio and the solution anneal temperature are very important in determining the sensitisation of the steel on further ageing. As the solution temperature is increased, (or the initial C level is increased) the temperature range over which sensitisation occurs is increased. Similarly, if the initial Nb content is decreased, the temperature range over which sensitisation is seen is increased. Lakshmanan and Kirkaldy and Sharma [154] review the solubility product of NbC in austenite.

Using the NbC/Nb/C solubility curves shown in Fig. 14, the concentration of C in solution after annealing may be calculated.

Fig 14 shows that after a 930°C anneal approximately 0.005 wt% C will be in solution. In service, cladding pins are filled with fuel and sealed by welding end caps to the cladding tube. The process of

welding may locally increase C solubility and may liberate more C into solution that that suggested for a 930'C anneal. The HAZ is thus potentially susceptible to sensitisation on subsequent thermal ageing.

3.9.1.2. Equilibrium considerations

After calculating the amount of C in solution prior to $M_{23}C_6$ precipitation, equation 4 (describing the $M_{23}C_6$ /Cr/C equilibrium) may be used to calculate the extent to which Cr depletion will occur. An effective Cr concentration is used to avoid considering the problem of activity coefficients that change with alloying element concentration. The use of an effective Cr concentration has been considered by Fullman [155] and Cihal [155a]. The effective Cr concentration used during modelling is given by an empirical relationship determined by Briant [65]

$$7. \quad [Cr \text{ eff}] = [Cr] - 0.18.[Ni]$$

$$8. \quad [C]^u. [Cr \text{ eff}] = S_{2(\tau)}$$

w

where $u = C/Cr$ ratio in the precipitate

$S_{2(\tau)}$ = the solubility product of $M_{23}C_6$.

The composition of the carbide varies with temperature and the extent of precipitation, though may be reasonably be approximated to $Fe_7Cr_{16}C_6$ as shown by EDX determinations on material aged at 550'C.

Therefore $u = 6/16$.

Equilibrium Cr concentration/C concentration data generated by the SAROC model are shown in Fig. 15. Using solubility curves from the Cr/ $M_{23}C_6$ /C diagram Fig. 15 it may be seen that after a 930'C anneal and ageing at a temperature of 550'C or above, the minimum equilibrium Cr concentration that is seen will be approximately 12.5 wt%. Therefore, if the criterion of the Cr level falling below 12 wt% is used sensitisation would not be seen, because after a 930'C anneal insufficient C is in solution. It may be seen that if these equilibrium values are used, more than 0.006 at% C (approximately 0.01 wt%) in solution results in Cr depletion at 600'C sufficient to cause sensitisation. The effect of lowering the ageing temperature is to reduce the amount of C required to bring the equilibrium Cr concentration below the threshold for sensitisation, and consequently sensitisation is predicted for lower levels of C.

An example of the use of SAROC is in considering the effect of solution anneal temperature on the Cr/ $M_{23}C_6$ /C equilibrium. The Cr concentration at the grain boundary at the start of ageing must first be calculated. Its value is calculated (as above) by first estimating the amount of C left in solution after annealing, and then prediction from Cr/ $M_{23}C_6$ /C equilibrium considerations.

Fig 16 shows the variation of the minimum Cr level attained at the

onset of precipitation with temperature for solution anneals of both 1050 and 1150°C. The curves are similar, though the minimum Cr concentration that results after a 1050°C anneal is greater than that for 1150°C. For the same material aged at the same sensitisation temperature, a higher solution anneal temperature results in more severe Cr depletion because a higher solution temperature puts a higher initial concentration of C into solid solution.

From Figs. 15 and 16 it may be noted that sensitisation is not expected for temperatures greater than about 700°C, because above this temperature the equilibrium level of Cr concentration does not fall below that necessary for sensitisation.

3.9.1.3. Prediction of Cr depletion profiles.

To examine the Cr profile (concentration with distance from the grain boundary) the Cr diffusion equation is solved as a function of distance from a boundary. For one-dimensional diffusion of C accompanied by precipitation Fick's second law may be written as

$$9. \quad \frac{dN_c}{dt} + \frac{d(N_c \cdot cr)}{dt} = D_c \cdot \frac{d^2 N_c}{dx^2}$$

$$10. \quad \frac{dN_{Cr}}{dt} + \frac{d(N_c \cdot cr)}{dt} = D_{Cr} \cdot \frac{d^2 N_{Cr}}{dx^2}$$

N_c or N_{Cr} = the mol fraction of C or Cr in austenite,

D_c or D_{Cr} = the diffusion coefficient for C or Cr in austenite,

$N_c \cdot cr$ = the number of moles of carbide

x = the distance from the grain boundary and t = time.

After each time step the total Cr lost from the matrix is calculated and hence the amount of C removed from solution by $M_{23}C_6$ precipitation is calculated. The value of the quantity of C remaining is then readjusted and the equation solved again to give a further set of Cr depletion concentrations at distances from the grain boundary.

Output from SAROC allows values of the Cr concentration to be evaluated considering distance from the grain boundary and ageing time and temperature.

Fig 17 gives an example of Cr prediction using the SAROC model. The data for the modelling concentration profiles were obtained from running SAROC [95] inputting the following parameters.

C wt% = 0.0375, Cr eff = %Cr - 0.18.%Ni, Grain size 12 μ m, Nb wt% 0.7

Values of the Cr level are generated at 2 nm mesh distances away from

the grain boundary for successive increments in ageing time (for a fixed temperature).

Fig. 17 shows how Cr profiles change shape with ageing time at 550°C. As ageing time progresses, profiles flatten out and become shallower and wider, and the minimum level of Cr at the boundary increases. The effect of two solution anneals is shown, it may be seen that the higher solution anneal increases the width of the Cr profile and decreases the minimum level of Cr at the boundary, ie the size of the Cr-depletion profile is larger. This is because the use of a higher solution anneal increases the level of C in solid solution, and therefore increases the activity of C prior to sensitisation. This results in more extensive Cr depletion.

The criteria suggested by Stawstrom and Hillert for sensitisation was for the level of Cr depletion to fall below 12 wt%, together with a depleted zone width of 20 nm at this level. The 12 wt% line is shown on Fig. 17. It is seen that all the profiles have Cr depletion below 12 wt%, however where the material has been aged for only 10 hrs at 550°C the profile width at the 12 wt% level is narrower than 20nm. If the criterion for sensitisation is correct, this material should appear unsensitised in corrosion tests. Similarly, if healing brings the profile minimum above the 12 wt% level, material should appear unsensitised in corrosion tests.

Fig. 18 shows how Cr profile shapes change with ageing time at 650°C, for a sample initially annealed at 1150°C. Again as ageing time progresses, profiles flatten out (become wider and shallower), and the minimum level of Cr increases.

Two suggested criterion for sensitisation are depicted on the diagram. Fig 18 shows that using Stawstrom and Hillert's criterion, only the sample sensitised for 2.5 hrs at 650°C would appear sensitised. If however, the necessary criterion is restated arbitrarily as Cr concentrations below 14 wt% together with a zone width greater than 32 nm all the samples apart from that aged for 250 hrs would appear to be sensitised. The criterion set to distinguish between sensitised and unsensitised is important if different corrosion tests respond to different extents of Cr-depletion and widths of Cr profiles, and we wish to compare response in corrosion tests with modelled profiles.

From such results it is possible to extract the time for the Cr concentration (at a set profile width) to fall and rise below a given Cr level.

Fig. 19 shows a TTS curve generated from SAROC data by considering the time for the Cr level to fall below, then rise again above 12 wt%, while the profile shape is such that the width of the zone depleted at the 12 wt% level is 20 nm. The concepts surrounding Cr depletion

profile and sensitisation are shown schematically in Fig. 19. Both a solution anneal of 1050 and 1150°C are considered. It may be seen that a higher initial anneal temperature results in sensitisation over a much wider range of time and temperature than the lower temperature solution anneal.

Fig. 20 shows a collection of such data, in the form of TTS curves. To generate such curves, it is necessary to assume criteria of levels of Cr depletion and zone width for sensitisation to occur. TTS curves for Cr levels of 13, 14 and 15 at% together with profile widths at that level of depletion of 12, 20 and 32 nm are shown for two different anneal temperatures (1050 and 1150°C).

The nomenclature is such that 11.12 indicates an 1150°C anneal and a chosen criterion of 12 nm zone width at the Cr level indicated on the Figure. 10.32 similarly indicates a 1050°C anneal and a zone width of 32 nm.

3.9.2. Diffusion Coefficients

Quantitative modelling of diffusion phenomena, such as the precipitation process which leads to sensitisation, relies on the availability of appropriate diffusion data. The lattice diffusion coefficient is a crucial parameter for calculating Cr depletion profiles. Often such data are obtained at high temperatures while precipitation may occur at much lower temperatures. This necessitates the dubious extrapolation of high temperature data. Furthermore, in stainless steels bulk and grain boundary volume diffusion coefficients vary with small changes in composition of the alloy. An important example is given by the work of Assassa et al [156] who studied the effect of Si content on the diffusion of Cr in various austenitic steels and found that the Cr diffusion coefficient varied by an order of magnitude for small Si concentration changes.

Data for the diffusion of Cr in type 304 stainless steel have been previously reported by Stawstrom and Hillert [129] who deduced their data from corrosion tests and measurements of the C concentration in the matrix of sensitised steel. More direct measurements of the volume and grain boundary diffusion coefficients for Cr have been made by microanalysis of the Cr depleted zone in sensitised steels using AEM methods such as STEM/EDX as by Briant and Hall [157] and Thorvaldsson et al [158]. Measurements using radiotracer techniques have been used to gain data for alloys containing 17 wt %Cr/12 wt %Ni by Perkins et al [159,160], and for 20 wt% Cr, 25 wt% Ni by Smith and Gibbs [161] and for 304 stainless steel by Bowden [162] and for 316 stainless steels by Smith [163]. These data are shown on Fig. 21a, Perkins [159] observed that the Cr diffusion coefficient decreases with Ni content. The volume diffusion data used for SAROC calculations used data by Perkins et al [159] and are shown in Fig. 21b.

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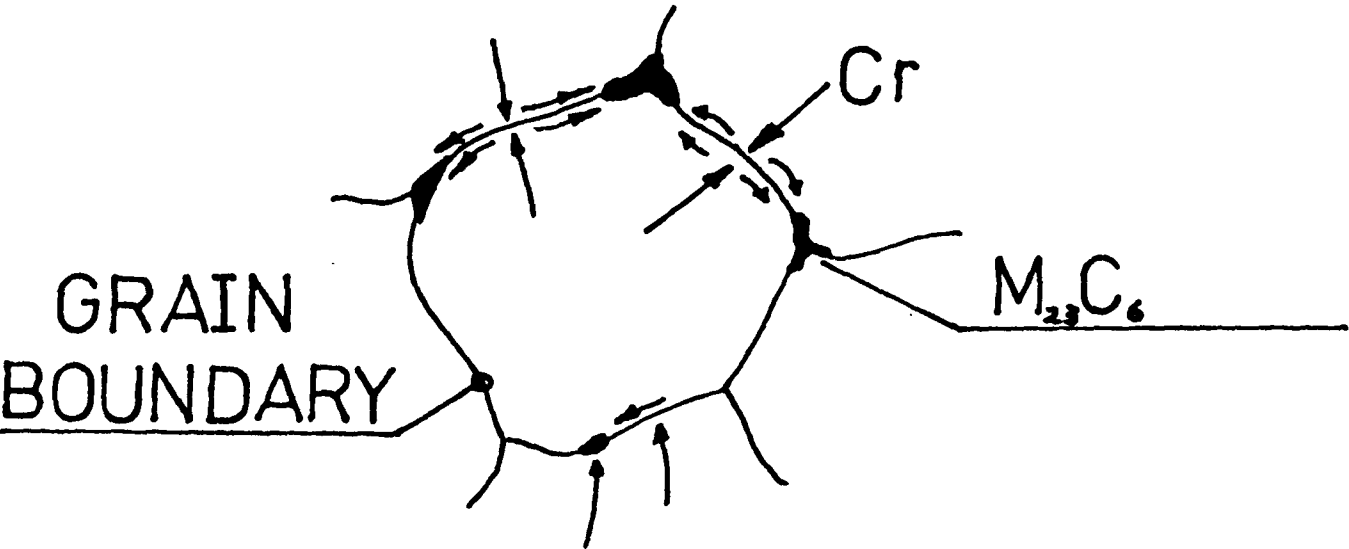
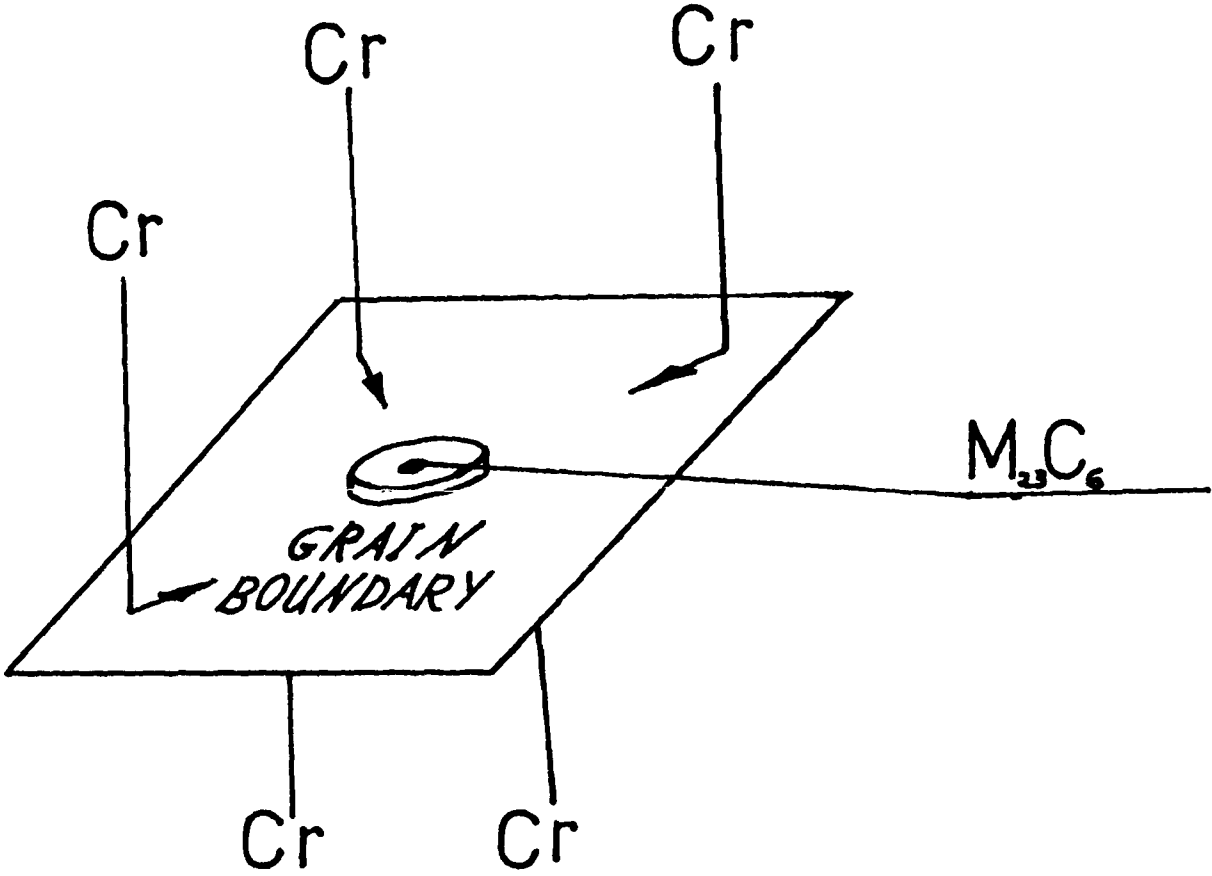
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Schematic showing the process of carbide formation and Cr depletion.



COLLECTOR PLATE MECHANISM.

FIG 1.3

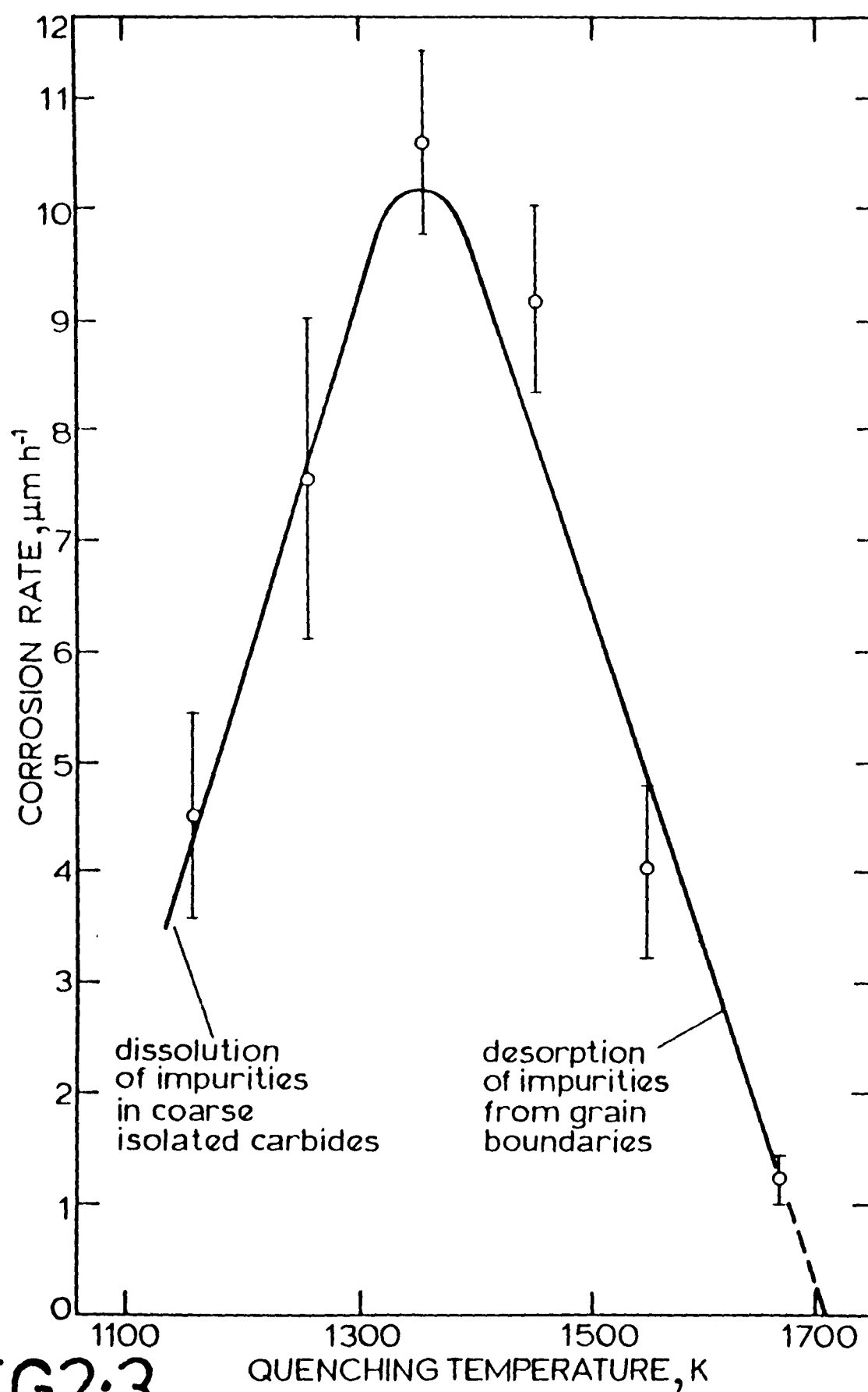


FIG2.3

Effect of heat treatment on intergranular corrosion rate of AISI 304 steel in 5N HNO₃ + 4 gl⁻¹ Cr⁶⁺ solution ref 52

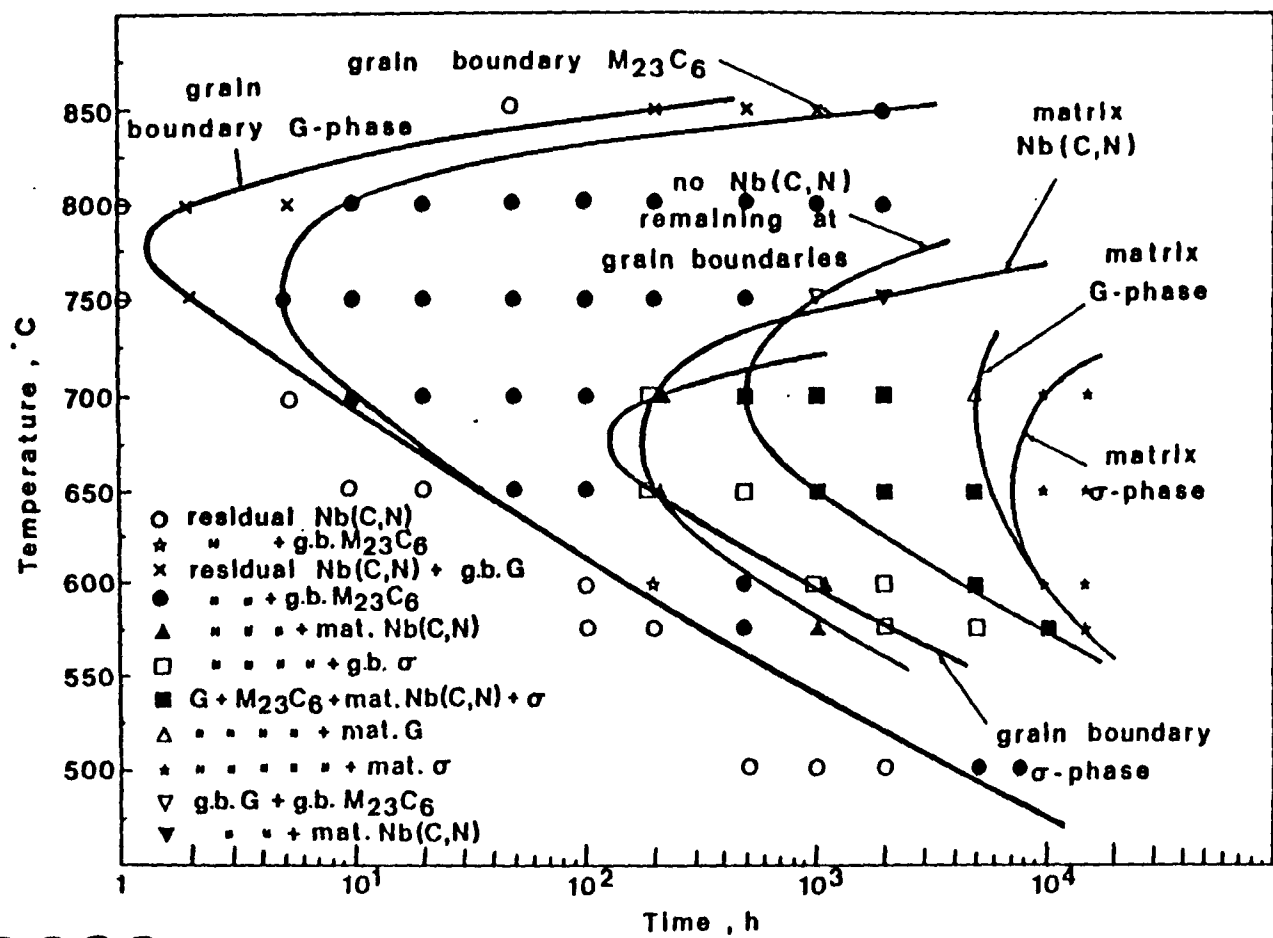
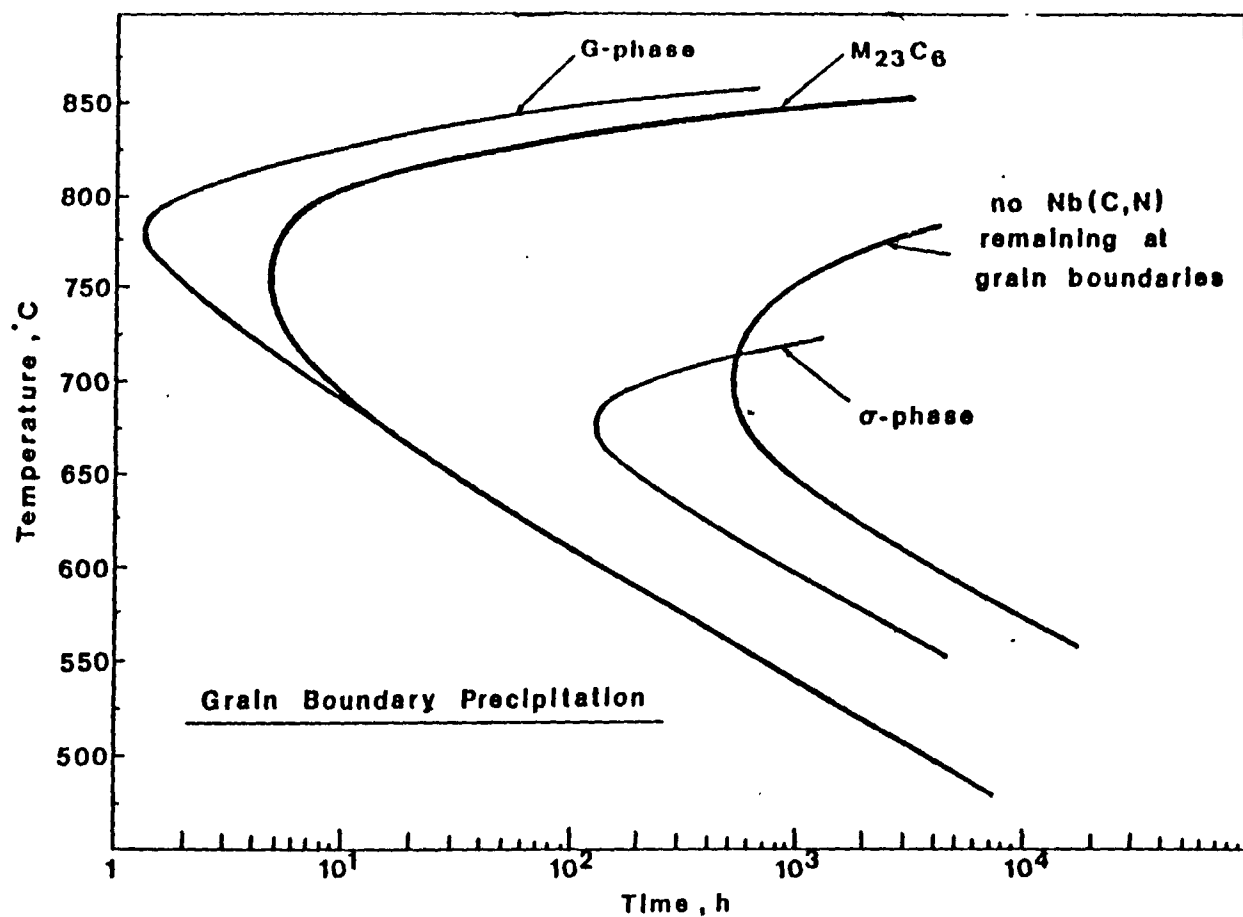


FIG33

A TIME-TEMPERATURE-PRECIPITATION (TTP) CURVES FOR THE PRESENT THERMO-MECHANICALLY TREATED MATERIAL AGED OVER THE TEMPERATURE RANGE 500-850°C.



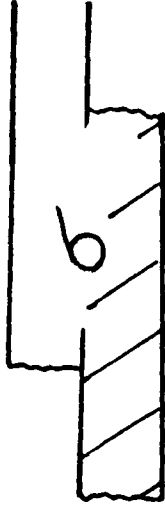
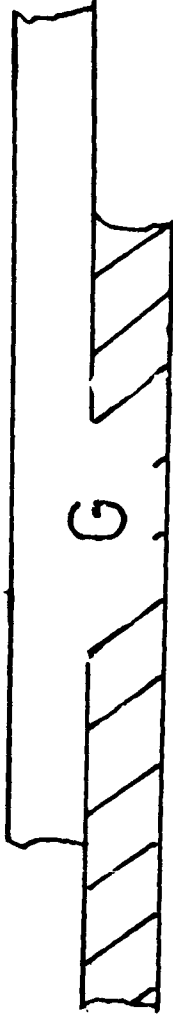
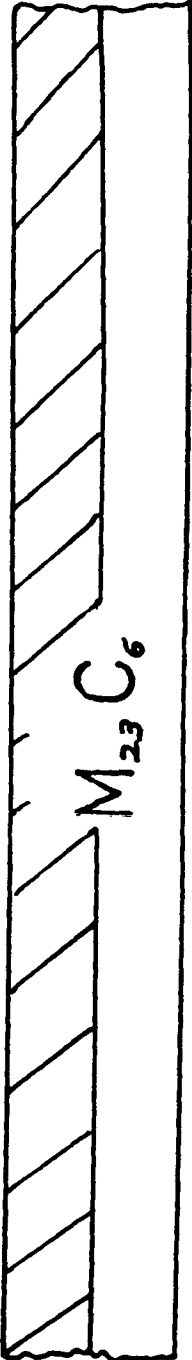
B TIME-TEMPERATURE-PRECIPITATION (TTP) DIAGRAM FOR THE GRAIN BOUNDARY PHASE TRANSFORMATIONS IN THE PRESENT MATERIAL.

Precipitation in 20% Cr, 25% Ni, 0.7% Nb stainless steel
Ref Powell (102) 1984.

FIG 4.3

AS RECEIVED
COLD WORKED

Ni_3Si (irradiation induced)



Nb(CN)

400 500 600 700 800

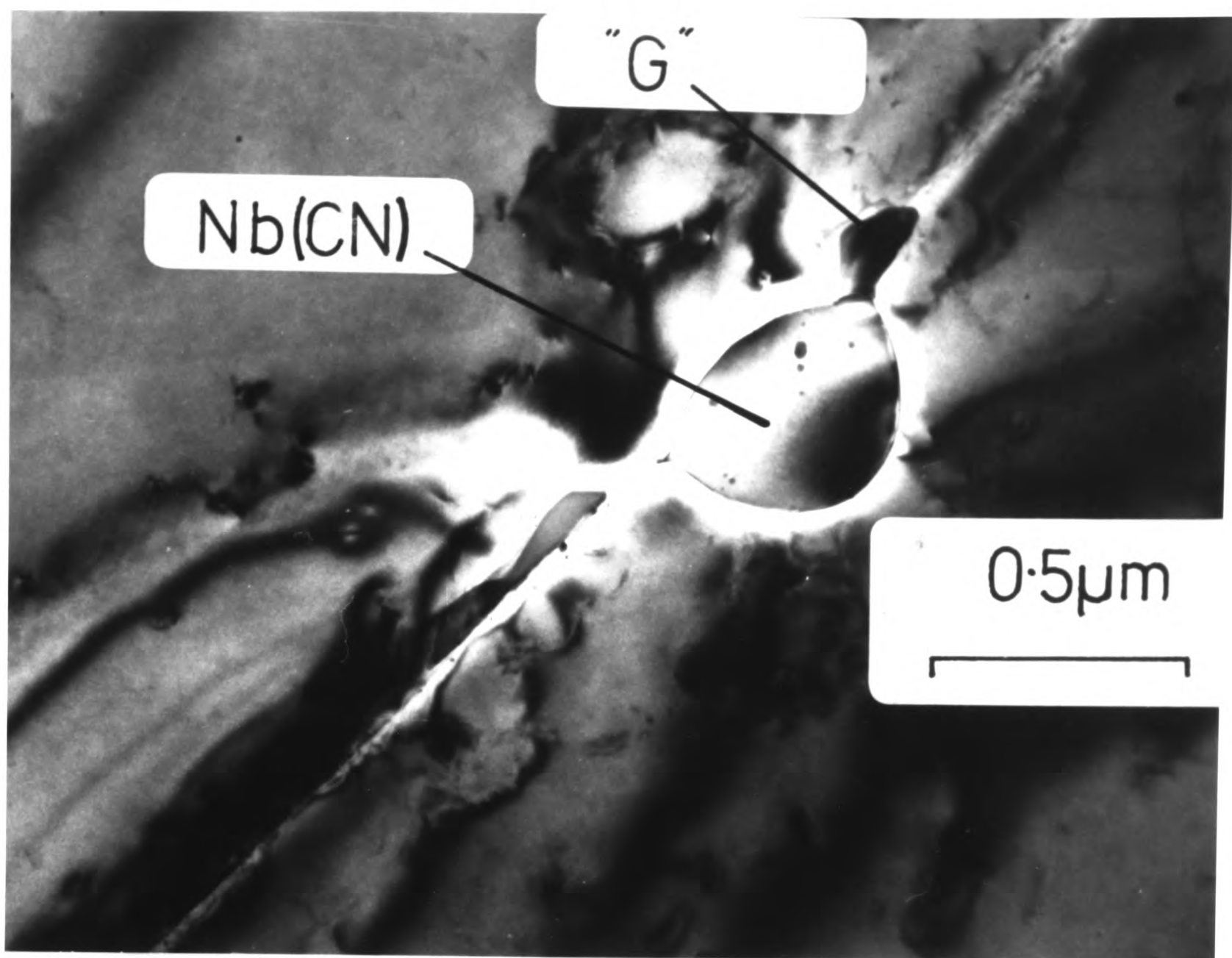
TEMPERATURE $^{\circ}\text{C}$

Temperature ranges for the formation of commonly observed phases
in 20% Cr, 25% Ni, X% Nb.

Figure 5.3

TEM micrographs showing carbide precipitation in material annealed at 1050°C and aged for 500 hours at 550°C

- A. Nb(CN) dissolution together with G phase precipitation
- B. G phase and $M_{23}C_6$ co-precipitation



A
B

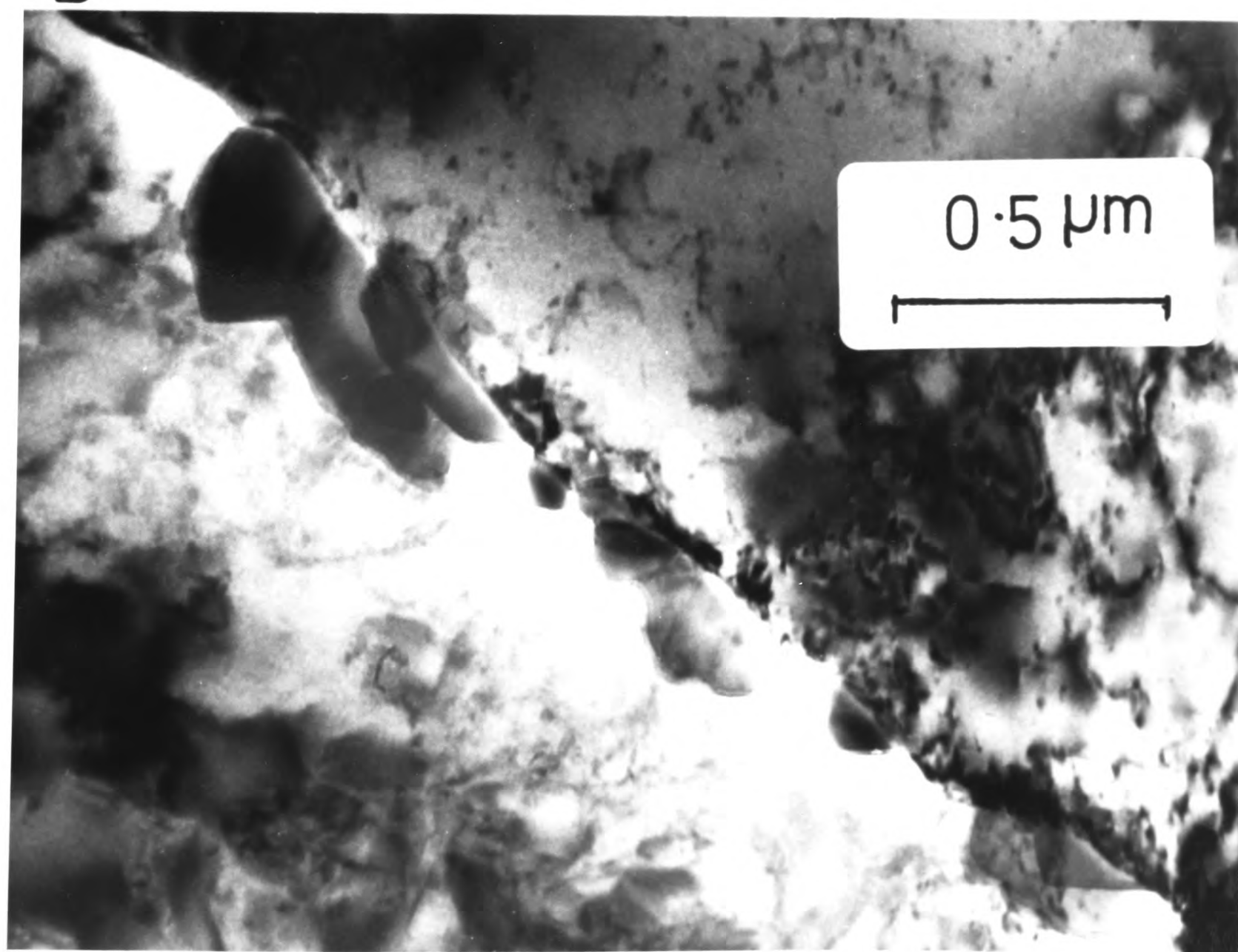


Figure 6.3

TEM micrograph showing $M_{23}C_6$ precipitates on a grain boundary.

Analysis of the diffraction pattern shows that

(111) $M_{23}C_6$ // (111) austenite
[110] $M_{23}C_6$ // [110] austenite



Figure 7.3

TEM micrographs showing carbide precipitation in material annealed at 1050°C 30 minutes and then

- A. aged at 550°C for 780 hours.
M₂₃C₆ precipitates.
- B. aged at 650°C for 130 hours.
M₂₃C₆ and Nb(CN) co-precipitation on grain boundaries
- C. aged at 650°C for 230 hours
M₂₃C₆ precipitation on matrix dislocations

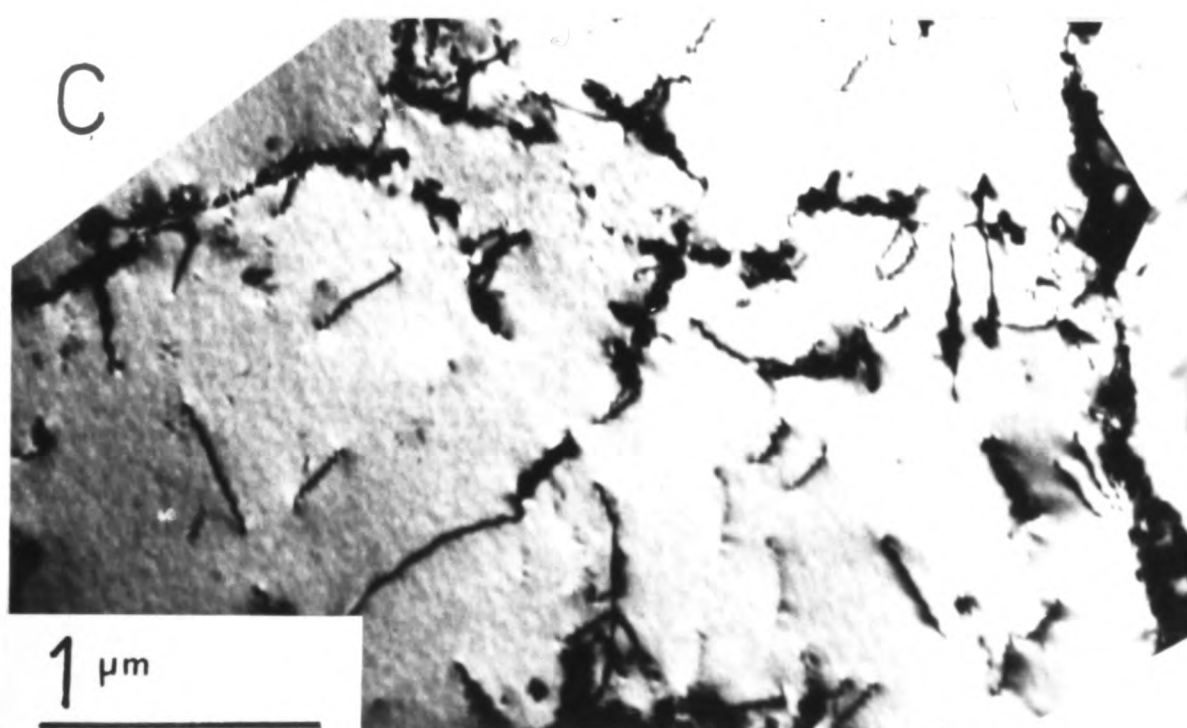
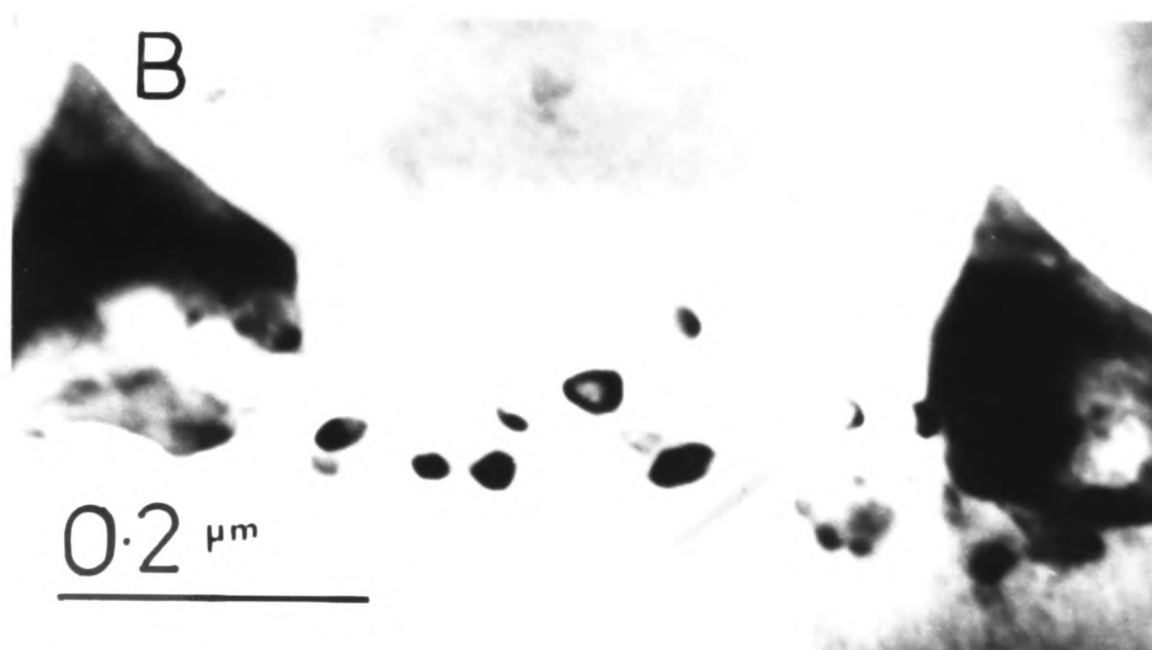
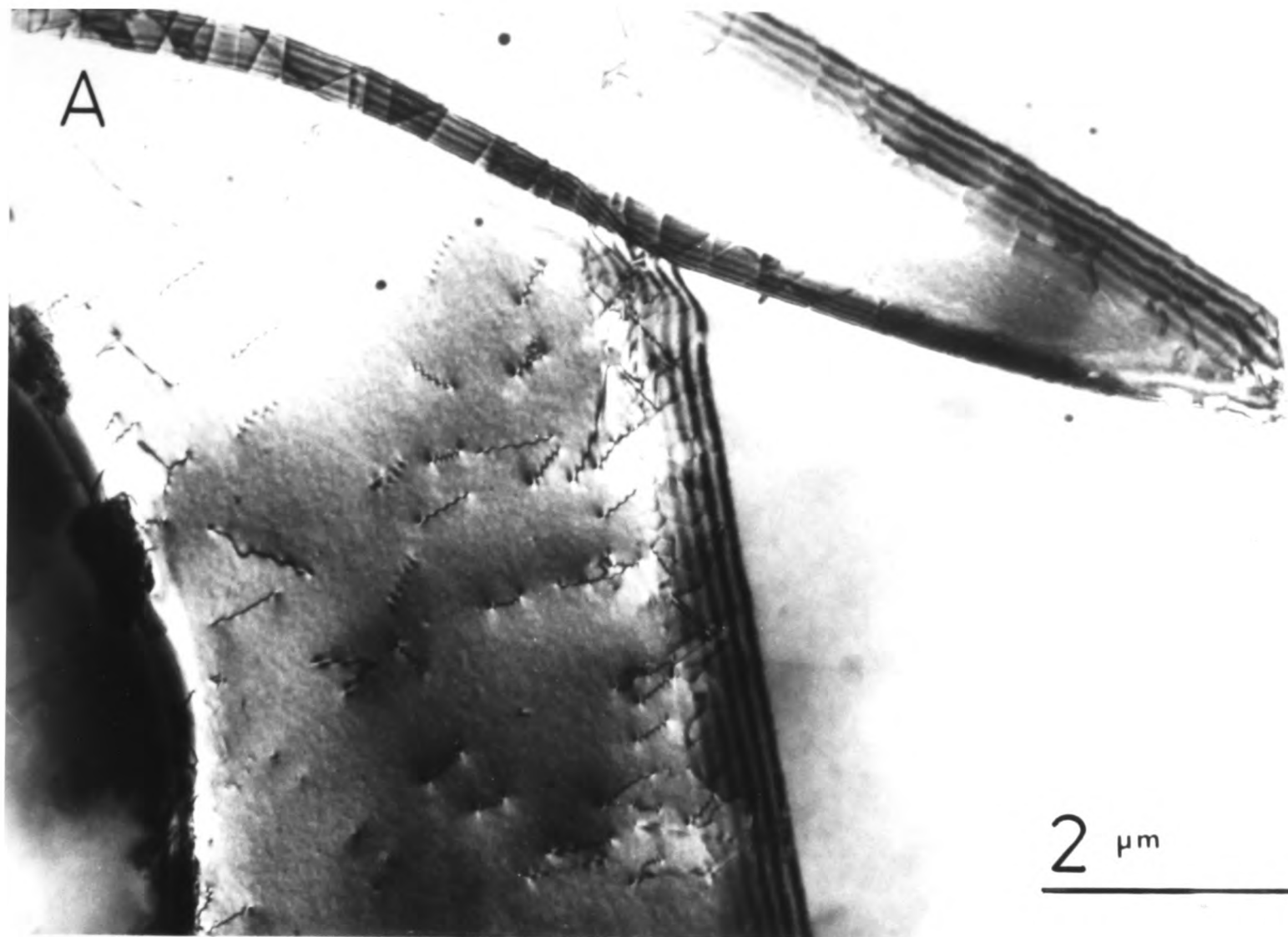


Figure 8.3

TEM micrographs showing grain boundary precipitation in material

A and B. annealed at 1150°C for 30 minutes and aged at 750°C for 130 hours

A. $M_{23}C_6$ precipitation

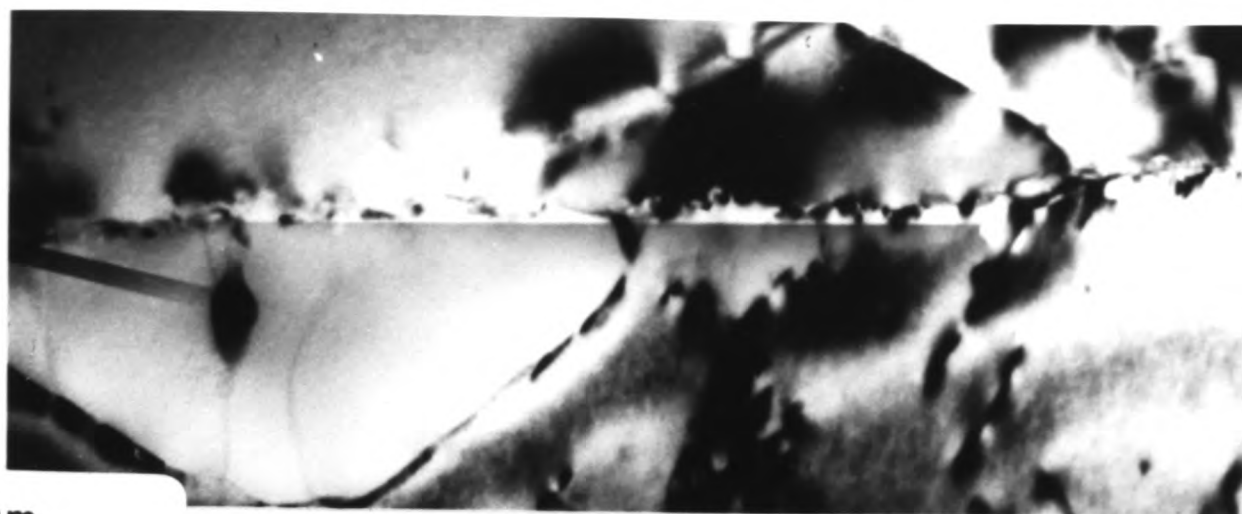
B. $M_{23}C_6$ precipitation

C and D. annealed at 1050°C for 650°C for 48 hours.

Large $M_{23}C_6$ precipitates with Nb(CN) precipitates on precipitate/boundary interface dislocations

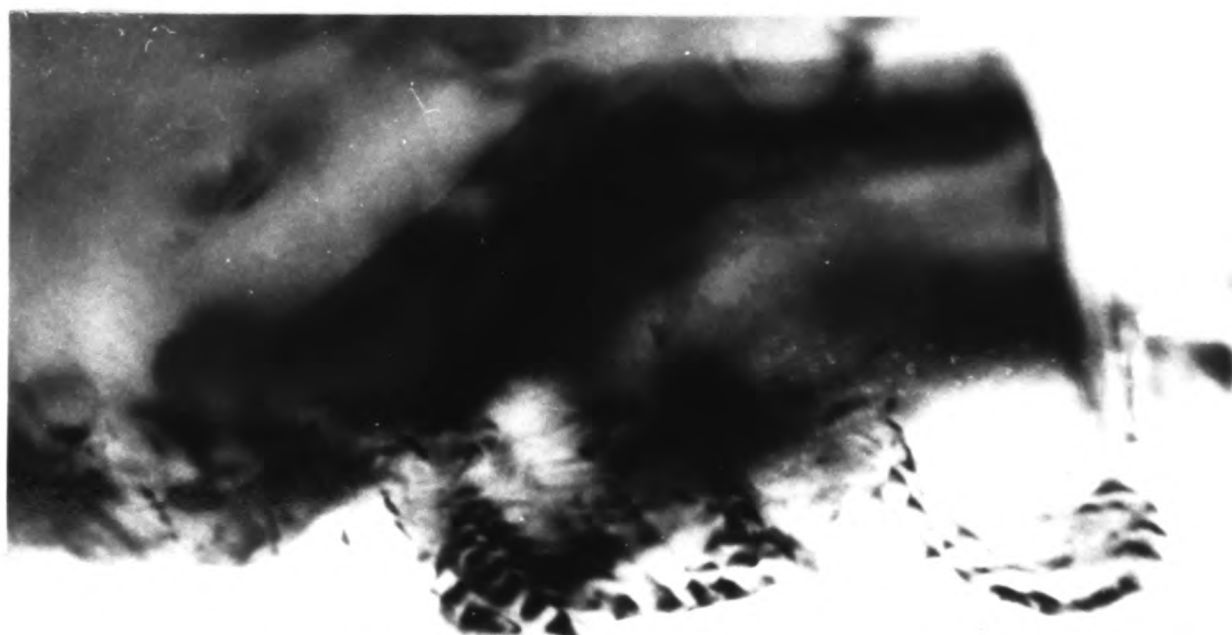
A 0.2 μm

B 0.2 μm



C 0.1 μm

D 0.2 μm



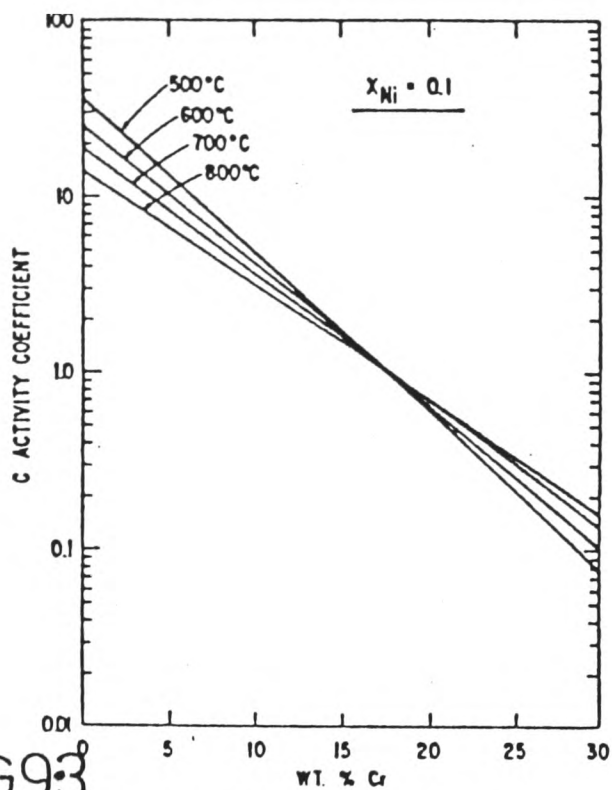


FIG9.3 Carbon activity coefficient vs. chromium content for an austenitic alloy containing 10% Ni, for various temperatures.

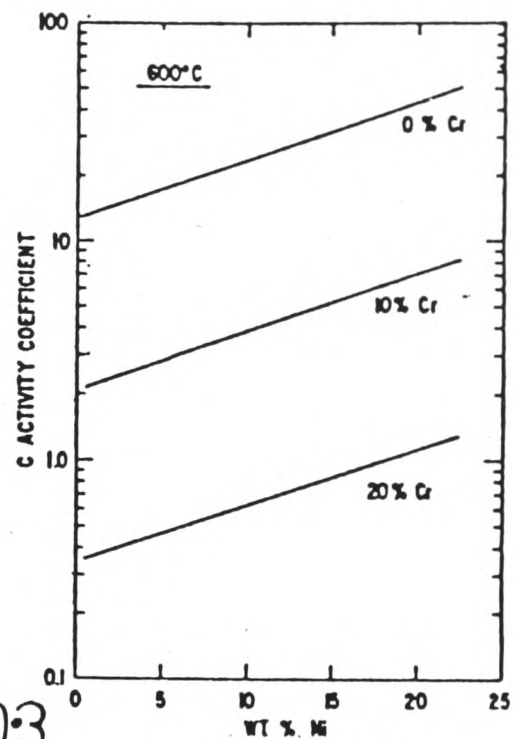


FIG10.3 Carbon activity coefficient in austenitic steel vs. nickel content at 600°C for various chromium levels.

after ref 130

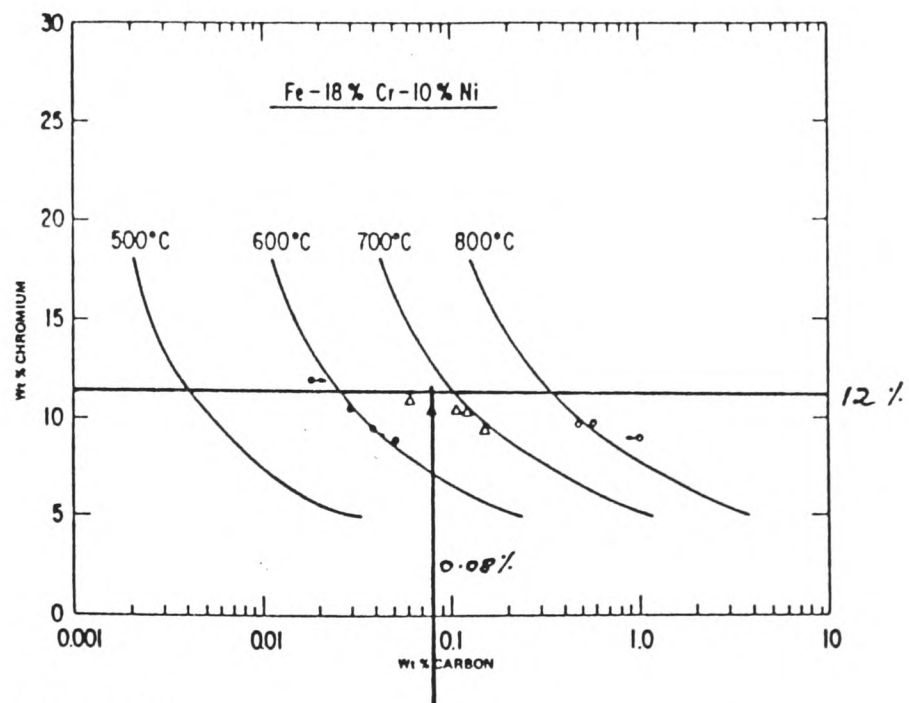


FIG11.3 Comparison of grain boundary Cr-C-Cr₂₃C₆ equilibrium data for Type 304 stainless steel with experimentally obtained corrosion data.

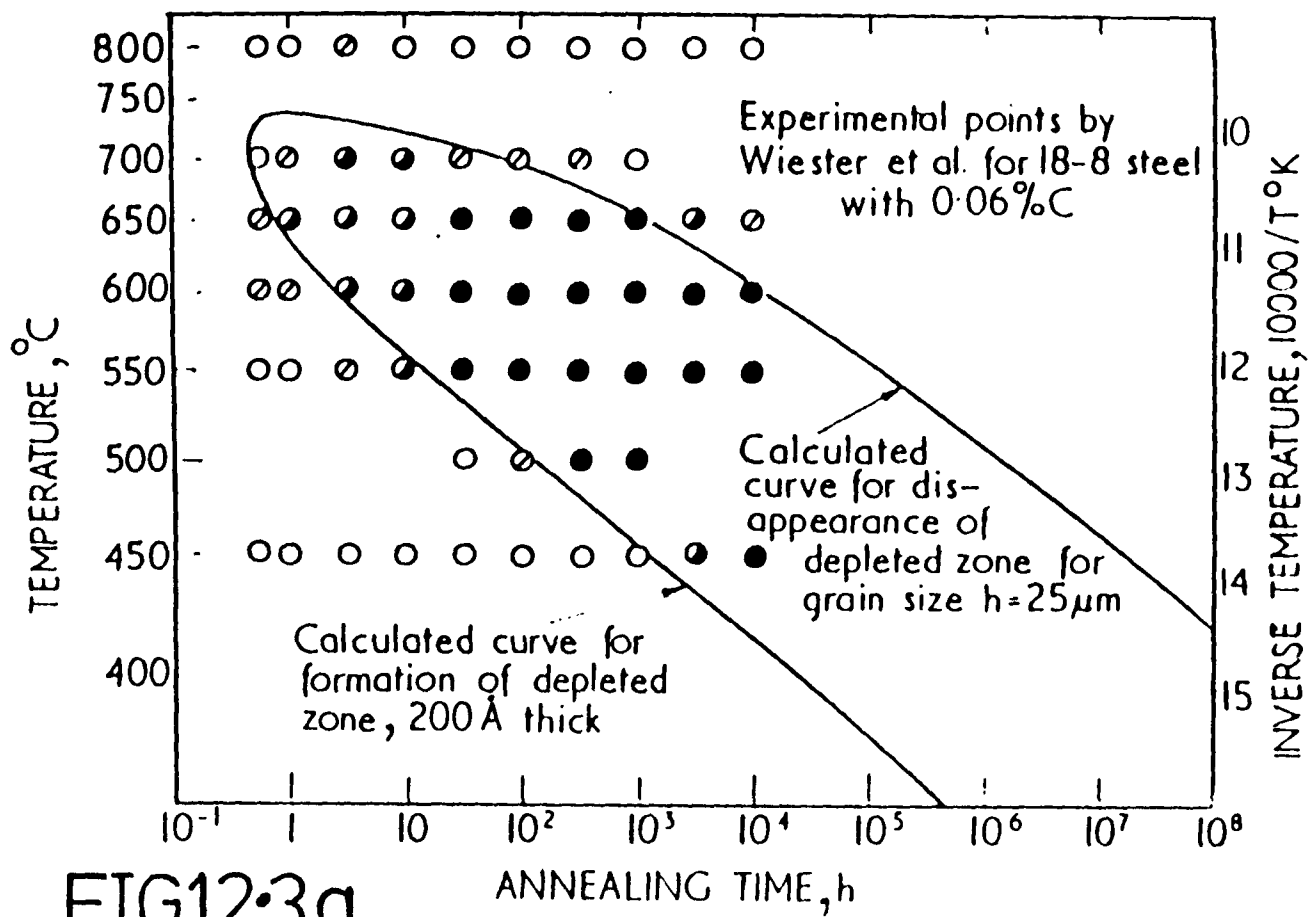
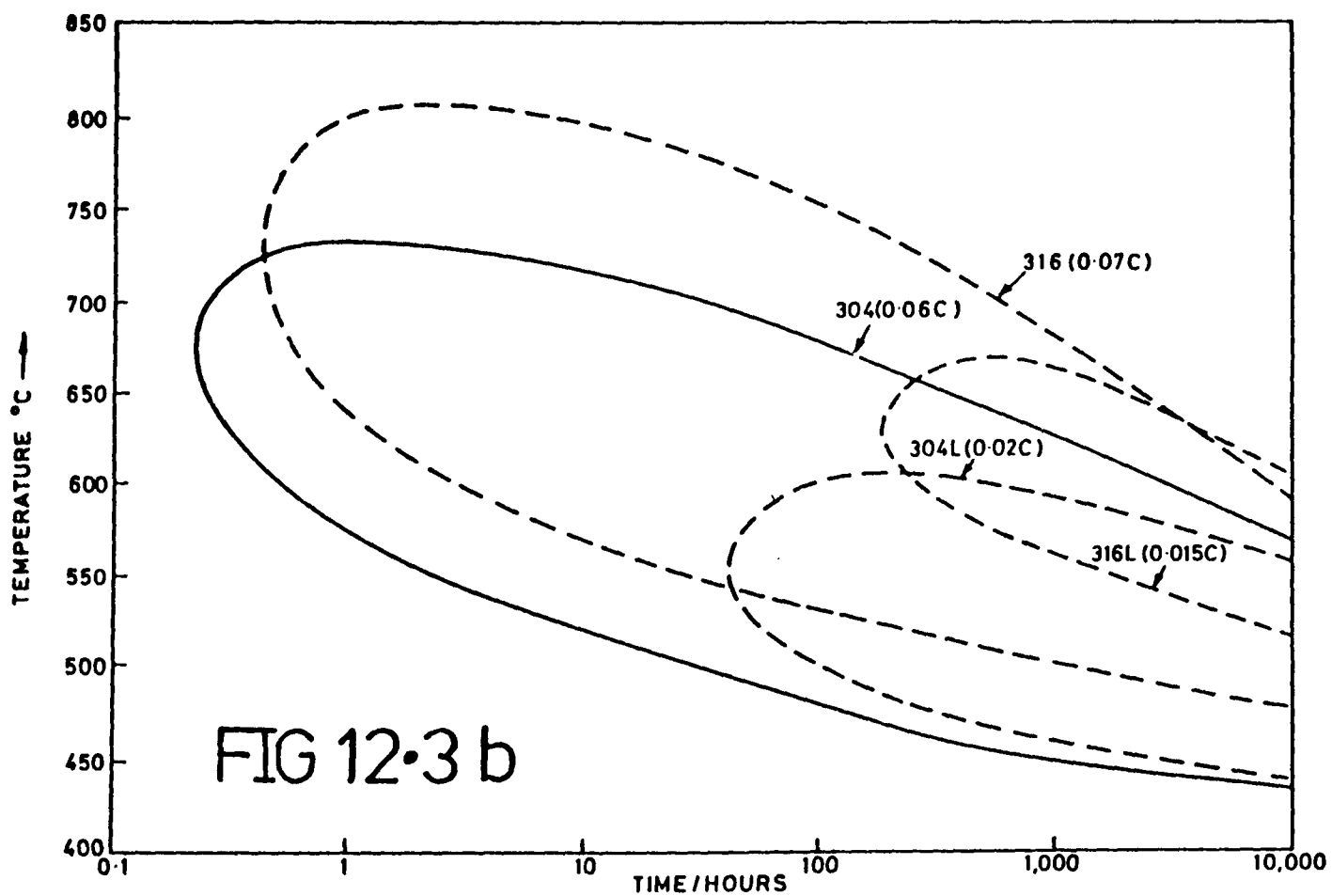


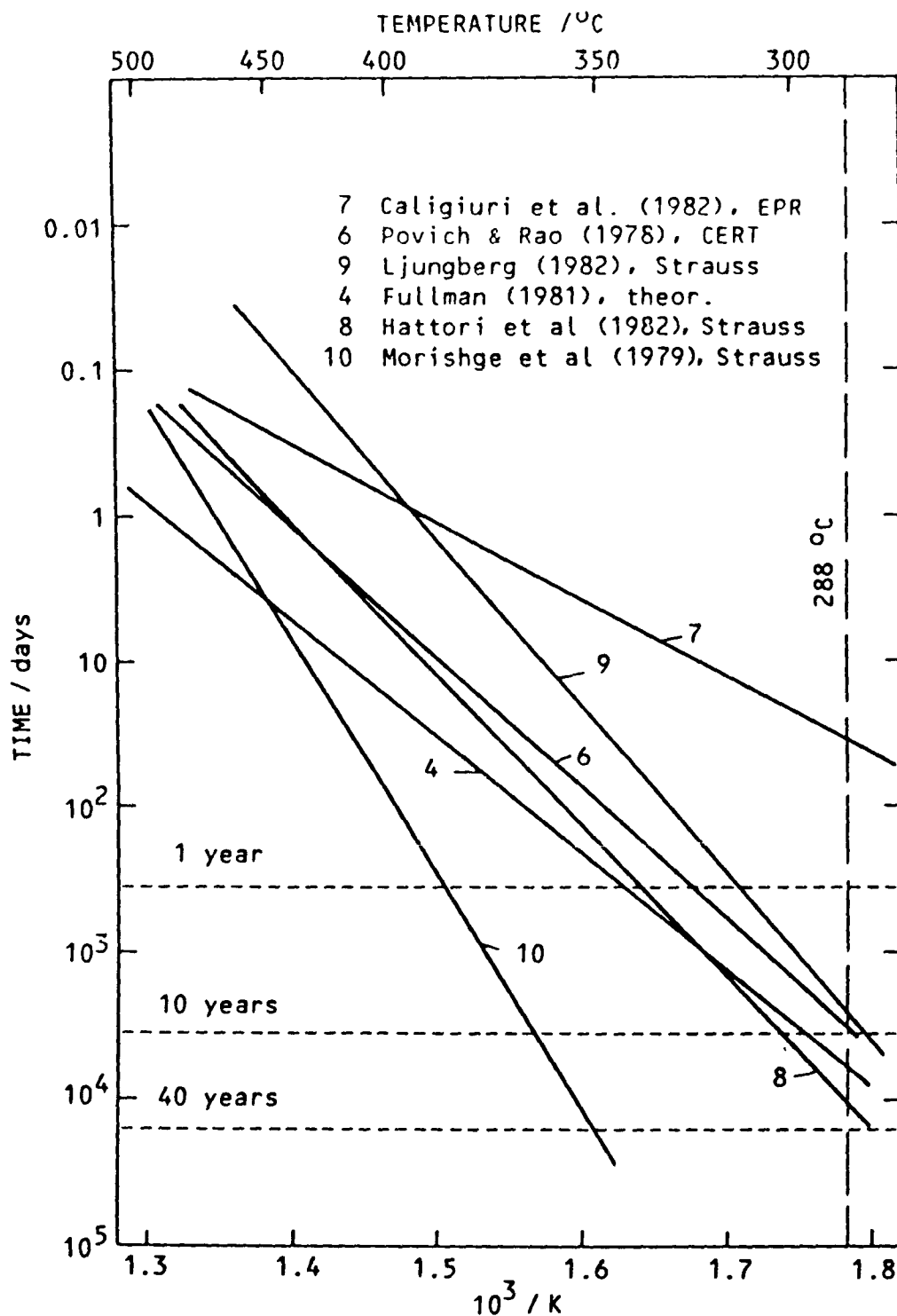
FIG12.3a

Comparison of corrosion tests with existence of depleted zone ref129



ref 147

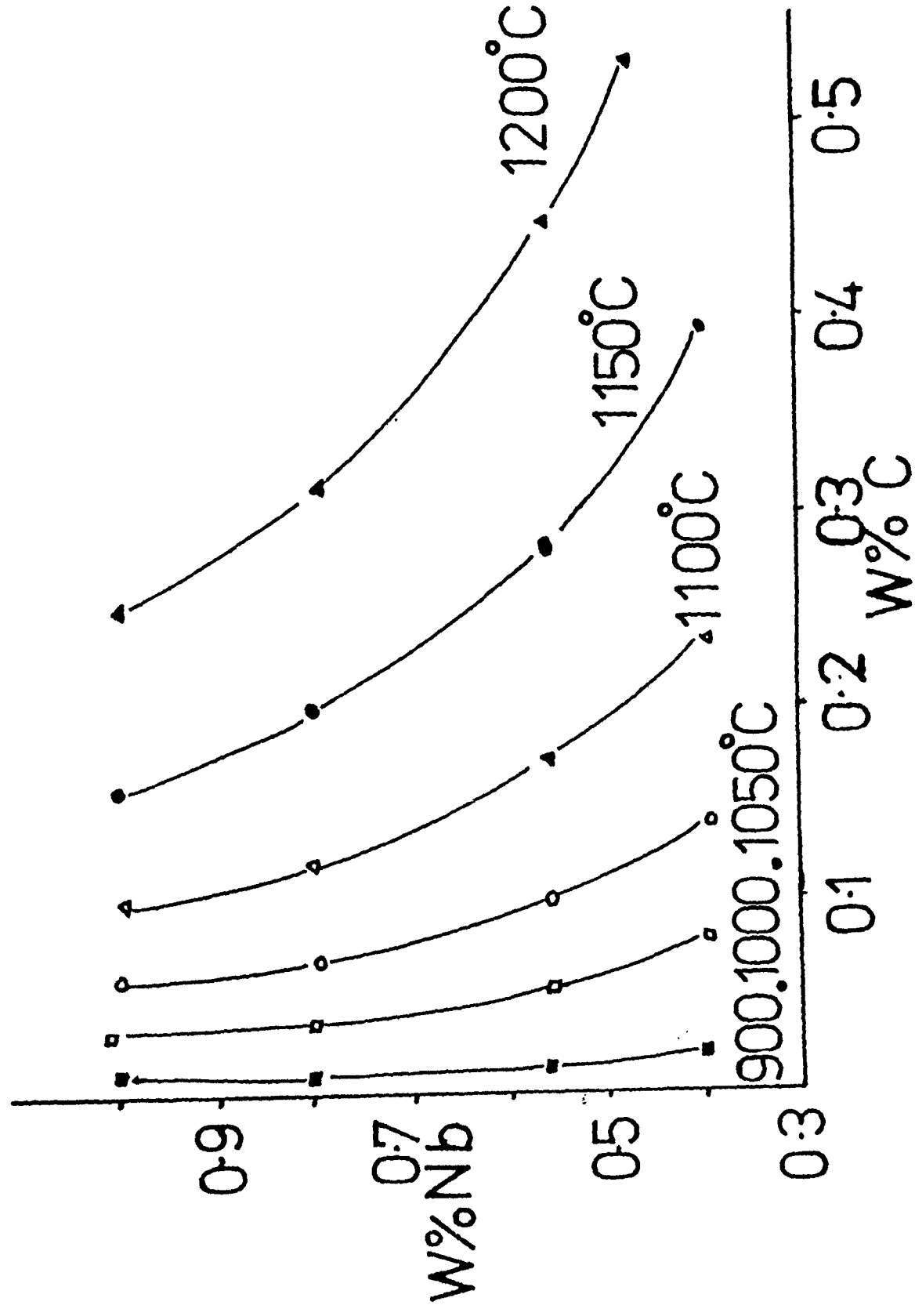
Comparision of predicted (a) and experimentally (b) observed regimes of sensitisation.



Several (T, t) dependences for low temperature sensitization of AISI 304 Type stainless steels.⁴⁻¹⁰⁾

4. R. FULLMAN, *Basic Studies of the Variables of Fabrication Related Sensitization Phenomena in Stainless Steels*. NP-1823, EPRI, Palo Alto, California, May (1981).
5. M. J. POVICH, *Corrosion* **34**, 60 (1978).
6. M. J. POVICH and P. RAO, *Corrosion* **34**, 269 (1978).
7. R. D. CALIGIURI, L. E. EISELSTEIN, C. G. SCHMIDT and S. S. WING, *Low-Temperature Sensitization of Type-304 Stainless Steel Weld-Heat-Affected Zone*. NP-3368, EPRI, Palo Alto, California, November (1983).
8. S. HATTORI, T. YOKOSUKA, Y. MORI and I. MASAOKA, *Low Temperature Sensitization in Austenitic Stainless Steel Pipe Welds*. EPRI International Workshop on Low Temperature Sensitization. Palo Alto, California (1982).
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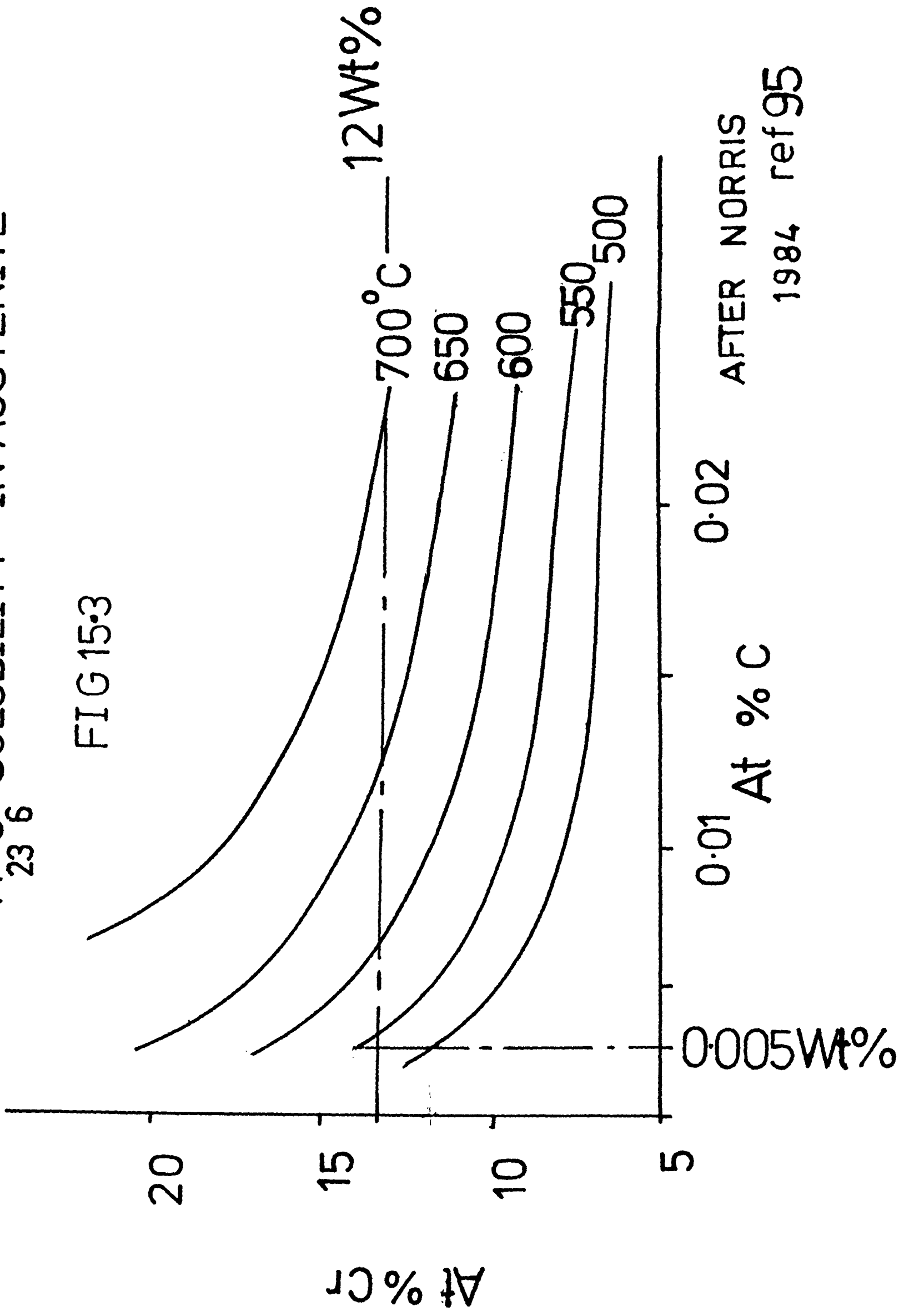
Ref Hanninen (135).



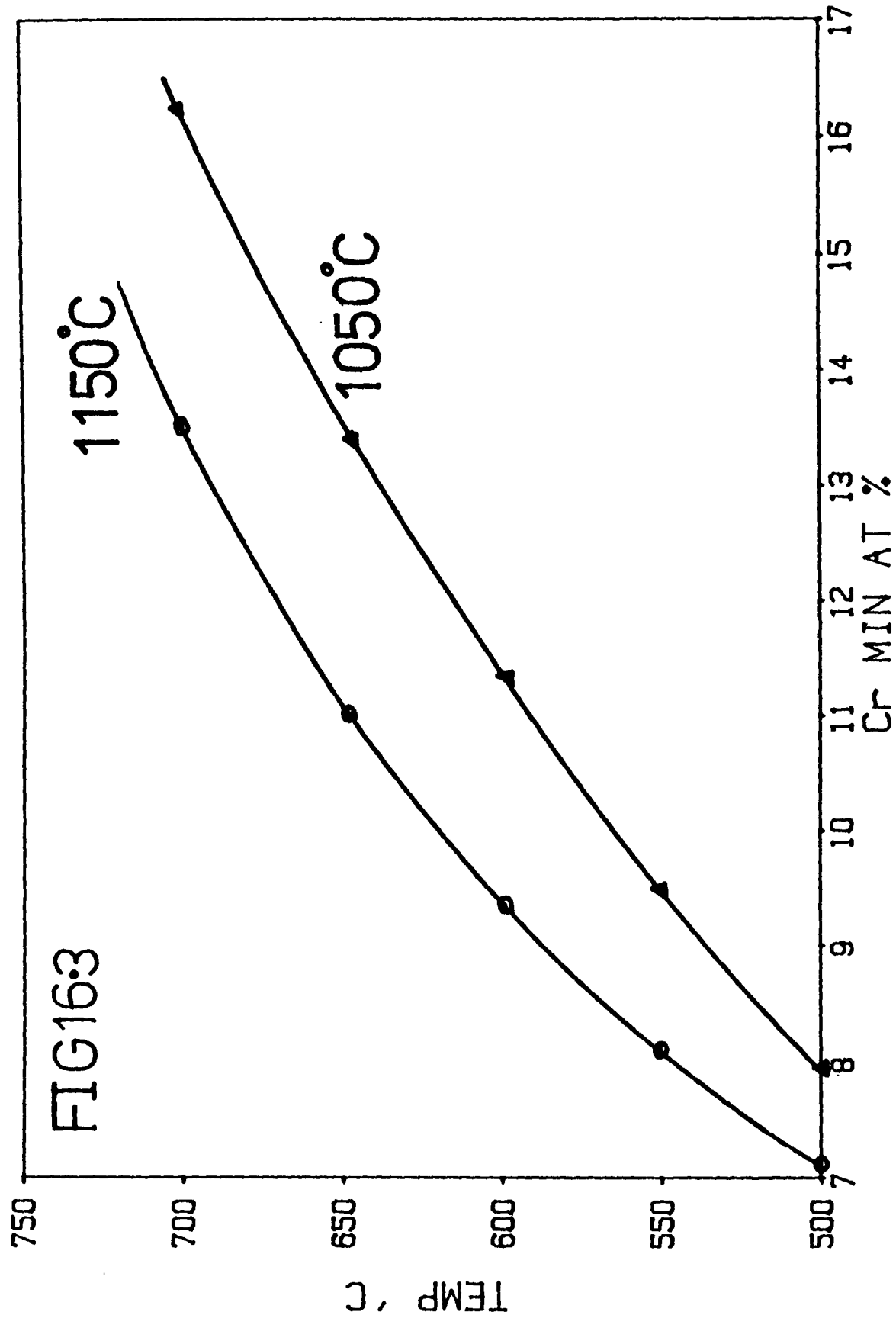
NbC SOLUBILITY IN AUSTENITE ref 154
FIG 14.3

M₂₃C₆ SOLUBILITY IN AUSTENITE

FIG 15.3



AFTER NORRIS
1984 ref 95



Minimum Cr concentration predicted at carbide / grain boundary interface.

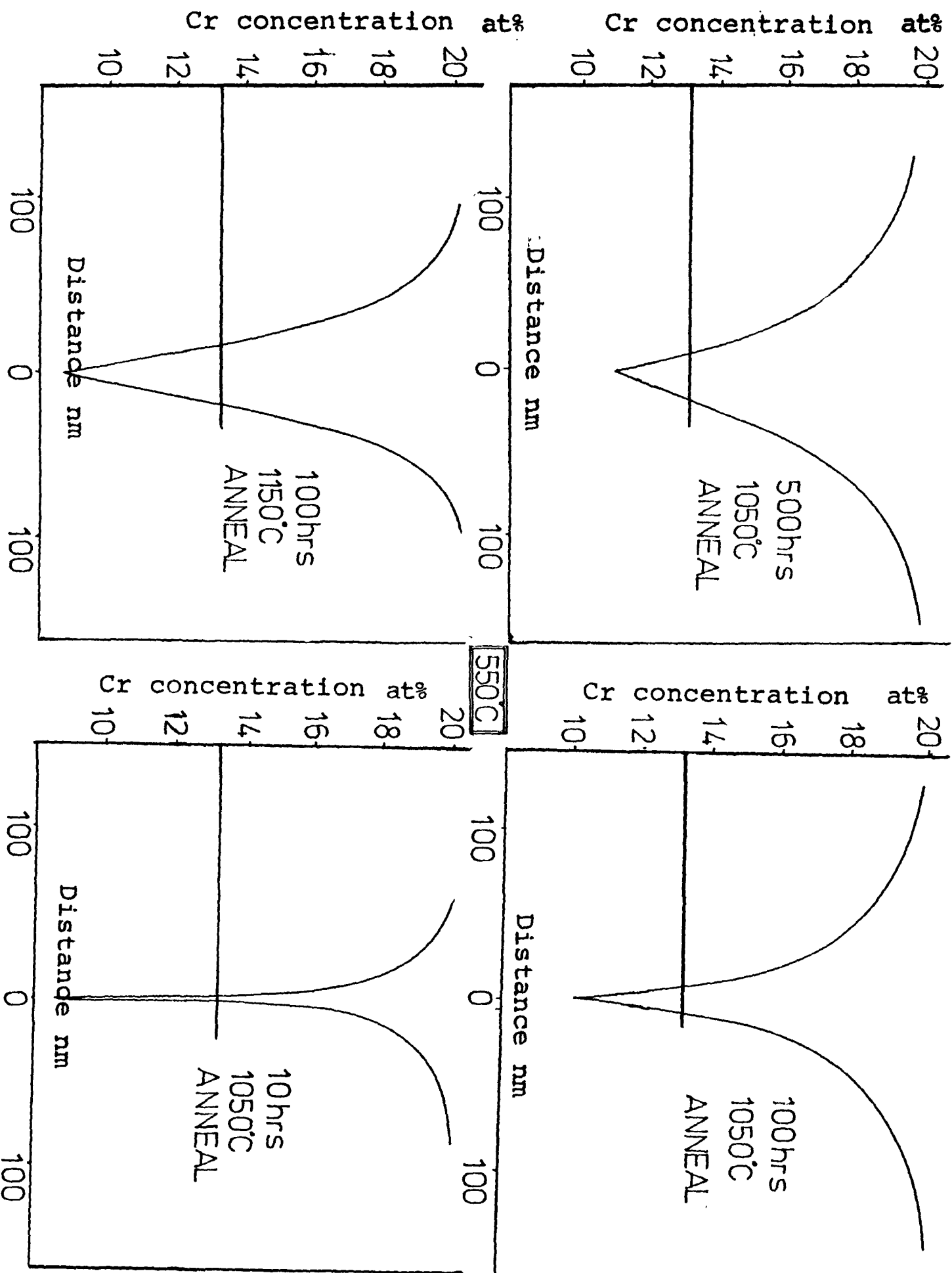
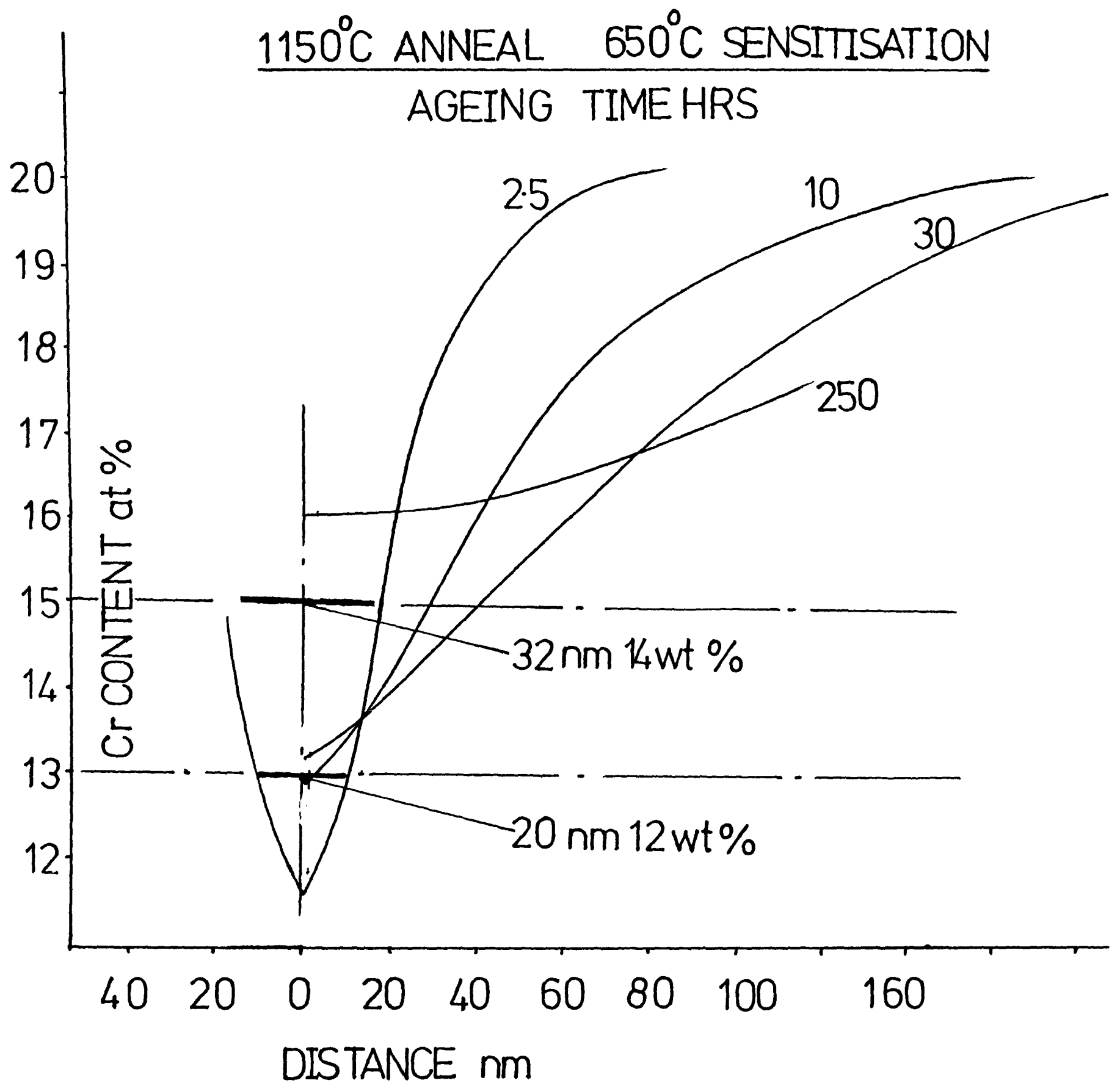


FIG 17.3

Prediction of Cr depletion profiles using the SAROC (95) model.



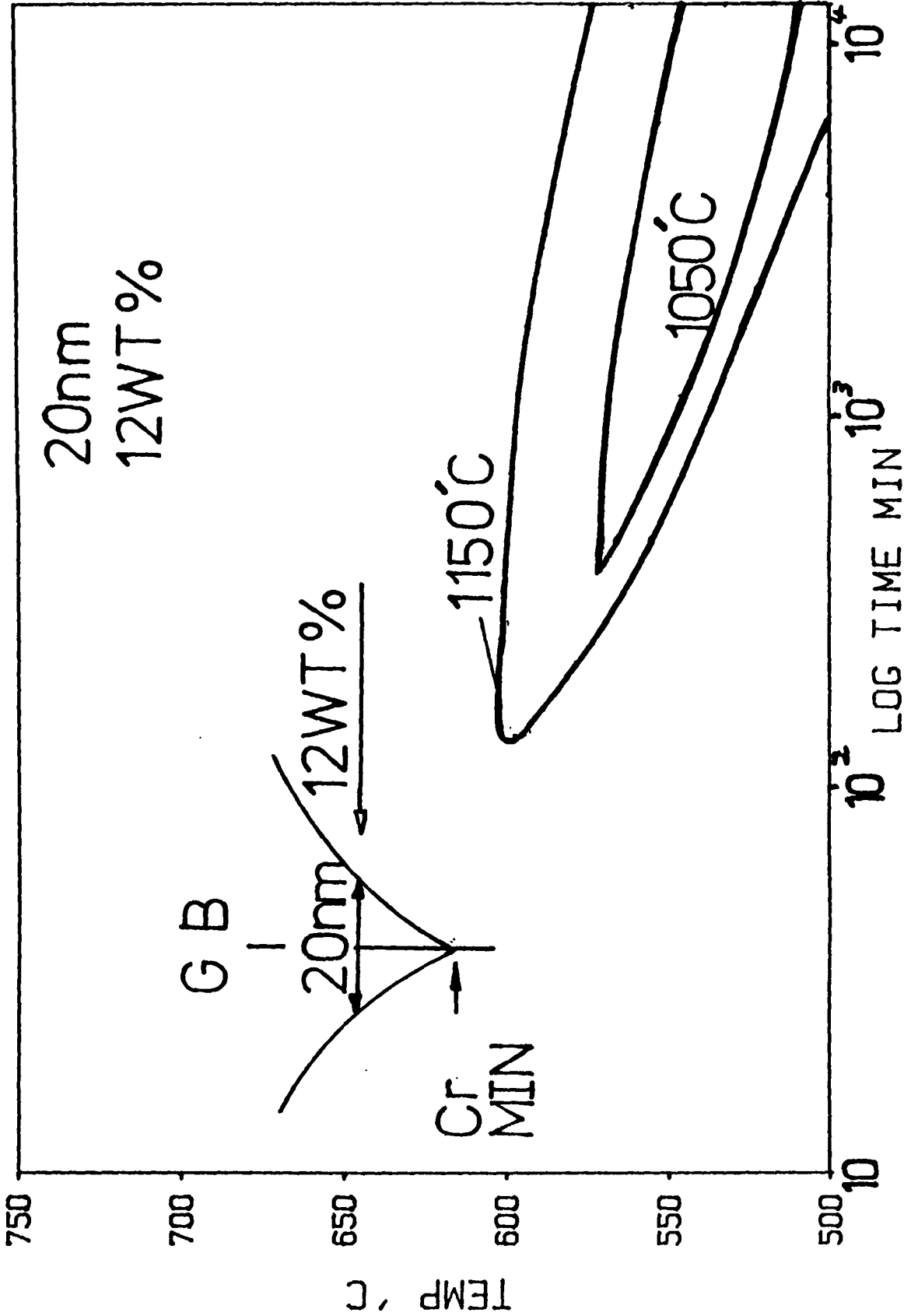
SAROC predicted Cr compositional profiles for different ageing times at 650°C, shown with two different criteria for sensitisation.

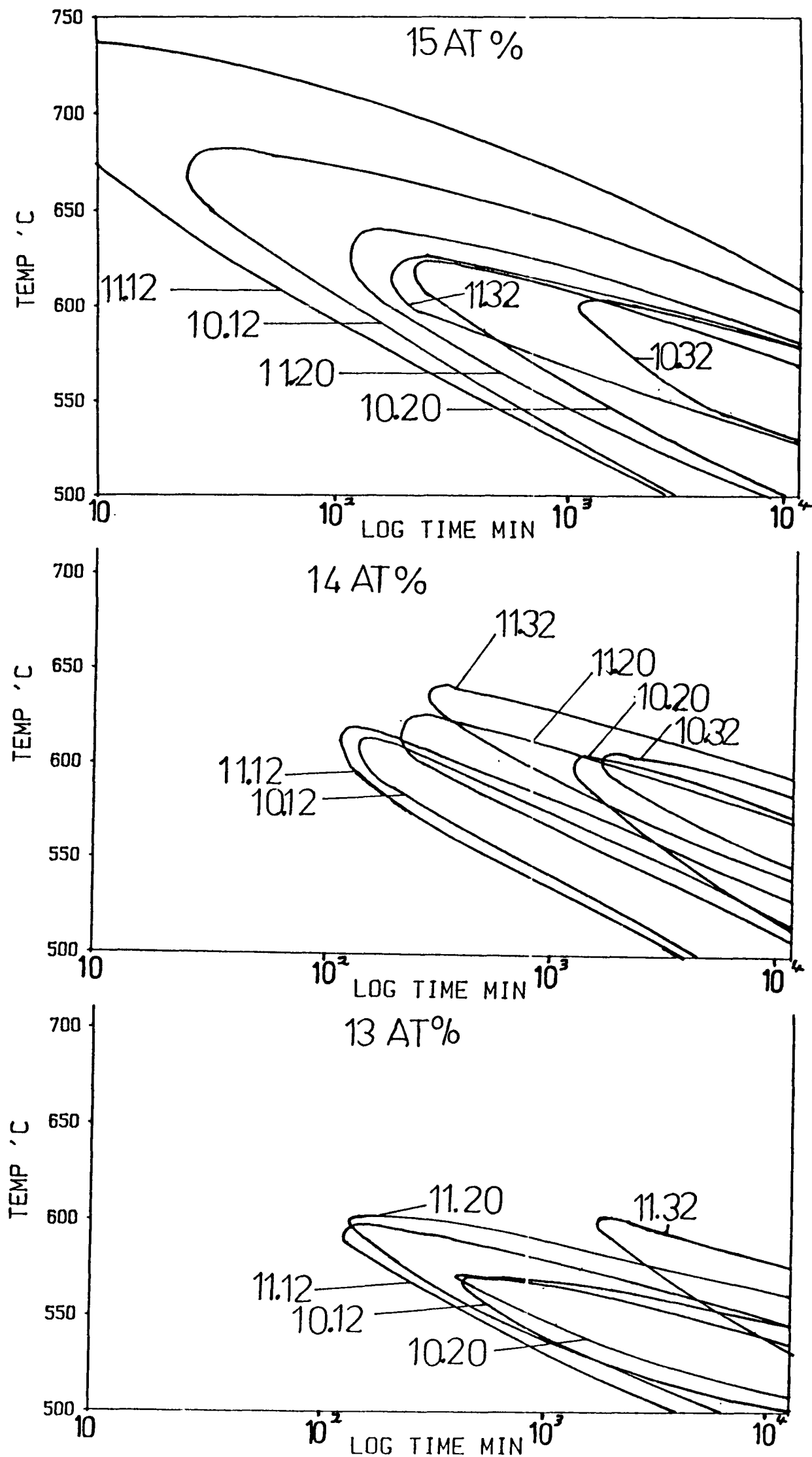
FIG 18.3

Prediction of sensitisation regimes by use of the SAROC model.

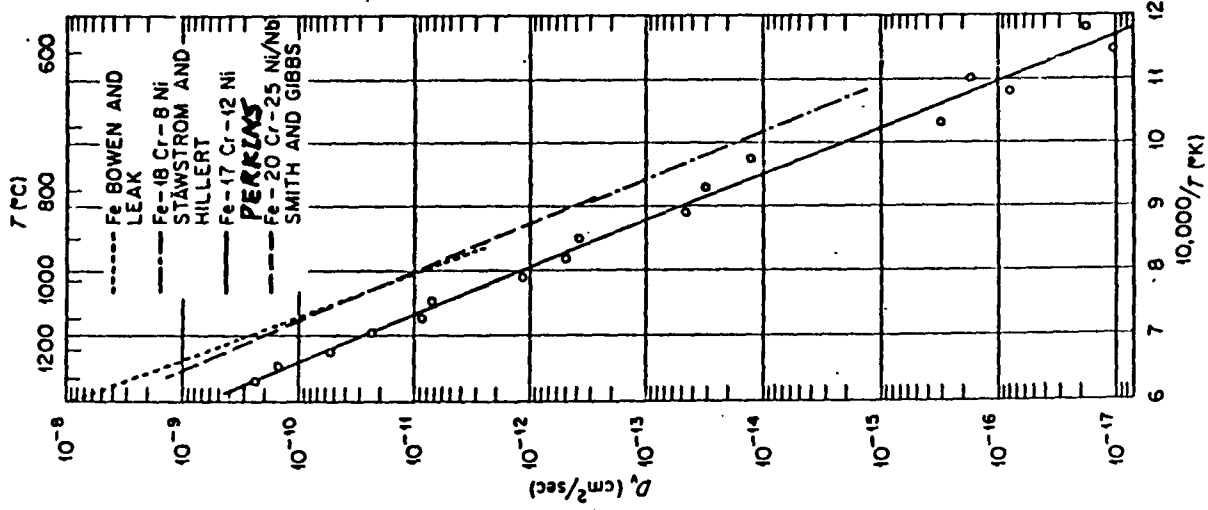
FIG19.3 ref 95

SENSITISATION 20/25 0.7%Nb



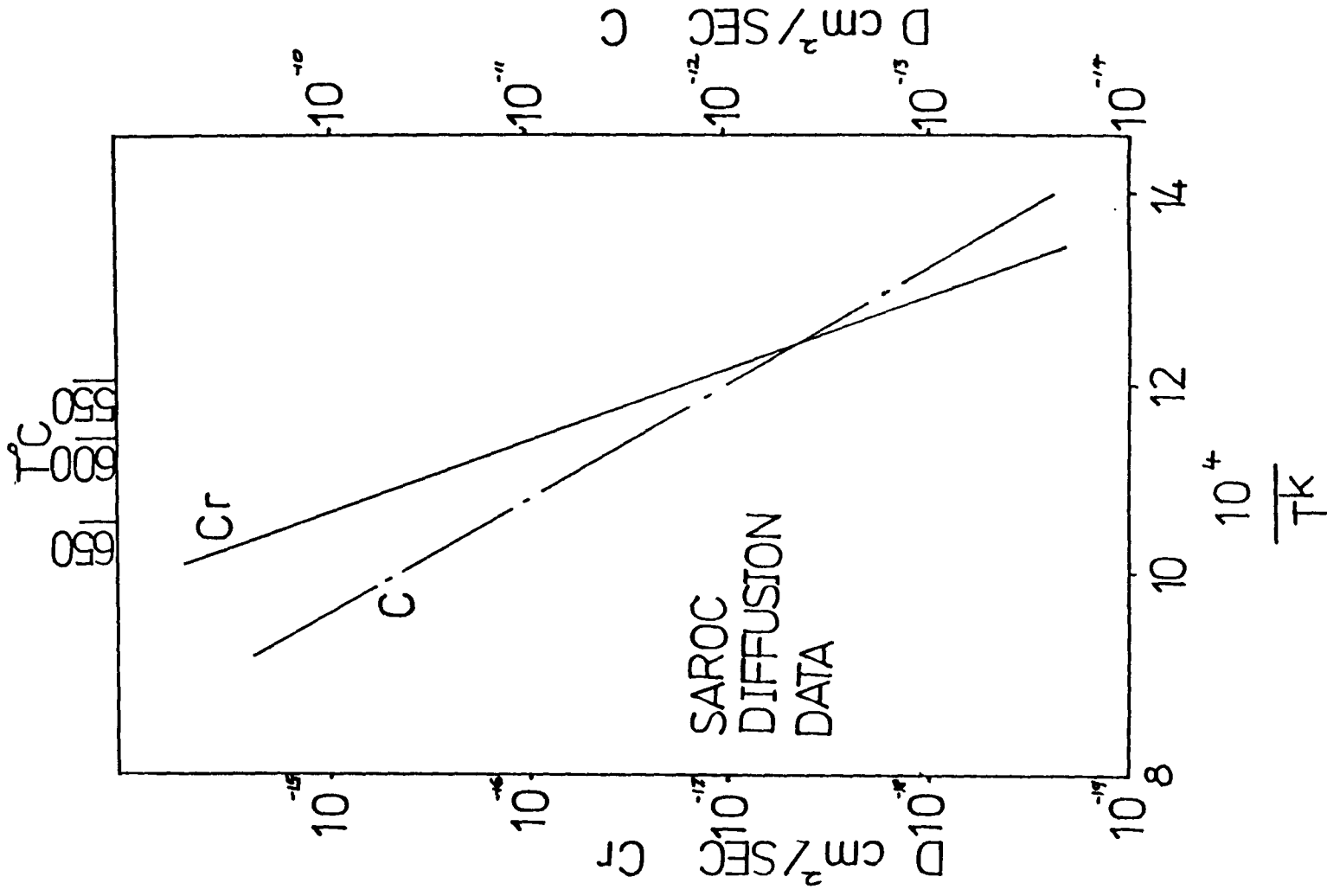


Prediction of sensitisation conditions using the SAROC model (95).
 11.12 indicates an 1150°C anneal, and a criteria of sensitisation of X at% (top of each figure) at a Cr depletion width of 12 nm.



Volume diffusion of ^{51}Cr .

FIG21•3



Comparison of diffusion data reported within the literature with that used for modelling sensitisation using SAROC.

CHAPTER 4

CHEMICAL AND ELECTROCHEMICAL TESTS

4.0 A Review of electrochemical tests

Intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC) are problems of utmost importance in the process and nuclear industries; the search for standardised tests to detect susceptibility to IGA continues. Since the early 1960's, many papers have been dedicated to work on possible mechanisms of IGA and on measurement of susceptibility to both IGA and IGSCC.

In commercial practice IGA of stainless steels has been observed in a number of common acids; these failures are either associated with incorrectly heat treated materials or bad welding practice. However, by far the major proportion of stainless steels manufactured are used under conditions which are not sufficiently aggressive to cause IGA. Because of the complexity of IGA a number of parameters are believed to play synergistic roles in causing attack eg. composition, applied and residual stress, thermal history, chemistry of environment, and inhomogeneities within the material [1]. Chapter 3 describes how both segregation of alloying elements and rogue impurities change the local electrochemistry of boundaries and lead to IGA. Chemical and electrochemical tests were developed in order to determine whether a material is susceptible to IGA before use in service. Screening tests are required to evaluate the condition of the material before use in plant and to compare different heats of material. Tests under the operating conditions of the plant are the most relevant, though accelerated "sorting" tests are also required.

The purpose of this chapter is to:

1. Describe the tests used to quantitatively evaluate the effects of heat treatment variables on the degree of sensitisation (DOS).
2. Report the results of such tests carried out on 20% Cr, 25% Ni, 0.7% Nb bar, reworked bar and tube material after a variety of heat treatments.
3. Attempt to relate test response to information gained from modelling Cr depletion profiles.

4.1 Test Procedures

Several reviews exist describing both tests for susceptibility and in-service observations of IGA in austenitic stainless steels [2 to 6].

Those tests regarded as reliable procedures by the ASTM are

incorporated into ASTM A 262 (1970), ASTM G28-72 (1972) and ASTM A 269-79 (1979). The solutions used in ASTM A 262 "Recommended Practice for Detecting Susceptibility to IGA" are summarised in table 1.

Table 1. ASTM A 262 test solutions for estimation of degree of sensitisation

- A. 10% Oxalic acid (electrolytic etching).
- B. Boiling 50% H_2SO_4 + 25 g/l $\text{Fe}_2(\text{SO}_4)_3$ (Streicher test)
- C. Boiling 65% HNO_3 (Huey test)
- D. 10% HNO_3 + 3% HF 70°C
- E. Boiling 16% H_2SO_4 + 5.87% CuSO_4 (Strauss test)

A comparison of ASTM tests is give by Streicher [7] and Brown [7a]. Streicher lists a set of suggestions for modifying ASTM 262 A tests to examine sensitisation in a more reproducible way.

Specimens are held in an aggressive environment at potentials such that the matrix remains passive whilst grain boundaries (of different composition to the bulk) are active. The redox potentials for the solutions listed in table 1 are shown schematically in Fig. 1. The different polarisation characteristics of the grain boundary region and matrix determines the rate and nature of attack. It must be noted that the potential at which specimens are attacked in these tests is different from test to test, and therefore the subsequent nature of attack differs. Tests carried out at a suitable potential will result in attack of the sensitised region. The value of the redox potential during the test is important as it controls the rate of IGA. A polarisation curve of a matrix of composition 18Cr,10Ni,balFe and a simulated Cr depleted zone of composition 10Cr,10Ni,balFe is indicated in Fig. 1. The lower Cr alloy is attacked over a wider potential range and much more rapidly under active corrosion conditions and therefore during testing the areas with higher Cr content will remain passive, whilst the Cr-depleted areas are active. Osazawa et al [8] conducted anodic polarisation measurements in deaerated H_2SO_4 . Alloys with lower Cr concentrations were found to show larger active peak current densities, shown in Fig. 2. These tests give rapid IGA and do not generate information on rates of attack in milder environments.

Details of the test procedures used during this study are now given.

4.1.1 Boiling HNO_3 test (Huey test ASTM 262 A practice C)

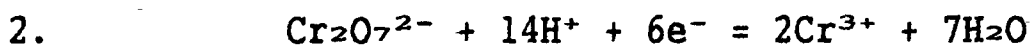
Evaluation of resistance to IGA by means of weight loss in boiling HNO_3 is widely used in the USA. The test consists of exposing pre-weighed ground specimens to boiling HNO_3 for successive 48 hr

periods. Specimens are cleaned, re-weighed and the corrosion rate calculated as $\text{mg cm}^{-2} \text{sec}^{-1}$. New solution is used at the start of each reflux. The test is commercially useful for evaluating steels that will encounter oxidising environments in service, such as in HNO_3 or urea manufacture. In commercial practice, upper corrosion rates are set to describe the onset of sensitisation, eg. a criterion suggested by DuPont for steels (type 304) used in HNO_3 manufacture is a rate of $0.54 \text{ gm m}^{-2} \text{hr}^{-1}$. If corrosion rates above this value are seen, then the steel is said to be sensitised. Grain dropping or "sugaring" takes place on fully sensitised materials. Care must be taken in obtaining specimens as sensitisation may result from cutting and grinding procedures [9], as the damaged layer may be several grains deep.

The corrosion potential ranges from 1.0-1.2 V(SHE), at which sensitised areas have a higher corrosion rate than the matrix. The potential of the test is determined by anodic dissolution and by the redox reaction



Acceleration occurs if oxidising ions are added to the test solution eg. $\text{K}_2\text{Cr}_2\text{O}_7$ at a concentration of 5 g/l. Oxidation of Cr^{2+} and Cr^{4+} from the dissolution of M_{23}C_6 also leads to the presence of oxidising ions in solution.



Aust [10], Armijo [11], and Westbrook [12] have shown that attack in the CrVI/HNO_3 test is not solely associated with Cr depletion, but also with impurity segregation. Armijo [13] and Joshi and Stein [14,14a] found that segregation was necessary to induce susceptibility to attack in unsensitised material.

4.1.2. Boiling $\text{H}_2\text{SO}_4/\text{CuSO}_4$ and Cu turnings (Strauss test ASTM 262 A practice E)

The Strauss test involves refluxing the solution, specimen and Cu turnings for 72 hrs in a solution of H_2SO_4 and $\text{Cu}(\text{SO}_4)_2$. To obtain quantitative data after testing the specimen is bent through 180° around a mandrel, and optical sections are prepared and the maximum depth of penetration measured at the apex of the bend. The test is used widely in the UK [15]; it is mild compared to the Huey test and little grain dislodgement takes place. The potential of the test lies in the range 0.3 to 0.58 V(SHE), just above the Flade potential of most steels. With increasing IGA, Cu^{2+} is reduced to Cu^+ and the redox potential is reduced in accordance with the change in the ratio of $\text{Cu}^{2+}/\text{Cu}^+$. A large difference between the rate of attack of regions of

lower Cr concentration and the matrix (the ratio of the rates of attack is of the order of 10,000) leads to rapid attack of Cr depleted regions. Attack is confined to the narrow depleted region and as such assessment is best made by measuring depth of penetration rather than weight loss. Weight loss measurements cannot be correlated with the degree of IGA because of grain dropping and because the narrow region of attack results in small weight losses.

Schenk [16] suggested the time of the test may be reduced by increasing the concentration of acid. However reducing the H_2SO_4 concentration results in a reduction in the minimum Cr content for passivation [17,18] because the Flade potential is made less noble, thereby reducing the aggressiveness of the corrodent. Thus a Strauss test has the capacity to examine different extents of Cr depletion by modifying test conditions.

4.2. Electrochemical testing.

New tests have been developed because chemical tests are time consuming, destructive and do not discriminate between specimens of moderate DOS. Evidence has shown that moderately sensitised materials can undergo IGSCC in environments that do not show IGA in the absence of stress. Conversely there are applications where a moderately sensitised material would not pass an ASTM test, but would perform satisfactorily in service. In such a case the use of a stabilised or low C grade C steel would be at an extra cost penalty. A test that provides quantitative information may provide more than a go/no go criterion.

4.2.1. Potentiostatic and Galvanostatic Tests.

Such tests etch out sensitised boundaries if specimens are held potentiostatically in a suitable electrolyte and under potential conditions where Cr depleted boundaries or second phases are active compared to the matrix [18,19]. France and Greene [19,20,21] maintain that it should be possible to predict service performance, a priori, by potentiostatic studies in the environment in question and by metallographic examination. ASTM Practice 262 A involves etching specimens in 10 % oxalic acid at $1 A/cm^2$ for 90 seconds.

This is often used as a rapid sorting test before moving on to more involved chemical tests. The test does not give a measure of the DOS but qualitatively indicates the extent of carbide precipitation. The surface is then examined after etching and the structure classified as having a step, dual, or ditch structure. The ditch or dual structure indicates that further testing is required. The ditch structure results from the high rate of attack on sensitised areas compared to the matrix. The step structure shows that the material is immune to

attack at grain boundaries; - attack is due to different rates of dissolution of different crystal planes. The dual structure is obtained when Cr carbides are present on grain boundaries, though not as a continuous network of precipitates.

Constant potential etching tests in 1M HClO₄ containing NaCl have been developed [22]. Other undesirable phases may be shown by etching. Table 2 shows suitable potentials for etching phases.

Table 2. Potentials (SCE) used for the selective etching of phases in 304 stainless steel in 0.5M and 20% H₂SO₄ [23,24].

Phase	0.5 M H ₂ SO ₄	20% H ₂ SO ₄
Ferrite	-0.25 to -0.4	-0.45
Sigma	-0.4 to -0.45 and +1.3	-
Austenite	-0.15 to -0.2	-0.35
Carbides	-	+0.8
Martensite	-	-0.5

4.2.2. Potentiodynamic Tests

Potentiodynamic tests consist of a controlled potential sweep from the free corrosion potential to a potential in the passive region. After some minutes rest, to allow a passive film to form, a reverse (cathodic) scan is made (reactivation). The activation/passivation and reactivation scans are shown schematically in Fig. 3. The test potential regions are limited to areas where secondary phases are passive, in order that response is only from Cr depleted regions.

The grain boundaries depleted in Cr are covered by a film of a less passive nature than the matrix. During the reactivation part of the polarisation curve, regions with a less passive film are preferentially attacked whereas regions with a sufficient concentration of Cr will not reactivate. The uneven reactivation behaviour indicates the extent of sensitisation because the high Cr regions do not reactivate (even in acid media) after passivation, whilst sensitised grain boundaries reactivate.

Potentiodynamic tests have the advantages over chemical tests of being rapid, non-destructive and are sensitive to variations of DOS. The growing interest in this kind of test is revealed by the increasing volume of literature giving test results for a wide range of materials. A portable cell system has been patented [25]. Application in the field has been reported [26,27]. The Electrochemical Potentiodynamic Reactivation test (EPR) is well documented and the ASTM form [28,29] was developed from work by Prazak [30] and Duffatt et al [31]. Different electrolytes have been proposed, composed of a "strong acid" and a salt which exerts a specific action with respect

to corrosion eg. H_2SO_4 and KSCN [32], or HClO_4 and NaCl [33]. KSCN or NH_4SCN is added as an activator to facilitate reactivation [34,35]. A summary of the different test methods reported is given in table 3.

Majdi and Streicher [36] investigated the effect of experimental variables on reproducibility and found that EPR measurements were dependent on surface finish, scan rate and solution temperature. The extent of grain boundary attack depends on the reactivation circumstances and the local quality of the built up oxide layer.

Majdi and Streicher [37] and Roelant and Vereecken [38] showed that problems of reproducibility could be overcome by using an anodic passivating scan before the cathodic reactivation sweep and an optimised scan speed.

Different criteria for examining IGA susceptibility have been adopted. A comparative measure of DOS is obtained from the resulting curves by ratios of either:

1. Critical passivation current densities during passivation and reactivation [39]
2. Areas under reactivation and passivation curves for an estimate of the charge passed for both the solution annealed material and the sensitised material.

Comparison of the areas under reactivation and passivation scans takes into account the width of the response peak; (eg lower Cr materials or depleted grain boundaries reactivate at higher potentials) together with the size of the peak. Measurement of the maximum current reflects the area of the sensitised grain boundaries and the extent of depletion.

The most widely used criterion for DOS is the ratio of charge passed during activation and reactivation (the area under a potentiodynamic activation or reactivation peak), as this compares the entire reactivation process of the whole surface with the reactivation process of the grain boundaries. Several authors [40,41] introduced the value of reactivation charge per unit of grain boundary area, to normalize the test data to grain size. Borello et al [42] suggested that charge measurement is more discerning than peak current measurement because the change in charge is larger than the corresponding change in peak current.

Pitting caused by the dissolution of inclusions may increase reactivation currents, though this is easily allowed for by performing comparison EPR tests on fully annealed specimens (annealed at temperatures above those at which inclusions dissolve). Hanninen et al [40] reported that the observed dissolution of carbides in EPR type environments does not take place under typical EPR test potential

conditions.

4.3 EXPERIMENTAL

To reiterate, the aim of the following experiments was:

1. To find the best test method to assess the extent of sensitisation in materials
2. To determine the optimum heat treatment conditions for sensitisation
3. To understand the process of sensitisation in terms of Cr depletion levels found at grain boundaries, and those predicted by modelling.

4.3.1. Material

The alloy used for these studies was 20% Cr, 25% Ni, 0.7% Nb stabilised stainless steel as used in Mk IV AGR fuel cladding material. It was supplied in two forms, 15mm diameter thin walled ribbed tube (AGR fuel cans) or 18mm diameter bar obtained from BNFL Risley. The compositions of these materials are listed in table 4. The bulk compositions are very similar, and only differ in Mn content. The bar is material extracted early in the thermomechanical processing en route to tube manufacture. Some of the bar material was rolled into flat strip and subjected to a treatment to mimic the finishing operations in tube production. The processing route for this "reworked" bar was:

1. 30% cold work
2. Anneal at 930°C for 1hr
3. 3% cold work
4. Anneal at 930°C for 1hr

4.3.2. Heat treatment

Heat treatment was carried out in two stages, solution annealing and ageing.

First tube was cut into thin strips and heat treated in silica tubes (under vacuum) for 0.5 hr at either 1050 or 1150°C, and then water quenched. Bar and reworked bar was heat treated in air, but the outer few mm were finally machined off to avoid any effects of oxidation or decarburisation. In some instances thin slices of bar 1mm thick, were heat treated in Ar to ensure a comparable severity of quench to the tube samples, but these samples behaved in essentially the same way as the larger sections of bar.

The second stage of heat treatment was ageing at temperatures between

550 and 750°C for times between 0.5 and 500 hours (tube in vacuum, bar in air).

4.3.3. Electrochemical tests

4.3.3.1. The EPR test method

A test procedure similar to that outlined in ASTM STP 656 [28] was followed, the differences from the ASTM procedure being that tests involved reactivation scans only, and were not carried out in de aerated solutions.

Small samples of 0.5 cm² area were hot mounted in perspex and an electrical connection was made through the side. The specimen surfaces were then ground to a 1200 grit finish, and washed in methanol and distilled water before the test. Tests were carried out in a small glass cell in approximately 250 ml of test solution, with a separate compartment for the standard calomel reference electrode connected by a Luggin capillary. A large platinised Ti counter electrode was placed around the specimen. The solution was stirred via a magnetic stirrer. A schematic of the test cell is shown in Fig. 4.

The test was carried out in freshly prepared 0.5M H₂SO₄ + 0.01M KSCN at ambient temperature. Solutions were always made from BDH AR quality reagents by mixing separate stock solutions of acid and thiocyanate immediately before the test, as it was found that reproducibility of tests was affected by solution age.

The test was carried out by a single negative-going sweep from a positive potential of +300mV (SCE) to -450mV (SCE) at a sweep rate of 100mV/min. Specimens were passivated for 60 sec at the upper potential limit before starting the scan. The sweeps were carried out under potentiostatic control (using a Thompson Ministat potentiostat), with an RML (Research Machines Ltd) 380Z microcomputer to control the signal potential. A schematic of the circuit is shown Fig. 5. The 380Z increments a Digital to Analogue converter (DAC) in steps of 1mV. The resulting analogue signal is fed to the external input of the potentiostat. The resulting current response is measured by a current follower circuit placed in the working electrode lead. A voltage proportional to the current flowing during testing is fed back to an Analogue to Digital converter (ADC). The analogue signal is converted to a digital equivalent, which is fed back to the microcomputer. This value is recorded 5 times and averaged for each reading, to reduce the effects of electrical noise. These data are then processed and presented as a potential/current plot, ie a polarisation diagram. These data were stored on disc for further processing.

Preliminary work examined the effect of varying solution concentrations (both acid and activator (KSCN) concentrations), scan speeds and start and finish potentials and the direction of the initial scan with the aim of optimising the reactivation response and its reproducibility, so that the difference between the response of the as received solution annealed (un-sensitised) and sensitised specimens was maximised. A single negative-going scan was adopted to ensure that reactivation occurred on a freshly unattacked specimen and to avoid damage during active corrosion so that correlation of the visible damage with reactivation behaviour was possible. A scan speed of 100mV/min gave the most reproducible results. The EPR conditions chosen for the test may be summarised as

Temp: 20'C	Area: 0.5 cm ²	Finish: 1200 size grit
No deaeration	Scan rate: 100 mV/min	
Reactivation scan only. Start at free corrosion potential, switch to 300 mV (SCE), delay for 1 min, then scan.		

The parameters and method of quantification of EPR experiments are shown schematically in Fig. 6. Area A (area under an activation scan) was obtained for a few samples only, and is not used in the comparison of results.

Specimens were examined in the SEM after testing to identify the nature of damage caused during reactivation, and to ascertain whether reactivation currents were associated with grain boundary attack.

4.3.3.2.Oxalic acid testing

Oxalic acid electrolytic etching was carried out on a smaller range of heat treatments. Oxalic acid electrolytic etch tests were carried out potentiostatically at 3, 1.2, 1 and 0.8 V(SCE) on samples prepared in the same way as for EPR testing.

4.3.4.Chemical tests.

4.3.4.1.Modified Strauss tests (ASTM 262 A 1970 practice E).

Heat treated specimens (either strips of tube or discs of bar material, ground to a 1200 grit finish) and copper turnings were immersed in a solution containing 35ml H₂SO₄ (1.84SG), 37.5g CuSO₄ and 318ml H₂O. The mixture was boiled in a conical flask for 72 hrs. After testing specimens were bent through 180° and conventionally mounted metallographic specimens were prepared to show the edge of specimens. These specimens were ground, polished and lightly etched and examined optically in order to gain an estimate of the depth of

penetration at the radius of the bend. Results for depth of penetration cited are the average of 10 such measurements.

4.3.4.2. CrVI+/HNO₃ tests.

CrVI+ / boiling HNO₃ tests were carried out on a smaller range of heat treatments than for Strauss testing. Specimens weighed approximately 2g and were ground to a 1200 grit finish and washed in methanol before testing. Tests were carried out in a flask containing approximately 200 ml of solution. During testing, specimens were periodically examined by removing, washing in distilled water then methanol and allowing to dry. Measurements were carried out to an accuracy of 0.2mg. The test solution was renewed after each weight measurement of specimens.

4.4. RESULTS

4.4.1. K₂Cr₂O₇ / HNO₃ test results.

In all cases the corrosive attack was intergranular in nature and continued until the entire boundary surrounding the grain was dissolved, at which point the grain fell out of the surface. Attack was monitored by recording weight loss with time. All the data are based on single experiments, apart from that gathered for tube annealed at 1050'C for 30 min, and aged at 550'C for 500hrs, for which 3 repeat experiments were carried out. Weight loss measurements were found repeatable for separate experiments to within approximately 20% error. Generally the rate of weight loss was constant for a particular specimen condition, though slightly faster in the first 10 hrs.

Fig. 7 shows the data for tube material. The fastest weight loss with time occurs for material sensitised by a heat treatment of 1050'C for 30 min, and aged at 550'C for 500hrs. Specimens only having undergone a solution anneal heat treatment (1050'C 30 min) showed the next fastest rate of weight loss with time. Heat treatment via a 1050'C 30 min, then 750'C 30 min route significantly reduced the rate of attack. The as received (AR) tube shows a much lesser response.

Fig. 8 shows data for bar material. Rates of attack are much less than those for tube material. The fastest attacked specimen is the solution annealed specimen, the slowest that treated at 750'C for 48 hrs. A solution anneal at 1050'C appears to increase the rate of observed attack, whereas 1230'C annealing appears to lessen the effect.

Fig. 9 shows that reworking the bar results in an increase in corrosion response. The AR material shows the greatest response at a rate comparable to the fastest case seen for the tube. Solution

annealing the reworked bar at 1150'C rather than 1050'C appears to decrease the rate of attack. It may be seen that ageing at temperatures between 600 and 750'C lowers the rate of attack compared to other heat treatments, whereas ageing at 550'C for 200 hrs greatly increases it. However, ageing for long times at 550'C gradually decreases the rate of attack.

4.4.2 Strauss test results.

This section describes Strauss test results for those tests which were carried out on material heat treated under an inert atmosphere. Appendix 4 gives results of surface observations on samples tested after heat treatment in an insufficiently inert atmosphere. Appendix 4 is included as a note of caution for specimen preparation and interpretation of Strauss test data.

The AR and annealed specimens of all materials (bar, reworked bar and tube) showed no response in Strauss tests. Only the tube material showed attack after annealing at 1050'C and then ageing. Bar and reworked bar remained unattacked after such heat treatments. After 72 hrs testing, tube samples regardless of the DOS showed a more or less constant depth of IGA along their length. Most boundaries were attacked along their whole length. The results of 72 hr Strauss tests on tube material are given in Fig. 10 and 11. Numbers indicate the number of repeat experiments for each point. The bulk of experiments are for a 550'C ageing temperature.

The rate of IGA (measured as the extent of IGA in 72 hrs testing) depends on the annealing temperature and ageing temperature and time. The depth of penetration first increases as ageing time increases, then decreases after a peak depth of penetration is seen. The change of depth of penetration with increasing ageing time shows that two processes are occurring, namely sensitisation due to Cr depletion, then healing as the level of Cr rises as Cr diffuses in from the bulk. Fig. 10 shows that the peak depth of penetration is reached in shorter ageing time as the temperature of ageing is increased. Samples annealed at 1150'C and aged at 600, 650 and 700'C achieve through tube wall penetration in 50, 5 and 0.5 hrs respectively. Samples annealed and aged at 750'C show little penetration, even for ageing times as short as 10 minutes. The time for which the maximum depth of penetration is seen is much narrower at higher ageing temperatures because the material is sensitised for shorter lengths of time.

Fig. 11 shows that samples solution treated for 30 min at 1050'C and aged at 550'C show gradually increasing penetration rates up to 500 hrs. The maximum depth of penetration seen in samples aged at 550'C was about 100 μm for material aged after a 1050'C anneal and about 70 μm for material aged after a 1150'C anneal. Furthermore, the

material annealed at 1150'C appears to reach the peak depth of penetration in a shorter ageing time than that annealed at 1050'C.

The observable maximum depth of penetration is limited to 120 μm penetration because of the finite thickness of the test samples. Once this depth of penetration is achieved specimens fractured and fell apart on bending. As severely sensitised material reaches this in less than 72 hrs the test saturates, and is unable to distinguish between different DOS in materials sensitised to give full width penetration of specimens in 72 hrs. To examine the change in the extent of attack with test time some specimens were examined after only 4 hrs and 24 hrs exposure. Attack was not uniform over the surface; only some boundaries are attacked, the number increasing with test time, though many remain unattacked. This phenomenon is seen even for materials which on further testing would show complete through width penetration after 72 hrs. Some samples showed complete failure after 24 hrs testing.

Fig. 12 shows the surface of a sample (1050'C anneal 600'C 50 hrs) after 24 hrs testing. Fracture of the specimen occurs where a linkage of sensitised susceptible boundaries is found through the thickness of the specimen. Fig. 13a shows the surface of a sample (1050'C anneal 550'C 500 hrs) after 24 hrs testing. Fig. 13b shows a similar sample after 72 hrs testing. It may be seen that attack remains narrow.

Fig. 14 shows the surface of a sample (1050'C anneal 650'C 5hrs) after 72 hrs testing. The surface is more severely attacked; much dissolution occurs and grains lose all shape. Fig. 15 shows the surface of a specimen (1050'C anneal, then aged at 600'C for 100 hrs) in the overaged condition where healing has begun. Attack is still seen to a depth of 15 μm .

The relationship between penetration depth and exposure time is linear. This is shown for material annealed at 550'C for 500 hrs in Fig. 16. The error bars show the spread in measurements of maximum penetration depth at several successive sections in the same sample.

The behaviour of the bar material in the Strauss test was in marked contrast to that of the tube. None of the samples, whether solution treated at 1050 or 1150'C and aged for temperatures between 550 and 750'C for times from 30 hrs out to 750 hrs showed any appreciable degree of IGA after testing. However it was found that solution ageing treatments of 1200 or 1230'C followed by subsequent ageing at 550 or 600'C led to significant grain boundary attack during Strauss testing. The form of this IGA is different from the tube material in that it was very narrow. The observed fracture surfaces showed little evidence of corrosive attack and were smooth and typical of a brittle intergranular fracture Fig. 17b. Fig. 17 shows the fracture surface of both tube and bar samples annealed at 1150'C aged at 600'C

for 50 hrs and then Strauss tested. The tube fracture surface Fig. 17a is more rounded, and grains corrode along facets. Reworking the bar material resulted in little change in the susceptibility to sensitisation as detected by Strauss testing.

4.5. Electrochemical test results.

4.5.1. Oxalic acid etching test results.

It was found that by varying the potential of etching, a range of microstructural features was etched, resulting in general pitting to specific grain boundary etching.

A potential of 6V was found to be too severe and led to rapid pitting. For tube sensitised via 1050'C 30 min, 550'C 500 hrs, an applied potential of 3V leads to grooving along grain boundaries and etching out of Nb(CN) particles; Fig. 18b shows gross pitting on the surface of sensitised tube etched at 3 V for 10 min. Fig. 18a shows a sample of bar annealed at 1050'C, then aged at 600'C for 50 hrs and etched at 1.2V. Fine etching and a ditch type structure may be seen, revealing the presence of twins and the location of prior annealing grain boundaries. The test potential used does not appear to pick out Cr depleted boundaries specifically. Fig. 19 shows a sample of bar annealed at 1150'C and aged at 600'C for 50 hrs etched at 0.8 V for 10 min. It may be seen that attack along most grain boundaries is narrow and continuous while some grain boundaries remain unattacked. Slight dissolution occurs around Nb(CN) particles, and the matrix is not attacked.

In conclusion, the test potential found best to discriminate between sensitised and unsensitised material was 0.8 V. All higher potentials lead to severe attack, pitting or attack of features other than sensitised grain boundaries.

4.5.2. EPR test results.

EPR tests were carried out on bar, reworked bar and tube material for a variety of heat treatments. To serve as a control, solution treated material of all three forms was tested. No increase in current was seen during the reactivation sweep. Peak currents for testing as received material were greater than those seen during the testing of solution annealed samples and were of the order of 10^{-5} Acm⁻² (two orders of magnitude less than for samples annealed and subsequently aged).

Experimental variables were optimised in an attempt to increase reproducibility between experiments. A selection of test results for tube material annealed at 1050'C and aged for 500 hrs at 550'C is

shown in Fig. 20. This shows the effect of some of the experimental variables that were optimised, eg scan speed, scan direction and solution concentration. The effect of different H_2SO_4 concentrations (0.5 and 3.75M H_2SO_4) was examined, for a fixed concentration of 0.05M KSCN. The higher concentration solution did not lead to significant increases in the reactivation peak size, but did lead to extensive general corrosion. Forward-going activation scans and negative-going reactivation scans show similar shapes though the maximum current observed is an order of magnitude greater for the original active peak than for reactivation. It was found that the most reproducible results were obtained with a single negative reactivation scan, rather than a double loop activation/reactivation scan, where the forward-going scan caused damage over the whole surface by general pitting. Scan speed was found to be important, and 100mV/min was used for all experiments. If 10mV/min was used, reactivation occurred earlier and the peak current was greater, though less reproducible. Reactivation scans were started by switching from the free potential to +300 mV SCE and holding for 1 minute before starting the sweep, to allow steady state conditions to be achieved. Peak current was measured rather than charge because charge was found to be very sensitive to scan rate. Reproducibility of the measured peak current between repeat experiments was of the order of $\pm 10\%$.

No EPR tests were carried out on tube materials aged at temperatures greater than 650°C or below 550°C. Tube samples annealed at 1050°C and then sensitised at 550°C for varying lengths of time were tested. Reactivation curves are shown in Fig. 21a, large active peaks are observed. The size of the peaks increases in magnitude with the time of heat treatment. This correlates to a similar gradual increase of test response seen in Strauss test results. Furthermore, it was seen that the start of reactivation occurred at higher potentials for specimens aged for longer ageing times.

A similar increasing response is seen for tube samples aged at 600°C after solution treatment at 1150°C, shown in Fig. 21b. A peak current response comparable with that obtained after 500 hrs at 550°C is obtained by heat treatment at 600°C for 100 hrs. Treatment for times longer than this results in a decrease in the size of the reactivation current due to healing. Material annealed at 1050°C then aged at 600°C showed a lesser response, the greatest response being 15 mAcm^{-2} for material aged for 50 hrs. Limited tests of samples aged at 650°C for 25, 100 and 200 hrs showed a peak of 10 mAcm^{-2} for the 25 hr aged sample and little response for the other samples.

The peak currents observed during EPR testing of the bar and reworked bar were at greatest an order of magnitude less than those of the tube

material. Normalising results (to account for grain size differences between the materials for comparable heat treatments of the differing materials) did not account for this difference. Fig. 21c shows a series of results for reworked samples aged for various times at 550'C. Increasing ageing time gives a gradual increase in the peak current, though the peak values are still an order of magnitude less than for similarly heat treated tube material. Some results obtained for bar and reworked bar are shown in Fig. 22. Results are the average of duplicate experiments. It may be seen that for comparable heat treatments the results of the reworked bar are greater than that of the bar. The bar response appears to decrease with ageing time whereas that of the reworked bar increases. For the reworked bar, a 1150'C anneal appears to have more effect than a 1050'C anneal. After long ageing times the current response for the reworked bar reaches values similar to those seen for tube. Surface examination after testing showed little evidence of grain boundary attack, though some local attack was seen around large carbides.

4.5.3. Surface attack after electrochemical and chemical testing.

It may be suggested that during EPR testing response may be generated from regions other than Cr depleted grain boundaries, such as around Nb(CN) particles. Direct SEM observation of the nature of attack was carried out after testing.

Fig. 23a shows the surface of sensitised tube after a positive going sweep followed by a negative-going sweep, passivation and then reactivation. Much general dissolution of the surface has taken place. Fig. 23b shows the surface of bar material sensitised via a 1150'C for 30 min and 600'C 50 hrs route, and subsequently tested in a double loop reactivation test. Attack is seen to occur along grain boundaries and locally around matrix and grain boundary precipitates.

Some crystallographic features such as twins are etched. It is notable that attack is patchy and does not run continuously along some grain boundaries.

To compare the extent of grain boundary attack for different tests, an EPR test and an Oxalic acid etch test were carried out on tube annealed at 1050'C and aged at 550'C for 200 hrs. The surface after a single reactivation scan is shown in Fig. 24a. The surface after etching in an oxalic acid test for 10 min at 1 V is shown in Fig. 24c. Both tests show similar numbers of grain boundaries attacked, and a similar width of attack. Estimation of the extent of grain boundary attack was attempted by using a linear mean intercept method. In both tests about 60% of all boundaries were attacked.

Fig. 24b shows bar annealed at 1150'C and aged for 230 hrs at 750'C and subsequently tested in an oxalic acid test. Cr-depletion in such material will have obviously healed above the Cr level commonly

regarded as necessary for sensitisation. Response in an EPR test or Strauss test is negligible, yet grain boundaries are etched in an oxalic acid test.

The width of attack after all chemical and electrochemical tests is much greater than any reported Cr concentration profile measured by AEM or predicted by modelling. The width of attack at grain boundaries on the surface is greater the higher the ageing temperatures, at higher ageing temperatures surface attack took the form of wide, shallow grooves. Fig. 25 shows the surface of a bar specimen aged at 600°C for 100 hrs after a 1150°C anneal. Figs. 25a and d show Strauss tested surfaces and Fig. 25b and c show Huey tested surfaces. The width of grain boundary attack in both samples is comparable; in Fig. 25b and c additional attack is seen around carbides and along twin boundaries. Fig. 25c and d show that most boundaries are attacked during Strauss testing, whereas during Huey testing attack is variable from boundary to boundary. The corroded sample groove widths after EPR, Huey, or Strauss tests measured some 0.5 to 2 μm . Both Briant [43] and Streicher [6] made the same observations. Briant [43] suggested a mechanism where degradation of the protective Cr_2O_3 film around grain boundaries was caused by Cr(VI)^+ in solution. Cr(VI)^+ formed at the low potentials involved because the pH of the solution increases by the local increase of Fe^{3+} in solution and subsequent oxidation of Cr^{3+} . Briant and Hall [45] suggested that the difficulty of diffusion along the crack may lead to solution conditions dissimilar from the bulk, and enhanced attack as the local environment becomes more aggressive.

4.6. FOIL ETCHING,

To observe directly which microstructural features are attacked in different chemical tests, TEM foils were examined then etched in the solutions used for testing, and re-examined. Etching was carried out until an effect was apparent. This method was first suggested by Younger et al [47].

Fig. 26 shows foils after etching in Strauss solution. Fig. 26a shows etching in material that had been aged via a 1050°C anneal and 550°C for 500 hrs. Attack occurs along most grain boundaries, though carbides are unaffected themselves. Fig. 26b shows etching locally around a carbide in tube material after 1050°C anneal and 600°C for 100 hrs. Etching occurs preferentially along grain boundaries and on one side of the carbide, one boundary remains unetched. Etching preferentially on one side of the carbide; indicates that asymmetric Cr depletion exists across the grain boundary. This result was confirmed by AEM, and such a Cr depletion profile is given in section 5.3. The shape of the corroded boundary observed by TEM reflects the

Cr profile, eg attack is seen preferentially on one side of the grain boundary as a result of boundary movement during $M_{23}C_6$ precipitation.

Fig. 27 shows a foil from material aged via 1050'C anneal 550'C 500 hrs ageing route etched in hot $HNO_3/Cr(VI)^+$, ie in a medium at a potential where regions showing segregation are attacked. Etching occurs continuously and uniformly along boundaries. Boundaries inclined perpendicular to the foil are completely removed, and inclined boundaries lose material where the surface meets the surface of the foil, the resulting contrast being simply due to the loss of section thickness. This effect was examined by specimen tilting experiments in the TEM. Attack in such media is attributed to impurity segregation rather than Cr depletion because the etching along grain boundaries is continuous rather than discrete for all heat treatments, including solution anneals where Cr depletion does not occur.

Fig. 28 shows further micrographs from foil etching experiments. All photographs apart from 28b show results for etching tube samples in hot Strauss solution. Fig. 28a shows etching in a sample annealed at 1050'C and aged for 50 hrs at 600'C. Etching is associated with incoherent twins only. Coherent twins, where precipitation does not occur are unaffected. Fig. 28b shows etching around a Nb(CN) precipitate on a grain boundary. Etching occurs both around the precipitate and along the grain boundary. The white line seen running across the precipitate results from grain boundary etching and is a contrast effect which occurs because the particle is embedded within the foil and etching reduces the amount of material in the way of the electron beam. Fig. 28c, d, and e show the patchy nature of attack that may result along some boundaries and around carbides in a sample annealed at 1050'C and aged at 550'C for 500 hrs. Fig. 28f shows that Cr depletion along boundaries may be continuous in a sample annealed at 1050'C and aged for 50 hrs at 550'C. The width of the attacked grain boundaries is no less than that for longer ageing times though the number of attacked boundaries is less. The narrow attack region emphasises how attack is concentrated in the plane of the grain boundaries (where Cr depletion occurs) with little matrix corrosion.

4.7. DISCUSSION.

4.7.1 Difference between bar and tube material.

The observed difference in response between the bar and tube material in sensitisation tests is consistent over a wide range of heat treatments, and indicates a difference between materials in ability to sensitise. Such a difference is unexpected because analysis (table 4) showed that both materials had similar chemical composition, though

differed slightly in Mn content. Microscopy (TEM and SEM of etched surfaces) reveals little difference between the tube and bar. Both materials show evidence of residual Nb(CN), and show $M_{23}C_6$ on grain boundaries after sensitisation ageing treatments. It is evident from the results that the bar material remains unsensitised while the tube material may be sensitised to varying degrees. Reworking the bar by giving the same thermomechanical processing route that the tube follows results in a greater response in both EPR and Strauss tests, though still much less than seen for the sensitised tube material.

Briant et al [60] suggested that the presence of Mn prevented sensitisation by changing the activity of C, and thus the amount of Cr depletion that took place. It was also suggested that Mn increased the ease of passivation of the alloy. The difference in Mn contents is 0.7 wt% for the bar material, and 0.4 wt% for the tube material.

The fact that an anneal of greater than 1200°C is required prior to ageing, to cause the bar material to show any response in a Strauss test points to insufficient C in solution after lower temperature anneals. This hypothesis is now examined.

As a way of determining the amount of C in solution after an annealing treatment, estimates of Nb concentration in the matrix at different temperatures, were made by electron microprobe analysis. A measurement of the amount of Nb in the matrix will give an indication of the amount of C locked up as carbide and therefore the amount in solution available for sensitisation.

The equilibrium solubilities of C in solution annealing can then be obtained by referring to the solubility product K for the corresponding temperature. Knowing the solubility product K:

$$1. \quad [Nb][C] = K$$

a value of [C], the amount of C in solution for $M_{23}C_6$ precipitation can be estimated.

Microprobe analysis measurements of the level of Nb (average for 10 measurements) in the matrix after solution annealing (for 45 min) at various temperatures, indirectly gave an indication of the amount of C not locked up as Nb(CN) and therefore available for sensitisation.

The data of the concentration of Nb measured in the matrix for a given solution temperature, are shown in Fig. 29 plotted in Arrhenius form (log concentration against reciprocal temperature).

0.7 wt% is the upper limit of Nb in solution, ie all the Nb content, resulting from the composition of the material. 0.4 wt % is the lower limit possible, because at this concentration all C is bound in the form NbC. This results from stoichiometric considerations. If

however a carbonitride forms, the level to which Nb in the matrix may fall is even lower (0.3 wt%) as less of the available C is required to maintain stoichiometry and precipitation may take place to a greater extent. If Nb(C₃N) forms [61,62] the value of Nb in the matrix may drop to 0.3 wt% at this is indicated on Fig. 29.

It may be seen that NbC dissolution in the 3 materials (bar, reworked bar and tube) differs, although the materials have nominally the same composition. The bar material maintained the same level of Nb in solution until 1150°C, after which levels of Nb in the matrix rapidly increased. Below 1150°C the level of Nb in the matrix stays constant, presumably because carbides do not dissolve and equilibrium is not achieved.

The Nb solubility in the tube and reworked bar follows an Arrhenius-type relationship, and solubility increases exponentially with temperature as expected. However the solubilities for the two materials differ. It would appear that Nb goes ~~into solution more~~ easily in the reworked bar than the tube for all solution temperatures. For comparison, data for the solubility of NbC in a stainless steel, obtained by Deighton [63], are shown. It may be seen that the data collected by Deighton lie parallel to that of the tube though not of the reworked bar. The heat of solution of Nb(CN) for the tube is the same as those determined by Deighton, though different from that of the bar material.

A further way of following Nb(CN) dissolution and subsequent C availability for the sensitisation process is to follow grain growth at different annealing temperatures. The migration of grain boundaries is strongly influenced by the presence of particles; Nb(CN) impedes movement by pinning grain boundaries. If Nb(CN) precipitates dissolve, grain growth is seen. Pinning is influenced by changes in the particle size distribution because Nb and C are both soluble in the matrix, at high temperature dissolution occurs and austenite grain growth occurs [64]. Limited measurements were made of grain size increases during annealing by use of a mean linear intercept method. Bar material was annealed at 1050, 1150 and 1200°C for 30 min and 2 hrs.

The data are shown in Fig. 30 in the form of mean linear intercept grain size (normalised to that of the as received bar) against annealing temperature. Despite the many limitations of the simple mean linear intercept method [65] it may be seen that the dissolution of NbC in the bar material leads to significant grain growth only for the 1200°C anneal. At temperatures less than this the loss of the pinning effect by Nb(CN) dissolution is time dependent and more grain growth is seen on ageing for 2 hrs rather than 30 min. Considerable grain growth is seen in the tube material on annealing at temperatures above 1100°C.

Why should the working the bar material enable the dissolution of Nb(CN) thereby allowing more Nb and C into solid solution at lower temperature? Both materials show evidence of residual Nb(CN) after solution treatments below 1150°C, though coarser particles are seen in the bar. The apparent size effect of the dissolution of Nb(CN) may be explained in that if Nb(CN) is able to dissolve, it is able to increase the C concentration in solution and thus a greater degree of sensitisation may be achieved. In the tube material, carbides are smaller and able to dissolve at lower temperatures, and thus sensitisation is seen in the tube material for lower solution anneal temperatures than is the case with the bar material. Reworking breaks up the carbides, to enable their dissolution in shorter times. In conclusion, the Nb to C ratio is important in determining sensitisation. If a higher solution anneal temperature is used, more NbC goes into solution, providing more C for sensitisation.

4.7.2. Comparison of tests in relation to each other.

The results of Strauss and EPR tests for tube material are, on the whole, as expected. As the ageing temperature is increased, the time to peak sensitisation is reduced. Ageing at 550°C produces a slowly increasing DOS, while for ageing at other temperatures the measured DOS first rises and then falls. The model described in chapter 3 predicts that with time the Cr level at the boundary slowly rises while the depletion profile widens. Therefore an increase of the rate of penetration in a Strauss test, or peak current in an EPR test, with ageing time appears to be associated with a widening Cr depletion profile. Little attack was seen in Strauss tests for samples aged at 750°C. The model shows that on ageing at this temperature, the minimum level of Cr at the grain boundary does not fall below 15 wt%, well above the levels of depletion suggested as necessary for attack. Observable attack in Strauss tests or EPR tests requires the Cr concentration at the grain boundaries to fall below a certain level. It has been suggested that in a Strauss test only grain boundaries with a Cr content of less than 12 wt% will be attacked. Fig. 31 shows the current density measured by Osozawa and Engell [49] for Fe 9% Ni samples containing different amounts of Cr. The tests were performed in H₂SO₄ at a potential close to that of the modified Strauss test. It is evident that for between 8 and 13 wt% Cr small changes in Cr content result in large changes in corrosion current. Therefore, compositional changes around these levels will control response in sensitisation tests.

The trend of EPR results is the same as for Strauss tests, though EPR

tests do not produce the same ranking order for all specimens, in particular, the process of sensitisation and healing is observed in shorter times in the Strauss test. The extent of attack depends on both the DOS and on the type of test used. This may lead to a different ranking order of DOS for different heat treatments depending on the test used. It is well established that both the EPR test and the Strauss test result in attack at grain boundary depleted regions [28 to 42,48,50]. Comparison of the response of tube material in Strauss testing and EPR testing shows that if the peak current is greater than 5 mAcm^{-2} the material appears to be sensitised in a Strauss test. This explains why it was noted that a gradual increase in response (up to a maximum peak current of 4 mAcm^{-2}) was seen during the EPR testing of bar material aged for increasing times at 550°C , whereas no response was noted during Strauss testing of the same material. The gradual increase in response arises because the EPR test is able to resolve segments of grain boundaries that appear as sensitised over the test surface whereas attack in the Strauss test requires more continuous Cr depletion for interlinking penetration into the specimen to be achieved. The ability of the EPR test to detect discontinuous as well as continuous sensitisation has previously been pointed out [35] to be a cause of discrepancy between the EPR and Strauss test.

The EPR test, as modified here, proved very sensitive in detecting grain boundary sensitisation in bar, reworked bar and tube material, discriminating between different levels of sensitisation for a wide range of heat treatments. The EPR test was able to distinguish between materials which showed a step or dual structure in the Oxalic acid etch test, and showed low corrosion rates in a Strauss test. Good correlation between the EPR test and chemical tests has previously been observed [40,41,42,46].

Strauss testing readily distinguishes between a great range of medium and severe Cr depletion and is unaffected by impurity segregation [17,18]. Such materials showed a ditch structure in the oxalic acid test. Care must be taken in the preparation of Strauss test specimens, because Cr depletion can arise through the formation of a Cr rich oxide film. A limitation during the test carried out was that the maximum observable depth of penetration is $120 \text{ }\mu\text{m}$ because through specimen penetration may be seen in a 72 hr Strauss test. The test was therefore unable to distinguish between higher DOS, where complete penetration is seen before the end of the test. The test may be made more sensitive to such high sensitisation regimes by decreasing the test time. The fact that the rate of penetration appears to progress linearly with test time suggests that there is no difficulty in the diffusion of species along etched out grain boundaries.

The response of EPR, Strauss and Oxalic acid tests in relation to each other is shown schematically in Fig. 32, (after ref [40]). Saturation of the oxalic acid test occurs when 100% of grain boundaries are attacked. The Strauss test saturates when complete penetration of the specimen is seen in a 72 hr test; if the test time is shortened, it is possible to discern higher DOS. The EPR test saturates when reactivation of the whole surface occurs.

The effect of heat treatment on corrosion rates in $\text{HNO}_3/\text{Cr(VI)}^+$ tests, can be explained by impurity segregation to grain boundaries [10 to 13,51,52]. Segregation is possible during the initial solution anneal. Electron microscope examination showed that the solution treated samples were free of grain boundary precipitates and thus increased corrosion was not the result of precipitation. The effect of heat treatment and the resulting weight loss measurements are explained by a model proposed by Armijo [11,13] and Aust [10]. According to this model, vacancies tend to annihilate at grain boundary sinks. Those solute/solvent systems with a positive vacancy binding energy may produce vacancy coupled uphill diffusion of solute atoms towards the boundary; impurities at grain boundaries then result in an increase in the rate of corrosion during testing. When heat treatment forms isolated second phase particles the corrosion morphology and rate are markedly changed. Heat treatment at temperatures greater than 650°C results in the formation of large carbides which can remove harmful solutes from grain boundaries and thus lower the rate of IGA. A sensitisation treatment at 550°C leads to rapid attack during $\text{HNO}_3/\text{Cr(VI)}^+$ testing. Briant [53 to 56] reported that corrosion was worst when both Cr depletion and P segregation occurred simultaneously and that segregation alone has less effect.

4.7.3. Comparison between predicted profiles and corrosion results.

This section aims to examine the shape of Cr depletion profiles (the value of the critical zone width and critical Cr concentration), that determine the borderline between "just sensitised" and "not quite sensitised". To do this SAROC predicted Cr depletion profiles are compared with depths of penetration seen during Strauss testing.

The corrosion data from Strauss tests were used to plot Fig. 33 and give the range of ageing times (temperature dependent) for which depths of penetration to levels of both 100 and 50 μm are obtained. These depths of penetration are arbitrary and are chosen purely to illustrate the method used to make the comparison, though Pascali et al [57] derived TTS curves for 304 stainless steel in similar way, and considered 50 μm depth of attack as the divide between "sensitised" and

"unsensitised". Changing the criterion of depth of attack necessary for sensitisation will change the regime over which sensitisation is observed.

Comparison may be made between the Strauss test generated TTS curves with modelled TTS curves (Figs. 17.3 and 19.3). The curves are similar in shape, and, as ageing temperature increases, the onset of sensitisation is seen after shorter times and the duration of sensitisation is less. Using the variables of Cr depletion profile width at a certain Cr level and depth of penetration, TTS curves may be compared. For instance, a level of attack of 100 μm will be seen if the Cr level falls below 15 at% for a profile width of 12 nm or greater. If the model (SAROC) predicts Cr depletion profiles well, sensitisation is seen to occur in material depleted to a much less extent than 13 at%, the criteria suggested by Stawstrom and Hillert. The regime over which sensitisation is seen, according to our Strauss test data, is much greater than would be predicted using this criterion.

The most significant difference is in the temperature above which sensitisation is not seen. The model suggests that after a 1150°C anneal, sensitisation should not be seen above 620°C, yet depths of penetration of 100 μm are seen after Strauss testing with ageing at 700°C. Decreasing the profile zone width for a given level of Cr depletion shortens the time to sensitisation and lengthens the time to healing, i.e. the regime over which sensitisation is seen is increased. Increasing the maximum concentration of Cr with sensitisation at a given profile zone width, raises the maximum temperature at which sensitisation may be seen. However, the difference between the suggested criteria for sensitisation, and temperature and time regime over which the model predicts sensitisation occur result because the predictions of the model are in error. The model may be in error because it does not consider the variation of the activity coefficient of C and Cr with temperature, but uses a "Cr effective" term (section 3.9.1.2) to calculate the change in alloying element concentration. The activities of both C and Cr are affected by the Ni concentration (described in section 3.8.1.). As both the Ni concentration at grain boundaries, and the composition of the carbide vary with ageing temperature and time, the activity coefficients of C and Cr vary, and the grain boundary Cr concentration will change. Because SAROC prediction is conservative in sensitisation prediction, the solubility of C must be less than indicated by calculations using a "Cr effective" term. Predictions of Cr depletion by use of the SAROC model are compared with microanalytical observations of Cr depletion in chapter 5.

4.8. Variation from boundary to boundary.

A TTS curve generated by modelling considers the time for the first incidence of sensitisation and healing only along one boundary. However the material is made up of many boundaries, and the extent of Cr depletion or impurity segregation may vary from boundary to boundary because different boundaries have different nucleation characteristics and diffusivities. During precipitation, a progressively larger number of boundaries becomes sensitised and then heals. At any particular time there will be a proportion of boundaries where the extent of Cr depletion is at one level, a further set at another level etc. The response in a test is made from the summation of these boundaries. For a level of response sufficient to describe the material as sensitised (as defined by a maximum depth of penetration in a Strauss test or peak current in an EPR test) to be achieved there must exist a certain proportion of boundaries with sufficient Cr depletion. For example, for a certain depth of penetration to be achieved, attack must find a linking path of sensitised boundaries. In material sensitised to a lesser degree, the probability of each attacked boundary adjoining to a linking path (a further sensitised boundary) is lower and the observed depth of penetration will be less. In specimens sensitised for 500 hrs at 550°C an almost continuous carbide network exists along grain boundaries and IGA is seen uniformly from grain to grain, Strauss attack penetrates uniformly to approximately 100 μm in 72 hrs. In samples aged for 25 hrs very few boundaries are sensitised and the deepest attack runs in only 15 μm (2 grains). The extent of linkage is related to the number of boundaries depleted to a sufficient extent in order to allow an attack path. Similarly it may be seen that on material sensitised to a lesser degree, attack over the surface is discrete rather than continuous. This is seen for short time Strauss tests only. Avalanche penetration of IGA is directly associated with the formation of continuous zones of Cr depletion, where corrosion can run freely from one grain to the next.

To describe observed crack length distributions in terms of both the variation of sensitisation throughout the material and the time of testing in a Strauss test would be very complex. The number of boundaries that need to be sensitised such that attack may run from one side to the other of the specimen, (through wall penetration), ie formation of an interlinking structure, involves ideas akin to percolation models. Reviews of percolation are given by Essam [58] and Welsh [59].

In summary, we may conclude that the effect of heat treatment variables on response in a variety of electrochemical and chemical tests has been examined. A wide range of responses is observed depending on the extent of precipitation. It is believed that variations in both Cr depletion and impurity segregation are the cause of the responses.

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Table 2

Analysis of materials used for sensitisation and stress corrosion experiments.

Wavelength Dispersive Spectroscopy Results

Wt%	Cr	Ni	Nb	Si	Mn	C	P	S
Tube	19.4	24.6	0.68	0.61	0.49	0.037	0.007	0.007
Bar	19.8	24.2	0.62	0.51	0.76	0.037	0.007	0.007

Balance Fe (≈54%)

Standard Deviation for all analyses < 0.4 Wt%

Table 3 .A summary of EPR test methods.

Ca = activation charge passed. Cp = reactivation charge passed
 ia = peak activation current. ip = peak reactivation current
 (GBA) = normalised to grain boundary area

Reference	Electrolyte	Conditions	Quantification
1.Cihal and Desestret Corrosion Sci 20,p737 1980	5N H_2SO_4	70°C Transpassive-passive	Ca/Cp
2.Charbonnier and Jossic Corrosion Sci 23,p1191 1983	3.75M H_2SO_4 0.001M NH_4SCN	23°C Transpassive-active 9V/Hr	ia/ip
3.Clarks, Cowan and Walker ASTM STP 656 1978	0.5M H_2SO_4 0.01M KSCN	30°C 200mV(SCE)-active 6V/Hr	Ca/Cp(GBA)
4.Streicher and Majidi Corrosion NACE 40,p584 1984 40,p393 1984	0.5M H_2SO_4 0.01M KSCN	30°C 200mV(SCE)-active 6V/Hr	Ca/Cp(GBA)
5.Cihal Corrosion Sci 19,p737 1979	1M H_2SO_4 0.5M NaCl	70°C -500 to 500 to -500 mV(SCE) 15V/Hr	ia/ip Ca/Cp
6.Mignone, Barbera and Borello Corrosion NACE 38,p360 1982 Brit Corr J. 17,p117 1982	0.5M H_2SO_4 0.005M KSCN	23°C Ecorr to 400mV(SCE) 30V/Hr	Ca/Cp(GBA)
7.Hanninen Corrosion Sci 25,p821 1985	0.5M H_2SO_4 0.01M NH_4SCN	23°C Ecorr to 200mV(SCE) 6V/Hr	Ca/Cp(GBA)
8.Lee Corrosion NACE 42,p107 1986	3 to 5N H_2SO_4	30°C active-passive 6V/Hr	Ca/Cp
9.Roelandt and Vereecken Corrosion NACE 42,p289 1986	1M H_2SO_4 10 ppm KSCN	25°C 880 to -350 mV(SCE) 2V/Hr	Ca ia
10.Duffaut, Pouzet and Lacombe Corrosion Sci 6,p83 1966	20% H_2SO_4 0.01M KSCN	23°C active-passive	ia

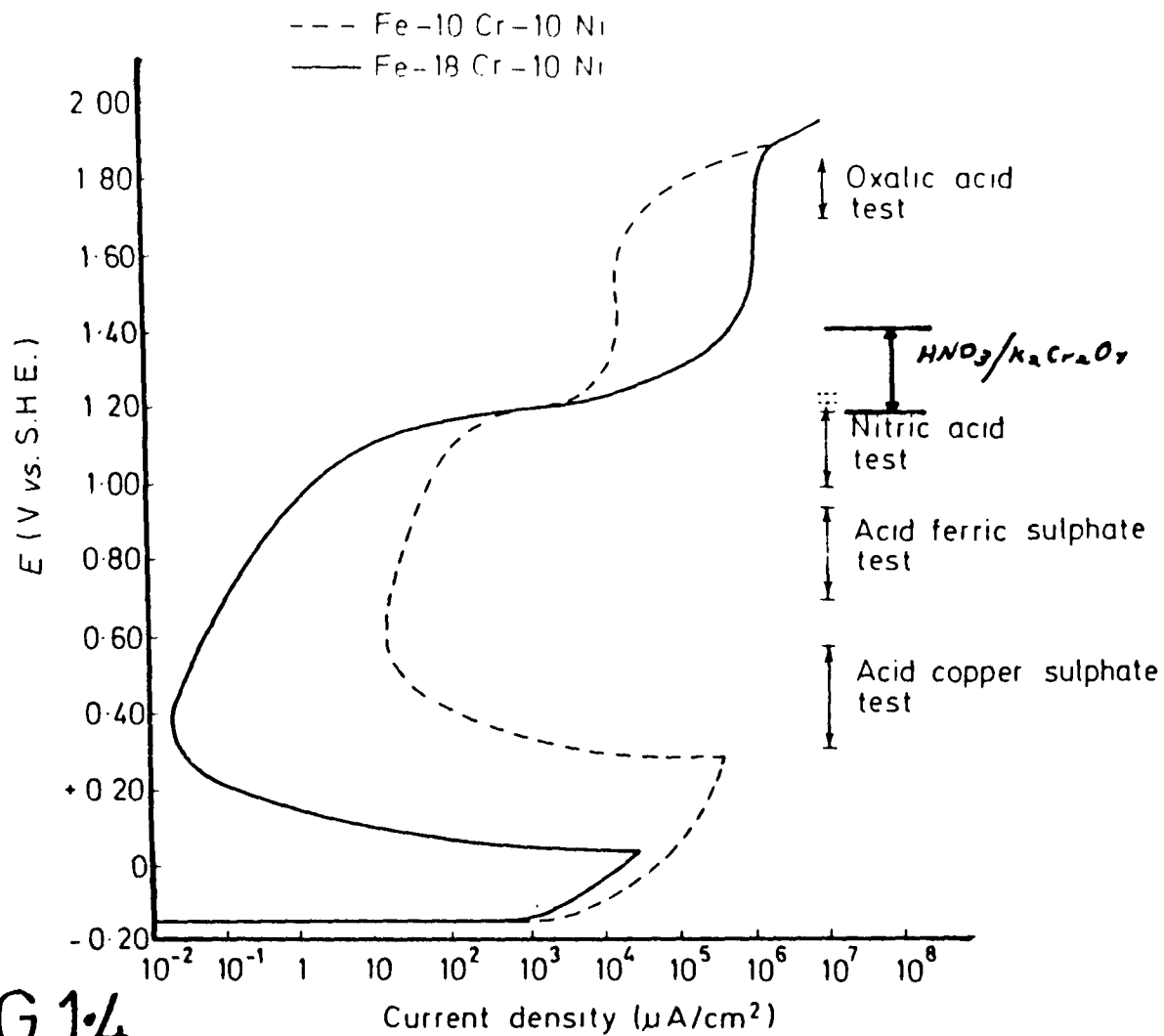


FIG 1.4

Schematic representation of range of corrosion potentials expected from various chemical tests for sensitisation in relation to the anodic dissolution kinetics of the matrix (Fe-18Cr-10Ni stainless steel) and grain-boundary alloy (assumed to be Fe-10Cr-10Ni) owing to depletion of Cr by precipitation of Cr carbides of a sensitised steel in a hot reducing acid after Cowan and Tedmon (2)

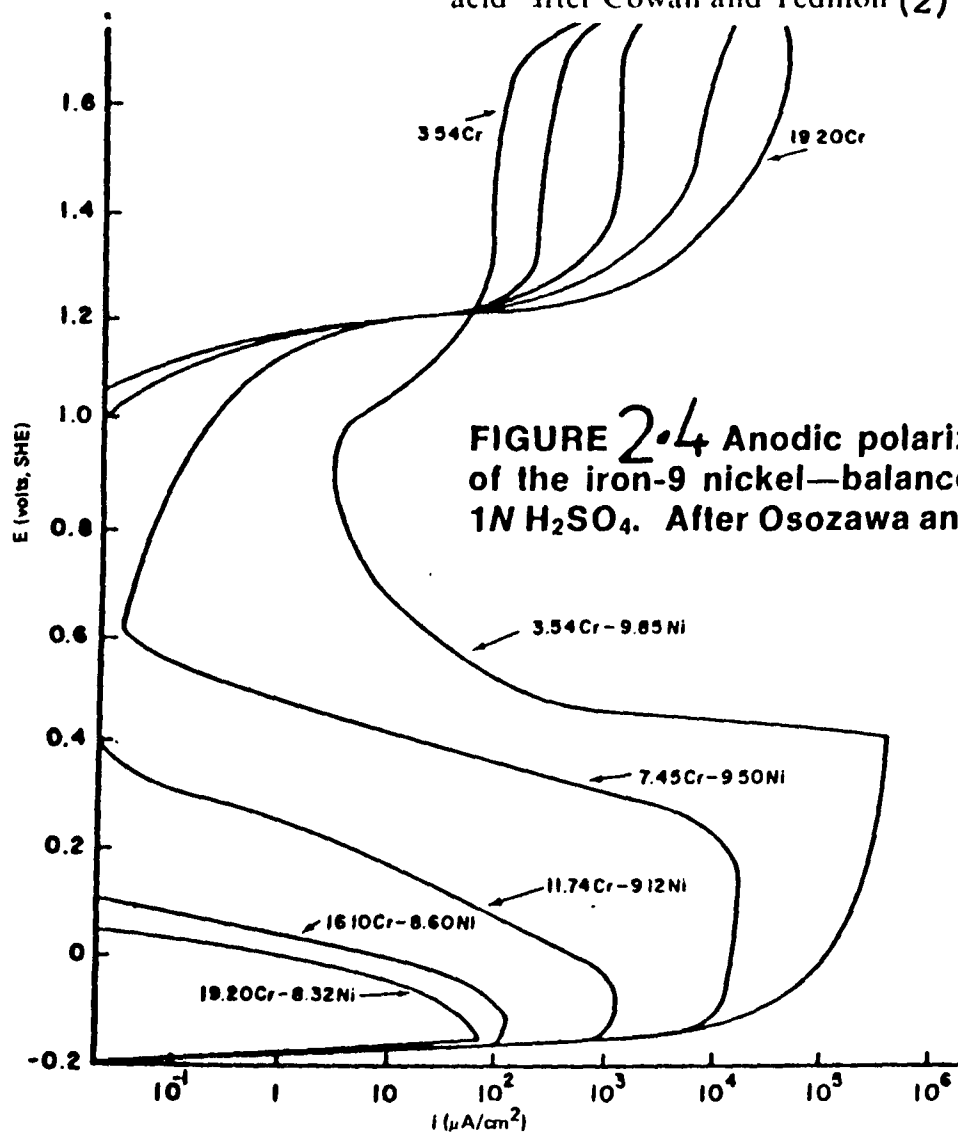


FIGURE 2.4 Anodic polarization curves of alloys of the iron-9 nickel—balance chromium system in 1N H_2SO_4 . After Osozawa and Engell (8)

Schematic of an EPR test

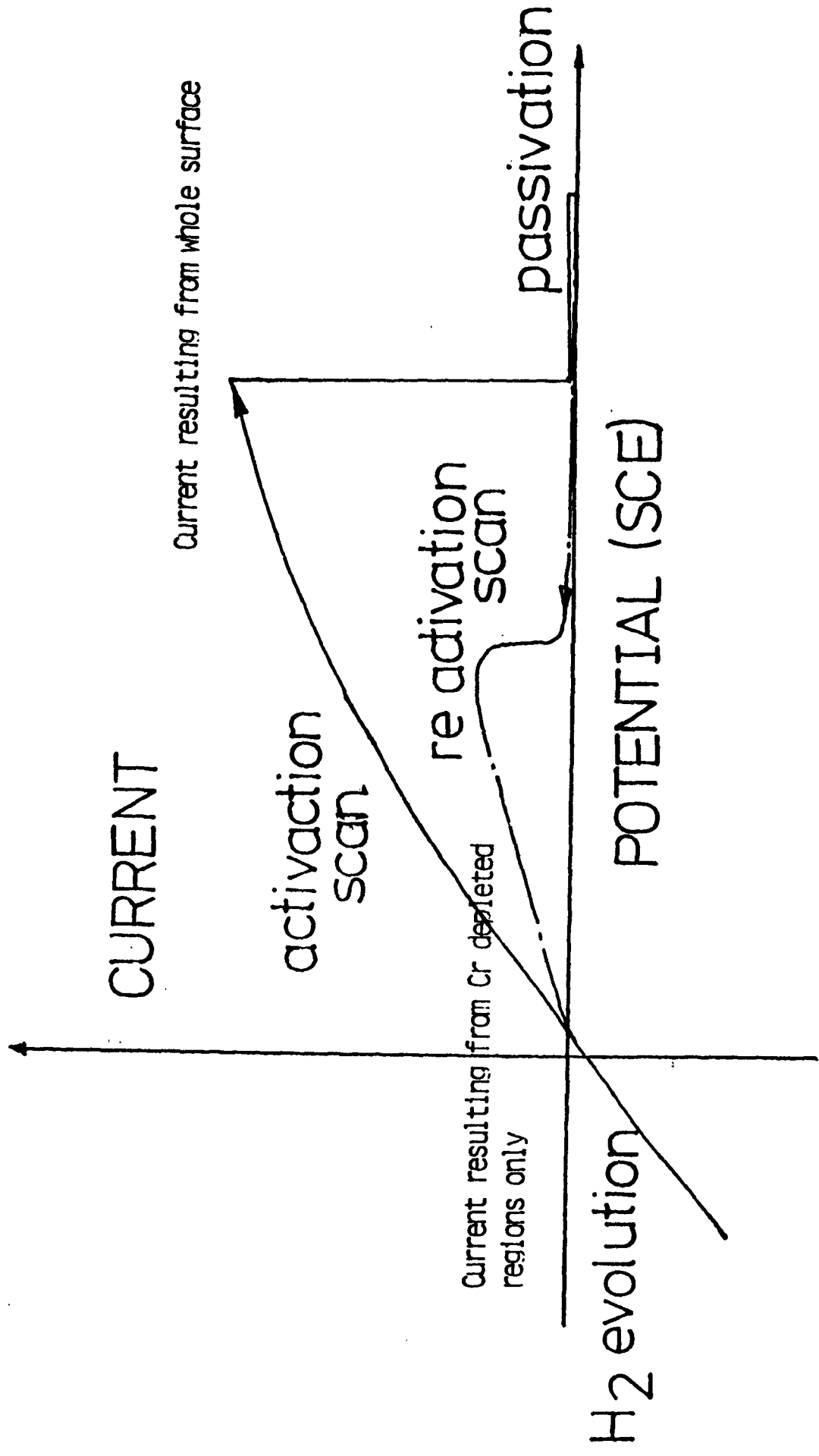
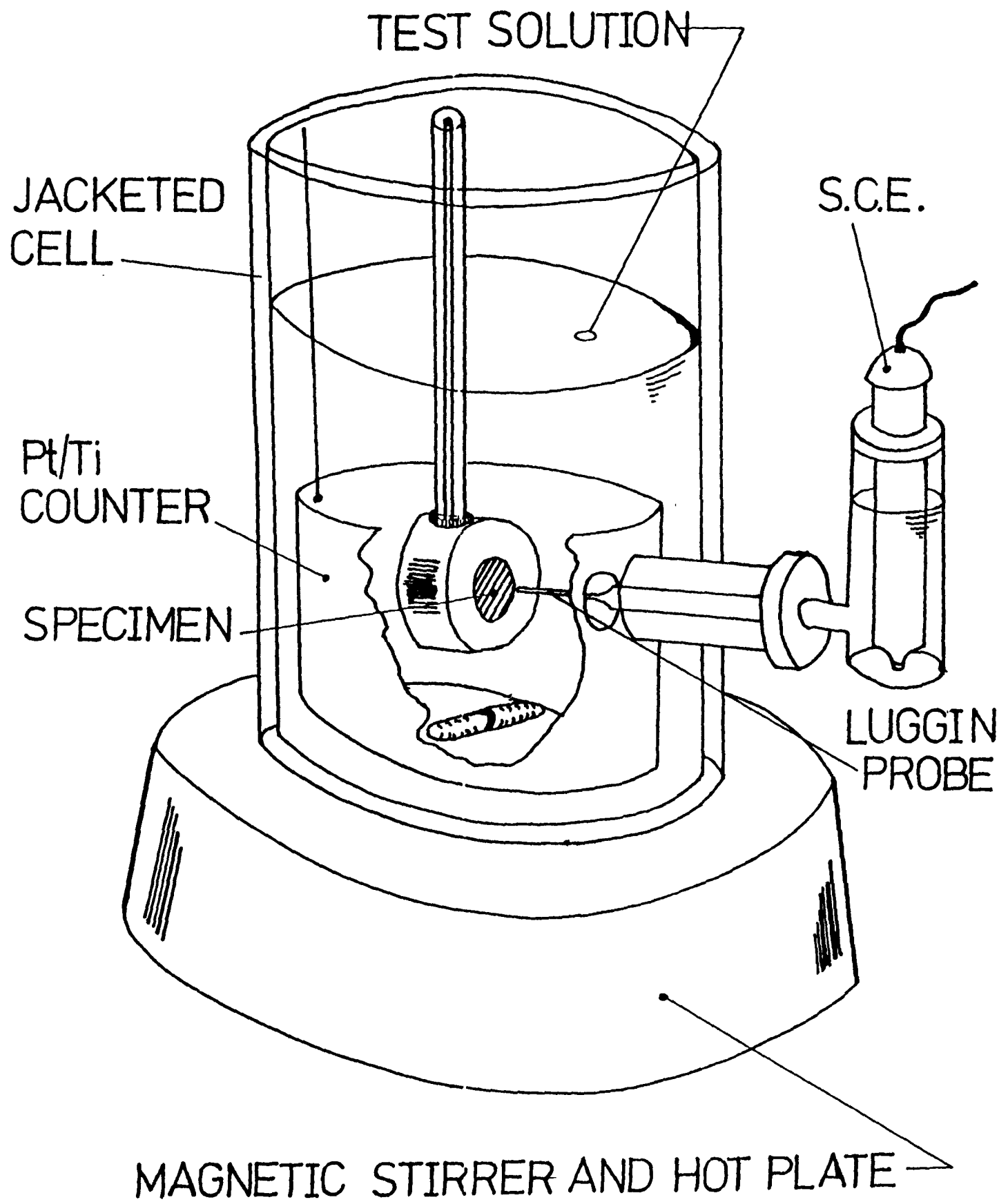


FIG 34

FIG 4:4 EPR TEST CELL



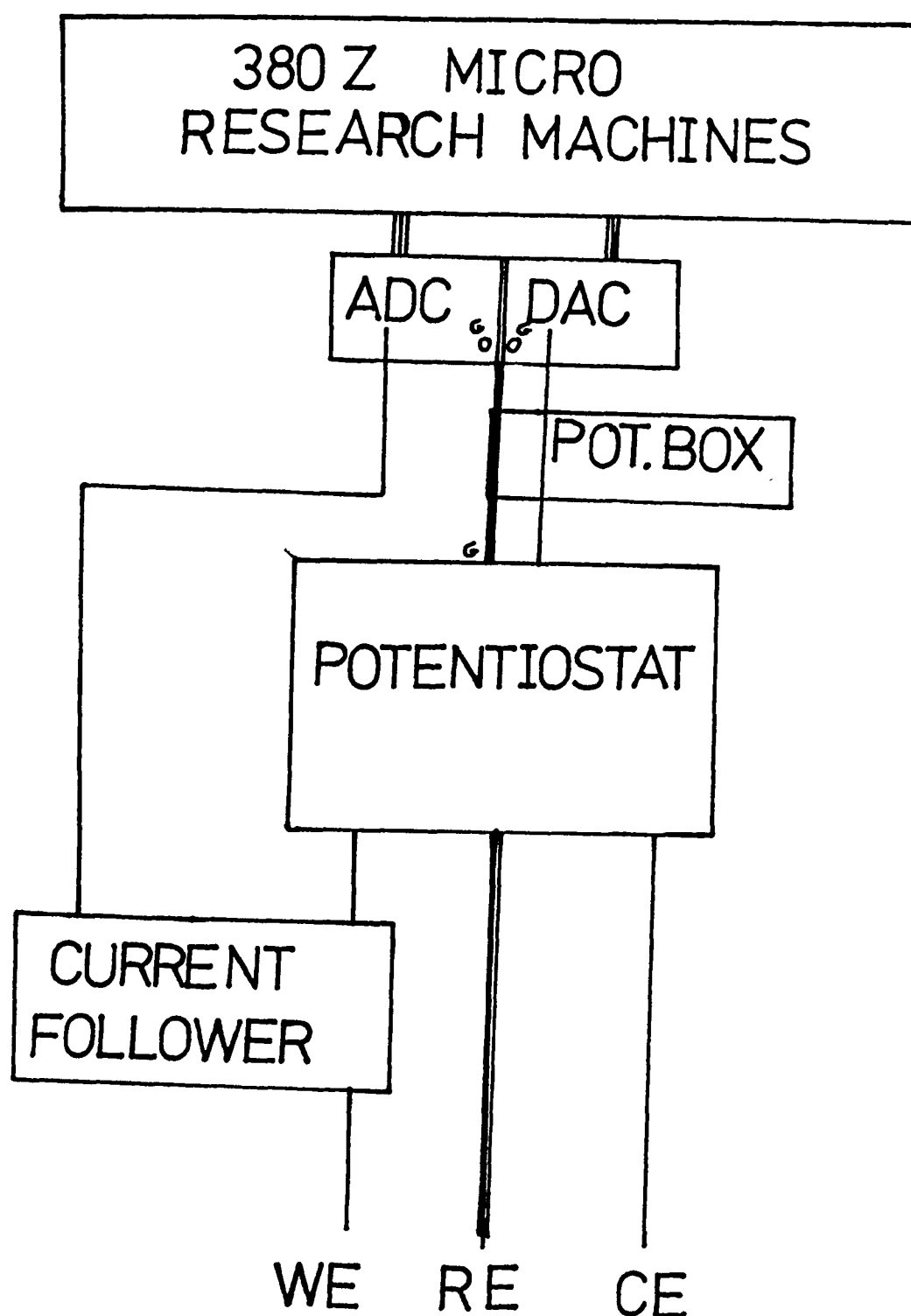


FIG 5.4

EPR TEST RIG SCHEMATIC

The 380Z micro-computer sends a digital signal to the digital to analogue converter (DAC). The DAC then sends an analogue signal to a potentiometer, and the resulting (offset) potential is fed to a potentiostat. Current is measured by a current follower circuit, the signal from which is fed to an analogue to digital converter (ADC) and then fed back to the micro-computer for data handling.

EPR TEST PARAMETERS

FIG 6.4

0.5M H₂SO₄ + 0.01M KSCN

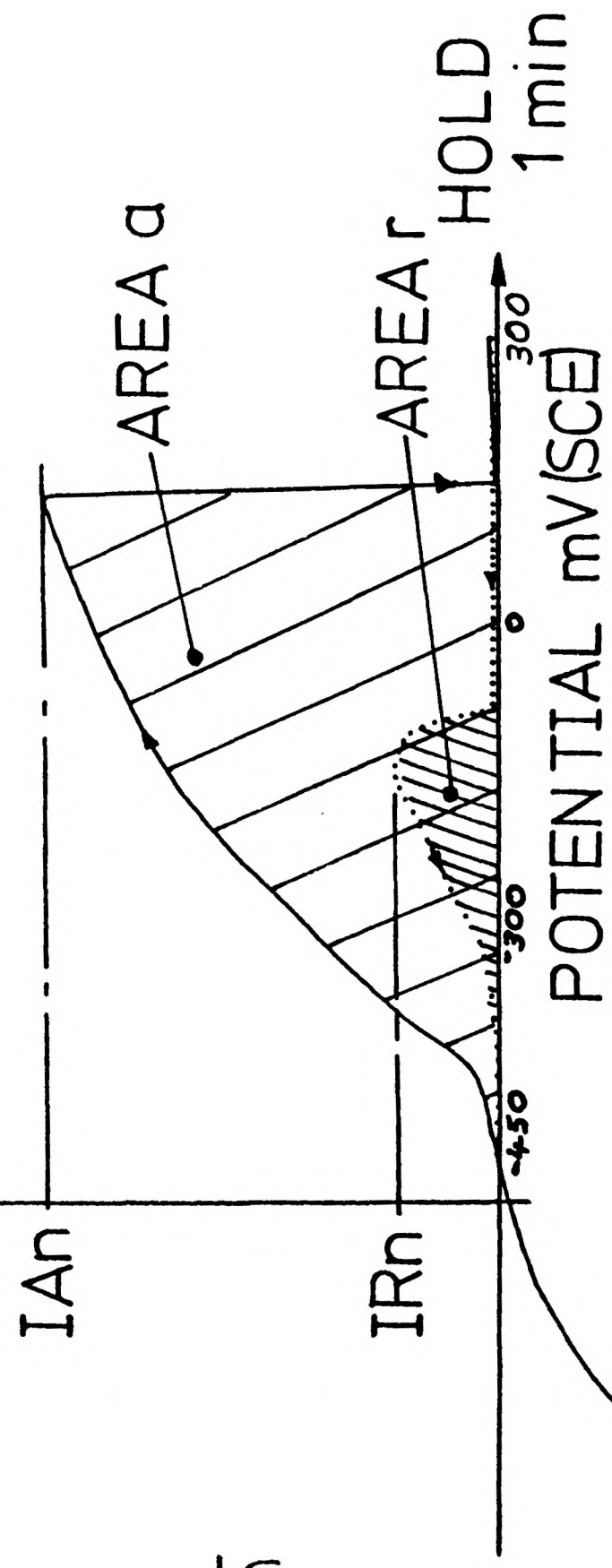
SCAN RATE 100mV/min

SCAN +300 → -450mV

CURRENT mA/cm²

$$Pa = \frac{a}{r}$$

$$Ia = \frac{I_{An}}{I_{Rn}}$$

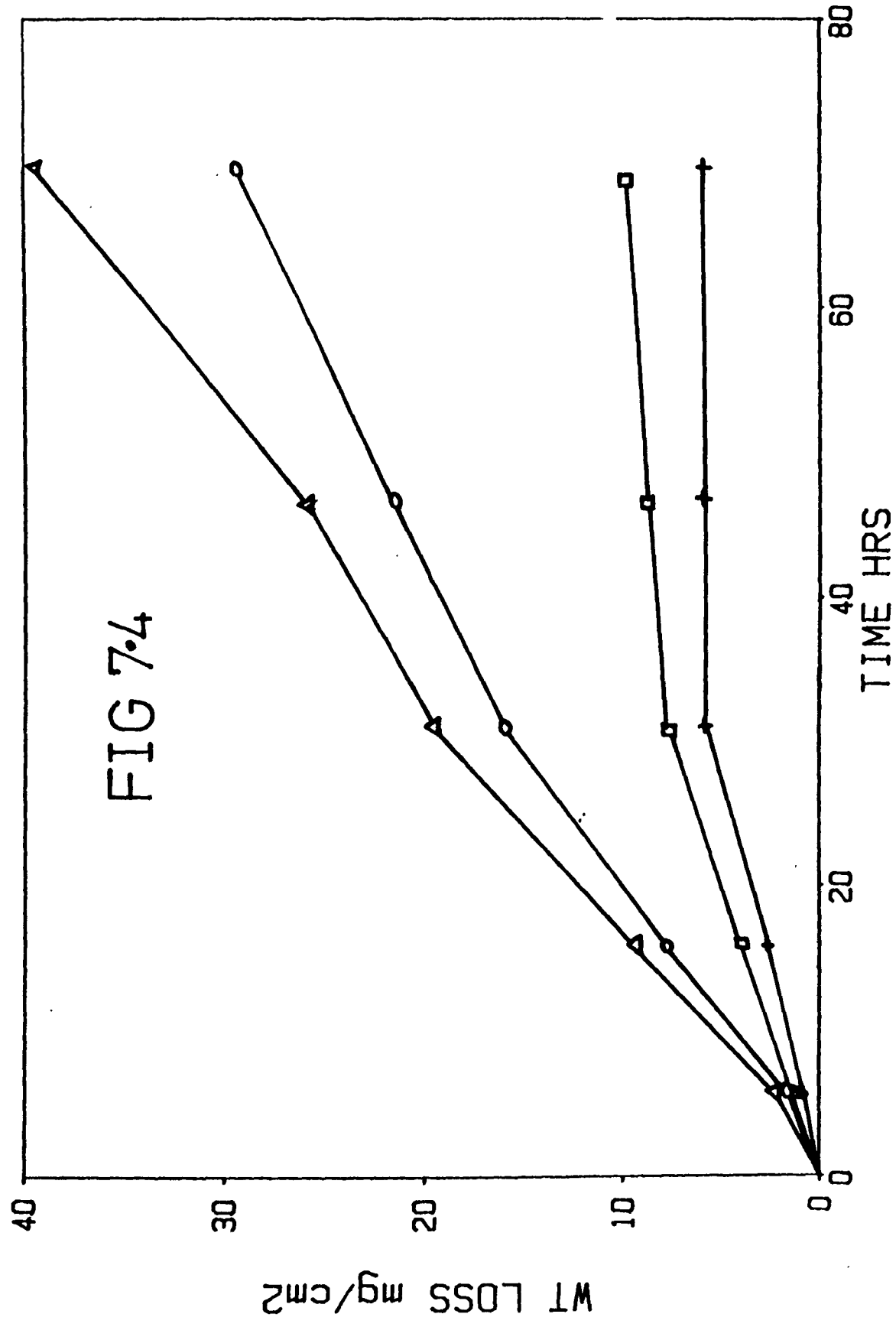


Test Parameters used for Electro Potentiodynamic Reactivation (EPR) tests.

Cr VI+ / HNO₃ weight loss tests

TUBE MATERIAL K₂Cr₂O₇/HNO₃

- + AR
- o 1050'C 30 min
- Δ " + 550'C 500 hrs
- " + 750'C 30 min



Cr VI+ / HNO₃ weight loss tests.
 BAR MATERIAL K₂Cr₂O₇/HNO₃

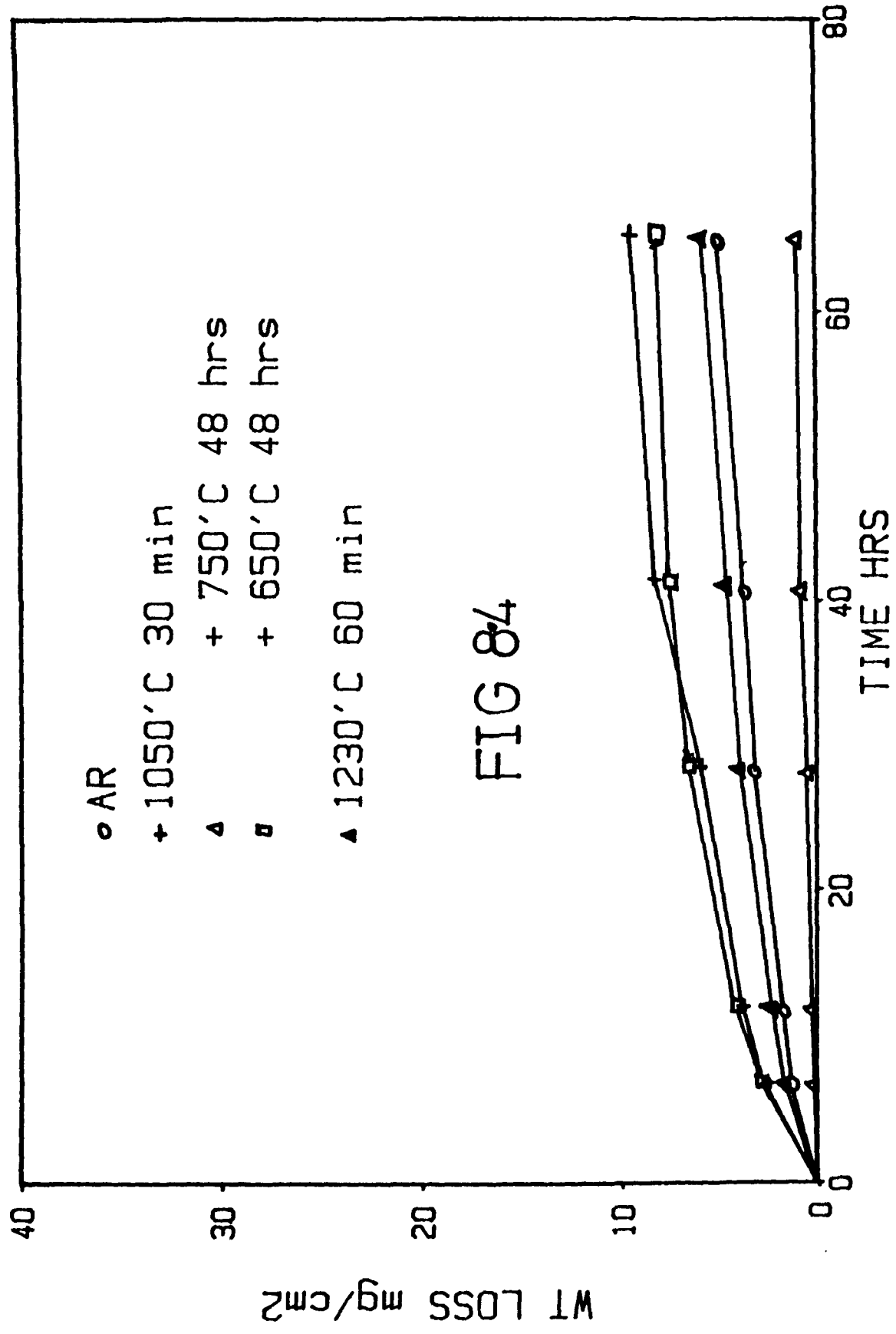
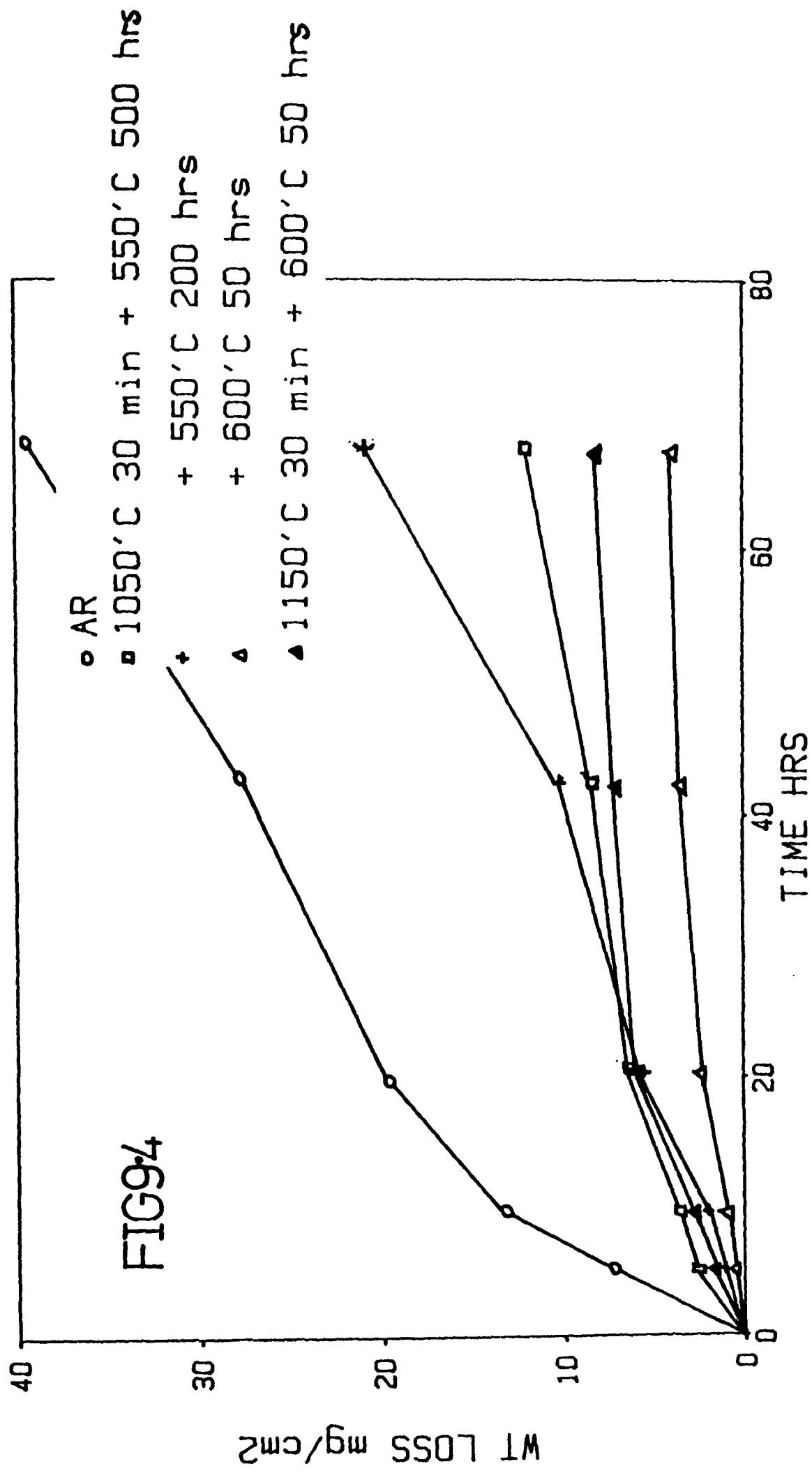


FIG 84

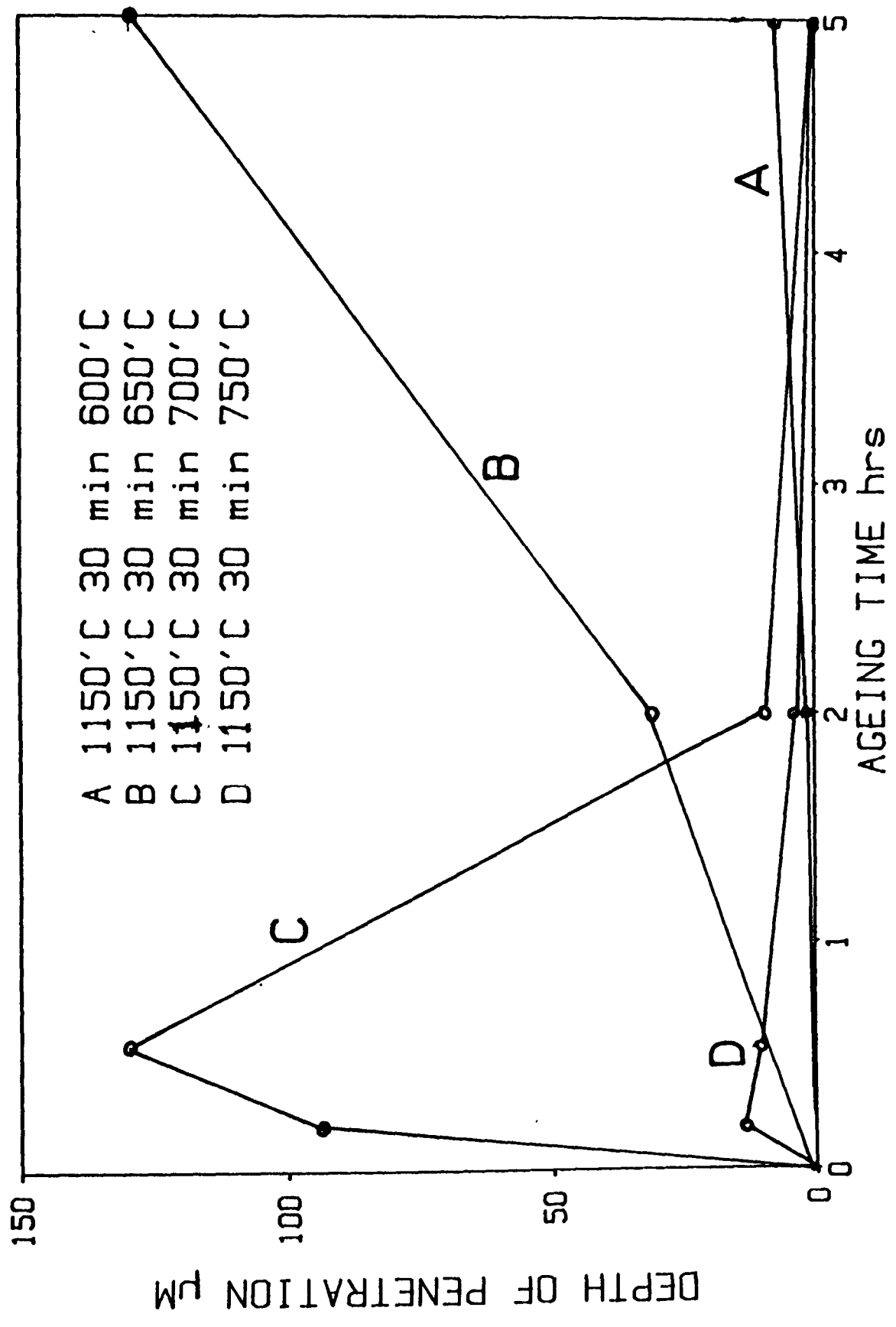
Cr VI+ / HNO₃ weight loss tests.

REWORKED BAR MATERIAL K₂Cr₂O₇/HNO₃



Depth of penetration in 72 hours Strauss testing.

FIG10.4 TUBE STRAUSS TEST DATA



Depth of penetration in 72 hours Strauss testing.

FIG 11.4 TUBE STRAUSS TEST DATA

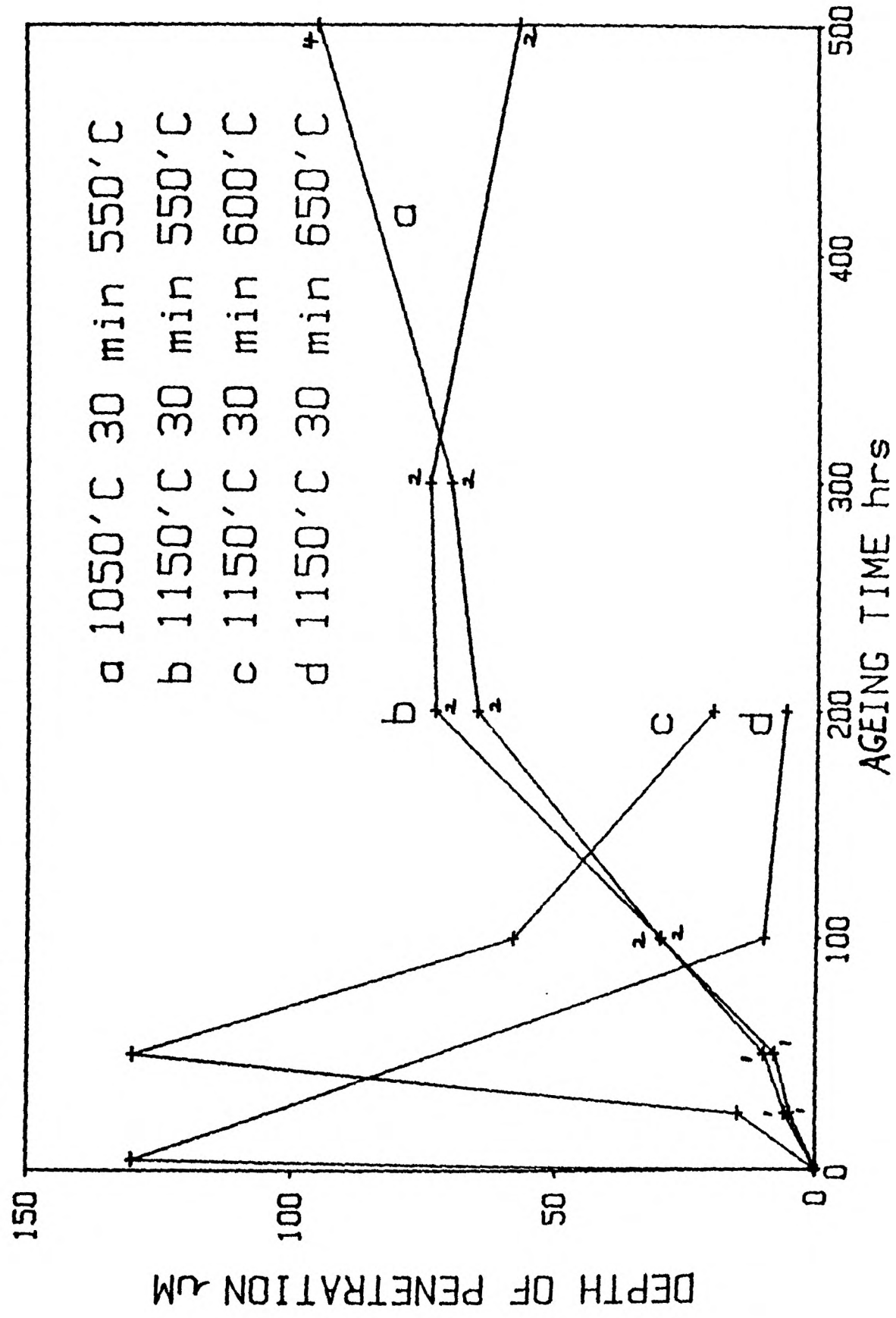
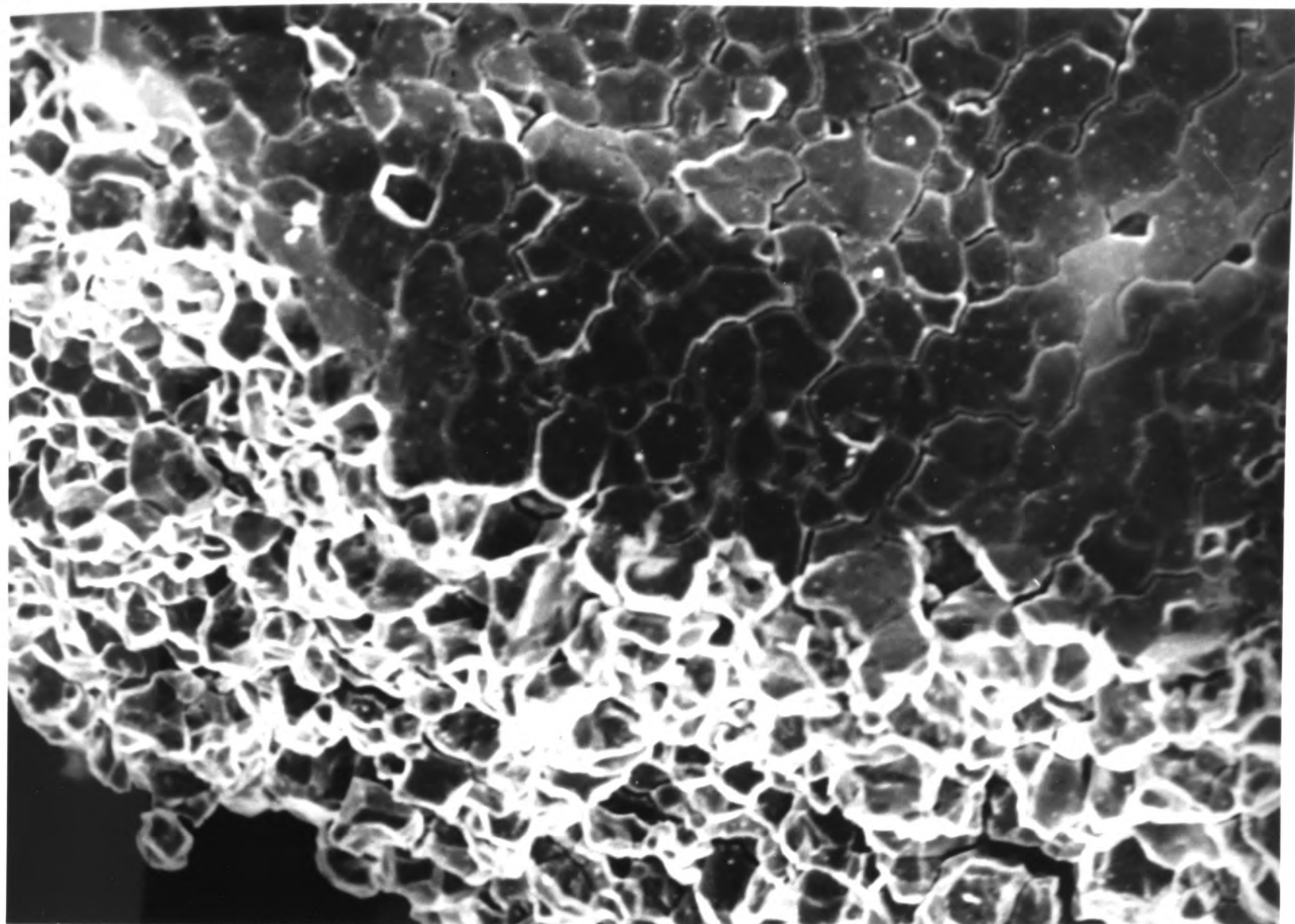


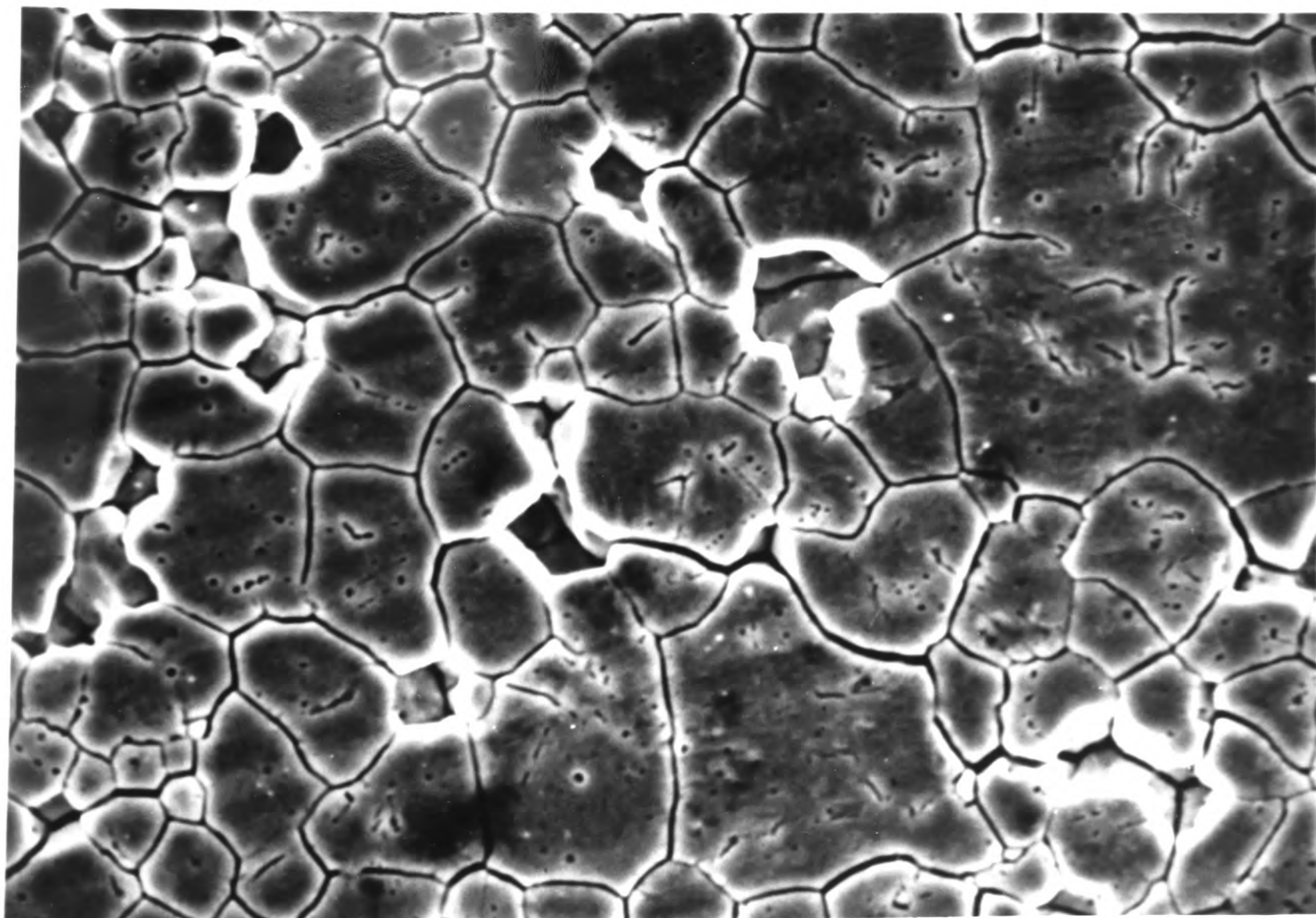
Figure 12.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes and then aged for 600'C for 50 hours and Strauss tested for 24 hours.



A

30 μm



B

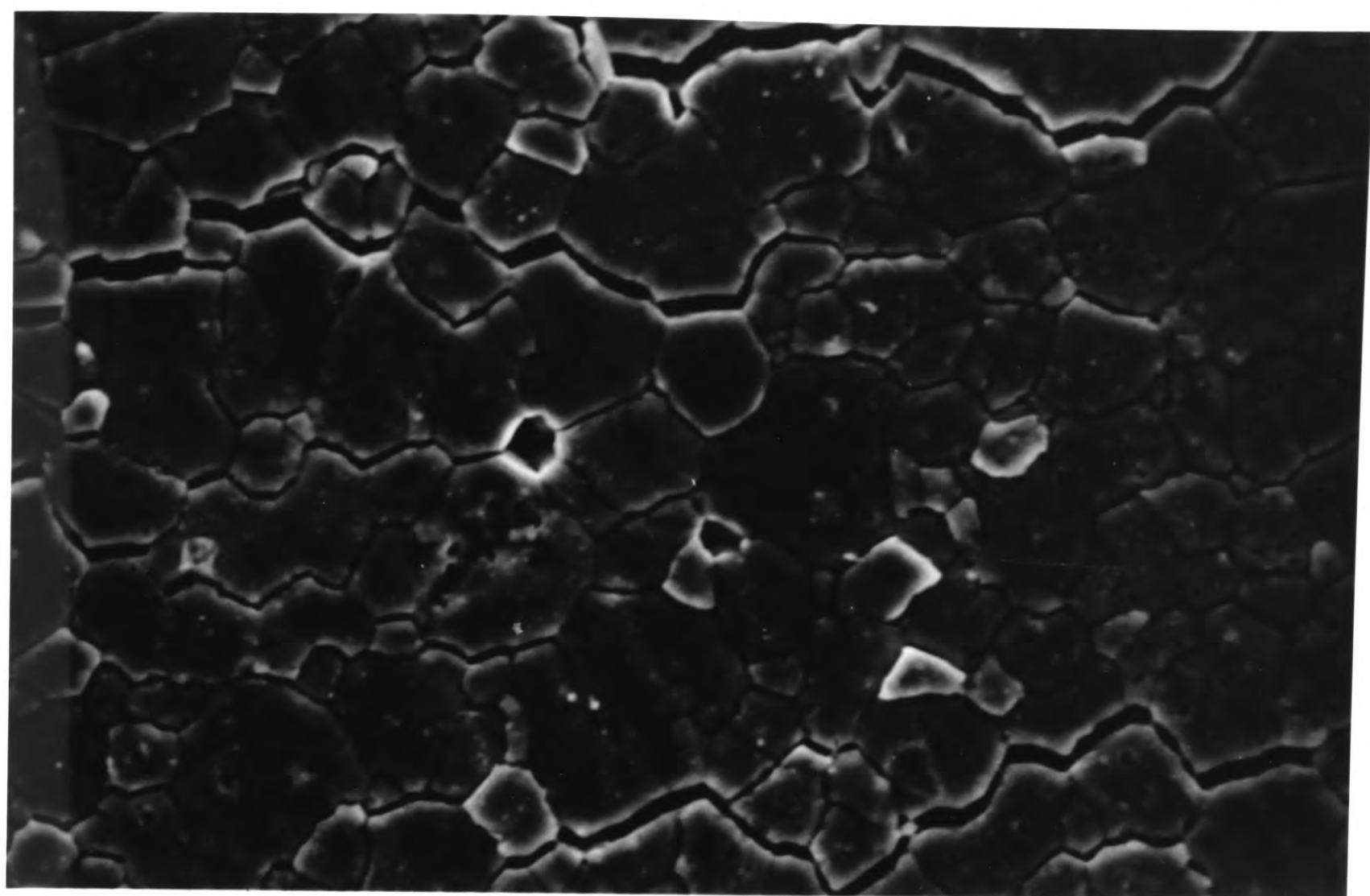
20 μm

Figure 13.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes and then aged for 550'C for 500 hours and Strauss tested for

A. 24 hours.

B. 72 hours.



A

25 μm

B

10 μm

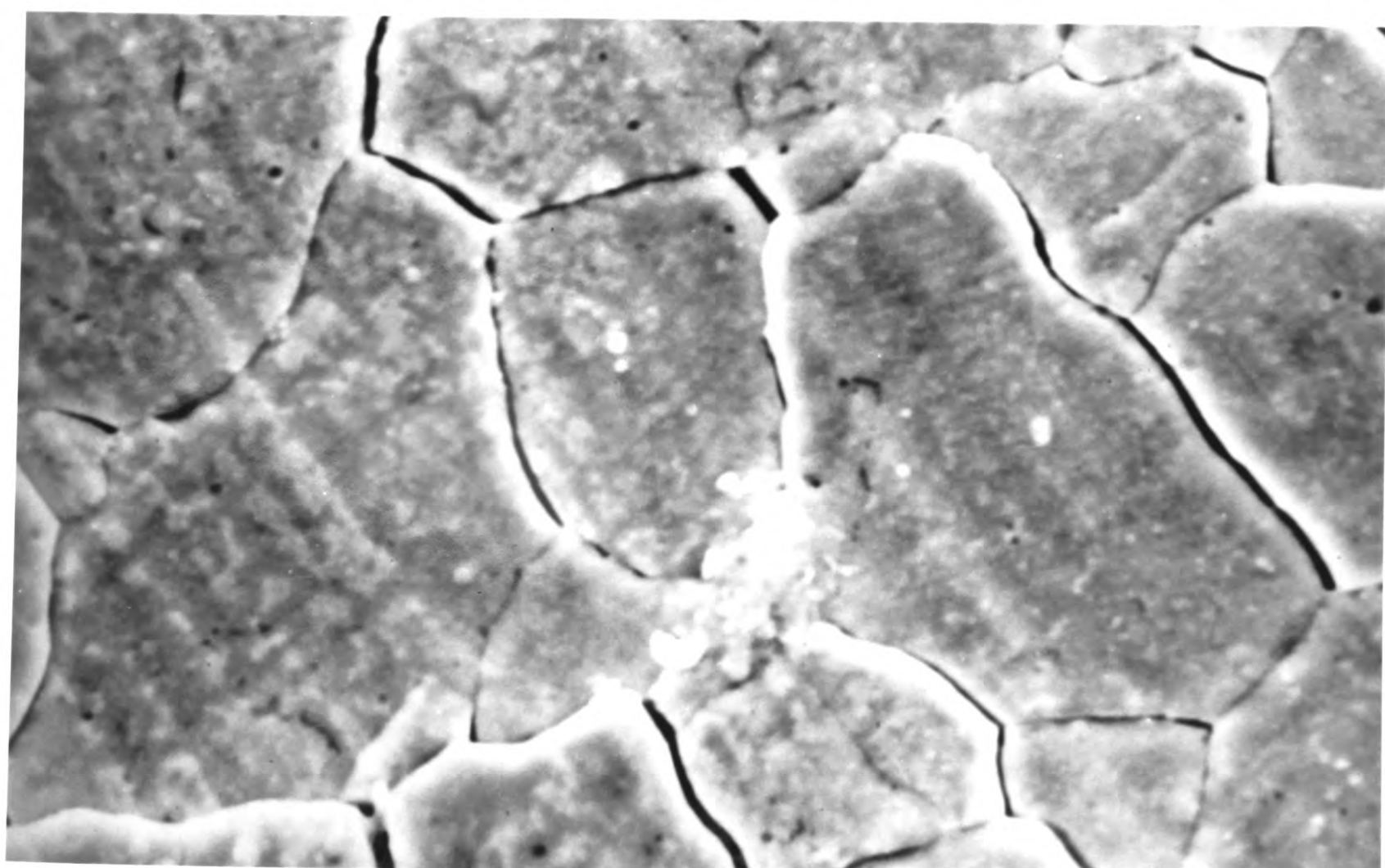
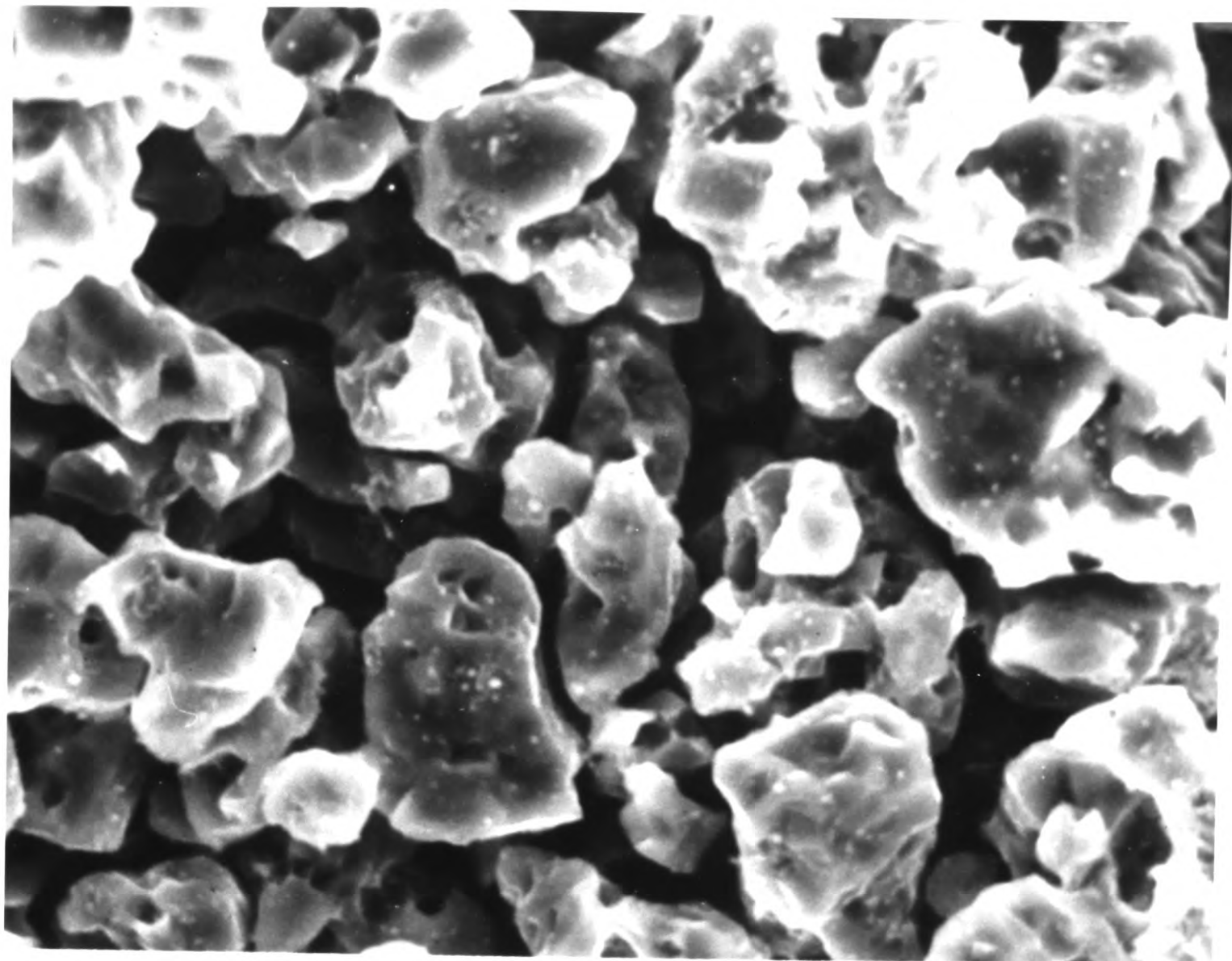


Figure 14.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes and then aged for 650'C for 5 hours and Strauss tested for

A. 24 hours.

B. 72 hours.

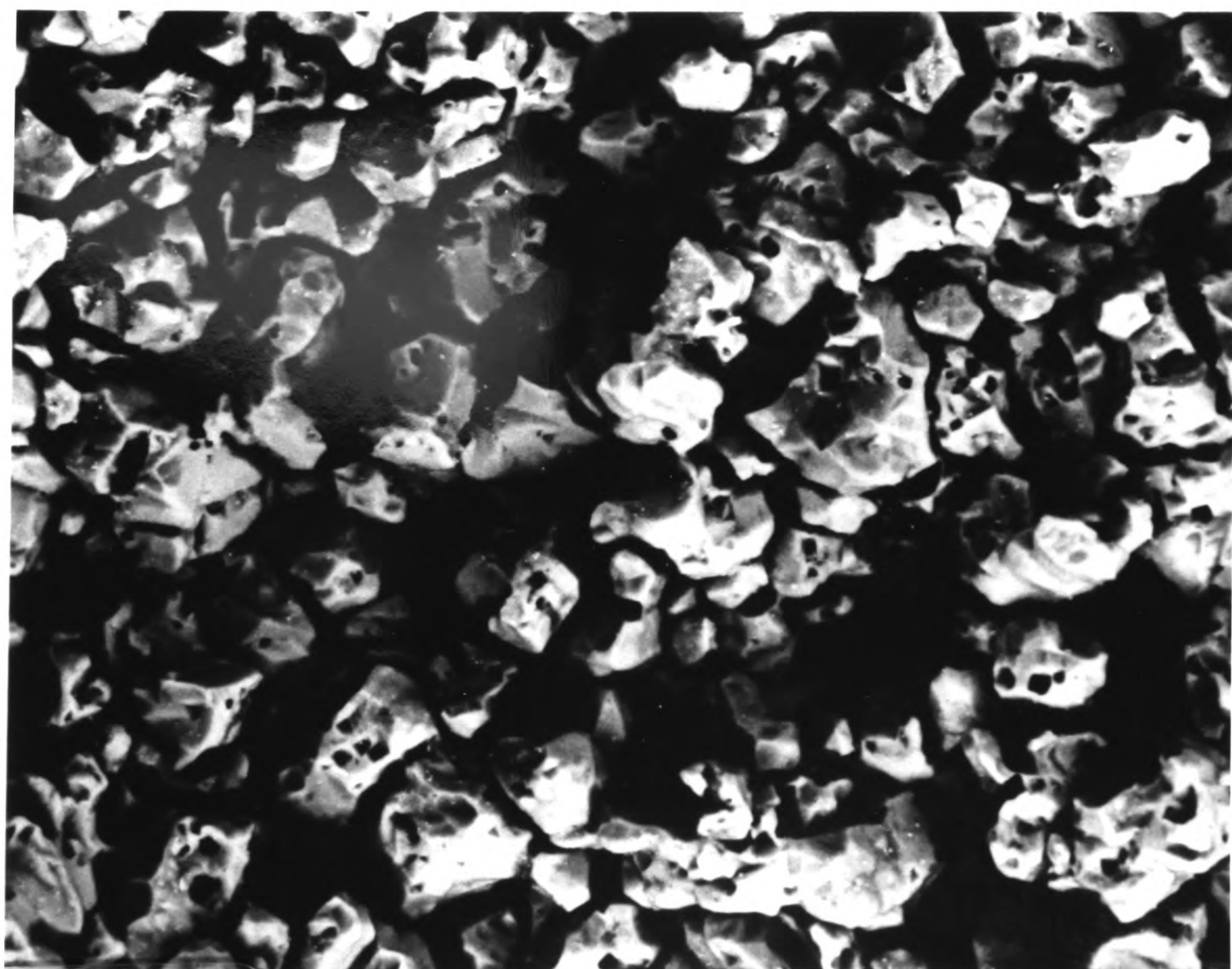


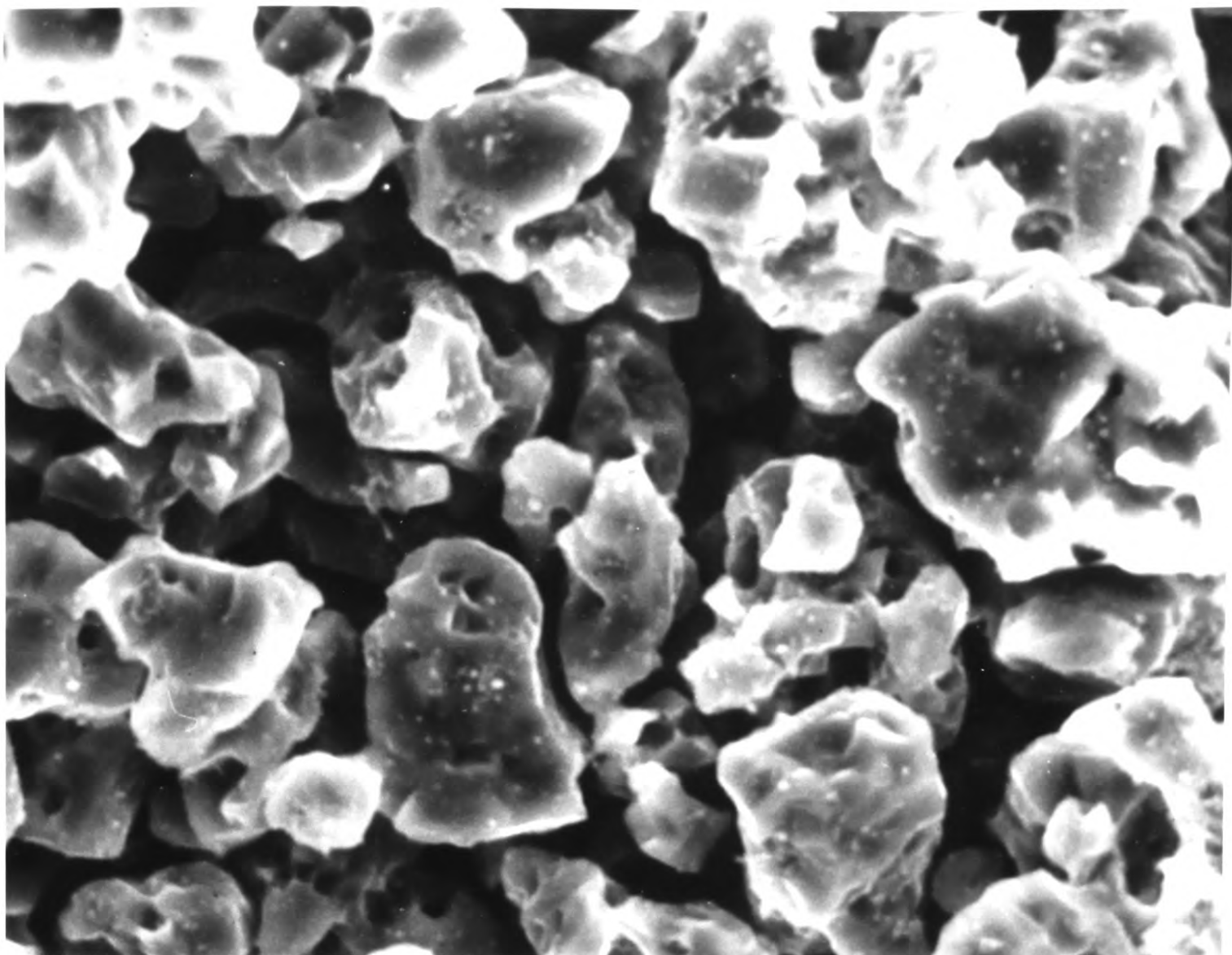
A

15 μm

B

10 μm





A

15 μm

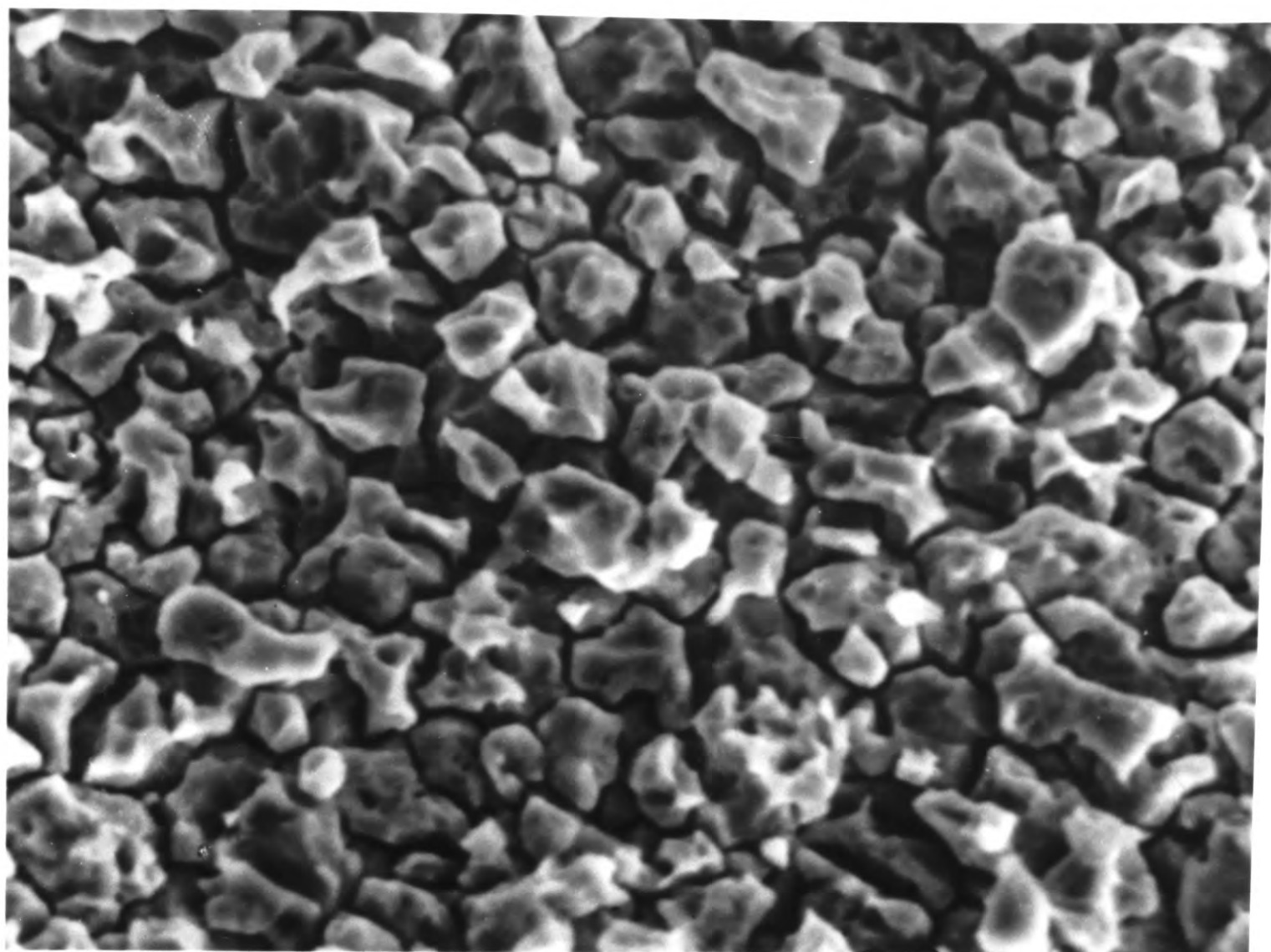
B

10 μm



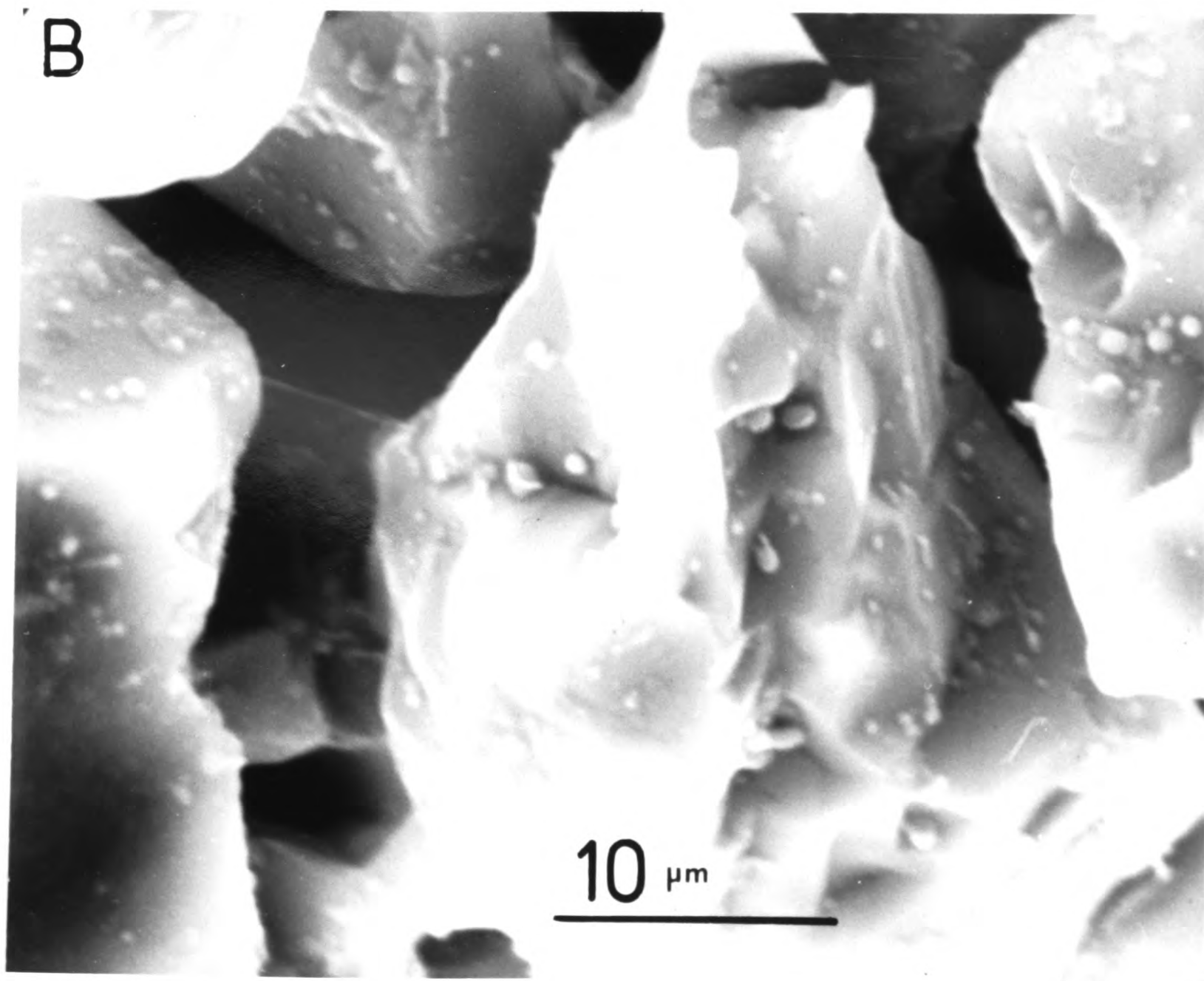
Figure 15.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes and then aged for 600'C for 100 hours and Strauss tested for 72 hours.



A

20 μm



10 μm

Change of depth of penetration with time, during a Strauss test, for material heat treated by a 1050°C anneal followed by 500 hours at 550°C.

STRAUSS TEST DATA

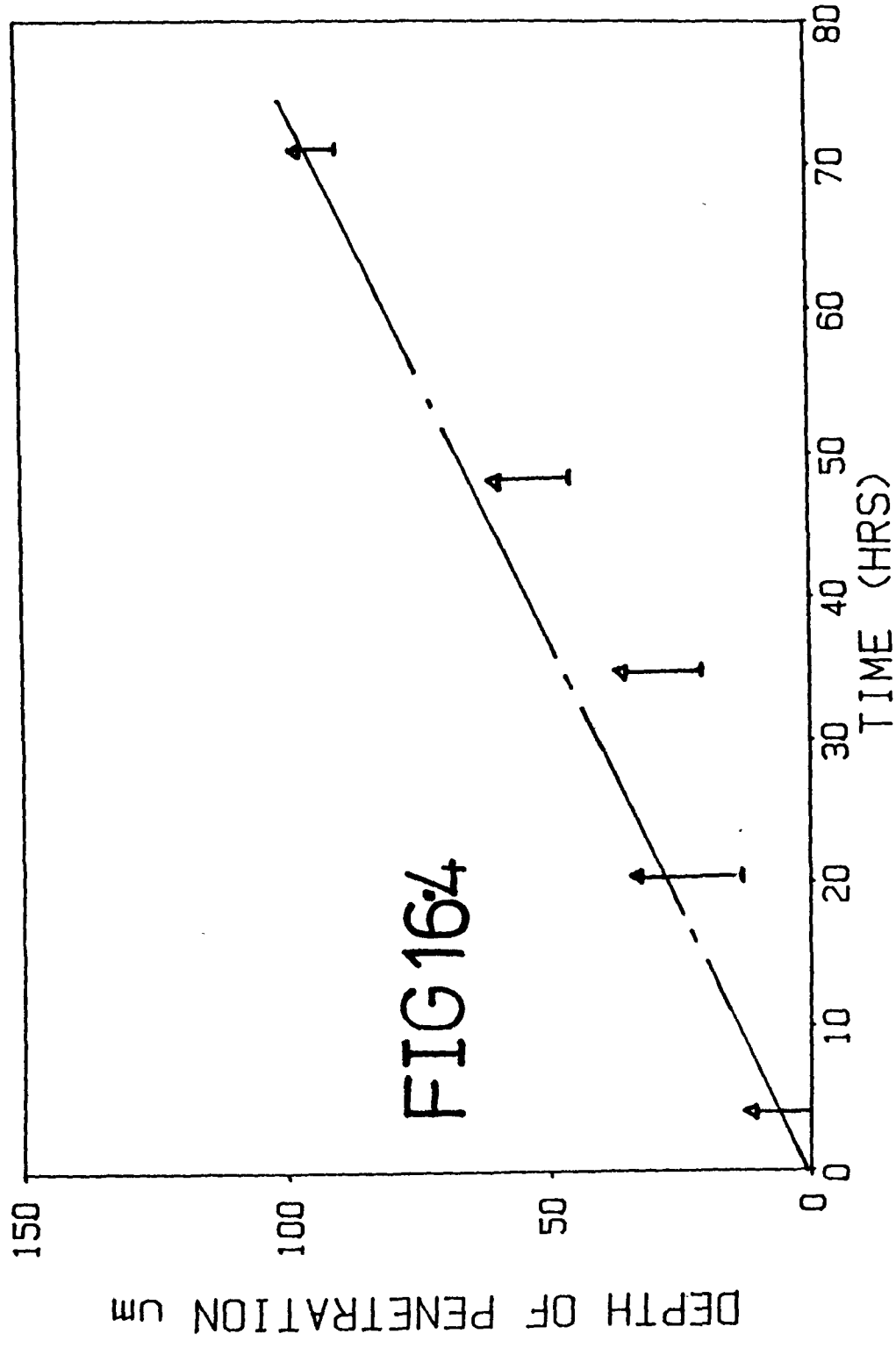


Figure 17.4

SEM micrograph of the fracture surface of (A) tube and (B) bar material annealed at 1150°C for 30 minutes and then aged for 600°C for 100 hours and Strauss tested for 72 hours.

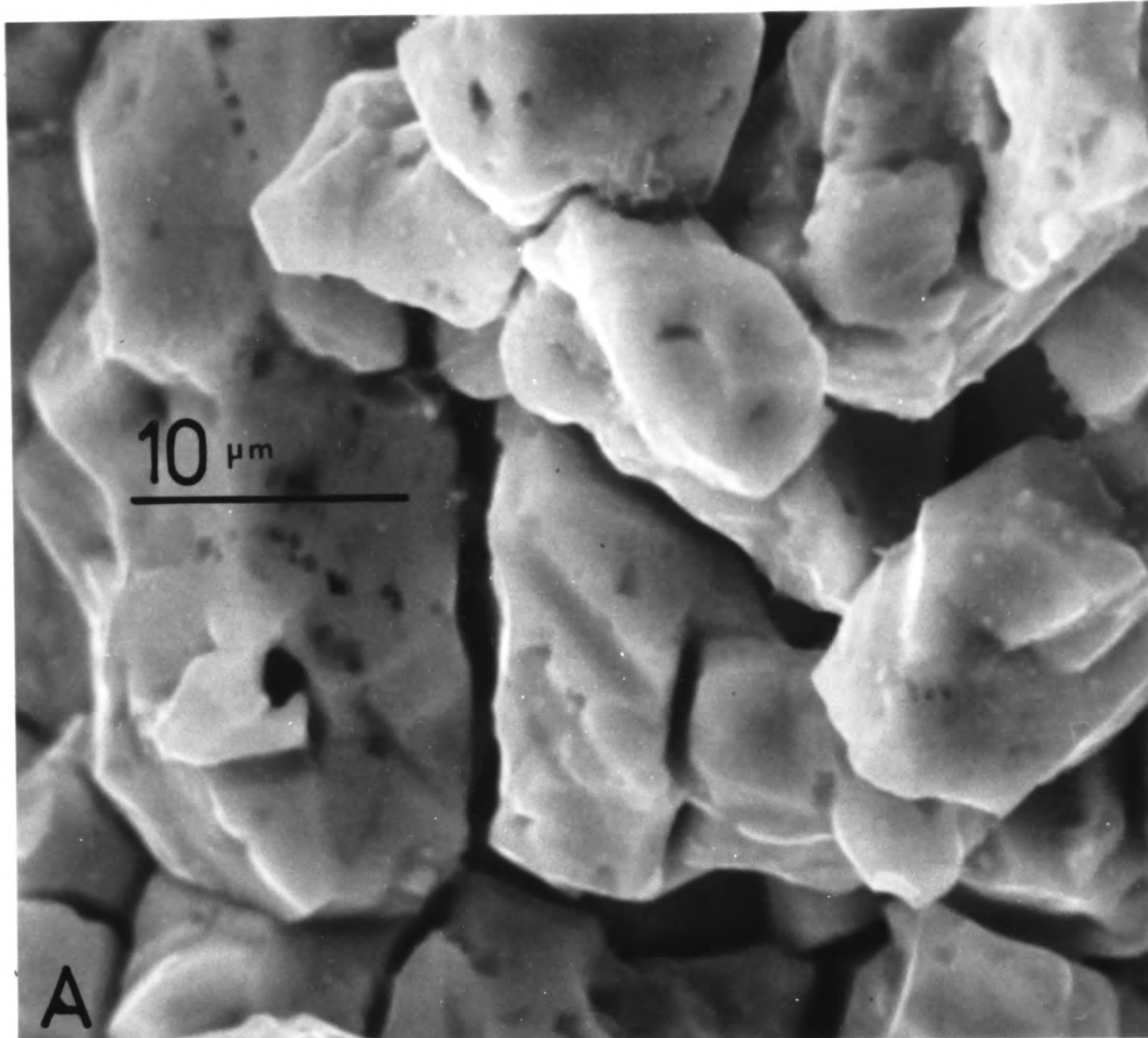


Figure 18.4

SEM micrograph of the surface of tube specimens after Oxalic acid electrolytic etch tests. Specimen annealed at 1050'C for 30 minutes then aged at

A. 600'C for 50 hours and etched at 1.2 V for 10 minutes .

B. 550'C for 500 hours and etched at 3 V for 10 minutes ..

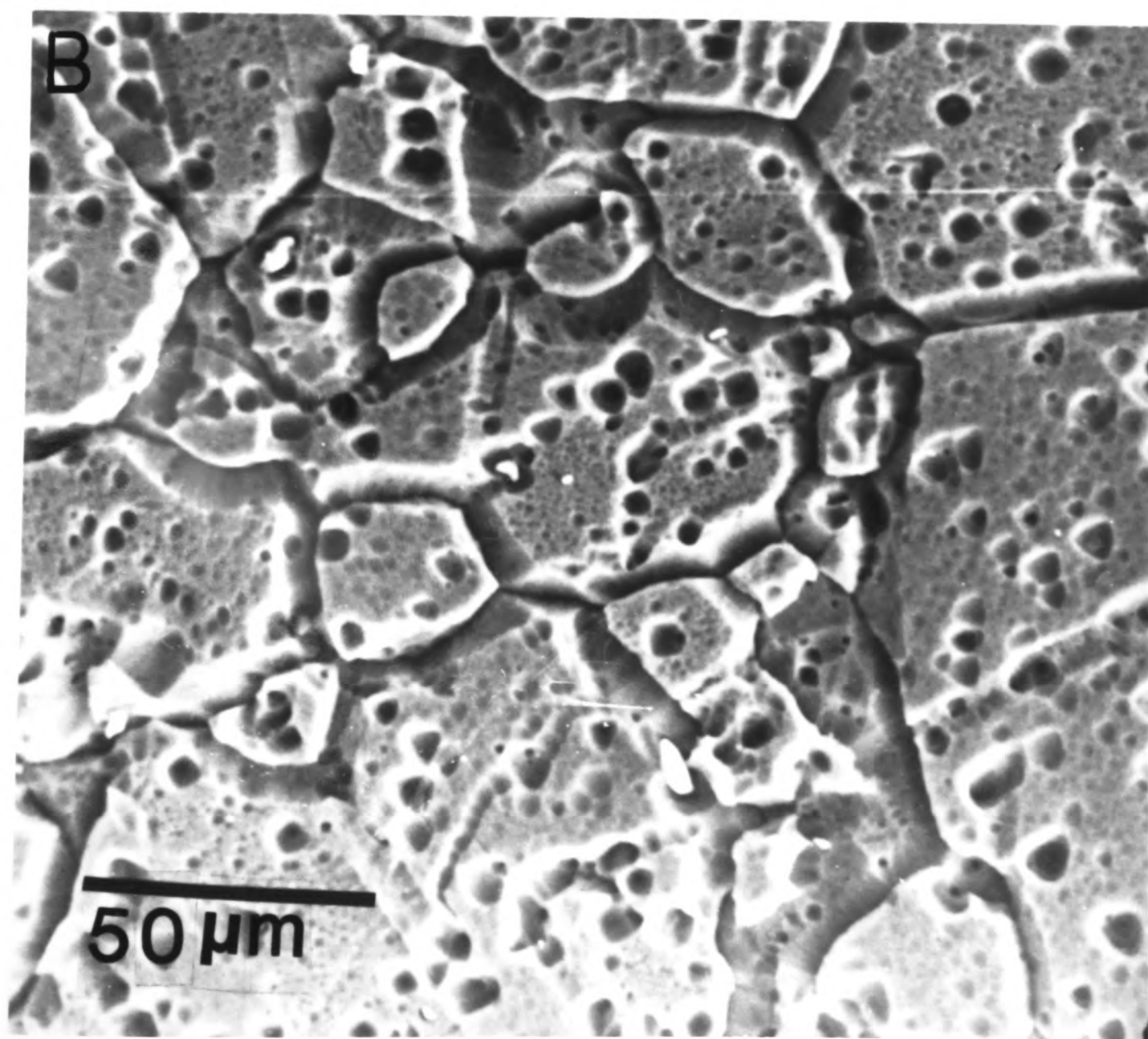
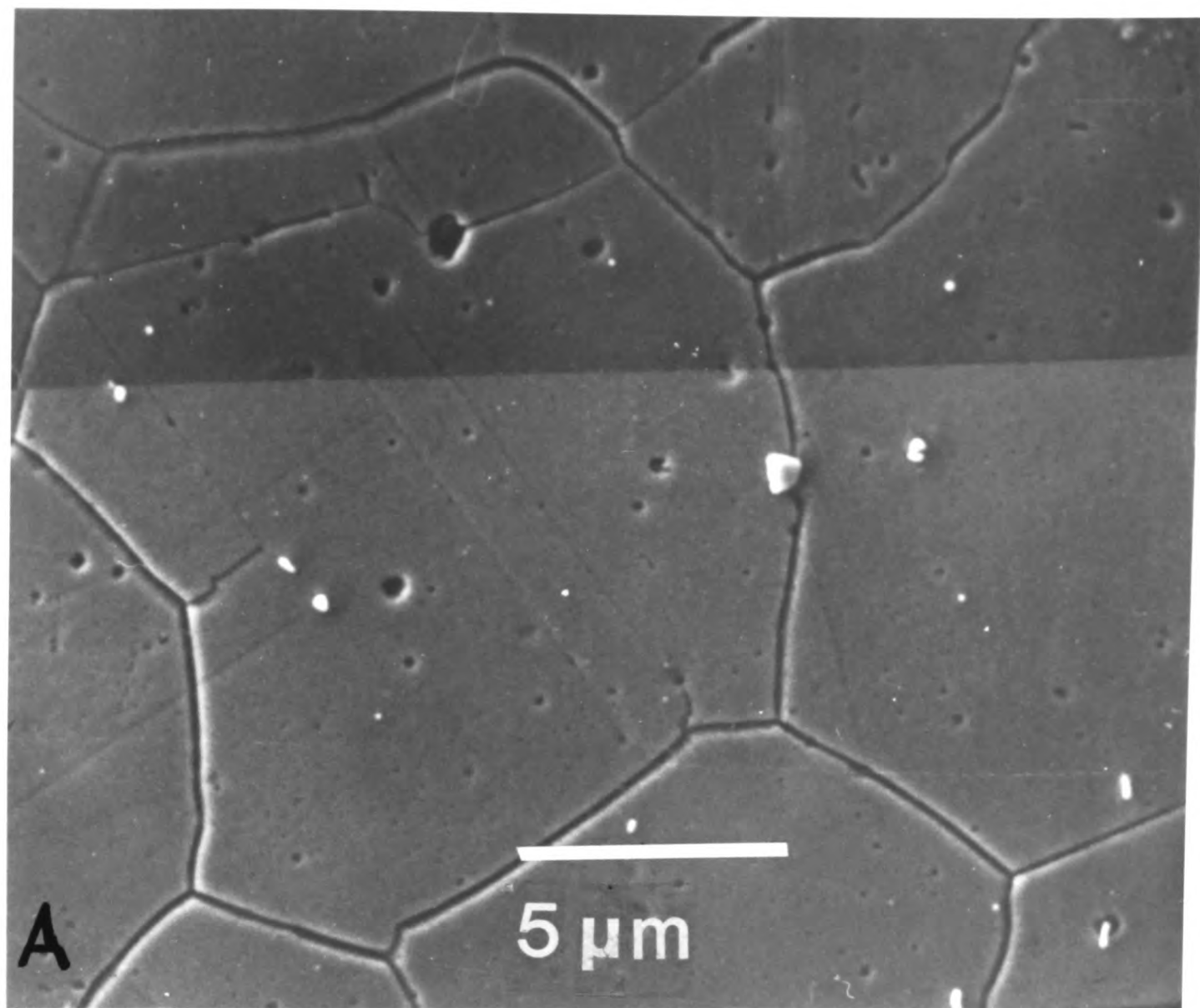
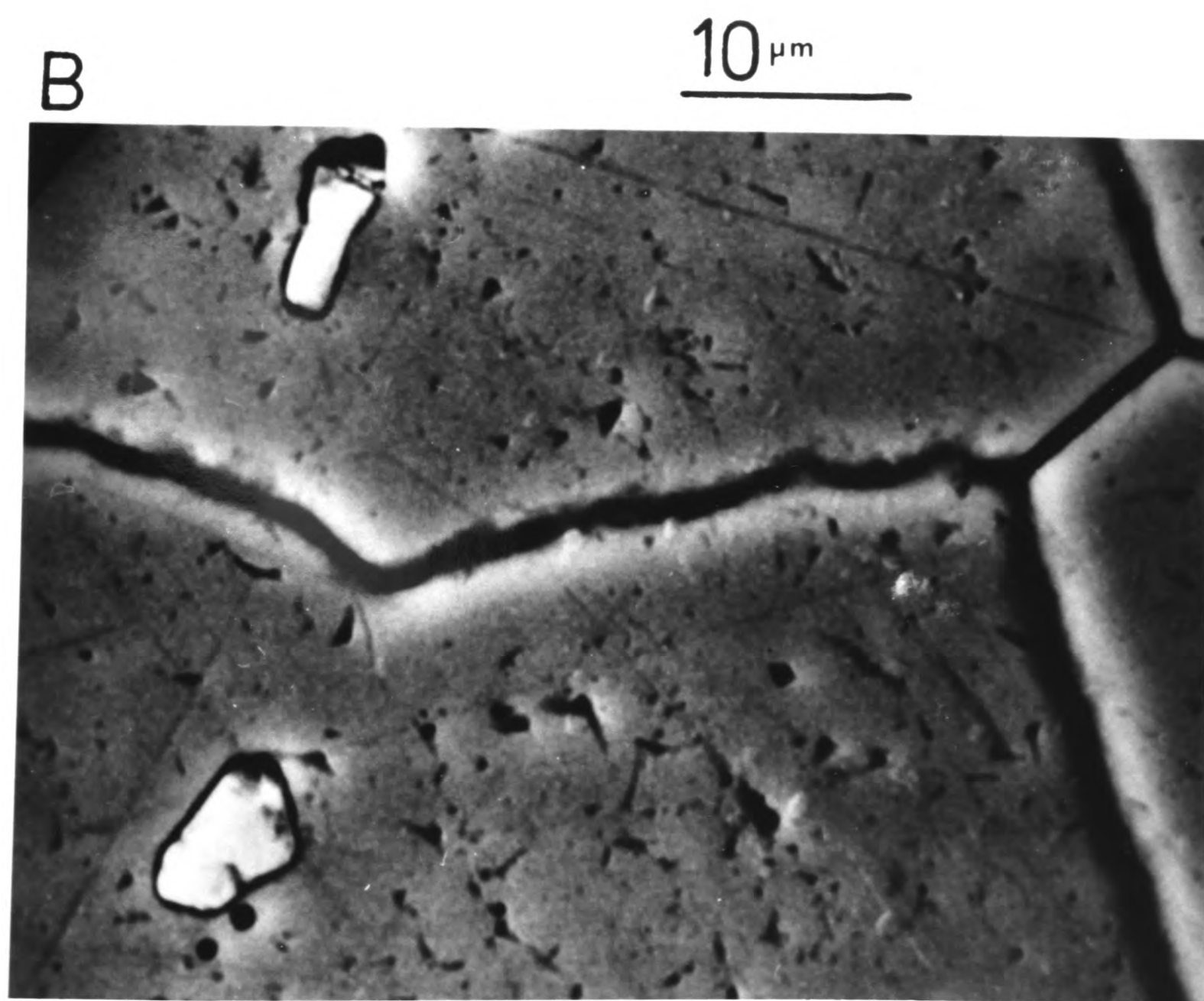
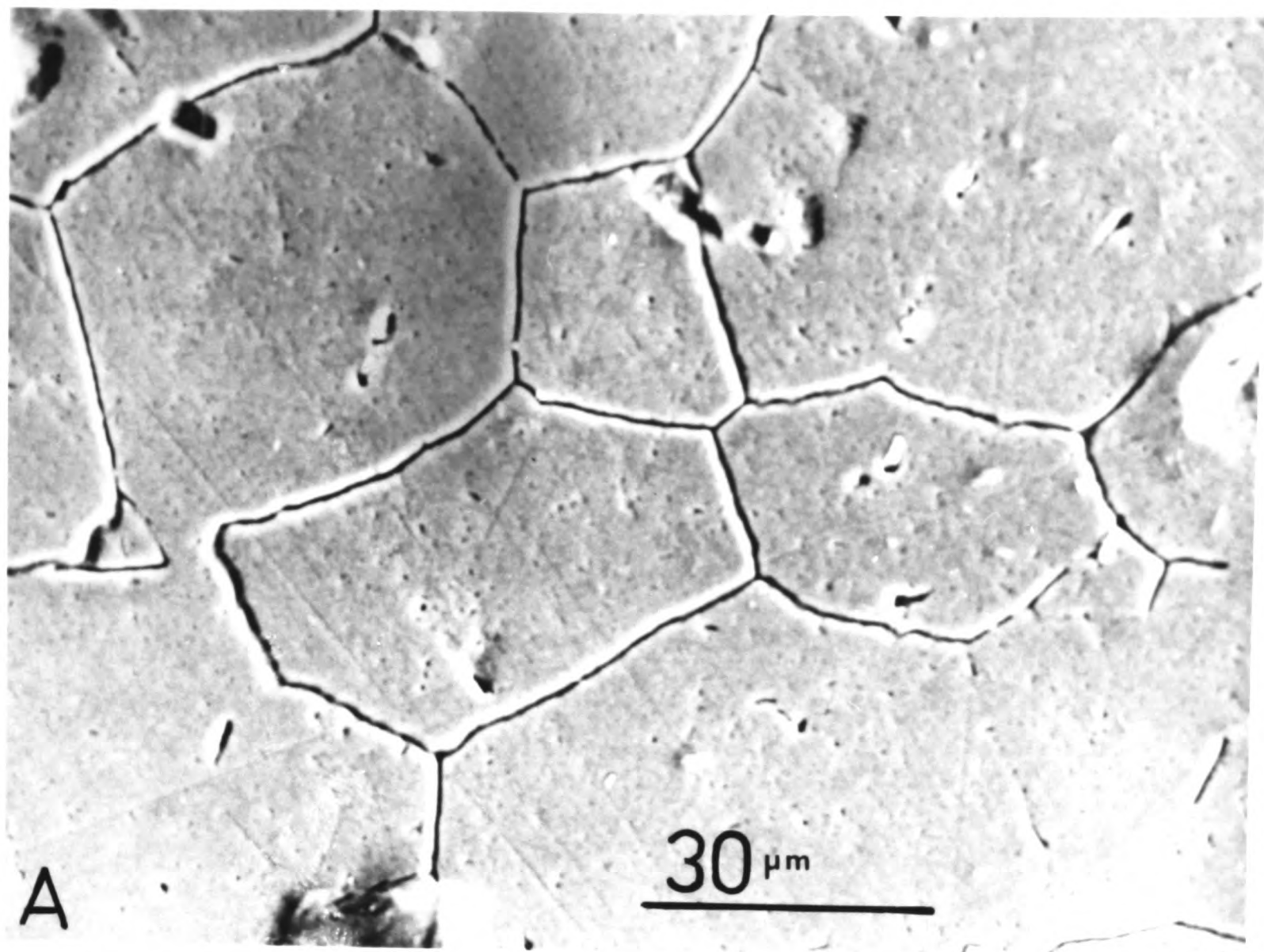
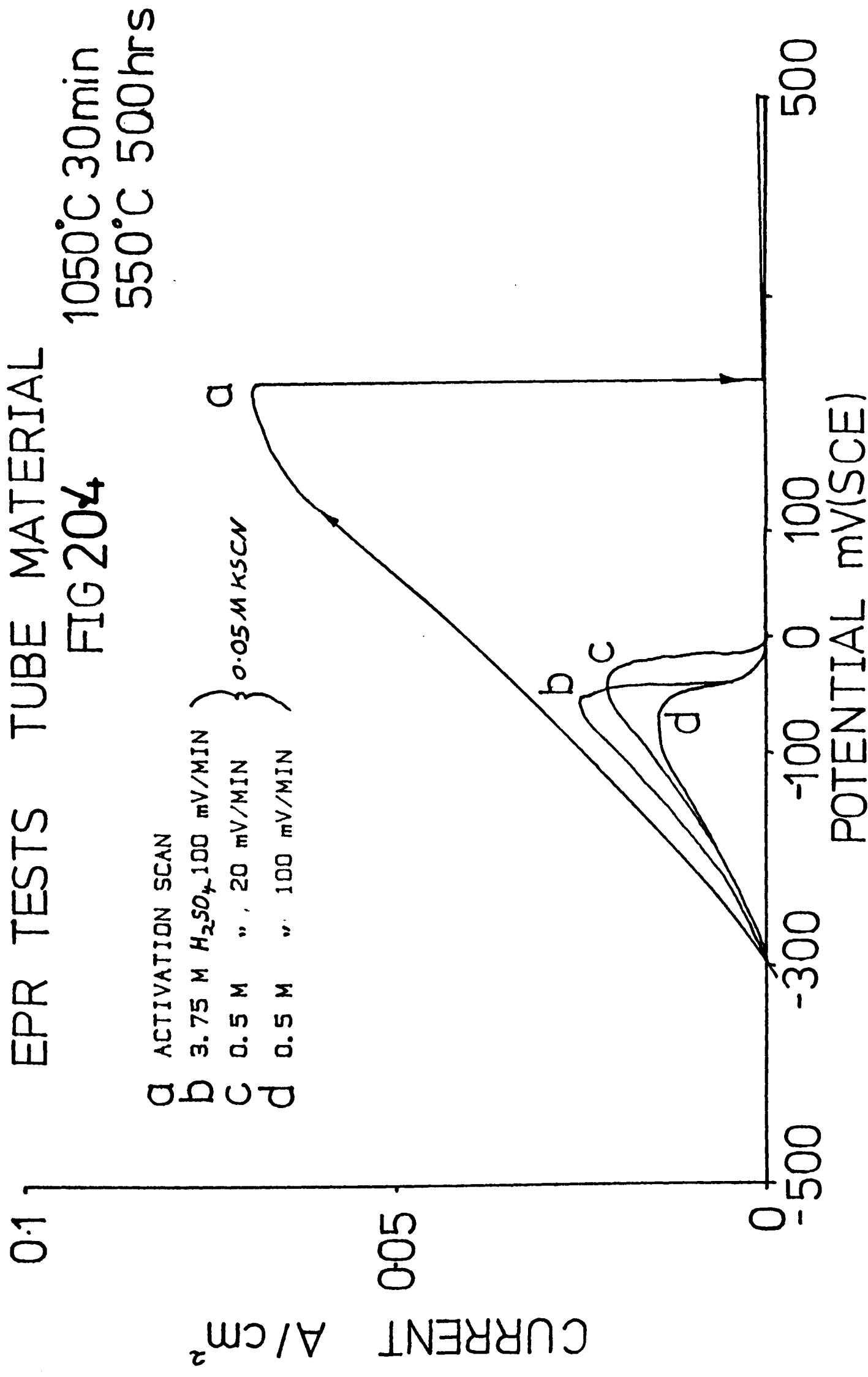


Figure 19.4

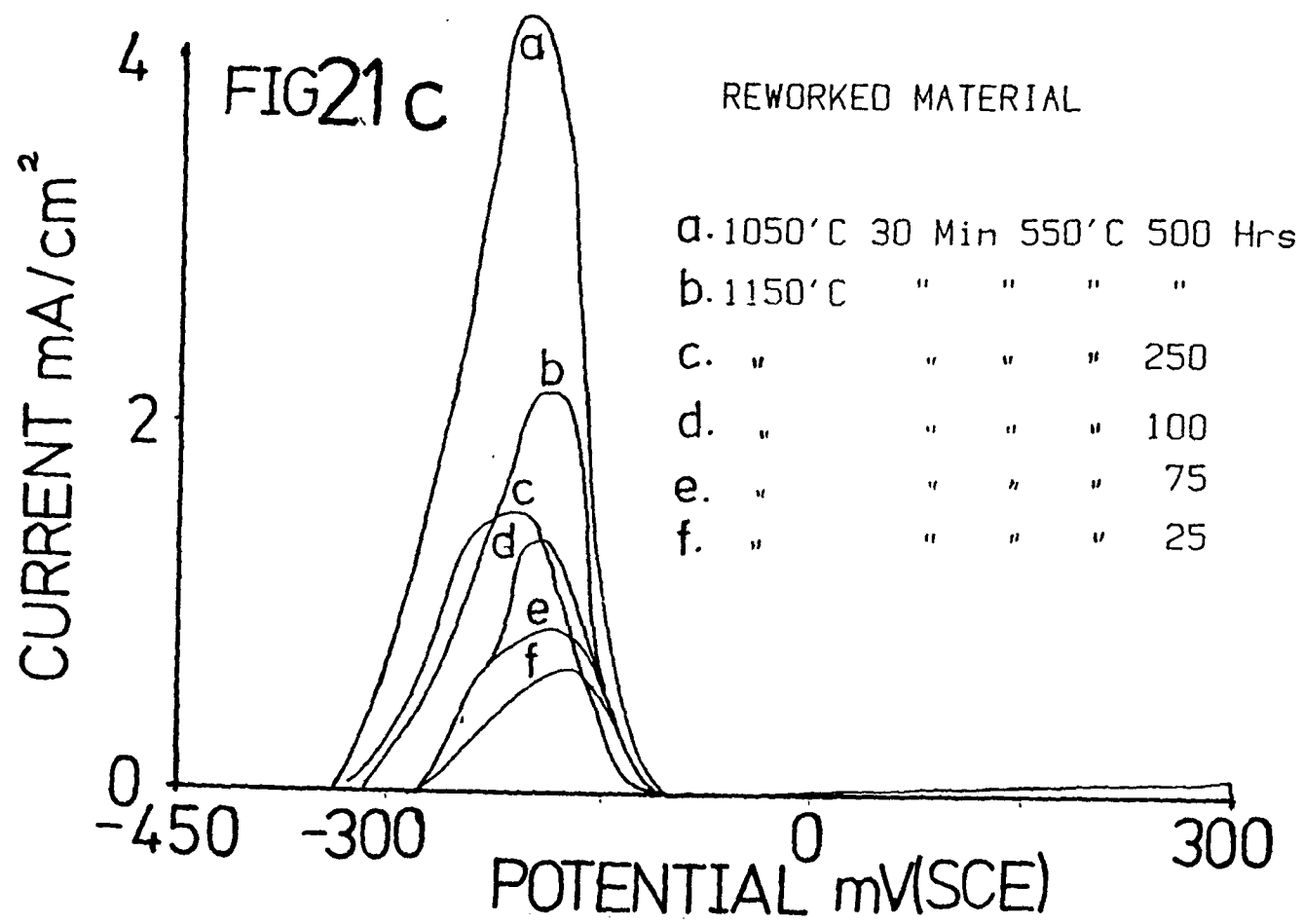
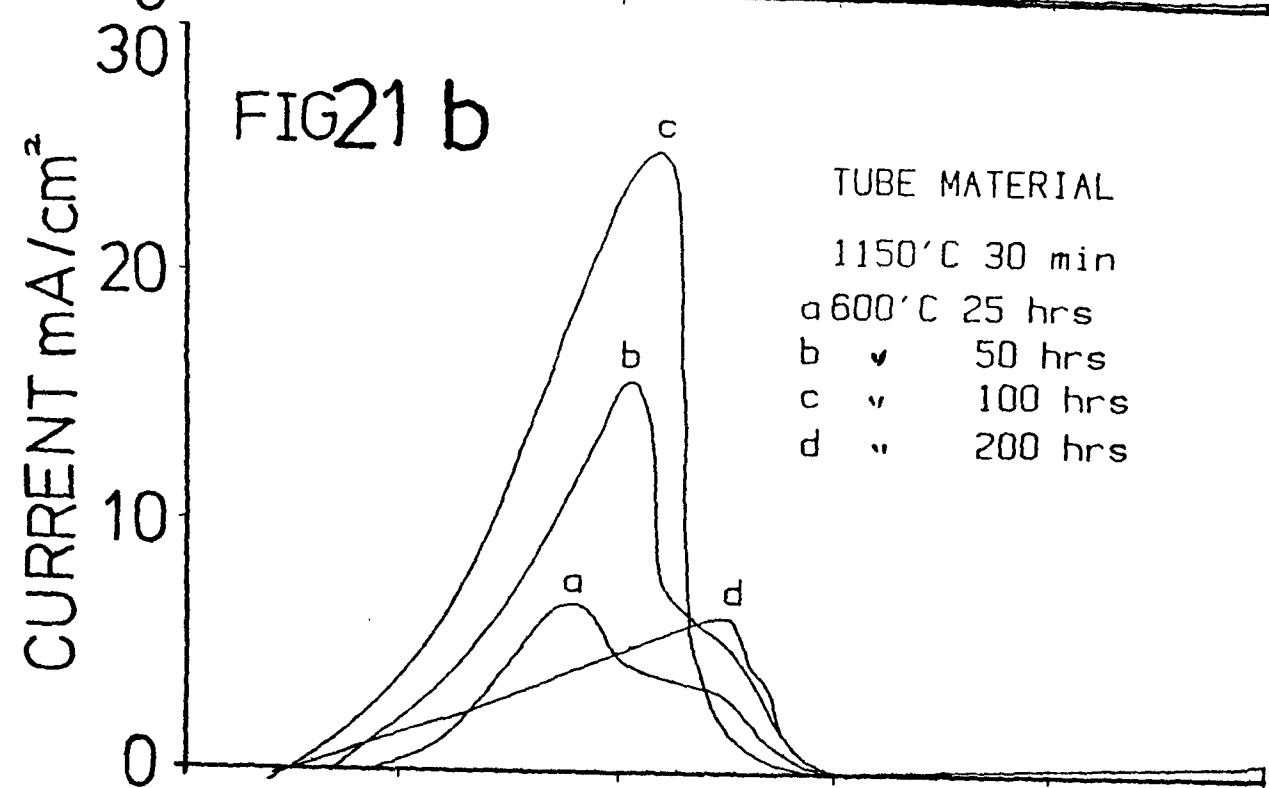
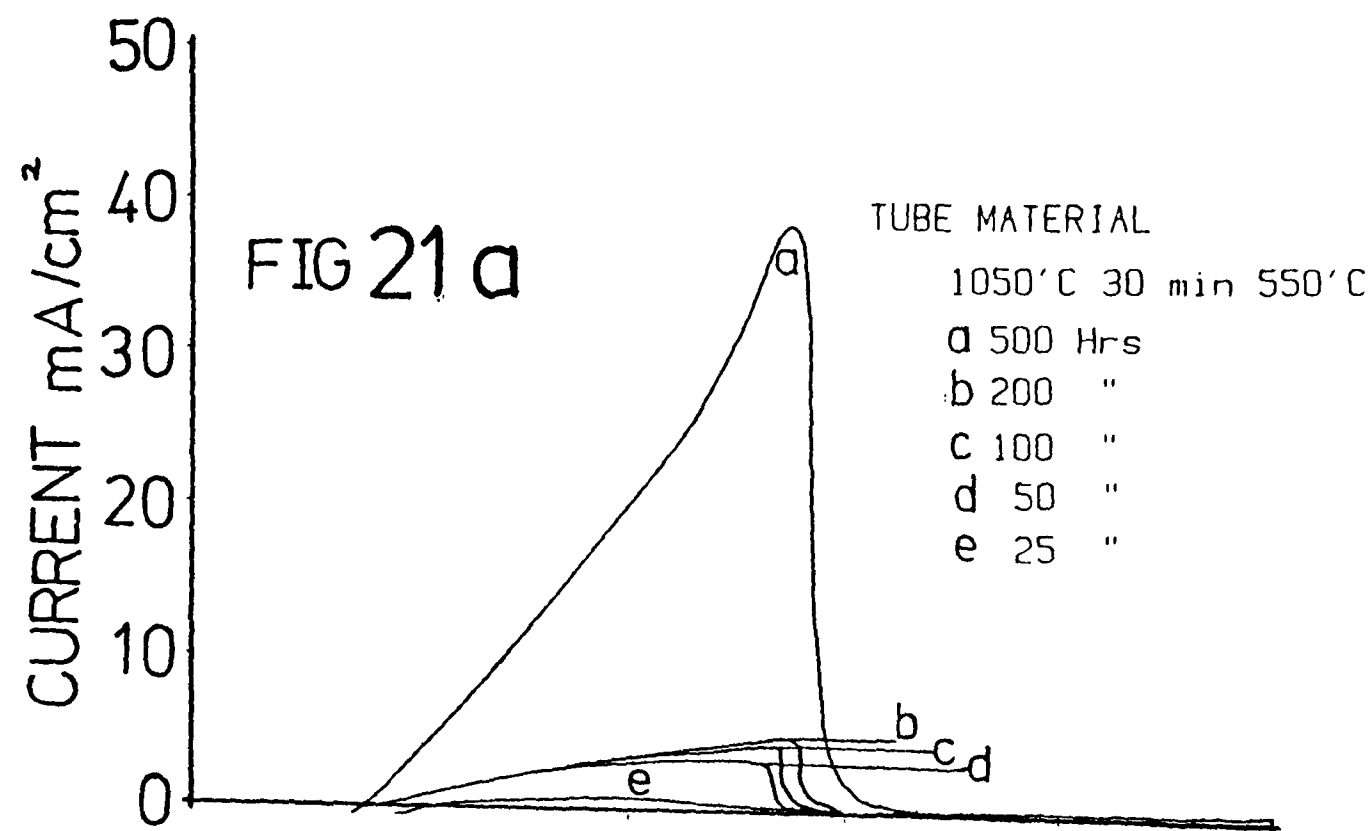
SEM micrograph of the surface of tube specimens after Oxalic acid electrolytic etch tests. Specimen annealed at 1150°C for 30 minutes then aged at 600°C for 5 hours. Etching at 0.8 V for 10 minutes.



Effect of test variables on EPR test results.

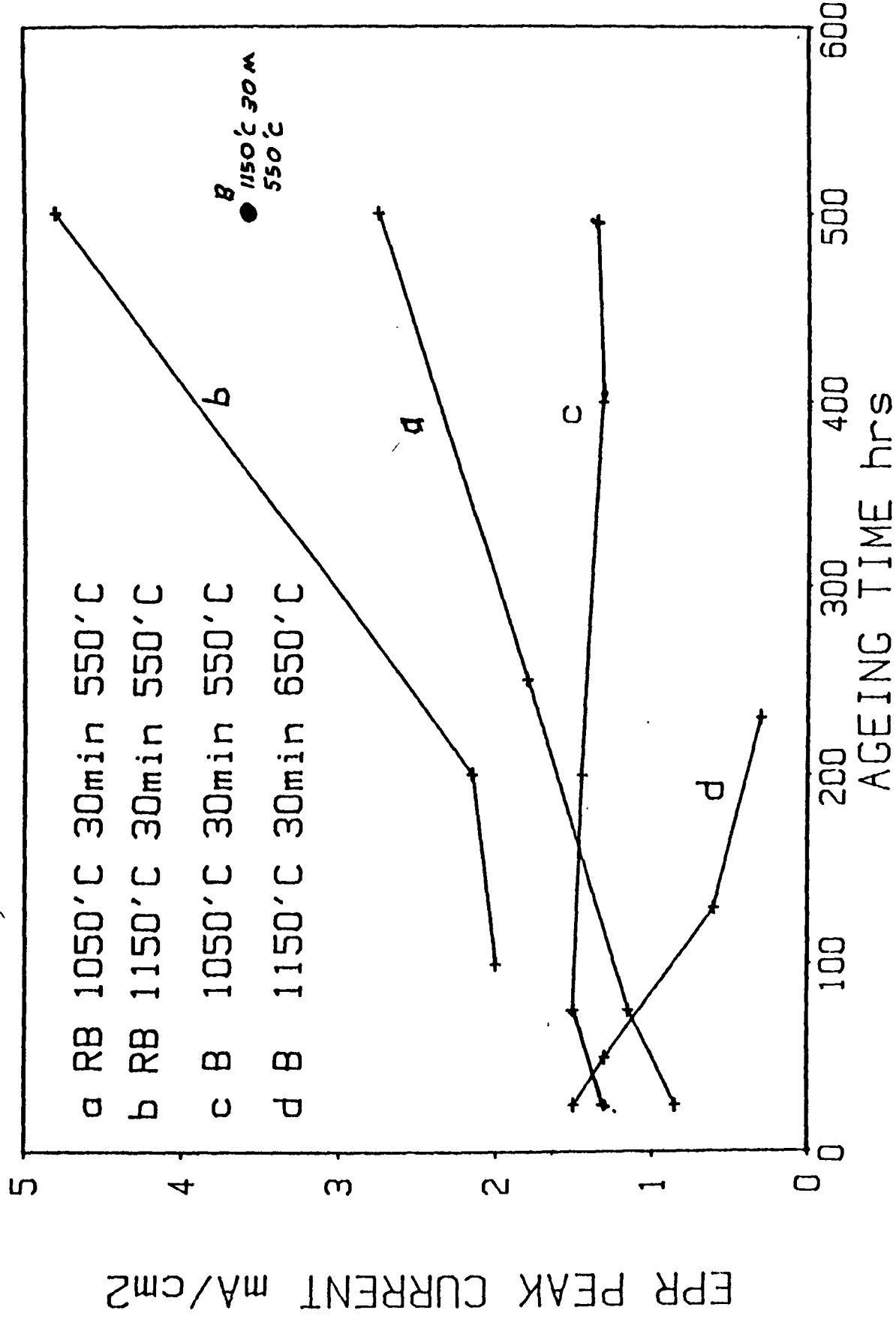


Reactivation scan results during EPR tests.



EPR TESTS FIG22.4

BAR(B) AND REWORKED BAR(RB)



Reactivation peak currents during EPR tests, for bar and re-worked bar material aged for different lengths of time.

Figure 23.4

Micrographs of the surfaces after EPR testing of

- A. tube annealed at 1050'C for 30 minutes then aged at 550'C for 500 hours**
- B. Bar material annealed at 1150'C for 30 minutes , and aged at 600'C for 50 hours**

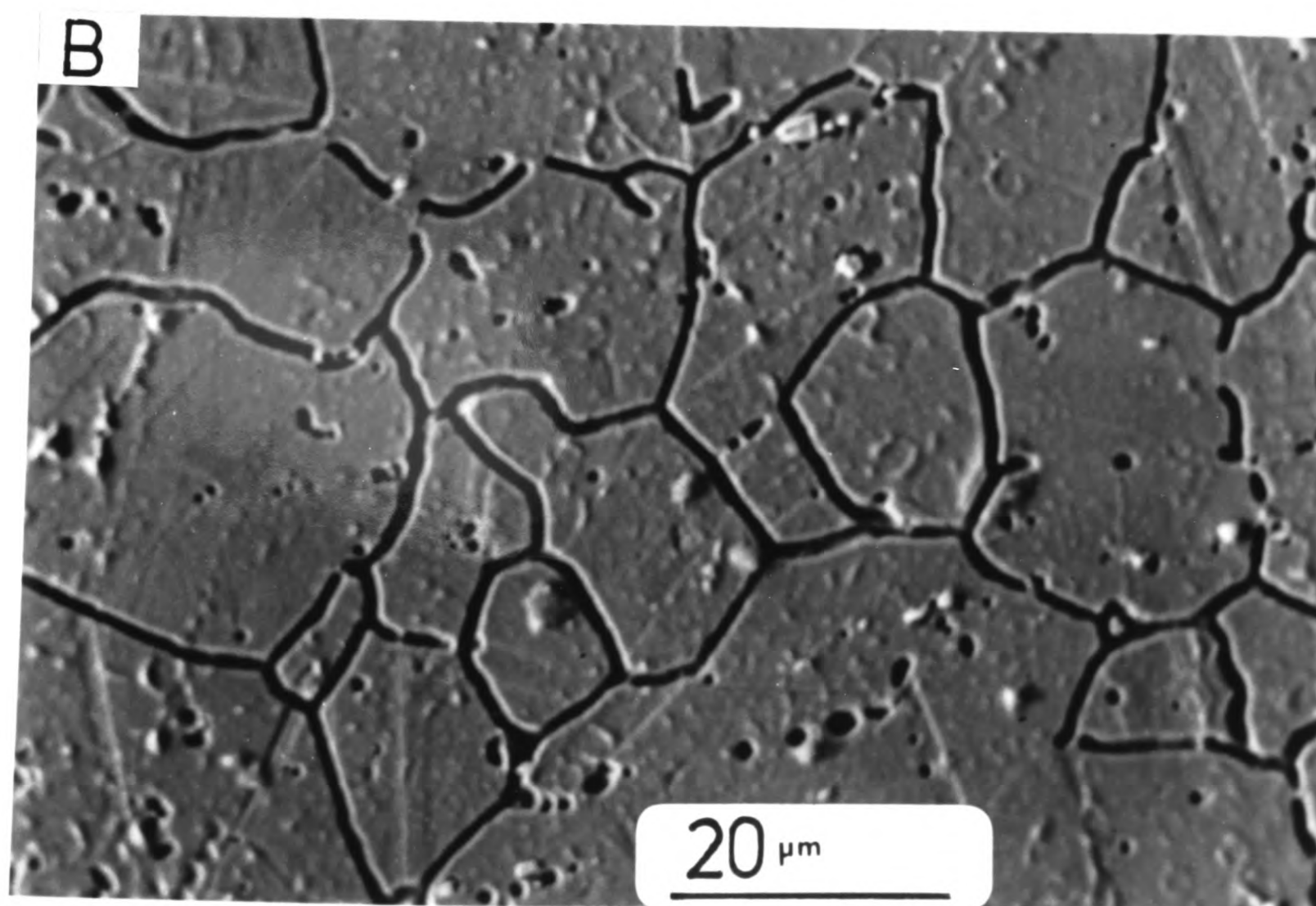
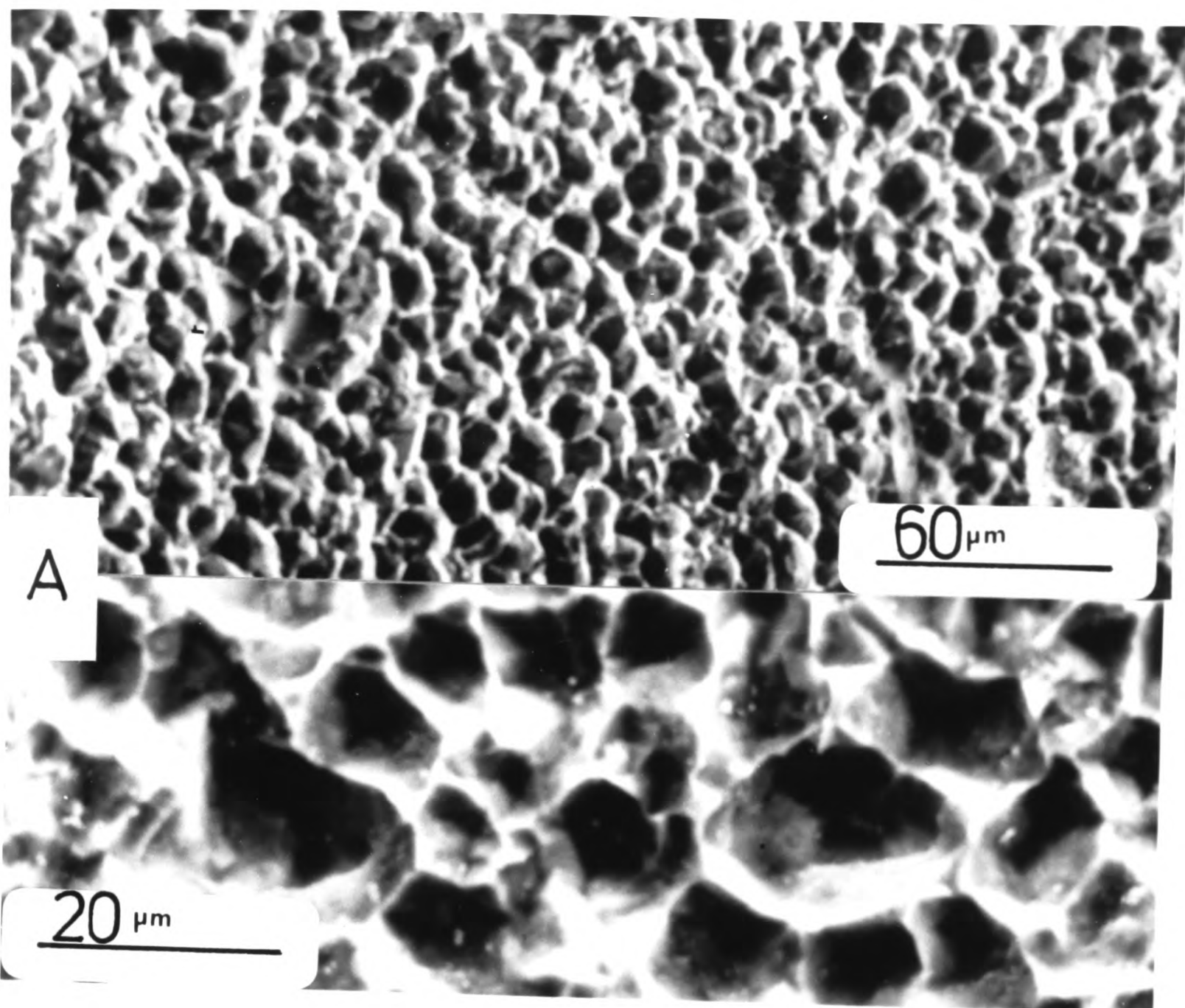


Figure 24.4

Comparison of the extent of surface attack after different tests

A and C. tube annealed at 1050'C for 30 minutes then aged at 550'C for 200 hours

A. EPR test

C. Oxalic acid etch 1V for 10 minutes

B. Bar material annealed at 1150'C for 30 minutes then aged at 750'C for 230 hours and etched in an Oxalic acid etch test at 1V. for 10 minutes.

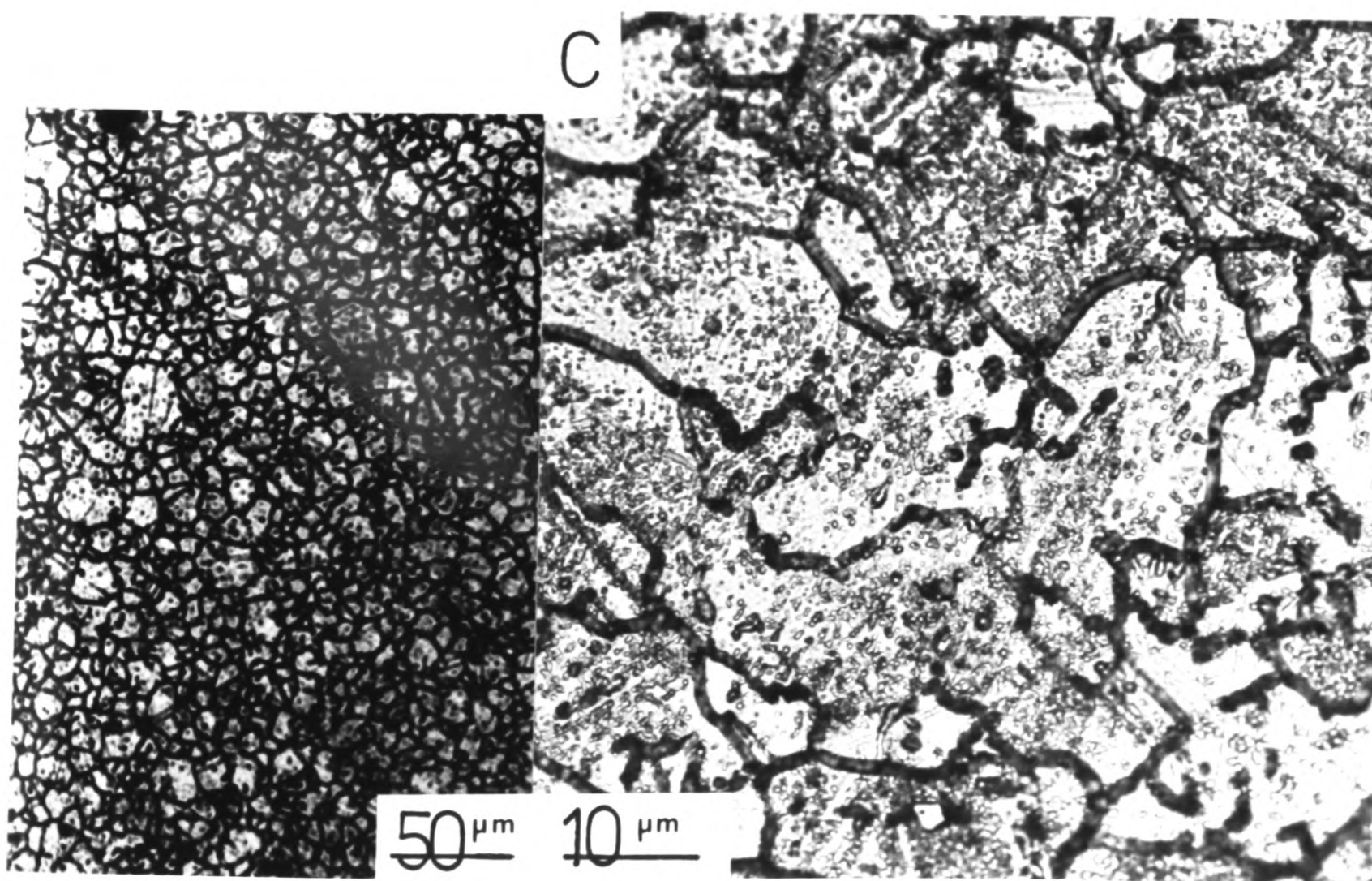
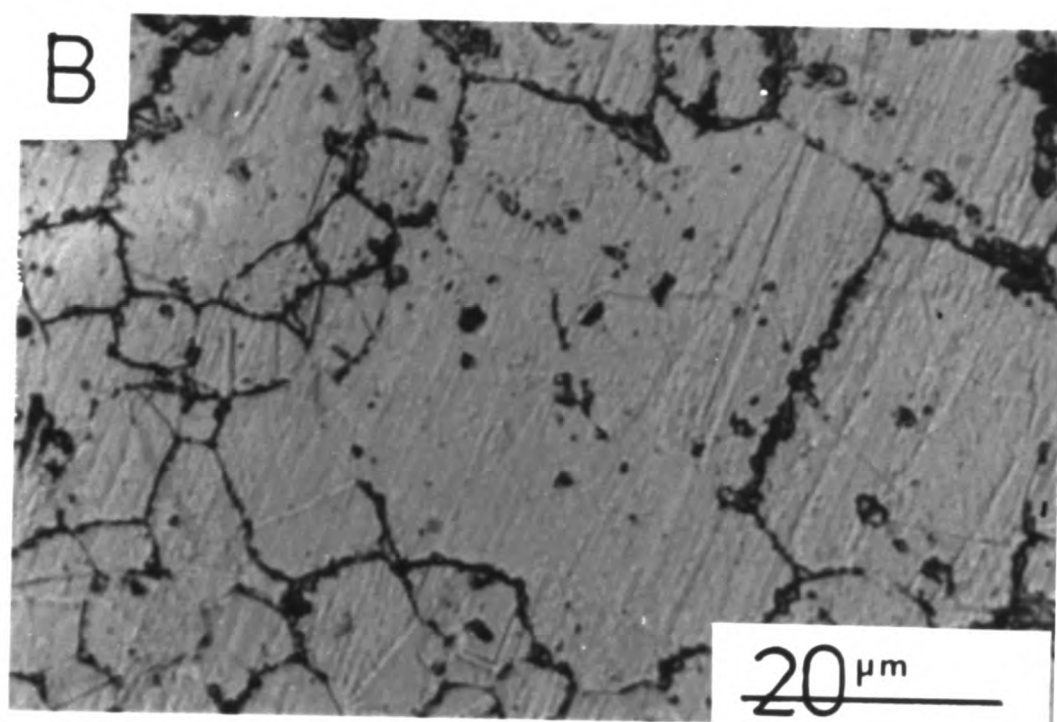
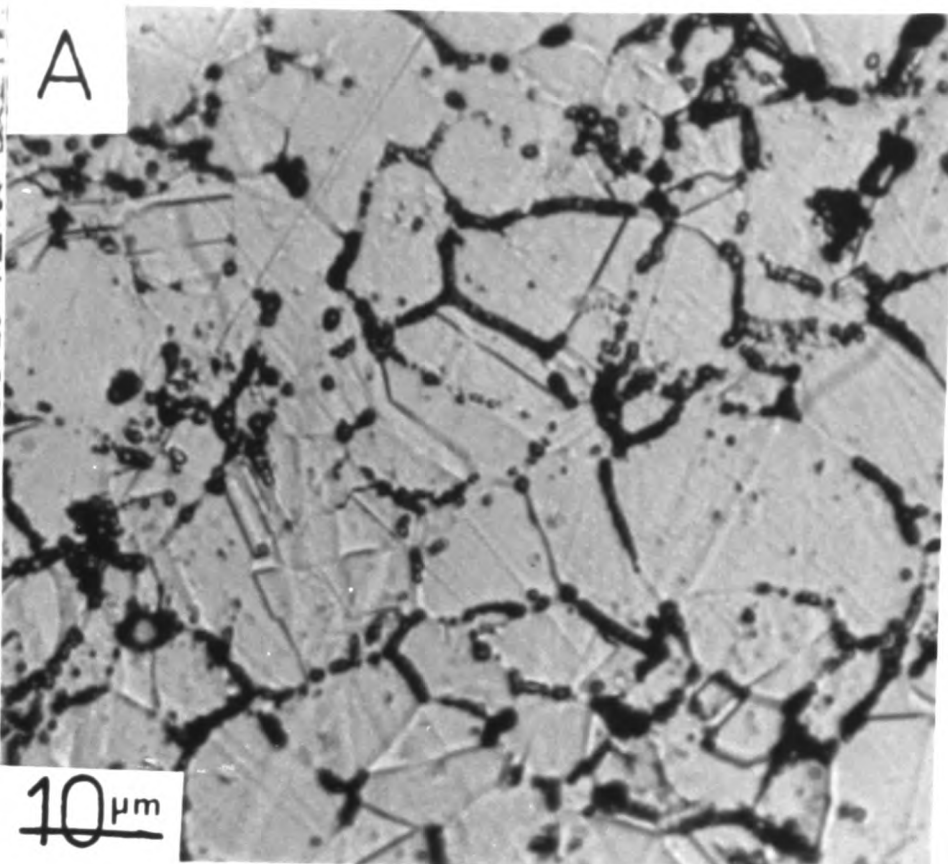
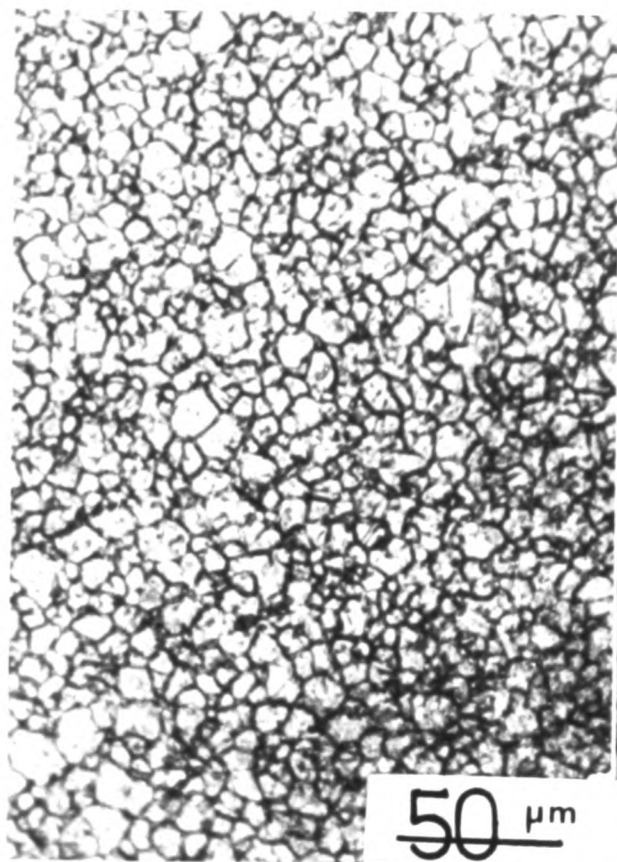
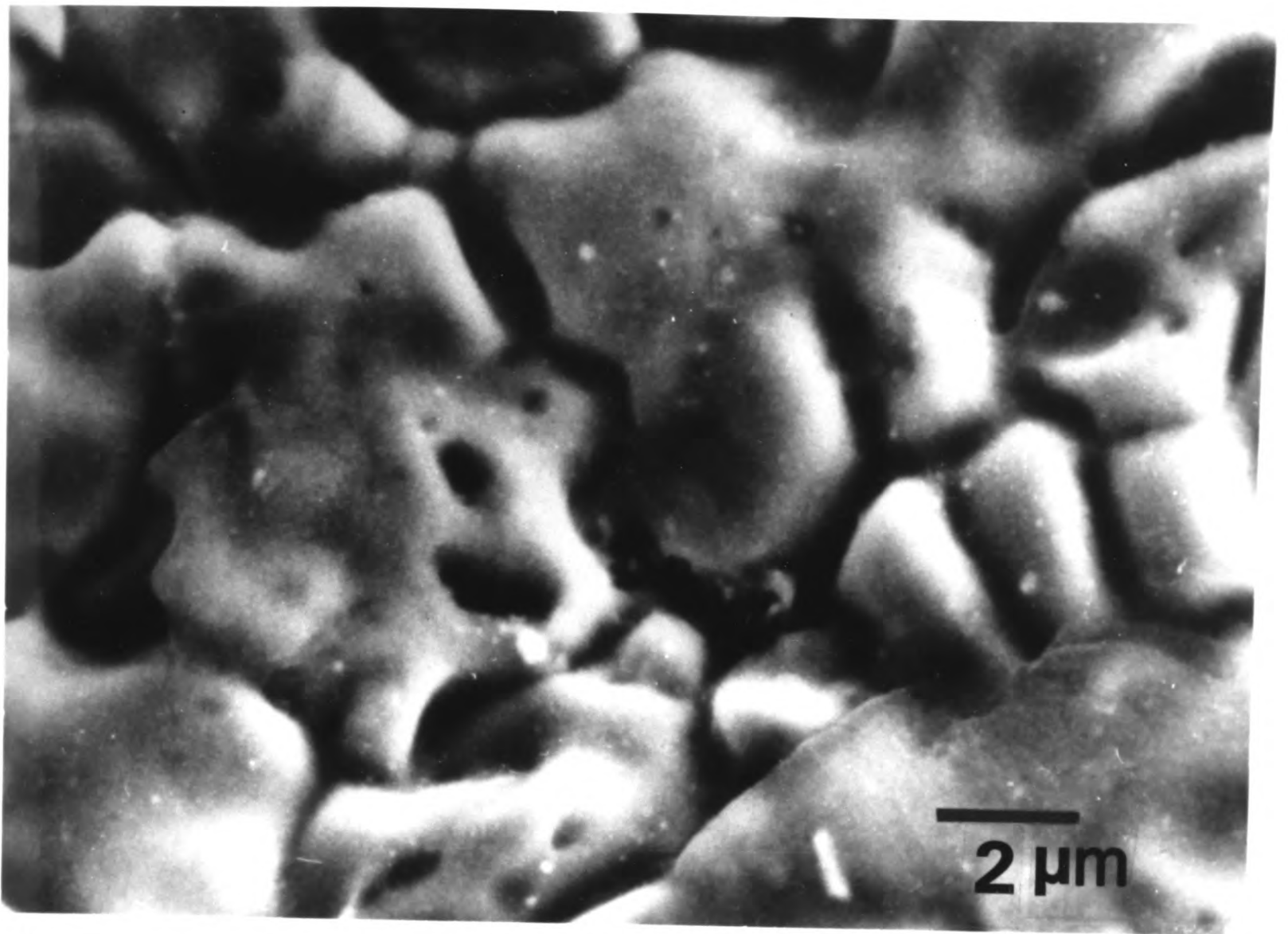


Figure 25.4

Comparison of surface attack of bar annealed at 1150°C for 30 minutes
aged at 600°C for 100 hours and

Strauss tested for 72 hours. A and D

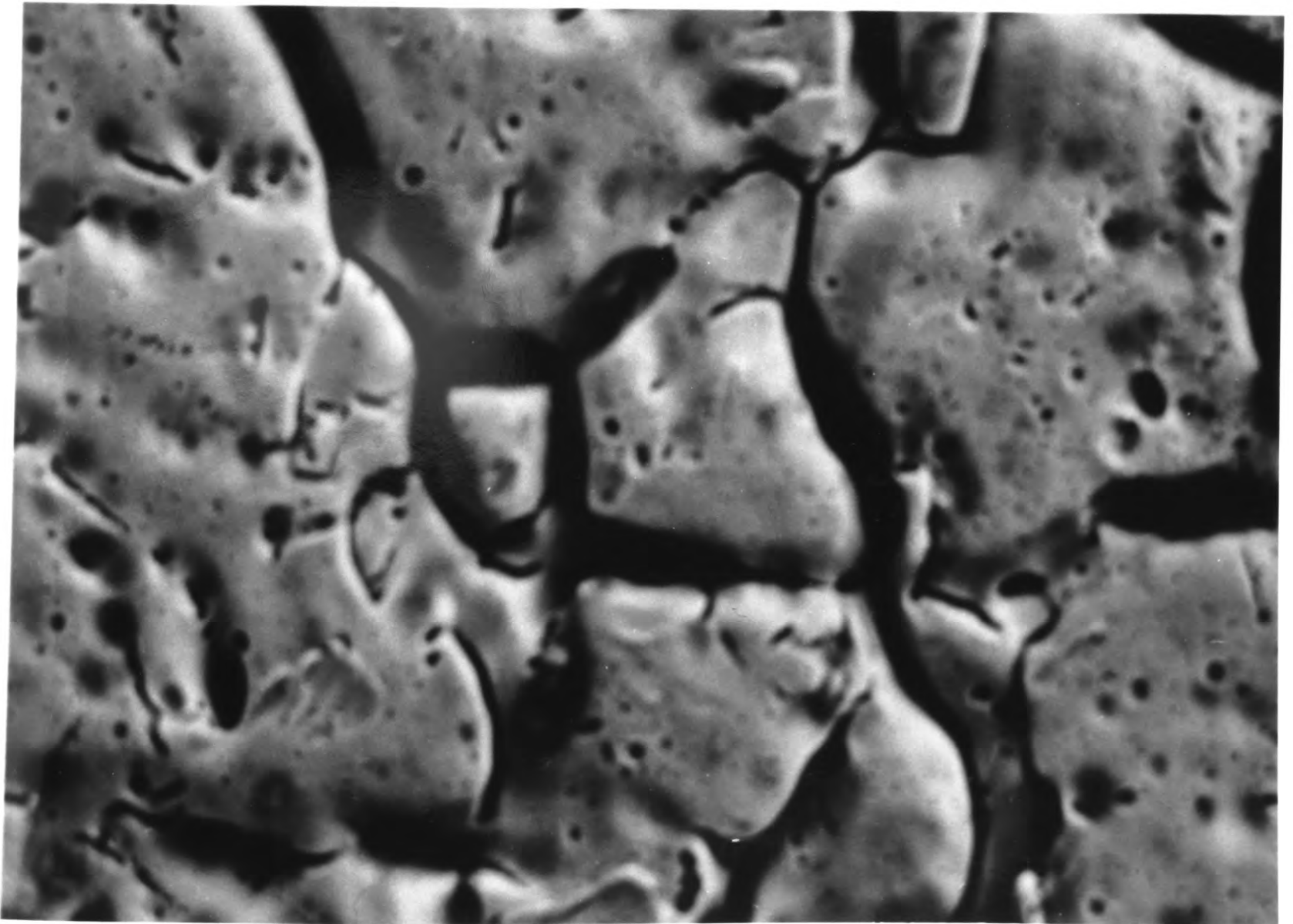
Huey tested for 48 hours. B and C

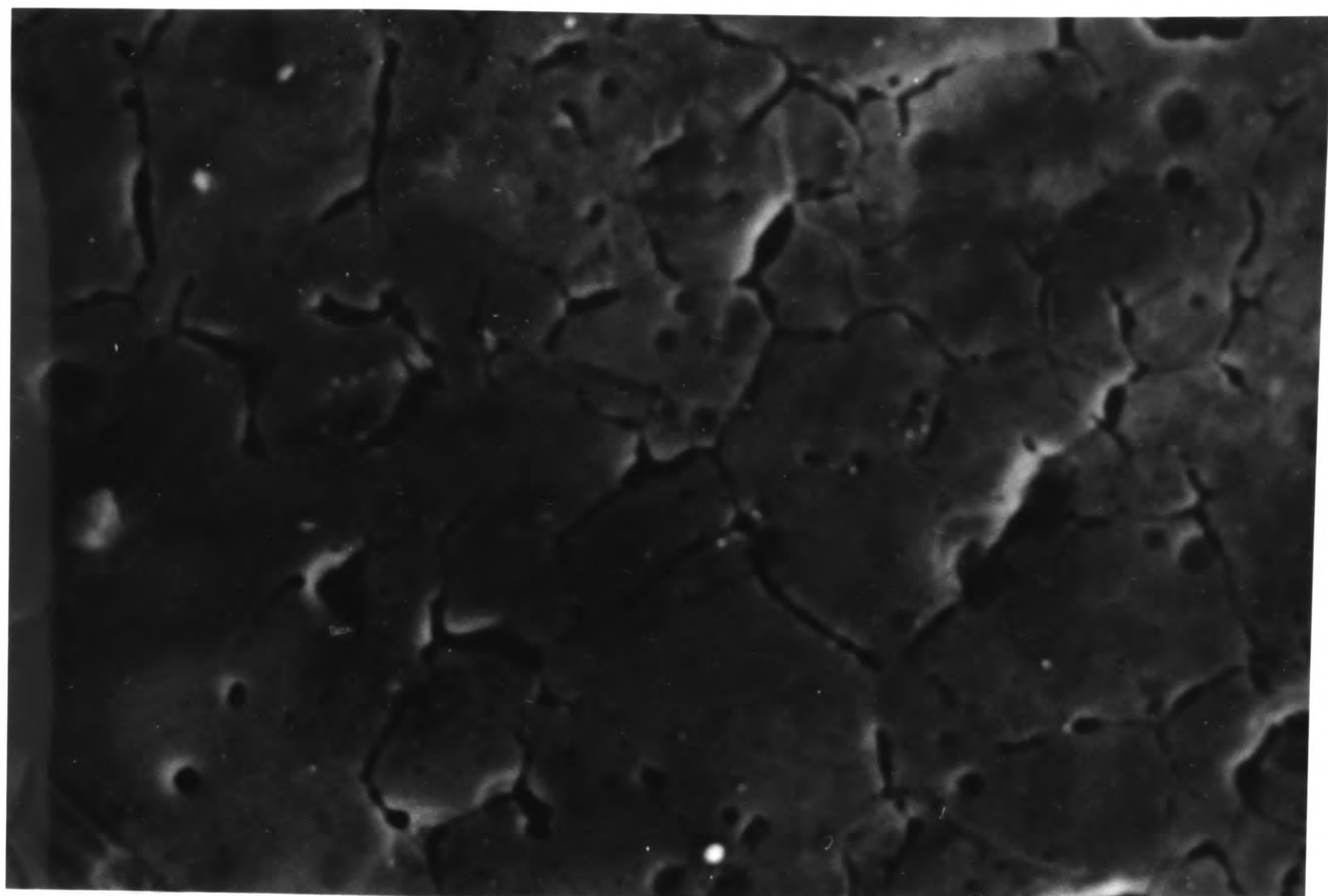


A

$3\ \mu\text{m}$

B





C

10 μm

D

100 μm



Figure 26.4

TEM foil etching experiments using Strauss test solution, tube annealed at 1050'C for 30 minutes then aged at

A. 550'C for 500 hours

B. 600'C for 100 hours

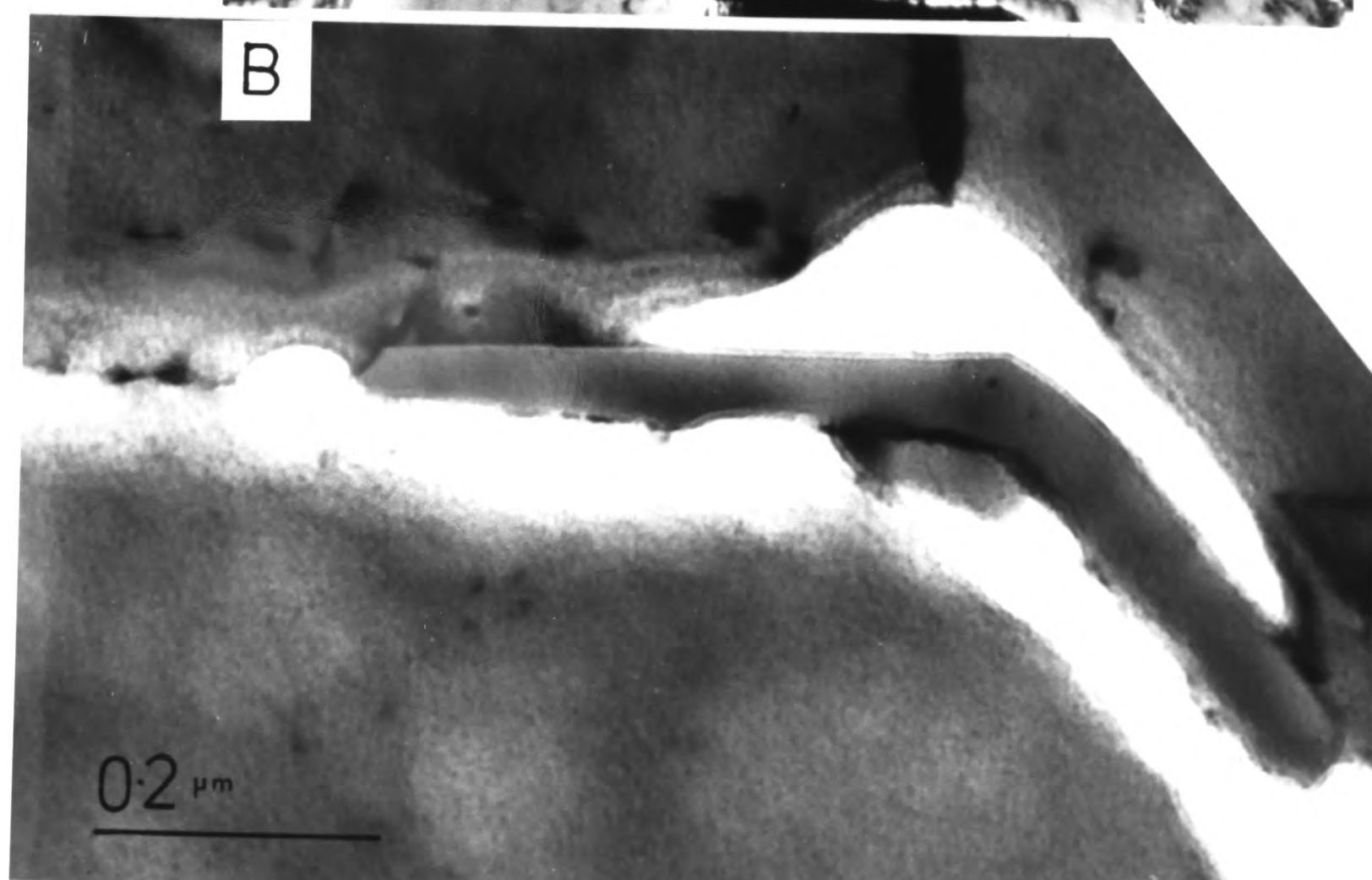
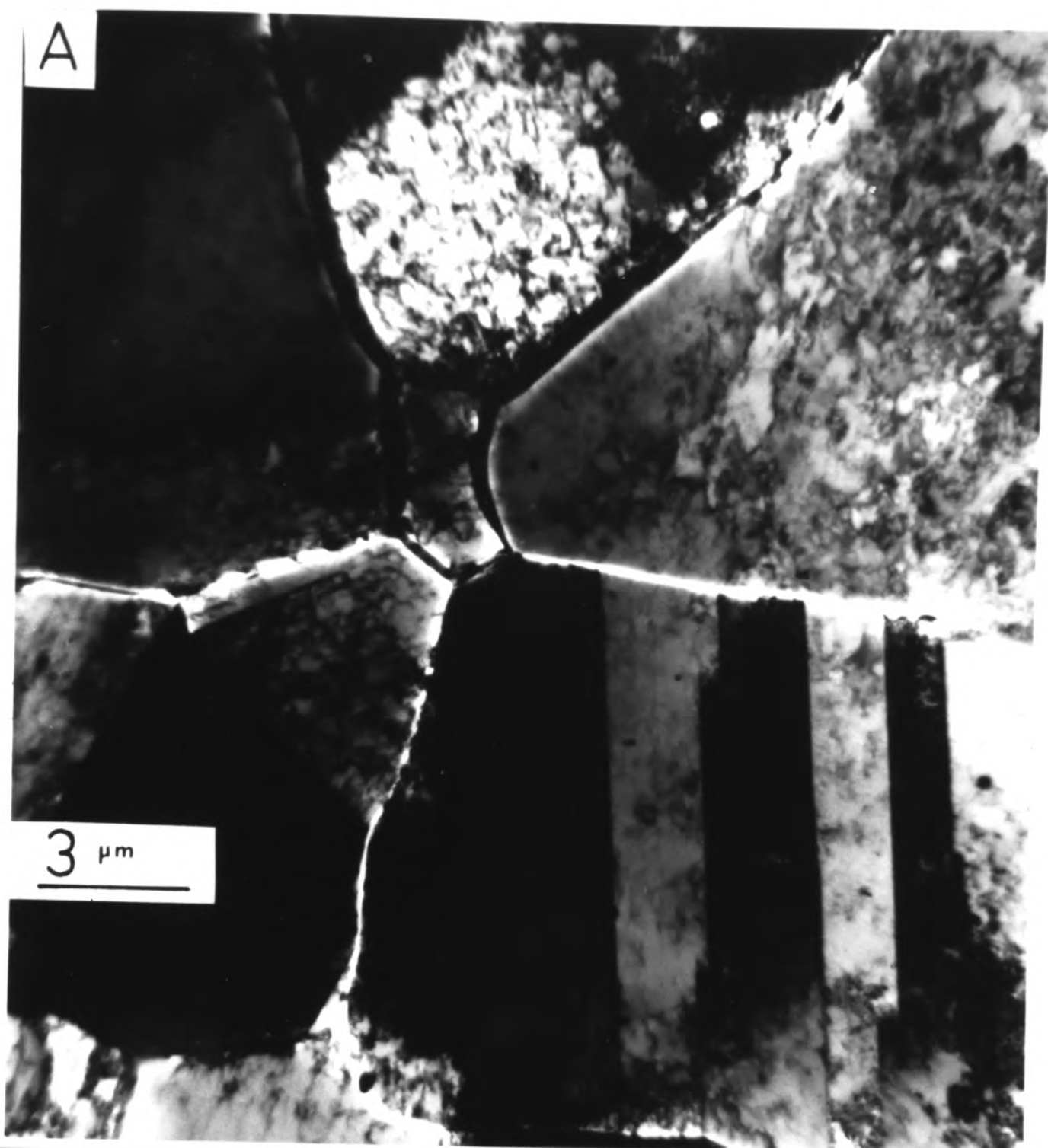


Figure 27.4

TEM foil etching experiment in hot $\text{HNO}_3/\text{Cr(VI)}^+$ solution. Tube material annealed at 1050°C for 30 minutes and then aged for 500 hrs at 550°C.

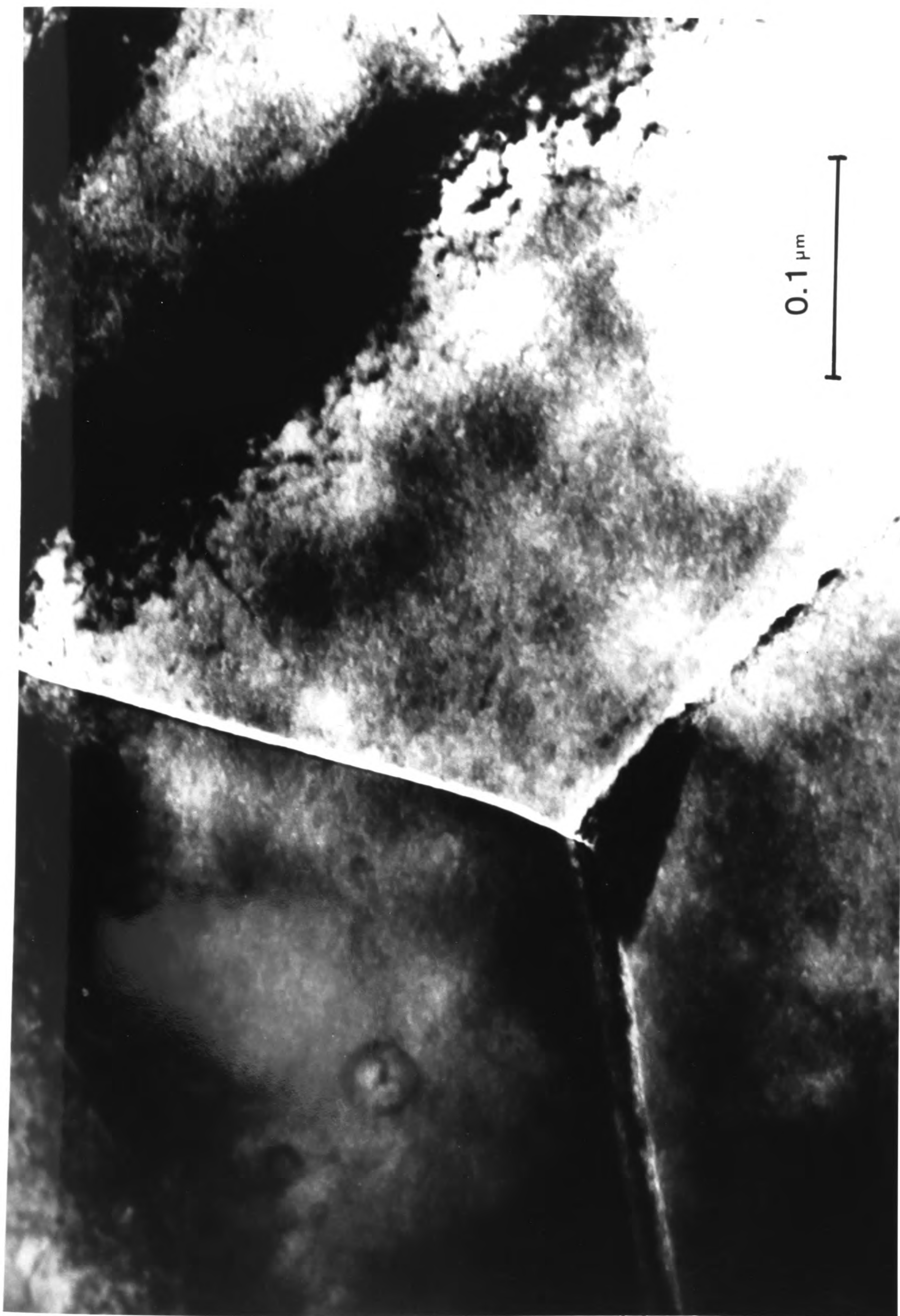


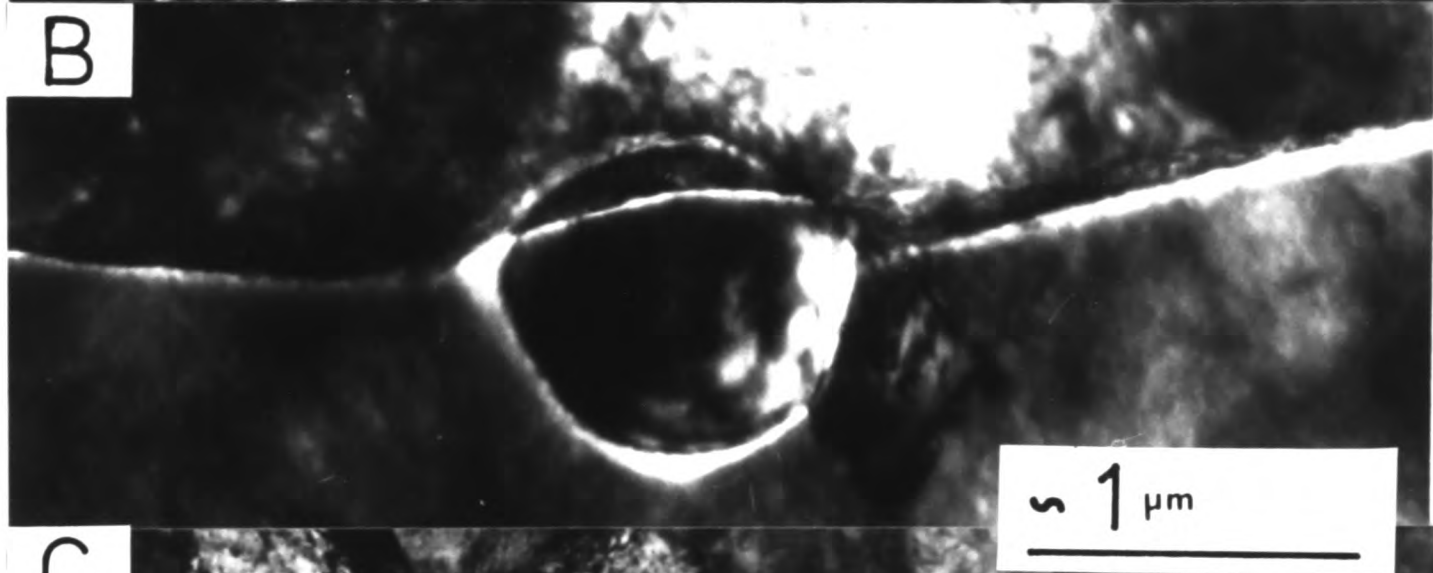
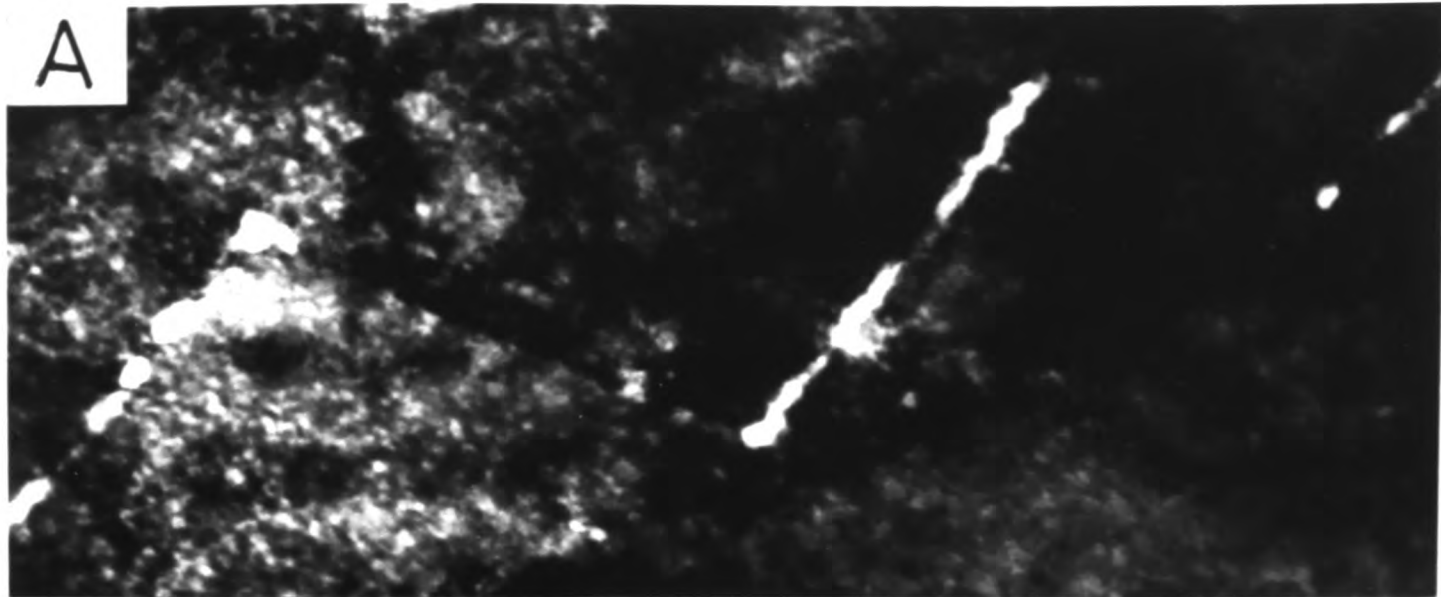
Figure 28:4

TEM foil etching experiments in tube material annealed at 1050'C for 30 minutes and then aged and etched in either Strauss test solution (A,C,D,E,F) or HNO₃ solution (B)

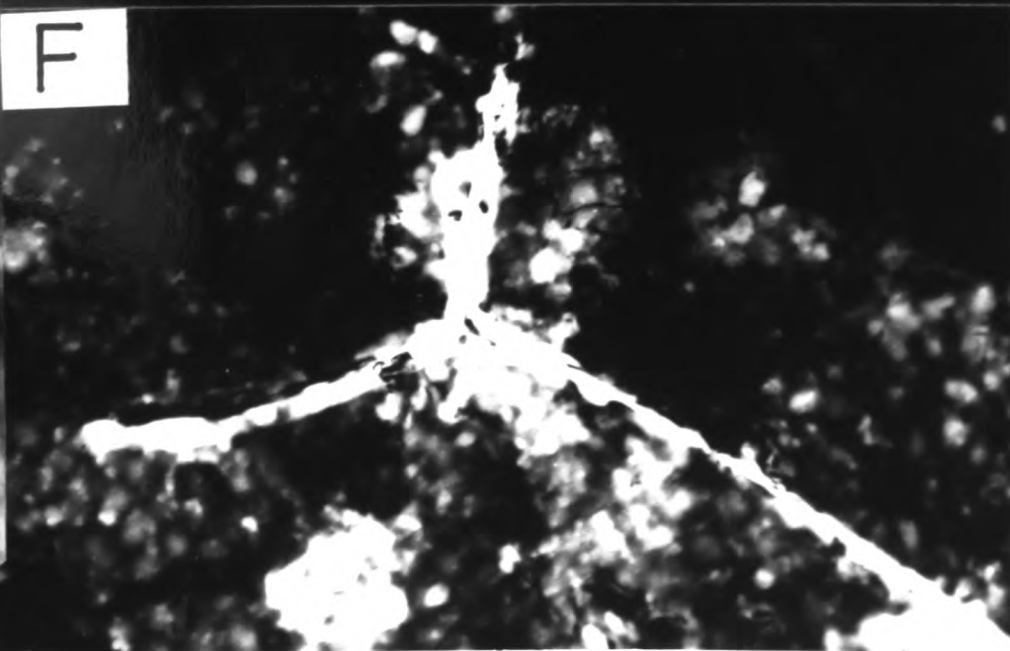
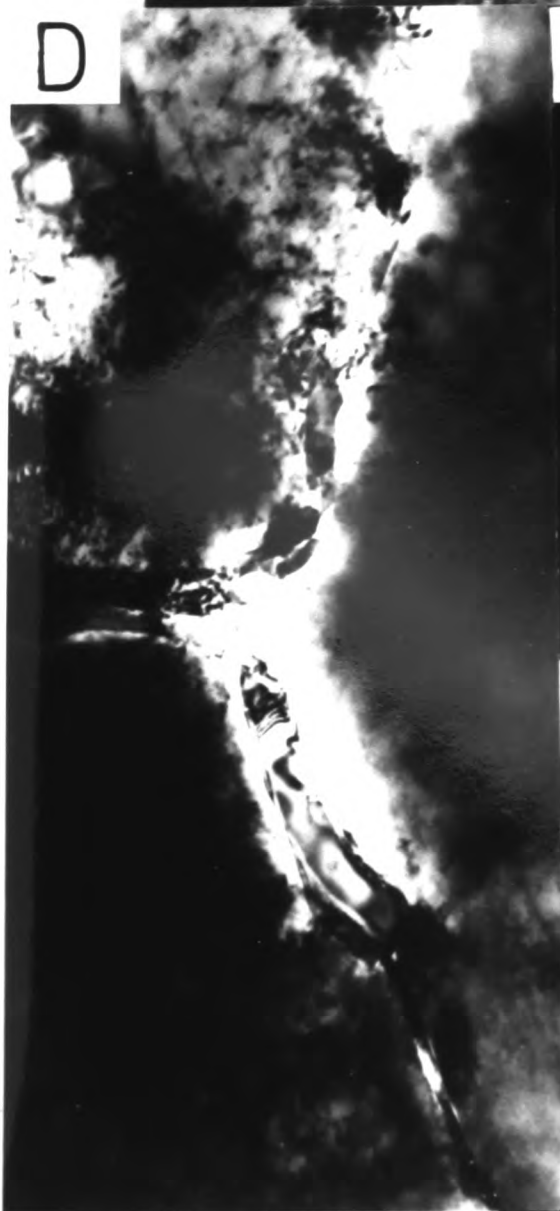
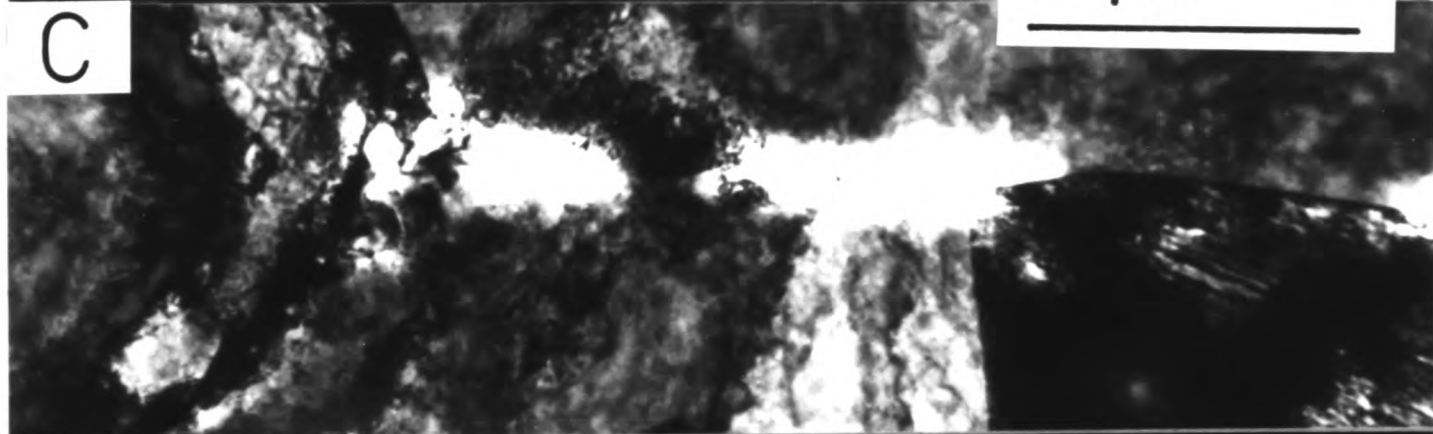
A and B. 600'C for 50 hours

C, D and E. 550'C for 500 hours

F. 550'C for 50 hours.

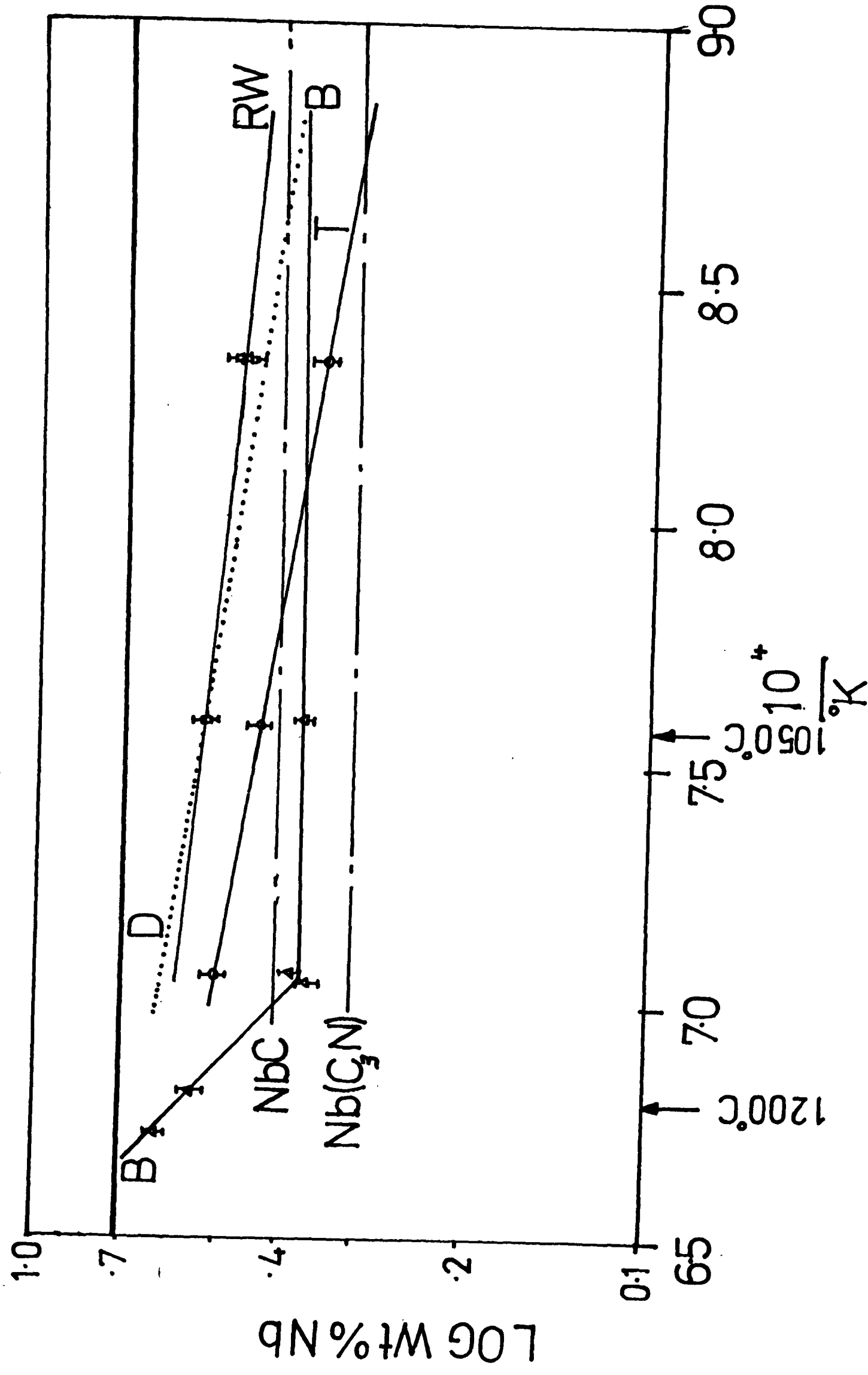


~ 1 μm

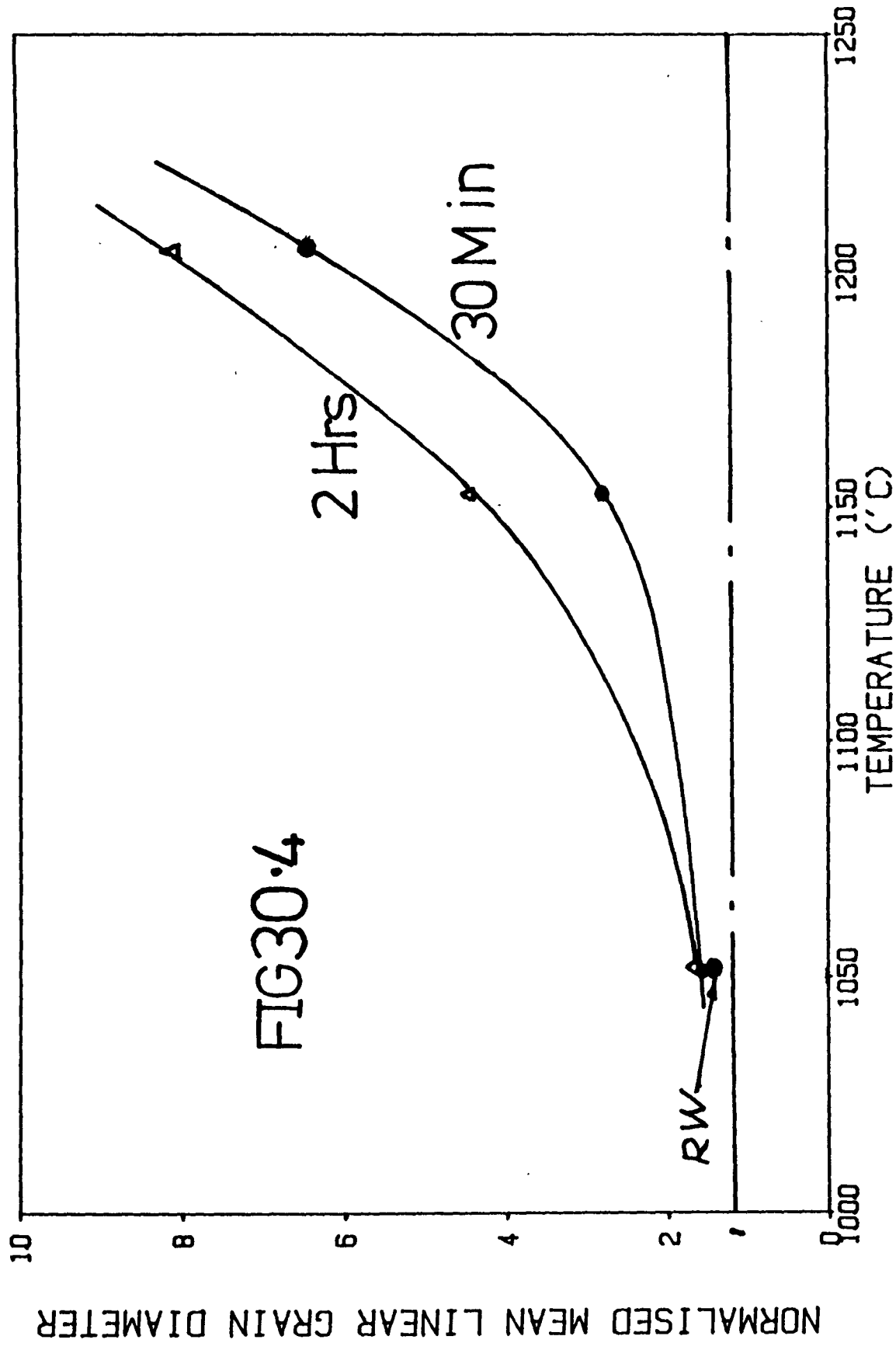


Microprobe data for the solubility of Nb(CN) precipitates in 20% Cr, 25% Ni, 0.7% Nb
 B= bar material, RW= reworked bar material, T= tube material, D= Deighton's data

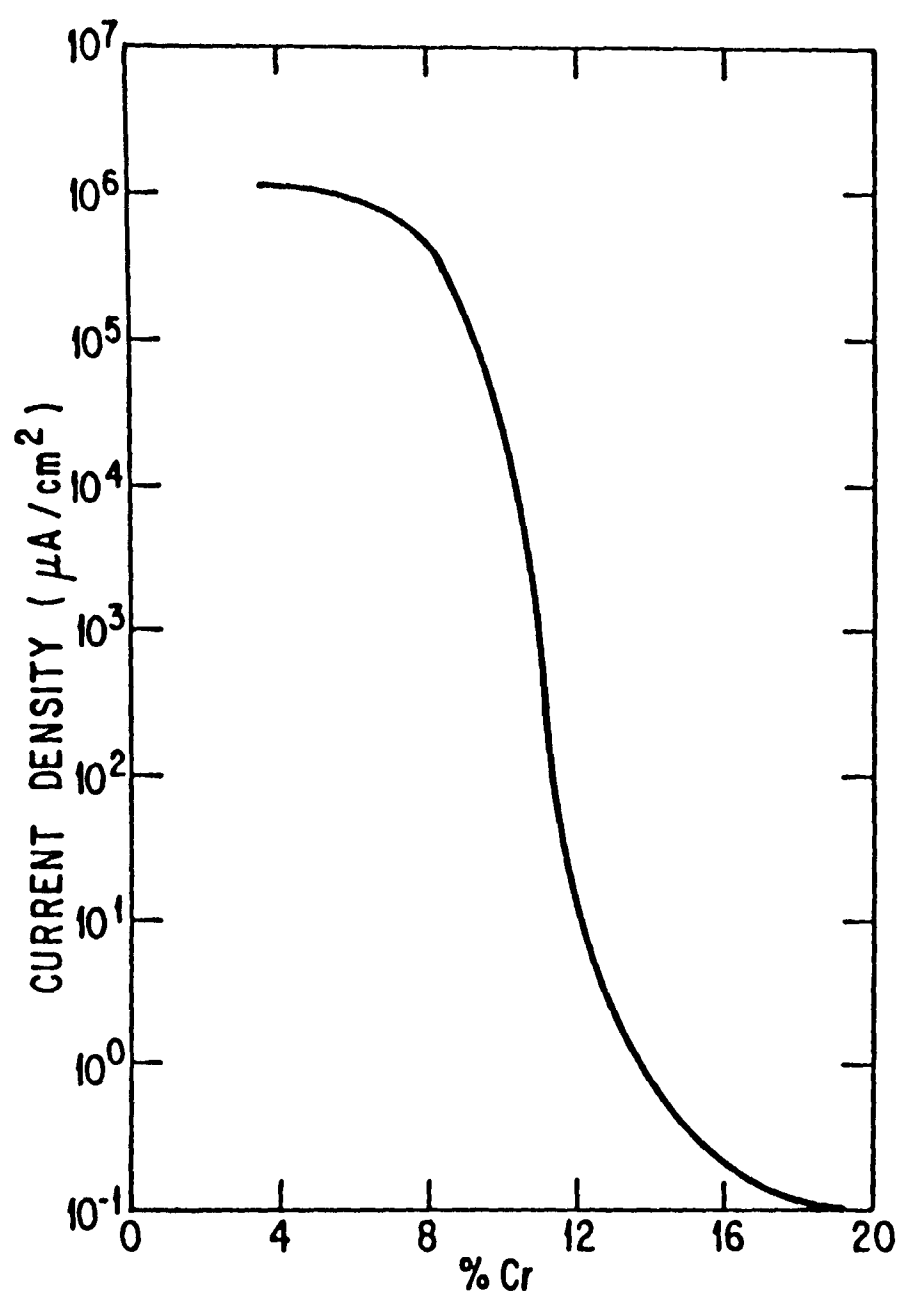
FIG 29.4



GRAIN GROWTH DATA (BAR)

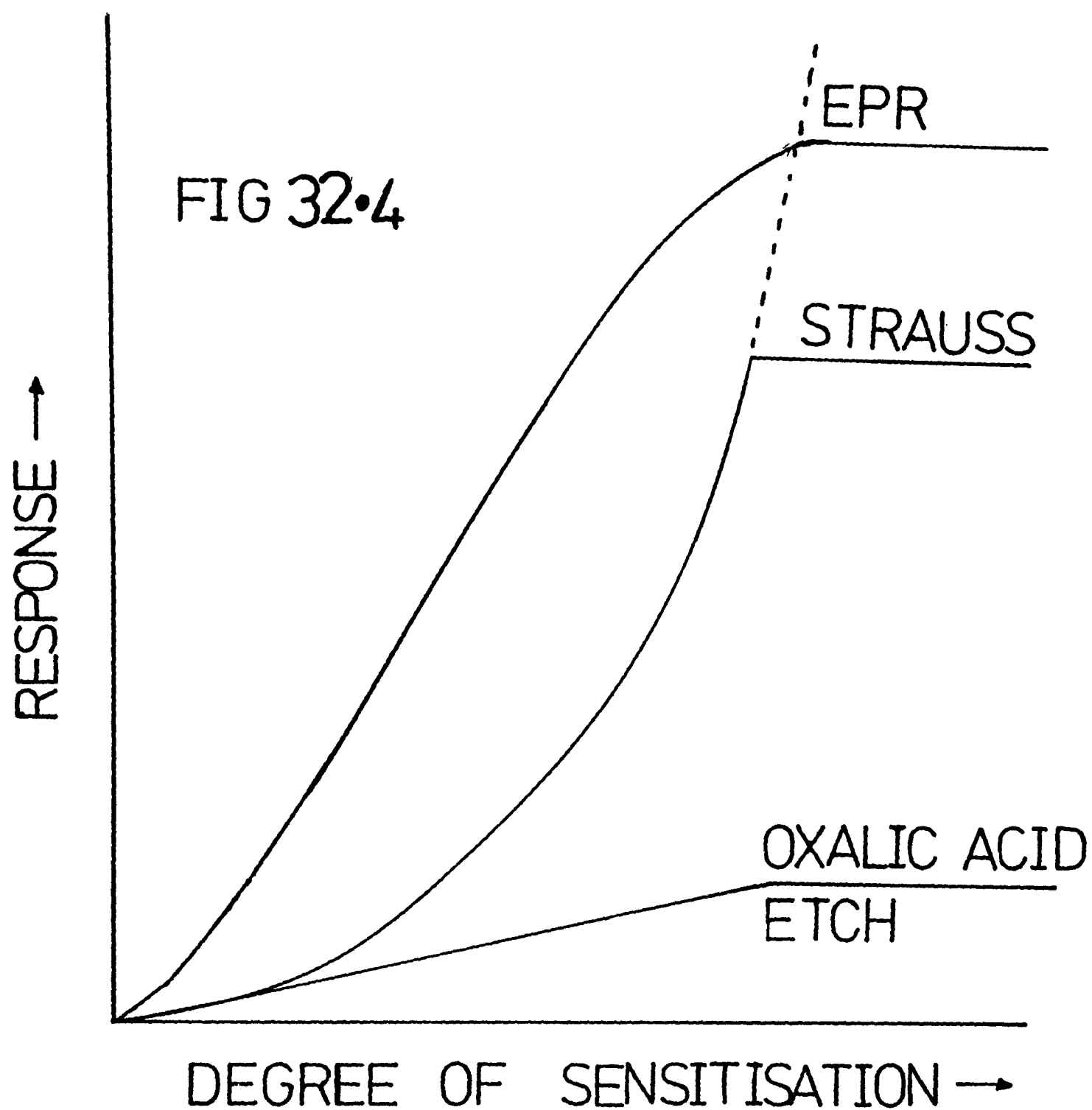


Grain growth at different annealing temperatures for the bar material.
 The pinning effect of the Nb(CN) precipitates is not removed until approximately 1150°C.



Anodic CD measured at 330 mV_{SHE} on Fe-10Ni-Cr alloys plotted as a function of chromium content. The data were taken from Reference [49]

FIG 31.4



CONCEPTUAL SCHEMATIC OF
TEST BEHAVIOUR (after[40]).

STRAUSS TEST DATA
SENSITISATION 20/25 0.7%Nb

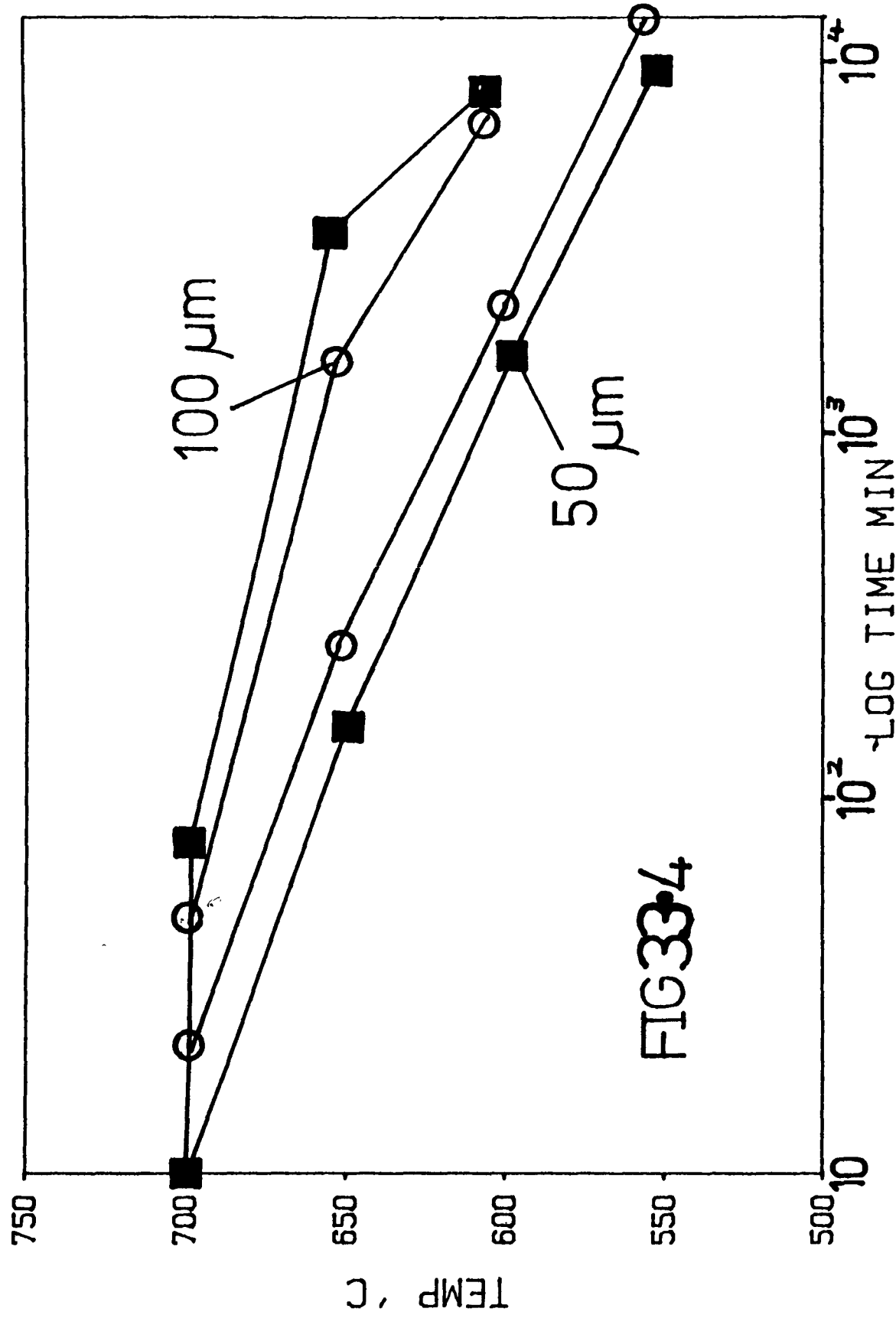


FIG 33-4

Experimental data from Strauss tests, showing the conditions necessary for a depth of penetration of 100 or 50 μm to be seen.

OBSERVATION OF Cr DEPLETION BY MICROANALYSIS

Prediction of sensitisation has been attempted by modelling the extent of Cr depletion at grain boundaries [1,2,3], and comparison has been made with corrosion test results [1,2]. However until about 10 years ago direct evidence of Cr-depleted regions was lacking, as instruments were unable to resolve such narrow regions [4]. More recently as microanalytical methods with sufficient spatial resolution became available, direct comparisons between measured and predicted Cr depletion profiles have been reported [5,6,7,8,9].

Direct comparison has been made using Analytical Electron Microscopy (AEM), and Scanning Transmission Electron Microscopy with Energy Dispersive X-Ray analysis (STEM/EDX). These techniques allow the carbide distribution along grain boundaries to be studied in detail and direct measurement of solute profiles across grain boundaries by using X-ray spectroscopy.

The purpose of this chapter is to describe the STEM/EDX work undertaken to characterise the depletion profiles resulting from various heat treatments. This study examined Cr concentration profiles after isothermal sensitisation in 20% Cr, 25% Ni, 0.7% Nb stainless steel, in order to gain an understanding of the process of sensitisation and to compare these results with predictions from a model (SAROC). The measured Cr depletion profiles are then related to responses in both EPR and Strauss tests.

5.1 Theory of microanalysis.

X-rays are generated when a high energy electron beam passes through a thin foil. The wave-length and energy of the characteristic X-rays emitted from the sample will be characteristic of its chemical composition. Quantitative microanalysis can be accomplished when the focused beam is positioned at a selected point on a specimen. The quantity of emitted X-rays are measured with an energy dispersive X-ray spectrometer. AEM has developed to a state where local compositional variations within a radius of 5 nm are routinely estimated. Several comprehensive reviews on the microanalysis of thin films have been written [10,11,12]. The practical resolution of the technique is now at best about 5 nm between successive analyses (HB 501 2 nm spot size at 200kV, [13]). The following review will briefly indicate the problems that may be encountered in STEM/EDX microanalysis.

5.1.1. Experimental considerations

In obtaining a concentration profile, the diameter of the electron probe determines the lower limit of spatial resolution. Ideally the probe should have a top hat distance-current distribution and be able to be positioned sequentially at distances from the grain boundary, while an energy dispersive X-ray spectrum is acquired at each point. The specimen is perfectly orientated with the flat grain boundary plane parallel to the incident beam. Fig. 1a shows the ideal situation and a more realistic representation of measurements. The current of the probe varies with radial distance and the probe size is not well defined. Furthermore the small probe size and small excitation volume lead to low count rates, which may limit the detection of small amounts of elements, as well as the accuracy of analysis. The problem of low count rates can be partly overcome by using a high brightness source, such as a Field Emission Gun (FEG) with an LaB₆ filament. Further problems arise because foil thickness variations occur and surface contaminant films may be present.

5.1.2. Quantification of X-ray data

In determining the local Cr concentrations in the matrix, X-ray intensities are converted to elemental concentrations at each point in the trace across the grain boundary.

To determine concentration values from X-ray intensities the Cliff-Lorimer [14,15,16] approximation is used since no standards are available for comparison during analysis and because of the geometrical factors that may not be evaluated to allow standardless analysis. The relative abundance of the major alloying elements is calculated from the ratios of the X-ray intensities and a single constant of proportionality K_{ab} [15,16].

$$1. \quad \frac{C_a}{C_b} = K_{ab} \frac{I_a}{I_b} \quad \text{The Cliff-Lorimer equation}$$

I_i = background corrected X-ray peak intensities

C_i = weight fractions of the elements

The K_{ab} values for the specimens in this study were evaluated by measuring matrix compositions far from any grain boundary where homogeneous composition exists and comparing these values to known bulk composition data using equation 1. The Cr k , Ni k , Fe k X-ray lines were used for quantification. This approximation is referred to as the thin film approximation and assumes that as the foil thickness varies intensity ratios (and therefore the C_a/C_b ratio) do not change. The accuracy of quantitative X-ray microanalysis by using the Cliff-Lorimer method is determined by the accuracy of the Cliff-Lorimer K_{ab} factor and the counting statistics of the X-ray

collection process. Gaussian statistics are applicable for X-ray peak shapes, for example, the standard deviation for an element A is given by $N^{0.5}$, where N is the number of accumulated counts corresponding to element A at a particular point of analysis. The value of twice the standard deviation is taken as the 95% confidence limit in Ia, and therefore the error in accumulated counts is $2*(N^{0.5})/N$.

The sensitivity limits for microanalysis are defined by the minimum detectable mass (MDM) and the minimum detectable mass fraction (MMF). These limits are set by the corrections listed above. Long count times and bright guns decrease the MDM, because X-rays from dilute regions become more statistically significant. The MMF is affected when peak overlap occurs, as deconvolution of the peaks from one another, and from the background, is difficult.

5.1.3. Beam spreading and concentration profiles.

The interpretation of information from the X-rays generated is impeded by the effects of finite probe size and broadening of the beam in the specimen. However, because thin specimens are used, limited spreading of the focussed beam occurs and a small X-ray source region is obtained. However, the volume of material from which X-rays are generated is somewhat greater than indicated by the nominal probe diameter; this is shown schematically in Fig. 1b. Spreading of the electron probe in the sample; due to elastic collisions between the incident electrons and the atoms of the sample has a strong effect on the measurement of profiles at grain boundaries using AEM [18,19] so that in some cases the value obtained for grain boundary chemistry can be significantly in error.

The probe measures an average composition around the location of the incident beam, and because steep compositional gradients are found at grain boundaries, the measured composition may be different from the real concentration at the grain boundary.

The effect of the finite beam size and radial electron distribution of the electron probe is to "smear out" the true profile. This is shown schematically in Fig. 1c. As the Cr concentration is a minimum at the grain boundary and increases sharply with distance perpendicular to the boundary, some of the collected X-rays will originate from regions near the boundary with a significantly higher Cr concentration. Though the profile width is relatively insensitive to beam broadening and probe diameter, the minimum Cr concentration measured using EDX is strongly affected. Because of beam spreading in the sample, the spatial resolution is a function of atomic number, specimen thickness (where the beam enters the specimen) and accelerating voltage. Maximum resolution is obtained when foil thickness and beam size are minimised and the accelerating voltage is

maximum.

A correction may be made to account for beam spreading and a measure of spatial resolution be estimated [20,21,22,23] and the true concentration be obtained. Broadening of a probe, given by a simple single scattering model was suggested by Goldstein [21]:-

$$2. \quad b = 6.25 \cdot 10^5 \cdot Z \cdot \left(\frac{P}{E_0} \right)^{0.5} \cdot \frac{t^{1.5}}{A} \quad \text{cm}$$

b = extent of beam broadening

t = foil thickness (nm)

Z = atomic number

A = atomic weight

E₀ = electron energy (eV)

P = density

Substituting the correct values in for 20% Cr, 25% Ni 0.7% Nb stainless steel this value becomes

$$3. \quad b_t = b_0 + 61.61 \cdot t^{1.5}$$

b_t = total beam size, b₀ = incident beam size

For a sample of thickness 100nm, the broadening at 100 kV for a 10 nm probe is about 20nm [17,18] for a high Cr steel, yielding a total source size of 30nm. The effect of probe size and hence specimen thickness on EDX profiles can be determined using a model which convolutes the electron intensity distribution in the probe with the assumed true compositional profile and compares this to the data [8,24]. In a region where elemental concentration varies linearly with distance, the expanded spot size has no effect on the resulting intensity. An estimate of the true grain boundary composition may be made using the following method [24].

Given the Cr concentration at point A, 50nm away from the grain boundary, and assuming that the Cr concentration varies linearly from the boundary to , the adjacent analysis point, then the concentration X(r) at distance r is given by

$$4. \quad X(r) = X_0 + r(X_A - X_0)/A$$

where X(r) = Cr concentration at r

X_A = concentration at point A

X₀ = true grain boundary concentration

r = perpendicular distance from grain boundary

A = distance from grain boundary to next measurement

Since X_0 is the true grain boundary concentration, and X_m the measured grain boundary concentration:-

$$5. \quad b_t \cdot X_m = 2 \int_0^{b_t/2} dr \cdot X(r)$$

Substituting the relation for $X(r)$ and solving for X_0 gives

$$6. \quad X_0 = \frac{X_m - (b_t/4A) \cdot X_A}{1 - (b_t/4A)}$$

Thus an estimate of the true value of grain boundary concentration may be determined.

Corrections to account for beam broadening through the finite probe size range from 1 at% for a steep Cr concentration profile, to 0 at% for a flat one.

One instrumental difficulty is that of specimen drift. This effectively enlarges the source size, and limits spatial resolution and must be avoided by the use of a cold finger, and by monitoring the location of the specimen and correcting for specimen drift.

5.3.4. X-ray generation

Problems in estimating the number of X-rays generated from a particular element may be classified in the following way:

1. Those due to differences in electron excitation and ionisation levels from atoms and lines of one element of atomic number Z to atoms and lines of another one (Z correction)
2. Those due to differences in X-ray photon absorption by atoms of the target, for the various characteristic lines considered (A correction)
3. Those due to indirect, or fluorescence, excitation of the X-rays generated inside the specimen, either from the characteristic or continuous spectra (F correction). When element A can be excited by continuum X-ray radiation or by fluorescence due to X-rays emitted by element B , a correction may be needed.

The correction considering these points is referred to as a ZAF correction. The importance of these corrections is reduced by the use of thin foil specimens, because the excitation volume is much less, and consequently less fluorescence and absorption takes place.

Various X-rays may be generated from regions other than where the beam is focused.

Spurious X-rays are caused from both:

1. Stray radiation in the illumination system
2. Specimen interaction with the primary electron beam.

The elimination of extraneous X-rays due to stray radiation in the AEM illumination system is a problem which is largely instrument design dependent. The sources of X-rays that may reach the EDS due to specimen interaction with the primary electron beam are summarised in Fig. 2. The possibility of self fluorescence by the specimen-generated continuum exists, particularly when the specimen is tilted at an angle away from the detector, and X-rays pass through the specimen to reach the detector. This effect can be minimised by using thin film specimens rather than discs, and by using detectors with high take-off angles.

In summary, the elemental concentrations determined by STEM analysis are subject to several sources of error, some of which may not be neglected and must be quantified. The points listed in table 1 were addressed during the following STEM microanalysis experiments by calculation and by reference to the literature.

Table 1. Difficulties that must be considered for accurate STEM analysis

Phenomenon	Correction
Beam broadening	Adjust grain boundary concentrations
Background count	Measure and subtract from raw intensities
Hole count	Measure and subtract from raw intensities
Counting statistics	Determine the uncertainty in X-ray counts by moving to thickish areas, and correct alignment with respect to X-ray detector. Use a bright gun. Use long count times.
Absorption	Adjust theoretical values by Cliff-Lorimer correction
Fluorescence	Adjust raw intensities
Intrinsic and spurious X-rays	Inherent in machine design
Grain boundary tilt and orientation	Tilt to optimise detector collection
Drift	Use a cold trap
Surface contamination	

Further information on high resolution microanalysis in steels is contained in references [25,26,27].

5.2. EXPERIMENTAL

Specimen heat treatment and foil preparation have been described in Chapter 3. Several specimens of bar and tube material were given a range of different heat treatments from 550'C to 750'C with ageing times of 25 to 500 hrs and were then examined. Foils were prepared and grain boundary depletion was examined. Data from the following specimens are given as representative of the process of Cr depletion:

Tube material	1050'C solution anneal for 30 min	550'C 500 hrs
	1150'C	600'C 100 hrs

Microchemistry data were obtained using a Philips model EM400 B S(TEM) equipped with a KEVEX energy dispersive X-ray detector. KEVEX software was used to apply a peak stripping routine and then a Cliff-Lorimer thin foil correction.

To aid counting statistics and obtain high count rates a FEG source (LaB₆ filament) was used. This was carefully aligned and saturated before analysis.

The boundaries chosen for compositional profile measurements satisfied two criteria:

1. That the plane of a chosen boundary was parallel to the electron beam when the foil was tilted to an orientation to obtain maximum efficiency for detection of X-rays. This was done experimentally by looking for a "thin" boundary, ie one which appeared in sharp contrast as a thin line.
2. That the chosen boundaries were radial to the central hole of the thin foil specimen. This increased the likelihood of obtaining constant foil thickness across the whole compositional profile because the specimen thickness tapers towards the hole edge.

Furthermore, boundaries with precipitation, but with no evidence of etching were selected. A STEM image was formed at 100K magnification and the image of the boundary rotated until aligned vertically. This made it possible to correct for drift, by checking the 0 point along the x axis after each measurement. Beam traces were made across boundaries, some 100nm away from carbides, to ensure no X-ray contribution from the carbides. The location of carbides was examined by imaging the precipitates under 2 beam conditions.

X shift movements were made by an attached XY controller, capable of 26.5 Å step resolution; X steps between analysis were usually made to be 13nm. Count times of 100 seconds were used, during which the spot location was periodically checked, and the specimen position corrected to account for specimen drift. The collected data were curve fitted by KEVEX software, assuming a Gaussian collection of data around an X-ray intensity peak for each element. Error bars for the compositional analysis were determined within the KEVEX software, as

the sum of the relative errors from the X-ray intensities (based on counting statistics) and from the Cliff-Lorimer factor. The value of twice the standard deviation was taken to be the 95% confidence limit in the value of I_a .

Contamination, resulting from carbon residues building up on the specimen surface at the incident beam point, was reduced by use of a cold finger and by exposing the specimen to an unfocussed beam for 10 seconds, achieved by removing the condenser aperture, to lock up all mobile C on the surface.

The results are presented with concentrations in atomic %, taking the concentration of $\text{Cr} + \text{Fe} + \text{Ni} = 100$.

5.3. RESULTS

In all the specimens examined, the size and density of precipitates varied substantially from grain boundary to grain boundary. Some grain boundaries were free of precipitates. Microanalysis indicated that there was considerable variation in Cr depletion from boundary to boundary.

The results and micrographs were taken from the "worst case" boundaries because Cr depletion profiles were measured on boundaries with copious precipitation. Such boundaries were used because they will govern the observed corrosion properties, and exhibit measurable Cr depletion profiles. For many of the boundaries examined the Cr depletion profile was too narrow, and the change in Cr concentration from the matrix was too small to be measured accurately by this technique.

Examples of the microstructures where profiles were determined are shown in Fig. 3. Fig. 3a shows a typical location for a profile (a-b) made across a boundary in tube material aged for 500 hrs at 550°C. Profiles were made midway between carbides, approximately 100 nm from the nearest carbide. Fig. 3b shows a M_{23}C_6 precipitate in tube material aged for 100 hrs at 600°C. The precipitate may be seen to be growing along two grain boundaries, though not along the third.

Profiles were taken on all 3 boundaries surrounding a similar carbide. Fig. 3c shows profile (c-d) made between large carbides in bar material aged for 130 hrs at 650°C.

The following points will be discussed:

- The minimum Cr concentration in equilibrium with the carbide at the carbide/matrix interface.
- The Cr depletion profile that exists between the matrix and growing carbide and comparison with modelled profiles.
- The symmetry of concentration profiles.

5.3.1 Concentration Profile data,

Fig. 4 shows the Cr and Ni profiles of tube annealed at 1050°C for 30 min followed by 550°C for 500 hrs. Similar profiles were obtained

for the several boundaries examined in two separate foils. The measured minimum Cr concentration was 13.1 at% at the boundary with a peak width at half height of about 40 nm. It should be borne in mind that the sample volume for a 10 nm probe is large on the scale of this profile, because of beam broadening, and 13.1 at% represents an average value across a region some 30 nm in size. The true Cr concentration at the boundary will be considerably lower than this value.

Fig. 5 shows a profile obtained from tube material annealed at 1050°C and aged at 600°C for 100 hrs. Three profiles are given for boundaries meeting at a triple point, their positions relative to the carbide are indicated in the inset sketch. The Cr levels vary considerably from boundary to boundary. Variations in profile may not be explained by the measurements not being carried out on profiles parallel to the beam, because the overall width for the separate profiles is similar. Anisotropy of depletion has been explained [28] by anisotropy of diffusion rate. Therefore depletion depends on the type (high angle or low angle) of the boundary.

5.3.2. Asymmetric profiles.

Some measured profiles show asymmetry of Cr depletion with distance from either side of the grain boundary. An example of an asymmetric profile is shown in Fig. 6 for tube material aged for 500 hrs at 550°C. Similar asymmetries have been seen in other systems where element depletion is present [7,29]. Experimentally a profile is sometimes slightly asymmetric due to specimen drift during the acquisition of the profile. However, the drift seen during measurement of most profiles was far smaller than the scale of the asymmetry shown in Fig. 6.

Such boundaries were seen in specimens aged at all temperatures, but were particularly prevalent for material aged at the highest ageing temperature, 750°C, where boundaries are more mobile. Where asymmetrical boundaries are seen, evidence of grain boundary movement is also seen. It has been proposed [7] that the asymmetry of measured Cr profiles may be explained by the mechanism of precipitation. Cr carbide precipitation involves either diffusion-controlled growth or discontinuous (cellular) precipitation. The diffusion-controlled growth is governed by the transport of Cr atoms through the bulk to stationary boundaries. Discontinuous precipitation involves nucleation of Cr carbides and their growth by grain boundary diffusion, together with simultaneous grain boundary migration. As grain boundaries migrate during discontinuous precipitation, wide Cr depleted or asymmetric zones may result. Several different reasons for grain boundary migration have been suggested. Turnbull and Tu [29,30] suggested that Cr carbides are precipitated discontinuously by an interfacial energy driven pucker

mechanism. Fournelle and Clark [31] suggested that the chemical driving force of precipitation could cause grain boundary movement. It is therefore important to note that the precipitation mechanism determines the nature of the Cr concentration profile across the grain boundary. Profiles at stationary boundaries where carbides grow by volume diffusion (Fig. 3a and c) are symmetrical, whereas asymmetric profiles are seen where precipitation occurs discontinuously (Fig. 3b). A wide Cr depletion profile is obtained behind the migrating boundary, whereas ahead of the boundary the Cr concentration increases sharply. The major consequence of boundary movement and the associated asymmetric profile is to greatly increase the width of the region adjacent to the grain boundary which is depleted in Cr.

5.3.3. Calculation of volume diffusion coefficients for Cr.

The volume diffusion coefficients for Cr were determined from the measured Cr profiles by using a method originally suggested by Doig et al [32] and by Thorvaldsson et al [33].

In the early stages of the precipitation process the matrix composition C_x at a point x can be described by the following solution of Fick's second law because the mass transport of Cr along grain boundary is much faster than in the bulk.

$$7. \quad C_x = C_o + (C_m - C_o) \operatorname{erf} \left(\frac{x}{2(D_v \cdot t)^{0.5}} \right)$$

where t = ageing time

C_o = experimentally determined equilibrium Cr concentration at the boundary

C_m = bulk matrix Cr concentration

D_v = volume diffusion coefficient of Cr

x = distance from boundary

These quantities are shown schematically on Fig. 7a.

An estimate of the true value of C_o was that determined by the application of equation 6 to the Cr depletion data. The value of D_v can then be calculated from experimental Cr profiles by first determining the concentration C_x (at distance x) for which the term $\frac{x}{2.(D_v \cdot t)^{0.5}}$ in the error function equation above equals 1:-

$$8. \quad \frac{(C_x - C_o)}{(C_m - C_o)} = \operatorname{erf}(1) = 0.84$$

The distance from the boundary (x) at which the calculated C_x value is obtained is then inserted into

$$9. \quad D_v = \frac{x^2}{2t}$$

in order that the volume diffusion coefficient of Cr may be calculated. Fig. 7b shows an Arrhenius plot ($\log D$ against reciprocal temperature). Shown on the same graph are data obtained by Smith and Gibbs [34] and by Perkins et al [35]. The data from our STEM experiments differ from reported data (obtained by radio-tracer methods), especially for diffusion coefficients obtained from material aged at higher temperatures.

The discrepancy between the experimental data obtained and those previously published is due to both of the following reasons.

1. The Cr depleted zone will eventually heal during prolonged ageing. This healing process is not accounted for by the error function solution of Fick's law.
2. If very low temperatures are used then a significant time is needed for the nucleation of the grain boundary carbide, thus giving rise to an overestimate of the time for diffusion associated with the formation of a depleted zone.

Healing was evidenced in materials aged at higher temperatures and used for measurement of STEM profiles by lack of response in both Strauss tests and EPR tests which pick up Cr depletion. A simple calculation of the time required for healing may be obtained by using equation 7. The criterion for sensitisation is assumed to be that the Cr concentration falls below 12 wt% with 20 nm depletion width [1] at that level of depletion, and the diffusion data of Perkins et al [35] is used. The calculated healing times are:

550°C : 1400 hrs, 600°C : 114 hrs, 650°C : 1.1 hrs

Therefore it may be seen that of the materials examined, the material aged at higher temperatures is predicted to have healed. Values of the diffusion coefficient may not be calculated using data from healed samples, because the solution of Fick's second law is inapplicable.

The value of D_v obtained by the above method may be substituted into equation 7, to generate values of the Cr concentration at various distances from the grain boundary. The profile obtained by this method may be compared with the initial STEM data. An example of STEM data / erf curve fitting is shown in Fig. 8 for tube material annealed at 1050°C and then sensitised at 550°C for 500 hrs. Good correlation is achieved between the data and the profile generated by this method.

We may conclude that the symmetric Cr depletion profiles measured perpendicular to the grain boundary (where healing has not occurred)

are described by a collector plate solution to Fick's law. Although rapid diffusion along grain boundaries plays an important role in the delivery of Cr to the growing carbide, the rate controlling step in the development of carbides and Cr depletion profiles is the bulk diffusion of Cr to the boundary. However, a discrepancy is seen between model prediction and experiment at higher temperatures, because healing is occurring together with additional precipitation processes (eg Nb(CN) precipitation) which affect the thermodynamics of $M_{23}C_6$ precipitation (by altering the level of C in solution). Therefore, at higher temperatures the solution of Fick's law is inapplicable.

5.3.4. Cr minimum levels.

As described in section 5.1.3, broadening of the electron probe by inelastic scattering of electrons within the specimen results in composition profiles and concentration values [17,18,19] that are different from the true values. Beam broadening leads to higher values of Cr than the true concentration being measured at the grain boundary. The model (SAROC) described above was used in order to obtain an estimate of the minimum Cr level that occurs at the carbide/boundary interface.

An estimate of the Cr minimum level was obtained by extrapolation of measured Cr depletion data using equation 6.

These values are listed in table 2.

Table 2. Predictions and measurements of Cr concentration (at%) at grain boundaries, together with response in sensitisation tests.

Specimen	SAROC model	measured STEM value	Corrected measured value	Width at half height(nm)	Depth in Strauss Test(um)	Peak EPR current mA cm ⁻²
1050'C anneal						
550'C 500 hrs	11.5%	13.1%	11.2%	33	95	37
1050'C anneal						
600'C 100 hrs	14.8%	16.6%	14.8%	30	20	7

The values obtained by modelling and deconvolution of the obtained profile are both significantly lower than the measured Cr minimum level, though not dissimilar from each other. Hall and Briant [7] similarly noted that AEM techniques could accurately measure Cr profiles, but differed from predicted values of Cr concentration at the grain boundary. Similarly Bruemmer [37] used a variety of models to compare predicted and observed minimum Cr concentrations, and found that predicted and measured Cr minimum concentrations differed in that the models tended to overpredict the Cr depletion during low temperature ageing.

Models may overpredict Cr depletion for low temperature ageing because of the following reasons:

1. C solubility at low temperatures is higher than extrapolation from high temperatures downwards would suggest.
2. C at low temperatures is bound up within the microstructure and only a proportion of it can diffuse to boundaries.
3. Models overpredict or do not consider the activity changes of C at low temperatures. This may arise because models do not consider the effect of the change in carbide and matrix composition with temperature on the activity coefficients of C and Cr, and on the equilibrium equation (section 3.8.1.)

5.4 Comparison between STEM measured profiles, modelling and corrosion tests.

A picture of the extent of Cr depletion may be obtained via modelling and by the direct measurement of solute profiles across boundaries using AEM. Only a few attempts have been made to obtain direct correlation of corrosion tests with experimentally measured AEM profiles together with theoretically derived profiles [eg. 37].

The purpose of the following discussion is to compare the profiles obtained by modelling and AEM with macroscopic corrosion data. Such comparison should allow corrosion test results to be interpreted more correctly in terms of true grain boundary chemistry.

The prediction of low temperature sensitisation and desensitisation times from extrapolation of experimental results by modelling is of great importance for the planning of replacement or maintenance operations of components.

By comparison of microanalysis data, Cr depletion and corrosion test data it is evident that a relationship exists between the occurrence of Cr depletion at grain boundaries and attack in Strauss tests and EPR tests. The limited amount of AEM data collected makes direct quantitative comparison between Cr profile and macroscopic corrosion difficult. Furthermore, to be able to resolve profiles, profiles that were wide enough to be determined accurately by microanalysis were examined; such material was usually in the "healed" condition (as revealed by estimates of Cr diffusion rates in such materials, section 5.3.3). Of the samples examined by AEM the one giving the greatest response in any of the electrochemical tests was that for tube material annealed at 1050°C and aged for 500 hrs at 550°C. The measured minimum value of Cr concentration in this material was 13.1 at%. This material was severely attacked in a Strauss test. This attack differs from the criterion of 12 wt% suggested by Stawstrom and Hillert. However it must be remembered that effects such as beam

broadening (resulting from inelastic scattering of the electron beam) will change the Cr concentration seen from the actual value.

Reasonable comparability between the measured STEM data and the model-generated profiles is seen. However, a discrepancy is seen between prediction and experiment at higher temperatures, because both healing is occurring together with additional precipitation processes (eg Nb(CN) precipitation) which affect the thermodynamics of $M_{23}C_6$ precipitation (by altering the level of C in solution). This does not explain the difference between the Strauss data and the regime that the SAROC model suggests as sensitised. A discrepancy could arise not because the criteria are wrong, but because the model is unable to predict sensitisation at higher temperatures. The SAROC model does not consider the change in the activity of Cr and uses a Cr eff term to by-pass the need for knowing the activity coefficients of C and Cr. The model does not take into account the fact that the Cr concentration at the boundary rises during healing.

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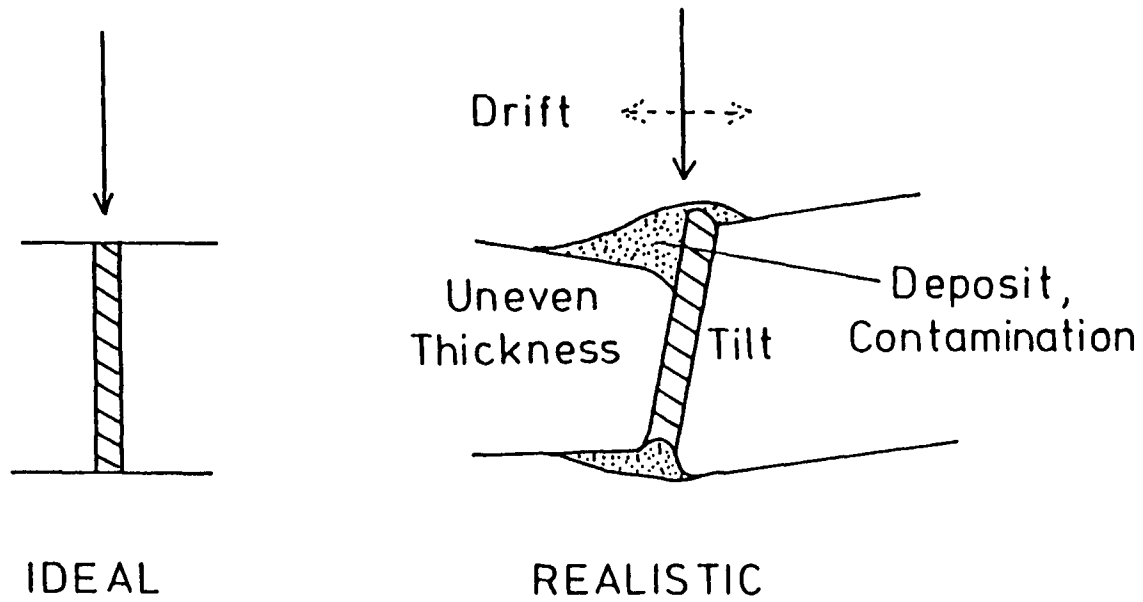
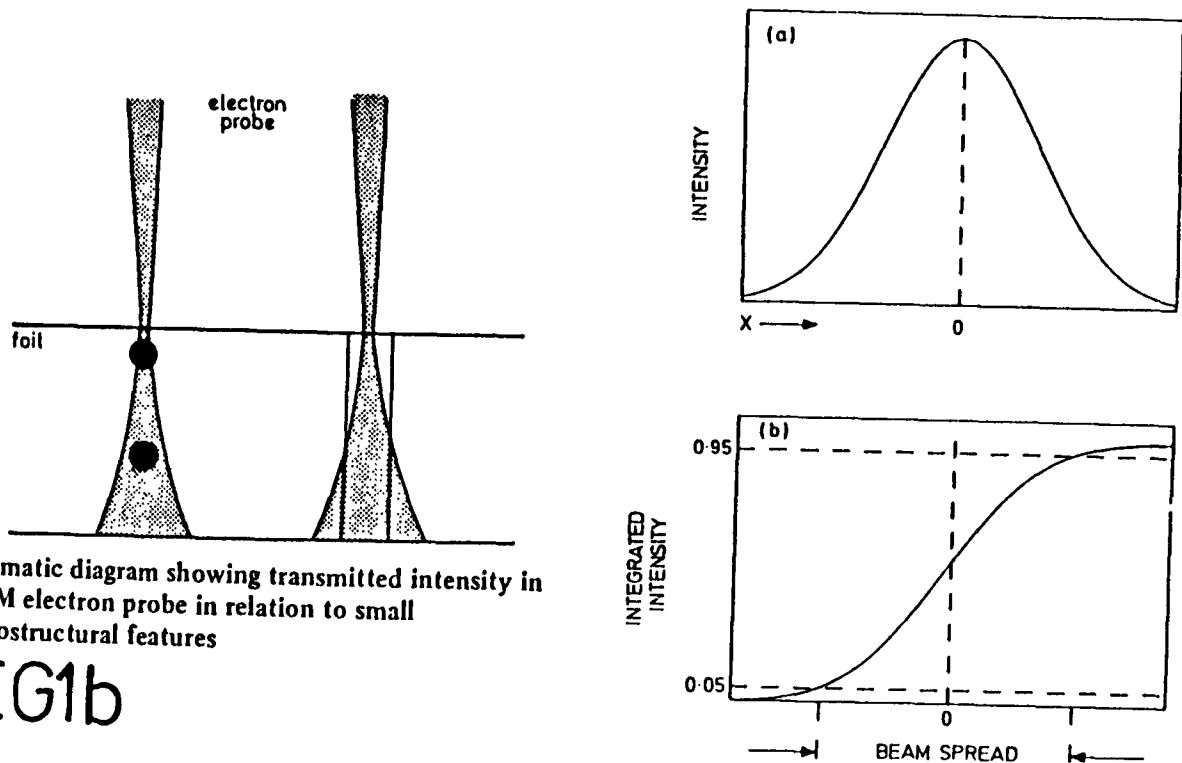


FIG1a Schematic representation of ideal and realistic grain boundaries oriented for analysis.



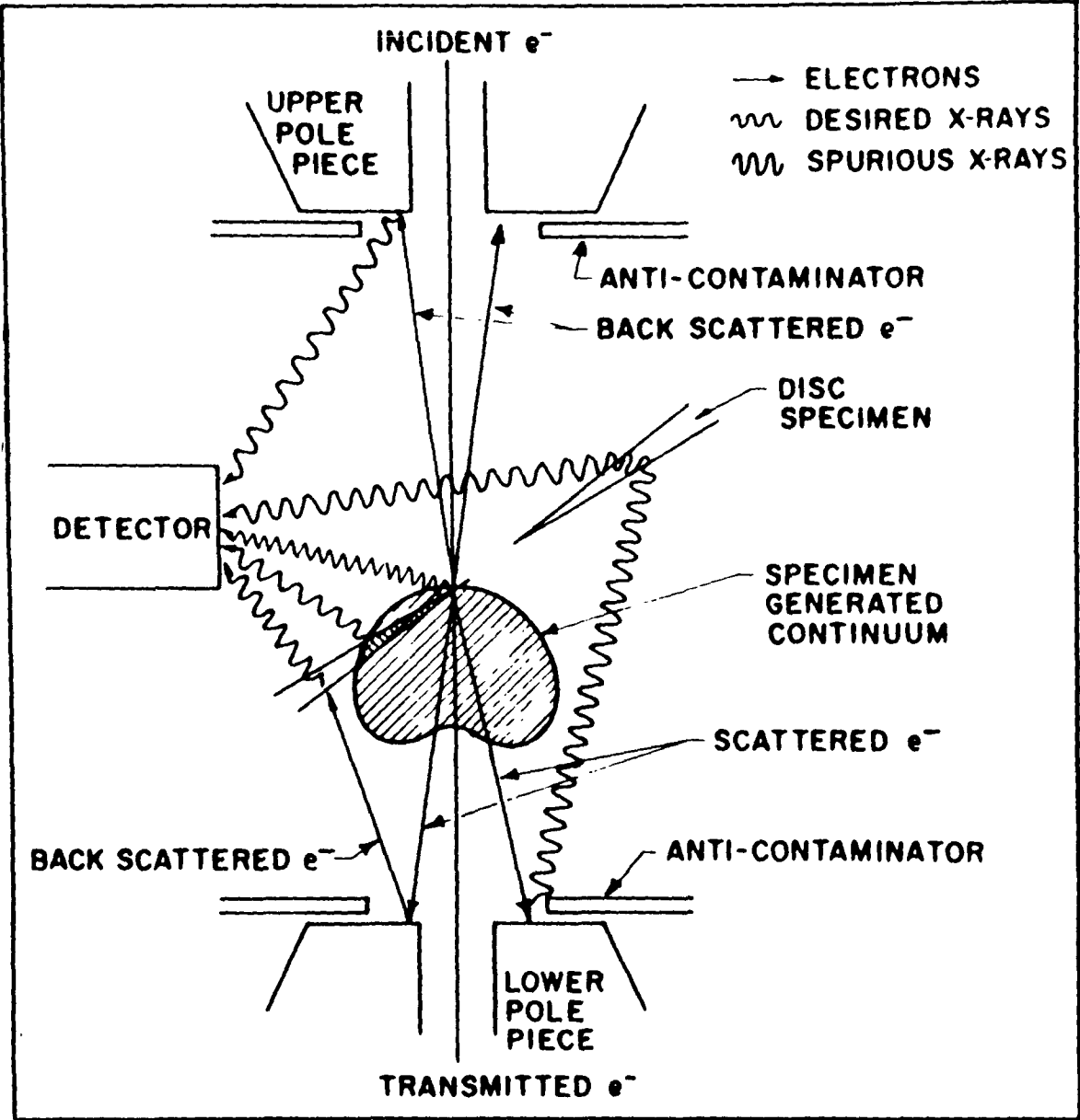
Schematic diagram showing transmitted intensity in STEM electron probe in relation to small microstructural features

FIG1b

FIG1c

Schematic: (a) radial electron intensity distribution in STEM electron probe; (b) relative intensity generated by traversing probe in X direction across boundary at $X = 0$

Instrumental characteristics that limit the resolution of X ray micro analysis.



Sources of spectral artifacts due to electron beam-thin disc specimen interaction in AEM

FIG 25[ref 12]

Figure 3.5

Typical locations for obtaining Cr depletion profiles

- A. Tube material annealed at 1050°C for 30 minutes and aged at 550°C for 500 hours.
- B. Tube material annealed at 1050°C for 30 minutes and aged at 600°C for 100 hours.
- C. Bar material annealed at 1050°C for 30 minutes and aged at 650°C for 130 hours.

A

a

b

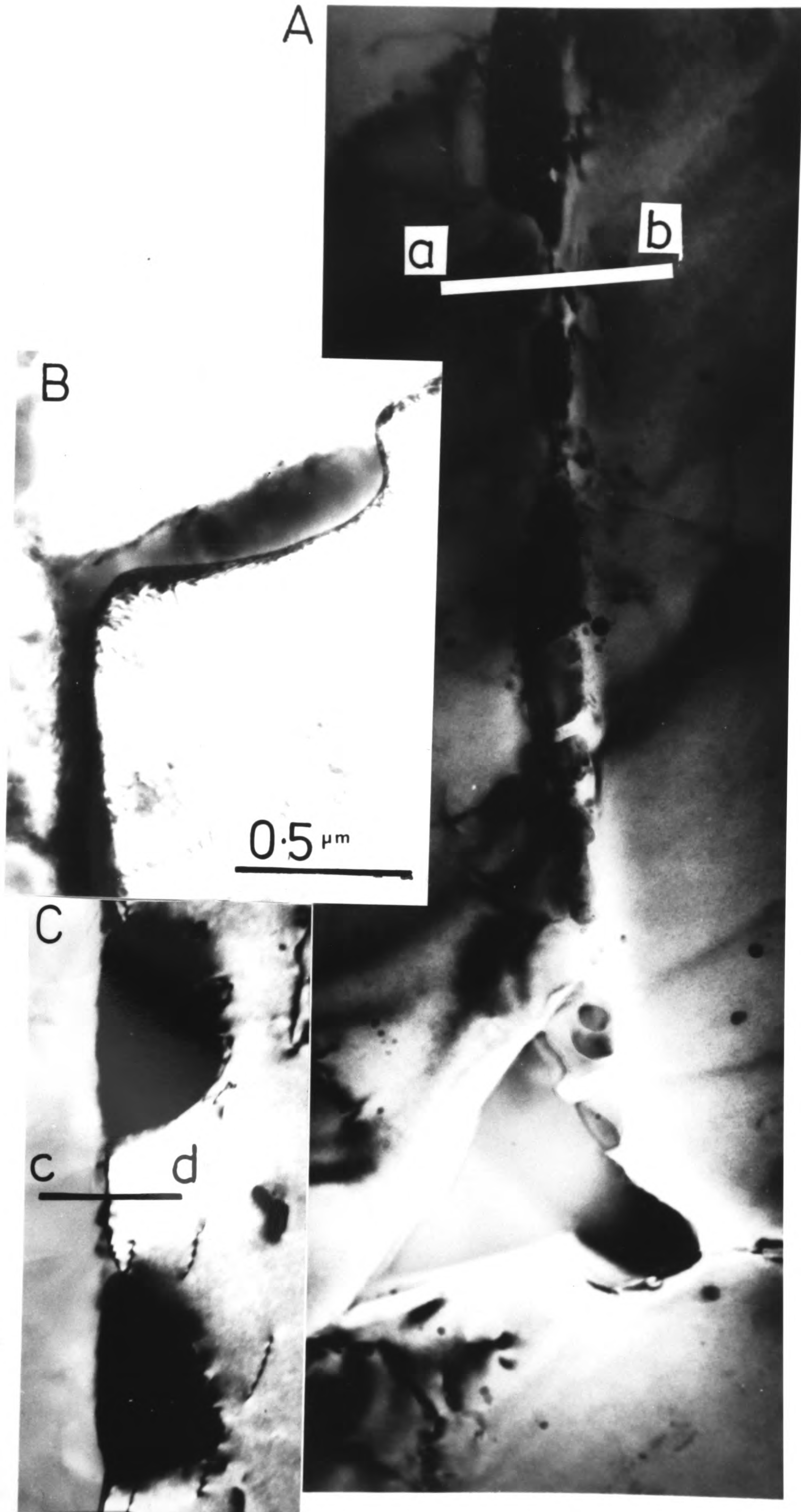
B

0.5 μm

C

c

d



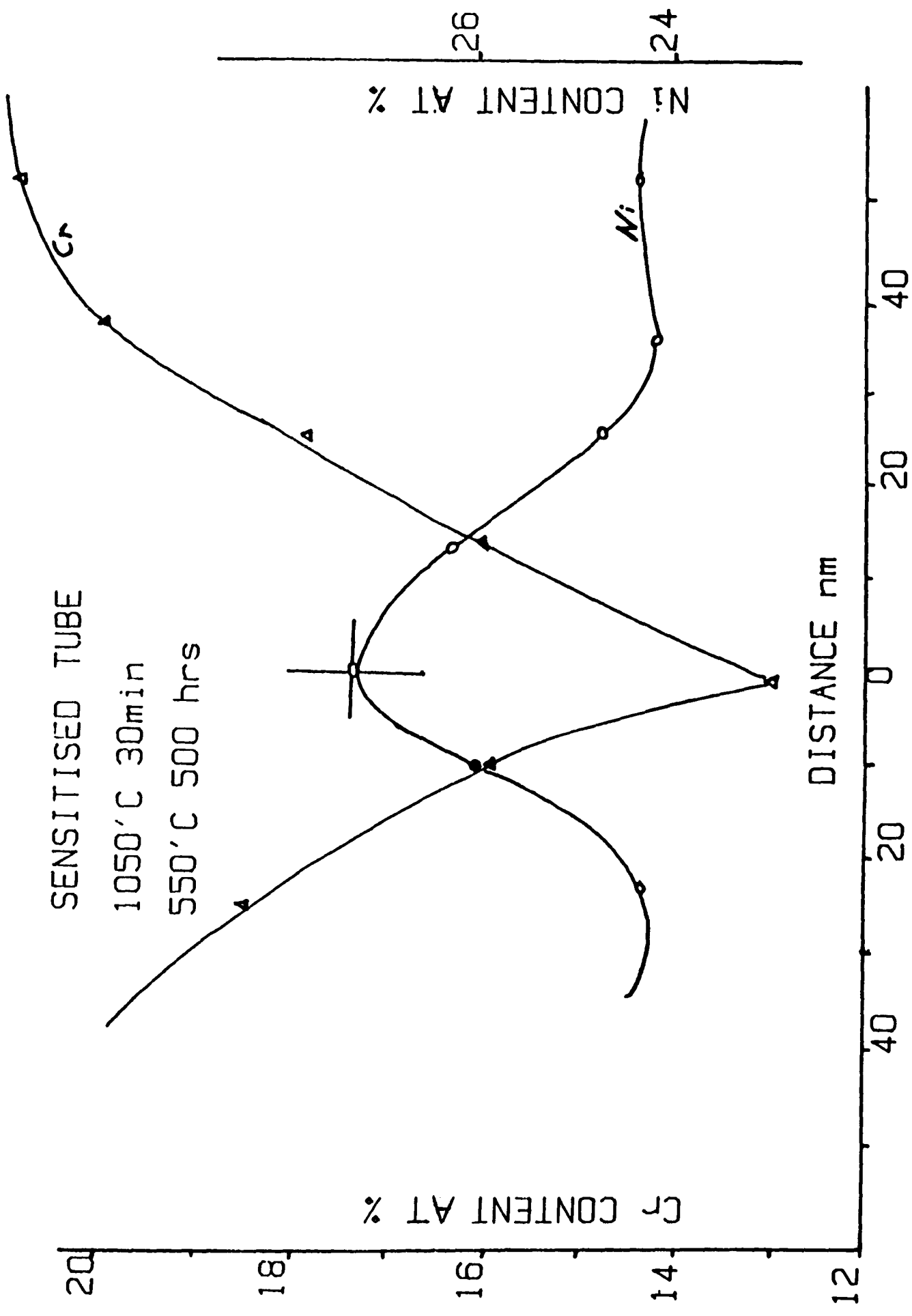


FIG 4.5

Ni and Cr compositional profiles, obtained using STEM microanalysis

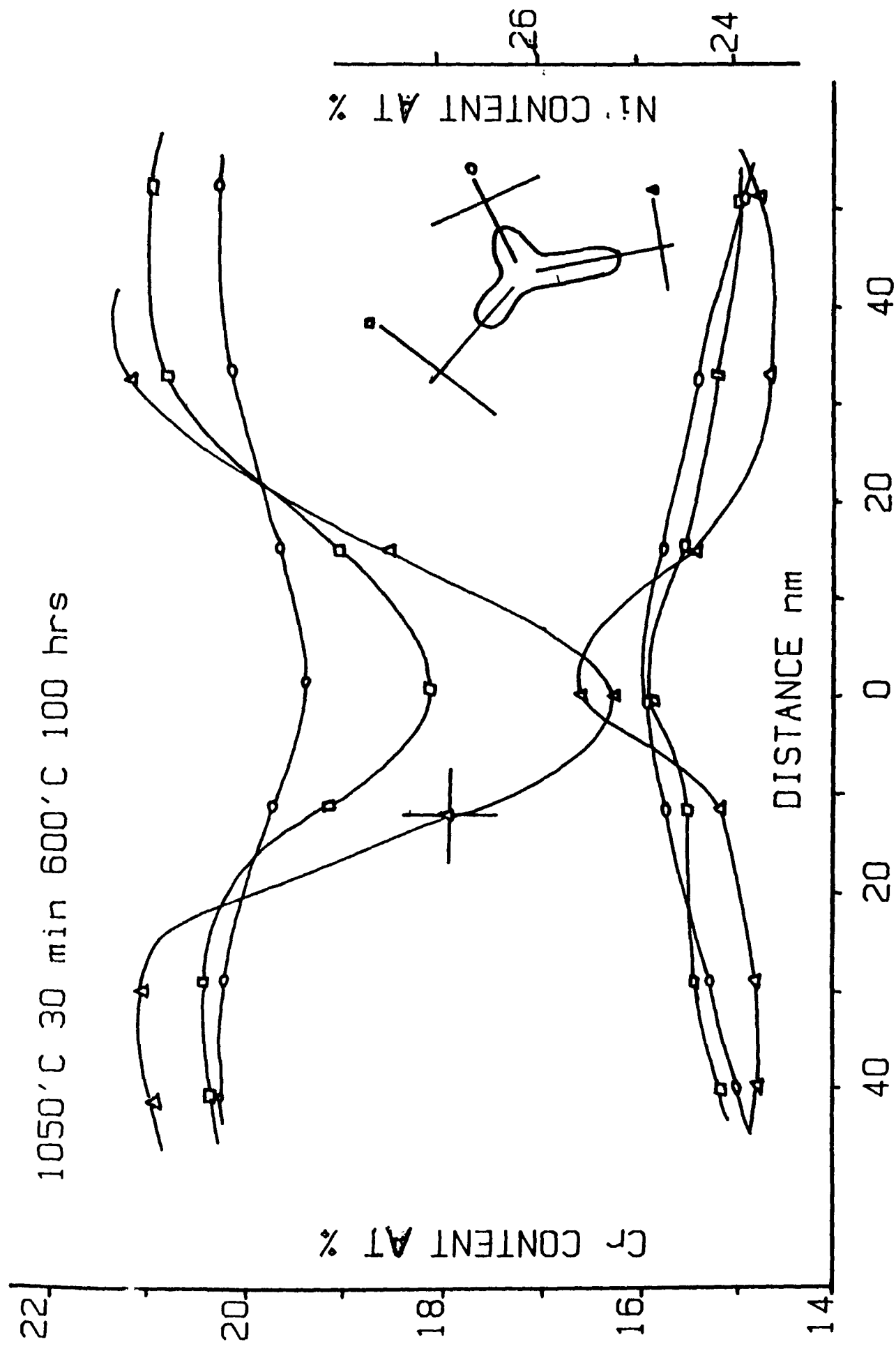
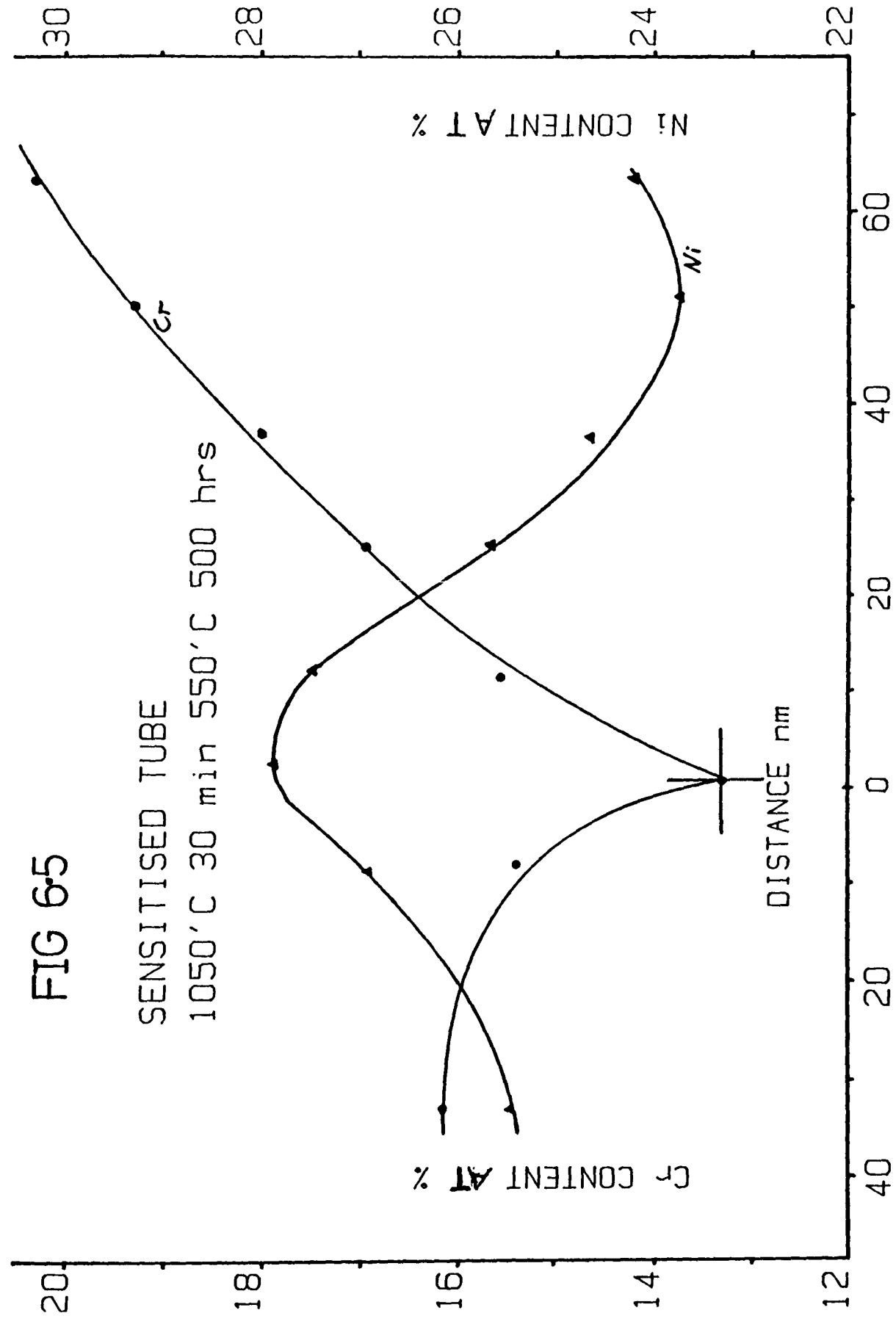


FIG 55

Ni and Cr compositional profiles, obtained using STEM micro analysis.



Asymmetric Cr and Ni compositional profiles, obtained using STEM micro analysis.

FIG 7.5a

Schematic of the parameters for the calculation of Cr diffusion coefficients.

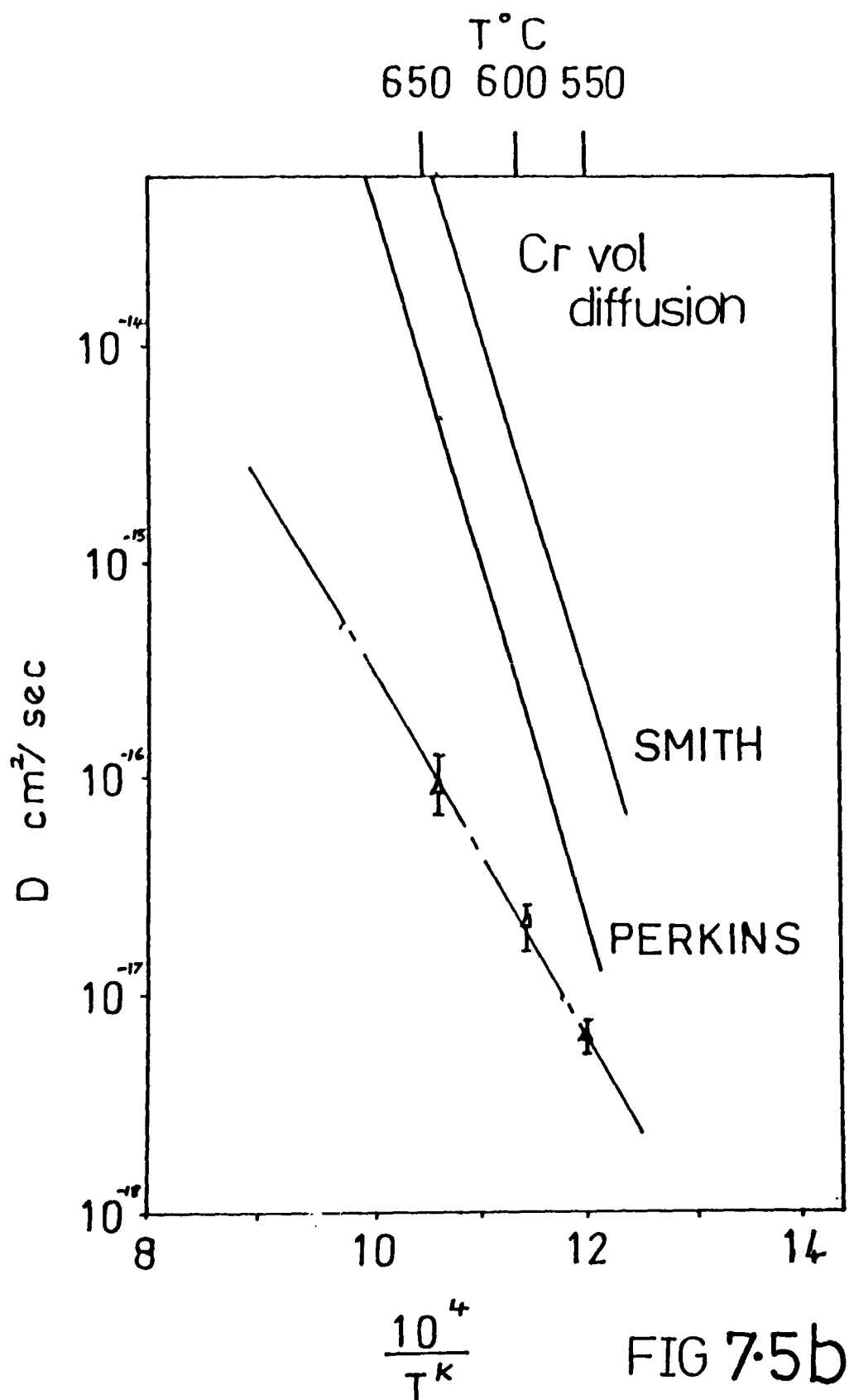
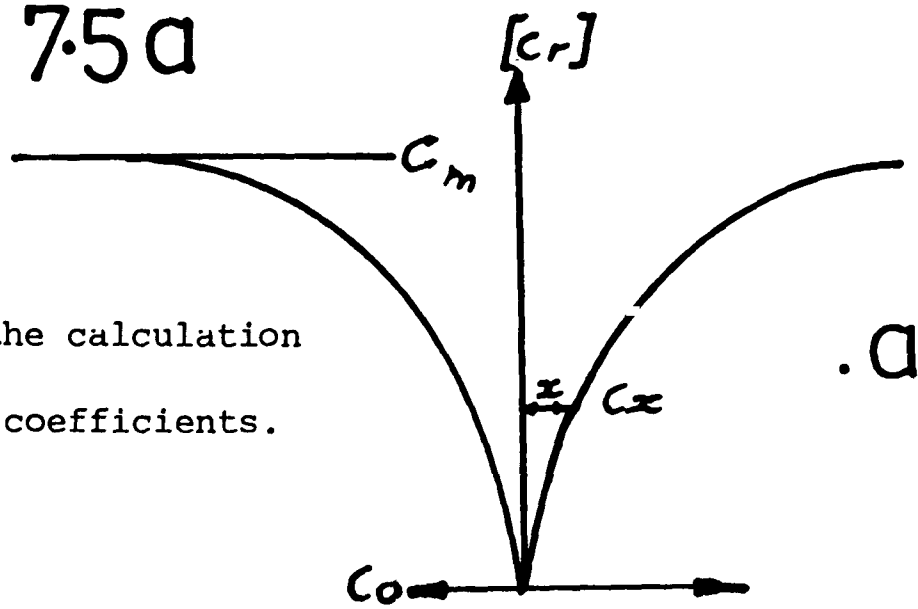
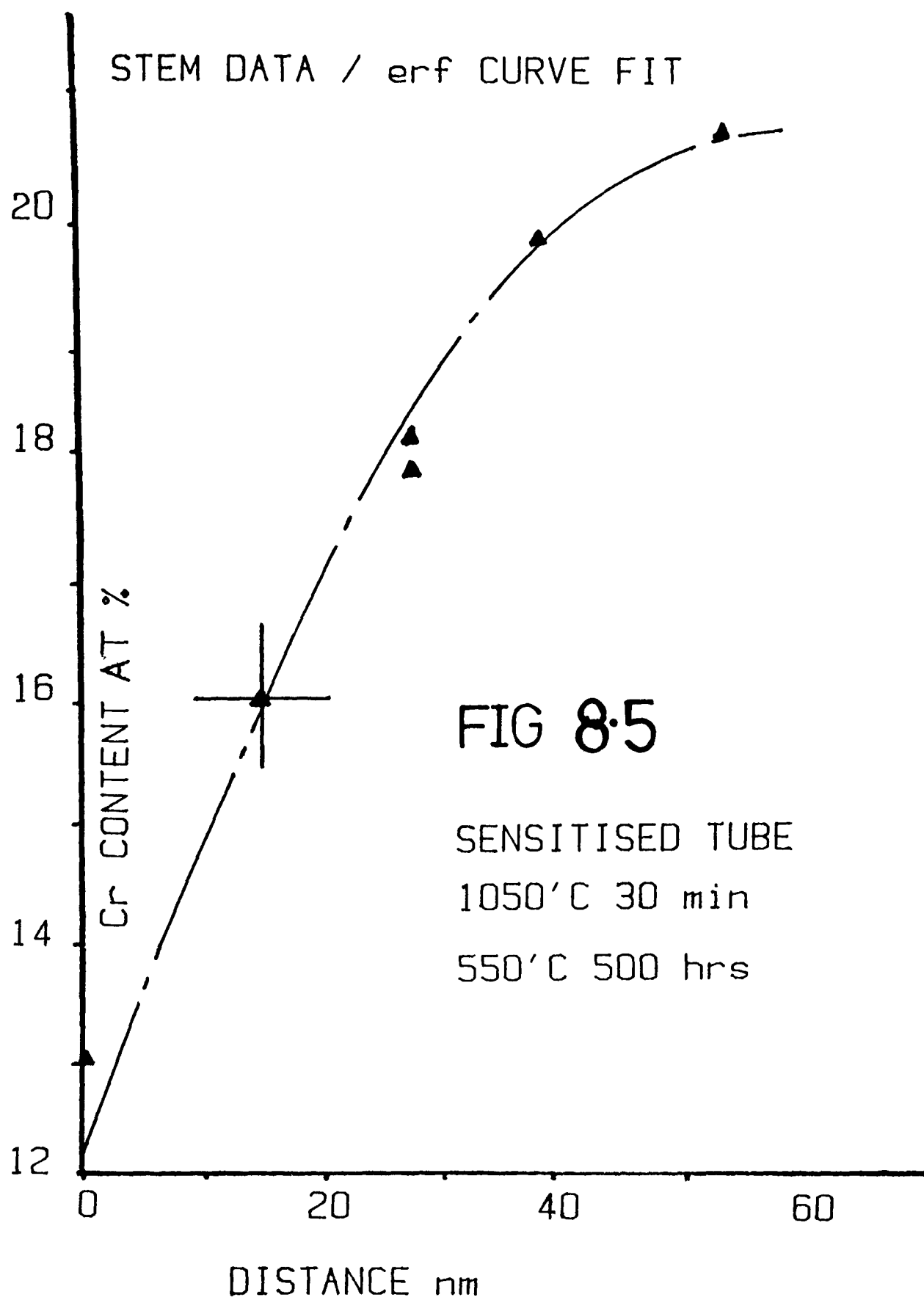


FIG 7.5b

Comparison of diffusion data from STEM micro analysis with that reported in the literature.



Curve fitting of STEM compositional profile data with
ERF analysis, to extract diffusion coefficients.

CHAPTER 6

The effect of Low Frequency Cyclic Stress on the Stress Assisted Corrosion Attack of 20% Cr, 25% Ni, 0.7% Nb stainless steel.

The need to achieve an understanding of the effect of stress on the corrosion behavior of materials has led to a range of tests. The starting point for gathering information is to simulate the practical situation, especially with regard to the microstructure of the material and environmental aspects in practice. There are many different methods of applying the stress to the test specimen, the most popular range from the constant strain and constant stress methods, through to constant strain rate methods. The disadvantages of these tests are that in a constant load or constant strain test attack initiation and propagation may be slow, while in a constant strain rate test the yield stress is rapidly exceeded. The presence of a cyclic stress superimposed on an existing tensile stress may accelerate corrosion attack rates and reduce initiation times. Such a method offers the opportunity to investigate SCC and stress assisted environmental attack under conditions of dynamic strain whilst at no time during the test exceeding yield stress, and is therefore more analogous to the practical situation, where stress levels above the yield stress are not usually encountered.

The purpose of this section is to present the method and results of low frequency cyclic stress on the SCC of sensitised 20% Cr, 25% Ni, 0.7% Nb stainless steel. The effects of both imposed low frequency saw tooth load cycling and static loads are examined. Thin-wall tensile specimens have been subjected to a static stress superimposed on which were low frequency (10^{-2} to 10^{-4} Hz) saw-tooth cycles. The effects of mechanical and electrochemical variables on crack propagation have been examined. Most cyclic testing was carried out at below-yield stress levels in HNO_3 environments.

6.1. EXPERIMENTAL

This section describes the apparatus and method used to impose a low frequency cyclic stress on top of an existing background tensile stress, on sensitised stainless steel held potentiostatically in HNO_3 solution.

6.1.1. Specimen manufacture

Material was delivered in the form of AGR fuel cladding, thin wall tube of wall thickness 0.32 mm and of dimensions 15.5 mm overall diameter by 1 m in length. The tube has ribbing machined on after tube drawing, to aid gas flow and consequent heat removal during service.

Tensile specimens were machined from the fuel cladding tube by filling 100mm lengths of the thin wall tube with a lead/tin ("Seribend") alloy to avoid gross distortion and tearing during machining. Tensile specimens were machined out of these lengths by removing 2 diametrically opposed scallops; splitting the can longitudinally yielded two specimens for stress corrosion experiments. Specimen dimensions are shown in fig. 3a.

6.1.2. Heat treatment.

Specimens for the bulk of stress corrosion tests were solution annealed at 1050'C (in an Argon atmosphere) for 30 min and then aged (in a vacuum of about $10E^{-6}$ Pa pressure) at 550'C for 500 hrs. This method was originally described by Miller and Roscoe [1] and produces a severe degree of grain boundary Cr-depletion while avoiding grain growth. Additionally some specimens were solution annealed at 1050'C then aged for times of 25, 50, 100, and 200 hrs at 550'C.

The heat treatment furnace was accurately calibrated, and the variation of temperature measured during heat treatment was found to be +/- 1.5'C.

6.1.3. Electropolishing.

For corrosion testing it is important to remove the oxidised surface layer resulting from heat treatment to ensure uniformity of specimen surface over individual specimens and from specimen to specimen. It is well known that surface condition may dominate corrosion behaviour.

Section 4.3.2. and Appendix 4 show that Strauss tests can vary markedly dependent on the degree of surface oxidation. Cr-depletion for vacuum annealed (10^{-4} Pa, 100 Hrs, 1000'C) 20% Cr, 25% Ni, X% Nb has been reported [2,3,4], to levels of 6 wt % Cr at the surface and depletion below the bulk Cr level extending in to samples as far as 100 um. Lobb and Evans [4] reported that the Cr-depleted layer after heat treatment at 850'C extends to 30 um and the Cr concentration at the surface drops to 15.2 wt%. It was therefore decided to electropolish specimens to remove oxidation and any residual surface damage resulting from machining.

Electropolishing was carried out (following ASTM recommendations [5])

for 10 mins in a 40 vol% orthophosphoric acid, 50 vol% glycerol, 10 vol% H₂O solution at 60°C. A current density of 50 mAcm⁻² was used. Lacomit stop-off varnish was used to ensure only the gauge length was polished. The solution was agitated by vigorous aeration. After polishing, specimens were ultrasonically cleaned in toluene, then methanol, and stored in a dessicator until later use. Detailed SEM and optical examination of the electropolished surface showed that the electropolishing process had resulted in a uniform smooth surface.

6.1.4. Apparatus

A low-frequency stress was imposed on top of an constant tensile stress by using a modified creep rig illustrated schematically in fig. 1. Three such creep rigs were used. Specimens were tested in HNO₃ whilst under potentiostatic control.

A background tensile stress was applied by weights (W) via the creep lever arm. A cyclic load was generated by water flowing into and out of the container (S), which flushed when the level reached the level of the outlet pipe (O). The resultant saw-tooth wave form is illustrated in fig. 2; a slow linear increase in load resulted whilst the container filled, followed by a rapid unload as the container was drained by the siphon (SH). As the water flowed from the container in to the tank (B), it was pumped by a motor pump (P) to a constant head tank (CH), which feed the container. Flow to the container was regulated by using either stop cocks (SC) or lengths of capillary tube. A thermostat was used initially to ensure constant temperature of the water and thus constant viscosity, however it was found unnecessary and was not used in further experiments. The reproducibility of the cycle time during experiments depended on the flow speed into the syphon, and was found to be +/- 5 % for cycle times less than 30 min, though less reproducible for longer cycle times, as the regulating stop cocks gradually blocked with dust. Two different sizes of container were used. The additional loads imposed by the container were found to be 2.4kg and 1.9kg by measuring the volume of the water that syphoned out repeatedly. An estimate of reproducibility was made over a number of cycles and variation found to be less than 50 grams. This translates to +/- 0.5 % in terms of the measured yield stress.

The specimen (SP) was located on the other side of a knife edge pivot (F) from the weights and container. The specimen received a stress proportional to the weight of the container and water and the static load which was determined by the ratios of the lengths (x, y, and z) shown in fig. 1. The creep rig arm was set to horizontal by a position transducer (HT), linked to a motor and gear, at the base of the specimen chain. The position transducer was not used while experiments were running.

Deformation in the specimen was followed by a transducer (T) at the end of the creep rig arm. Two types of transducer were used, a "Novatech" transducer with a 2V output for 25 mm travel and a "Schaevitz" DC transducer with an output of $\pm 5V$ for 25 mm travel. To ensure that the creep rig was functioning reliably, and that displacement of the transducers truly represented strain in the specimens, the response of both transducers was checked in relation to the response of strain gauged specimens. The method of calculation of the change in strain from the measured output, for transducers and strain gauges is given in Appendix 2. Good correlation between the two methods of strain measurement was seen, as is shown in fig. A.1 in Appendix 2 in the appendix. Comparison of the change in strain measured by the transducers with that measured by strain gauges was excellent, and agreement was seen to better than $\pm 0.01\%$ strain. It was concluded therefore that the transducers accurately revealed displacement in specimens. The transducers and their output/displacement characteristics were calibrated using a stage micrometer. Both the transducer and the strain gauge had linear characteristics over the range of strains seen in both cyclic stress corrosion and cyclic creep experiments. The limit of reliability for the strain gauge was about 2% specimen strain, whilst the limit of travel of the transducers limited strain measurement to about 8% specimen strain.

Inaccuracy of the measurement of the true overall strain resulted during transducer use because during initial loading of the specimen slack is taken out of the system. To off-set initial transducer movement, a potentiometer box was placed in the transducer output circuit. Before starting strain measurement, the specimen was lightly loaded to remove all slack in the loading system and the transducer base line set at zero, and then loading started.

As the gauge length was off-set from the axis of the tube specimen, grips were designed so that the stress axis of the testing machine lay along the mid wall position of the can. A schematic drawing of the specimen/grip assembly is shown in fig. 3c.

Specimen/cell assemblies were loaded into position using the jig shown in fig. 3b. Use of the jig ensured no pre-deformation of the delicate thin wall tube before testing and aided correct alignment of the specimen assembly.

The stress applied to the specimen was calculated (described in Appendix 3) knowing the width and cross section of the specimen, the applied weight, the quantity of water flowing in and out of the syphon and the beam ratios of the creep rig. The loading stress during the experiment is quoted in terms of the yield stress, which was determined as 300 N/mm² under loading conditions similar to those used in SCC experiments. This value was measured at a constant loading

rate (of 100 g/min) on the modified creep rig described above, by allowing water to flow continually into a large container on the end of a creep rig arm. The limit of proportionality was chosen to represent the yield stress. Plots of stress against strain for both the as received and sensitised materials are shown in fig. 4. It was found that the measured yield stress was not dependent on loading rate (for the limited range of rates used). The Youngs Modulus determined from these data was 100 GPa for both sensitised and as-received tube material.

The cell design is shown fig. 5. Sealing the specimen into the cell was awkward because of the specimen geometry. To overcome this problem a tapered mould was used to cast a rubber bung round the specimen.

The rubber used was a two-pack butyl rubber supplied by DEVCON (Flexane 94). Experiments were conducted in solutions made from analytical reagents (BDH) and singly distilled water.

Potential was controlled using either potentiostats constructed from operational amplifiers (circuit shown appendix 1), or conventional potentiostats (Thompson ministats).

Current was applied using a platinised titanium counter electrode, (a Luggin probe for the calomel reference electrode was thought not to be necessary as the solutions used were conductive). Potential was measured with respect to a Standard Calomel Electrode (SCE). Temperature was controlled to 25°C $\pm$ 0.5°C by electrical heaters controlled by thermostats.

Specimens were placed in cells, loaded on the creep rigs, the cells filled and then load applied. Load was gradually applied to the specimens by lowering the weights on to the creep rig arm by using a jack (J). An oil dashpot ensured that load was applied smoothly.

Specimens were then left to creep out for about 30 min before the potential was applied.

Current was measured as a voltage generated across a resistor in the counter electrode lead. This signal went to a multiplexer controlling the signals from 3 such cyclic stress corrosion tests. The multiplexer simply switched from one signal to the next in turn separately, and fed inputs to a buffer amplifier and single pen chart recorder.

A schematic of the potentiostat control and measuring and recording apparatus is shown in fig. 6. Appendix 1 lists the references used for the construction of the electronics used in experiments.

The information stored on the chart recorder was thus:-

1. Displacement/time data from the transducer or strain gauges.
2. Current/time data from the voltage drop in the resistor in the counter lead.

6.1.5. Examination of crack growth rate.

Because existing techniques of crack (or penetration) depth measurement are difficult to apply to thin wall tube and because no in-situ techniques could be used the only option available to monitor the appearance of short multiple IGA was to examine penetration after experiments and to build up a matrix of penetration depth/time for different mechanical and electrochemical conditions.

Two methods were used to estimate penetration depths in samples.

1. Specimens were mounted edge-on in bakelite (shown schematically in fig. 7) and polished to a 6 μm finish. To enable better (un-bevelled) edge preparation, some samples were plated in Ni. Light etching was used to reveal tight penetration paths and allowed better estimation of the depth of penetration. The etching reagent used was dilute Aqua Regia (20 vol% HCl, 5 vol% HNO₃, remainder H₂O). Penetration depth was measured by examining cross sections at 200X magnification on an optical microscope. The 10 longest penetration depths along a section were measured, and an average determined. The section was then ground back further and the process repeated, to ensure that the initial average was representative of the sample.
2. Samples were fractured on either a Hounsfield tensometer or an Instron tensile test machine at a strain rate of about 5×10^{-4} /sec. The fracture surface was then examined in an SEM. Comparison of crack length with those of unstrained specimens showed that mechanical fracture did not extend the cyclic stress corrosion generated attack but simply widened tight penetration paths and made examination easier. The transition between penetration by cyclic stress assisted corrosion and the final mechanical fracture was clearly seen. Fracture generally occurred at the location of deepest penetration.

Comparison of penetration depths measured from fracture surfaces and from cross sections showed that both methods gave similar values of penetration depth and gave an unambiguous result for the maximum penetration depth attained.

6.1.6. Experimental Variables.

The following variables were used.

A. Specimen Potential

The test potentials used were -300, -200, -100, 0, 100, 300 mV SCE and the free corrosion potential. The solution used was 1M HNO₃. Most results are for tests carried out potentiostatically at -200mV as this was found to be the potential where IGA was most rapid.

B. Specimen Condition

The majority of specimens were in the fully sensitised condition ie had been heat treated via a 1050'C anneal followed by 550'C for 500hrs. Some as-received specimens and some which had been annealed and then aged for various lengths of time at 550'C were also tested.

C. Loading Conditions

The following mechanical test variables were used

1. Static : A constant load conditions at various stress levels.
2. Dynamic : A saw tooth stress waveform was used; the stress ratio varied from 0.1 to 0.7 for a peak stress level between 30 and 90% of the determined yield stress; cycle times between 400 and 5000 sec were used.

Loading conditions are connected in the following way. It is apparent from fig. 8 that for the same maximum-stress a decrease in R (a larger stress amplitude achieved by moving from min stress.1 to min stress.2) results in a decrease in the mean stress. Furthermore, a decrease in frequency for a constant value of R means that the rate of applying the stress decreases. Two alternative container volumes were used in tests, R was also adjusted by varying specimen width and cross section.

In total, some 180 cyclic stress and static stress corrosion experiments were carried out.

6.2. RESULTS

All potentials refer to Standard Calomel Electrode (SCE), and all the quoted stress levels are in terms of the measured yield stress (ie % of 300 MPa).

6.2.1. Effect of test potential on cyclic stress assisted intergranular attack.

The free corrosion potential of sensitised tube in 1M HNO₃ gradually rises with time then falls and settles at about -200mV, shown in fig. 9. A number of test potentials were examined during low frequency cyclic stress testing. It was found that the potential for stress assisted corrosion was an important parameter, and cyclic stress assisted corrosion of artificially sensitised 20% Cr, 25% Ni, 0.7% Nb stainless steel was found to occur readily at -200mV. However, at potentials outside a band some 30mV above or below this value, a much lower rate of attack was seen. At potentials other than -200mV rates of IGA were as much as an order of magnitude less and often no attack is seen at all. Attack at potentials other than -200mV was shallow,

patchy and often associated with individual carbides. An example of the different morphologies of attack is shown in fig. 10 and fig. 11.

Figs. 10a and b show pitting over the surface of specimen held at 300mV and a peak stress level of 70% and cycled with 1800 sec cycles (5.5×10^{-4} Hz) with $R=0.6$. Testing was carried out for approximately 72 hrs. Attack is localised around grain boundary carbides.

Fig. 10c shows attack in a specimen tested in a similar way though held at 100mV, again attack is shallow, and localised to carbides.

Figs. 11a and b show surface attack on the surface of a specimen held at 100mV, and cycled with peak stress levels of 75 and 120% yield stress respectively. A cycle time of 1800 sec was used with $R=0.1$ for a test lasting approximately 72 hrs. Attack is extensive where the specimen has been cycled at above yield stresses. Fig. 11b' shows a cross-section of the specimen tested at 120% yield stress, attack extends to a depth of about 18 μm .

Attack at test potentials of -100, 0 and 100mV occurs preferentially on grain boundaries normal to the direction of stress, not every boundary is attacked, many remain immune.

6.2.2. Cyclic stress assisted intergranular attack at -100 and -200mV.

The bulk of tests were carried out at -200 mV because this was found to be the potential at which stress assisted intergranular attack occurred most readily. The majority of other tests were carried out at the more passive potential of -100mV. Attack for all tests at both potentials occurred uniformly along the gauge length and no notable effect was associated with specimen geometry.

NOTE: The bulk of tests were carried out for 72 hrs. As a simple basis for comparison the average rate of penetration or crack growth rate was obtained by dividing the measured maximum crack length or penetration depth by the test duration. This procedure has widely used elsewhere, but implies that the rate of propagation throughout the test is constant, and that no time is taken for attack initiation.

The methodology behind the organisation of the following section is to describe the IGA rates observed for the experimental variables, and then to discuss the microscopically observed variation of crack morphology. The direction of the applied stress during testing is indicated on photographs.

In parallel with the low frequency cyclic tests, static loading tests were carried out at comparable peak stress levels. Static load test data are shown in fig. 12. The rate of grain boundary penetration at -200mV is more than an order of magnitude greater than that at -100 mV

for a given stress level. The rates obtained for "dead-loaded" tests are shown on stress against IGA rate parameter graphs, because cyclic stress corrosion data are later described in terms of how damaging the effect of cyclic stress is in comparison to static loading at the same peak stress level. It is notable that increasing the applied static stress (even for below yield stress levels) results in faster attack than where stress is absent.

In the absence of stress, IGA is slight ($<2\mu\text{m}$) at -100mV though penetration reaches $30\mu\text{m}$ deep in 100 hrs at -200mV .

6.2.3. -100 mV results.

Penetration rates at -100mV are up to an order of magnitude less than those at -200mV for the same peak stress level, and at low stress levels only pitting around carbides or along grain boundaries takes place.

Fig. 13 shows IGA rate plotted against peak stress for specimens cycled with an R ratio of 0.6, for tests lasting 72 hrs. It may be seen that for low stress levels the rate of IGA for both 600 sec and 1200 sec cycle times ($16 \times 10^{-4}\text{Hz}$ and $8.4 \times 10^{-4}\text{Hz}$ respectively) is less than that for the static load tests. Furthermore, for a given peak stress level the rate of IGA for a cycle time of 1200 sec is similar to that for 600 sec cycles.

Fig. 14 shows the effect of stress amplitude. It is found that larger amplitude cycles (smaller R values) leads to larger rates of IGA. The rate of IGA is now larger than those seen during static loaded tests carried out at the same peak stress.

Figs. 15a and 15b show the surface of samples tested at $R=0.7$ with a peak stress of 55 % of the yield stress and 600 sec cycles for 48 and 72 hrs respectively. Although no opening of grain boundary fissures can be seen in fig. 15a it is apparent that the grains have slid over one another and although corrosive attack is not observed grain boundary separation must have occurred. Fig. 15b shows the surface of a specimen well away from the final fracture. Fissures have opened up normal to the direction of stress, and slight grain boundary attack may be seen. However, many grain boundaries remain unattacked. The surface is rumpled because grains constrain each other at unattacked grain boundaries and separate at grain boundaries where dissolution has occurred.

Figs. 16a and a' shows samples tested at $R=0.4$, with a peak stress of 60% yield stress, and 600 sec cycles. Fig. 16a shows the surface of a sample about 1mm back from the fracture surface. It is observed that some small grains have dropped out from the surface. Fig. 16a'

shows the same specimen in cross-section and that attack varies significantly from boundary to boundary. Attack along boundaries remains tight and narrow. In figs. 16b and 16b' a sample tested at $R=0.6$ with a peak stress of 60% yield stress is shown. Boundaries are only part attacked along their length, and, although the depth of penetration is shallow IGA is widespread over many grains. Cross-sectioning shows that the extent of attack varies both from grain boundary to grain boundary and also along individual boundaries.

Fig. 17a shows a sample tested at $R=0.5$, with a peak stress of 60% of the yield stress. Deformation of some grains is seen. Fig. 17a' shows the sample in cross-section; extensive linking between boundaries perpendicular to the specimen surface has occurred. Plates of connected grains slid as they were stressed during fracture. Fig. 17b again shows that small grains fall from the surface.

Fig. 18 shows further examples of grains rumpling over each other, in samples tested at $R=0.3$, with a peak stress of 80% of the yield stress for 100 hrs. Much variation of attack from boundary to boundary is seen over the specimen. Fig. 18a shows attack viewed in cross-section at the root of a machined rib. Both figs. 18b and 18c show that not every boundary at the surface of the specimen is attacked, though the deepest penetration extends to a depth of several grain diameters.

6.2.4. -200 mV results.

Attack in samples tested at -200mV was much more extensive than at other test potentials. For testing at -200mV there was little distribution in depth of IGA across individual specimens, and the longest estimated depth of attack was representative of the depth of attack.

Fig. 19 shows penetration data for specimens cycled with an R value of 0.6. The average rate of penetration was generally faster than that for static loaded samples, though only by twice. Penetration rates were seen to increase with of peak stress level for both static and cyclic loading. Furthermore, the difference in penetration rate between cyclic and static loading was seen to increase with peak stress level. Cycle frequency appears to have little effect for $R=0.6$, for the narrow range of frequencies examined.

Fig. 20 shows the effect of stress amplitude. Penetration rates were faster for larger amplitudes (smaller R values) and for slower cycle times. However, for data taken at $R=0.4$ and cycle times of 400 sec, the rate of penetration was lower than that of the static loaded

samples for all values of peak stress.

Observed attack was typical of IGA and attacked grain boundaries linked throughout the structure. With time the surface became disrupted completely as grain boundaries were attacked. Much material was removed from grain boundaries at the surface and grains tended to lose their sharp faceted shape. Material close to the limit of attack has undergone little dissolution, that at the surface has been exposed for longer and will be more rounded. Attack did not only occur on boundaries perpendicular to the direction of applied stress, and attack extended parallel to the direction of applied stress. Presumably this is because as penetration advances the stress in ligaments between such regions is eased, and such regions are less influenced by stress.

Fig. 21 shows the surface and edge of a sample tested at $R=0.6$, peak stress 60% yield stress, cycle time 600 sec. Surface damage appears slight, grains rumple over each other, and only tight penetration is seen. Fig. 21a' shows an optical cross-section which reveals the narrow penetration. When the sample was fractured, shown in fig. 21b, the attack was seen to extend some 50 μm into the sample. The remaining material failed in a ductile manner by mechanical overload. Fig. 21c shows the fracture cross-section of a specimen tested in a similar way. Penetration is intergranular and at the penetration front grains are faceted. Where grains have been exposed to solution for longer times, grains are more rounded due to dissolution. The transition between corrosion attack and ductile fracture is well marked. No evidence of striations resulting from the cyclic nature of loading was found.

Fig. 22 shows a sample tested at $R=0.6$, with a peak stress of 50% yield stress. Figs. 22b and 22b' show the variable nature of attack from boundary to boundary. The region of attack along grain boundaries is narrow, and on pulling after the test grains separate with no constraint and small grains drop from the surface. The observation that the region of attack is narrow shows that dissolution occurs mainly at the furthest extent of penetration rather than at the sides.

Fig. 23 shows samples tested at $R=0.5$, with a peak stress of 50% yield stress. Micrographs are taken 1mm back from the final fracture resulting from straining after the test.

Fig. 24 shows samples tested under stress conditions of $R=0.8$, with a peak stress of 80% yield stress. The extent of boundary attack still varies from boundary to boundary and some surface boundaries remain unattacked. Again, deep fissures are seen to be regularly spaced

together with a distribution of attack parallel to stress direction linking inbetween.

Fig. 25 shows further examples of variability of attack along individual boundaries and from boundary to boundary, for samples tested at $R=0.5$, with a peak stress of 60% yield stress.

Fig. 26a shows attack at higher stress levels, in a sample tested at $R=0.5$, with a peak stress of 70% yield stress. Fig. 26b shows the narrowness of the attacked zone; penetration is only resolvable after the final fracture. When examined in cross-section, as shown in fig. 26c, estimate of the overall extent of attack may be made. It is seen that, in general, more material has been removed at triple points than along grain boundaries. Many of the longest penetrations are seen to terminate at triple points.

Fig. 27 shows further examples of the morphology of penetration in samples tested at $R=0.6$, with a peak stress of 60% yield stress. It is evident that attack progresses both normal and parallel to the direction of stress, though the most severe attack is seen in boundaries normal to the stress.

Fig. 28 shows specimens tested at $R=0.5$, with a peak stress of 80% yield stress, and it is evident that most boundaries are attacked and much material around the boundaries has been removed. Slip lines are seen on the surface of the grains which have active slip systems. Slip is possible in some grains although the macroscopic yield stress has not been exceeded

Fig. 29 shows two samples tested under the same stress conditions of $R=0.4$, with a peak stress of 65% yield stress, for 72 and 120 hrs respectively. Surface damage in fig. 29b is much more extensive, and grains lost their shape, gross dissolution of the surface took place and the sample became a light grey colour.

6.2.5. Initiation times and the kinetics of "crack" growth.

Penetration rates so far have been arrived at simply by dividing the final grain boundary penetration depth by the test time in the conventional manner of determining penetration rates or - crack growth rates. Such a method makes no allowance for initiation time and grain boundary attack is assumed to be initiated at the outset of the test. Furthermore, the previous plots of peak stress against grain boundary penetration depth/time (figs. 13, 14, 19 and 20) do not take into account the kinetics of attack.

The validity of this assumption was investigated by running tests for different lengths of time at a peak stress of 60% yield stress, $R=0.6$,

cycle time 600 sec. The results are shown fig. 30. It may be seen that the penetration rate for cyclic loading at -100mV is linear whereas that for cyclic loading at -200mV is parabolic. The -100mV relation is based on 8 data points and that for -200mV on 10 data points. From this plot it may be noted that the kinetics of penetration are different for -100 and -200 mV under the same test conditions.

Both lines when extrapolated back to the time axis show an initiation time, that for -200mV being 20,000 sec (about 5.5 hrs) and that for -100mV being 150,000 sec (about 41 hrs). Intergranular attack for static loading at -200mV also appears to show a linear relationship with time, (4 data points).

Fig. 31 shows these data plotted as log time/log grain boundary penetration depth and confirms that depth of IGA increases as a $t^{0.5}$ relationship for cyclic loading at -200mV. For long times (greater than a couple of days) a linear relationship is seen for both cyclic loading at -100mV and for static loading at -200mV.

Penetration or crack growth may therefore be described by:-

$$1. \quad K(t - I)^n = a$$

where a = depth of attack
 I = initiation time
 K = constant

The exponent $n = 0.5$ in the case of cyclic loading tests carried out at -200mV, and $n = 1$ in the case of tests carried out at -100mV or for static loading at -200mV. Defining a parabolic attack factor K , given by grain boundary penetration depth divided by (test time) $^{0.5}$, data may be replotted (assuming that attack progresses as $t^{0.5}$) as K against stress.

Figs. 32 and 33 show K against mean stress for testing at -200mV. It is evident that the rate of grain boundary attack is strongly affected by the level of stress and that the rate of attack increases for large amplitudes, and longer cycle times. It is important to bear in mind that when applied stresses are compared in terms of peak load, cyclically loaded specimens see a much smaller "average" load, which reduces the apparent effect of cyclic stress. Even though the comparison is unfavourable it appears that penetration (after 72 hrs testing) is generally larger for very low levels of stress, but at high stress levels cyclic loading results in greater penetration.

In order to compare rates of attack, the different time dependence of penetration growth for static and cyclic loading must be considered. Information on rate of attack or crack growth rate may be obtained by measuring the slope of penetration depth/time plots shown in fig. 30,

if we consider the parabolic case (equation 1, above) where $n = 0.5$, then the rate of penetration da/dt is described by:-

Differentiation of equation 1., with $n = 0.5$,

2.
$$\frac{da}{dt} = 0.5Kt^{-0.5}$$

substitution gives:-

3.
$$\frac{da}{dt} = \frac{0.5K^2}{a}$$

For static loading, differentiation of equation 1., with $n = 1$,

4.
$$\frac{da}{dt} = K$$

Thus for short penetration depths (small a) typical values of K yield very high rates of penetration, higher than for static loading. An example illustrates this point. Considering the data presented in fig. 30 for experiments carried out at -200 mV, and calculating crack growth rates for cyclic and static loading by use of equations 3. and 4. respectively;

Crack depth	Cyclic Growth Rate	Static Growth Rate	Static Growth Rate/Cyclic Growth Rate
μm	$\mu\text{m sec}^{-1}$	$(\times 10^{-4})$	
20	8.0	1.3	0.1625
100	0.87	1.3	1.5

It may be seen that as cracks grow the calculated growth rate for static loading exceeds that for cyclic loading. Whilst the measured grain boundary penetration depth after short test times for cyclic loading is larger than that for static loading, after a time the penetration depth resulting from static loading becomes as large as that resulting during cyclic load testing. To examine the effects of stress for both static and cyclic loading it is important to consider the different penetration growth kinetics resulting from each method of loading. However, the limitations of the testing matrix (limited variations of test time and stress) must be remembered, and assumptions may not be universal.

If we take into account the different kinetics, by plotting log penetration depth against log time we can predict what stage the depth of penetration during static loading equals that resulting during cyclic loading. This is shown schematically in fig. 34. A parameter

may be described (t_T) as the time taken for the depth of attack during a static loaded test to equal that for cyclic loaded test (carried out at the same peak stress). If it is assumed that a $t^{0.5}$ dependence applies to cyclic data collected at -200mV, and that a linear dependence on t applies for static data collected at -200mV, extrapolation may be made to obtain t_T . This assumption is based on the data shown in fig. 30 of measured grain boundary penetration depth for different test times, and on other data sets (though by far less complete) which show that the kinetics of similar attack are maintained for slower rates of penetration growth, and for tests lasting longer than 72 hours. t_T occurs at a grain boundary penetration depth l_T . t_T and l_T were evaluated from data for $R=0.6$ and $R=0.4$. Results are shown in fig. 35 and 36.

The stress at which the penetration depth resulting during static loading exceeds that during cyclic loading is seen to increase as R decreases (ie as large amplitude cycles are used) and as cycle frequency decreases. It is evident that the time (or penetration depth) for the transition is very short at low stress levels and longer at higher stress levels. At higher peak stress levels (for the same R value), the effect of frequency becomes less important on attack and curves for different frequencies merge.

These predictions may not be correct, because it has been assumed that linear behaviour continues indefinitely for static loading. However, as growth continues kinetics may change as (for instance) penetration becomes diffusion controlled. If this is the case then the extrapolation used above would not be justified.

6.2.6. Current measurements and mechanical response during testing.

The current and mechanical response of specimens was followed with time in all potentiostatic tests.

For tests carried out at -200mV, current was seen to gradually drift more cathodic with time, while for tests at potentials other than -200mV currents were small ($<0.1 \text{ mAcm}^{-2}$) and unvarying. For tests carried out at -100mV the current did not vary throughout the test, and remained at approximately 0.1 mAcm^{-2} . Cathodic current densities for tests carried out at -200mV could drift as cathodic as 5 mAcm^{-2} . For tests carried out without potentiostatic control the corrosion potential drifted more anodic. Potential drifts to a maximum of 500mV (SCE) were observed after 72 hrs cycling.

Fig. 37a shows an example of the gradual drift in cathodic current as cycling progresses, for a sample held at -200mV. No irregularities are seen in the trace. Fig. 37b shows deformation and current response for a specimen tested until fracture. It may be seen that during cycling the specimen extended and an additional strain resulted with

each cycle. Rapid penetration occurred over the last 10 cycles, indicated by the increase in the compliance of the specimen, as the remaining area of material supporting the load became rapidly smaller. The observed current response during this process was erratic, and electrochemical noise was seen during active dissolution.

Fig. 38a shows the deflection and current time trace for a specimen held at -100mV during load cycling. The current is small and unvarying. Figs. 38b and 38c show the mechanical response for two specimens also held at -100mV, though cycled at slower speeds than in fig. 38a. In fig. 38b the peak stress used was 60% of the yield stress and in fig. 38c 80% of the yield stress.

The observed mechanical response was complex and requires description. A number of features were seen such as:-

1. Strain remained constant during a period immediately after the unloading part of the cycle, although the applied load was increasing.
2. The overall strain envelope continuously increased, (ie "cyclic creep softening") although the specimen was loaded to stress levels below yield,

These observations are discussed in chapter 7.

During static loading tests, for specimens loaded at stress levels below the yield stress, there was little difference in the observed current between tests. Again, the -100mV test currents remained constant whilst those of the -200mV tests gradually drifted more cathodic. However, for specimens loaded to levels at, or above, yield, rapid anodic current fluctuations of around 1 mAcm^{-2} were seen at the start of the experiment. The appearance of a specimen where only a few current fluctuations have taken place is shown in figs. 39a and b, for a specimen loaded at 110% yield stress, held for 24 hrs at -100mV. The largest fluctuations were seen for a specimen loaded at 130% yield stress and removed after 10 hrs testing, shown in fig. 39c. Gross surface damage resulted during testing and the morphology of penetration was different than for the cases 39a and 39b, as shown in fig. 39c, where attack is seen to extend less than one grain diameter. Specimens loaded at -200mV to above yield stresses failed rapidly, and much dissolution took place.

In summary, the current showed no relation to the imposed loading pattern or to the resulting mechanical response of the material, for loads lower than the yield stress. The mechanical response of cyclic loading tests showed that plastic strains occurred, although below-yield stress levels were used. Cycling was found to induce strain softening; such phenomena are discussed in chapter 7.

6.2.7. Stress assisted intergranular attack in materials with

other heat treatments.

To investigate the effect of heat treatment on low frequency cyclic stress corrosion behaviour, several specimens were aged at 550°C for different lengths of time, ranging from 25 to 200 hrs. These different heat treatments lead to different susceptibility to attack in a Strauss test (reported in chapter 4), the degree of sensitisation increasing with ageing time at 550°C. Specimens were tested under the same conditions of low frequency cyclic loading, $R=0.5$, with peak stress of 65 % yield stress, cycle time 600 sec in 1 M HNO_3 at -200mV. A range of attack morphologies and rates of attack was seen. Rates of attack were all much slower than for specimens aged for 500 hrs.

Fig. 40a and b shows attack in samples sensitised by ageing for 50 and 100 hrs respectively at 550°C. It is seen that grain boundaries, slip bands and twins are all etched out. For different ageing heat treatments there was a large variation in the proportion of grain boundaries attacked, and the depth of attack throughout individual specimens.

As-received tube material was tested under a variety of mechanical conditions at stress levels both above and below the measured yield stress. Tests were carried out potentiostatically at -200mV in 1M HNO_3 . No penetration or attack of any form was seen. This was so, even when above-yield stresses were used. Figs. 41a and b show the surfaces of specimens tested in 1M HNO_3 at -200mV, and at 80% of the yield stress with $R=0.5$ and 70% of the yield stress with $R=0.4$ respectively.

6.3. DISCUSSION

The purpose of this section is to discuss the phenomenon of intergranular corrosion observed during low frequency cyclic stress testing of sensitised 20% Cr, 25% Ni, 0.7% Nb in 1M HNO_3 . Although attack is stress assisted the term SCC is not strictly applicable because attack occurs along grain boundaries both parallel and normal to the direction of applied stress, and is only seen for heavily sensitised specimens. The terms environmentally assisted fracture or stress assisted intergranular attack are more appropriate.

The majority of tests were carried out at stress levels below the measured yield stress, though undoubtedly some grains will have had active slip systems. The yield stress was taken as the limit of proportionality on a stress/strain curve produced under slow constant loading rate conditions, at loading rates similar to those used for load cycling stress corrosion experiments.

The observed phenomena may be listed as follows:

1. The rate of IGA was strongly dependent on the applied test potential. For the same conditions of given peak stress, frequency and amplitude, the rate of grain boundary attack during cyclic loading was often as much as an order of magnitude larger at -200 mV than that at -100 mV, which was again an order of magnitude larger than that observed at the free corrosion potential. The free potential for unstressed material stabilises at -200 mV (fig. 9) though during cycling at the free potential the free corrosion potential moved away from -200 mV.
2. For exposure at -100 and -200 mV the rate of grain boundary attack increased with:
 - a. Cycle amplitude
 - b. Peak stress level
 - c. Cycle time
3. For experiments held potentiostatically at -200 mV:
 - a. IGA was seen in the absence of stress
 - b. The penetration depth increased linearly with time for static loading.
 - c. The penetration depth increased parabolically with time for cyclic loading experiments.
 - d. At low stress levels static loading results in deeper penetration after 72 hrs testing than cyclic loading at the same peak stress, although initially during cyclic load tests rates of penetration are faster than for static load tests.

At higher stresses cyclic load tests result in deeper penetration after 72 hrs testing. A critical stress level may be defined below which static load tests result in deeper penetration, and above which cyclic load tests result in deeper penetration, after 72 hrs testing at the same peak stress level.
 - e. The observed current became increasingly cathodic; no evidence of anodic transients or cyclic variations of current were seen.
4. For experiments held potentiostatically at -100 mV:
 - a. Where no stress was present attack did not extend greater than a few microns.
 - b. Penetration depths (for both cyclic loading (at longer times) and static loading) increased linearly with time.
 - c. Penetration depths during cyclic loading only exceeded those seen in static loaded tests when large amplitudes and long cycle times were used.

5. No grain boundary attack was seen in as-received test samples cycled at below yield stress levels in 1M HNO₃ at -200mV; attack was only seen with sensitised samples.
6. Changing the degree of sensitisation by ageing 1050'C annealed specimens for shorter times than 500 hrs at 550'C changes the morphology of attack. In such samples penetration extended only a few microns, and twin boundaries as well as grain boundaries were attacked.

In this system stress-assisted corrosion is linked to IGA and penetration was only seen after testing sensitised material in the potential region where IGA occurs. Establishing the role of stress in enhancing penetration rates is not straightforward because at -200mV the environment alone causes penetration greater than a couple of grain diameters to occur even in the absence of stress.

6.3.1. Stress-assisted intergranular attack.

The observation that at -200mV penetration kinetics depend on whether load is statically or cyclically applied deserves particular attention. Observations showing this are shown schematically in fig. 34, whilst the data showing this are given in figs. 31, 35 and 36. A number of reasons may be suggested to explain the difference in kinetics between static and cyclic loading:

1. Cyclic loading maintains crack tip plasticity (and consequently dissolution) at lower stress levels than where it is seen during static loading.
2. A difference in crack tightness may result for the two loading modes and hence diffusion along the penetration path may differ, eg a "crack closure" or "crack narrowing" type mechanism may occur as a result of cycling.
3. Build up of aggressive ions within the crack or penetrated grain boundary may be different between the two loading modes as a result of, for example, solution pumping effects.
4. The extent of mechanical or dissolution blunting of the penetration front of crack tip may differ for the two loading modes.
5. Deformation-induced phase transformation may occur at the crack tip during cycling and enhance the possibility of hydrogen embrittlement.

6.3.1.1. Loading conditions.

The question of what is the role of mechanical variables on penetration rate kinetics in low frequency cyclic stress-assisted

attack may be posed.

The role of mechanical variables requires consideration. Recalling the inter-relationship of test variables and their effect on strain rates:

- i. A high frequency means that for a given R value and peak stress the application of load occurs in a shorter time and, thus, the resultant elastic strain rate is larger. It was found that for higher frequencies the overall plastic strain and "creep" rate was smaller.
- ii. Smaller R values (larger amplitudes) means that for a given frequency the resultant elastic strain rate is larger. However, smaller R values means that for a given peak stress the mean stress will be lower (as shown in fig. 8). It was found that for smaller R values the overall plastic strain and "creep" rate was larger.

The effect of cyclic loading was seen to become more significant at higher stress levels. A stress level (dependent on R) exists such that the penetration depth resulting (after 72 hrs testing) during cyclic loading is longer for the throughout the test duration than that resulting from static load tests (at the same peak stress level). Below this critical stress level penetration depths resulting from static loading will, by the end of a 72 hr test, exceed those seen as a result of cyclic loading at the same peak stress level.

The ways by which the strain at the crack tip or penetration front may accelerate dissolution by either yield-assisted dissolution or by repeatedly rupturing the film and preventing passivation are reviewed in chapter 2. There is much evidence to suggest that where attack is stress-assisted, the role of stress is to provide a strain or strain rate sufficient to rupture the passive film and allow dissolution at the bared surface. Dissolution at the tip of the fissure then continues until the strain rate falls below a certain threshold and repassivation begins when the current decreases. The factor controlling attack rates will be the occurrence of a finite rate of plastic strain leading to film rupture, (elastic deformation of underlying metal may result in film rupture of brittle films if sufficient strain is transferred from the underlying material).

During static loading little plastic deformation (and therefore film rupture) will occur unless penetration has been deep enough to induce further additional deformation by an increase in the stress intensity or extension of the plastic zone. If attack is slow penetration is shallow and creep exhaustion follows initial loading, and non-propagating attack is seen. The static case relies on crack advance to maintain crack tip plasticity. If crack growth is not fast enough work hardening brings "creep" to a standstill. However, under

cyclic loading conditions the movement of mobile dislocations sustains deformation throughout the material and a continual increase in strain is seen, which presumably results from cyclic induced plastic strain. Cyclic loading may maintain the strain rate at a level necessary to produce film rupture and result in bare metal at the penetration front. The plastic creep strain that results from cyclic loading continuously increases and will either accelerate penetration by increasing the time that dissolution may occur or possibly retard it due to blunting of the crack tip. Plastic strain rates at the penetration front rather than the observed overall elastic strain rate will control the frequency of film rupture seen during cycling. The important strain rate to be considered is, therefore, the plastic strain rate rather than the elastic strain rate. Plastic strain rates were seen to increase as the amplitude and peak stress of cycling was increased (chapter 7).

We assume that rapid penetration in the case of cyclic loading tests is also a result of the much higher plastic strain rates than for static load tests. Evidence of repassivation and reinitiation, as strain rates fall below a critical level and then exceed that level on reloading, might be expected. None was found from fracture surface examination. Dissolution of the crack surfaces may remove evidence of the mechanism of grain boundary attack. Furthermore, no evidence was noted from the current response during experiments because anodic behaviour was masked by the dominating cathodic reactions of HNO_3 .

6.3.1.2. Diffusion effects.

The linear dependence of penetration rate observed during static loading suggests that the limiting process for attack is the rate of anodic dissolution. The $t^{0.5}$ dependence of penetration observed during cyclic loading at -200mV may be a result of the crack coming under diffusion control as the penetration path becomes longer. The rate of IGA under cyclic loading would become diffusion limited if the anodic processes at the penetration front were faster than mass transport could cope with. We may hypothesize that the parabolic behaviour observed during cyclic load tests occurs because once penetration reaches a certain depth the current becomes limited by diffusion. The depth at which diffusion starts to control will depend on the size of the anodic current at the crack tip. For fast dissolution diffusion control sets in early during testing. Under diffusion control the dissolution rate or size of the maximum current decreases as the penetration depth increases. It was observed that for static loading we have smaller currents than for cyclic loading, and it was found that although static loading stimulated active behaviour at the penetration front the current remained small during experiments (at maximum 1 mAcm^{-2}) and rates of propagation were low, and thus growth did not become diffusion controlled. The greater

degree of anodic activity induced by cyclic loading (maximum currents were of the order of 10mAcm^{-2}) may result in diffusion control. If this line of argument is correct the penetration depth of statically loaded specimens should never exceed that of cyclically loaded specimens for the same test conditions. This is because if the penetration depth during static loading approaches that observed during cyclic loading, then penetration during static loading would start to come under diffusion control as a result of the length and narrowness of the penetration path. If this is the case, penetration rates for cyclic and static loading should tend to the same value for deep cracks and comparable stress conditions. This is implied in figs. 35 and 36.

It is also notable that without loading penetration rates slowed down with time, and presumably even for small currents diffusion may play a part in penetration as the path is tighter because there is no stress to "yawn" (open) the fissures.

It must be borne in mind that comparison of cyclic and static penetration data has been carried out at the peak same stress level. Static loading keeps the opening at a maximum, and penetrated grain boundaries yawn, whereas during cyclic loading the mean stress is lower and the size of opening will be much less for much of the time. Therefore, for the same peak stress, penetration paths during cyclic loading will be narrower and consequently the diffusion path more restricted. Static load tests do not become diffusion controlled because of the much smaller dissolution currents involved. At low peak loads the greater penetration rates observed during static loading than cyclic loading are perhaps a direct result of the larger mean stress yawning cracks. At higher stress levels narrowing of the penetration path is less and transport of ions faster.

Prater et al [16] formulated a model to describe observed crack growth rates in sensitised 304 stainless steel, exposed to cyclic stress and high temperature water environments, in terms of time spent above a critical stress intensity level, K_{ISCC} , and other experimental variables. However, for our work where IGA is wide-spread across the specimen, and for short cracks in thin wall tube a meaningful value of stress intensity may not be determined and it is therefore not possible to use such a model.

6.3.1.3. Crack tip chemistry.

The rate of attack during SCC is known to be a function of the crack tip chemistry and the potential of the solution at the crack tip [6]. Although the bulk potential may be held potentiostatically, conditions within the crack enclave may differ from the bulk [7], and both potential and solution composition will vary. However, potential-drop down fissures in this system are likely to be small because of the

high conductivity of HNO_3 . The concentration of potent environments within cracks may markedly change the local electrochemistry eg. within a pit, crack or penetration fissure the pH may drop as a result of hydrolysis of metal ions; however, in our experiments the pH was already low. The intense anodic activity concentrating metal ions within the crack will attract anions to maintain electroneutrality. If these ions are aggressive, passivity is retarded.

The build up of oxidising species within a stagnant crack can produce a more corrosive environment, eg the localised corrosion of 304 stainless steel in HNO_3 is known to proceed autocatalytically when conditions allow oxidation products to build up [7]. It is known that ferric (Fe^{3+}) and chromate (CrVI^+) ions which are corrosion products of stainless steel in acid solutions can both lead to autocatalytic corrosion processes, because as these ions build up, the oxidising character of the acid is enhanced and corrosion rates increase [8].

The cathodic reactions of HNO_3 may be depolarised in stagnant cracks of penetrated grain boundaries. It is known that when HNO_2 builds up in stagnant HNO_3 it depolarises the cathodic reactions leading to faster reduction [9].

For tests carried out at the same R value and peak stress, but at different frequencies, longer cycle times (smaller frequencies) resulted in faster attack rates. The role of cycling may be to pump solution in and out of the crack; however, the frequency of cyclic loading used during experiments was much lower than for frequencies where pumping is believed to play a role in SCC or corrosion fatigue [10]. Furthermore, if aggressive ions build up within the penetration fissure and accelerate attack, it would be expected that the penetration rate during static loading would accelerate rather than show linear kinetics. It is therefore concluded that solution changes down fissures are not a dominant part of the mechanisms of stress assisted corrosion in the system studied. Slower cycle frequencies resulted in greater plastic strains. The effect of frequency may lie in the plastic strain rate at crack tips rather than in solution effects.

6.3.1.4. Crack blunting.

Crack propagation is influenced by crack tip acuity, and if the crack tip is blunted the crack is less able to propagate and crack growth rates decrease. Dissolution, together with simultaneous mechanical blunting may result in a less sharp crack or penetration front. Cycling is known to prevent blunting (if the mechanical conditions are "severe" enough, ie large enough amplitude at a high enough peak stress) by "mechanically" sharpening the crack. However, if stress cycling conditions were too severe the crack tip would blunt by plastic deformation and the crack growth rate decrease. The evidence against such a mechanism being dominant in the cyclic stress assisted

corrosion study above is that firstly metallographic examination of penetration morphologies of both cyclic and static loading test specimens showed little difference and secondly the fact that penetration rate for both static and cyclic loading did not show signs of decreasing with increasing peak stress level, as observed by Mendoza [18].

6.3.1.5. Hydrogen embrittlement.

Hydrogen embrittlement is unlikely to be a dominant mechanism in systems exhibiting IGA. Hydrogen embrittlement in austenitic stainless steels is often (but not always) associated with local strain induced martensite transformation at the crack tip. The possibility of strain induced martensite transformation at the penetration front is small for 20% Cr, 25% Ni, because the high Ni content of the steel places it in a region of a phase diagram where austenite is a thermodynamically stable phase.

6.3.2. Estimates of crack growth rates.

An attempt is now made to arrive at a semi-quantitative estimate of crack growth rates assuming growth is controlled by either diffusion or potential drop along the cracks. We shall start by assuming that the crack has the simplest geometry, namely that the crack sides are parallel. For this geometry the width of the crack mouth is the same width as the dissolution zone at the crack tip.

6.3.2.1. Diffusion control.

We have attempted to explain the parabolic behaviour observed during cyclic load tests by assuming that once penetration reaches a certain depth the current becomes limited by diffusion. The depth at which diffusion starts to control the crack growth rate will depend on the size of the anodic current at the crack tip. For fast dissolution diffusion control sets in early during testing and crack growth rates are limited by rates of mass transport. If crack growth is diffusion controlled we may assume that attack is limited by the diffusion of metal cations from the crack tip. Two effects that we shall not consider in our analysis are the possibility of the precipitation of a salt film that would stifle anodic dissolution or opening (yawning) of the crack to assist diffusion of cations from the crack tip. This is because firstly the nitrate salts that form are known to be reasonably soluble and secondly we wish to estimate the minimum growth rate of a diffusion controlled crack.

Suppose (for the sake of argument) that the mixed nitrate has a solubility (C_{sat}) of 1 mole litre⁻¹ (10^{-3} mol cm⁻³). Therefore for a crack of length a the concentration gradient dc/dx is given by:-

$$5. \quad \frac{dc}{dx} = \frac{C_{sat}}{a} \quad \text{mol cm}^{-4}$$

The flux along the crack is given by:-

$$6. \quad J = \frac{D.C_{sat}}{a} \quad \text{moles cm}^{-2} \text{ sec}^{-1}$$

where D = the diffusivity of the cations (about $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$)

Now 1 mole of salt forms from 1 'mole' of stainless steel ie about 50g or 5cm^3 . Therefore the rate of crack growth is :-

$$7. \quad \frac{da}{dt} = \frac{5.D.C_{sat}}{a} = \frac{10^{-5}.10^{-3}.5}{a} \quad \text{cm sec}^{-1}$$

Considering crack lengths of 20 and 100um, as previously, gives crack growth rates of 0.25 and 0.05 um sec^{-1} . It is apparent from this model that short cracks grow at a much faster rate than long cracks. However, comparison with the crack growth rate data presented earlier shows the crack growth rate as a result of this model is some three orders of magnitude larger than experimental values.

6.3.2.2. Ohmic Drop.

Our experiments have shown that ^{we} can suppose the potential at the crack tip must remain within about 100mV of a potential of -200 mV or the crack growth rate slows right down. Calculating the ionic resistance of the crack:-

$$8. \quad R = \frac{p.a}{A} \quad \text{Ohm cm}^2$$

where R = ionic resistance (Ohms)

a = crack length (cm)

p = resistivity of 1M HNO₃ (= 1/conductivity $\approx 2 \text{ Ohm cm}$)

A = area of parallel sided crack (assumed equivalent to area of crack tip)

If the maximum likely iR drop is 0.1V, calculating the maximum current density (i) by Ohm's law:-

$$7. \quad i = \frac{0.1}{2.a} \quad \text{Amps cm}^{-2}$$

As stated above this equation assumes that no dissolution of the crack sides takes place, and that the crack area is the same as the dissolving crack tip.

From Faraday's law; given in chapter 2, equation 1; it is possible to estimate the crack growth rate as:-

$$8. \quad \frac{da}{dt} = \frac{i.M}{p.F.n} = \frac{i.56}{7.9 \times 9.6 \times 10^4 \times 2} = \frac{1.84 \times 10^{-6}}{a} \text{ cm sec}^{-1}$$

Where:-
 i = current density (Amp cm^{-2})
 n = valence of solvated ion (2)
 F = Faraday's constant (9.6×10^4 Amp sec moles $^{-1}$)
 M = Molar mass of metal (56 g mole $^{-1}$)
 p = density of metal (7.9 g cm^{-3})

Considering crack lengths of 20 and 100 μm again gives current densities of 25 and 5 A cm^{-2} and thus the crack growth rates are approximately 9.2 and 1.84 $\mu\text{m sec}^{-1}$ respectively. The crack growth rates calculated are an order of magnitude larger than those calculated for diffusion controlled growth, and are about four orders of magnitude larger than the experimentally observed rates.

Because of the difference between predicted and observed crack growth rates it may be concluded that the external potential is effective in controlling the crack tip potential and potential drop along the crack is negligible. This is to have been expected, because with short cracks and a concentrated solution of low pH the potential drop is likely to be small.

It is difficult to explain the observed parabolic crack growth rates, seen during cyclic loading, on the basis of diffusion or ohmic drop because the observed crack growth rates are much smaller than either a diffusion or Ohmic drop mechanism would support. However, calculations of experimental crack growth rates were made by assuming that crack growth was continuous, and that crack growth rate was determined as maximum crack length divided by the duration time of the experiment. The crack growth rate may fall below the theoretical rates calculated above to an extent that depends on the competitive processes of film growth, to prevent dissolution, and plastic strain to rupture such films and exposure bare metal. If crack passivation took place, and cracks lay dormant for much of the time during each cycle, the crack growth rate during periods of crack extension would be calculated to be much larger. To achieve the theoretical crack growths predicted above cracks would have to be active for only a few seconds of each cycle. Simple calculation of the time to set up a concentration gradient for diffusion control gives an answer of the order of seconds. Therefore, if crack extension occurs in a cyclic manner, where the crack is passive for much of the time, is conceivable that diffusion or ohmic drop mechanisms could come into play. However, no morphological or electrochemical evidence was found to indicate a cyclic nature of passivation and attack during crack growth.

6.3.3. Role of sensitisation.

Some variation of attack from boundary to boundary was seen and some boundaries remained unattacked during testing. Furthermore, variation in the morphology of attack was seen between samples heat treated to a different level of sensitisation, with the as-received material being unattacked. Such observations require an explanation of the role of sensitisation in cyclic stress assisted corrosion. Grain boundary attack is undoubtedly due to the fact that material is heavily sensitised. Devine et al [11] suggested that IGA of sensitised steels in oxidising acids was due to impurity segregation at grain boundaries, leading to accelerated dissolution. However, at the test potentials used, Cr-depletion is the generally accepted reason for IGA [12]. Only Cr-depleted regions undergo active dissolution, and anodic activity is confined to the tip of the fissure where Cr-depletion is greatest. Little lateral spreading was observed and penetration paths remained narrow, because Cr-depletion is less in these areas and passivation occurs [12].

Stress may aid IGA by making boundaries more active by causing localised deformation at the penetration front and therefore hindering passivation. Attack may then occur on boundaries which would otherwise not be attacked could because the extent of Cr-depletion is insufficient. Applied stress may be able to assist attack by "bridging" between unconnected areas or "clusters" of sensitisation. Solomon [13] and Takaku et al [14] found that the extent of IGSCC increased as the DOS increased, similarly Clarke et al [15] were able to make a correlation between the degree of sensitisation (DOS) determined by EPR and the measured rate of IGSCC, ie. IGSCC can occur in material which is not fully sensitised though the rate at which attack occurs is dependent on the proportion of fully sensitised boundaries.

Intergranular attack has been modelled in terms of percolation theory [17]. According to this theory the penetration pattern that develops depends on the number of linking sensitised boundaries and the imposed stress system. In this work the material used for the bulk of experiments was heavily sensitised and continuous pathways of sensitised boundaries existed throughout the microstructure, and cyclic stress corrosion at -200 mV progressed by "broad front" IGA where attack to the same depth is seen across specimens. For such attack IGA was not controlled by the probability of finding linked sensitised boundaries for attack to advance along. However, variation of attack was seen across the surfaces of specimens, though most grain boundaries at the surface were attacked due to the ease of initiation and IGA penetrated the structure until limited by mass transport gradients.

In summary we have found that the superposition of low frequency cyclic loading on top of an existing tensile stress to give a peak stress below the yield stress increased the rate of IGA above that for static loading (at the same peak stress) for 20Cr, 25Ni, Nb in 1M HNO₃. Attack was most severe at a potential of -200mV (SCE).

It was found that cyclic loading lead to plastic strain even though stress levels below the nominal yield stress were used.

A number of mechanisms were discussed to explain the increased activity (and dissolution) at crack tips as a result of cyclic loading. The difference in kinetics between cyclic and static loading stress corrosion was explained in that the larger currents during cyclic loading lead to diffusion controlled growth and parabolic growth rates; whereas the smaller dissolution currents and wider crack opening, due to a higher mean stress, for static loading resulted in linear growth rates. However, simple analysis showed that the experimental rates of crack growth were some three to four orders of magnitude less than those expected for where diffusion control or ohmic drop would dominate corrosion mechanisms. This discrepancy is perhaps explained by discontinuous crack extension during cyclic loading, for which the crack growth rates during periods of crack extension are much larger than the overall calculated experimental crack growth rate.

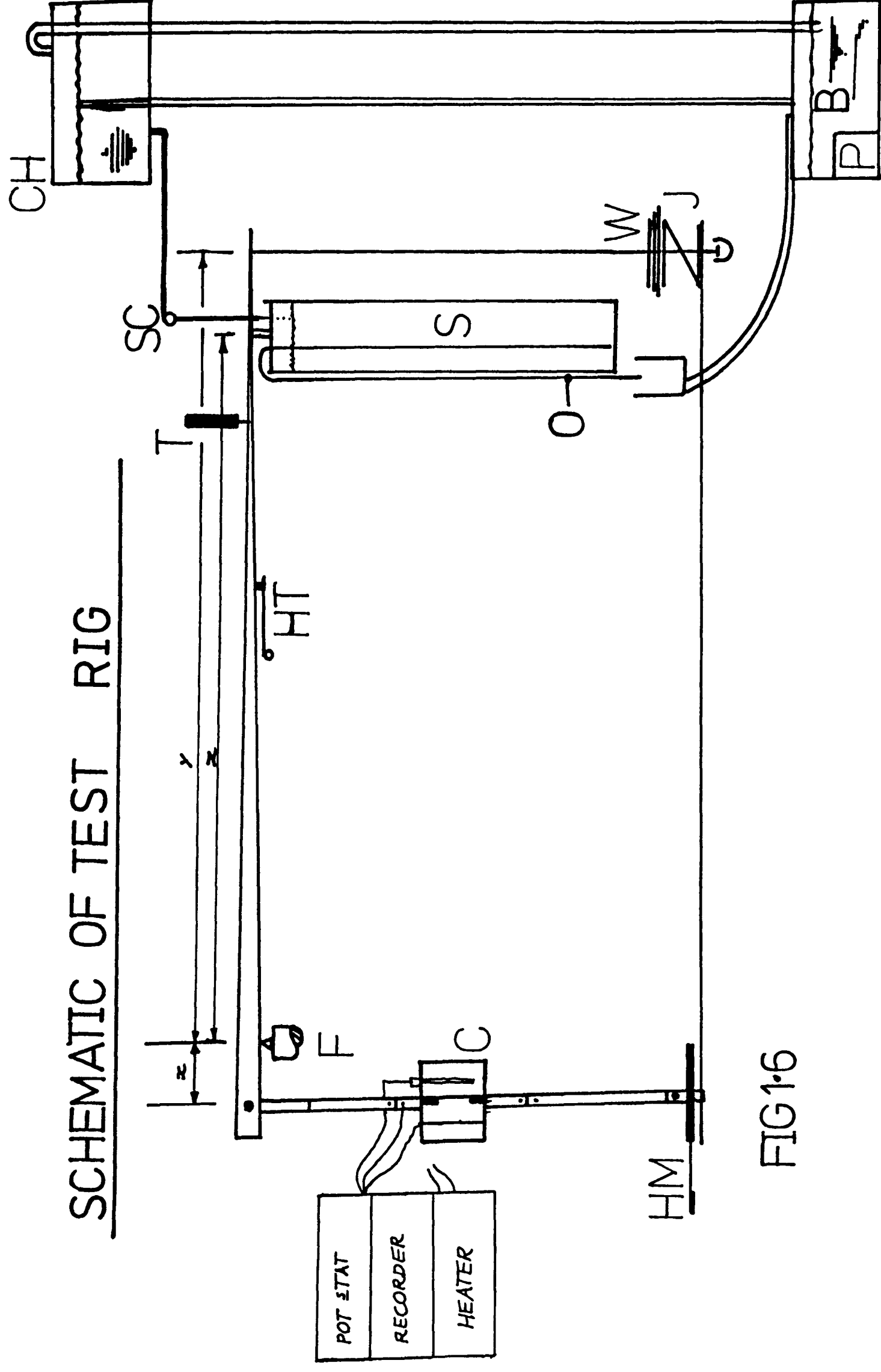
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Figure 1.6
Schematic of the low frequency cyclic stress rig.

B = basin
C = cell and specimen assembly
CH = constant head tank
F = fulcrum
J = jack
HM = horizontal levelling motor
HT = horizontal levelling transducer
P = pump
S = syphon
SC = stop cock
T = transducer
O = outlet tube
W = weight

SCHEMATIC OF TEST RIG



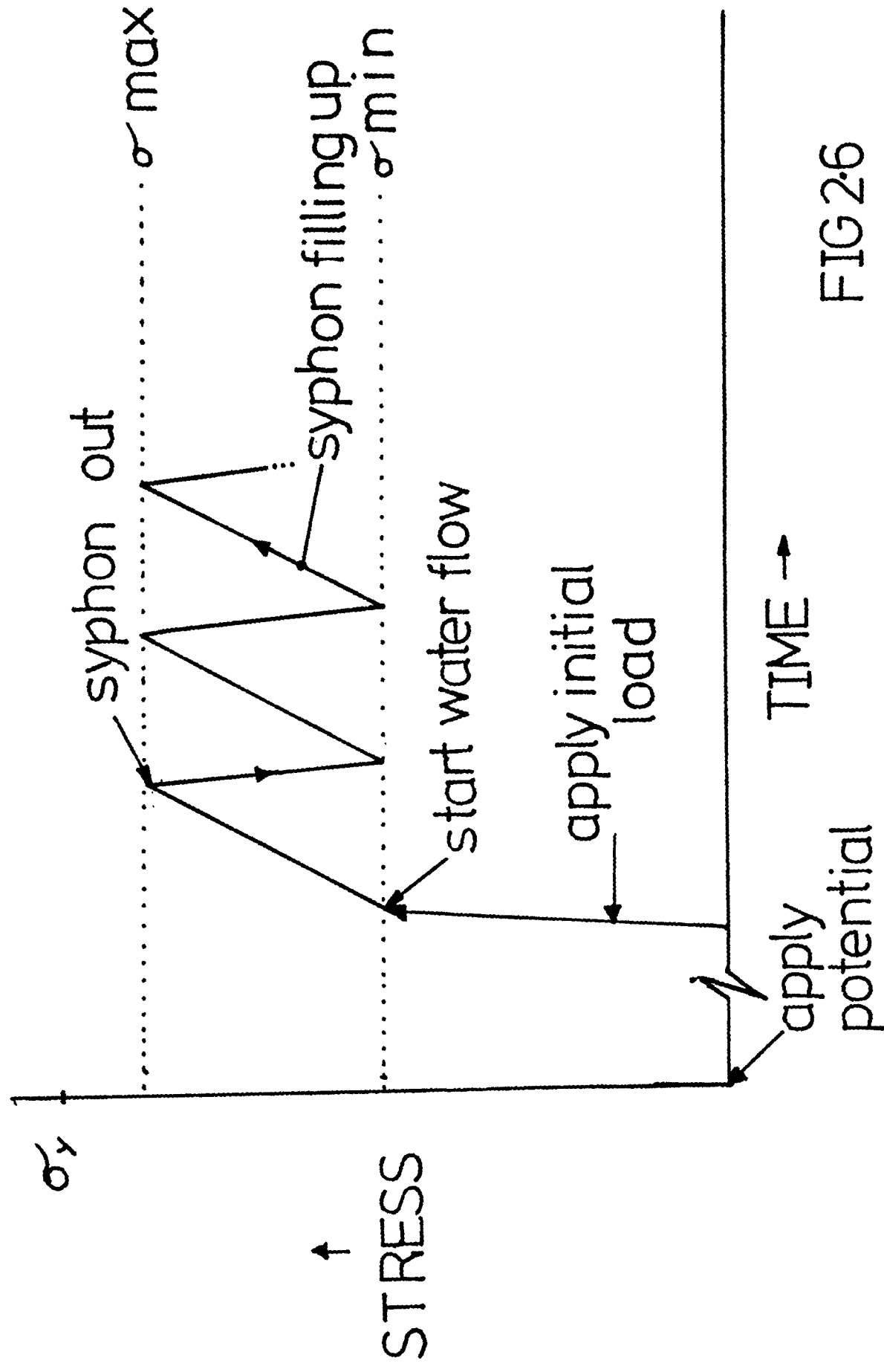
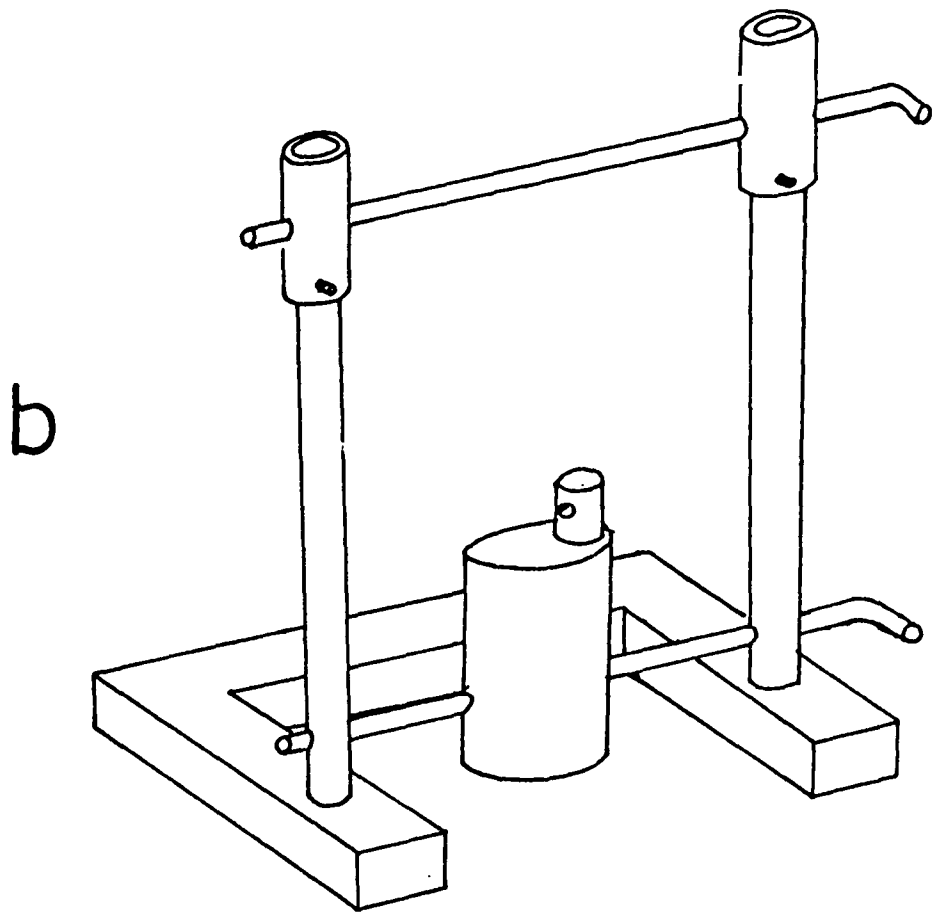


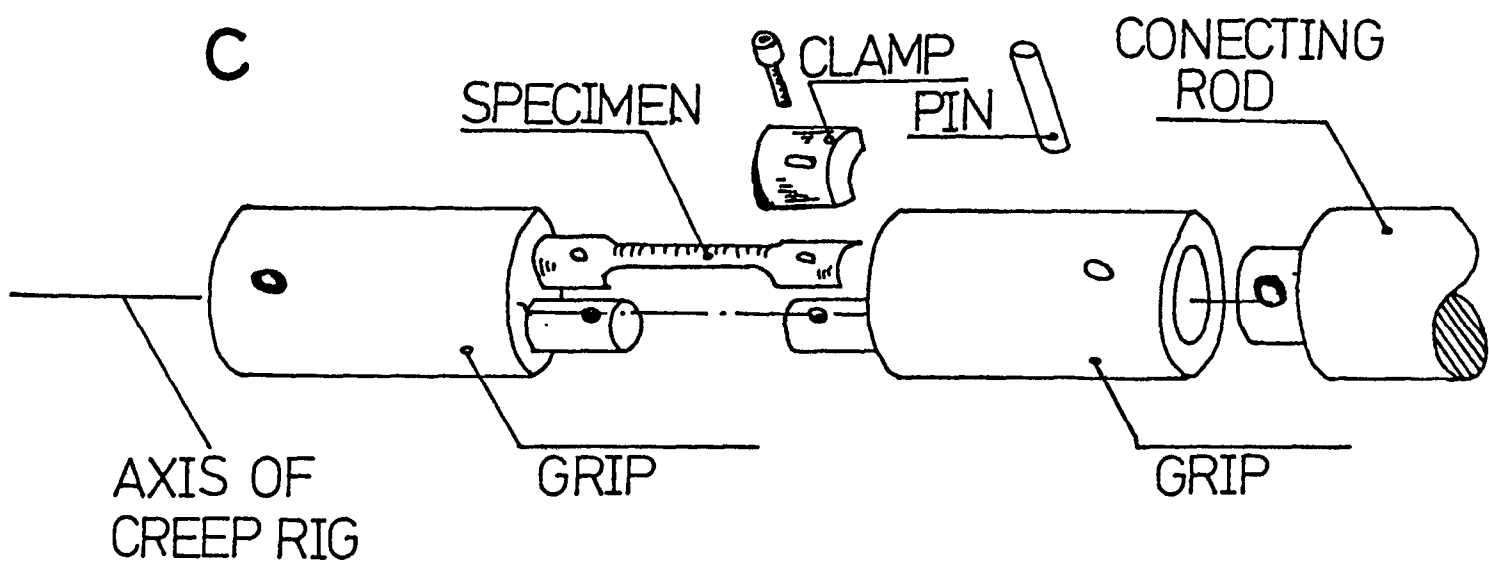
FIG 2.6

Schematic of low frequency cyclic stress applied during SCC tests.

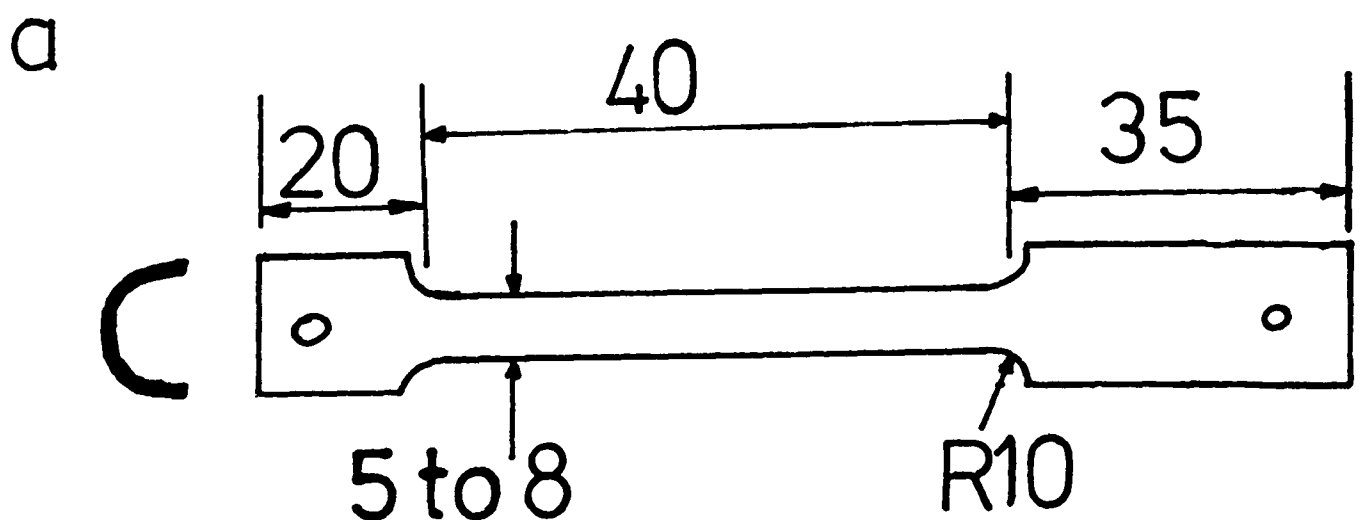
FIG3·6



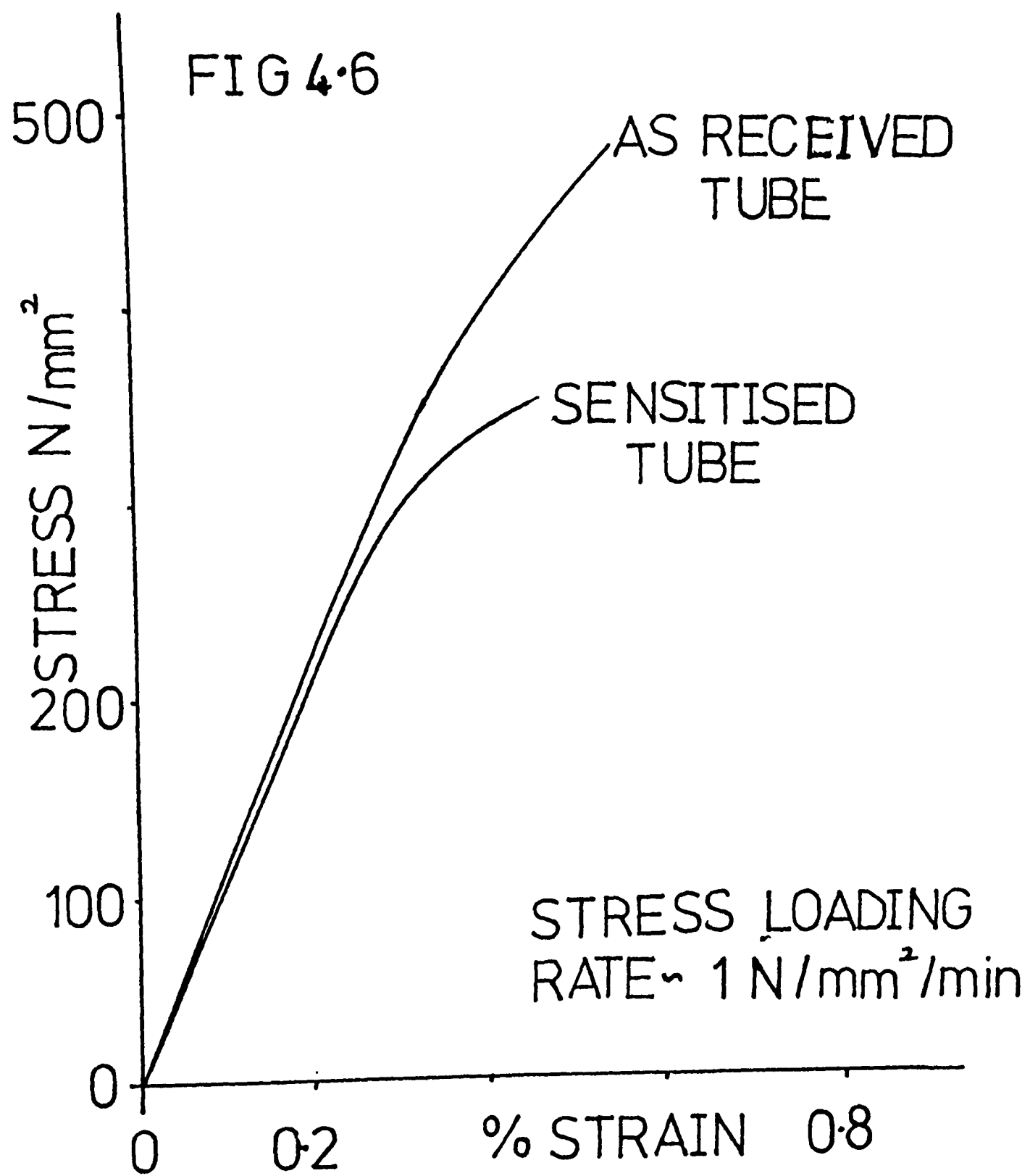
LOADING JIG



SPECIMEN/GRIP ASSEMBLY



SPECIMEN DIMENSIONS(mm)

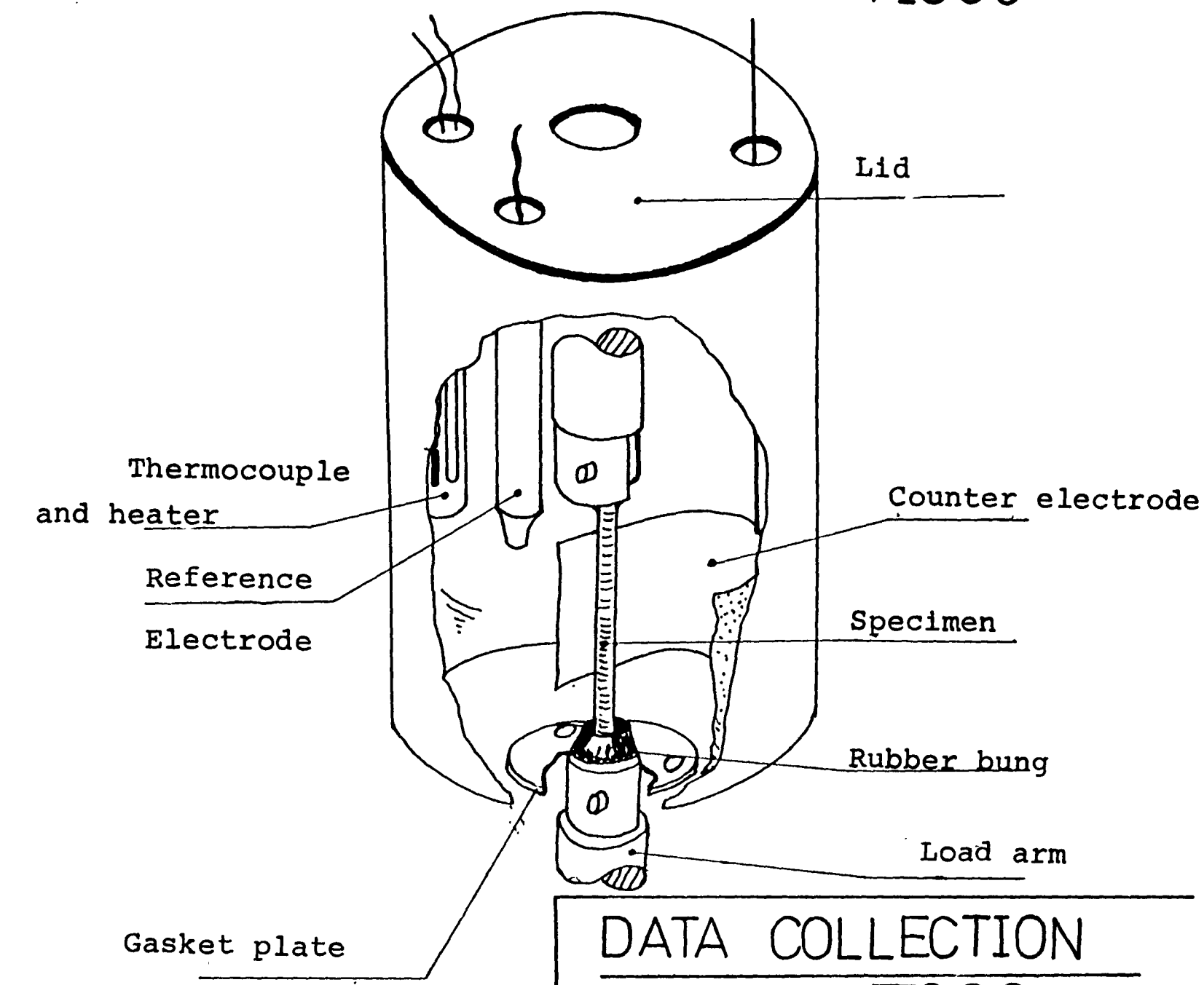


Stress / strain data for loading tube material at a constant rate.

Yield stress for sensitised tube taken as 300 N/mm^2 .

SCHEMATIC OF CORROSION CELL

FIG 5.6



DATA COLLECTION

FIG 6.6

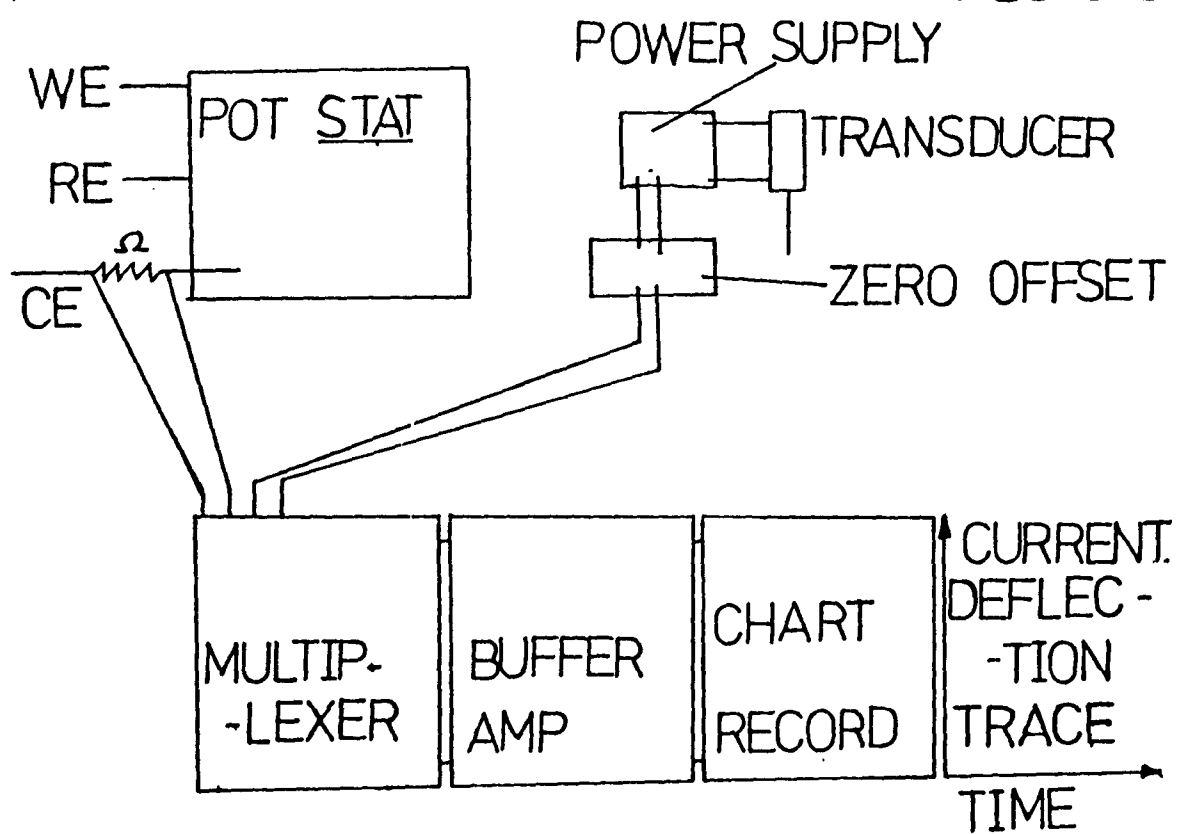
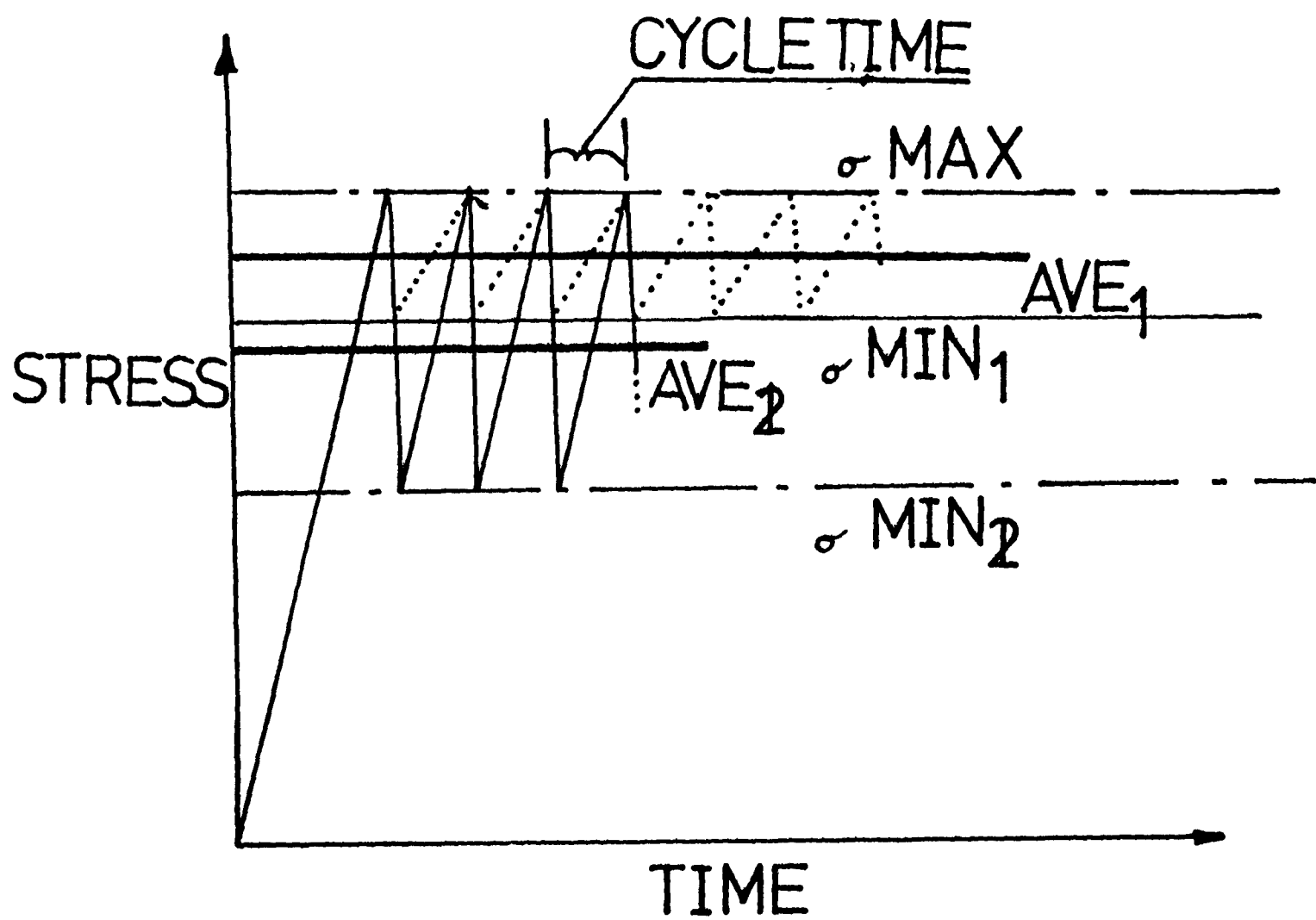
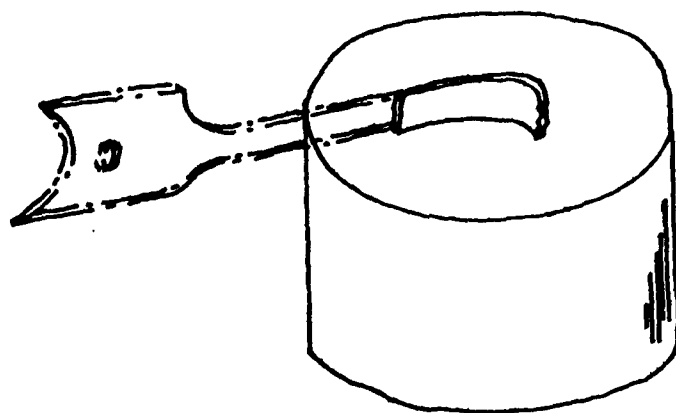


FIG 86



MECHANICAL PARAMETERS

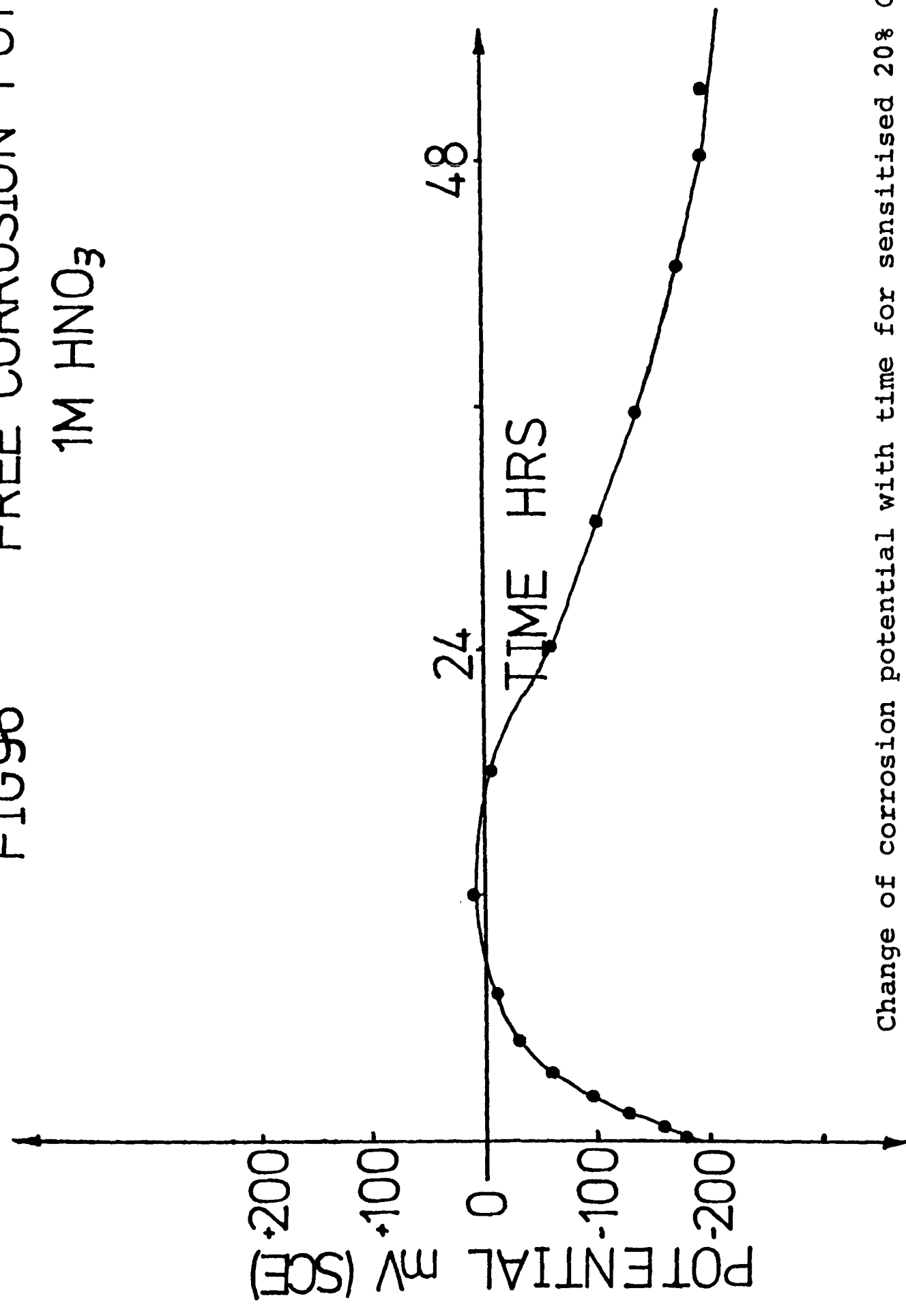
$$R = \frac{\sigma_{MIN}}{\sigma_{MAX}}$$



SCHEMATIC OF OPTICAL

FIG 7.6

FIG96 FREE CORROSION POTENTIAL
1M HNO₃



Change of corrosion potential with time for sensitised 20% Cr, 25% Ni, 0.7% Nb

Figure 10.6

- A and B. Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of +300mV (SCE). A peak stress of 70% of the yield stress was used, together with R = 0.6 and 1800 second cycles.
- C. Surface of a sample tested under the same mechanical conditions but at +100 mV (SCE).

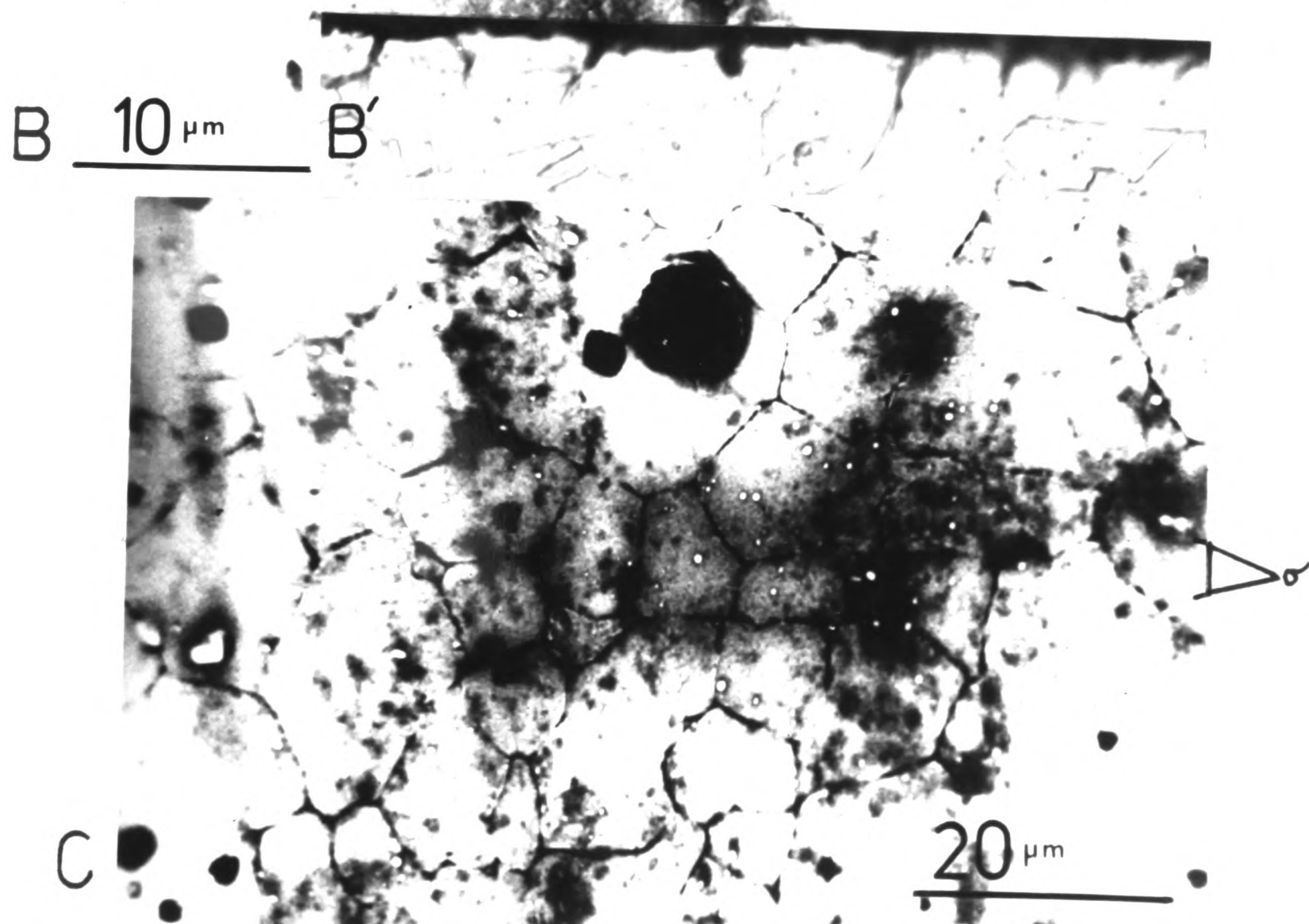
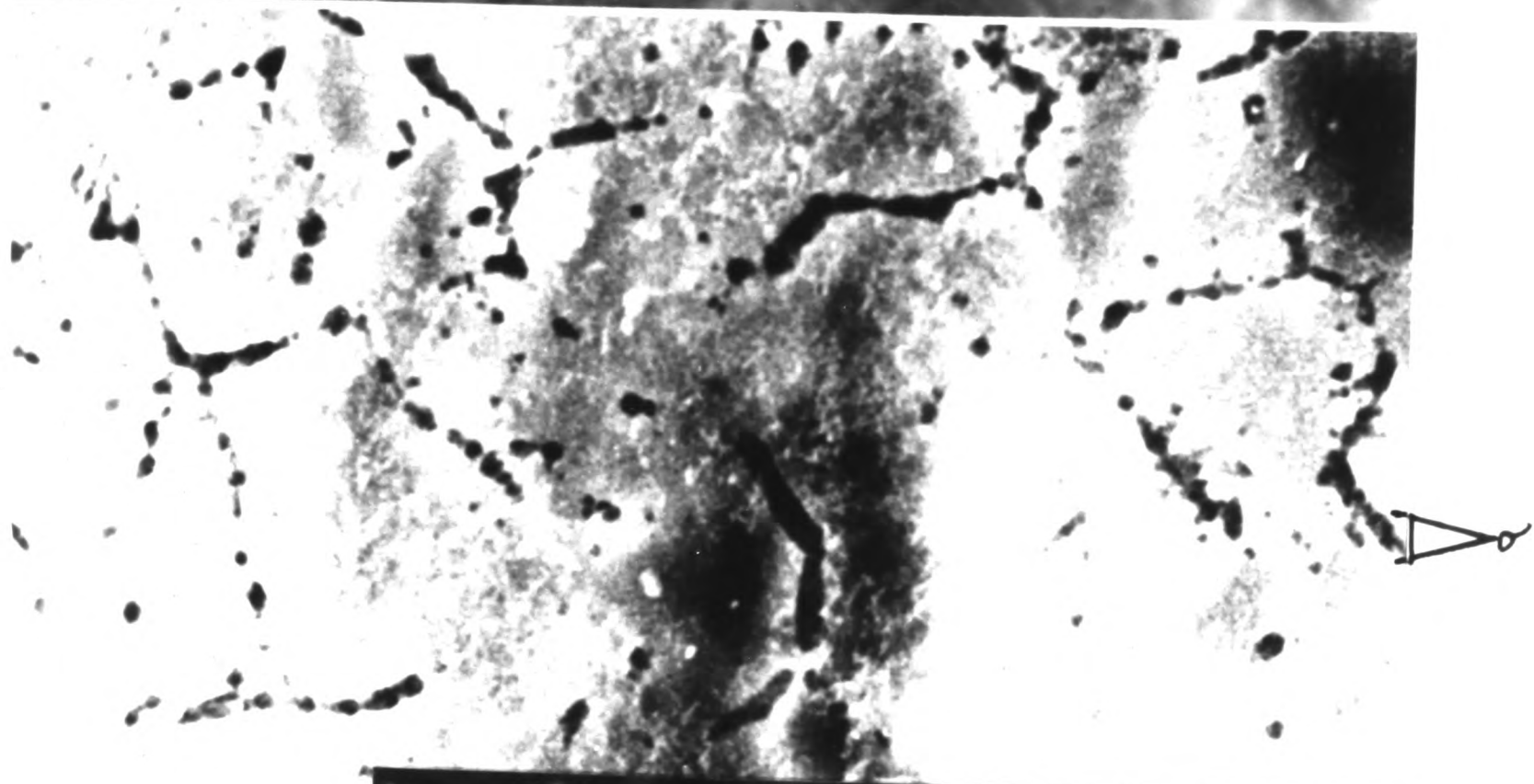
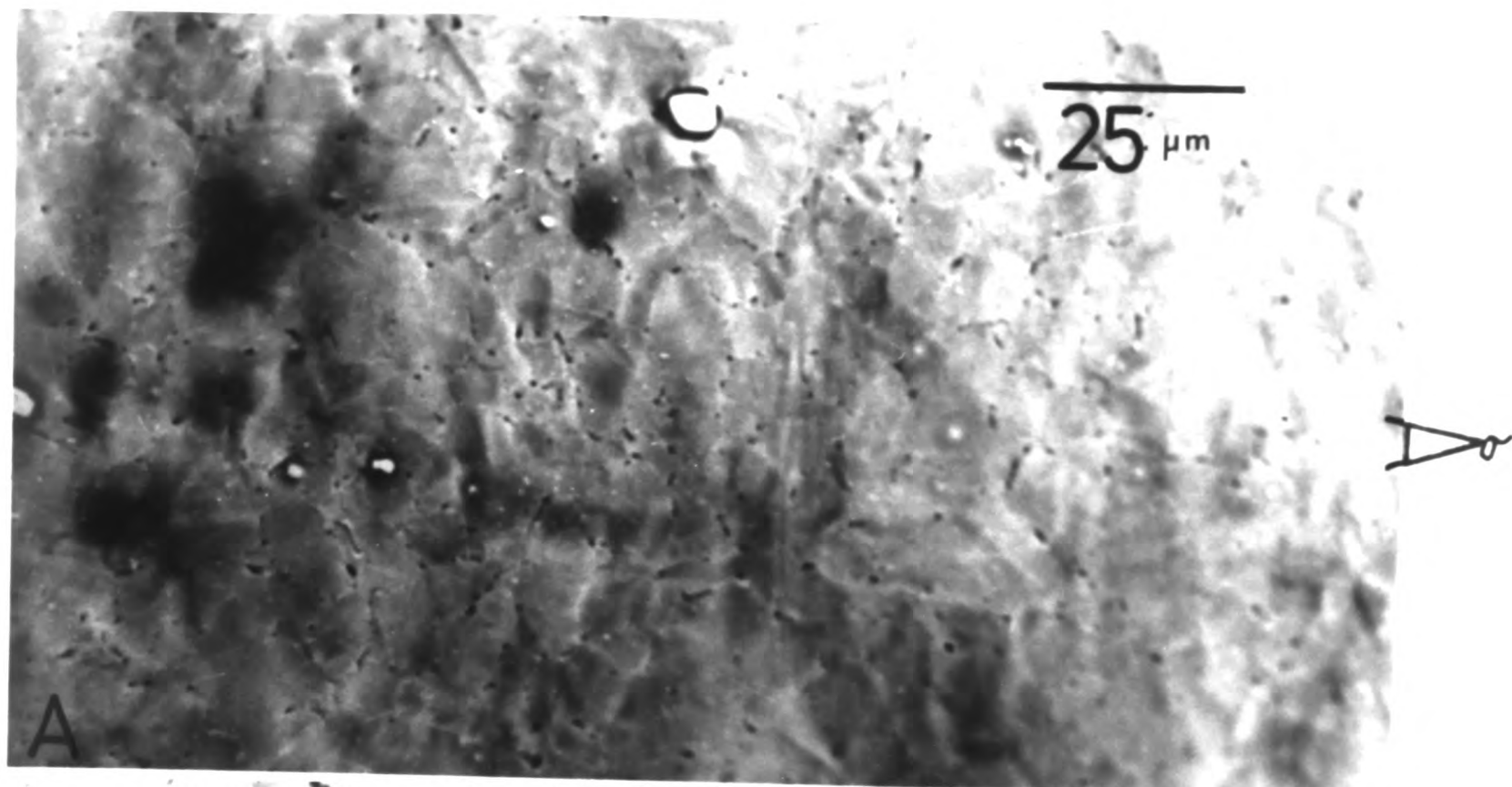
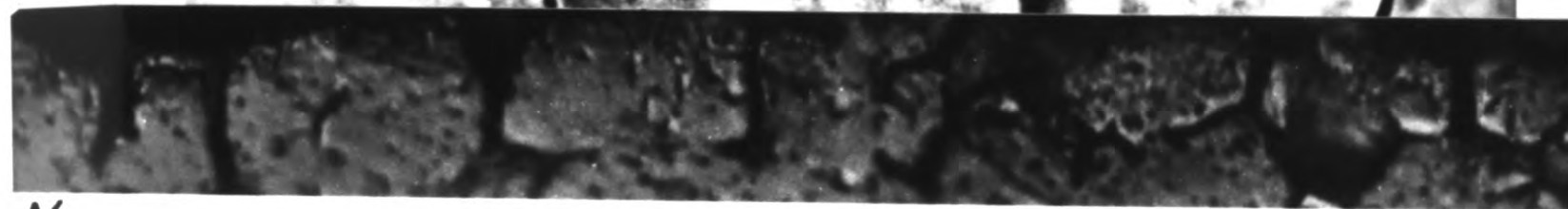
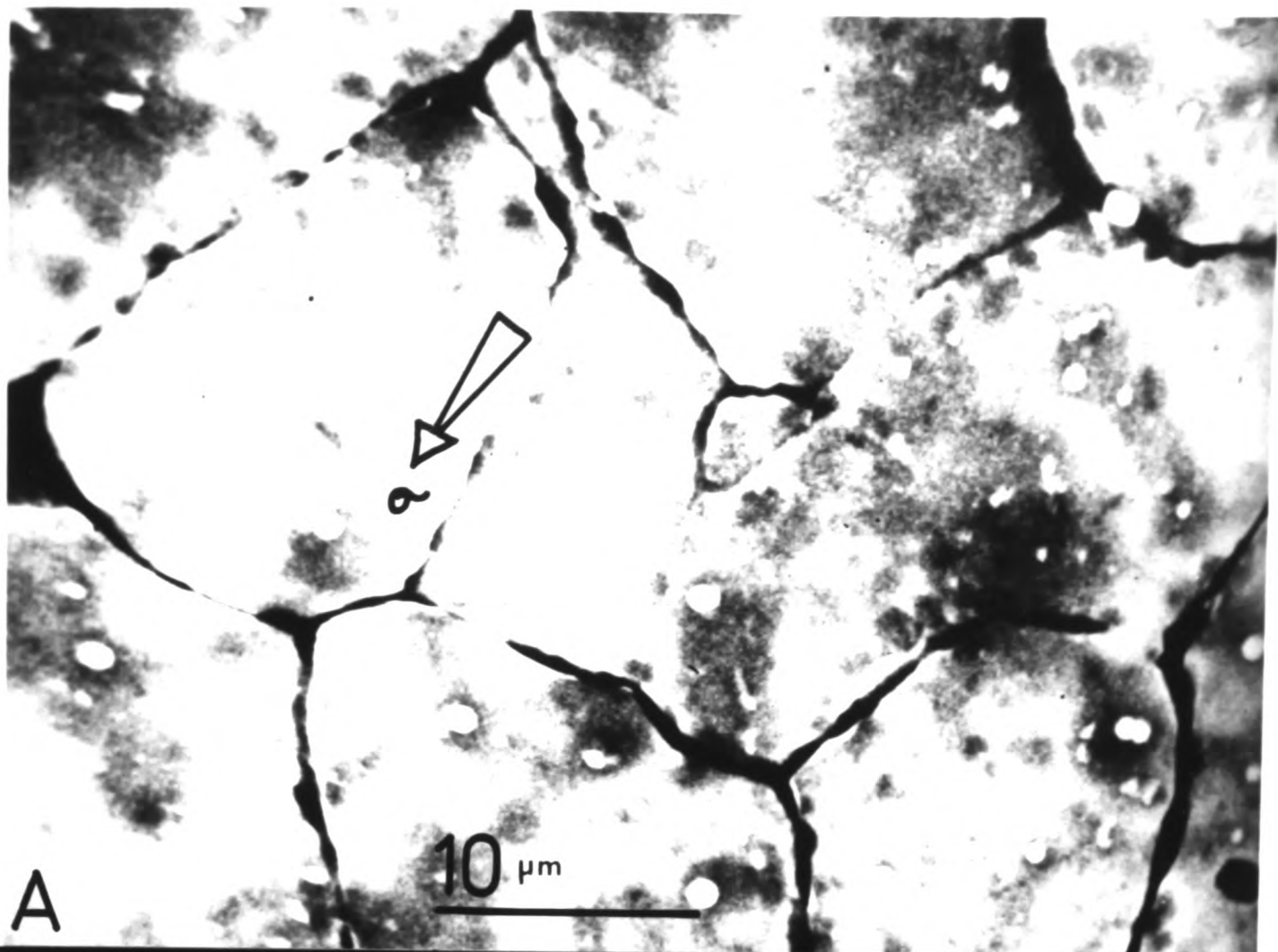


Figure 11.6

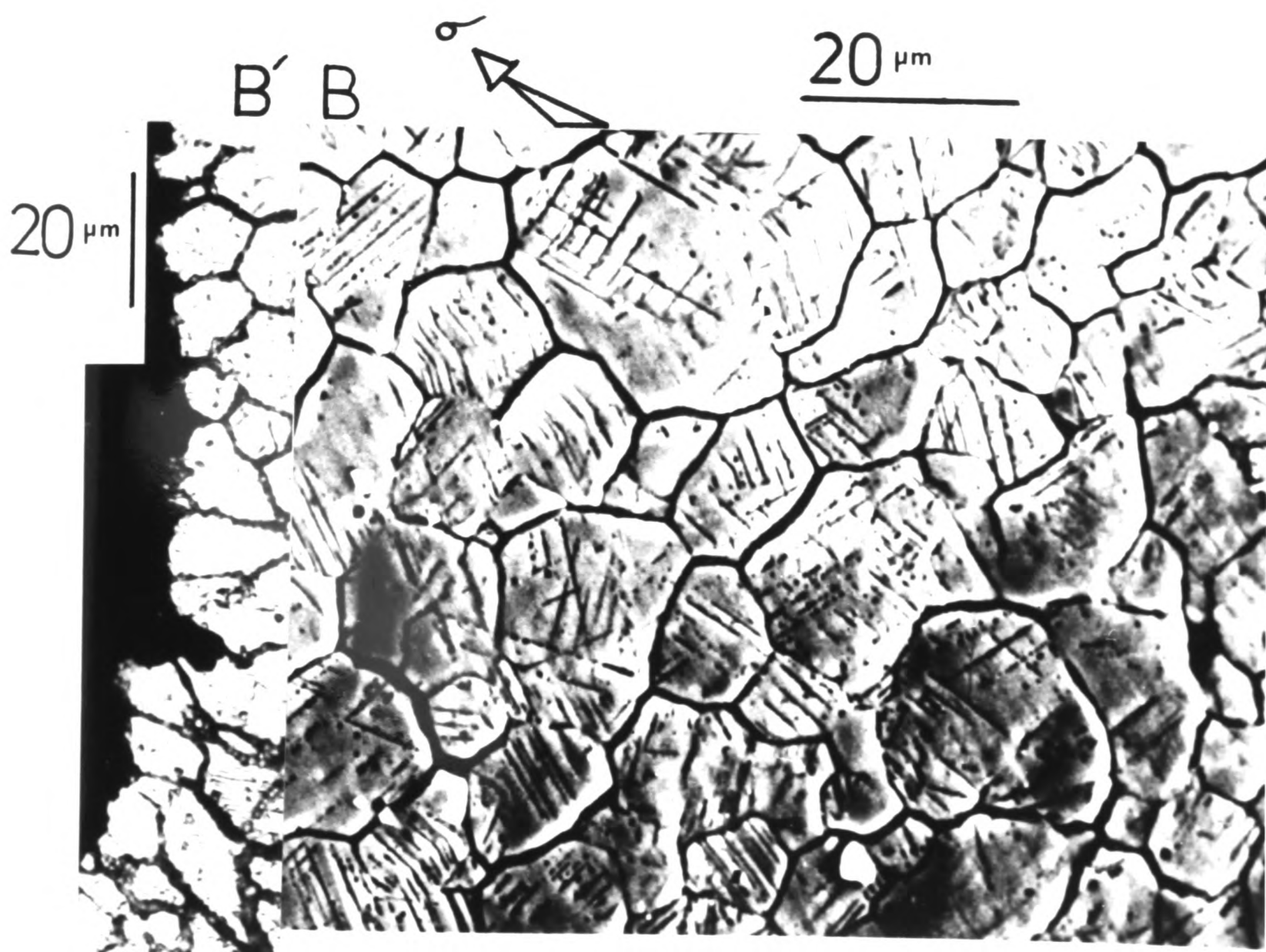
Surfaces of sensitised specimens tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of +100mV (SCE). A cycle time of approximately 1800 seconds was used.

- A. A peak stress of 75% of the yield stress with $R = 0.1$
- B. A peak stress of 120% of the yield stress with $R = 0.1$. Note the slip lines on the surfaces of grains.



A'

$10\ \mu\text{m}$

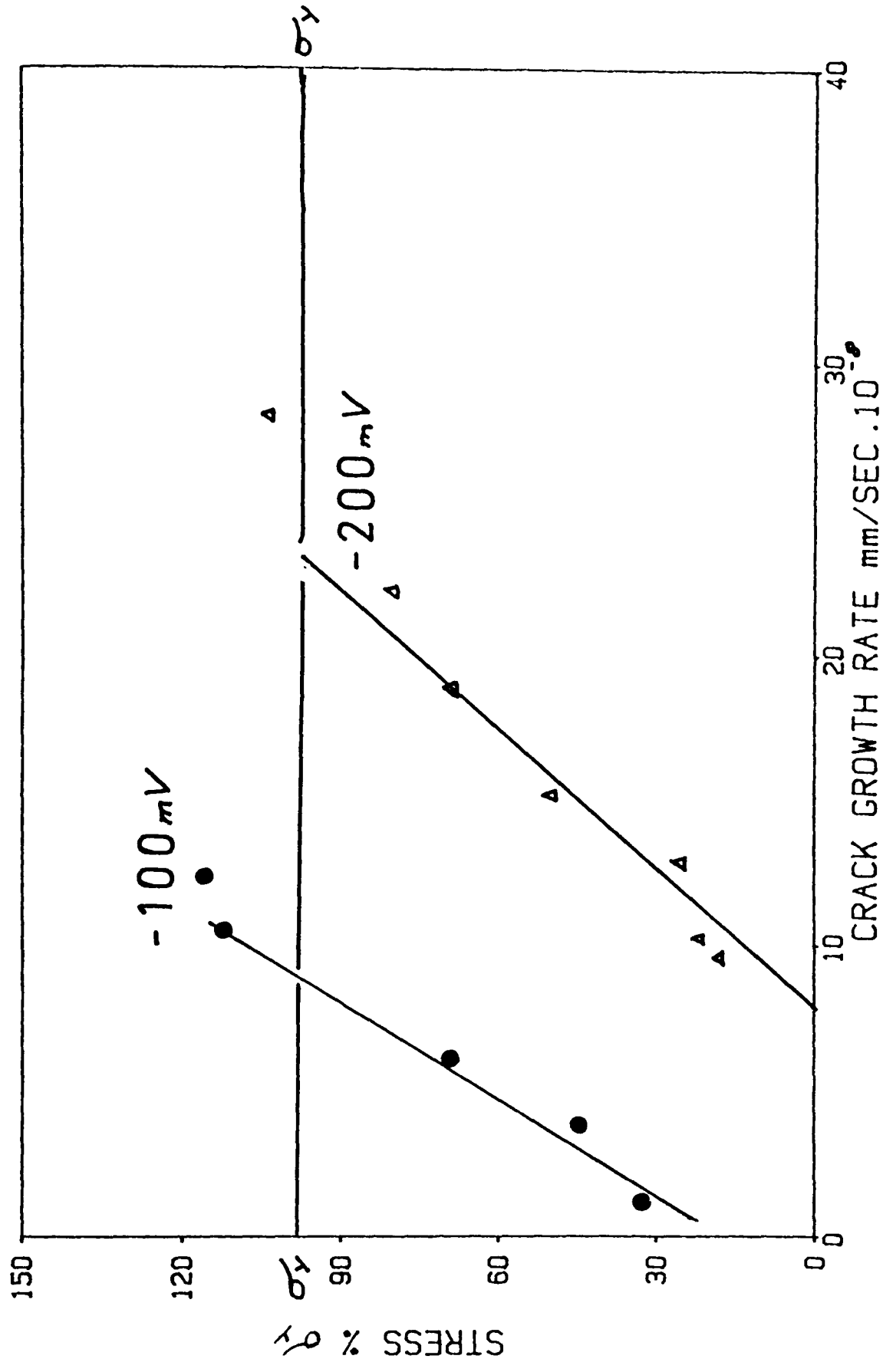


B' B

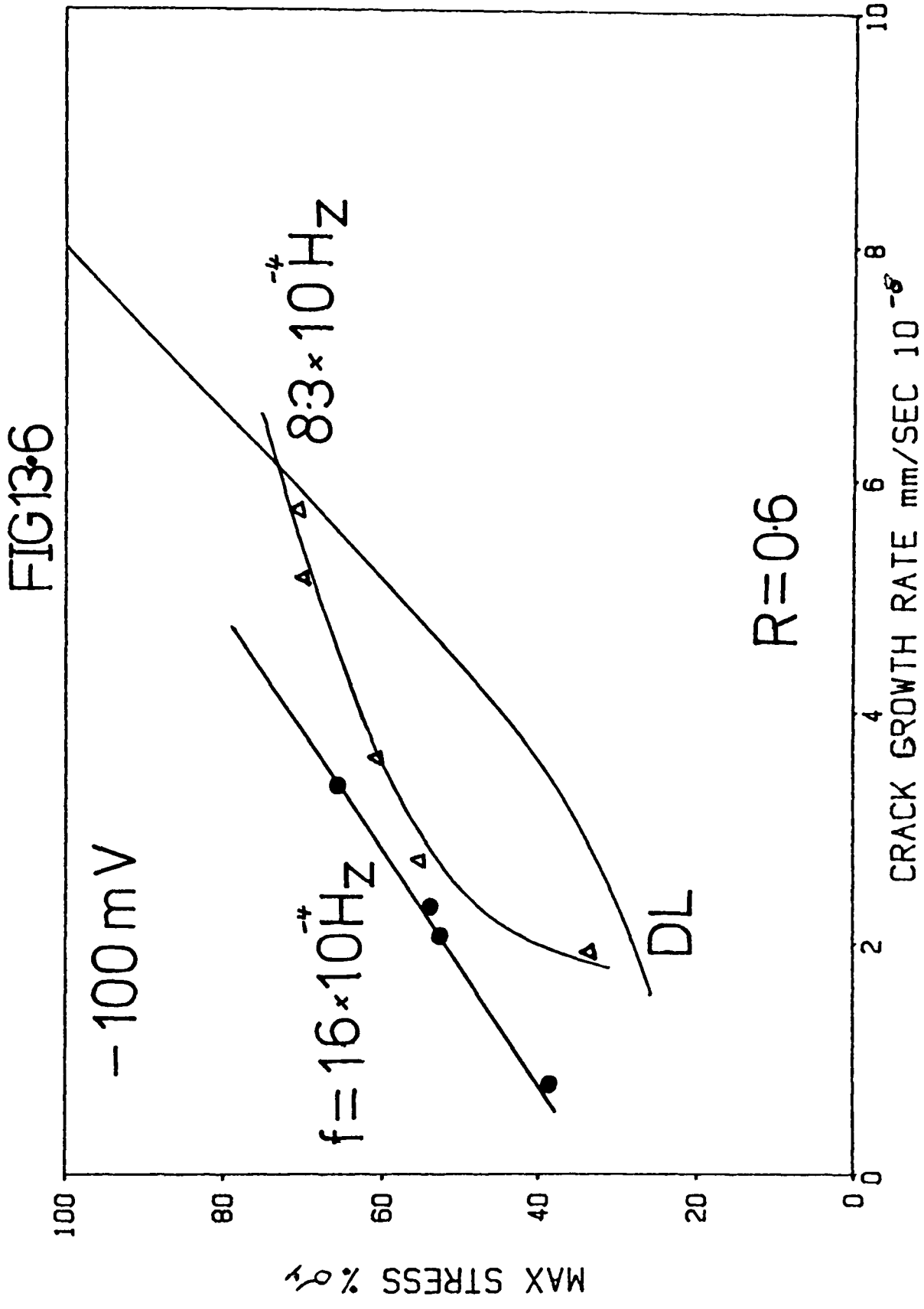
$20\ \mu\text{m}$

$20\ \mu\text{m}$

DEAD LOAD TESTS FIG12.6



Crack length / time data for sensitised tube material, for loading statically at the indicated stress levels.



Crack length / time data for low frequency cyclic stress experiments.

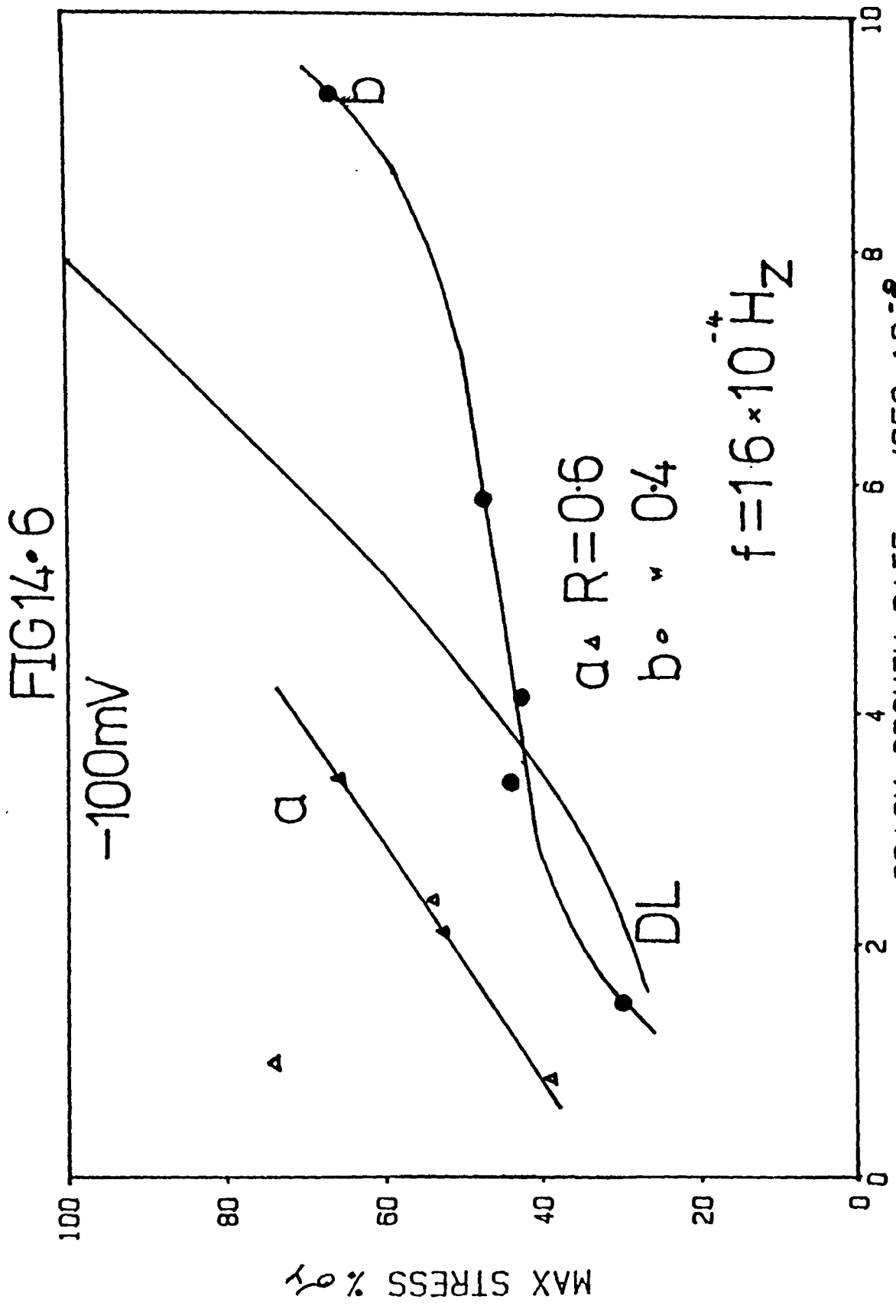


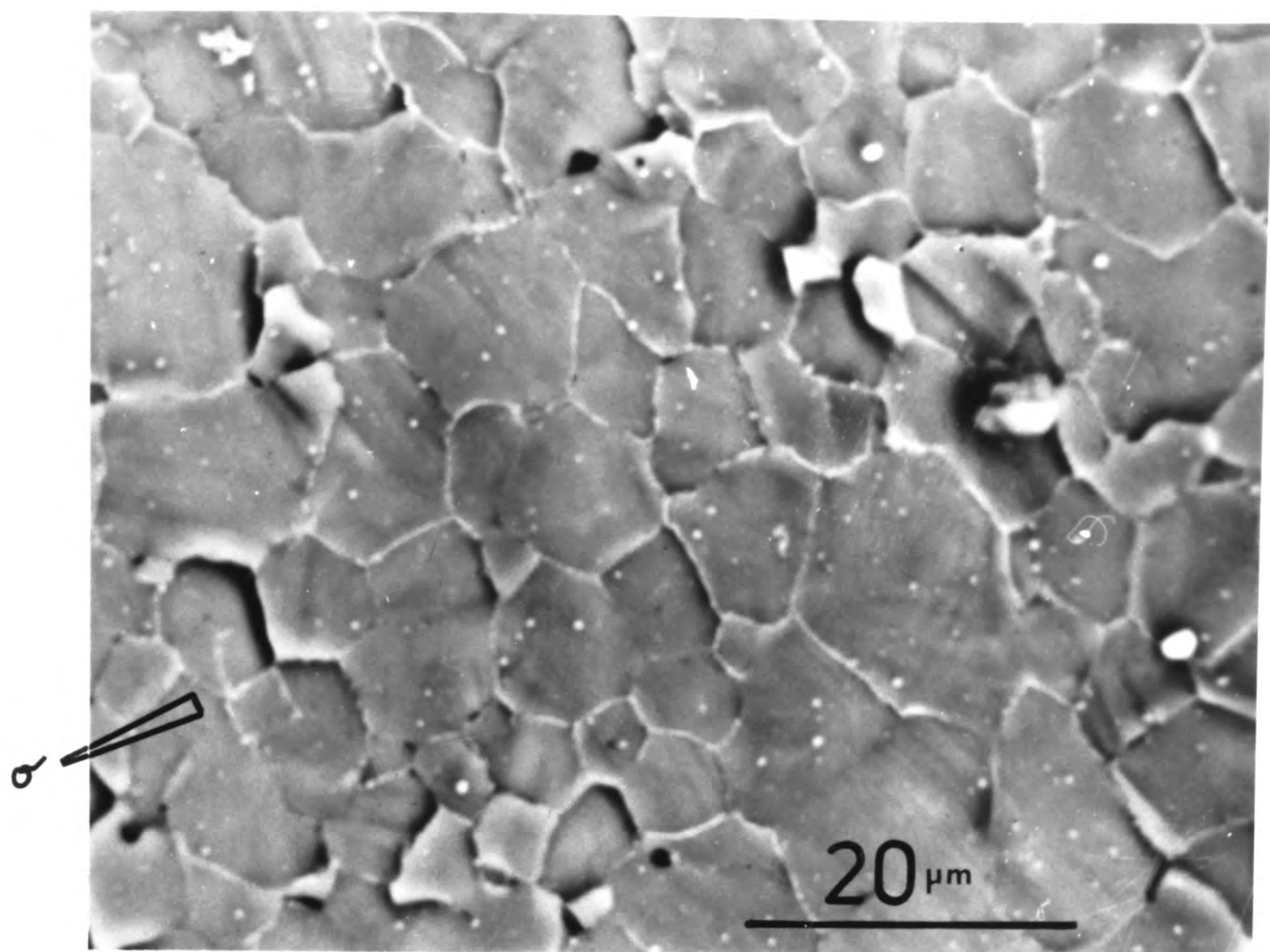
FIG14.6

Crack length / time data for low frequency cyclic stress experiments.

Figure 15.6

Surfaces of sensitised specimens tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -100mV (SCE). A peak stress of 75% of the yield stress with $R = 0.6$ and 600 second cycles were used.

- A. after 48 hours testing
- b. after 72 hours testing



A

B

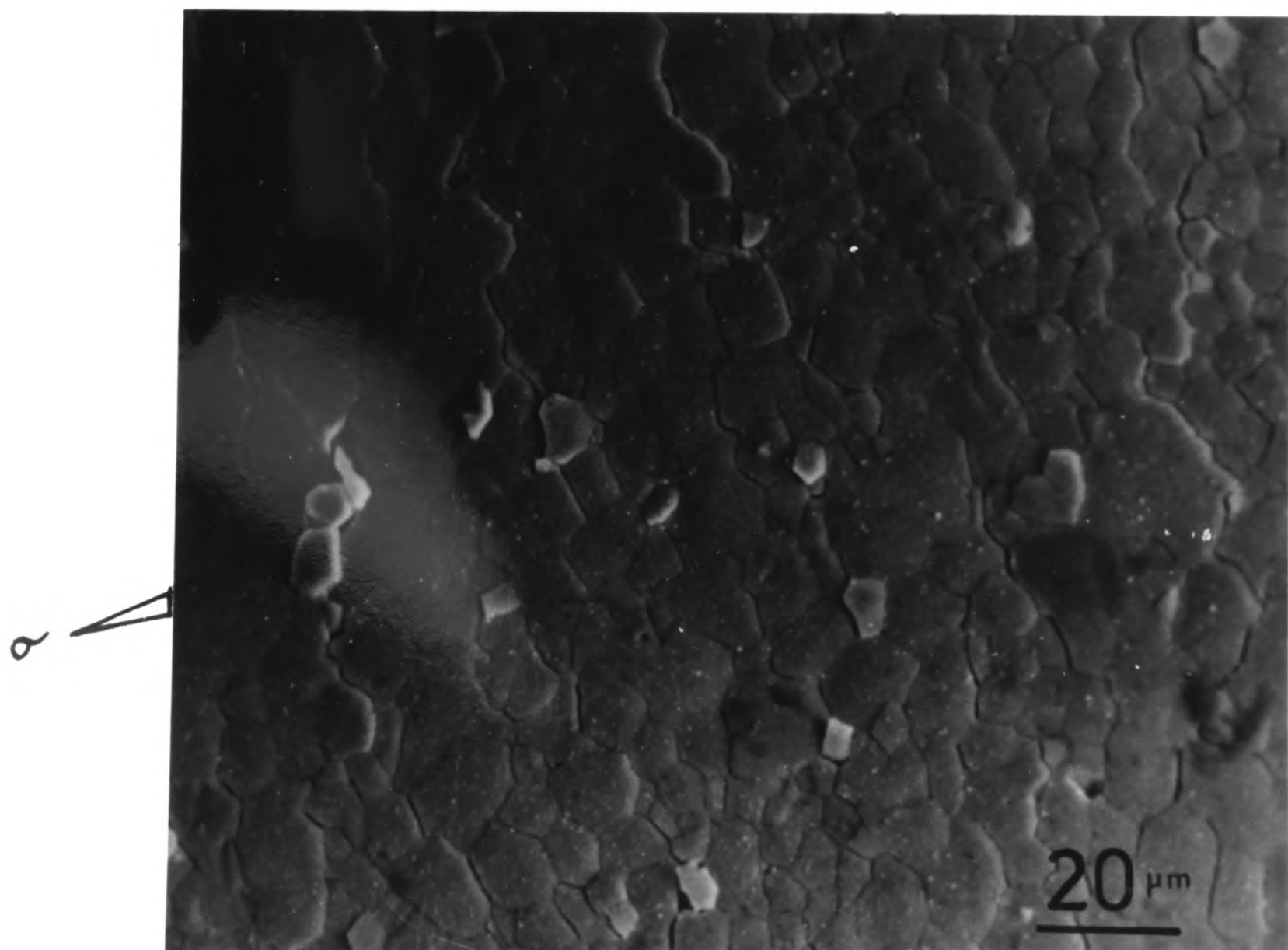
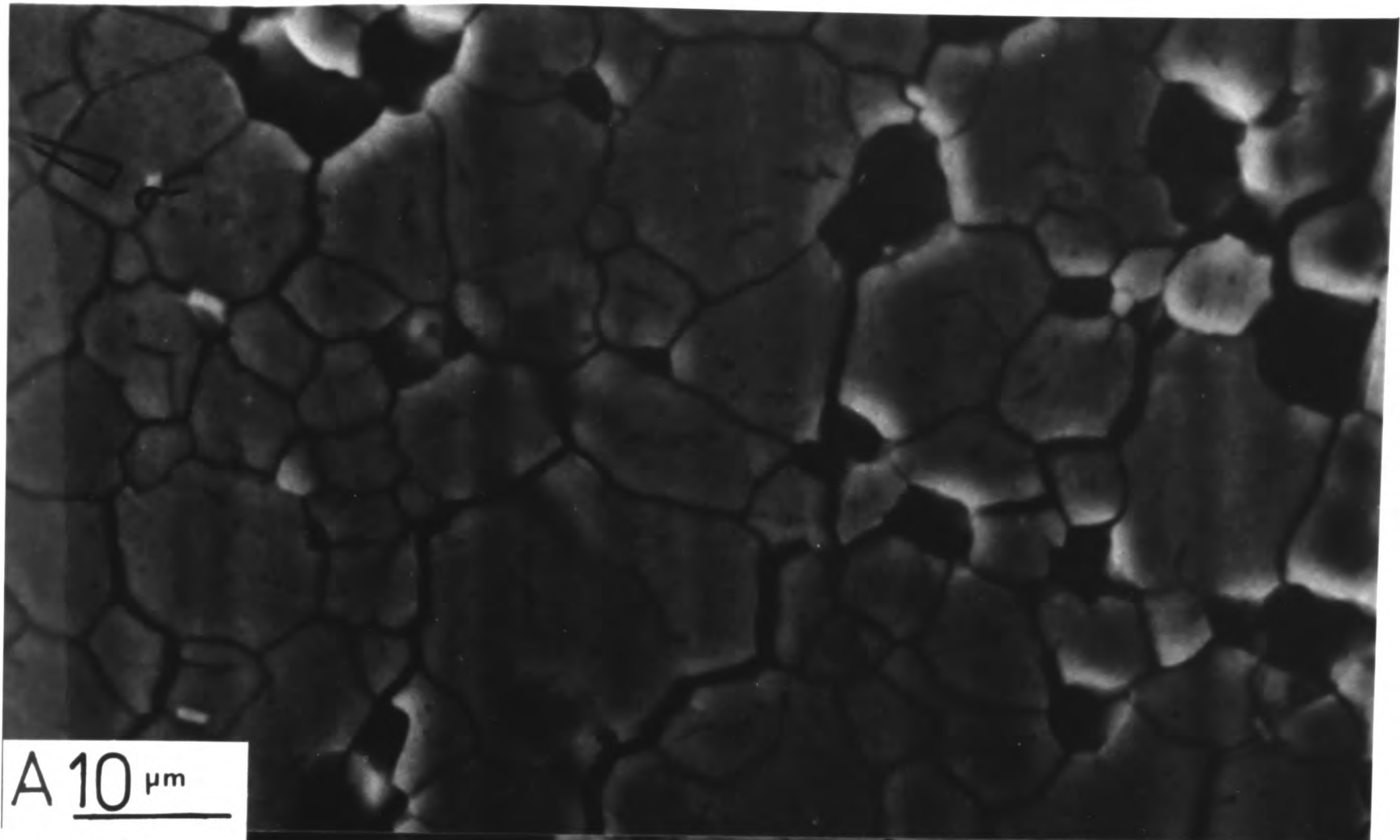


Figure 16.6

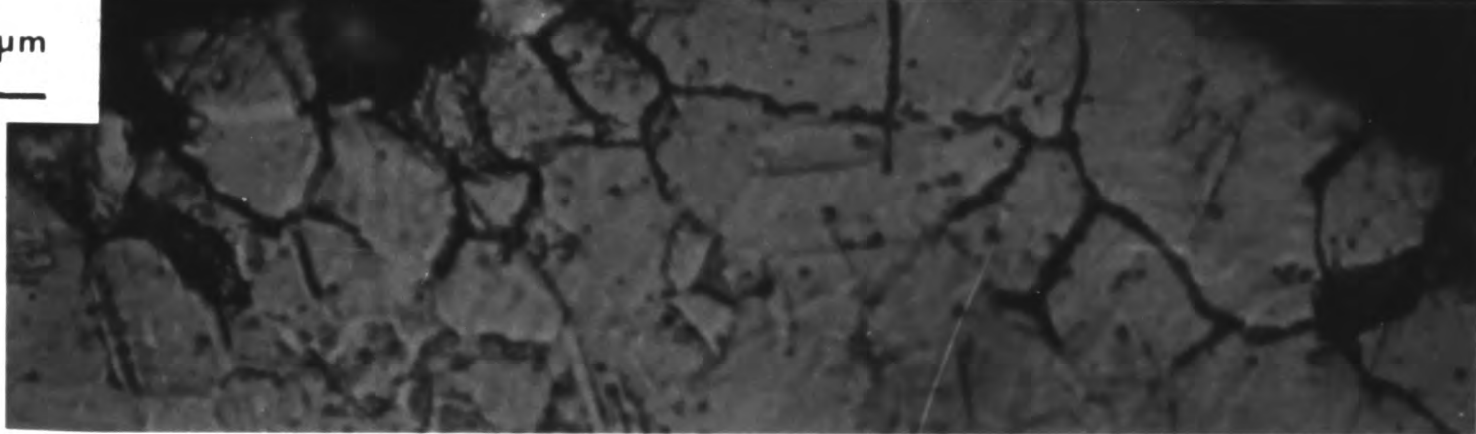
Surfaces of sensitised specimens tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -100mV (SCE). A peak stress of 60% of the yield stress and 600 second cycles were used.

- A. $R = 0.4$
- B. $R = 0.6$



10 μm

A' 10 μm

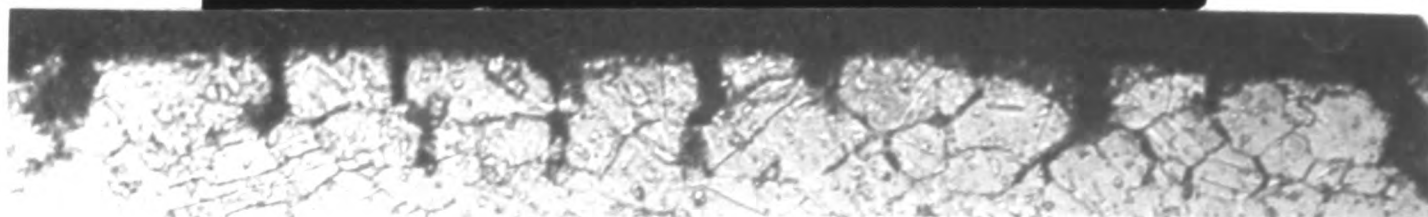


B



B'

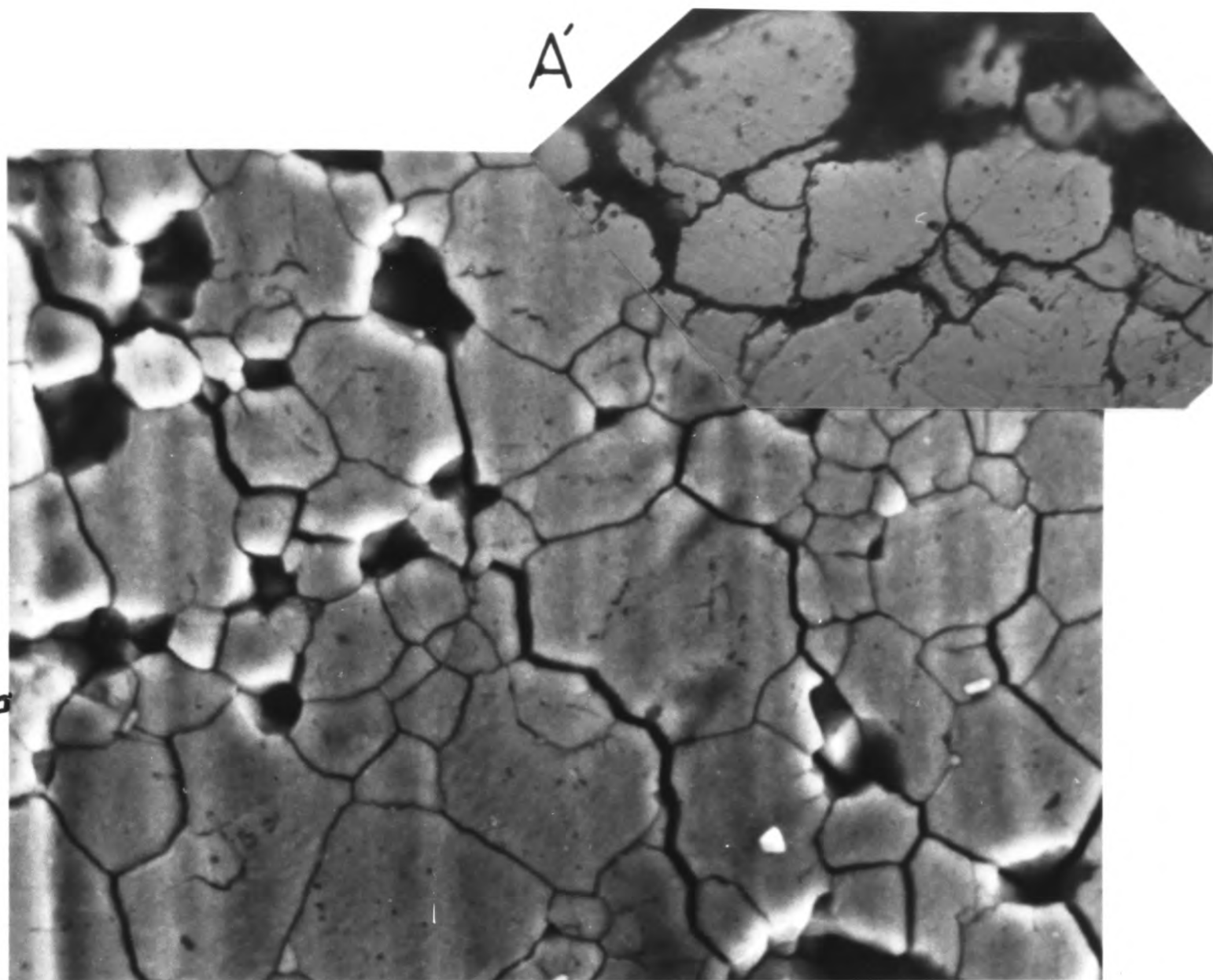
40 μm



20 μm

Figure 17.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -100mV (SCE). A peak stress of 60% of the yield stress with $R = 0.5$ and 600 second cycles were used.



A

15 μm

B

25 μm

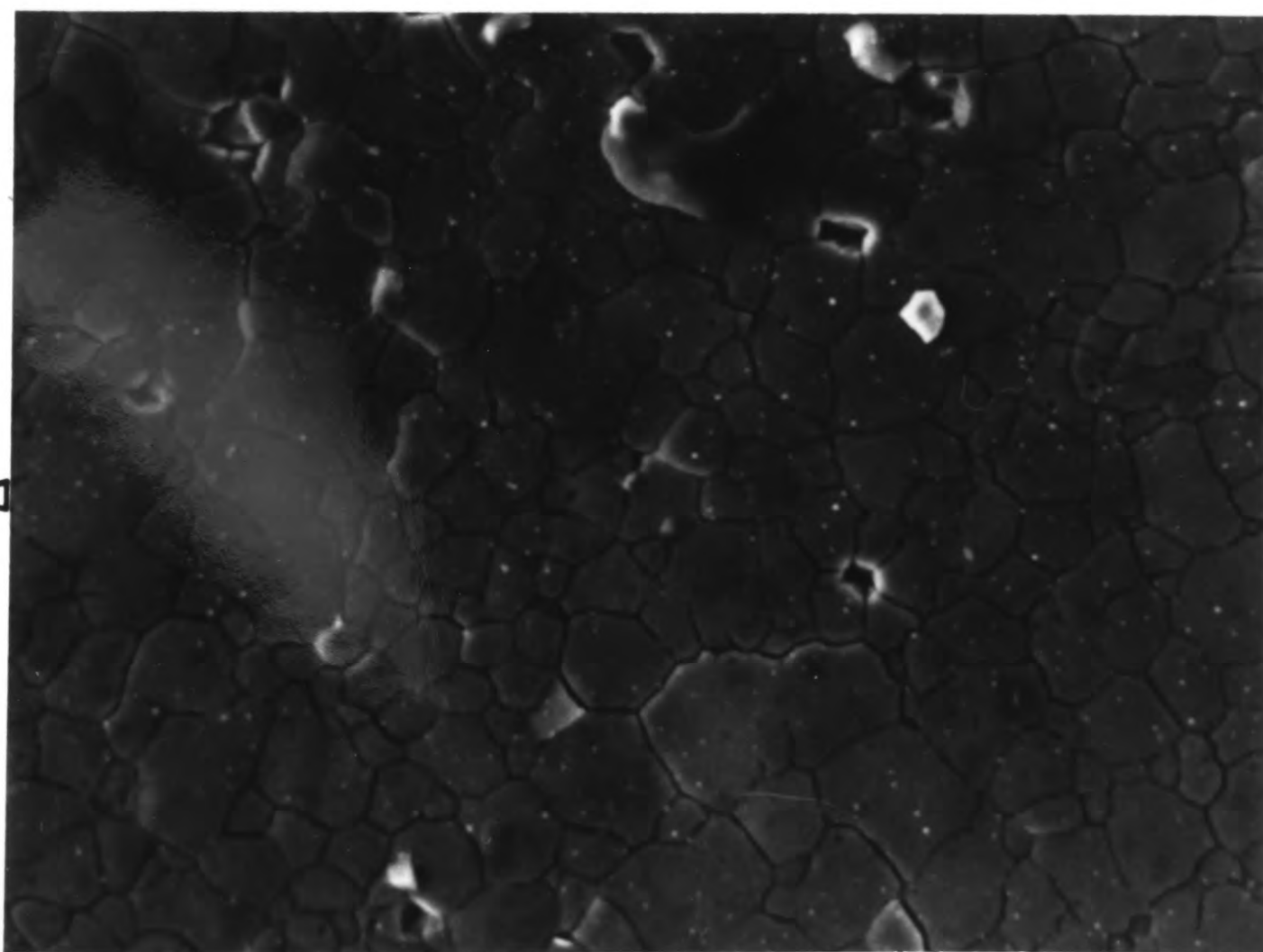


Figure 18.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -100mV (SCE). A peak stress of 80% of the yield stress with $R = 0.3$ and 600 second cycles were used. The test lasted 100 hours.

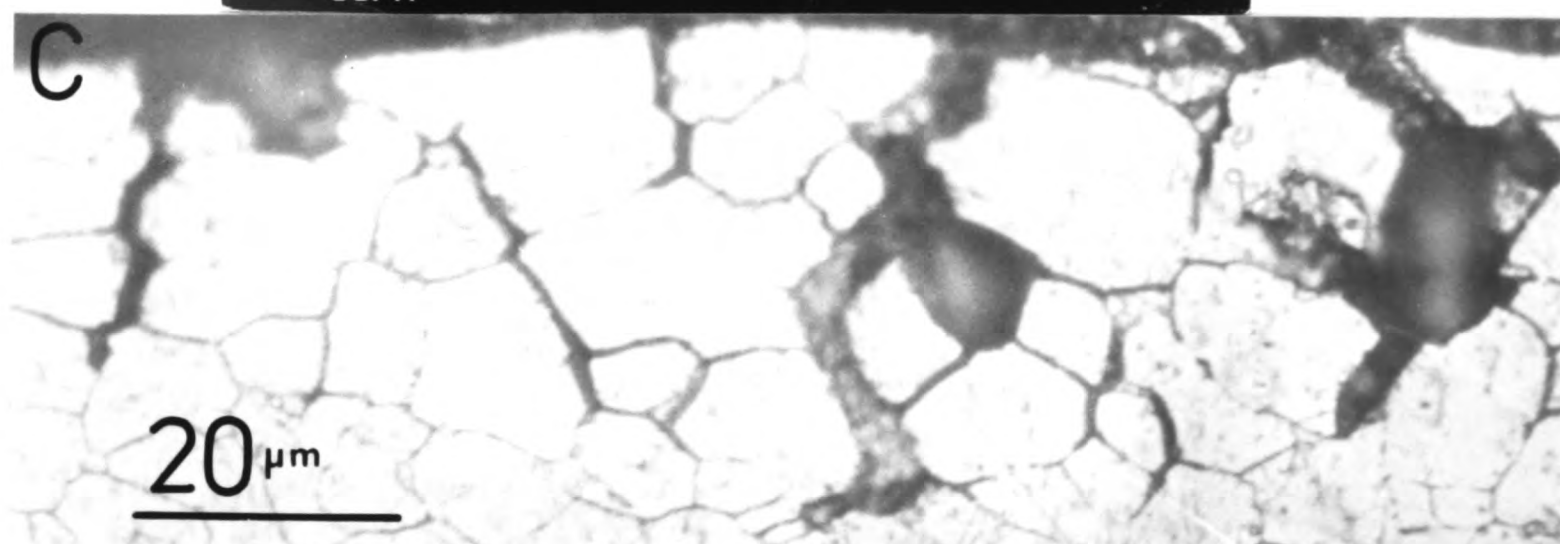
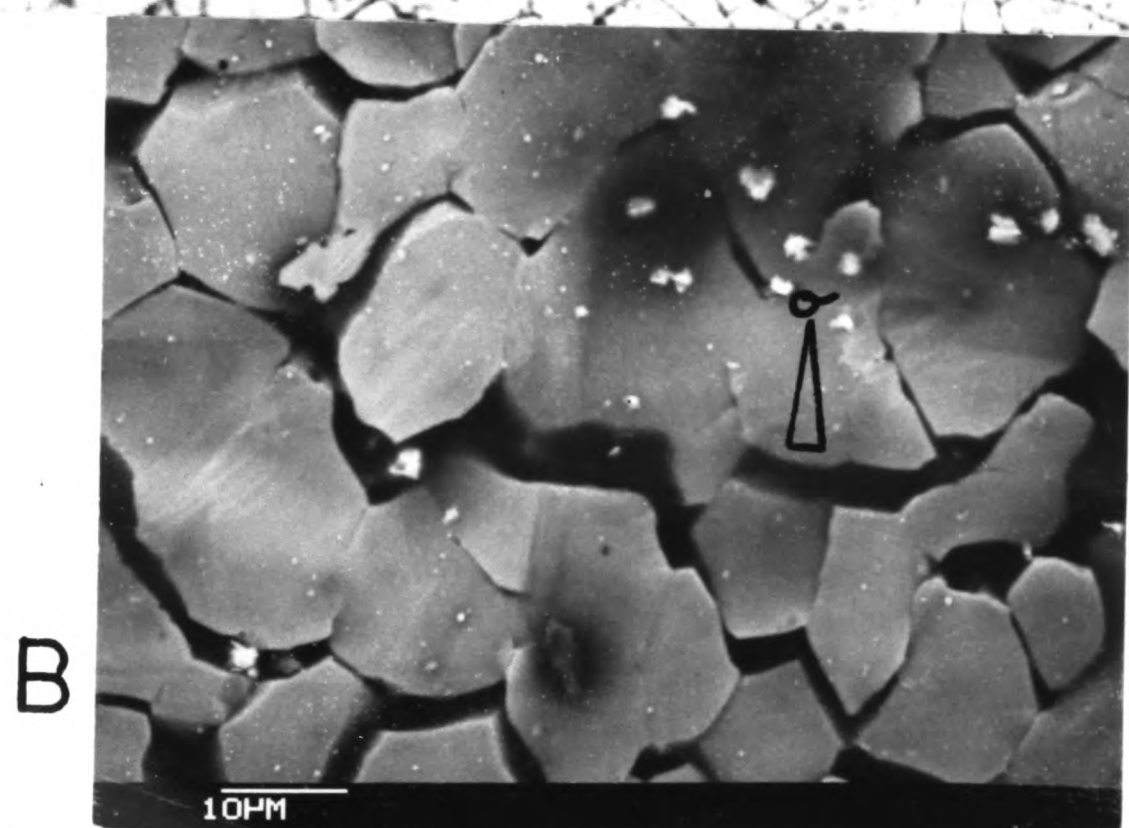
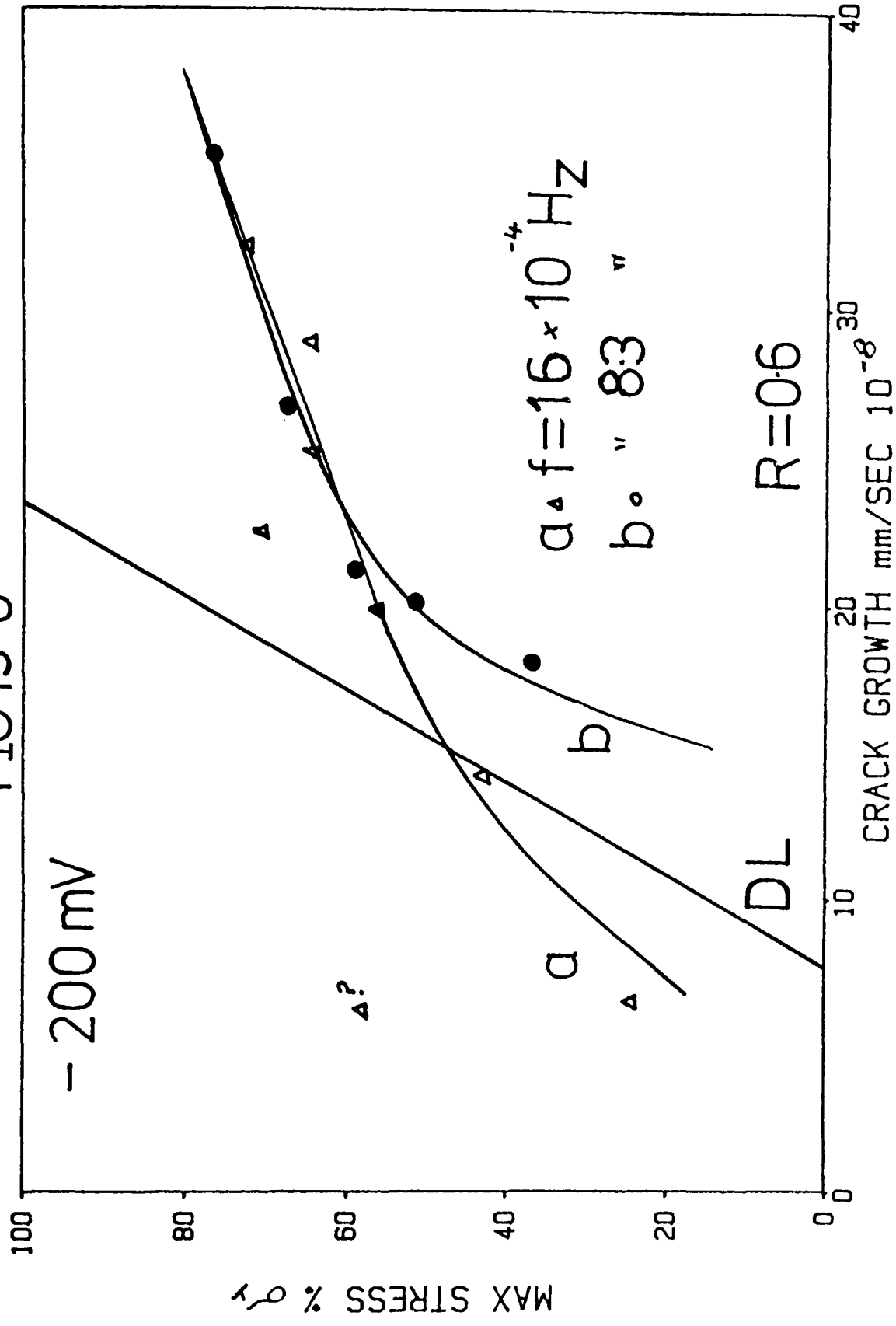
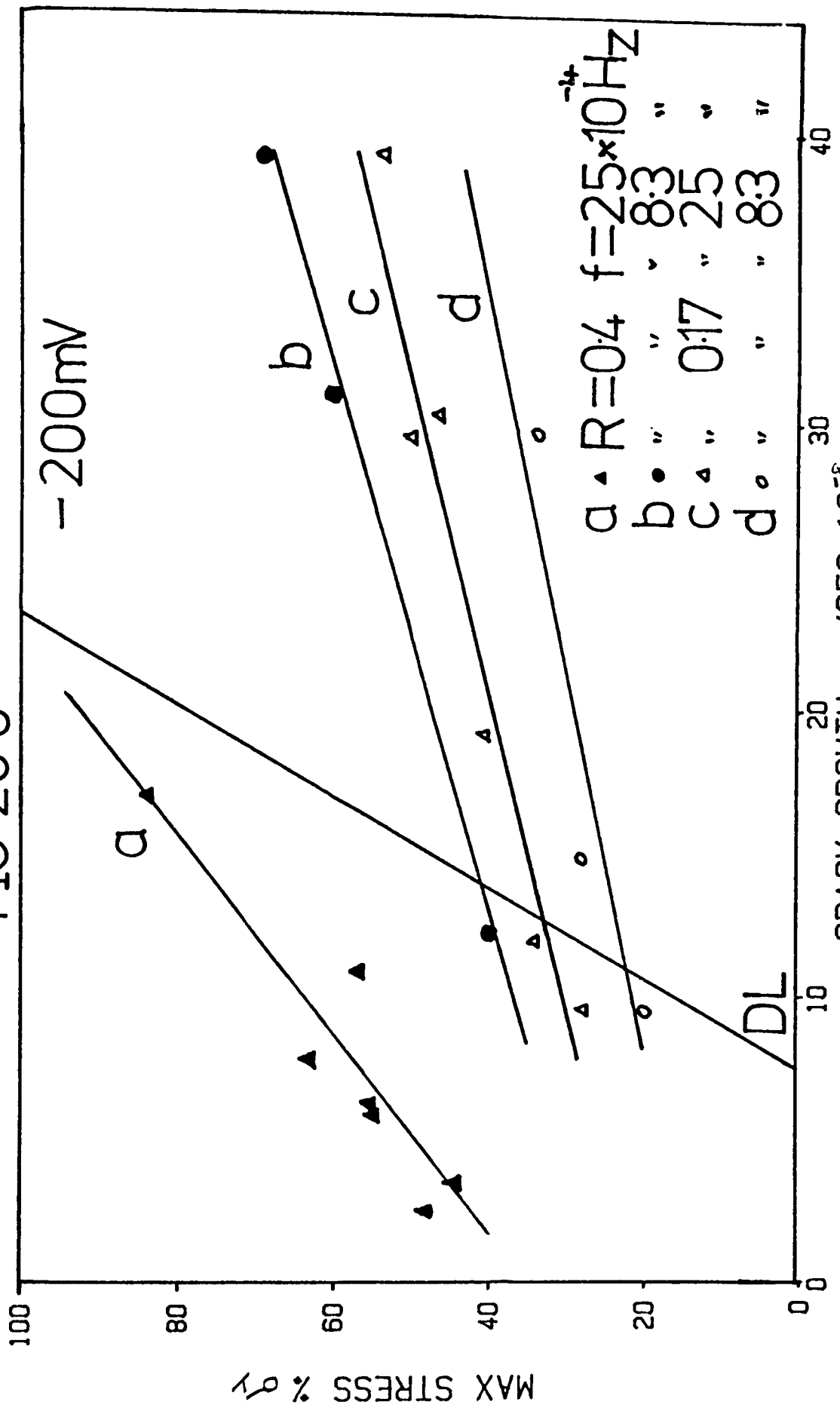


FIG19.6



Crack length / time data for low frequency cyclic stress experiments.

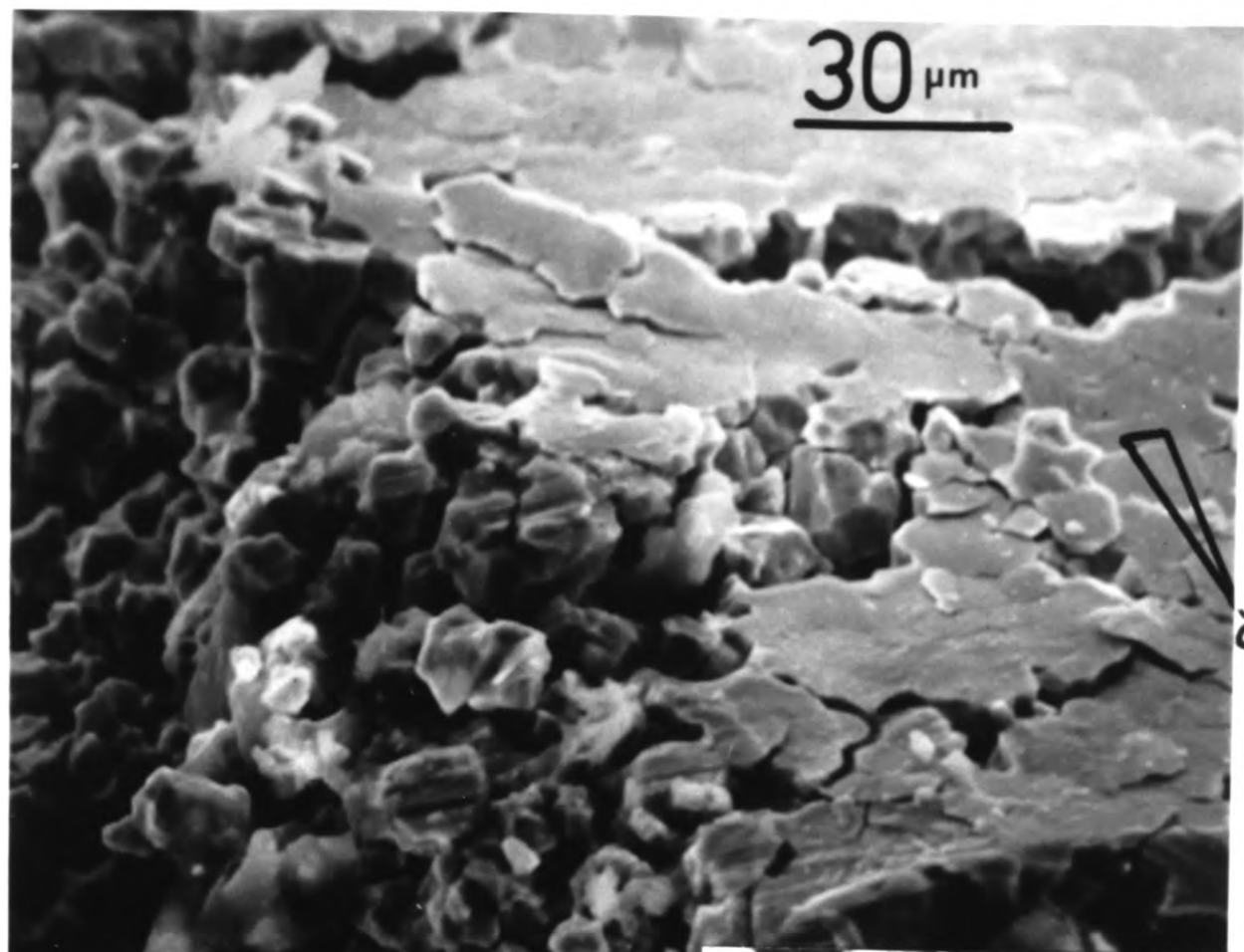
FIG 20.6



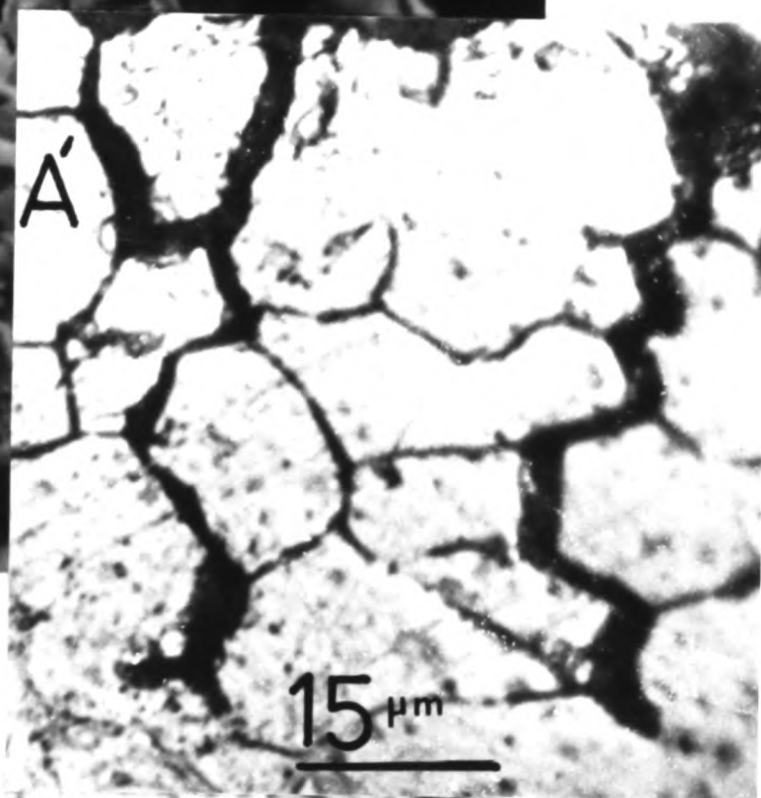
Crack length / time data for low frequency cyclic stress experiments.

Figure 21.6

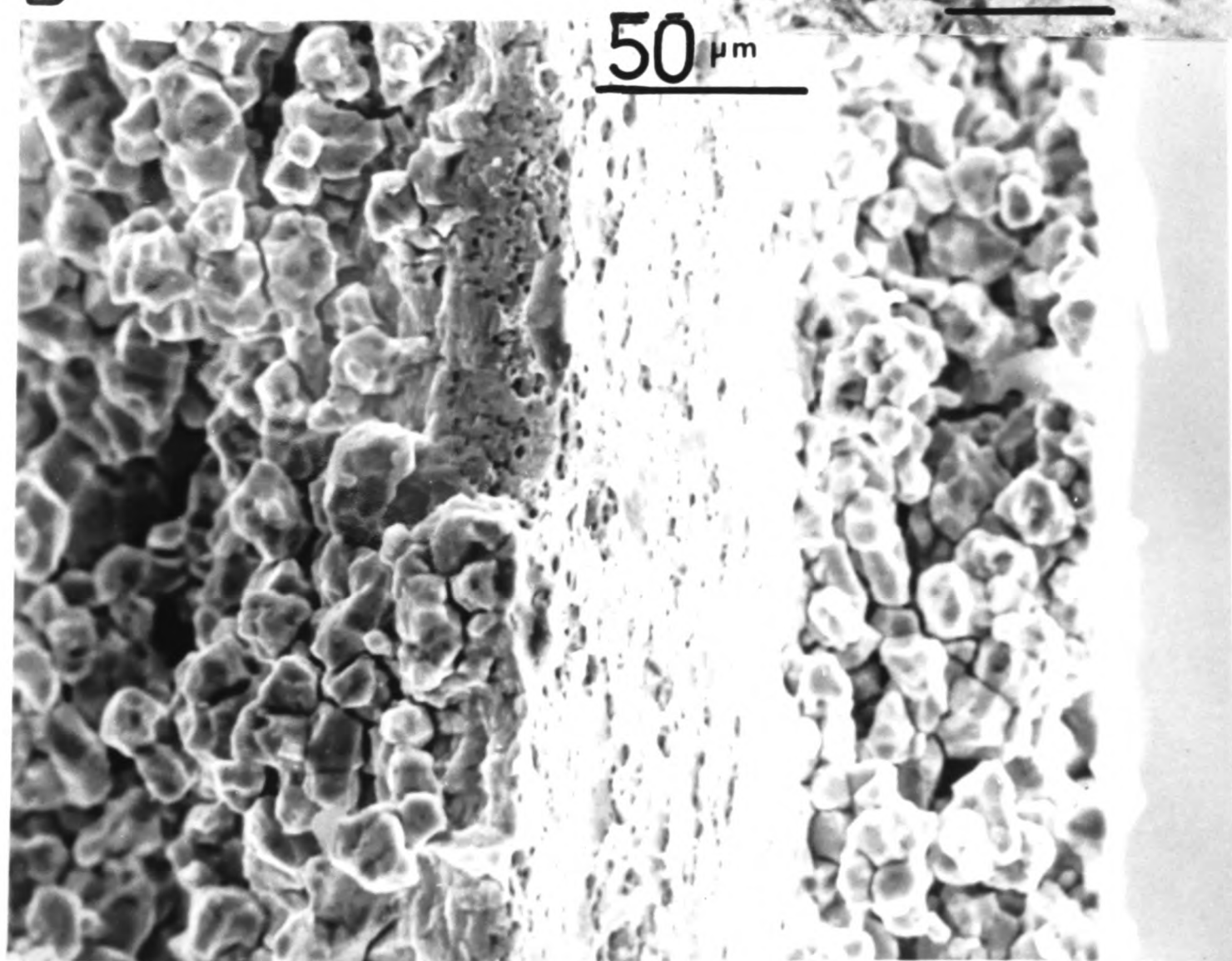
Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -200mV (SCE). A peak stress of 60% of the yield stress with $R = 0.6$ and 600 second cycles were used. The test lasted 72 hours.



A



B



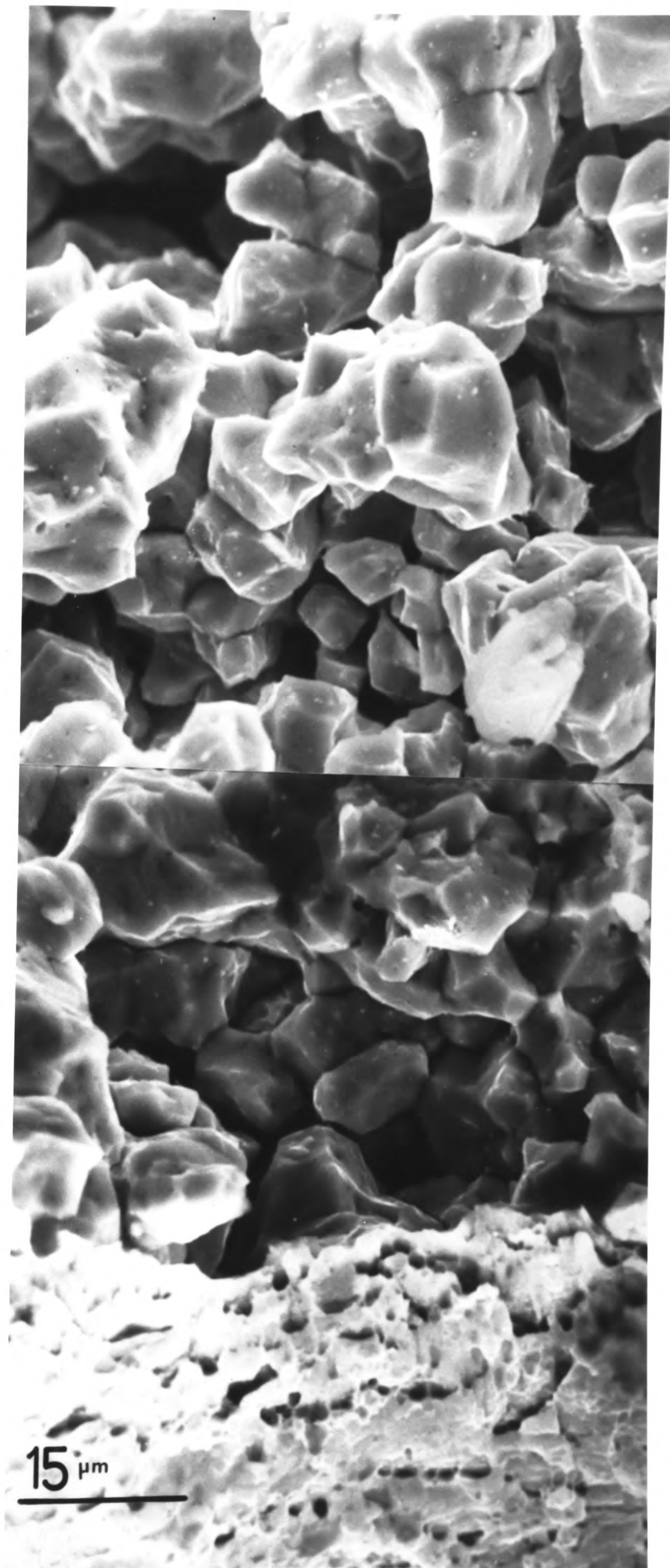
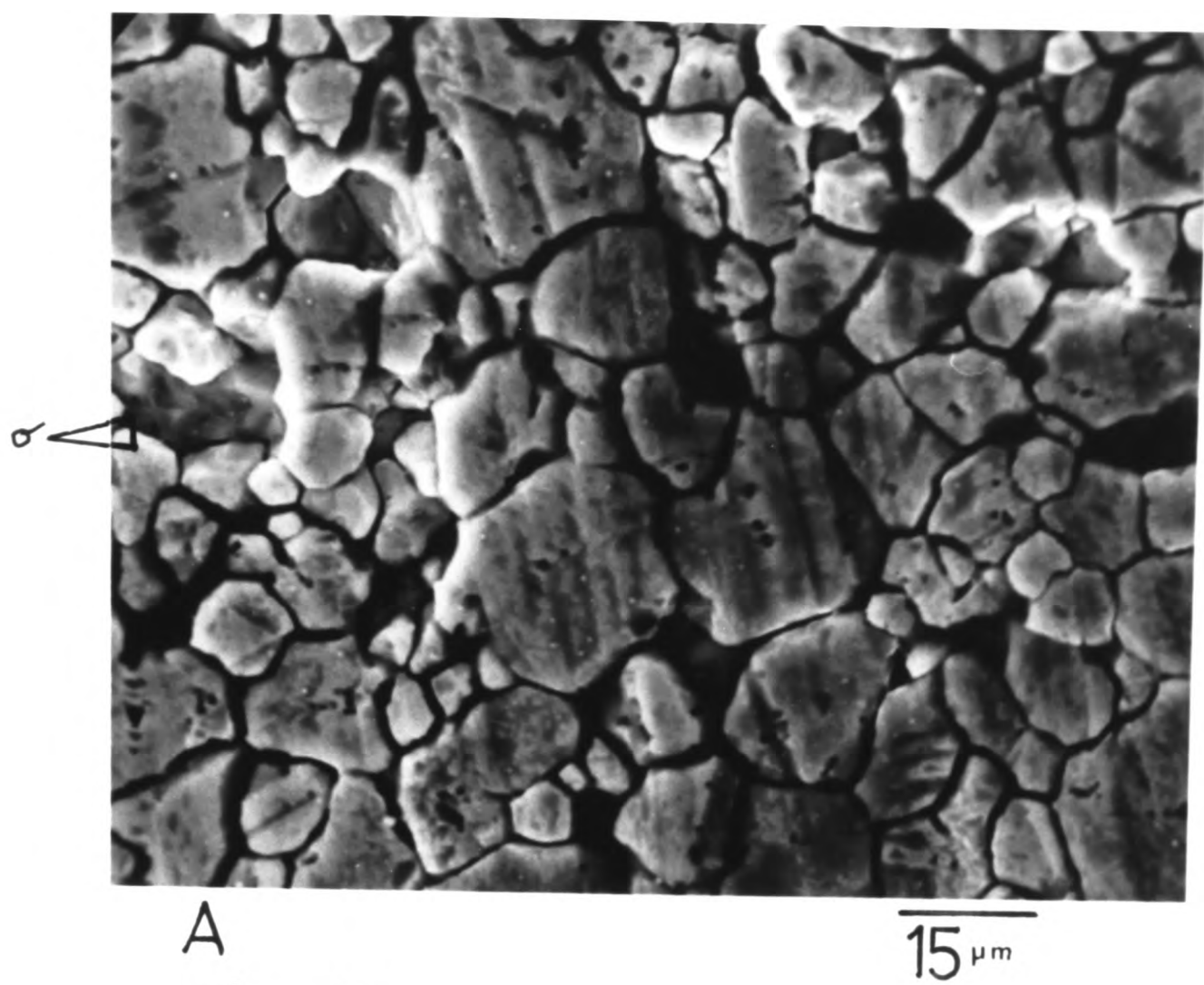


Figure 22.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). A peak stress of 50% of the yield stress with R = 0.6 and 600 second cycles were used. The test lasted 72 hours.



B' B

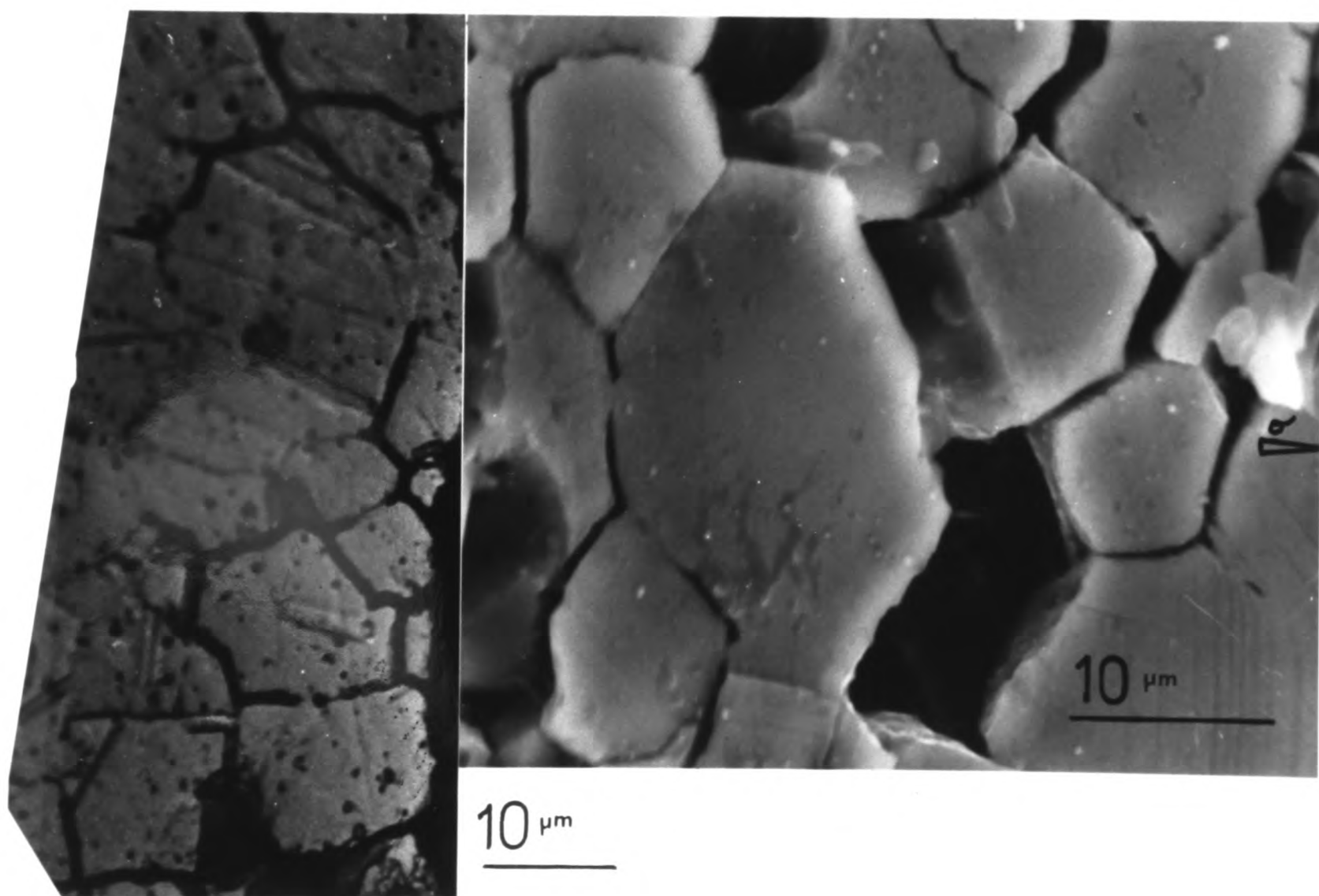
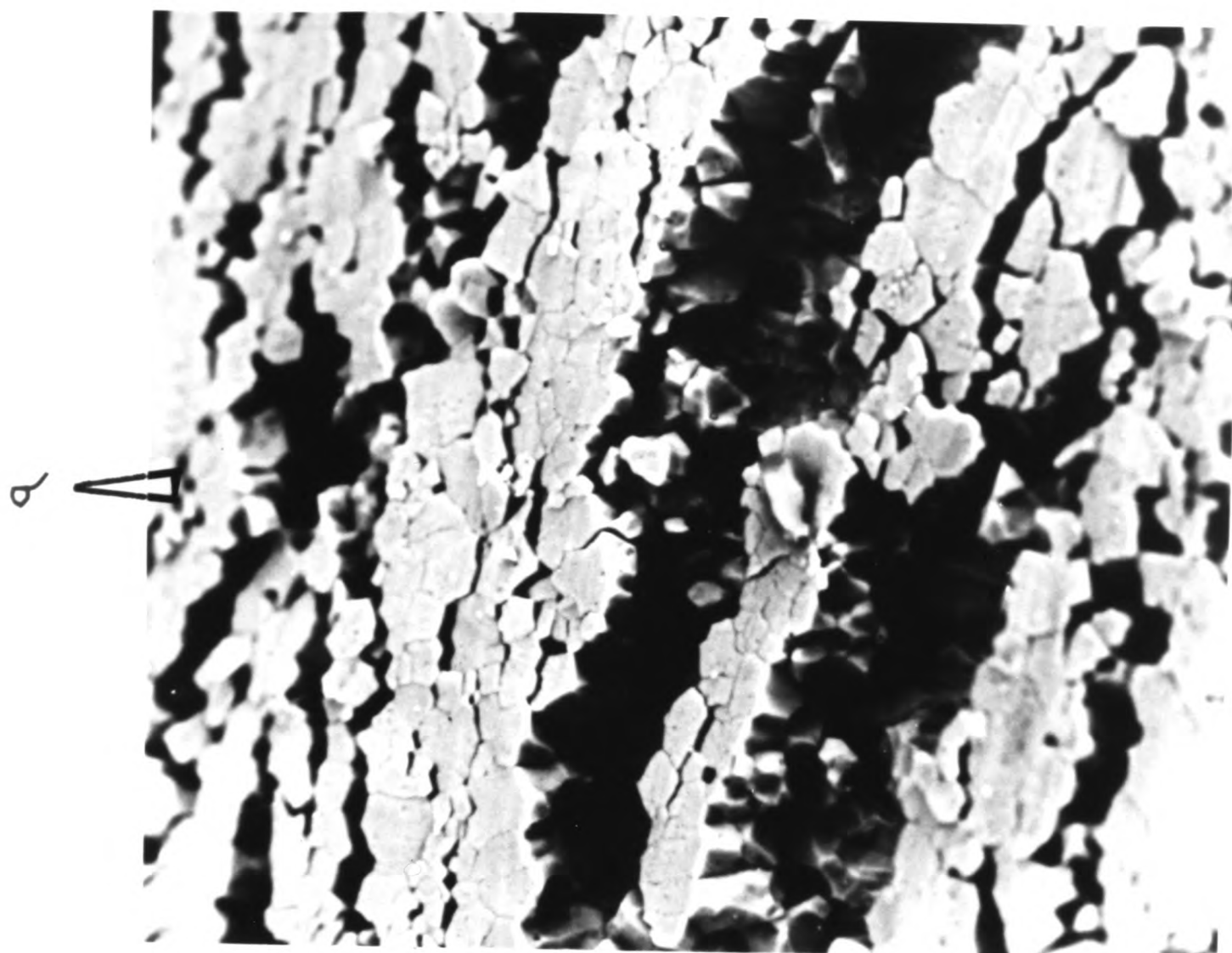


Figure 23.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). A peak stress of 50% of the yield stress with R = 0.5 and 600 second cycles were used. The test lasted 72 hours.



A
B

20 μm

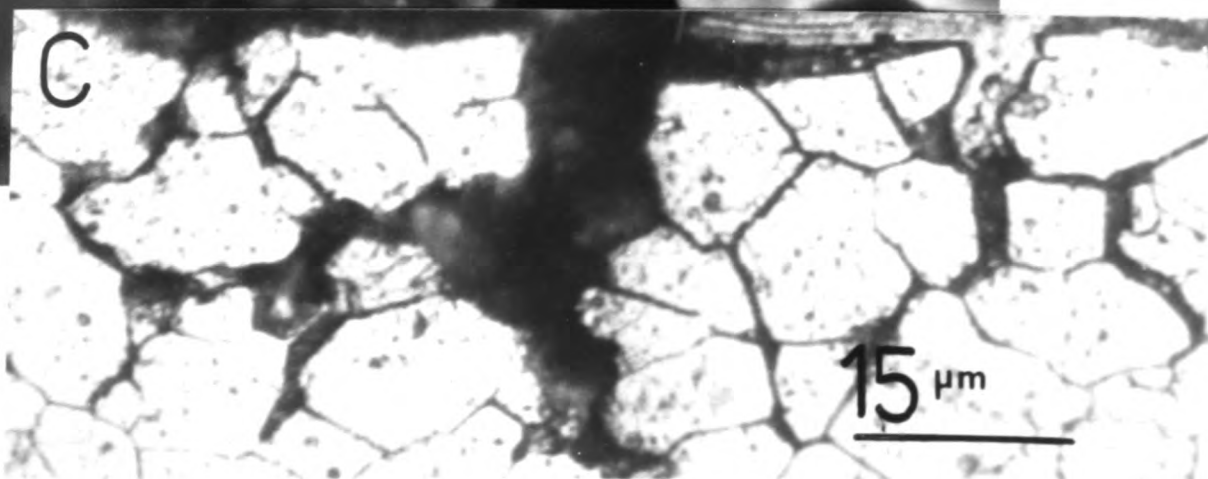
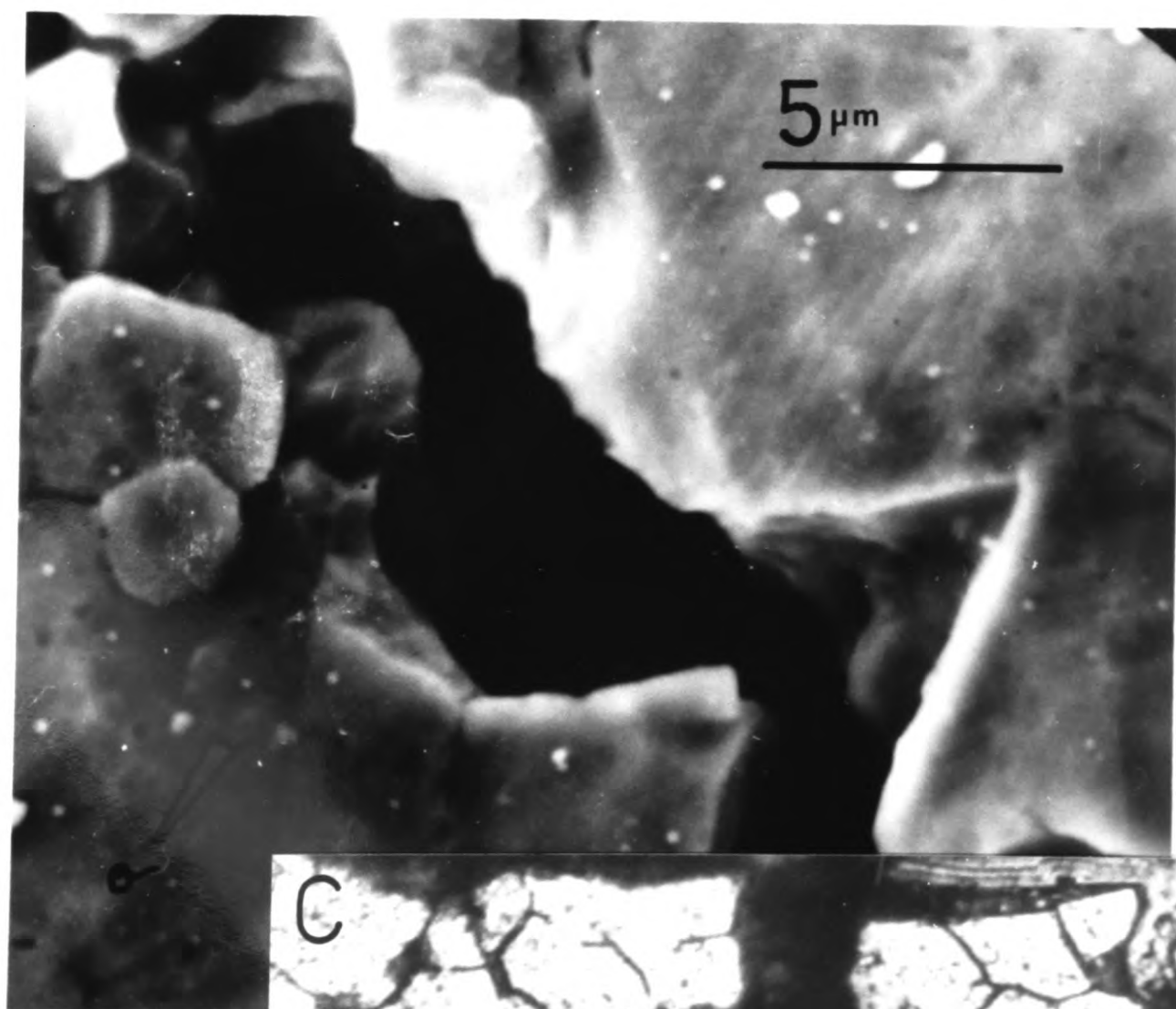
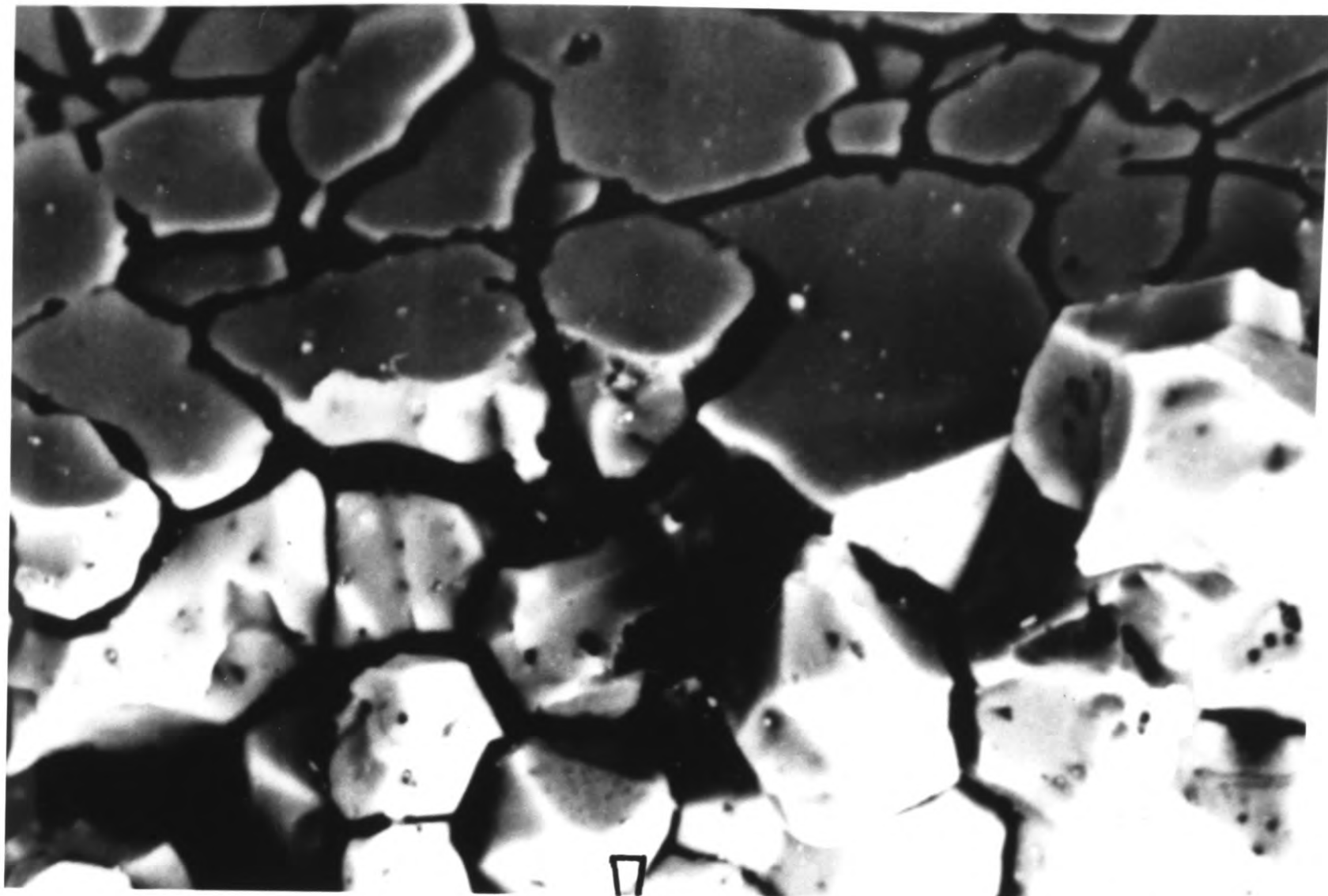


Figure 24.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). A peak stress of 80% of the yield stress with $R = 0.8$ and 600 second cycles were used.



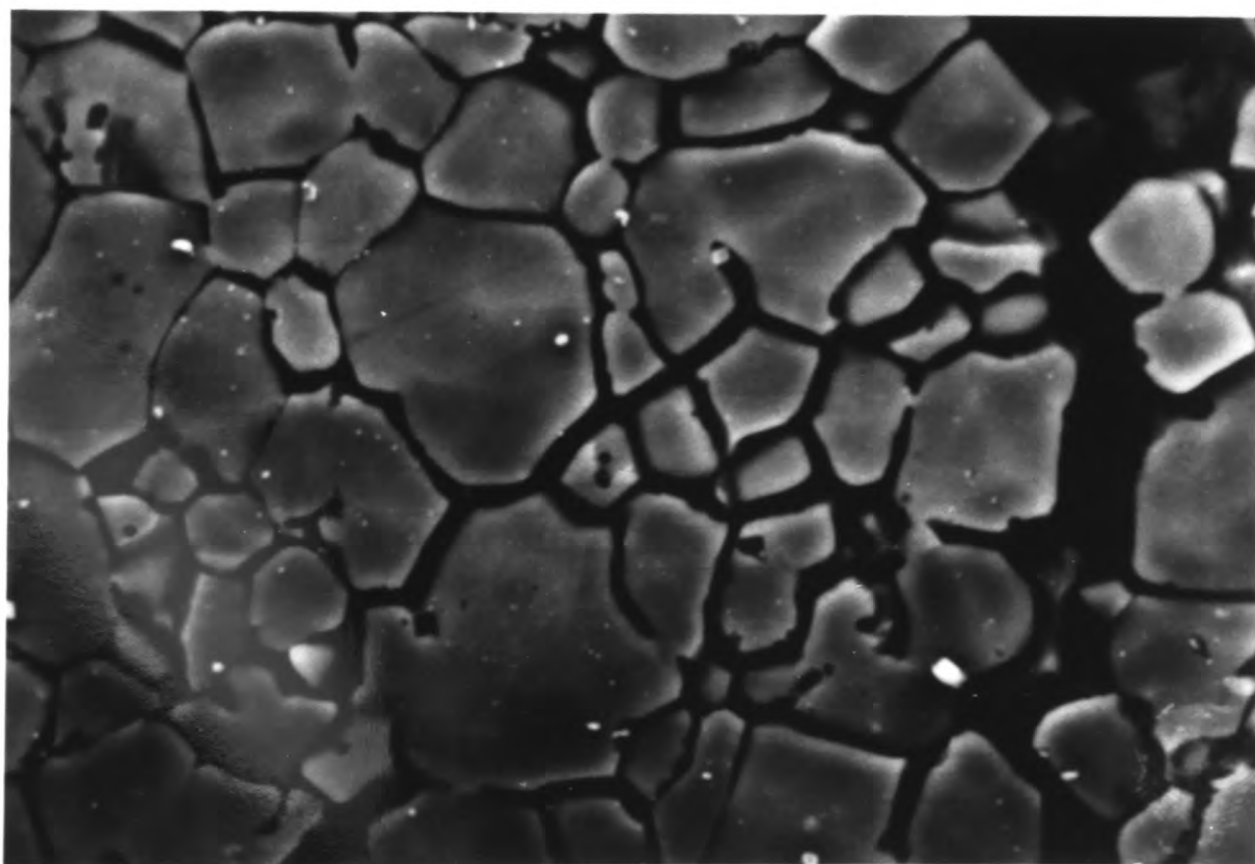
A



10 μm

B

20 μm



C

50 μm

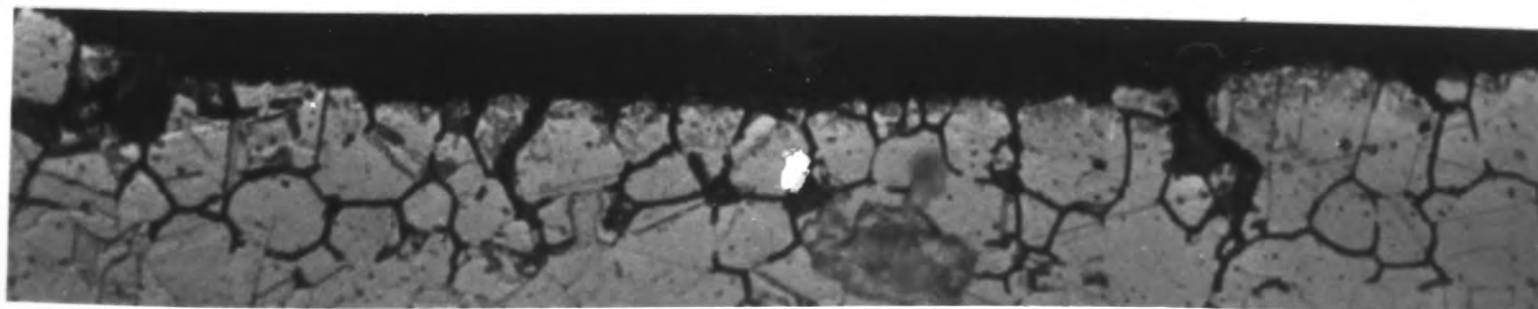
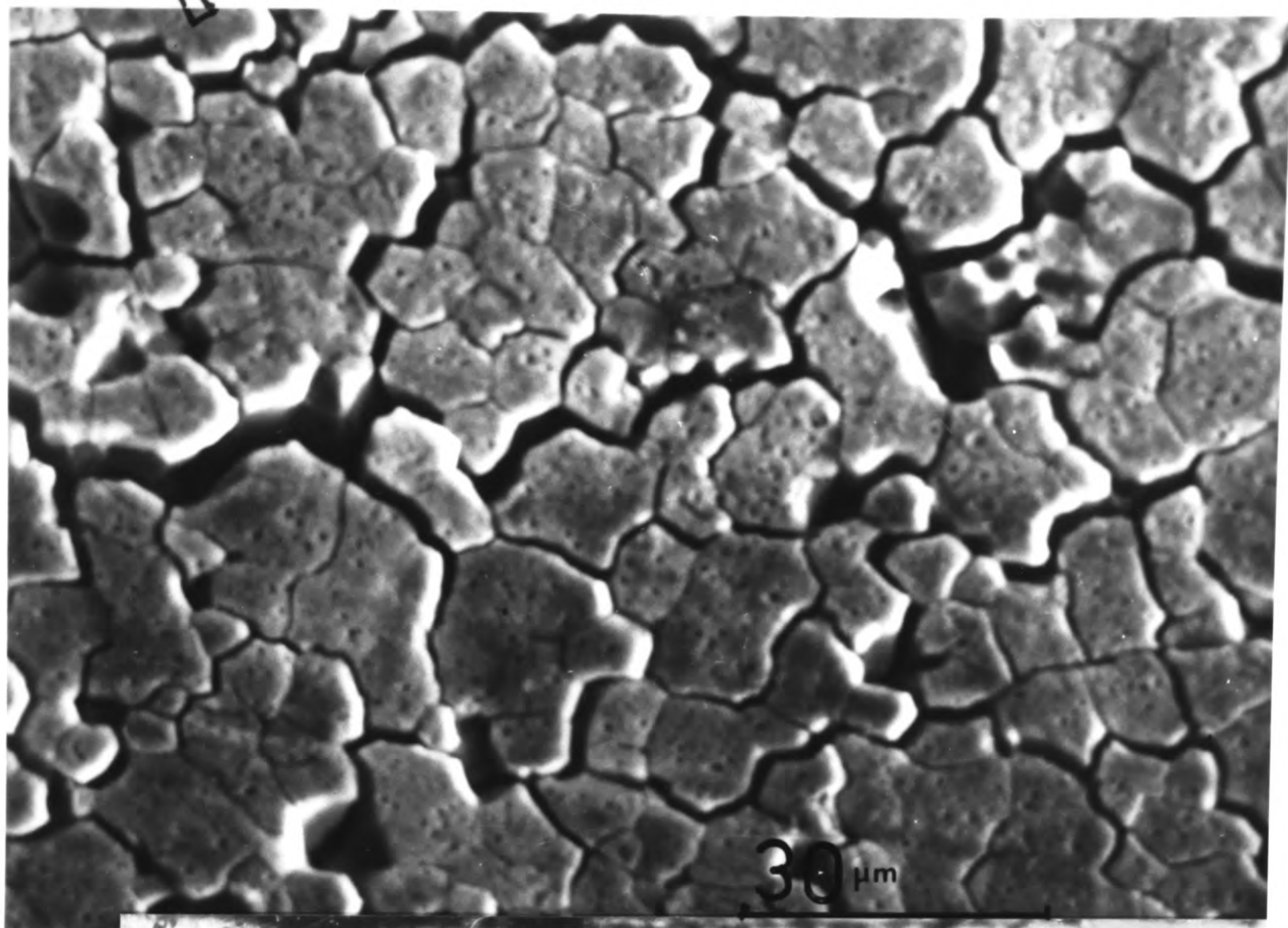


Figure 25.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). A peak stress of 60% of the yield stress with R = 0.5 and 600 second cycles were used. The test lasted 72 hours.



A

A'

B

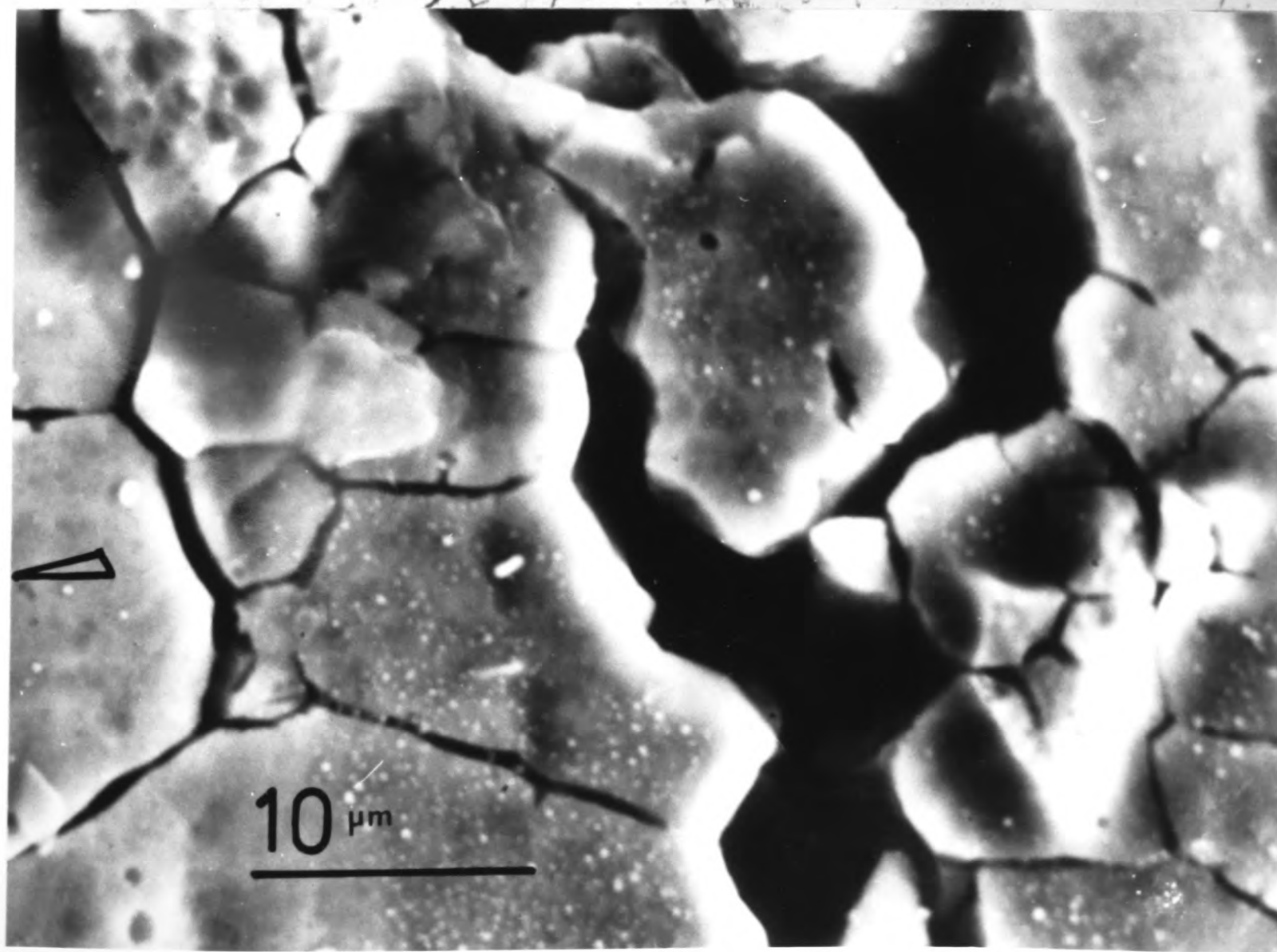
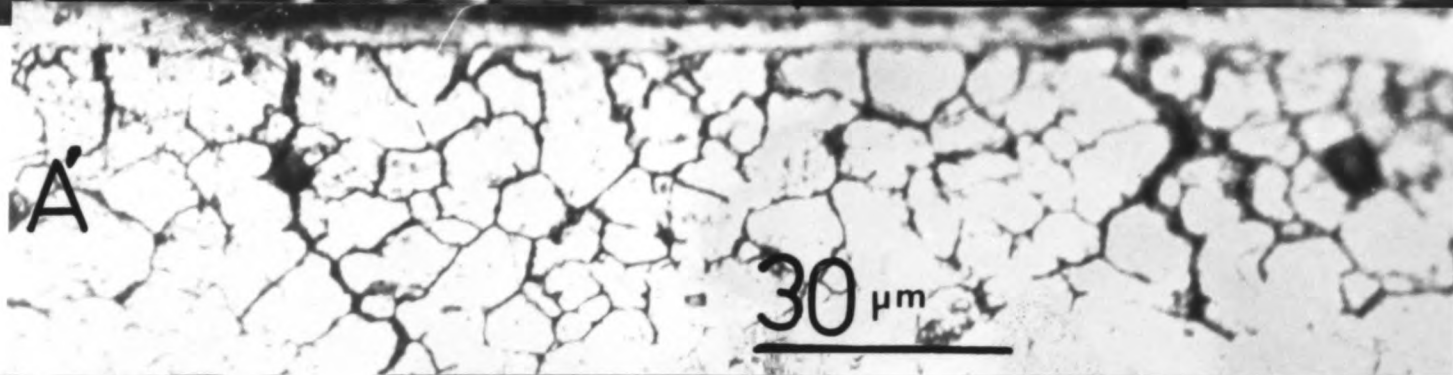
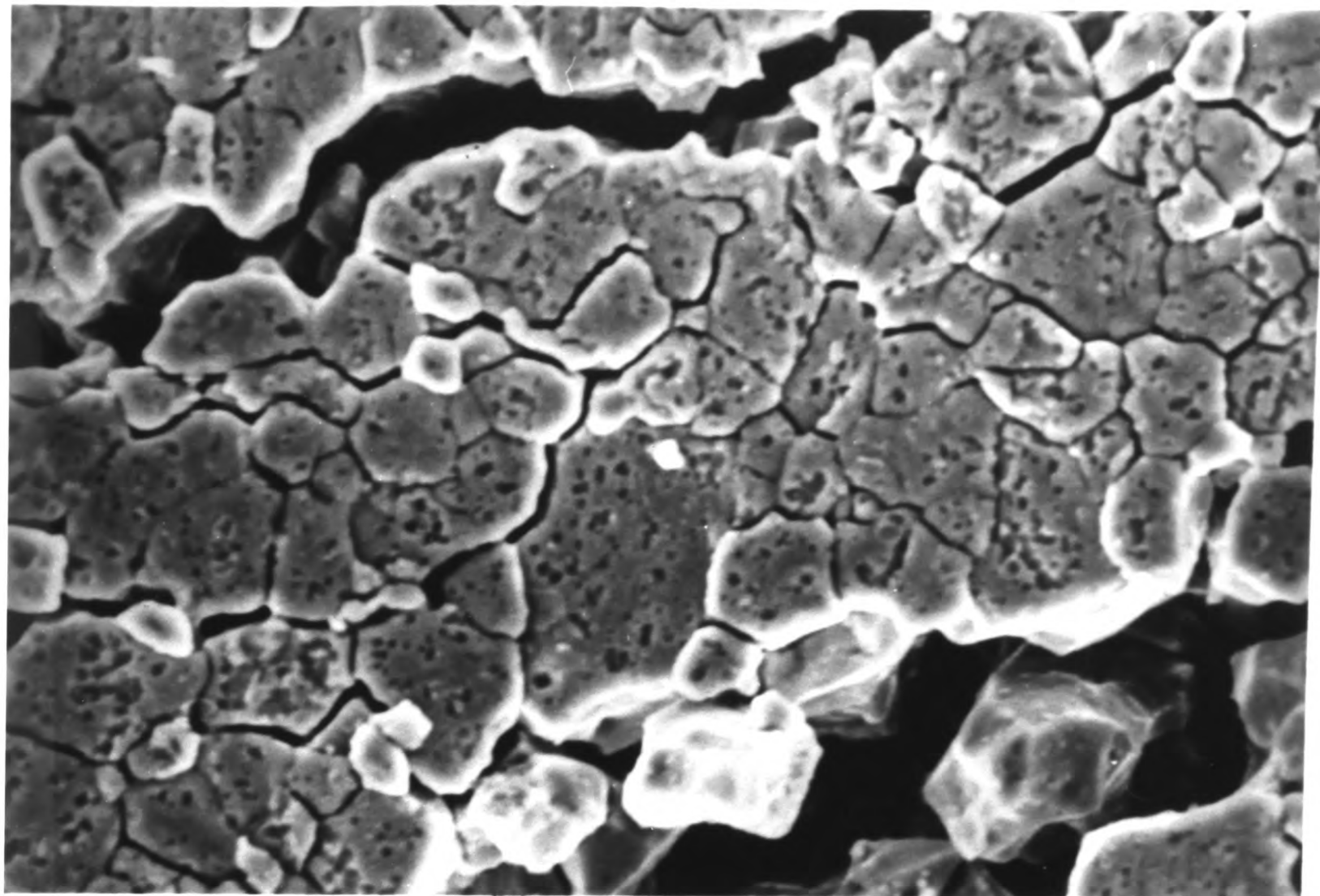


Figure 26.6

Surfaces of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -200mV (SCE). A peak stress of 70% of the yield stress with $R = 0.5$ and 600 second cycles were used. Tests lasted 72 hours.

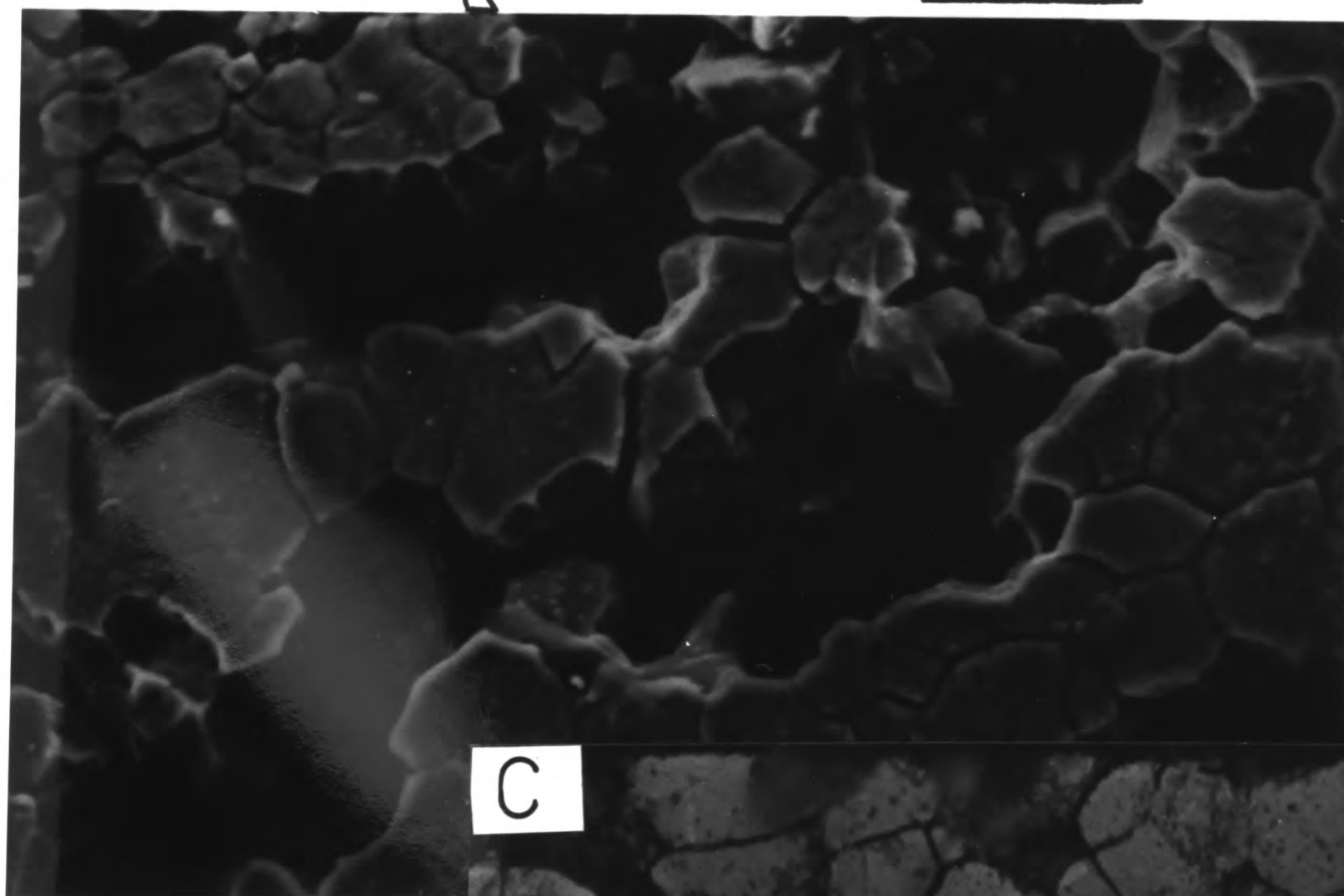


A

20 μm

B

20 μm



C

15 μm

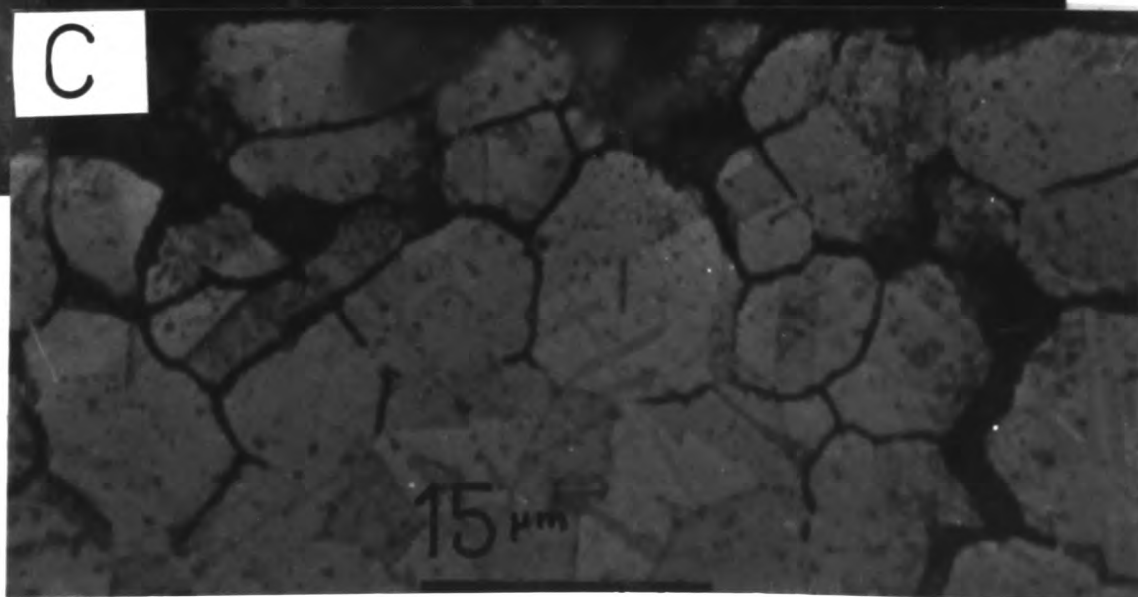
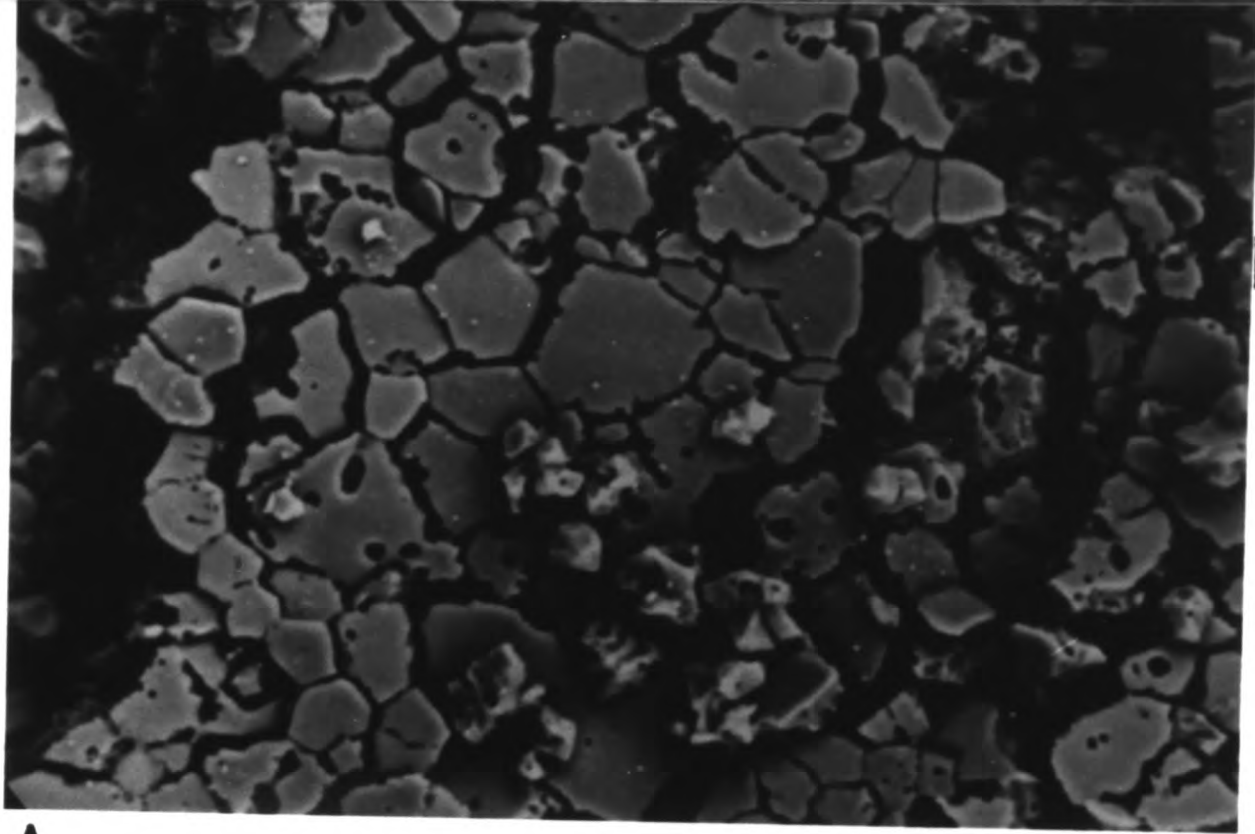
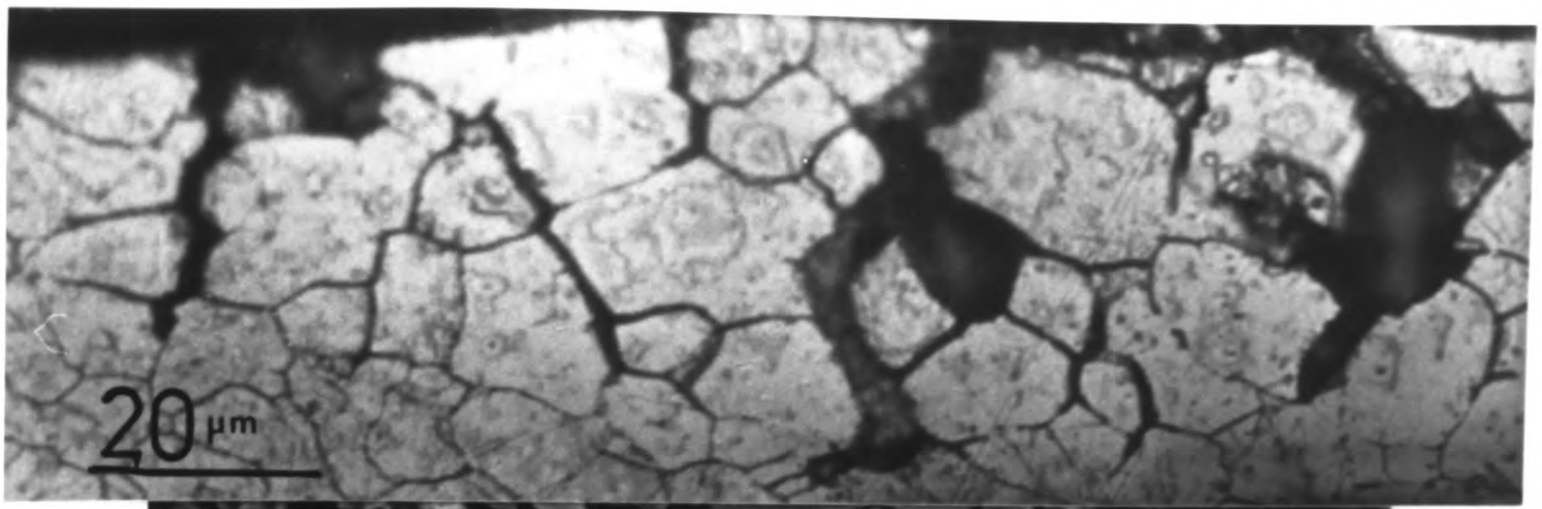


Figure 27.6

Surface of a sensitised specimen tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). A peak stress of 60% of the yield stress with R = 0.6 and 600 second cycles were used. The test lasted 72 hours.



20 μm
10 μm

B

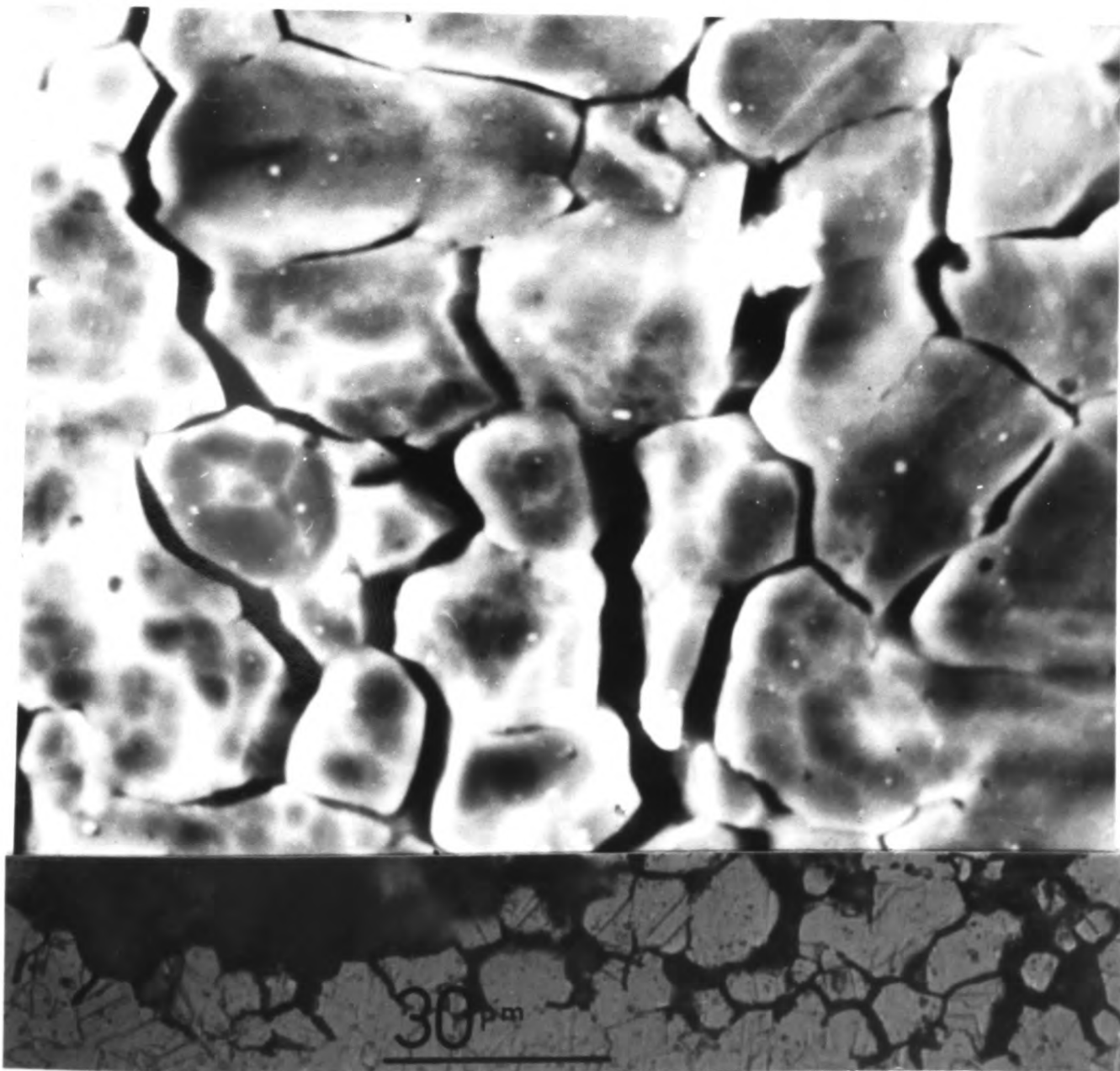
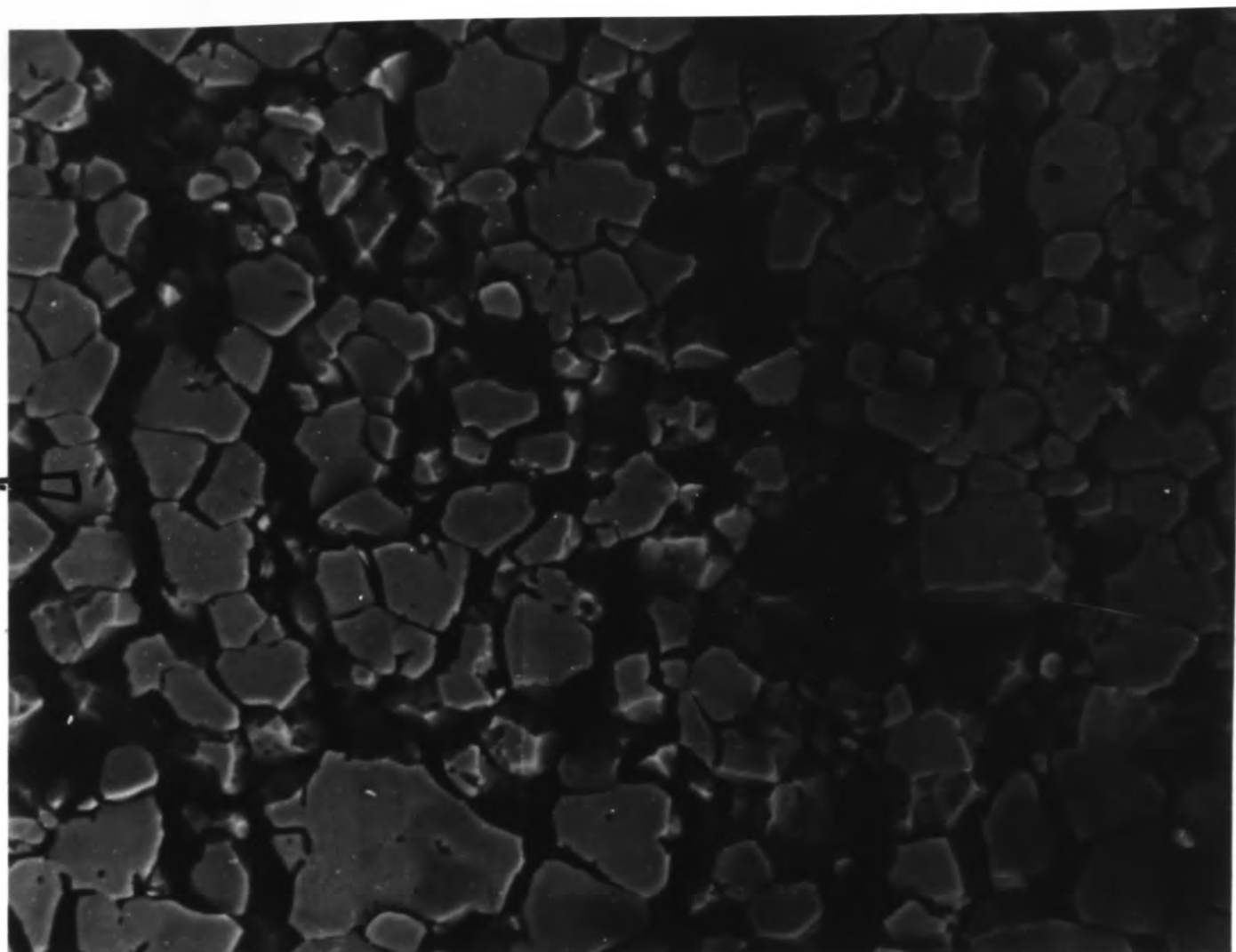


Figure 28.6

Surfaces of sensitised specimens tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -200mV (SCE). A peak stress of 80% of the yield stress with $R = 0.5$ and 600 second cycles were used. Tests lasted 72 hours.

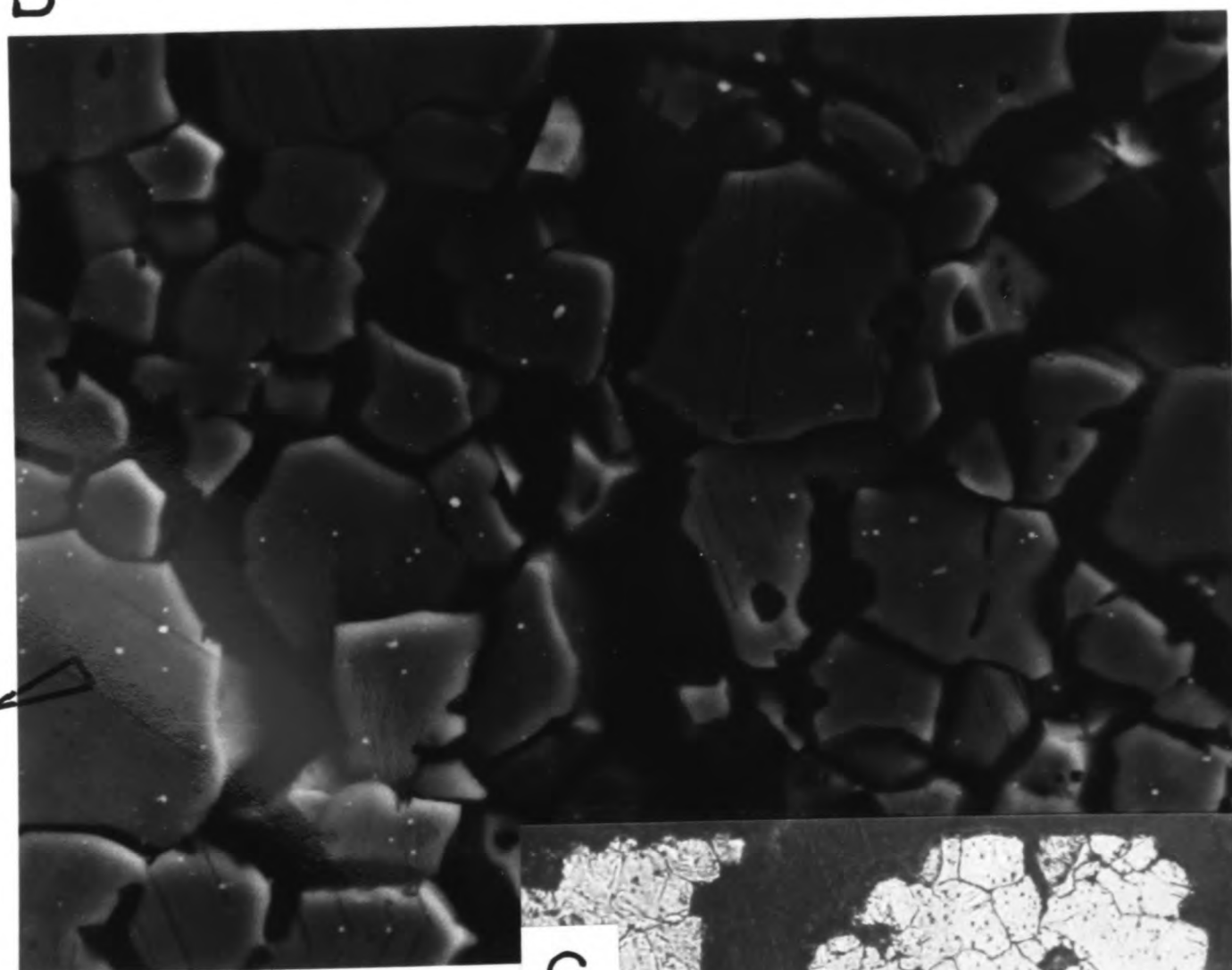


A

20 μm

B

10 μm



C

15 μm

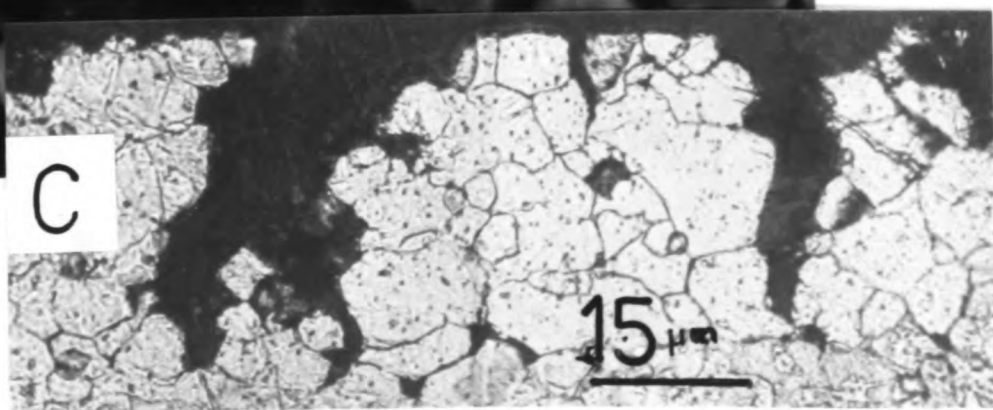
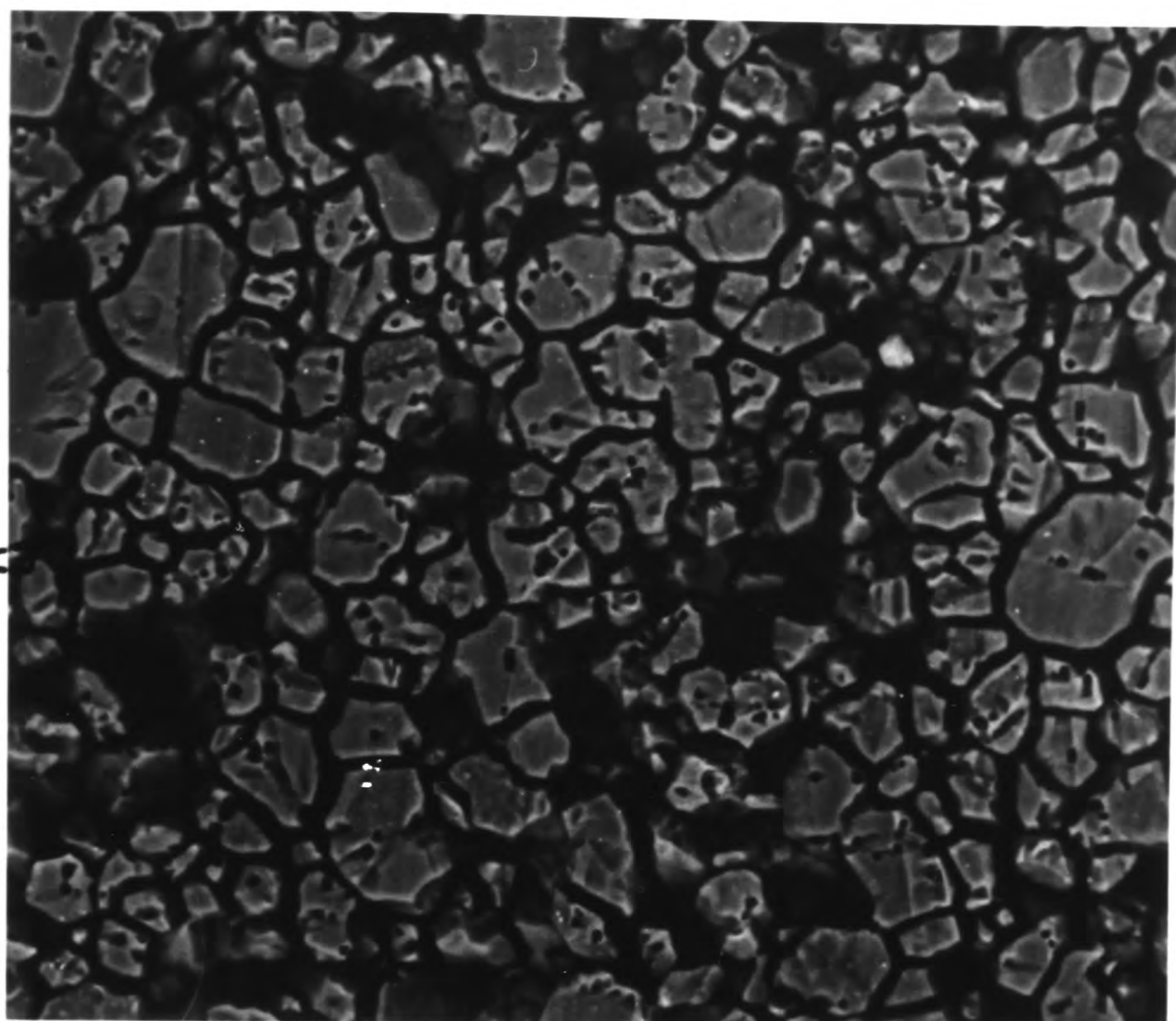


Figure 29.6

Surfaces of sensitised specimens tested under low frequency cyclic stress conditions in 1M HNO_3 at a potential of -200mV (SCE). A peak stress of 65% of the yield stress with $R = 0.4$ and 600 second cycles were used.

- A. 72 hours testing
- B. 120 hours testing

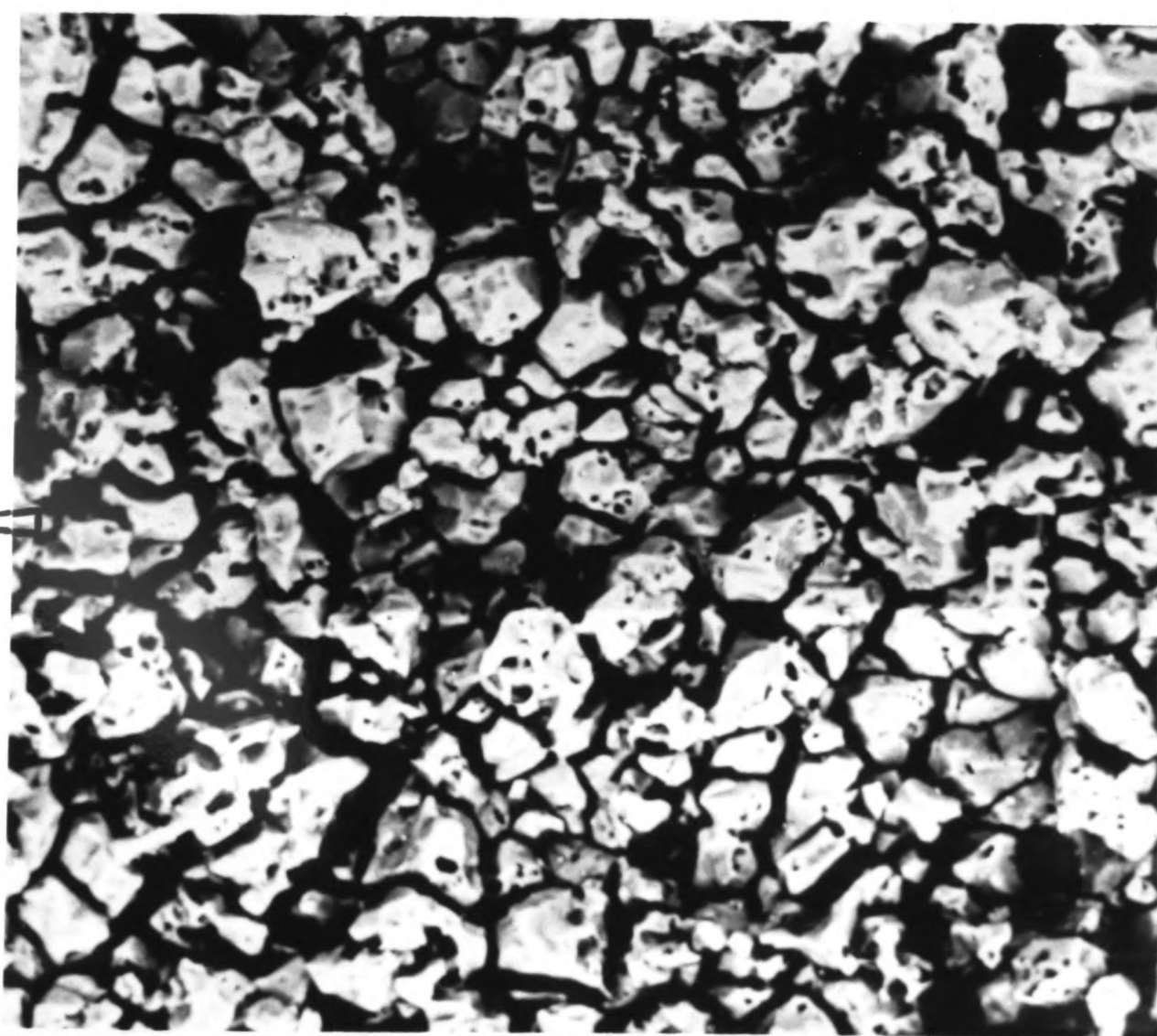


A

25 μm

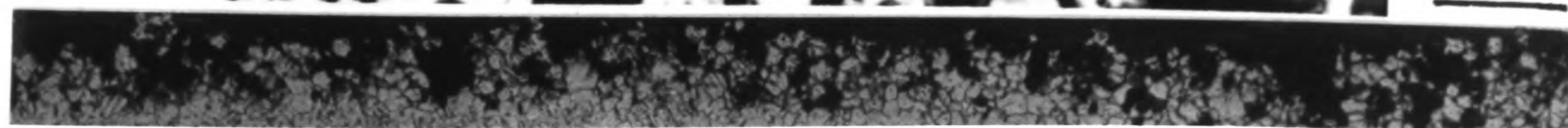
B

25 μm

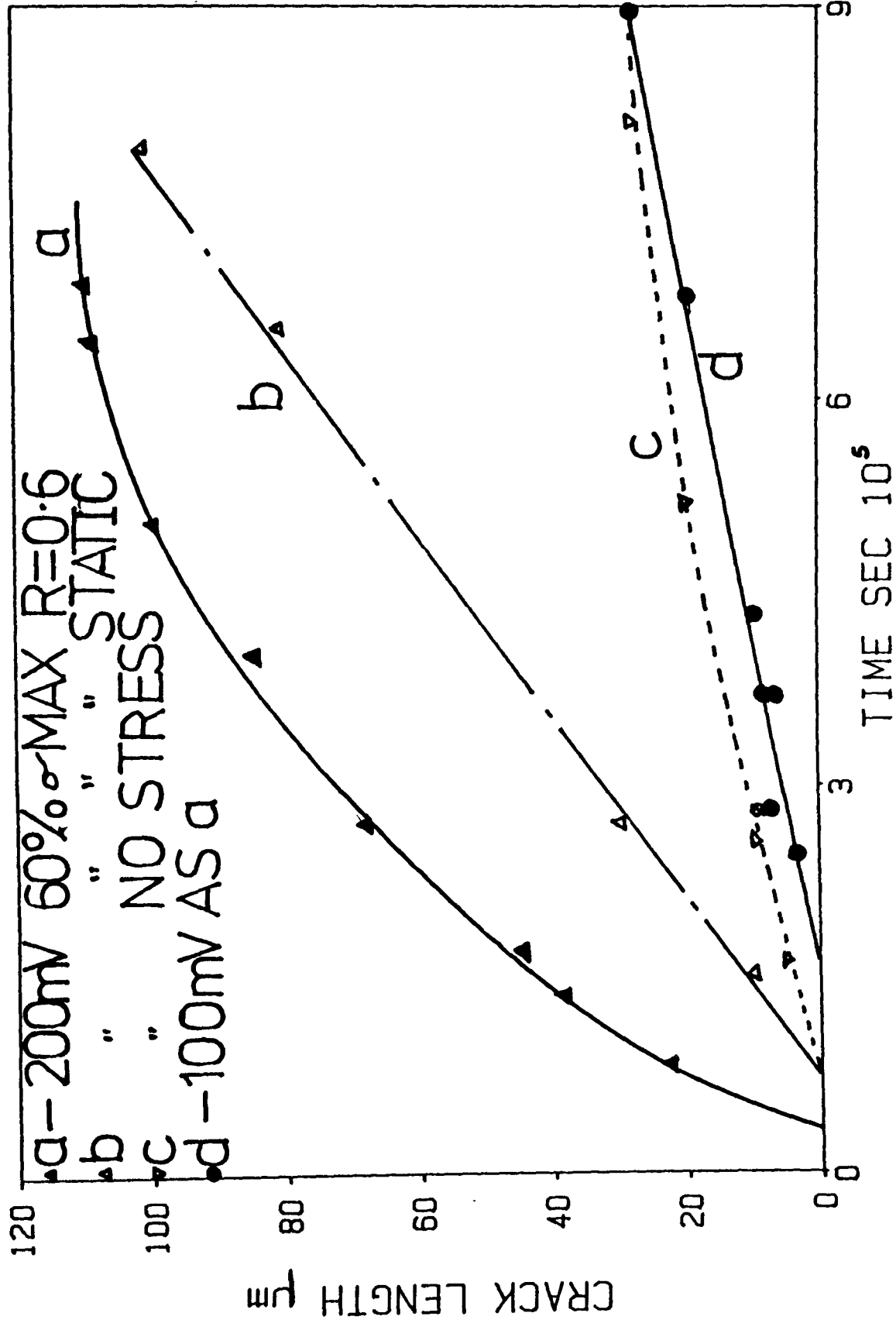


C

60 μm

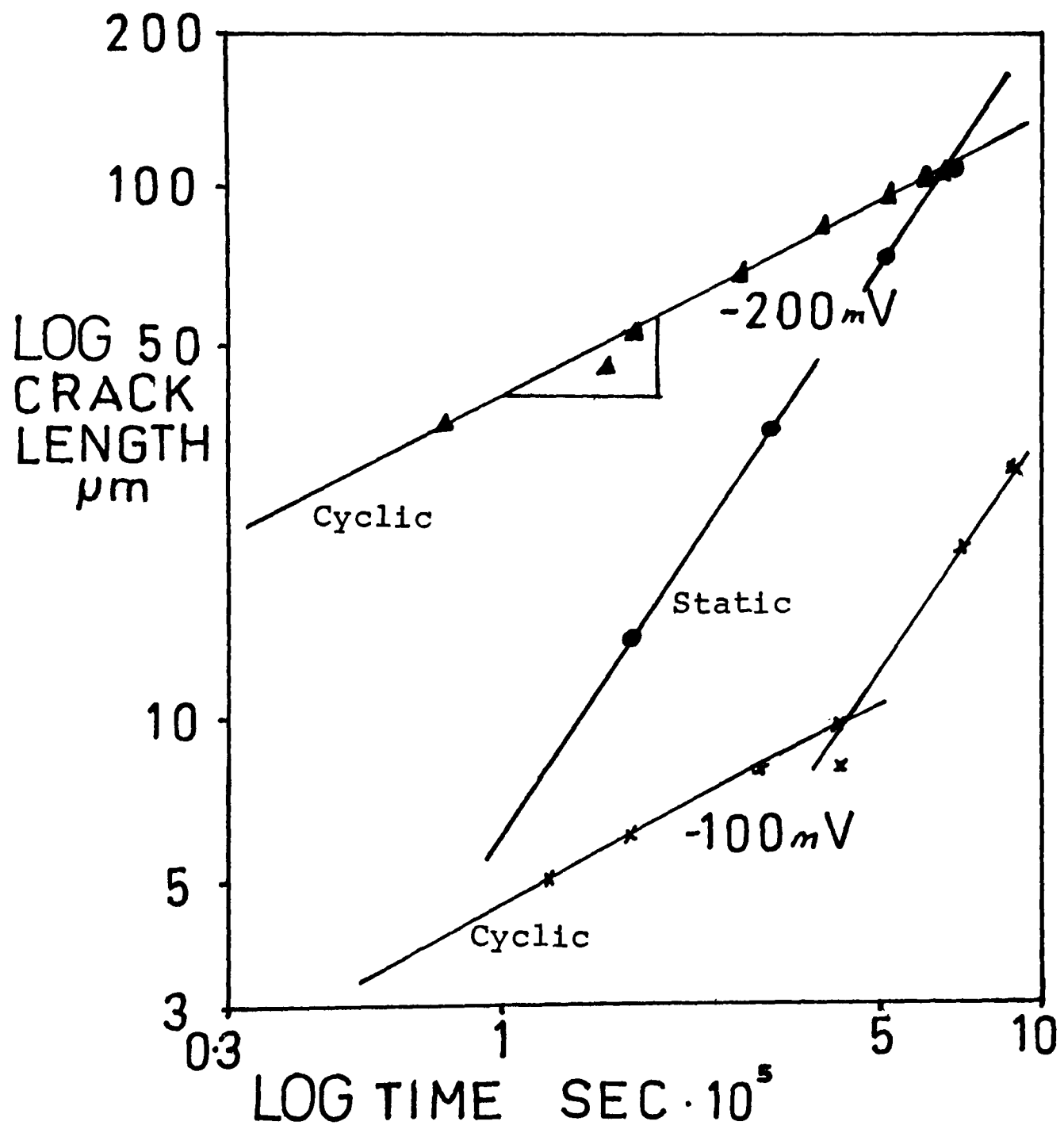


CRACK LENGTH/TIME PLOT FIG30.6



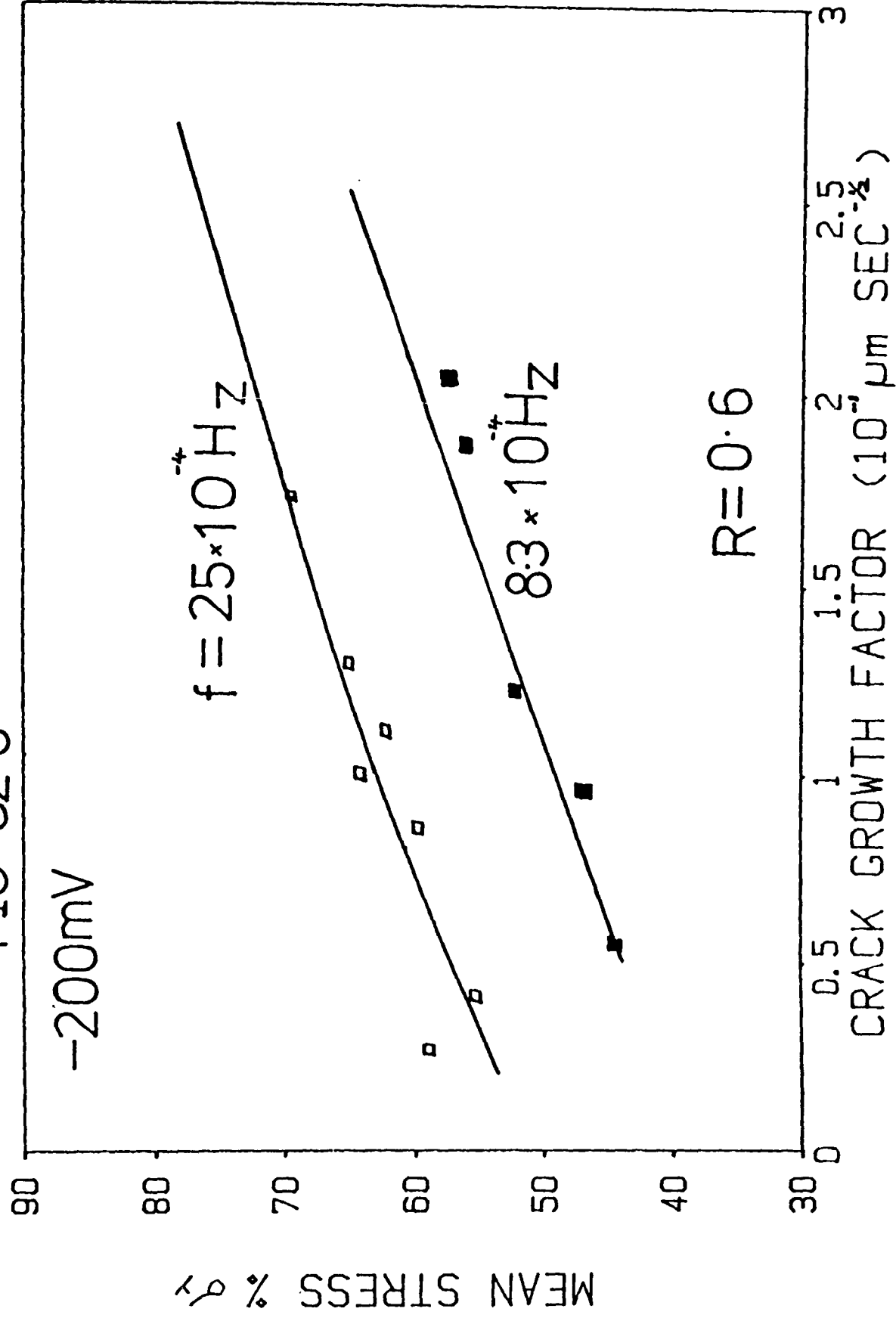
Influence of testing time on crack length, for statically loaded and cyclically loaded tests.

FIG 31.6



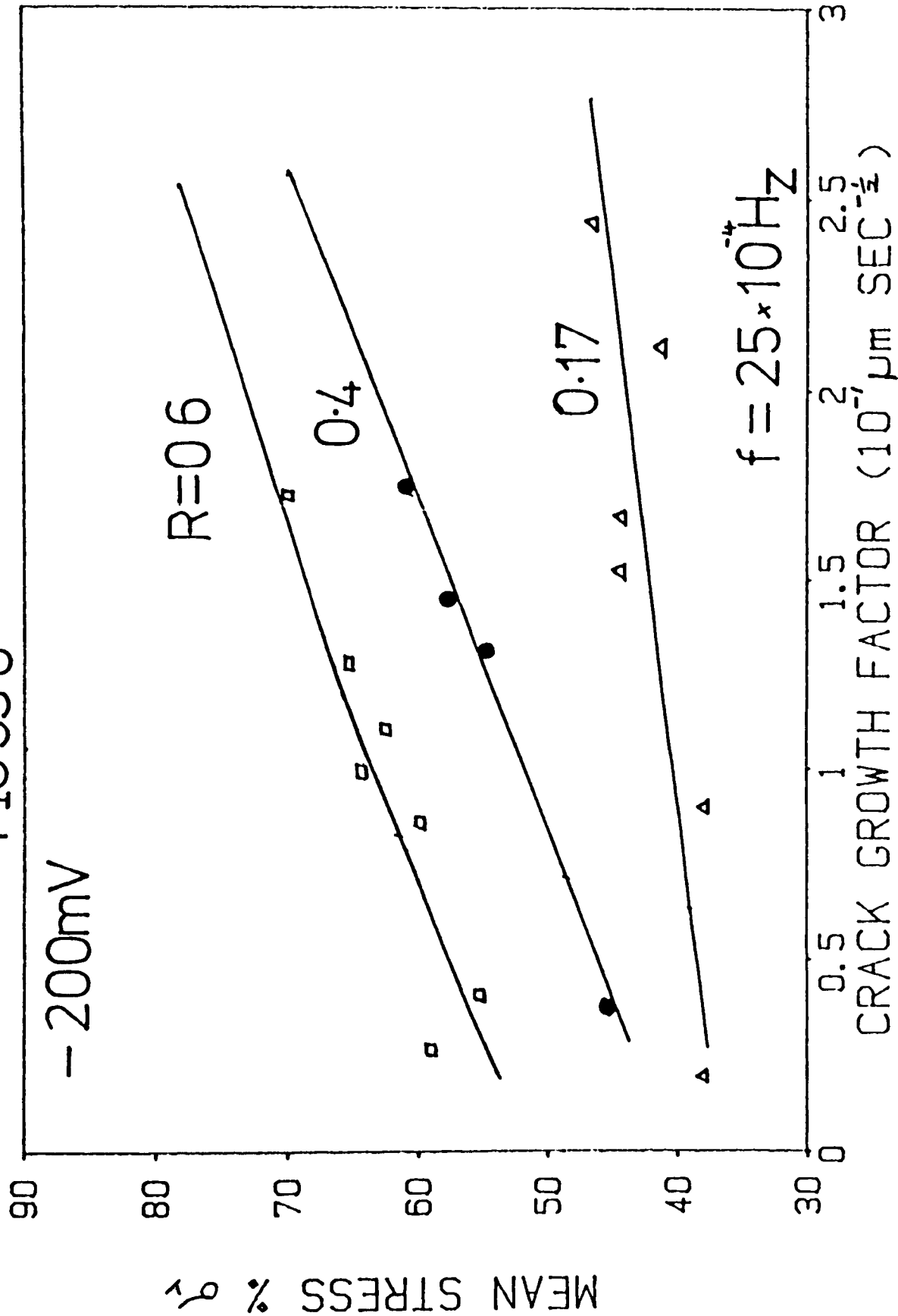
Log crack length against log time of test for cyclically loaded and statically loaded specimens.

FIG 32.6



Crack length / (time)^{0.5} for low frequency cyclic loading tests.

FIG 33.6



Crack length / (time)^{0.5} for low frequency cyclic loading tests.

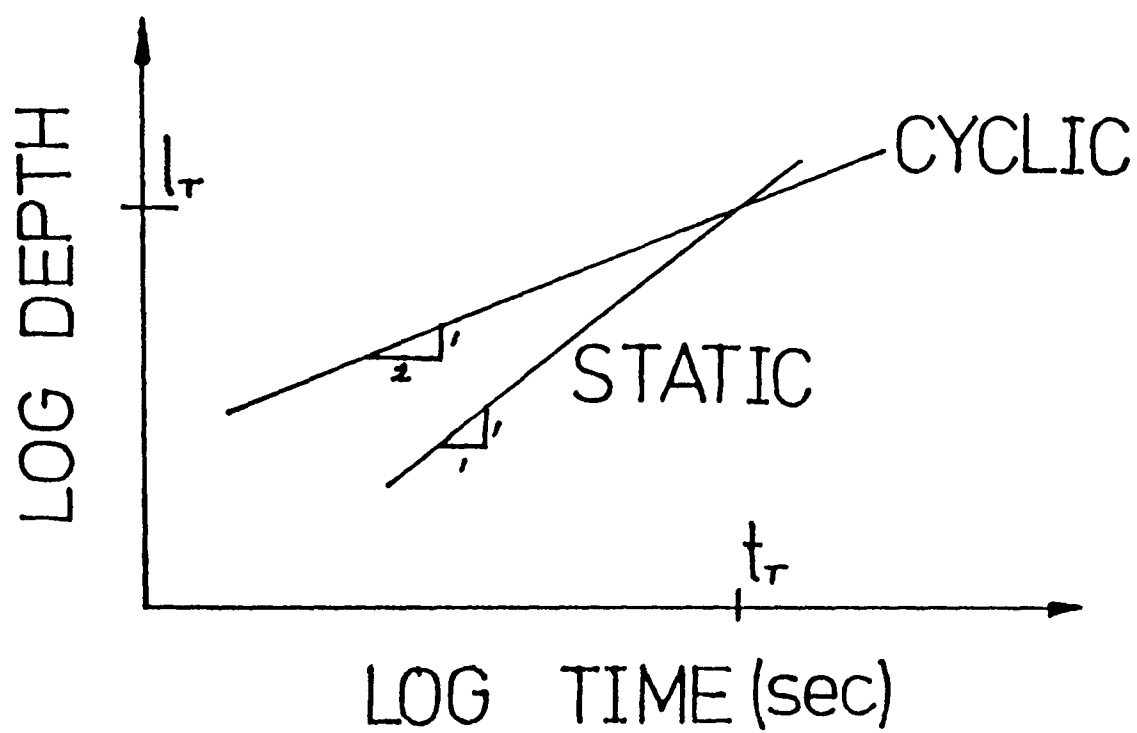
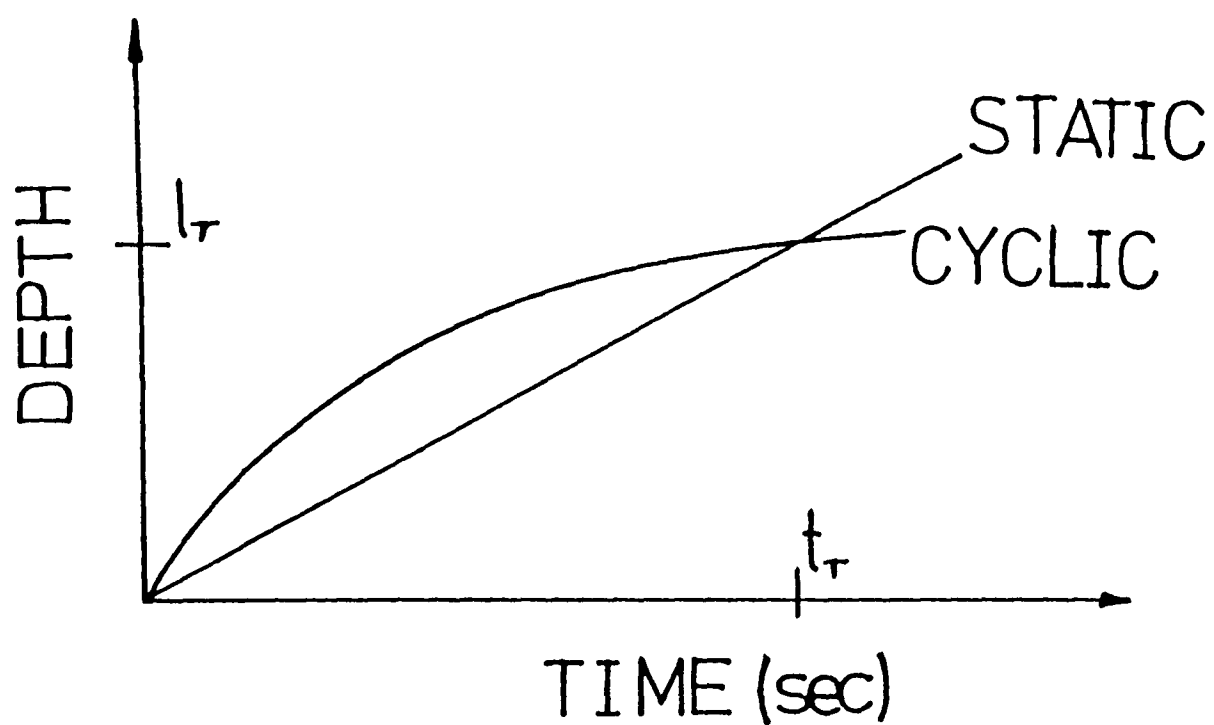
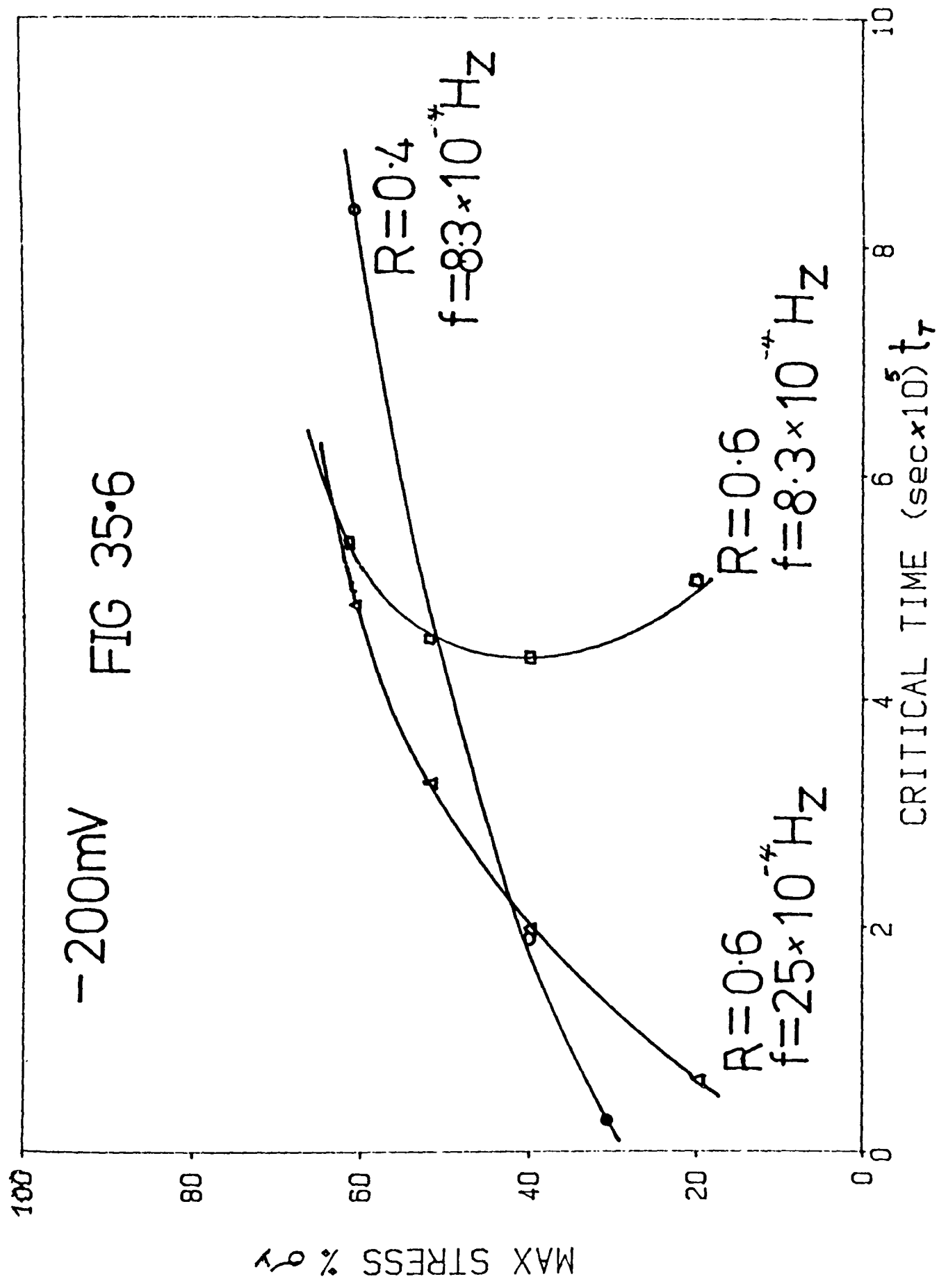
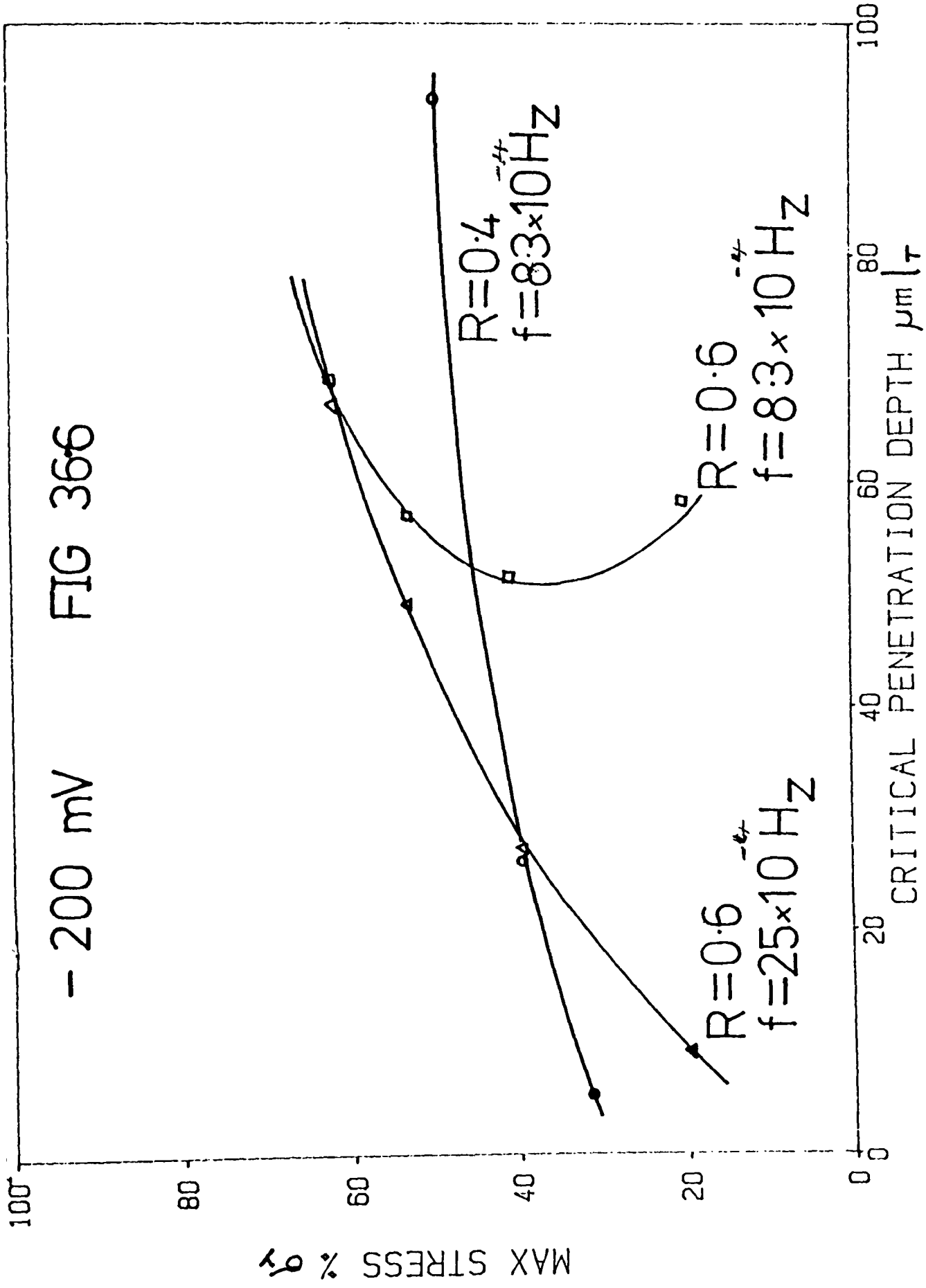


FIG 34.6

Schematic showing the method of extrapolation of data to find t_T , the time for the static loading crack length to exceed that for cyclic loading (for the same peak stress level). The crack length at this time is l_T .





Examples of current and mechanical
response during tests at -200 mV.

FIG 376

B

$i =$
 $\sim 0.1 \text{ mA/cm}^2/\text{cm}$

$\xi =$
 ~ 0.05
 $\%/\text{cm}$
 0.5 mm/sec

A

FIG 386

Examples of current and mechanical response
for tests carried out at -100 mV

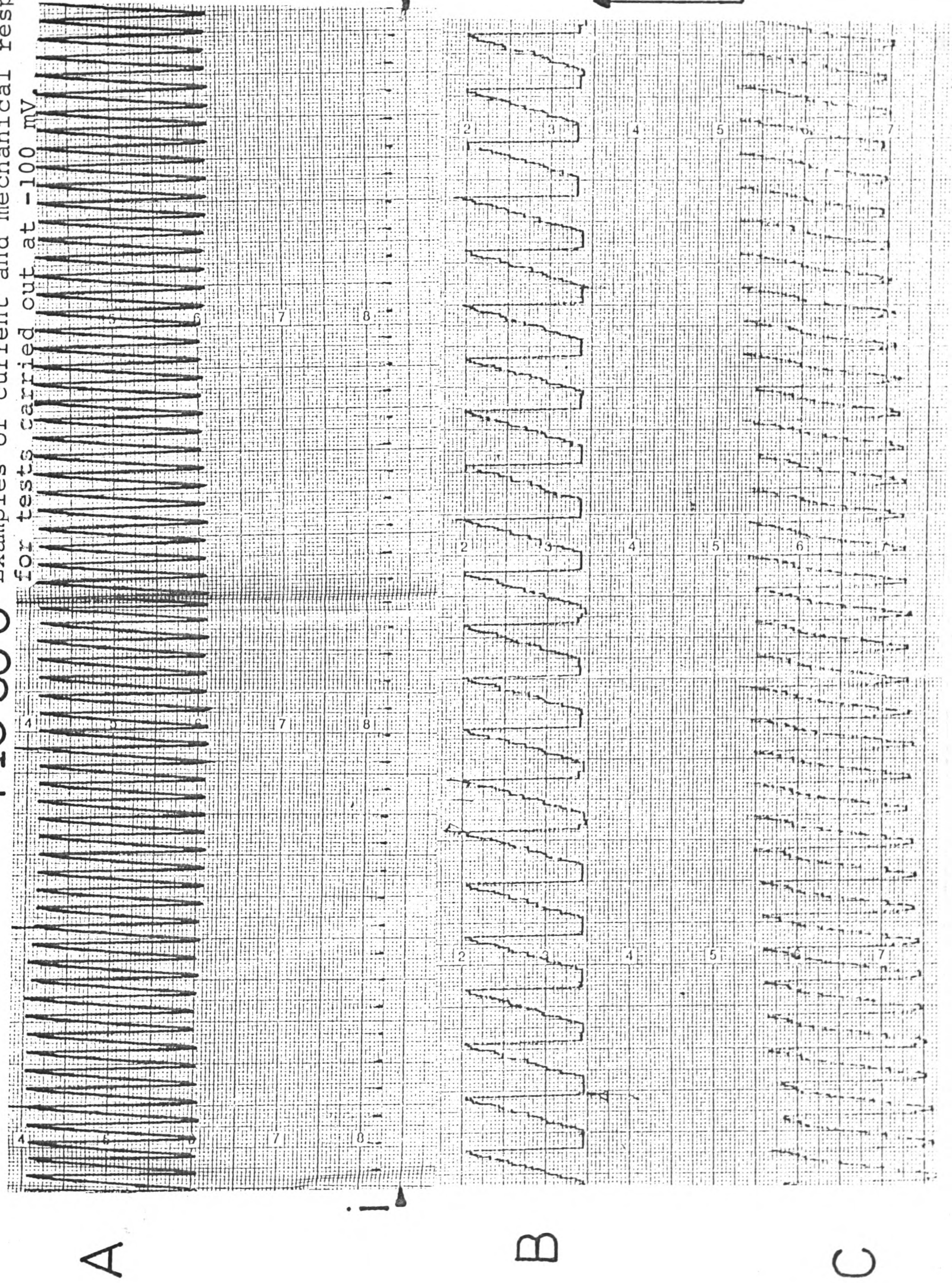
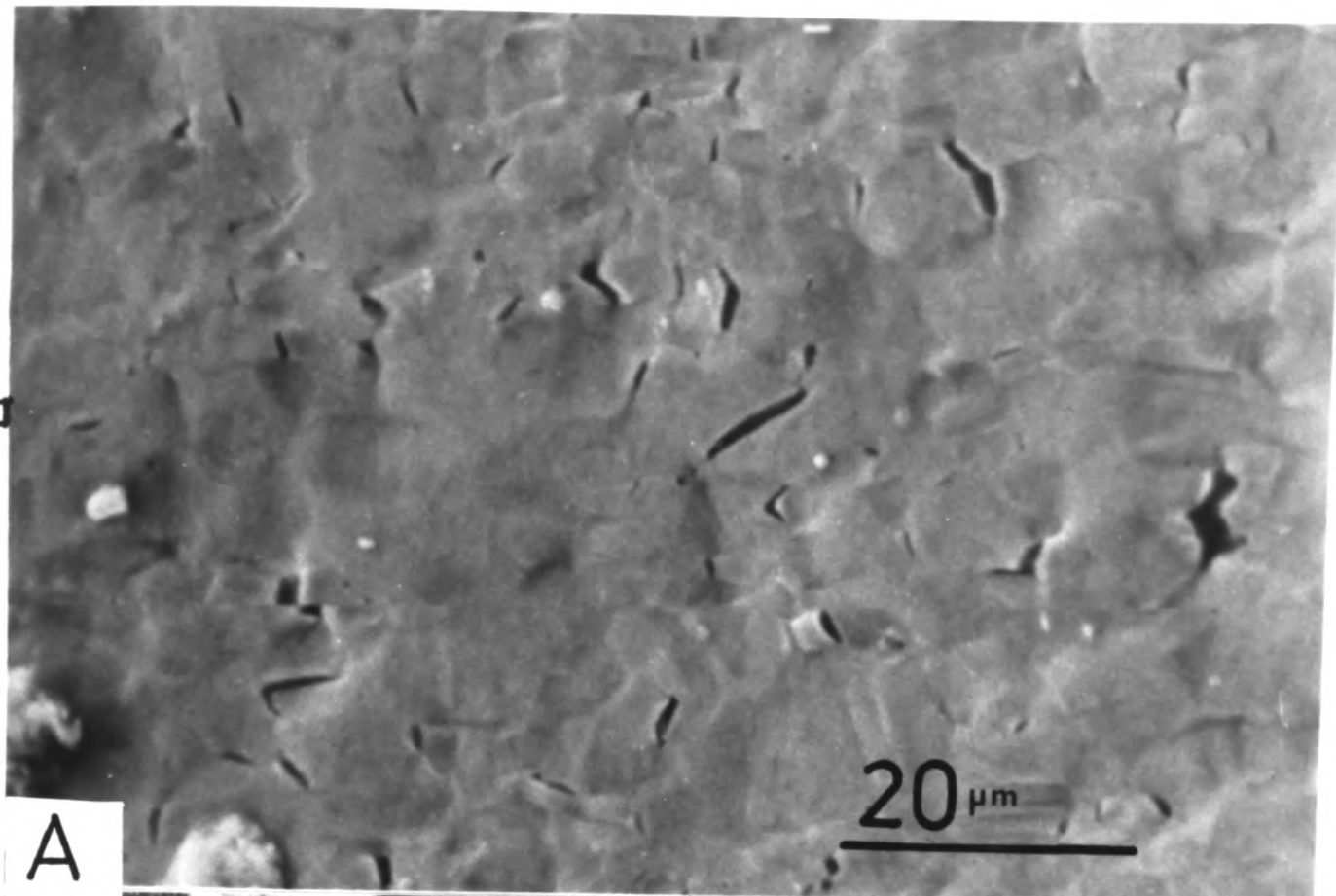


Figure 39.6
SEM micrographs of surfaces after static loading in HNO_3 at -100 mV (SCE)

- A and B. 110% yield stress for 24 hours
- C. 130% yield stress for 10 hours

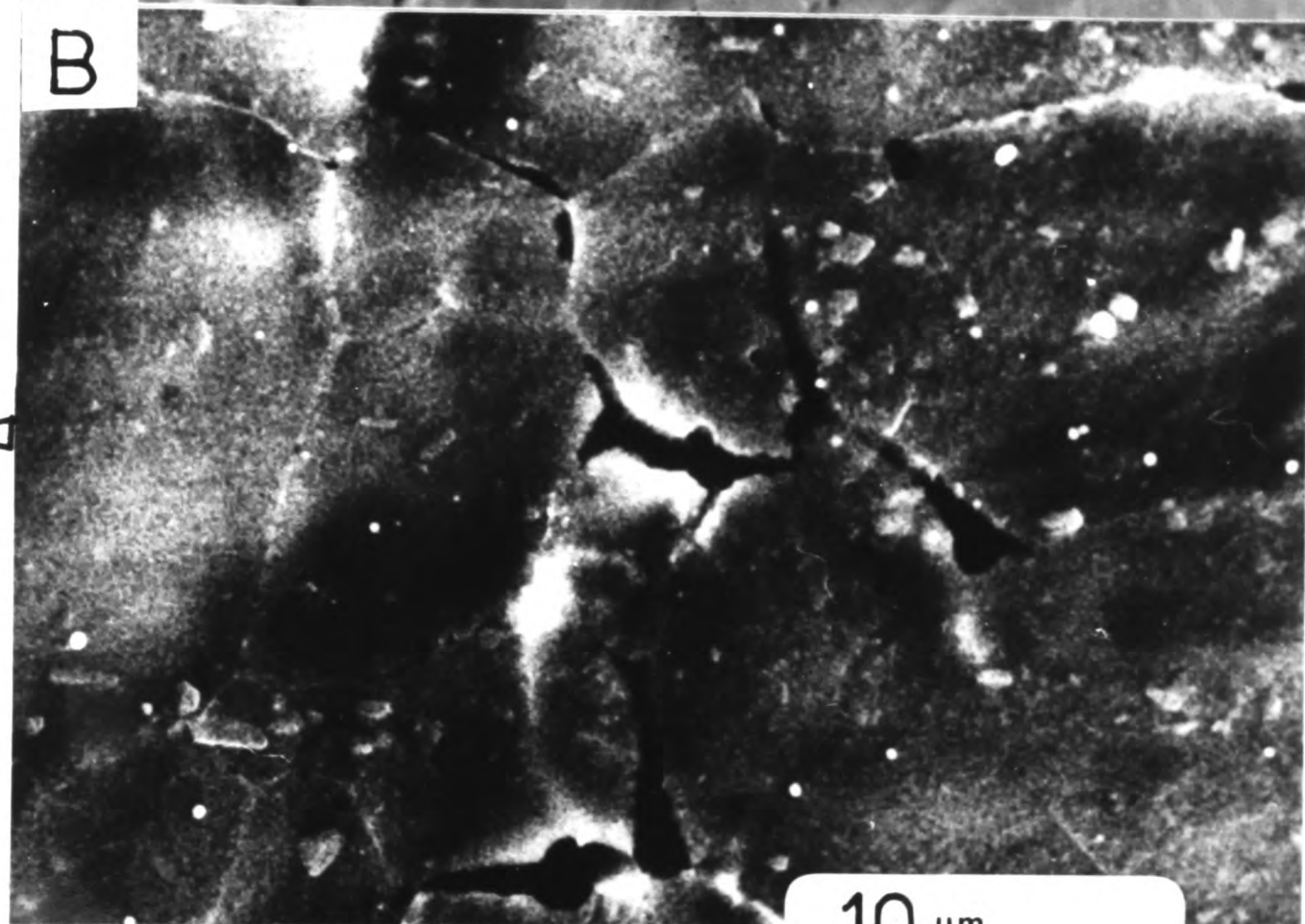
○△



A

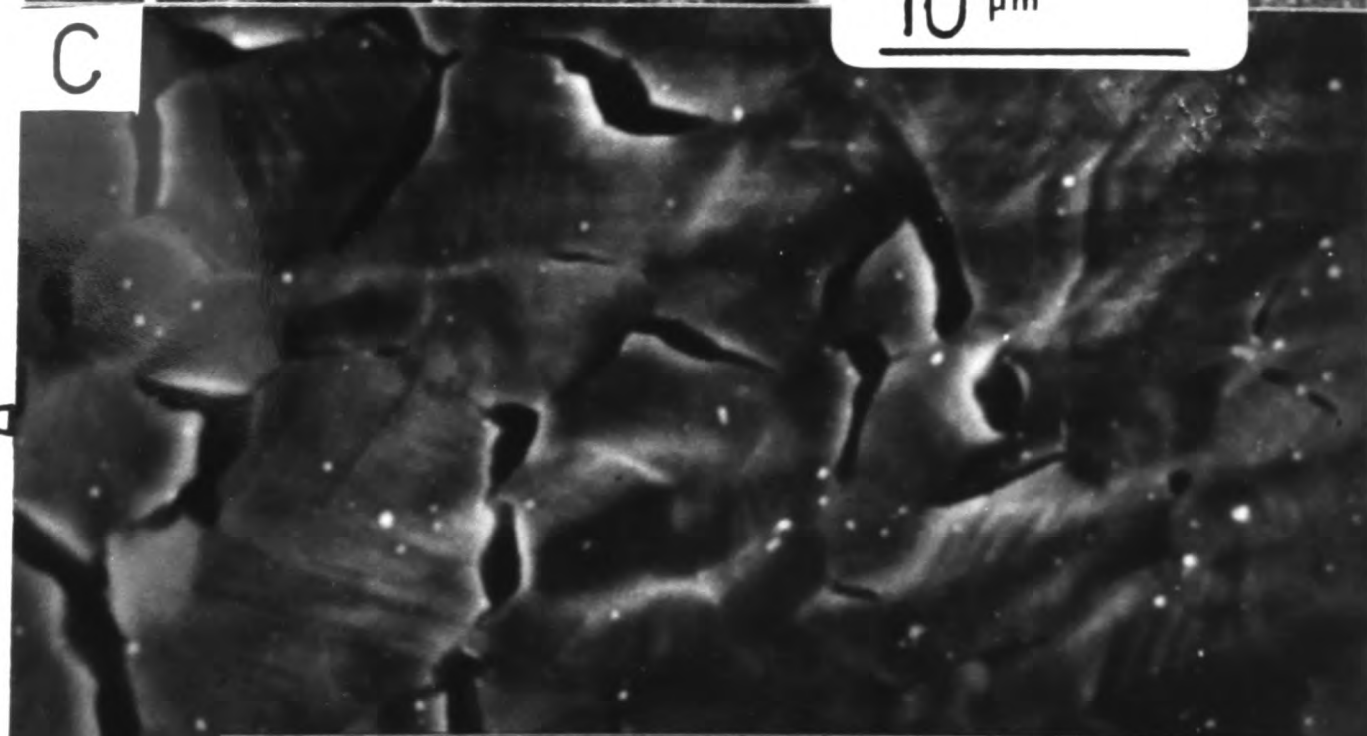
B

○△



C

○△



C'

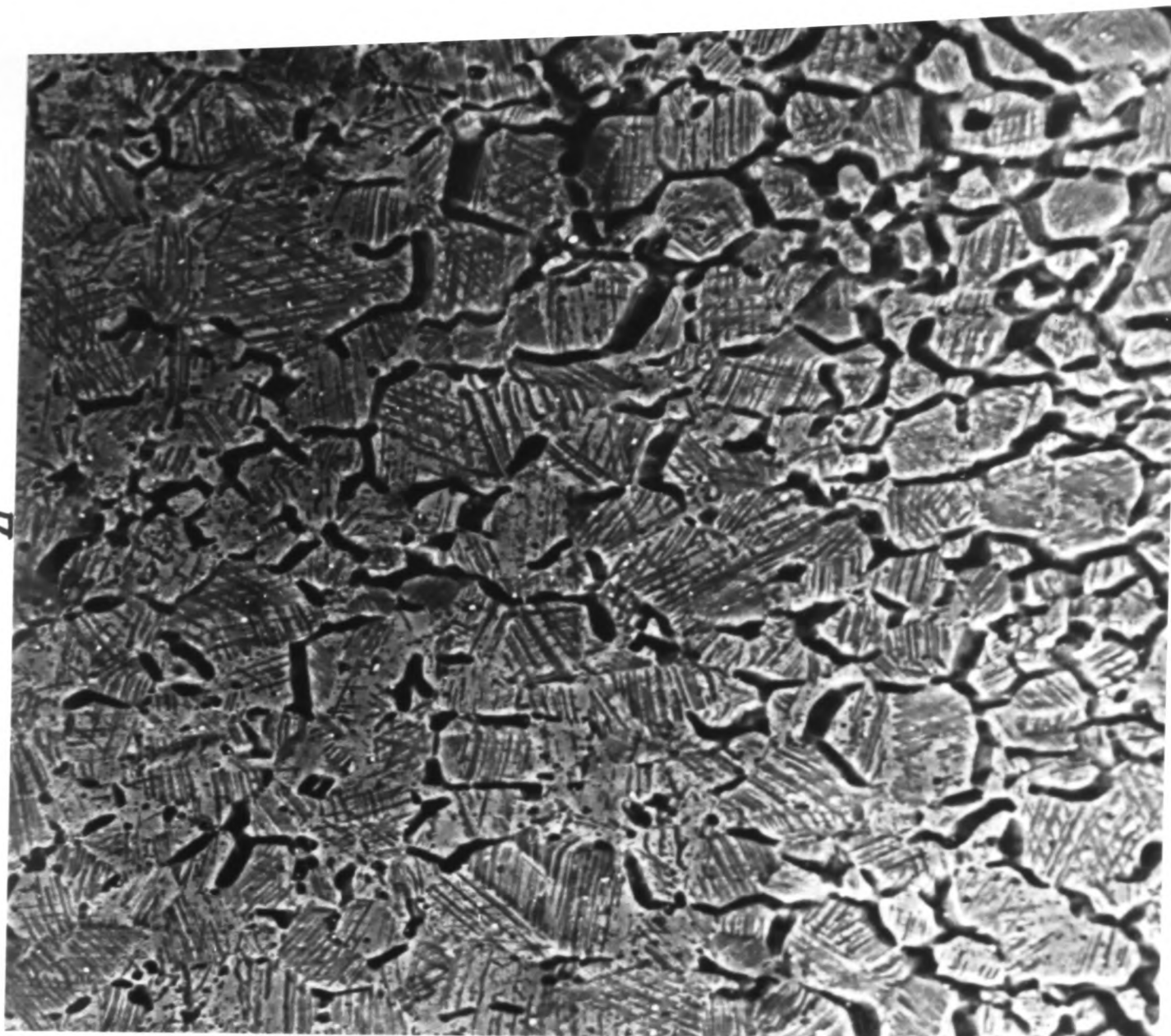
25 μm



Figure 40.6

Surfaces of specimens sensitised for different lengths of time at 550°C and tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). The peak stress was 65% of the yield stress and R = 0.5. 600 second cycles were used.

- A. 50 hours sensitisation
- B. 100 hours sensitisation

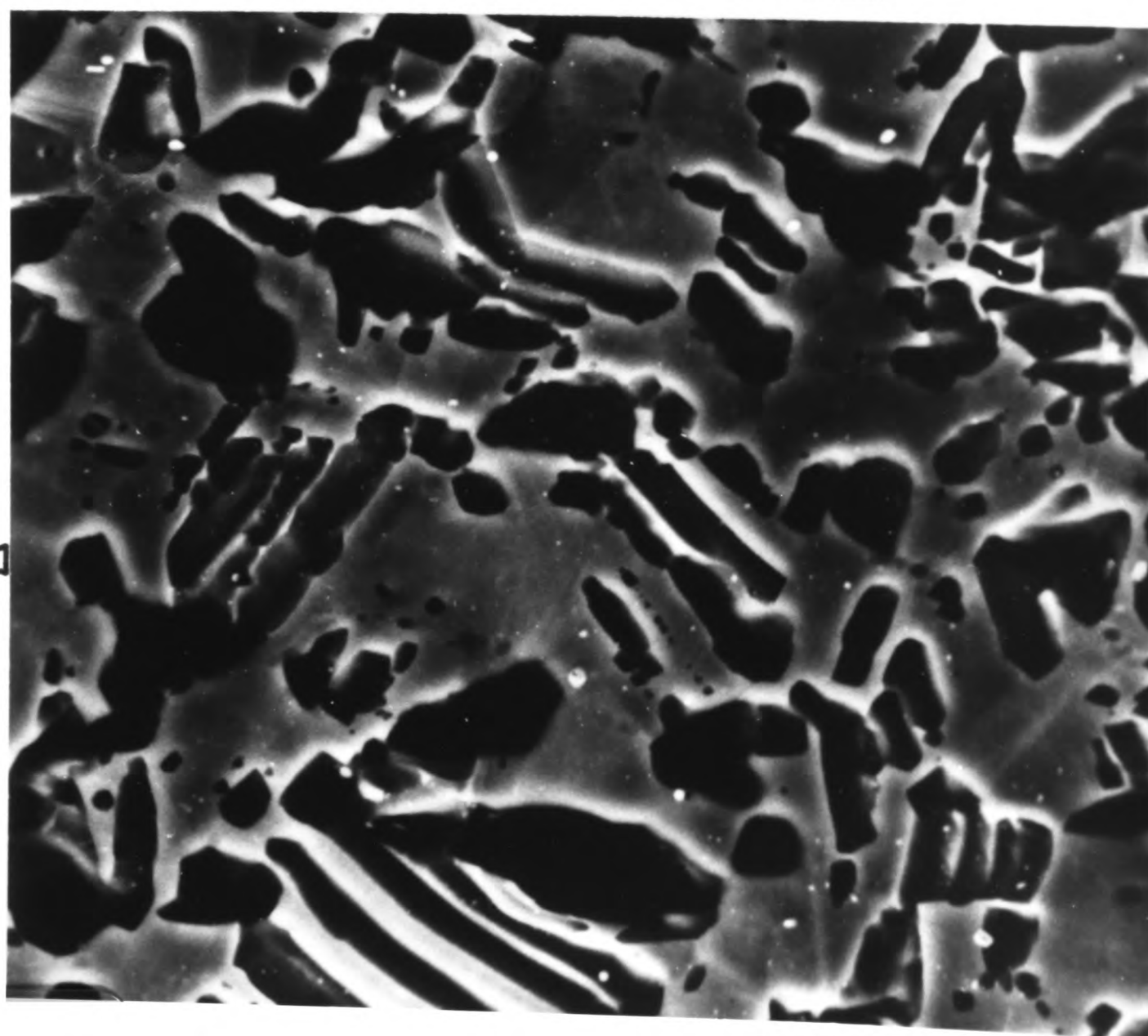


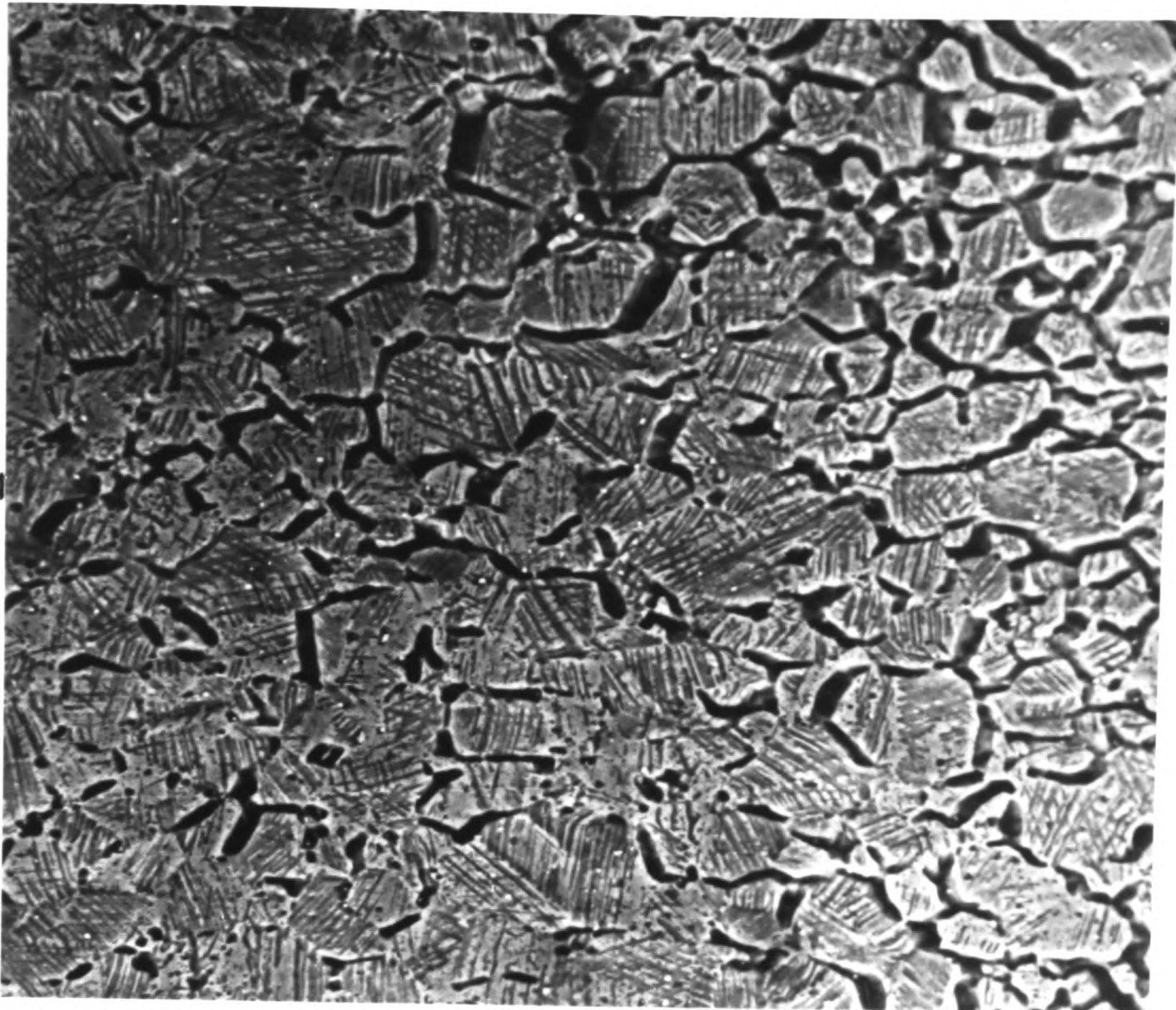
A

10 μm

B

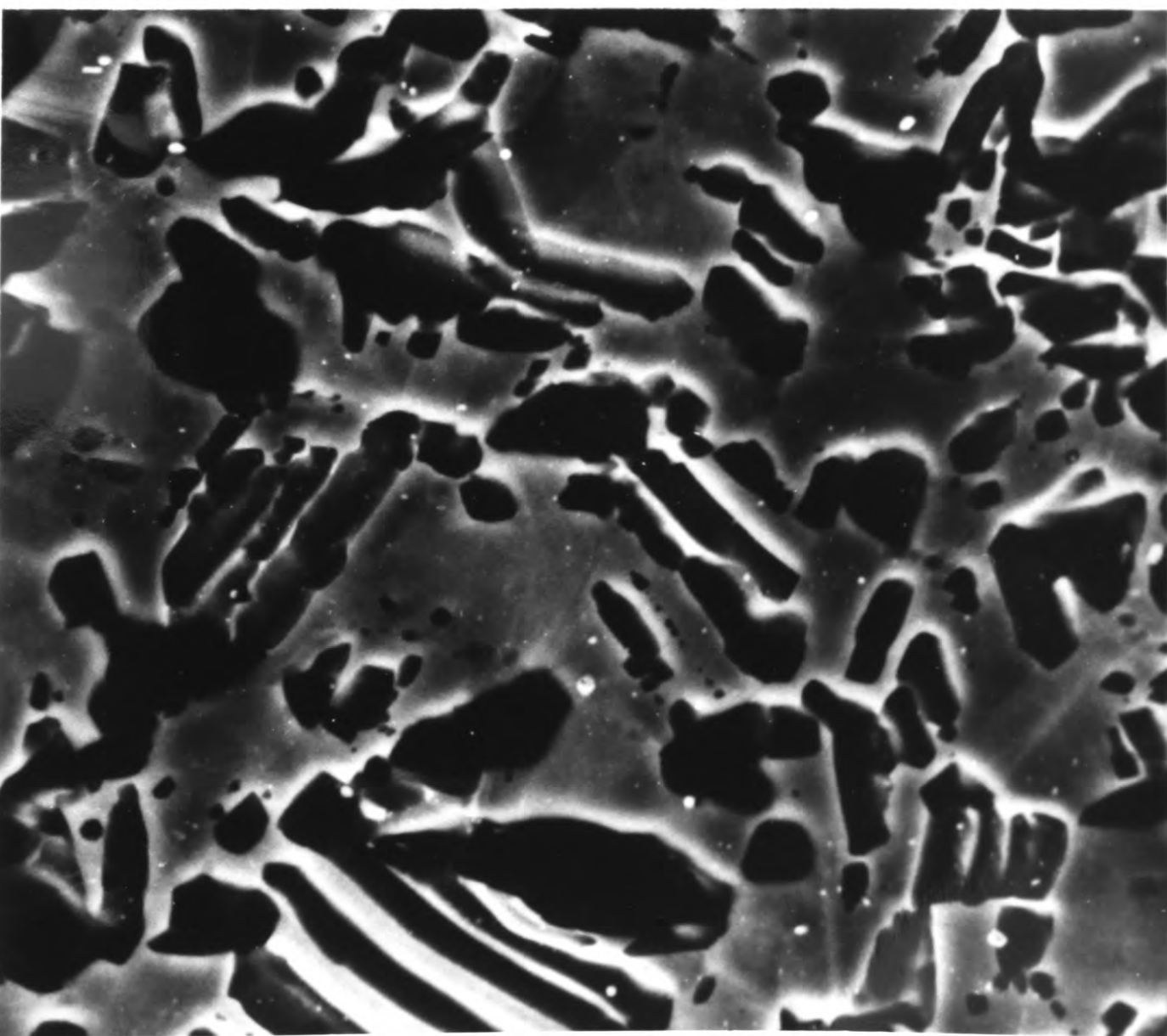
15 μm





A

10 μm



B

15 μm

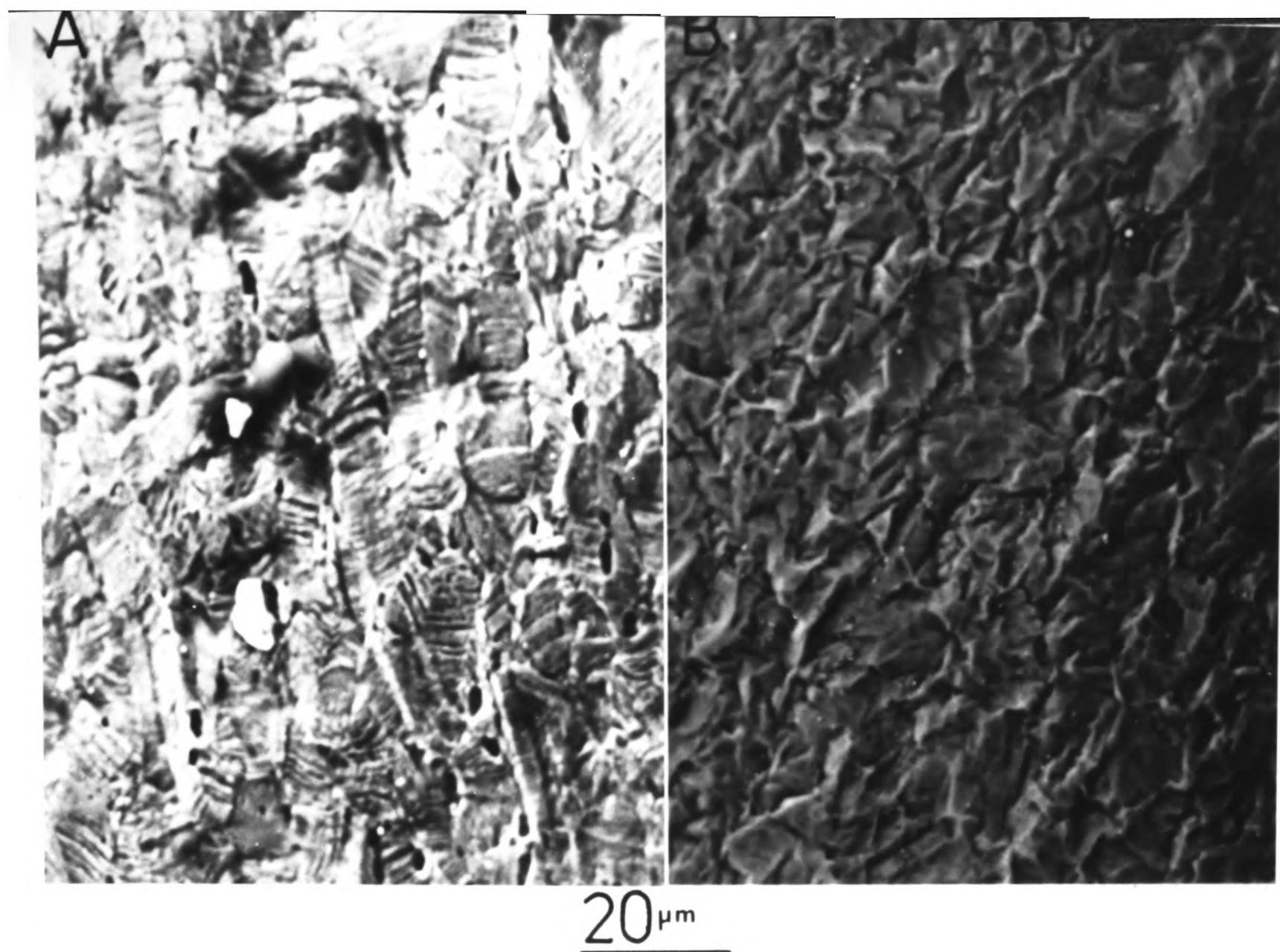


Figure 41.6

Surface of As-Received specimens tested under low frequency cyclic stress conditions in 1M HNO₃ at a potential of -200mV (SCE). Tests lasted approximately 100 hours.

- A. at a peak stress of 80 % of the yield stress with $R = 0.5$
- B. at a peak stress of 60 % of the yield stress with $R = 0.4$

Strain softening by cyclic loading

It was observed that during the low frequency cyclic stress corrosion experiments (described in chapter 6), where specimens were subjected to cyclic stress conditions superimposed on a background tensile stress, an irrecoverable plastic strain increment was seen with each cycle.

It was evident that load cycling produced strain ("creep") which was not seen on loading statically at the same peak stress levels. This is shown schematically in fig. 1. The envelope of the cycles shows the magnitude of permanent plastic deformation that occurs.

It was noted that plastic strain increments were produced for a wide spectrum of loading conditions of various frequencies, amplitudes and peak stress conditions, for stress levels below the "yield stress".

The fact that cyclic loading allows plastic strain to continuously increase, whereas with static loading, strain rates rapidly decrease as strain becomes exhausted has great significance for SCC and stress assisted attack. Cyclic loading experiments were carried out in an attempt to relate the strain response phenomena seen during cyclic loading experiments to cyclic creep softening phenomena. This chapter reviews some of the information on continuous plastic strain induced by load cycling, and describes a very limited number of the observations made on the phenomenon of cyclic load strain softening.

7.1. INTRODUCTION

Static creep refers to creep under a constant stress, cyclic creep refers to that resulting because of a varying or alternating tensile stress. Note that the phenomena discussed are for tests carried out at temperatures within 200°C of room temperature, ie. a small fraction of the melting point temperature.

It has been known for many years that cyclic loading can promote the accumulation of plastic strain although carried out at low mean stress levels. Under service conditions many components are subjected to combinations of static and cyclic stresses. Difficulty may arise because the deformation behaviour of materials under service conditions is not predictable from creep and fatigue test data.

When metals are subjected to cyclic stress they harden or soften depending on the initial structure; annealed materials harden, cold worked materials soften [1]. Each increment in strain results in an increase in back stress which reduces the ability of dislocations to flow. Changes in the deformation resistance are seen as changes in the flow stress, damping response and changes in cyclic stress/strain response. Such dislocation structures are unstable and change may

occur (ie dislocations may flow) if the material is either heated (thermal activation) or the load partially removed. It is well documented [2,3] that during a creep test if the stress is decreased to a lower value, the structure will recover to a state which is characteristic of the lower stress. At low temperatures ($<100^{\circ}\text{C}$) creep is limited by work hardening. On reloading additional creep may result until the rate is again reduced by work hardening. During cyclic loading creep occurs until a characteristic saturation or steady state strain is achieved. This strain is determined by the stress amplitude or magnitude and temperature in materials of wavy slip mode. On the other hand, where the slip mode is planar the steady state strain is dependent on the deformation and thermal history of the material.

Cyclic loading effects are known to be cumulative [1], so that plastic strain may be observed repeatedly. Recovery is cumulative, with repeated unloading, and large strains may result after sufficient numbers of cycles. An early review article by Meleka discusses such information [4].

Cyclic load strain softening effects are very significant in strain rate controlled stress assisted attack, because cycling allows the strain rates that are necessary for attack to be obtained, whereas with static loading the strain rate will gradually diminish as the material work hardens.

Creep acceleration as a result of stress cycling has been seen in a variety of materials:

Al alloys	Feltner [5], Shetty and Meshii [6], Bradley et al [7,8] Bennett and Evans [9]
Cu alloys	Shetty and Meshii [10], Meleka and Evershed [11]
Pb	Kennedy [12], Greenwood [13]
High temperature alloys	Lazan [14]
Stainless steels	Morris and Harris [15,16]

Theories to explain cyclic creep softening have been proposed ranging from strain assisted dissolution of precipitates, where cycling causes mechanical scrambling of atoms in precipitates and softening [9], through to ideas where change in internal stress allows creep recovery [4,10]. In this latter mechanism reverse movement of dislocations takes place during unloading as a result of high back stress, and on subsequent loading barriers to dislocation motion are passed.

All the following observations were made on partial unloading experiments, where a positive load was maintained continuously.

Evans and Parkins [17] and Bennett and Evans [9] suggested that, as a result of cycling, obstacles were passed by dislocation cross slip.

This mechanism is shown schematically in fig. 2a. They consider dislocation change during unloading to be crucial to cyclic strain softening and discuss two classes of dislocation, mobile or potentially mobile dislocations and obstacle dislocations. Obstacle dislocations are unable to move further than a few Burgers vectors due to dislocation interactions. Before unloading, the strain rate falls to a small rate, ie. the applied stress is cancelled out by long range internal stresses and short range friction stresses. On removal of the applied stress the mobile dislocations move backward under the action of the long range internal stress. Recovery takes place as segments of mobile screw segment cross slip by rearrangement of obstacle dislocations as a result of the altered state of internal stress. On reloading the cross slipped screw segments move forward as the long range back stress is insufficient to prevent their movement at positions away from the blocked regions in the primary slip plane. On reloading rearrangement is assisted by the forward motion of the cross slipped segments, and the efficiency of the obstacles to prevent plastic flow is reduced. Evans and Parkins [17] further suggested that obstacle dislocations may become rearranged during the unloading part of the cycle. Morris and Harris [15,16] suggested that internal stresses develop during unloading, which result in anelastic relaxation.

Meleka and Evershed [11] suggested that the application of a cyclic stress causes dislocations to oscillate. They suggested that the effect of the oscillating stress during cyclic loading was to increase mobility and this provides a means to overcome obstacles in the slip plane. A large number of vacancies is supposedly produced, which diffuse to moving dislocations to produce a retarding effect. Steady state creep results from the balance between increased dislocation mobility and resistance to movement produced by vacancy pinning. This is shown schematically in fig. 2b.

Kennedy [12] considered creep to be the sum of two opposing effects, work hardening and thermal recovery. He suggested that vacancies were produced by fatigue loading and that cyclic loading resulted in a greater vacancy concentration. This increased concentration assists dislocation climb and hence dislocations may climb past pinning obstacles to other slip planes. Similarly Feltner [5] assumed that point defects created by cycling diffuse along dislocations, the majority of which are destroyed at jogs. This process is shown schematically in fig. 2c. As defects are annihilated segments of the dislocations climb after the pinning action of point defects is lost. The process repeats until the affected dislocation climbs far enough to escape the pinning obstacle, after which it can move by glide. Shetty and Meshii [6] disputed this because they observed greater cyclic creep at 77K rather than 298K. This finding indicates that vacancy movement cannot be the dominating mechanism because at higher temperatures more point defects would be thermally activated. They

maintained that the most important factor was the unstable nature of the work hardened state, and the greater the degree of work hardening the greater the effect of load cycling on subsequent strain softening. Lorenzo, Laird, Finney and Feltner [18,19,20,21,22] showed that a prerequisite to cyclic strain softening was reversed plastic strain. They suggested that incomplete revision of the dislocation structure resulted when the reversed plastic strain was small, and when cross slip was difficult (such as in planar slip mode materials). They suggested that strain softening occurred by subtle interchanges of glide between dislocations, and that the role of point defects was minor.

Until recently the focus for experiments was on load variations and net elongation. Recent investigators [7,8,20,21] found that creep acceleration was seen when reverse plastic strain was observed on unloading, ie when the stress cycle was symmetric and the plastic strain amplitude large, though it is not necessary for the load to go into compression for creep straining to be restarted [23].

7.2. EXPERIMENTAL

The starting point for an interpretation of the effect of low frequency cyclic loading on SCC is understanding the shapes of incremental creep vs time curves from experiment. To investigate the influence of stress cycling on strain, low frequency cyclic stress experiments were performed. The following work describes experiments carried out at low stress levels (below yield) and at room temperatures.

Cyclic loading tests were carried out on specimens in the AR and the sensitised condition by use of the modified creep rig apparatus and specimen assembly described in chapter 6. Figure 1 schematically shows the method of loading. Displacement was monitored continuously by either strain gauges mounted on the specimens or transducers positioned at the end of the creep rig arm. Displacement was recorded on a chart recorder and translated into strain by the method described in Appendix 3. Tests were carried out in air or distilled water.

7.3. RESULTS

Fig. 3 compares static and cyclic creep for specimens tested at the same peak stress. Specimens were cycled in air and a cycle time of 500 seconds (2×10^{-3} Hz) was used. A constant amplitude was used on top of a background stress. The limit of proportionality for the AR material was determined at 400 Nmm². SEM examination after testing revealed no cracks and little change in surface relief after testing. It may be seen that average creep rates resulting during cyclic loading were greater than the corresponding values for static loading

(at the same peak stress). The accumulation of plastic strain observed during cyclic loading was greater than that for static loading although the mean stress during cyclic loading was 52.5 N mm^{-2} less than the static load.

Fig. 4 shows these data as accumulated plastic strain against log time. The accumulated plastic strain is the strain that is seen beyond the elastic strain, ie only plastic and anelastic strain.

Fig. 4 shows that accumulated strain increases with loading stress. Furthermore, cyclic loading at the same peak stress level increases the rate of plastic strain. The plots of strain against log time are linear, apart from the cyclic load test at the highest stress. The type of observed creep is known as logarithmic creep and is described by:

$$1. \quad e = e_E + e_P + e_0 \log(1+Yt)$$

e = observed strain

e_E = elastic strain

e_P = plastic and anelastic strain

t = time

e_0 and Y are constants

The data in fig. 4 show that e_0 is larger for cyclic loading than for static loading, as a result of increased dislocation mobility [7,8].

Fig. 5 shows strain/time curves obtained from transducer outputs during cyclic loading tests. Fig. 5a shows the rate of plastic strain accumulation for a sensitised tube material specimen loaded to a peak stress of 65% of the yield stress and cycled with $R = 0.4$ with a cycle time of 600 seconds. The rate of strain accumulation is approximately 0.04% per hour, whereas no additional extension is seen on a sample statically loaded at the same peak stress. Fig. 5b shows strain data for a specimen loaded at a peak stress of 75% of the yield stress and cycled with a 600 second cycle time with $R = 0.5$. At the start of each loading period, a dormant period is seen, where no extension is observed. During this period anelastic recovery takes up the deformation resulting from elastic extension, and a "dead strain" period is seen. The effect of frequency change is also shown in fig. 5b. The proportion of the dead strain period in relation to the loading up period remains constant, a further indication that anelastic recovery takes place. Fig. 5c shows the beginning of a cyclic loading test for a sample loaded to a peak stress of 65% of the yield stress and cycled with 600 second cycles with $R = 0.7$. Again the dead strain period is seen, together with the initial elastic strain from loading to the peak stress.

Fig. 6a and 6b shows TEM micrographs from an AR section of AGR

cladding that was cycled for 8 days at a mean stress level of 80% yield with an amplitude of $\pm 15\%$. The initial structure has a very low dislocation density. However, after cycling the interiors of grains are characterised by the first stage of dislocation cell formation, where dislocation tangles divide large subcells that are relatively free of dislocations. Such a structure generated by strain ratchetting has been likened to those seen after high temperature, low cycle fatigue [23]. Wall-like dislocation tangles comprising relatively short and incomplete cell wall segments are mostly composed of trapped and piled-up mixed dislocations.

Figs. 6c and d shows micrographs of a conventional bright field and a 3G weak beam image of the same area, of a specimen after cycling at $R=0.6$, 60% of yield stress and 600 sec cycles. The test was stopped after about 100 cycles. Dislocation cell structures build up because of cross slip, and further interaction of these segments with obstacles. Such observations tie in with the models suggested by Evans and Parkins [17] and Bennett and Evans [9].

7.4. DISCUSSION

It has been shown above that different stress conditions influence the rate and magnitude of the observed accumulated plastic strain.

The extent of creep softening during load cycling was seen to increase when the following increased:

1. Test frequency
2. Stress amplitude
3. Peak stress

The cyclic loading test observations allow us to attempt to describe the microscopic behaviour during cycling.

A schematic of the shape of a cycle in terms of the elastic, anelastic and plastic components is shown in fig. 7. The strain time diagram shows an instantaneous elastic strain increment and time-dependent anelastic and plastic strain increment. During the maximum load period the creep rate decreases to a relatively constant value at longer times. As stress is applied, dislocations rearrange until internal stresses develop. If the stress is removed, strain may be recovered anelastically. Anelastic recovery during unloading allows plastic strain to be seen on loading. This plastic strain is seen during each cycle and allows accelerated stress assisted intergranular attack during low frequency cyclic stress corrosion tests.

The introduction to this chapter suggested that such effects were explainable by the anelasticity of the material during loading, and slow recovery of this anelastic deformation during unloading periods. The work hardened structure is unstable on unloading, and dislocation

rearrangement allows further strain increments on reloading. Unrecoverable creep only occurs by dislocation link activation and does not accumulate until dislocation links become fully bowed. Partly bowed dislocations lead to the transient effects seen during cyclic loading and to the recovery seen in stress relaxation experiments. It is likely that strain softening is associated with the reverse movement of mobile dislocations during unloading [7,8]. If reverse movement is prevented by dislocation pinning the creep produced during cyclic loading is greatly reduced.

The magnitude of recoverable anelastic strain depends on the frequency. Smaller anelastic recovery is seen for fast cycles as time is required to recover all anelastic strain. Dislocations therefore do not have time to take up fully bowed morphologies.

Therefore higher average stress levels will lead to a greater creep rate. Faster cycles do not allow anelastic recovery and thus restrictive immobile dislocation networks do not build up although dislocations bow, and therefore creep acceleration is seen. Time spent at higher stress levels generates more creep.

The effect of load cycling on plastic strain and strain rates at the crack tip may be a significant factor on the rate of propagation of SCC cracks. Further, and more extensive systematic, research on the effect of load cycling on strain softening is required to understand the effect of low frequency cyclic stress on the SCC of materials.

References Chapter 7

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Schematic showing the effect of low frequency cyclic loading and static loading on the strain response of specimens.

FIG1.7

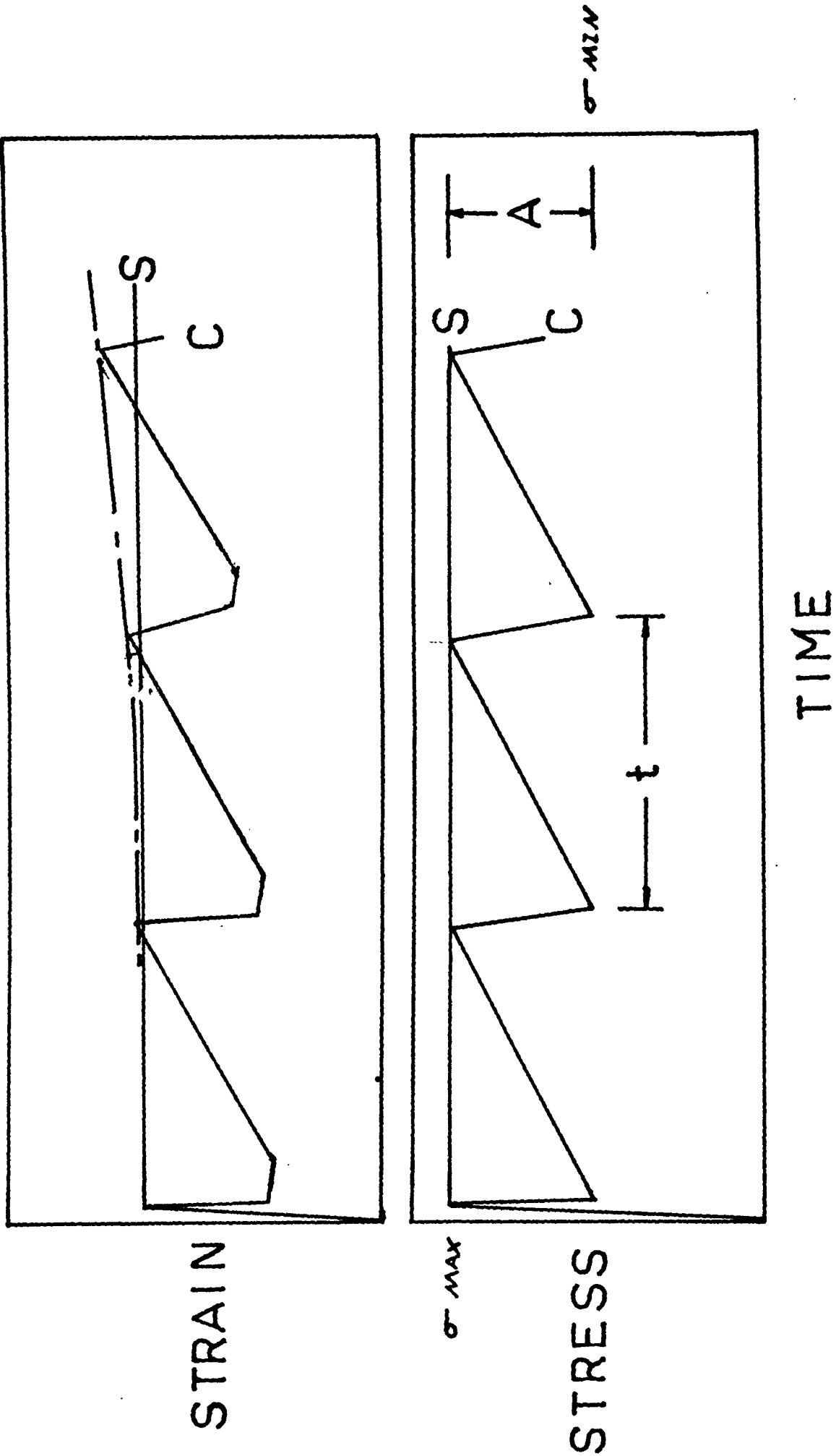
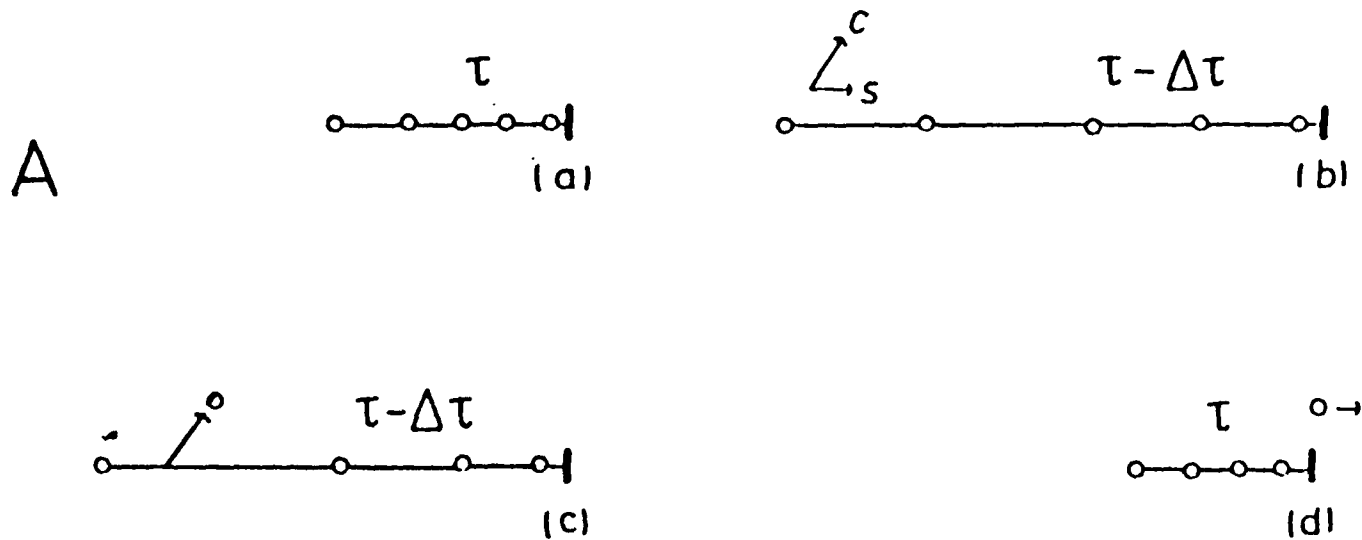


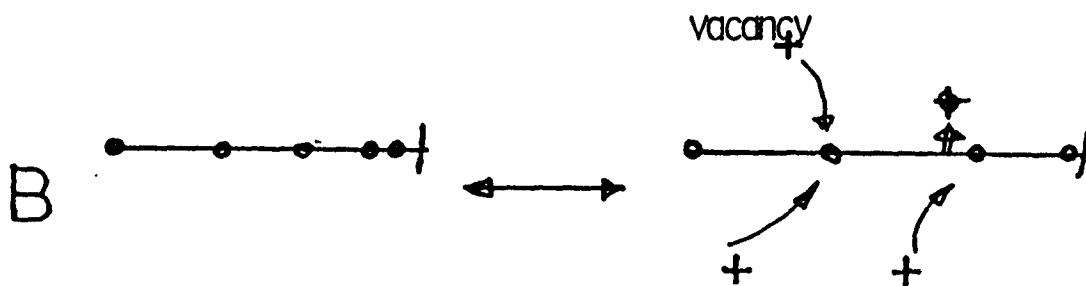
FIG 2.7

Proposed different mechanisms of cyclic stress softening.



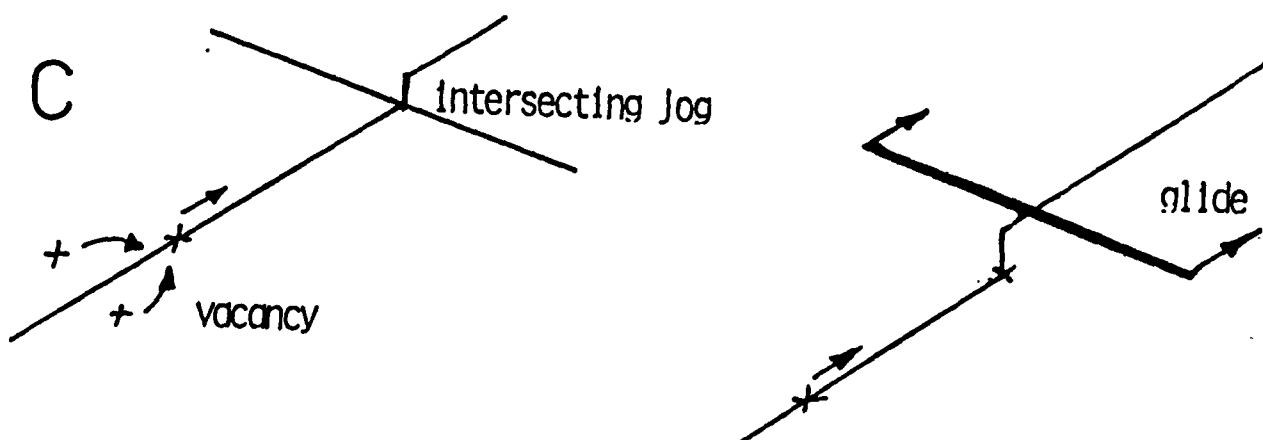
Mechanism A

illustration of the cross slip produced by backward motion of screw dislocations, (ref Evans and Parkins [17]; and Bennett and Evans [9]).



Mechanism B

Vacancy production by dislocation motion allowing increased mobility and bypass of obstacles on a slip plane, (ref Meleka and Evershed [4]).



Mechanism C

Vacancies annihilate allowing dislocation climb as action of point defects is lost,
(ref Feltner [5]).

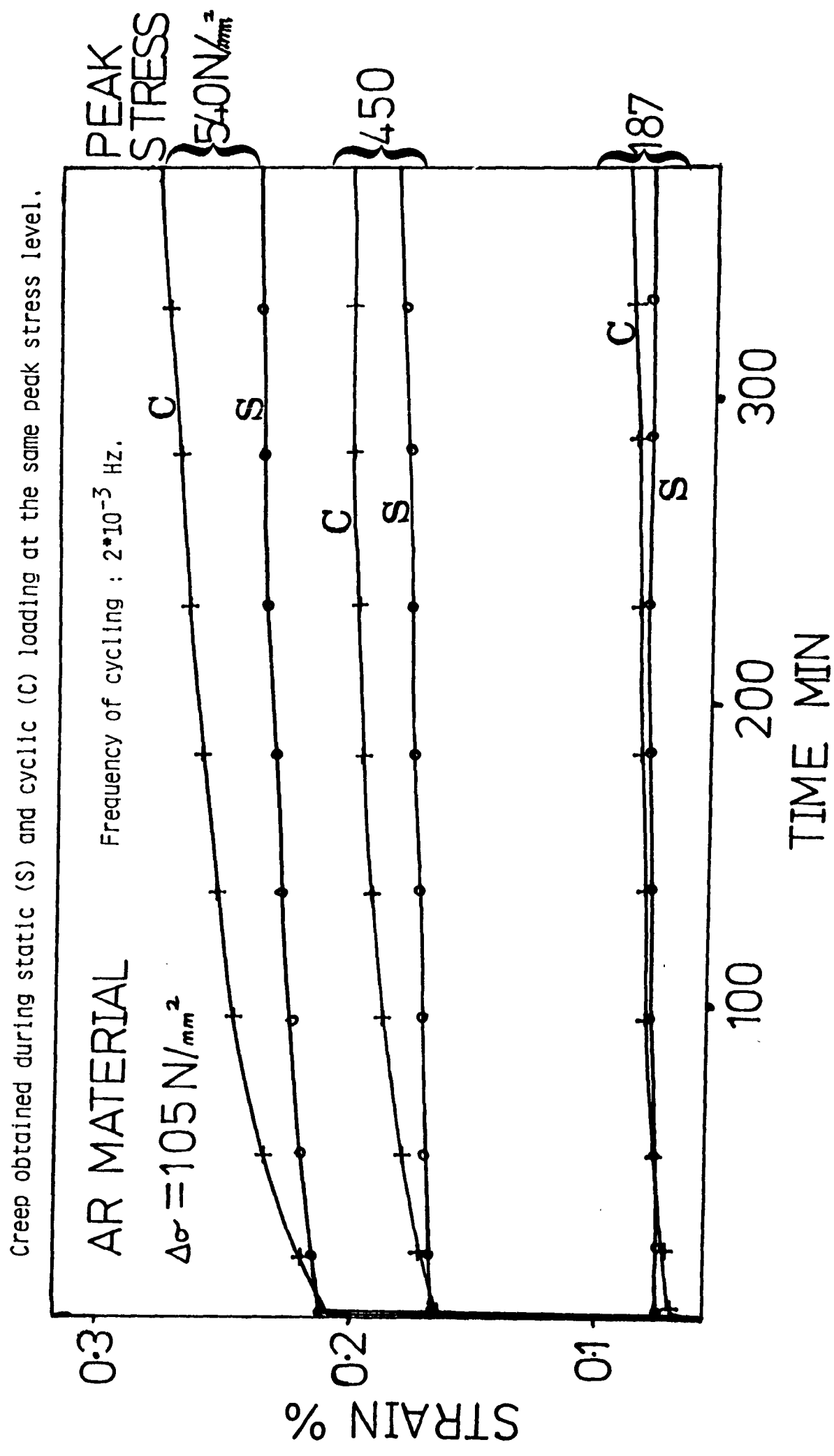


FIG 3.7

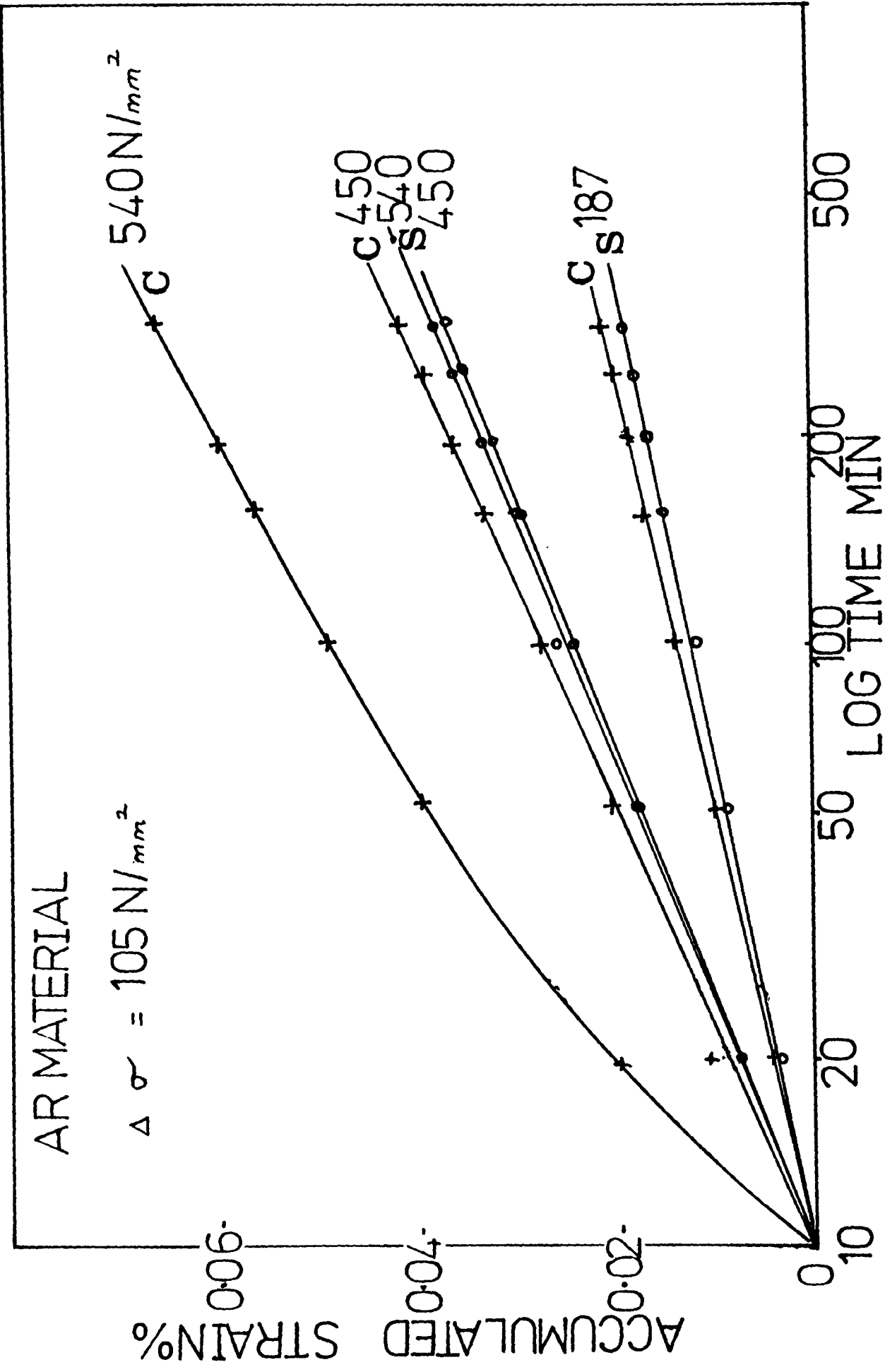


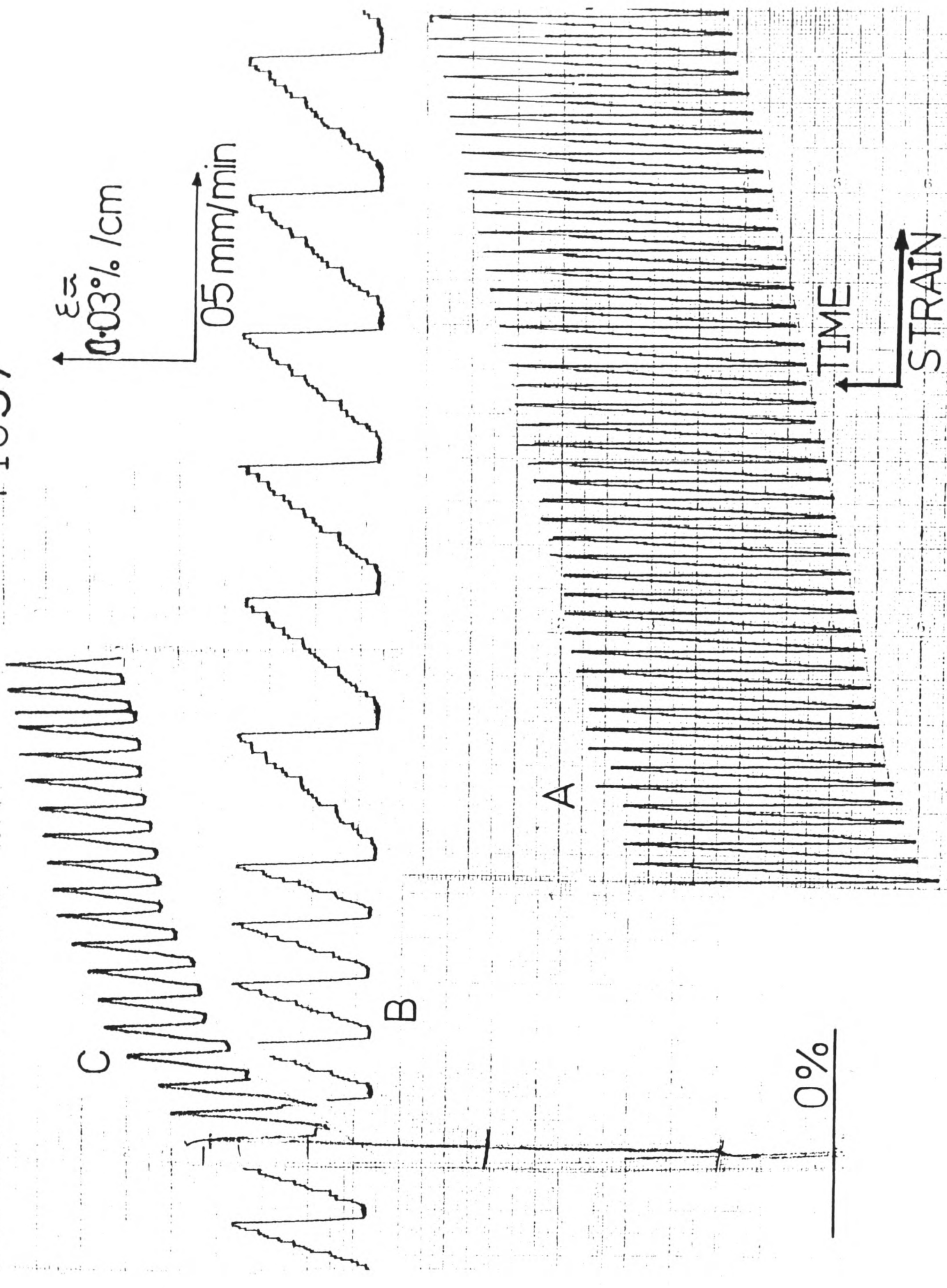
FIG 4.7

Figure 5.7

Transducer output (strain measurement) during load cycling for specimens cycled at

- A. a peak stress of 65% of the yield stress with $R = 0.4$ and 600 second cycles. Plastic strain accumulation as a result of load cycling is seen.
- B. a peak stress of 75% of the yield stress with $R = 0.5$, with 1000 second and then 2500 second cycles.
- C. a peak stress of 65% of the yield stress with $R = 0.7$ and 800 second cycles. The start of the load cycling experiment is shown.

FIG 5.7

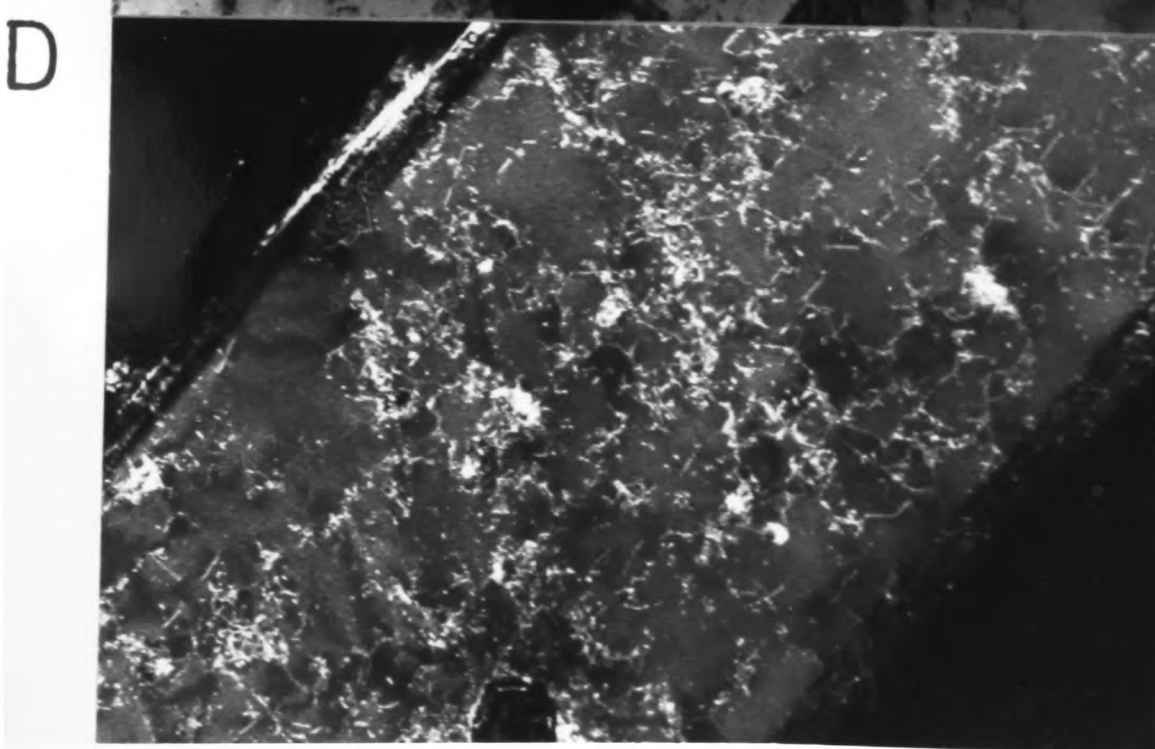
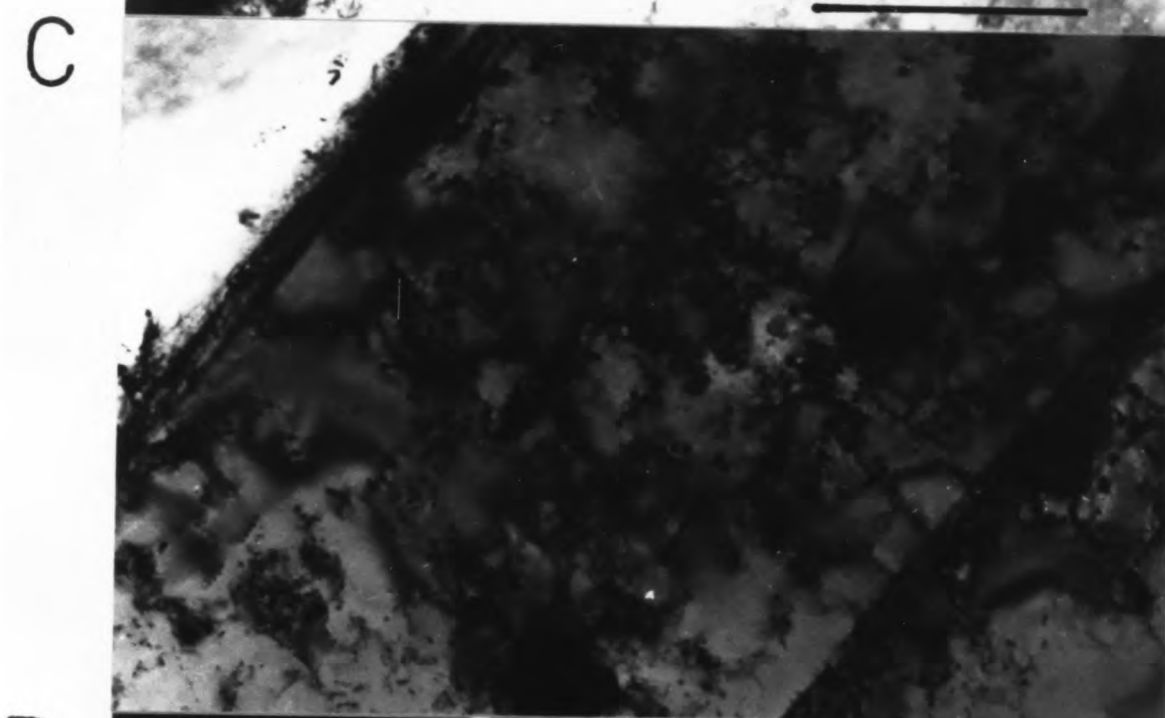
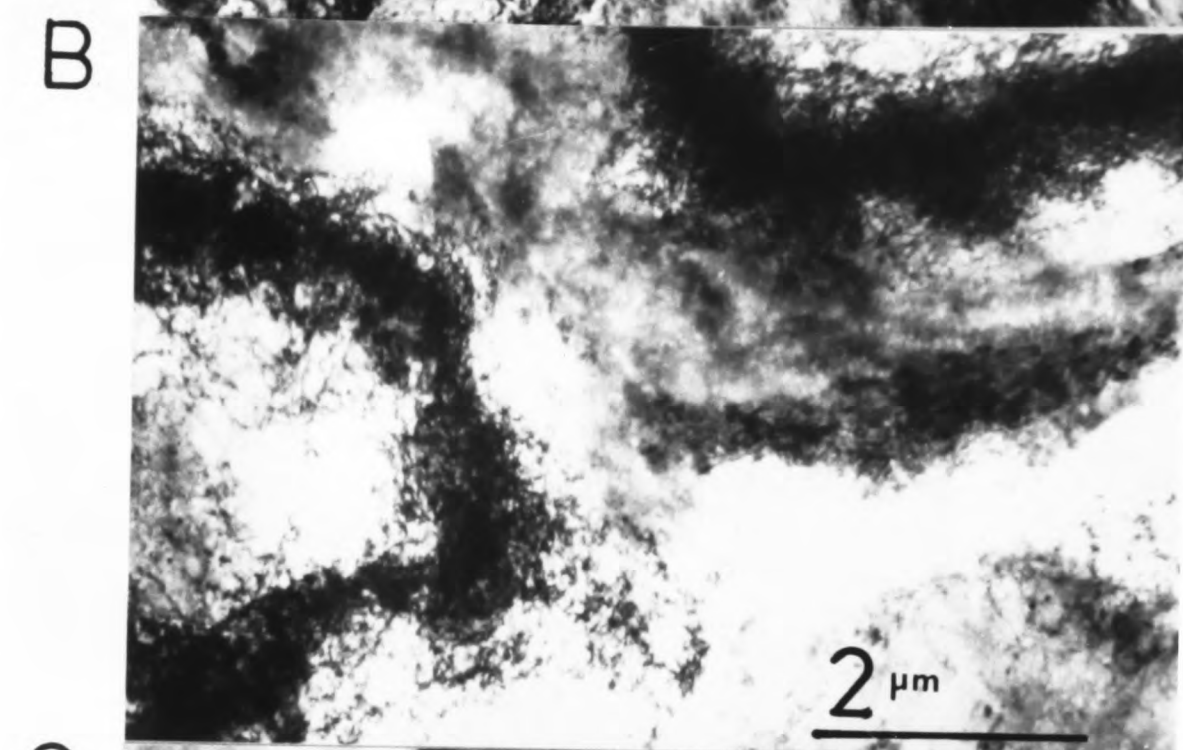
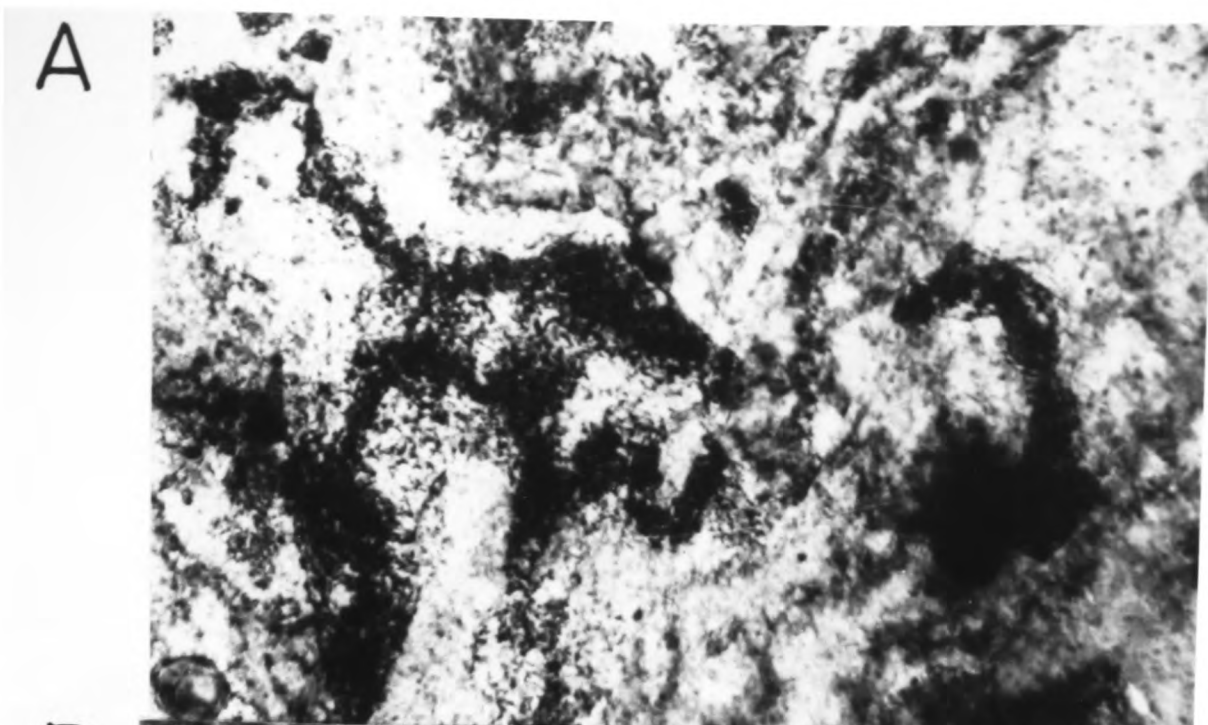


Transducer output (strain response) for cyclic loading experiments.

Figure 6.7

TEM micrographs from specimens after load cycling experiments

- A and B. Bright field micrographs after cycling As Received material at a peak stress of 80% and amplitude of ± 15 of the yield stress.
- C and D. Bright field and weak beam micrographs of specimens cycled at $R = 0.6$ and a peak stress of 60% of the yield stress.



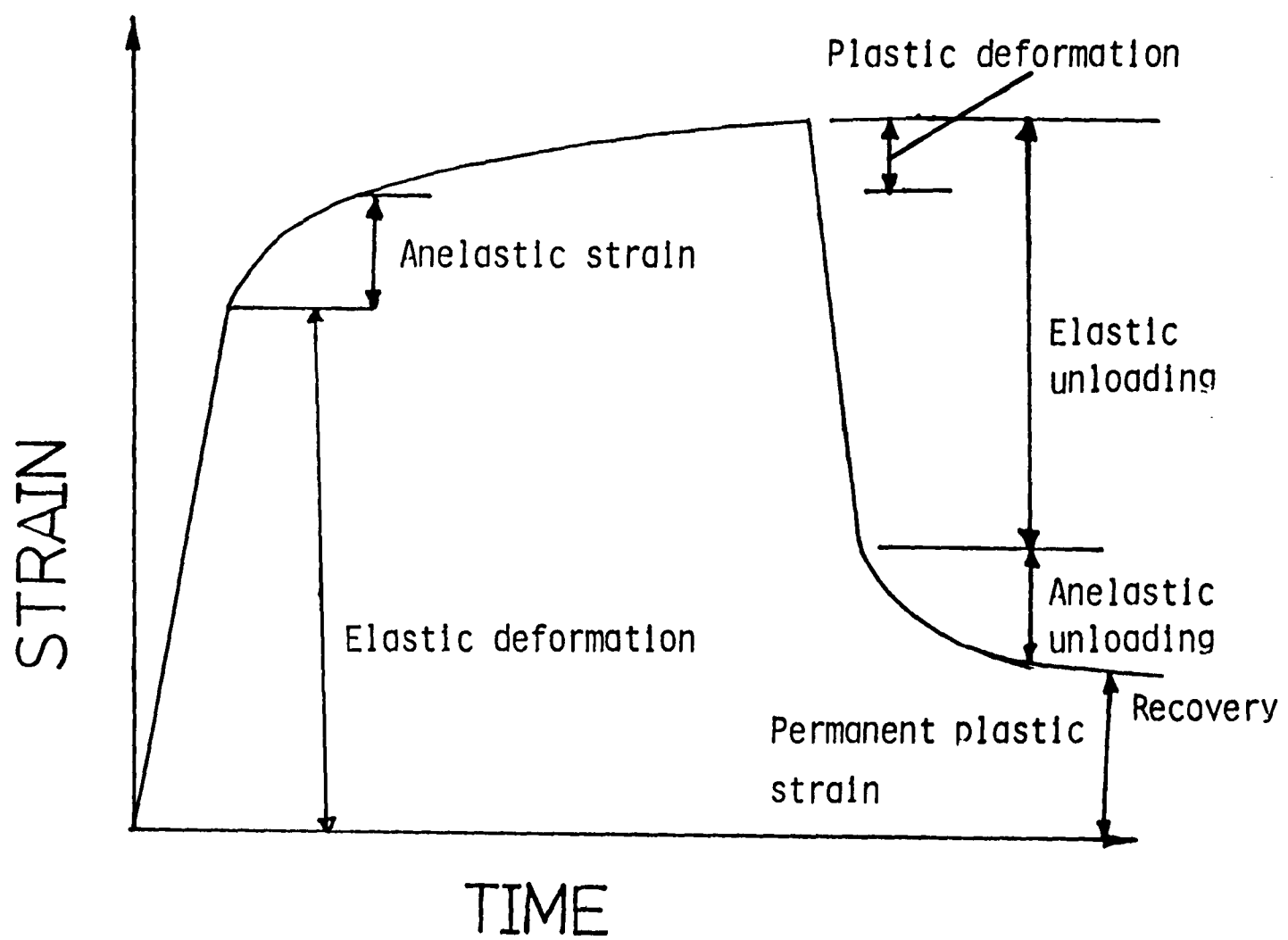


FIG 77

Schematic of strain response during stress relaxation experiments.

Chapter 8

8.1. GENERAL C

1. Stress assisted intergranular corrosion attack has been observed in thermally sensitised 20% Cr, 25% Ni, 0.7% Nb stainless steel tested in 1M HNO₃ solution. Attack was observed at stress levels as low as 30% of the "yield stress" for material sensitised by annealing at 1050°C for 30 mins and ageing at 550°C for 500 hrs. Such material is severely attacked in a Strauss test. Little attack was observed in material annealed at 1050°C then aged for 25 or 50 hrs; such material also showed little response in a Strauss test. As-received AGR fuel cladding showed no IGA or stress assisted corrosion attack when tested under similar conditions.
2. Dissolution in all tests was intergranular. Attack occurs fastest at an applied potential of -200mV SCE. For potentials greater than 30mV away from this potential, the rate of attack was an order of magnitude less. The attack observed at -200mV was narrow, and activity is confined to the penetration front.
3. For static loading at low stress levels the rate of attack is little faster than the rate of IGA for unstressed material. For tests carried out at stress levels greater than the yield stress rapid intergranular penetration was observed. For tests carried out at -200mV where a low frequency (10^{-4} to 10^{-2} Hz) cyclic load was superimposed on a static load, an increase in peak stress caused up to an order of magnitude increase in the rate of penetration. The extent of the increase in penetration rate with peak stress was greatest when large amplitudes and low frequencies (long cycle times) are used.
4. The penetration depth for static loading tests at -100 and -200 mV increased linearly with time. The penetration depth in cyclically loading tests at -200 mV increased with the square root of time. The penetration depth in cyclically loading tests at -100 mV increased linearly with time.

A number of different mechanisms were discussed to explain the parabolic rate of grain boundary penetration during cyclic loading. The mechanisms discussed included the difficulties of ion transport down narrow dissolution paths, dissolution enhanced by plastic strain, crack tip or penetration front blunting, pumping of solution in and out of dissolution paths and localised martensite formation aiding hydrogen embrittlement. It was concluded that although the most plausible reason for the parabolic rate of penetration at -200 mV was

that dissolution became diffusion controlled because of high anodic currents and a narrow penetration path. The observed crack growth rates were far below those where rates would become diffusion limited.

5. During cyclic loading, although stress levels below the yield stress were used, continuous plastic strain resulted. Plastic strain rates were far greater than those seen during static loading at the same peak stress. Cyclic stress resulted in elastic, anelastic and plastic deformation whereas if the same stress is applied statically, very limited strain was seen. The "creep" resulting during cycling and static loading was described by a low temperature logarithmic creep law.

Cyclic creep rates are fastest for large amplitudes and high mean stress levels.

6. The process of sensitisation was examined for 20% Cr, 25% Ni, 0.7% Nb stainless steel in three forms (tube, bar and reworked bar). The tests used to determine the extent of sensitisation of materials with a variety of heat treatments were the Oxalic acid test, the modified Huey test ($\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$), the Strauss test and the EPR test. The response observed in all tests depended on prior heat treatment and shows that both Cr depletion and impurity segregation can occur in 20% Cr, 25% Ni, 0.7% Nb stainless steel.

7. As the temperature of ageing was increased, the maximum depth of penetration observed during Strauss testing and the maximum current observed during EPR testing were achieved in shorter ageing times and sensitisation extended over a shorter range of ageing times.

The largest degree of sensitisation observed during Strauss testing was obtained for AGR fuel cladding samples heat treated by a solution anneal of 1050°C for 30 min followed by ageing at 550°C for 500 hrs. High levels of sensitisation were also achieved by solution annealing at 1150°C for 30 min followed by ageing at 600, 650 and 700 °C for 50, 5, and 0.5 hrs respectively. The largest response during EPR testing was attained for AGR fuel cladding samples heat treated by a 1050°C anneal for 30 min followed by ageing at 550°C for 500 hrs, or by annealing at 1150°C for 30 mins and ageing at 600°C for 100 hrs.

A depth of penetration greater than 100µm occurs in a Strauss test for tube material heat treated in the following ways:

1050°C for 30 min and aged at 550°C for 500 hrs

1150°C for 30 min and aged at 600°C for times between 40 and 75 hrs

650°C for times between 4 and 25 hrs

700°C for times between 20 min and 1 hr

8. The potential of 6V during Oxalic acid etching was found to be too severe, leading to rapid pitting, and a reduced potential 0.8V was found to result in less surface damage and better ability to discriminate between heat treatments.
9. Little response was seen in the above tests for bar material annealed at temperatures up to 1150'C for 30 min and aged at temperatures between 550 and 750'C for times from 30 to 750 hrs. Bar material was only sensitised when a high solution anneal temperature (greater than 1200'C) was used. Examination of the bar and tube material by TEM and STEM revealed that the only difference in microstructure able to account for sensitisation was that the carbon in the bar material was locked up in the form of large Nb(CN) particles which only dissolved during very high temperature annealing. Reworking the bar material broke down such particles and allowed their dissolution, and subsequent sensitisation of the material.
10. Weight loss experiments were carried out on bar and tube material in boiling $\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$ solution. Response was dependent on prior heat treatment, and both solution anneals around 1100'C and ageing heat treatments at temperatures less than 650'C showed the presence of impurity segregation at grain boundaries. Ageing temperatures above 700'C produced large carbides and resulted in a much reduced response.
11. The SAROC model predicted that the criterion of 12 wt% Cr and a depletion width of 20 nm at that level, was met over a much smaller time and temperature regime than that where sensitisation was actually observed during Strauss and EPR testing. Time/Temperature/Sensitisation (TTS) data from the SAROC model predicted the following times for sensitisation and healing:
- | | 1050'C anneal | | 1150'C anneal | |
|-------|---------------|-----------|---------------|-----------|
| | sensitisation | healing | sensitisation | healing |
| 500'C | @1000 hrs | >2000 hrs | 460 hrs | >2000 hrs |
| 550'C | 122.5 hrs | > 500 hrs | 52.5 hrs | >1000 hrs |
| 600'C | | | 9.5 hrs | @200 hrs |
12. The model predicted that the activity of C in solid solution increases as ageing temperature increases or the initial C content is increased. The model illustrates the importance of the initial Nb:C ratio in determining the degree of sensitisation. If the Nb concentration is increased, sensitisation is predicted over a narrower temperature regime. If the initial C concentration is increased or if a higher solution anneal temperature is used, more C is available in solid solution and sensitisation occurs over both a wider temperature and time regime. After a 1050'C anneal, sensitisation is predicted not

to occur above 570°C, and after a 1150°C anneal sensitisation is predicted not to occur above 620°C, whereas 100 µm depth of penetration is actually seen during Strauss testing in materials aged at temperatures up to 700°C.

13. Zones of Cr depletion and Ni enrichment were found adjacent to grain boundaries in all the specimens examined by STEM with EDAX. Profiles obtained by STEM X-ray microanalysis showed that for material showing a depth of penetration of 95 µm in a Strauss test, and a peak current of 37 mAcm⁻² in an EPR test, the minimum Cr level measured at the grain boundary was 13.1 at%. If broadening of the electron probe in the thin foil specimen was considered, the estimate of the minimum concentration at the boundary was 11.2 at% (@10.1 wt%). Similarly, material that showed a depth of attack in a Strauss test of 20 µm and a peak current of 7 mAcm⁻² in an EPR test, had a minimum measured Cr level of 16.6 at%. If beam broadening was considered this value became 14.8 at% (@13.6 wt%).

The corrected measured Cr minimum levels compare well with the values obtained by modelling.

AEM showed evidence of asymmetric Cr depletion profiles. This is believed to be because of grain boundary movement during discontinuous precipitation.

8.2. FURTHER WORK

Suggestions for further work divide into three areas:

1. To understand how the number of sensitised boundaries varies with heat treatment time and temperature.
2. To examine the influence of the variables of sensitisation on the stress assisted corrosion process.
3. To examine further the influence of low frequency cyclic loading on the stress assisted corrosion of sensitised stainless steel.

During ageing, at any particular time there are a proportion of boundaries that are sensitised. A progressively larger number of boundaries first becomes sensitised and then healed. The depth of penetration measured in both Strauss tests and stress corrosion tests depends on both the test variables and the extent of sensitisation throughout the structure. Attack advances until a non-sensitised boundary is met and then stops, as the susceptible pathway for attack does not continue. Further work could be carried out on material sensitised by different heat treatments, containing different numbers of sensitised boundaries throughout the structure. Investigation should be carried out on how the distribution of sensitised boundaries

affects both sensitisation test response and stress corrosion processes.

Deconvolution of test results would require an understanding of how microstructure was related to test response. Such information would require the determination of a large number of accurate Cr depletion profiles to enable statistical handling of such data for each heat treatment condition. Accurate analysis is becoming routine as AEM technology advances. Further analysis could be carried out using a dedicated STEM, capable of smaller probe sizes and thereby greater spatial resolution.

The inability to sensitise the bar material other than with a high temperature solution anneal is an important observation that should be investigated with further AEM.

Because it was found possible to sensitise the bar material (although later on during the project) sensitised bar material (rather than thin wall tube) could be used for stress assisted corrosion experiments. Bar material could be easily machined to a reproducible test specimen geometry. The use of conventional tensile specimens would ensure that as grain boundary attack progressed, the compliance of the specimen would remain almost unchanged. However, the use of bar material for tests is yet further divorced from the plant situation because high temperature annealing results in grain growth which consequently results in a change in the thermodynamics and kinetics of sensitisation.

The measurement of current density during stress corrosion experiments gave little information on the process of corrosion because the redox reactions of nitric acid dominated the electrochemistry. Further low frequency cyclic stress experiments could be carried out in a medium where the electrochemical reactions are more simple. A medium relevant to the nuclear power industry, known to cause both SCC and IGA in sensitised stainless steels is polythionic acid. The proposal that crack propagation observed during cyclic loading was a result of mass transport conditions could be investigated by the use of different concentrations of media.

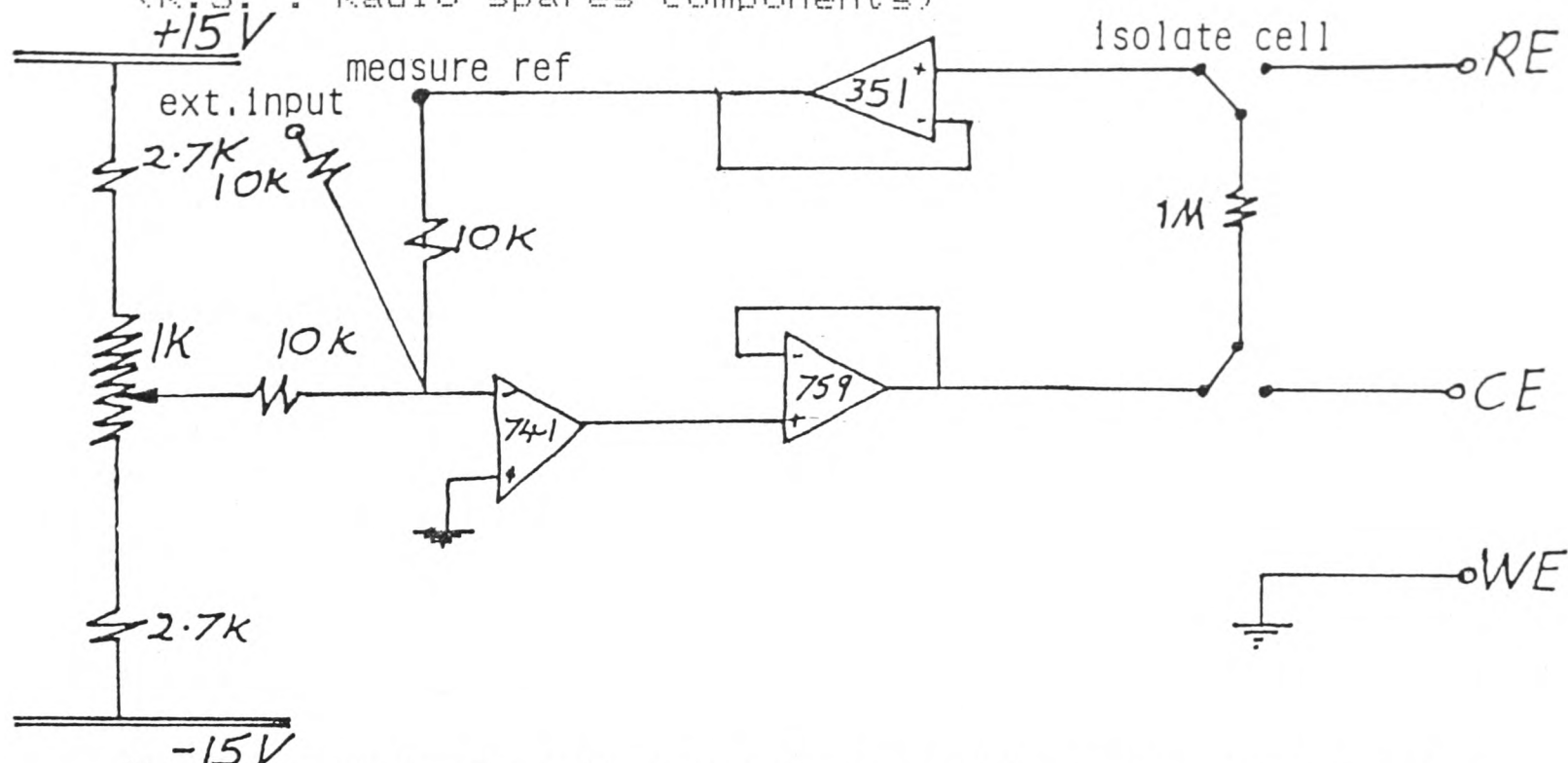
Although there is an increasing amount of literature on strain softening resulting from stress cycling, little work has been carried out on stainless steels. Further mechanical testing could be carried out on strain gauged specimens, cycled at low frequencies and at below yield stress levels. Detailed TEM work would be required to analyse dislocation interactions that resulted during cyclic strain softening.

We have shown that cyclic loading increases the rate of intergranular attack during stress corrosion experiments. Fundamental work is required on how the reactivity of the material (and sensitised

boundaries) changes whilst elastic and plastic conditions exist at the specimen surface, and at penetration fronts or crack tips.

Appendix 1. Notes on electronic circuitry used.

(R.S. : Radio spares components)



Potentiostat circuit (requires stabilised $\pm 15V$ supply)

759 power amplifier. R.S. data sheet 5386

351 high impedance JFET operational amplifier

741 operational amplifier

Heater circuit

741 comparator circuit, soldering iron heater elements
bead thermistors. R.S. data sheet 1867

Strain gauge measurement

R.S. strain gauges and strain gauge amplifier
R.S. data sheet 6266

Multiplexing circuit

Reed relays and double pole relays
Digital logic gates and counter. R.S. data sheet 7275

Buffer circuit

351 high impedance JFET operational amplifier powered by
9V batteries

Transducer power supplies

Schaevitz: $\pm 5V$ stabilised power supply
Novatech: $\pm 2V$ power supply

Appendix 2

Calculation of Strain from Transducer and Strain Gauge Output

$$\text{strain} = \text{extension} / \text{original length}$$

Original gauge length = 40mm

Calculation of strain from:

A. Transducer Output

Novatech transducer constant $\Rightarrow 1\text{mm} = 70\text{ mV}$ } K
Schaevitz transducer constant $\Rightarrow 1\text{mm} = 454\text{ mV}$ }
Beam ratio = 6.5

$$\text{Therefore strain} = \frac{\text{mV change}}{(40 \times 6.5 \times K)}$$

B. Strain gauge amplifier output

Strain gauge used in quarter bridge configuration (fig. 1)

Gauge factor = 2.1

Bridge voltage = 10 Volts

Strain gauge amplification gain factor = 1000

$$\text{Therefore strain} = \frac{V_{\text{output}} \times 4}{1000 \times 10 \times 2.1}$$

Strain gauge limit of linear response = 2% strain $\Rightarrow 0.8\text{mm}$ extension.
An example of the comparison of response from the Novatech transducer and from a strain gauge is shown in fig A.1

Quarter bridge (3 wire)

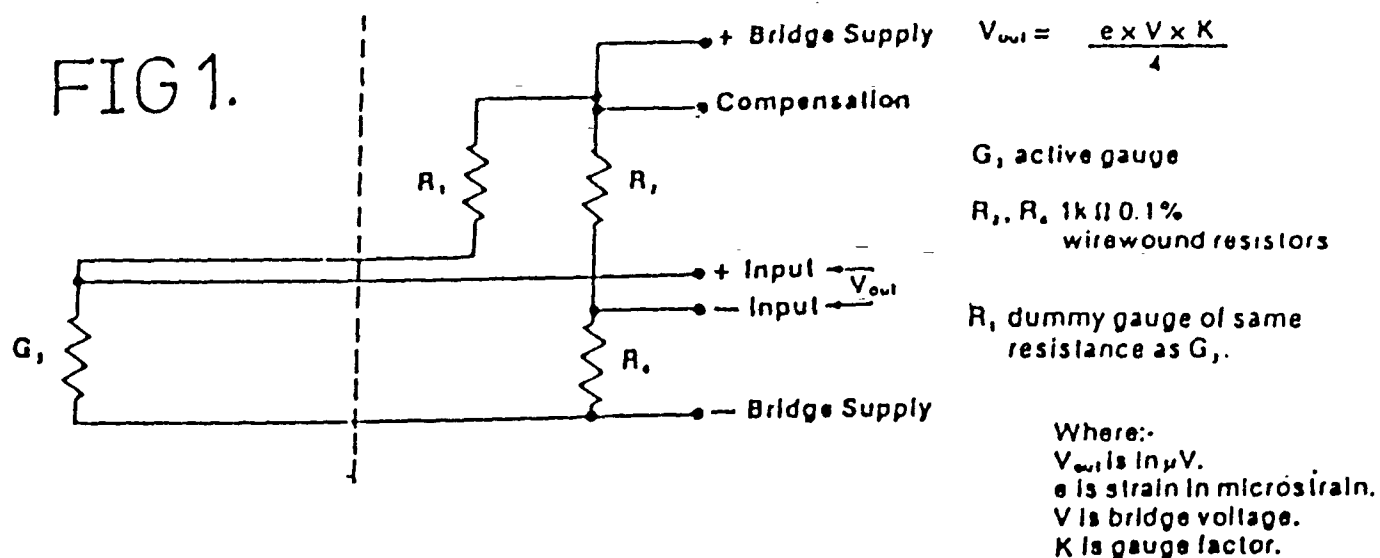
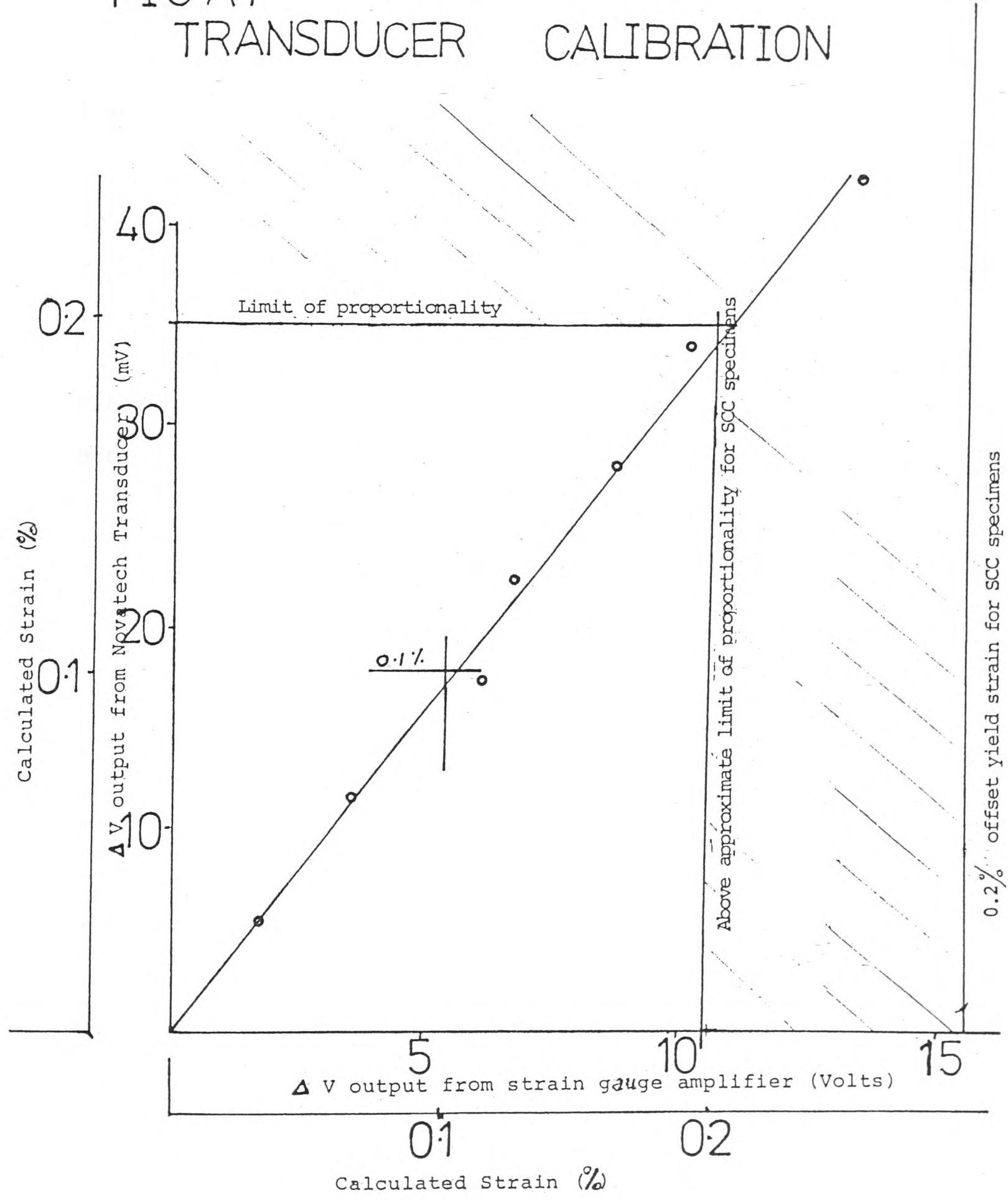


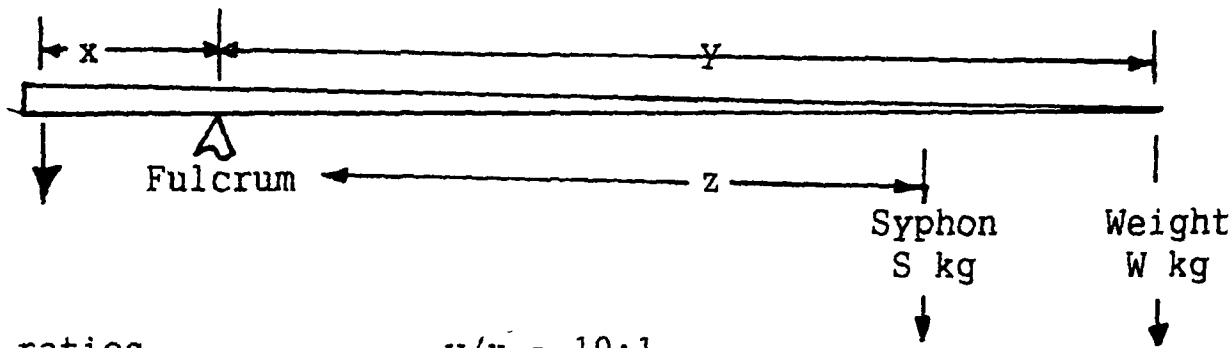
FIG A.1
TRANSDUCER CALIBRATION



Appendix 3

Calculation of the applied stress level in SCC tests.

The stress applied to specimens was calculated in terms of the measured yield stress in the following way.



Beam ratios $y/x = 10:1$
 $z/x = 9.5:1$

Total force applied to the specimen $L = (W \times 10 \times 9.8) + (S \times 9.5 \times 9.8) \text{ N}$

Cross sectional area of specimen $A = w \times t \text{ mm}^2$

w = cross section width (5 to 8 mm)

t = cross section thickness (0.35mm)

The effect of the ribs was ignored.

Measured yield stress of sensitised 20%Cr,25%Ni,0.7% Nb = 300 Nmm^{-2}

Stress applied to specimen in terms of yield stress

$$\frac{L \times 100}{A \times 300} \quad \% \text{ of the yield stress}$$

Appendix 4. Surface Intergranular Attack in Strauss tests.

In this section, anomalous results that may arise from Strauss tests are described. The purpose of describing such results is to demonstrate the care required in Strauss test experiments, and to show why specimens were electropolished during the preparation of stress corrosion test specimens. Furthermore, such results show that sensitisation may be a surface phenomenon only, where the bulk of the material remains unattacked.

It was found that Strauss testing of some 20% Cr, 25% Ni 0.7% Nb stainless steel specimens in the annealed condition could result in surface IGA, though the bulk of the material was resistant if the surface was removed and the specimen again tested. This observation cannot be explained by the presence of carbides at grain boundaries. The observed phenomenon is due to changes in the chemical composition of the surface layer which take place during the anneal at 1050°C.

Air may be present (though at low partial pressure) due to insufficient evacuation of the silica tube prior to heat treatment.

During this treatment a Cr-rich scale may form at the expense of Cr content at grain boundaries, and as a result the sensitivity of the material to IGA corrosion can increase. To investigate this phenomenon thin wall AGR clad was annealed at 1050°C in either an air atmosphere or an argon atmosphere then water quenched. Samples were then taken and taper sectioned at a slight angle to the surface. Samples were Strauss tested to determine the thickness of the layer sensitive to IGA.

Fig. 1 shows a sample of tube material after a 1050°C anneal in air. Etched-out boundaries are seen on the surface whereas the bulk remains unetched by the dilute HNO_3/HCl etchant. In samples where the surface was removed by either electro-polishing or mechanical grinding or annealed in argon before etching, IGA was not seen. Preferential attack at grain boundaries is seen to a depth of several grain diameters. Fig. 1b shows an optical section of the same sample after a 72 hr Strauss test. Attack runs in about one grain diameter (12 microns). Fig. 1c shows the same sample where the surface was ground at an inclined angle after treatment and before testing. It may be seen that the only part of the sample attacked is that near the surface, the bulk remains unattacked.

Figs. 2 and 3 show that a range of surface morphologies may result after heat treatment in insufficiently inert atmospheres. All samples were treated via a 1050°C anneal in slow-flowing Ar followed by 500 hrs under vacuum at 550°C. Figs. 2a and b show that not all boundaries are depleted to an extent sufficient to cause attack and a variation of the extent of attack is seen. Dissolution-rounded grain boundary edges are seen in fig. 2b. The width of IGA is greater than that seen for samples heat treated using the standard procedure, and

speckles of the oxide remain on the surface. Fig. 3 shows that if the annealing atmosphere is more inert grain boundary attack over the surface is more regular, though still differs from material heat treated in an inert atmosphere. Fig. 4a shows a sample that was annealed and only aged for 50 hrs at 550'C. Surface attack is much less, indicating that attack shown in figs. 2 and 3 is not only due to oxidation of the surface, but due additionally to Cr depletion from carbide precipitation. Fig. 4b shows the surface of this sample which was ground back, and then tested. It is notable that the extent and depth of attack resulting from oxidation is variable from boundary to boundary.

The surface corrosion seen in these tests is due to the changes in the chemical properties of the surface which take place during heat treatment such as oxidation and scale formation. Electron probe microanalysis showed that as a result of annealing, samples formed a Cr-rich scale. The formation of such a scale requires diffusion of Cr from the bulk of the material to the surface. Diffusion takes place faster along grain boundary paths which operate as a collector plate mechanism. Electropolishing removes this surface chemical inhomogeneity and as a result IGA is not seen. Samples for low frequency cyclic loading stress corrosion experiments were annealed in a fully inert atmosphere and electropolished before testing in case the presence of such a Cr-depleted surface layer favoured initiation of stress assisted corrosion attack.

Figure 1.4

Surface attack on a sample of tube annealed at 1050'C in air for 30 minutes.

- A. Etched in dilute HNO_3/HCl solution
- B. Strauss tested
- C. Ground at an inclined angle to the surface and Strauss tested.

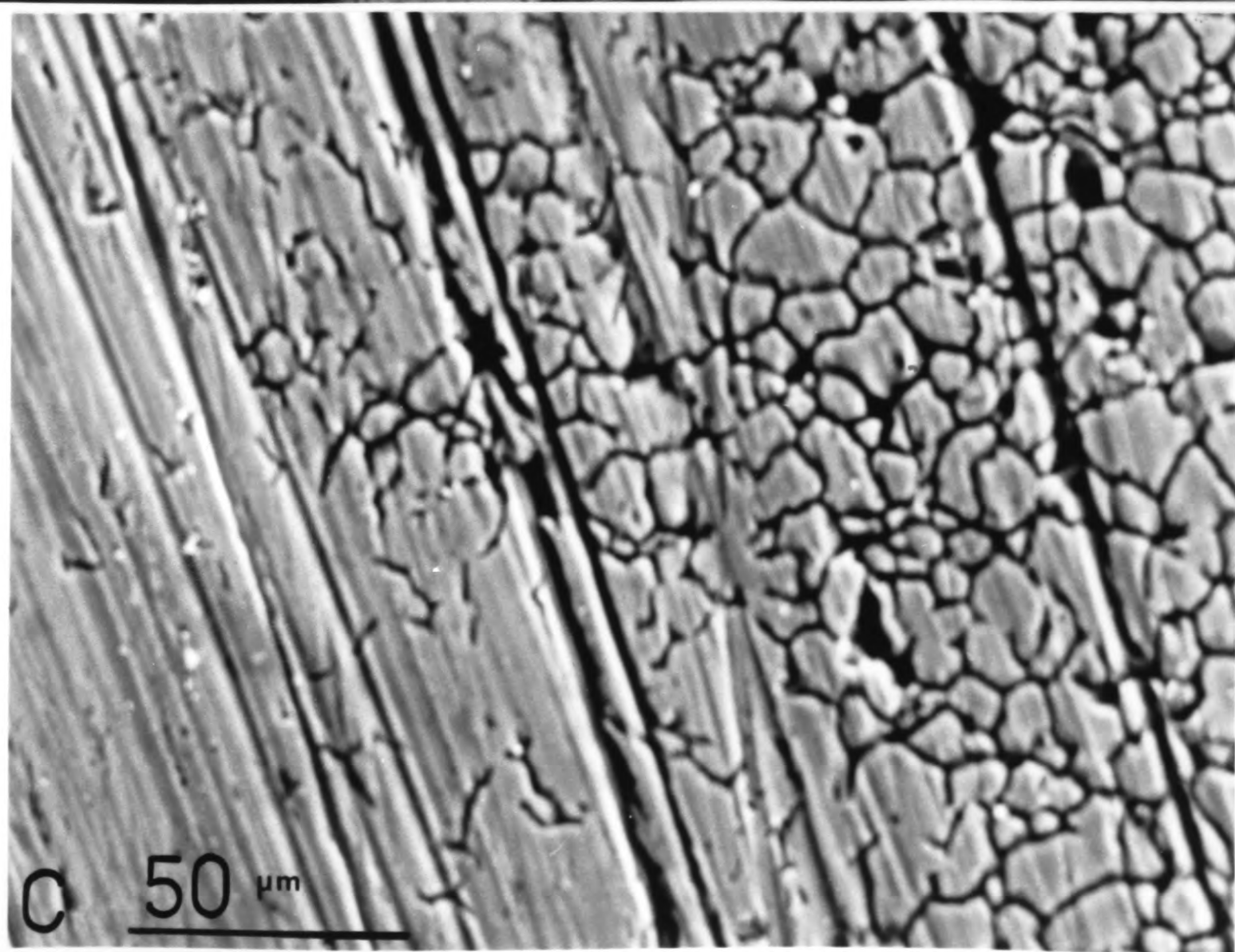
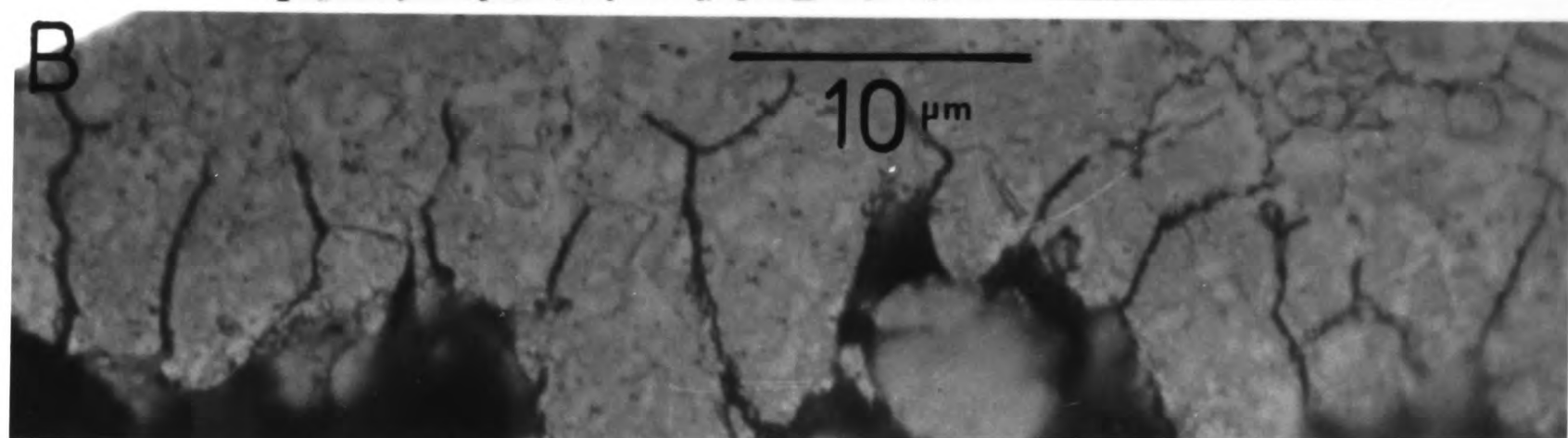
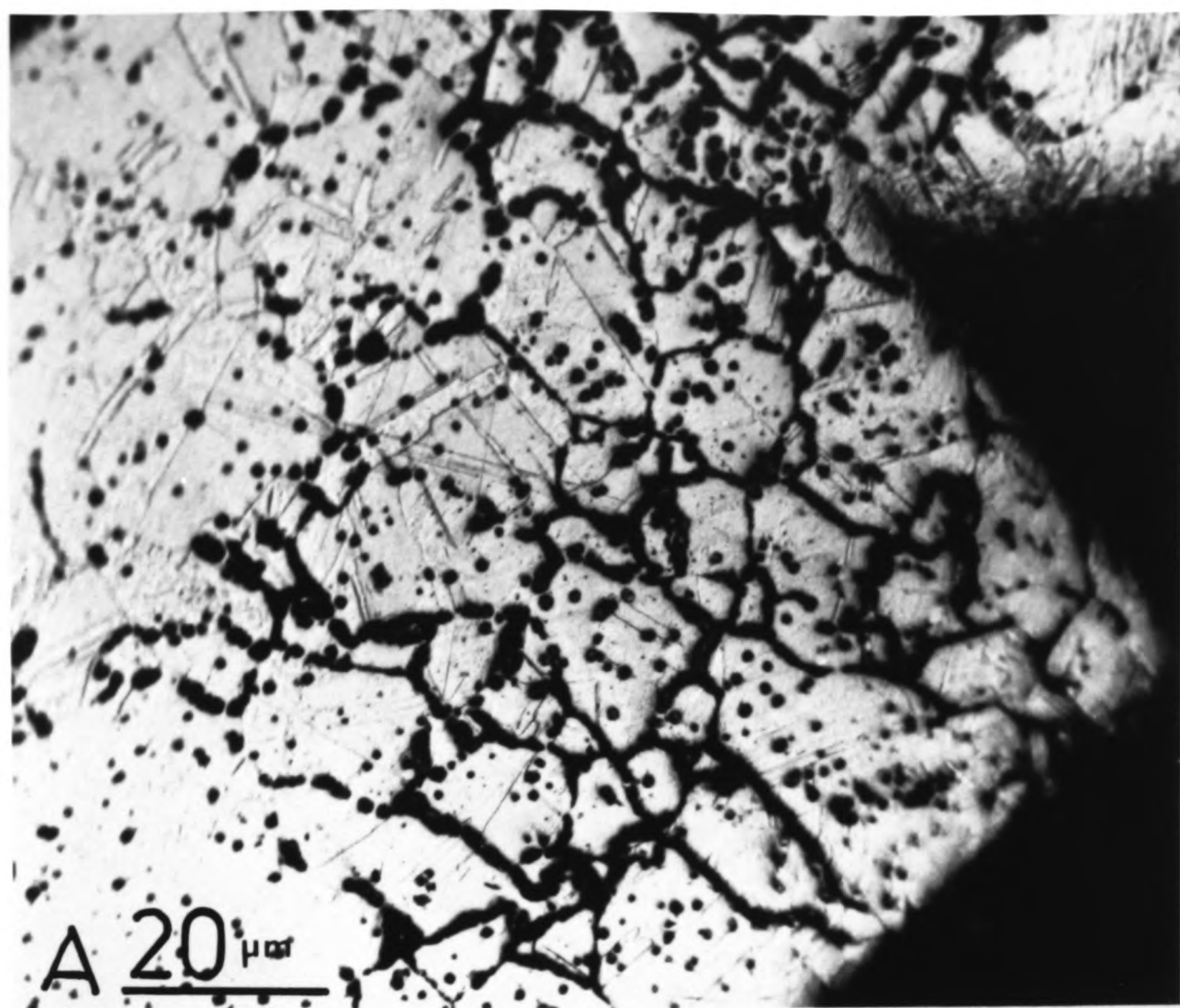
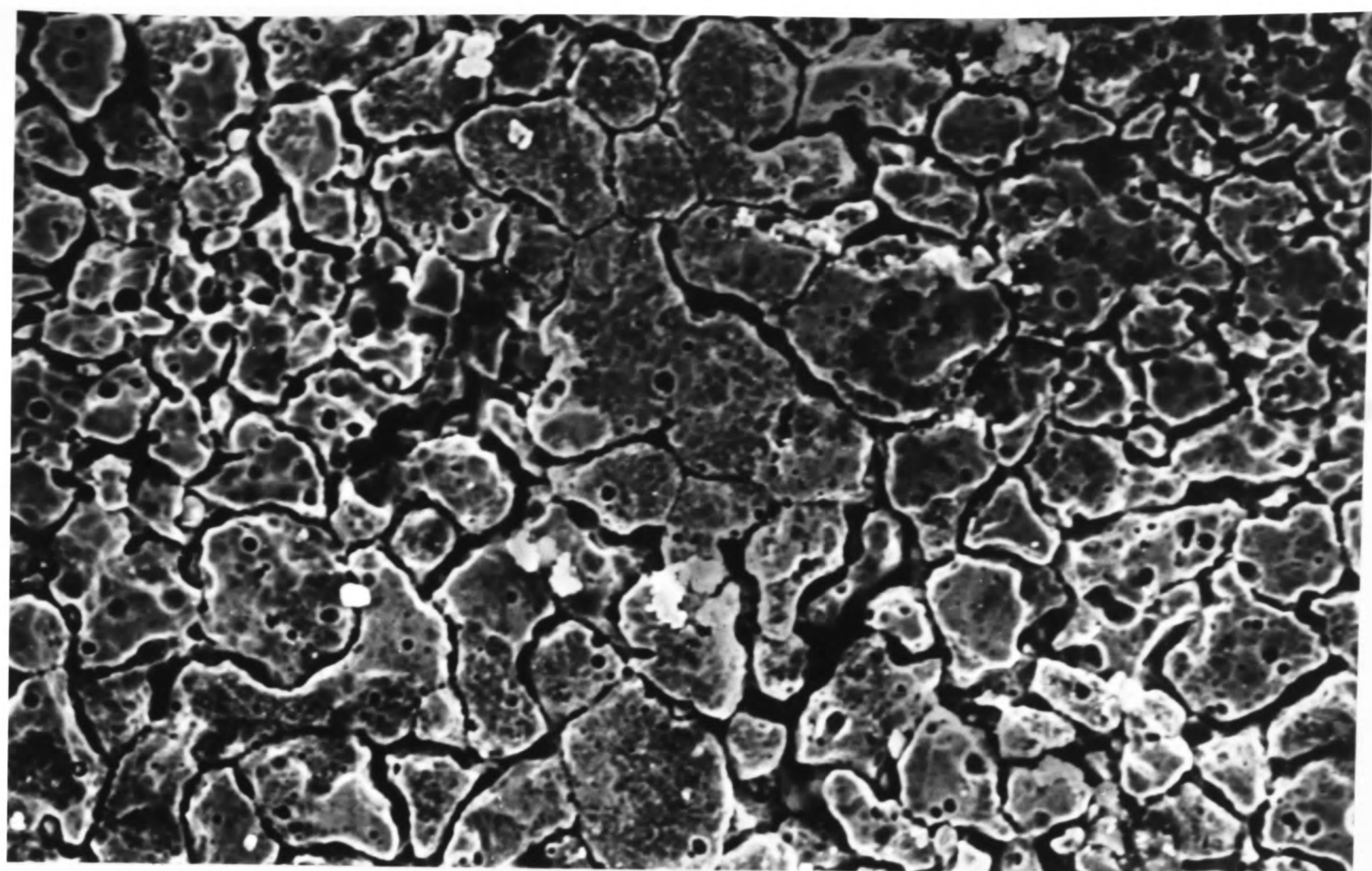


Figure 2.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes in an air/argon mix, aged at 550'C for 500 hours and then Strauss tested for 72 hours.

Considerable variation is seen in the extent of attack from boundary to boundary.



A

25 μm

A'



B

15 μm

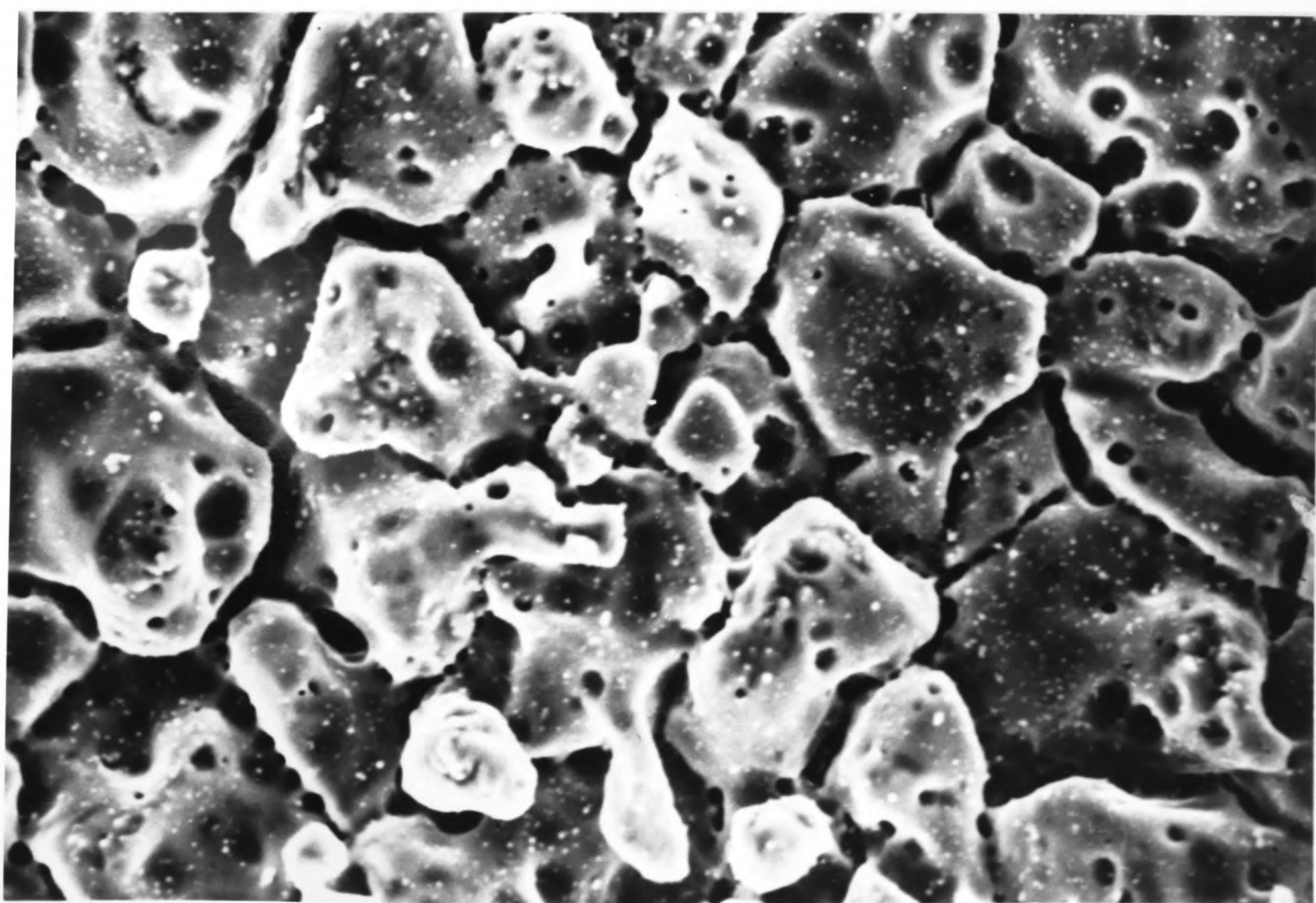
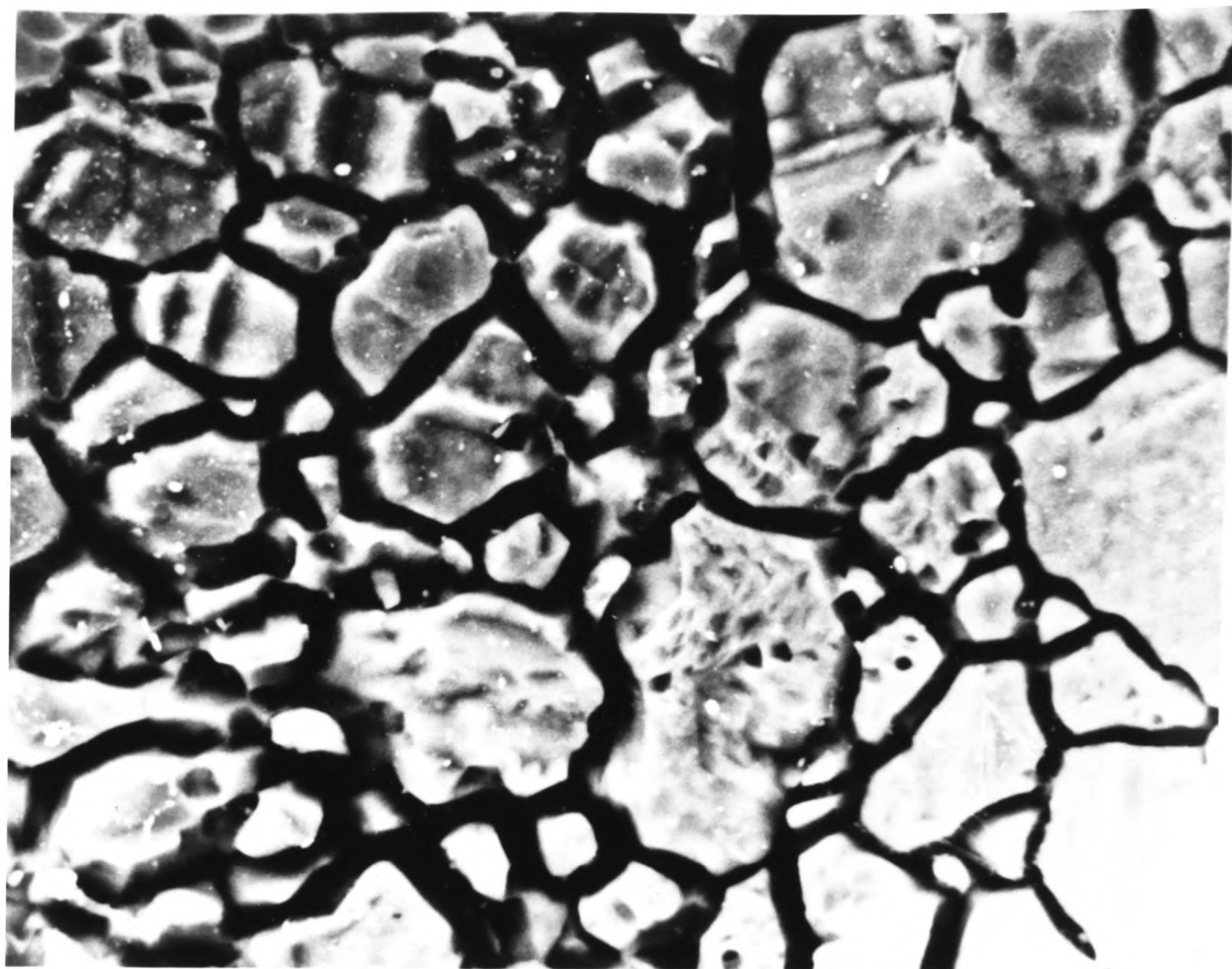


Figure 3.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes in an air/argon mix then aged at 550'C for 500 hours and Strauss tested for 72 hours.



A
B

15 μm

20 μm

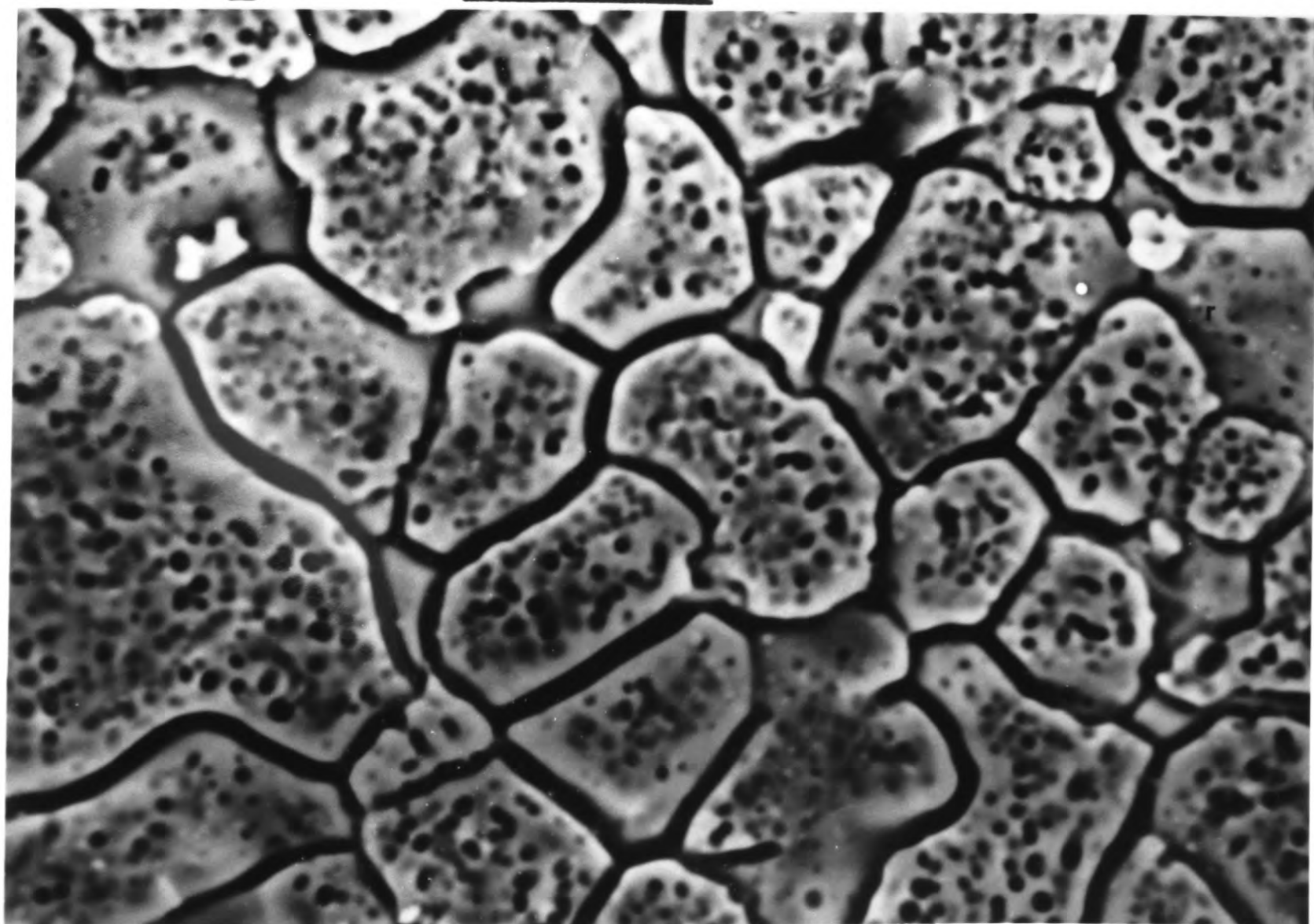
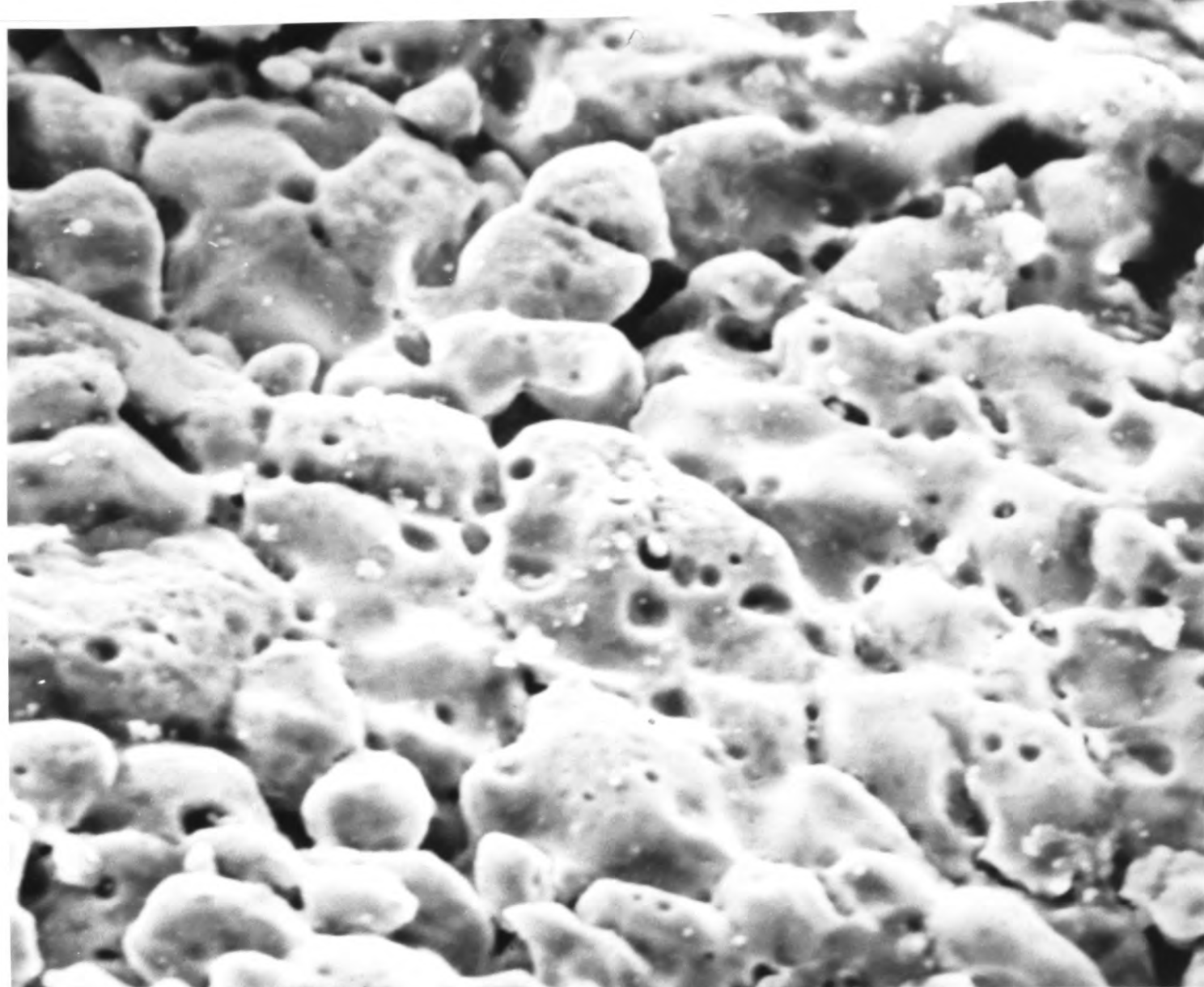


Figure 4.4

SEM micrograph of the surface of tube annealed at 1050'C for 30 minutes in an air/argon mix then aged at 550'C for 50 hours and

A. Strauss tested for 72 hours

B. Ground back and Strauss tested for 72 hours



A

20 μm

B

50 μm

