

**THE HIGH TEMPERATURE OXIDATION OF CHROMIUM AND CHROMIUM
IMPLANTED WITH CERIUM.**

A Thesis submitted for the degree of Doctor of Philosophy

by

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ABSTRACT

The oxidation of pure chromium and of chromium implanted with cerium ions has been investigated at temperatures between 700°C and 1000°C using techniques of light and electron microscopy. The differences in growth and morphology of the oxides that form on the two substrates have been studied in order to determine the mechanisms whereby the cerium addition increases the protective nature of the chromia scale. A heat treatment of 3 hours in hydrogen at 1500°C has been found to be necessary to convert the electrolytic chromium used in the study into a good substrate for oxidation. The surface microstructures of the implanted and unimplanted metals have been studied and the chromium has been found to have a large grain size and a strong $\langle 111 \rangle$ fibre texture; the cerium-implanted metal has been found also to have a thick, amorphous native oxide film.

The nucleation and growth of the oxide film has been studied in-situ using an environmental cell in a 1MeV transmission electron microscope. The initial oxide film forms with a preference for its {0001} plane to be parallel to the {111} plane of the metal and its grain size varies between 50 and 400 nanometres. The grain size of the oxide film on the cerium-implanted metal is initially smaller than that on the unimplanted metal.

The oxide film on unimplanted chromium is generally adherent but contains areas where the film has buckled. Contamination of the surface is found to be the major cause of decohesion. Cerium implantation causes the oxide to become fully adherent and reduces the thickness of the oxide films in comparison to equivalent unimplanted specimens. Cerium has been found to segregate to the grain boundaries in the oxide and it is thought that this gives rise to blocking of the diffusing cation species, thereby providing the increased protection.

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1 INTRODUCTION

As a commercial material, chromium has found only two major uses: in the bright electroplating of components and as an alloying element. Chromium is a valuable alloying element since the selective oxidation of the chromium to form a chromia scale gives good corrosion protection to many industrially important alloys such as stainless steels and some nickel-based superalloys. The oxide film is, thus, of high technological importance and a thorough understanding of its properties and growth mechanism is needed. The best method for achieving this is to study the oxidation of the metal in a pure form.

The addition of certain oxygen-active elements such as yttrium and cerium to the metal vastly improves the protective capability of the oxide film by reducing the growth rate of the film and increasing its adherence to the metal substrate (1). The reasons for these improvements are not yet fully understood. There has been much research on the effects of adding these elements to alloys containing chromium but little on the pure metal itself. The oxygen-active elements have their main effects in the surface of the metal and one of the most efficient methods of introducing an active element into the surface of a metal is by ion-implantation.

This study investigates the effects on the oxidation of pure chromium of implanting the metal with a large dose of cerium ions. In order to do this, the oxidation behaviour of the pure metal itself needs to be fully understood and the effects of ion-implantation need to be separated from the effects of the cerium addition. To this end, this study consists of an investigation of the oxidation behaviour of the pure metal, of pure chromium implanted with a neutral species and of pure chromium implanted with cerium. The neutral species chosen for implantation is chromium as the only effect this will have will be physical.

1.1 Chromium

Before the oxidation of the metal can be discussed, the properties of the substrate need to be considered. If the metal is to be used as a model, it needs to be as pure as possible as other elements may affect the oxidation process. Chromium is a transition metal of atomic number 24. It has a body centred cubic structure up to 1840°C whereupon it undergoes a phase transformation to a face centred cubic structure. Of its four naturally occurring isotopes, the most abundant is that of mass number 52 (2). A list of the major physical properties of chromium is given in table 1 (2-5).

A comprehensive review of the properties of chromium metal and the production of high purity chromium is given in the book by Sully and Brandes (6)

Table 1

A table of the physical properties of chromium and chromium(III) oxide (2-5)

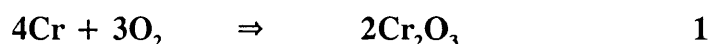
Chromium	
Melting point	1875°C
Boiling point	2860°C
Phase transformation temperature	1840°C
Structure below 1840°C	b.c.c., cI2 (Im3m), a = 0.28846 nanometres at 20°C
Structure above 1840°C	f.c.c., a = 0.38 nanometres
Density at 20°C	7190 kgm ⁻³
Young's modulus	250 GPa
Thermal conductivity	67 Wm ⁻¹ K ⁻¹
Coefficient of linear thermal expansion	(7.3 + 0.00829T)x10 ⁻⁶
Chromium(III)Oxide	
Melting point	2266 ± 25°C
Boiling point	4000°C
Structure	corundum, D5 ₁ , a = 0.4954 nanometres, c = 1.3584 nanometres
Density at 20°C	5210 kgm ⁻³
Young's modulus	292.7 GPa
Coefficient of linear thermal expansion	(6.7974 + 0.0008468T)x10 ⁻⁶

which deals with all of the work on the pure metal carried out prior to 1967. The two main methods of producing chromium of high purity are by electrolytic deposition and by the thermal decomposition of chromium iodide. This latter method is only practical on a small scale due to cost and production time; iodide chromium can be used for oxidation purposes although at higher cost than electrolytic chromium. Pure chromium manufactured by a powder metallurgical route has recently become available but details of its production are still confidential.

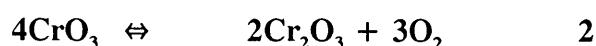
Electrolytic deposition is the most widely used method of production, mainly for hard and bright plating of components and both thick and thin coats can be achieved. The majority of the technical literature about chromium published since 1967 has been on electroplating (7 - 10) and the electrolytic chromium used in oxidation studies is just a thicker electrodeposit that has been stripped from the cathode. The electrolytic bath used in electrodeposition contains chromic acid and sulphuric acid in a ratio of roughly 100:1, the metal is deposited onto a cathode, usually copper, and the anodes are either antimonial lead or a tin/lead alloy. The purity of the final electrodeposit is dependent upon the purity of the acids used in the bath and very low levels of metallic impurities are possible; large quantities of oxygen and hydrogen, though, are absorbed by the metal during deposition, the amounts depending upon the electroplating conditions used in the bath. The metal is also highly microcrystalline and contains a large amount of inherent strain which is relieved by cracking of the metal. These problems and their solutions are covered well by Sully and Brandes (6) and updated by references (7 - 10).

1.2 Chromium Oxide

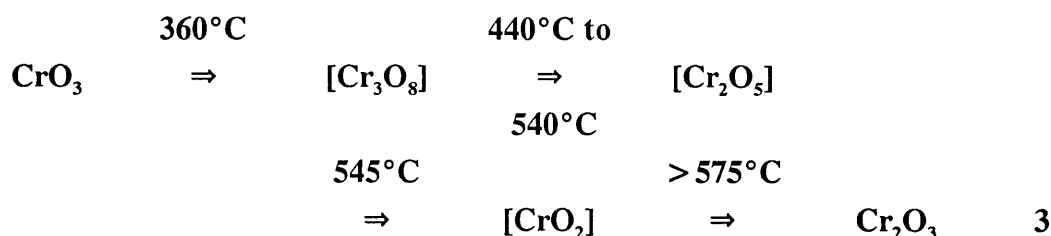
When chromium metal is heated in oxygen a layer of chromium oxide forms on the surface via the reaction:



A list of the major physical properties of Cr_2O_3 are given in table 1 (2,3,4,5). There have been many other forms of chromium oxide reported in the literature apart from Cr_2O_3 (11,12) the most stable of these being CrO_3 , Cr_3O_8 , Cr_2O_5 and CrO_2 (11). All of these other forms, except CrO , are intermediate between Cr_2O_3 and CrO_3 and they will all decompose to Cr_2O_3 on heating. At high temperatures, the only solid oxide formed is Cr_2O_3 , CrO_3 melts at 196°C and then decomposes into a mixture of Cr_2O_3 , O_2 and CrO_3 (11) via the reversible reaction:



the other oxide species are all vapour species. The decomposition of CrO_3 at high oxygen pressures and low temperatures is reviewed by Chamberland (11). The other metastable forms of chromium oxide exist mainly at higher oxygen pressures and Chamberland (11) gives the full decomposition route of CrO_3 as:



Chamberland also characterises the structure, properties and reactions of CrO_2 . The structure and properties of Cr_3O_8 and Cr_2O_5 are detailed by (13). Above 1000°C in excess oxygen, reaction 2 proceeds in reverse and Cr_2O_3 volatilises (12,14-16). The volatilising species was first determined by Caplan and Cohen (14) and the mechanisms and kinetics of the process were determined by Graham and Davis (15), Stearns, Kohl and Fryburg (12) and Grimley, Burns and Inghram (16). The rate determining step in the process is the gas phase transport of CrO_3 across the stagnant boundary layer that forms at the surface of the oxide and Greskovich (17) quotes the rate constant for the reaction as:

$$\log K = \frac{-2.46 \times 10^4}{T} + 6.16 \quad 4$$

1.3 Scale Morphology

The morphology of the oxide film that forms during the high temperature oxidation of chromium is varied and its microstructure and adhesion has been reviewed by Hindam and Whittle (18). Most workers have noted the buckled and deformed appearance of the scale and have tried to explain it in terms of various stress-generating mechanisms. The earliest studies of the oxidation of pure chromium (19-22) mention that the oxide scale was found to have spalled on cooling but do not otherwise mention the appearance of the scale. Of the later studies, only two (23,24) have reported adherent, undeformed oxide scale. The amount of deformation observed depends mainly upon the surface preparation and the oxygen partial pressure that was used in the study.

Electropolished specimens tend to produce the most highly deformed scales, ranging from partially adherent scales with as many as eight distinct layers of oxide formed by repeated through-scale cracking and re-oxidation of the exposed metal

surface (25), to a single, completely non-adherent scale growing via chromium evaporating from the surface across to the underside of the scale (26). Etching a surface that has been electropolished can cause a complete transformation of morphology to the production of a scale that has porous, polycrystalline nodules among areas of thin, adherent, monocrystalline oxide (25,26). The majority of scales that have been reported on mechanically polished surfaces have been deformed, with two or three layers (27,28). The multilayered scales are generally cracked on the outside with a number of the cracks healed by the growth of new oxide. Several authors have reported whisker formation on the outer surface of the oxide (28-30). This is thought to be due to the surface diffusion of cations along a tunnel centred around a core of a screw dislocation or of a bundle of dislocations (30). The outer surfaces of some scales were also found to be porous (28,30).

At lower partial pressures of oxygen, the ability of the scale to deform seems to increase. Lillerud and Kofstad (29) and Cadiou and Paidassi (31) both used thermally etched surfaces in their oxidation studies; the oxide formed at low pressures reported by Lillerud and Kofstad had deformed substantially whereas that reported by Cadiou and Paidassi at atmospheric pressure had suffered far more through-scale cracking. Hindam and Whittle (28) also noted that the scales formed during oxidation at low oxygen pressures were deformed and non-adherent but were only single layered; no cracking of the scale had occurred. This increase in the ability of the scale to deform is thought to be due to the creep rate increasing with decreasing oxygen partial pressure (29).

The grain size of the oxide scales formed after short periods are reasonably uniform across the scale thickness (28,32). Cotell noted that for oxide scales formed after 18 hours at 900°C, the grains were approximately equi-axed and between 100 - 200 nanometres in size. After longer times, grain growth occurs (29). Caplan and Sproule (26) reported that, after 100 hours, the grain size of the oxide formed varied from 500 nanometres at the scale/metal interface to 2 - 5 micrometres at the outer surface.

The spallation of the scales occurs only on cooling (29) and is due to the difference between the thermal expansion coefficients of the oxide and metal. The adherent areas of the scale spall explosively whereas the non-adherent areas tend to break off as a whole (25). The cause of the oxide deformation is more controversial. The stress that causes the deformation occurs during oxidation and, thus, must be connected with the growth mechanism of the scale. The stress must be lateral and compressive. The most widely accepted mechanism is that the stress is generated by new oxide forming in the interior of the oxide scale due to a countercurrent of oxygen down fast diffusion paths (33,34). The fast diffusion paths may be grain boundaries (33) but may also be microcracks or pores (34). Atkinson (35) has shown that oxide

can form within the oxide scale from the interaction of defects if both are interstitials or if one is an uncharged interstitial and the other is a charged vacancy. Microcracks can develop in growing oxide films as a result of grain growth and plastic deformation which can then act as paths for oxygen diffusion leading to increased stress in the scale (36). The formation of microcracks is only likely to occur, though, for relatively thick scales and cannot explain the deformation seen in oxide films only 12 nanometres thick (37).

Evans (38) and Srolovitz and Ramanarayanan (39) have analysed the formation of new oxide at grain boundaries in the oxide film during oxidation and have determined that, for thin scales, the growth stress is very sensitive to the oxide film thickness. Srolovitz and Ramanarayanan (39) concluded that the oxide film will either fail by buckling, the stress generation will cease or the growth mechanism of the oxide will change in order to minimise the generated stress. From descriptions of the oxide scale morphology that occurs on oxidised chromium, it appears that the oxide film fails by buckling in preference to the other two mechanisms. Evans (38) detailed a stress generation mechanism whereby the stress was caused by oxide intrusions into the metal. These have not been observed in practice.

There have been several reviews on the general subject of stresses in oxide scales; the most comprehensive is that by Stringer (40) who discussed all aspects of stress generation and relief in growing oxide films, the most recent is that by Evans and Cannon (41). A general review of the mechanical behaviour of oxide coatings is given by Evans, Crumley and Demaray (42); Robertson and Manning (43) studied the theoretical basis of the adherence of oxide films to metal substrates and their paper includes valuable data on the properties of Cr_2O_3 . Very few workers have investigated stresses in oxide films formed on pure chromium, probably due to the difficulty in forming adherent oxide scales. Stout, Gerberich, Lin and Lii (3) studied the residual stresses in chromia films grown on chromium at 900°C and found them to be compressive. They concluded that a significant component of the residual stress is a compressive growth stress. Most of the scale failure on pure chromium is by buckling of the oxide film; Evans and Hutchinson (44) have analysed the mechanics of the buckling process. There has been very little work carried out on the origin of the interfacial separation needed to initiate buckling (41).

1.4 Scale Growth

The growth mechanism for Cr_2O_3 on chromium, its defect structure and the nature of the diffusing species have been the subjects of several reviews, the most notable of which are by Hindam and Whittle (18) and by Atkinson (45). The oxide scale on chromium has been found to grow by the outward diffusion of cations with

the oxide forming at the scale/gas interface. The most frequently used method of determining the direction of growth has been to place inert markers on the surface of the metal prior to oxidation and to determine their position after a scale has developed. Hagel (27) quotes Seybolt and Felton as both having found that the Cr_2O_3 scale grows at the scale/gas interface using platinum markers. There was some debate as to whether there was an anion contribution to scale growth; Phalnikar, Evans and Baldwin (46) argued that the scale grew by the inward diffusion of oxygen and Caplan, Harvey and Cohen (25) used an analogy of the Rhines and Wolf (33) theory to postulate some anion flow in order to explain the buckling of the oxide scale.

More recently, other methods have been used to determine the growth mechanism of chromium oxide. These involve sequential oxidation in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ and then determining the position of the two isotopes in the scale. The first method of determining the distribution of the isotopes was a nuclear method, using the $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$ and the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reactions (47,48). The second method, now more commonly used, is to use Secondary Ion Mass Spectrometry (SIMS) to detect the variation in the amount of the tracer with depth (49). All found that the scale grows by the outward diffusion of cations but Graham, Eldridge, Mitchell and Hussey (49) determined that, for an adherent scale, approximately 1% of the scale was formed by inward anion diffusion.

The tracer diffusion data for oxygen and chromium in Cr_2O_3 are plotted in figure 1.4.1 as tracer diffusion rate versus inverse temperature and the activation energies are given in table 2. These diffusion experiments were carried out using both polycrystalline and single crystal Cr_2O_3 . Apart from the single crystal data found by Walters and Grace (52), the diffusion rates for similar processes lie in similar areas of the graph. The diffusion rate for chromium in sintered Cr_2O_3 determined by Hagel and Seybolt (51) agrees with that determined by Lindner and Åkerström (50) yet the diffusion rate in hot pressed Cr_2O_3 is quite different. Kofstad, in his review of the diffusion data (60), and Hagel and Seybolt both discuss this and believe that the difference is due to the hot pressed oxide being more dense; they conclude that the diffusion data from the hot pressed oxide is a true representation of the tracer diffusion rate of Cr in Cr_2O_3 . Hay, Hicks and Holmes (55) give chromium diffusion rates that are in rough agreement with the data of Hagel and Seybolt (51). They also express reservations regarding the validity of the diffusion data up to that time (50-52,56) for reasons of sample purity and equilibrium but do not give any further details.

Hoshino and Peterson (53) and then Atkinson and Taylor (54) determined the diffusion rate of Cr in single crystal Cr_2O_3 and found that the rate was five orders of magnitude lower than the previous results. This discrepancy in the results was thought to be due to grain boundary diffusion in the polycrystalline samples but this

Figure 1.4.1

A graph of the diffusion rates of oxygen and chromium through Cr_2O_3 , determined by previous workers, plotted on a logarithmic scale against inverse temperature.

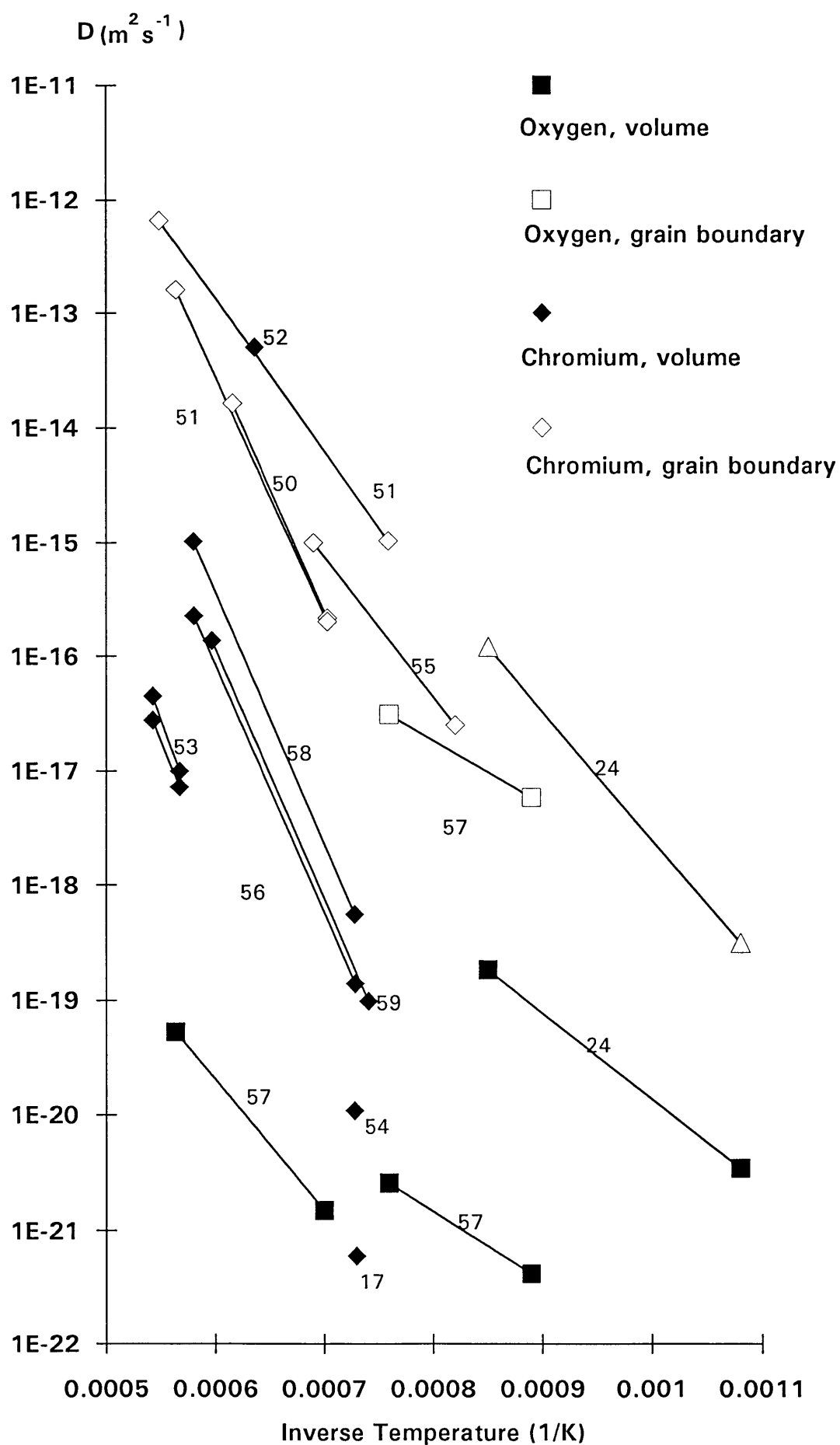


Table 2

A table giving the samples used, the activation energies measured and the temperature range used in the determination of the diffusion rates plotted in figure 1.4.1.

Reference	Sample	Measured activation energy kJmol ⁻¹	Temperature range °C
Chromium			
Lindner and Åkerström (50)	polycrystal, sintered	420	1150 - 1350
Hagel and Seybolt (51)	polycrystal, sintered	420	1150 - 1500
Hagel and Seybolt (51)	polycrystal, hot pressed	255	1045 - 1550
Walters and Grace (52)	single crystal		1300
Hoshino and Peterson (53)	single crystal	500	1490 - 1569
Atkinson and Taylor (54)	single crystal		1100
Hay, Hicks and Holmes (55)	polycrystal	250	950 - 1150
Greskovich (17)	single crystal		1100
Oxygen			
Hagel (56)	volume diffusion	420	1100 - 1450
Socket, Saal and Heilmaier (57)	polycrystal, volume diffusion	125	850 - 1050
Socket, Saal and Heilmaier (57)	polycrystal, grain boundary diffusion	100	850 - 1050
Schwanke (in 55)	single crystal	218	1100 - 1500
Hagel, Jorgensen and Tomalin (58)	sintering, volume diffusion	423	1100 - 1450
Burton and Reynolds (59)	creep, volume diffusion	468	1077 - 1402
Hussey, Mitchell and Graham (24)	polycrystal, volume diffusion	143	650 - 900
Hussey, Mitchell and Graham (24)	polycrystal, grain boundary diffusion	214	650 - 900

does not explain why the single crystal results of Walters and Grace (52) are similar to the polycrystalline results. The result determined by Greskovich (17) is in good agreement with the rates found by Hoshino and Peterson (53). A parabolic rate constant for oxide growth can be calculated from the diffusion data and the polycrystalline diffusion rates agree well with the rate constants found by experiment (54). Rate constants calculated from the later single crystal diffusion rates (53,54) are between four and seven orders of magnitude lower than the measured parabolic rate constants. This leads to the conclusion that the cation transport through the polycrystalline oxide film, during growth, is via grain boundaries (45). Similar results have been found for NiO (61) and microstructural evidence (30) also supports this view. Evidence for the growth of monocrystalline oxide on chromium by dislocation pipe diffusion through the oxide layer is given by Przybylski and Yurek (62) and the parabolic rate constant for this was an order of magnitude lower than for the growth of polycrystalline oxide, implying that the diffusion paths in the polycrystalline oxide allowed faster diffusion than did dislocations. The single crystal diffusion rates determined by Hoshino and Peterson (53) and by Atkinson and Taylor (54) appear to be in rough agreement when the lines on the graph are extrapolated to lower temperatures.

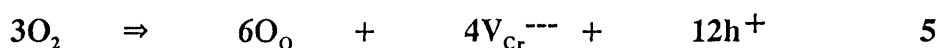
Oxygen diffusion rates in Cr_2O_3 have been measured by tracer diffusion through compacts (56,57), by Burton and Reynolds from Nabarro-Herring creep rates (59), by Hagel, Jorgensen and Tomalin from initial sintering rates (58) and by Hussey, Mitchell and Graham from SIMS analysis of ^{18}O tracer distributions in oxide scales grown on pure chromium (24). In contrast to the chromium tracer diffusion rates, the oxygen diffusion rates are more contradictory. The volume diffusion data determined by Hagel (56) are in good agreement with the volume diffusion rates determined from sintering by Hagel, Jorgensen and Tomalin (58) and by Burton and Reynolds from creep (59). The volume diffusion rates determined by Sockel, Saal and Heilmaier (57) are slightly different to the rates determined by Schwankeⁱⁿ (57); although the lines are in approximately the same area of the graph, the activation energies for the two sets of data differ by a factor of two; both are in disagreement with the other volume diffusion data. The volume diffusion data determined by Hussey, Mitchell and Graham (24) are two orders of magnitude higher than the volume diffusion data determined by Sockel, Saal and Heilmaier (57) whereas these authors' sets of grain boundary diffusion data are more in agreement.

The diffusion rates determined by Hussey, Mitchell and Graham (24) should be the most relevant and possibly the most accurate, being the only rates determined from oxide grown on chromium, in contrast to the other rates determined from compacts of Cr_2O_3 produced by another route. It has previously been believed (58) that the rate of oxygen diffusion in Cr_2O_3 is at least three orders of magnitude below

that for chromium diffusion whereas, from the data given in the figure, it appears that the diffusion rates for the two species are similar, with oxygen volume diffusion possibly even being more rapid than chromium volume diffusion. It must be noted that the data determined by Hussey, Mitchell and Graham (24) was for transport down fast diffusion paths, not necessarily grain boundaries. Kofstad (36) has determined a mechanism whereby microchannels can open in the scale and this may allow an increased diffusion rate.

Hussey, Mitchell and Graham (24) report that the net transport of oxygen in their oxidation experiments was several orders of magnitude too low to be responsible for oxide growth and that the diffusion rates of oxygen are also too low to account for the observed oxidation rates. They also report that the net transport of oxygen was always around 100 times lower than the net transport of chromium and suggest that this indicates a coupled diffusion process. In a given time period, the net transport will be a function of both the diffusion coefficient and the number of ions available for transport. As the diffusion coefficients for chromium and oxygen diffusion along fast diffusion paths appear to be similar, figure 1.4.1, the control of the oxidation process by outward cation diffusion is probably due to the low numbers of available oxygen ions. The diffusion rates for chromium have not yet been determined in a growing oxide film and so there can be no real comparison with the diffusion data determined by Hussey, Mitchell and Graham (24).

Having determined the ionic species responsible for the growth of the oxide and the diffusion path, the nature of the diffusing point defect species is still a subject for investigation. Kofstad (60) reviewed the early work on the point defect properties of oxygen and chromium in Cr_2O_3 . The deviation from stoichiometry in Cr_2O_3 has been measured by Hay, Hicks and Holmes (55) and by Greskovich (17). Hay, Hicks and Holmes (55) determined the nonstoichiometry to be approximately 10^{-4} mol fraction and Greskovich (17) determined the formula of chromium oxide to be $\text{Cr}_{2-\delta}\text{O}_3$ with $10^{-4} > \delta > 10^{-5}$ at 1100°C with $10^{-1}\text{Pa} > p(\text{O}_2) > 10^4\text{Pa}$. The diffusion rates for the cationic species through the oxide at different oxygen partial pressures have also been investigated in order to determine the nature of the diffusing species. The diffusion rate will vary with oxygen activity in a different manner depending upon whether the diffusing species are interstitials or vacancies. For vacancies diffusing through Cr_2O_3 that is in equilibrium with the surrounding oxygen activity, the cation vacancies are formed according to:



$$K = \frac{A[\text{V}_{\text{Cr}}^{\text{---}}]^4[\text{h}^+]^{12}}{[\text{a}(\text{O}_2)]^3} \quad 6$$

with O_o denoting oxygen on oxygen sites, V_{Cr}^{---} denoting triply charged cation vacancies, h^+ denoting positively charged electron holes, K being the rate constant, A a constant of proportionality and $a(O_2)$ being the oxygen activity (63). In order for the oxide scale to be electrically neutral, the concentration of holes has to be three times the concentration of cation vacancies or, in the notation used here, the system has an electroneutrality condition of:

$$3[V_{Cr}^{---}] = [h^+] \quad 7$$

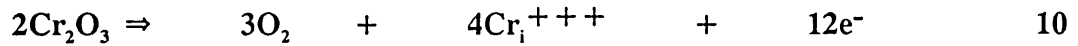
Which gives equation 6 as:

$$K = A'[V_{Cr}^{---}]^{16} / [a(O_2)]^3 \quad 8$$

and, so

$$[V_{Cr}^{---}] = K[a(O_2)]^{3/16} / A' \quad 9$$

The equivalent equations for interstitials are:



$$K = B[Cr_i^{+++}]^4[e^-]^{12}[a(O_2)]^3 \quad 11$$

with an electroneutrality condition of:

$$3[Cr_i^{+++}] = [e^-] \quad 12$$

so:

$$[Cr_i^{+++}] = B'[a(O_2)]^{-3/16} / K \quad 13$$

with Cr_i^{+++} denoting triply charged cation interstitials, e^- denoting electrons and B , B' being constants of proportionality. Thus, if the diffusion rates for cation transport through Cr_2O_3 are plotted against oxygen activity using logarithmic scales on both axes, then the graph should be a straight line with slope $+3/16$ if the diffusing species are vacancies and $-3/16$ if the diffusing species are interstitials (63).

Walters and Grace (52) measured the variation of the cation diffusion rate within a range of oxygen activities of 1×10^{-6} and 5×10^{-6} at a temperature of $1300^\circ C$ and determined that the diffusing species were vacancies. Hagel and Seybolt (51)

suggested that their data may imply that, below 1250°C, electron holes are the diffusing species. Kofstad and Lillerud (64) suggest that the data given by Walters and Grace (52) are open to interpretation due to the scatter in the results. They also re-analyse the results of Lindner and Åkerström (50) and Hagel and Seybolt (51), suggesting that these results are due to interstitial diffusion rather than grain boundary diffusion. Hoshino and Peterson (53) found that in a range of oxygen activities of 10^{-8} to 10^{-4} at 1570°C the diffusing species were cation vacancies; Atkinson and Taylor (54) determined that, at 1100°C, interstitials are the diffusing species below oxygen activities of 10^{-10} and vacancies above this activity. These results were all from experiments carried out upon Cr_2O_3 rather than on growing oxide scales.

The diffusing species in isolated Cr_2O_3 at different oxygen activities can be determined by other methods such as conductivity measurements and thermoelectric power measurements. The early work on the semiconducting properties of Cr_2O_3 has been reviewed by Kröger (65) who concludes that the pure oxide is n-type at low $a(\text{O}_2)$ and p-type at high $a(\text{O}_2)$ although, above 1200°C, the oxide is an intrinsic electronic conductor. This latter conclusion is directly contradicted by the later work of Hoshino and Peterson (53). If Cr_2O_3 is an electronic conductor then the diffusion rate of Cr ions would be proportional to $[a(\text{O}_2)]^{3/4}$ whereas Hoshino and Peterson (53) found that, at 1570°C, the diffusion rate is proportional to $[a(\text{O}_2)]^{3/16}$ implying that the oxide is p-type, with vacancies being the diffusing species. Thus it is more likely that Cr_2O_3 is p-type at all temperatures for a high $a(\text{O}_2)$.

Young, Gerretsen and deWit (66) have also studied the electrical conductivity of Cr_2O_3 and its variation with $a(\text{O}_2)$ at temperatures between 1000K and 1800K. They have also found that the oxide is n-type at low $a(\text{O}_2)$ with Cr interstitials being the main diffusing species and p-type at high $a(\text{O}_2)$ with Cr vacancies being the main diffusing species. Their transition from n-type to p-type is at a similar oxygen activity to Matsui and Naito (67) and also agrees fairly well with that found by Atkinson and Taylor (54). The diffusion data determined by Hoshino and Peterson (53) indicates vacancy diffusion but lies in a region that should have a majority of chromium interstitials according to Young, Gerretsen and deWit (66). They also report that the conclusion reached by Kofstad and Lillerud (64), that Cr_2O_3 is an intrinsic conductor, is invalidated due to an error in their calculations. The transition between n-type and p-type conductivity is reported to be irreversible below 1770K or, at least, very slow. This is confirmed by Young and Cohen (68). The very slow kinetics for the reverse transition could be due to one of two models (66); for p-type oxide to transform to n-type, chromium interstitials must be formed and must diffuse through the p-type material. In the first model, interstitials are assumed to diffuse more rapidly than vacancies and the rate determining step is the creation of oxygen vacancies at the surface of the oxide; in the second model, vacancies are assumed to

diffuse more rapidly than interstitials and the rate-determining step is the creation and diffusion of the interstitials through the p-type oxide. In their review of the electronic properties of Cr_2O_3 , Przybylski and Yurek (62) report that, below 1100°C , the diffusion rate for interstitials is much greater than for vacancies. This would imply that the first model given above is correct but it is not possible yet to be definite. It would also imply that the lattice diffusion of chromium in p-type oxide would be very slow.

The determination of the diffusing species in Cr_2O_3 forming upon Cr in an oxidising atmosphere has received less coverage. The growing scale has an oxygen activity gradient across its thickness, from the equilibrium $\text{Cr}/\text{Cr}_2\text{O}_3$ dissociation pressure at the oxide/metal interface to the oxygen partial pressure of the oxidising gas at the gas/oxide interface and, if the oxide is quick to reach equilibrium with the ambient oxygen activity as assumed by Kofstad and Lillerud (64), then there should be a region of n-type oxide near the oxide/metal interface and a region of p-type oxide near the oxide/gas interface. As the oxide grows by outward cation diffusion, the diffusing species in the growing oxide film should be the point defect species that is in the majority at the metal/oxide interface, that is interstitials (62). The oxide will be formed at the oxide/gas interface and should, thus, be p-type for the high oxygen partial pressures used by those studying the oxidation of chromium. If vacancies are the diffusing species then the parabolic rate constant will vary with oxygen activity according to:

$$k_p = E\{[a(\text{O}_2)]_0^{3/16} - [a(\text{O}_2)]_1^{3/16}\} \quad 14$$

and if interstitials are the diffusing species then the parabolic rate constant will vary according to:

$$k_p = F\{[a(\text{O}_2)]_0^{-3/16} - [a(\text{O}_2)]_1^{-3/16}\} \quad 15$$

where E, F are constants of proportionality, $[a(\text{O}_2)]_0$ is the oxygen activity at the oxide/metal interface and $[a(\text{O}_2)]_1$ is the oxygen activity at the oxide/gas interface (63). For oxidation experiments, the oxygen activity at the oxide/metal interface is constant and, so, equation 14 says that the parabolic rate constant would vary as $[a(\text{O}_2)]_1^{3/16}$ if vacancies were the main diffusing species. In oxygen partial pressures close to atmospheric, the second term in equation 15 would be negligible compared to the first term, which is constant, which would imply that the parabolic rate constant would be independent of the oxygen partial pressure if interstitials were the main point defect species. The parabolic rate constant for the oxidation of chromium has been found to be independent of oxygen partial pressure by several authors (28-

30,62), indicating that interstitials are the main diffusing species. Interstitials are the major diffusing species in n-type oxide which would imply that the growing oxide is n-type. For thick scales, near the metal/oxide interface, the oxide should be n-type because the equilibrium oxygen activity is that for the dissociation of $\text{Cr/Cr}_2\text{O}_3$. Young, Gerretsen and deWit (66) point out that this implies that the oxide would have to undergo the transition that they reported to be extremely slow, as the oxide will form as p-type. Taken with the very low rate of chromium diffusion in single crystals reported by various authors, this seems unlikely and it is probable that the bulk of the oxide is frozen into the p-type configuration (66) produced at the oxide/gas interface where oxide formation occurs. The main diffusion paths in the oxide, though, are thought to be grain boundaries which are fast diffusion paths and it is possible that the oxide immediately adjacent to the grain boundaries reaches equilibrium with the ambient oxygen partial pressure far more rapidly (30). It is also possible that the scale is not in equilibrium with the ambient partial pressure of oxygen yet the diffusion rate of chromium interstitials is still sufficiently high that their mobility makes up for their lack of numbers in the p-type scale.

The classical theory for the formation of thick oxide films on a metal is the Wagner theory. This assumes that the oxide layer is compact and perfectly adherent and that diffusion of charged particles through the scale is rate determining (45). The theory predicts that the thickness of the scale will increase as:

$$X^2 = kt \quad 16$$

where X is the thickness of the scale, t is the time of oxidation and k is the parabolic rate constant. This rate constant is most easily accessible from experiment by thermogravimetric analysis where the increase in mass of a sample is measured at a given temperature of oxidation. This leads to:

$$W^2 = k_p t \quad 17$$

where W is the mass gain per unit area and k_p is the parabolic rate constant. k_p is related to k by:

$$k_p = 2k[M_x/VZ_x]^2 \quad 18$$

where M_x is the relative atomic mass of oxygen, V is the equivalent volume of scale and Z_x is the valency of oxygen (63). k_p should also obey the Arrhenius equation for temperature dependence:

$$k_p = B \exp(-Q/RT) \quad 19$$

where B is the frequency factor, Q is the activation energy for the process, R is the gas constant and T is the temperature. The data derived from thermogravimetric analysis is usually given as a graph of the parabolic rate constant plotted against temperature according to:

$$\ln(k_p) = \ln(B) - \frac{Q}{RT} \quad 20$$

where $\ln(k_p)$ plotted against $1/T$ gives a straight line and allows the activation energy to be determined. The kinetic data given by the authors that have studied the oxidation of chromium are plotted in this form in figure 1.4.2. This set of kinetic data has been determined at various oxygen partial pressures but, as the parabolic rate constant should not change significantly with oxygen activity for values close to atmospheric, the data in the set should be entirely comparable in this respect.

The scatter in the data is large but the lines have a roughly similar slope indicating that their activation energies are similar. This is not surprising given that the same process is being measured. The activation energies calculated from the lines are given, in order of magnitude, in table 3. The mean activation energy for the growth of chromium oxide on pure chromium is 230kJmol^{-1} which should be compared with the mean activation energy for diffusion of cations through Cr_2O_3 of 340kJmol^{-1} . The activation energy for oxide growth is much closer to the 250kJmol^{-1} determined for cation grain boundary diffusion by Hay, Hicks and Holmes (55) and by Hagel and Seybolt (51) for hot pressed Cr_2O_3 ; the mean value for cation diffusion through Cr_2O_3 is raised by the less reliable (51) data determined by Hagel and Seybolt (51) and Lindner and Åkerström (50) for sintered Cr_2O_3 .

The wide variation in the kinetic data, up to four orders of magnitude, is a direct result of the deformation of the oxide scale and the differing degrees of break-away oxidation that occur during oxidation (18). Other factors may include sample purity, oxide grain size and oxide structure (24). The amount of oxide deformation that occurs will depend upon such factors as surface preparation, oxidation conditions, the state of the metal surface and sample purity (25). The methods of preparation of the samples used, their surface preparation and the oxidation conditions for each of the lines in the graph in figure 1.4.2 are tabulated in tables 3 and 4. The kinetic data given in figure 1.4.2 are also marked as to the final surface preparation that was used in their determination. Where a sample has been ground, this means that the final abrasion was with a large grit grinding paper, mechanical polishing implies polishing with at least 1 micrometre size particles, electropolishing was usually carried out with a perchloric acid solution and etching was carried out after an initial electropolish in

Figure 1.4.2

A graph of the parabolic rate constants for the oxidation of pure chromium determined by previous workers, plotted on a logarithmic scale against inverse temperature.

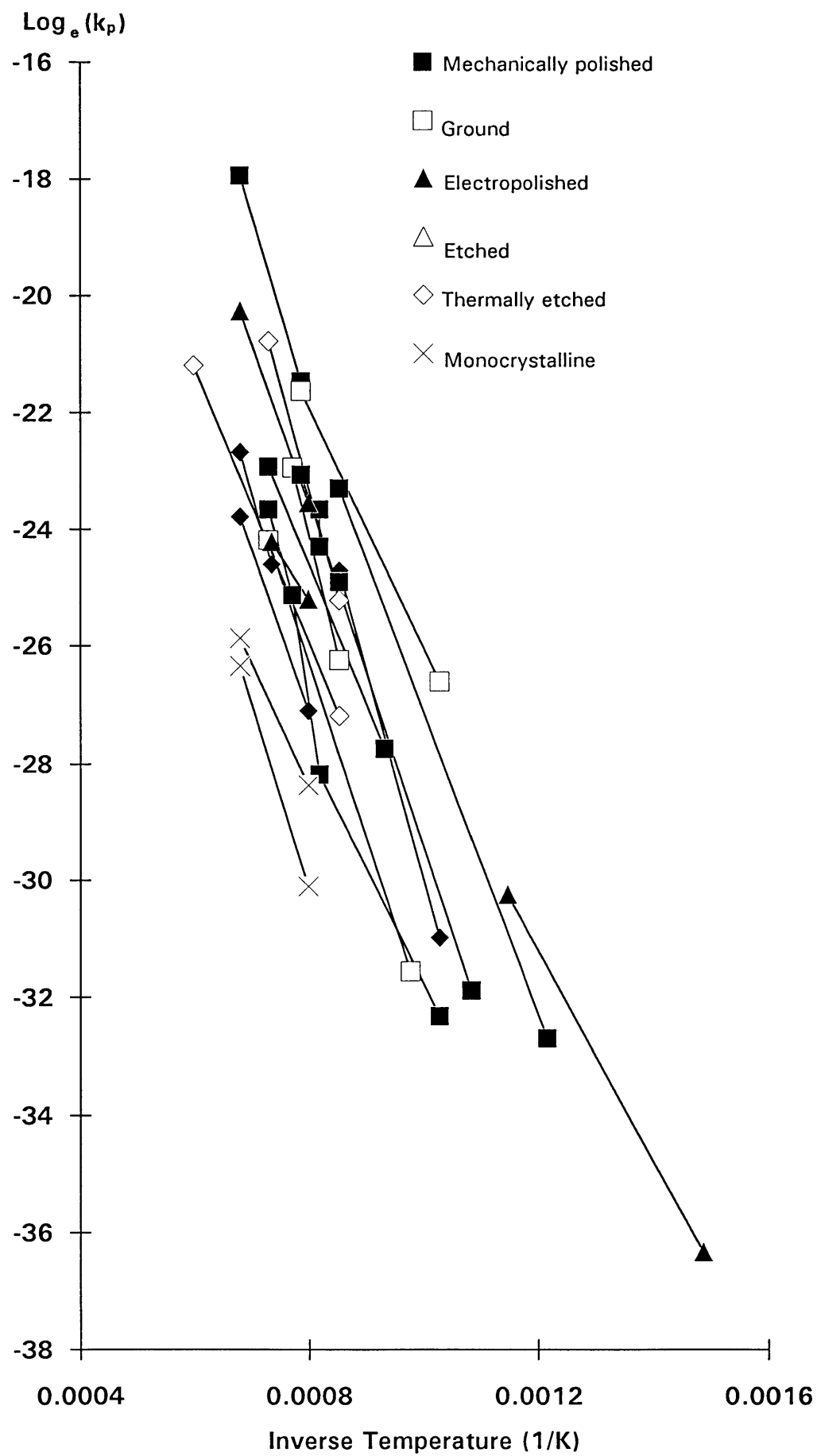


Table 3

A table showing the type of chromium used, given with the measured impurity levels quoted by the authors, and the activation energies measured in the determination of the parabolic rate constants plotted in figure 1.4.2. The values are arranged in ascending order of the activation energies for the studies.

Author	Chromium	Impurities	Activation energy, kJmol ⁻¹
Caplan, Sproule (26)	Hot rolled electrolytic	300ppm Fe, no O quoted	129
Young, Cohen (37)		800ppm O	148
Hatfield (19)	Cast		171
Caplan, Harvey, Cohen (25)	Hot rolled electrolytic	300ppm Fe, no O quoted	174
Cadiou, Paidassi (31)	Iodide	100 - 200ppm O, 150 - 250ppm C	195
Giggins, Pettit (70)	Cast		196
Hussey, Mitchell, Graham (24)		800ppm O, 39ppm C, 31ppm N	216
Caplan, Harvey, Cohen (25)	Hot rolled electrolytic	300ppm Fe, no O quoted	229
Caplan, Harvey, Cohen (25)	Hot rolled electrolytic	300ppm Fe, no O quoted	231
Gulbransen, Andrew (21)	Sheet	0.05wt% Si, 0.01 - 0.1wt% Al	232
Hagel (27)	Arc melted iodide	34 - 37ppm C, 12ppm O	245
Mortimer, Post (69)		300ppm O, 20ppm N	247
Phalnikar, Evans, Baldwin (46)	Electrolytic		260
Caplan, Sproule (26)	Hot rolled electrolytic	300ppm Fe, no O quoted	264
Gulbransen, Andrew (20)	Vacuum cast electrolytic	Traces of tin, lead, silicon	280
Caplan, Sproule (26)	Hot rolled electrolytic	300ppm Fe, no O quoted	292
Kofstad, Lillerud (29)	Electrolytic	4150ppm O	297
Cotell <i>et al</i> (32)	Cast		330

Table 4

A table of the surface preparations and oxidation conditions used in the determination of the parabolic rate constants plotted in figure 1.4.2. The information is arranged in ascending order of the activation energies measured in the studies.

Author	Final surface preparation	Oxidation conditions	Activation energy, kJmol ⁻¹
Caplan, Sproule	Electropolished	100 hours, 980-1200°C, 1atm flowing O ₂	129
Young, Cohen	Electropolished	10 ⁴ s, 400-600°C, 0.53Pa	148
Hatfield	Ground	24hours, 700-1000°C, 1atm	171
Caplan, Harvey, Cohen	Etched	100 hours, 980-1200°C, 1atm flowing O ₂	174
Cadiou, Paidassi	Thermally etched	20 hours, 900-1400°C, 1atm flowing O ₂	195
Giggins, Pettit	Ground	20 hours, 800-1200°C, 0.1atm O ₂	196
Hussey, Mitchell, Graham	Mechanically polished, annealed	2.5 hours, 600-900°C, 5x10 ⁻³ torr O ₂	216
Caplan, Harvey, Cohen	Electropolished	100 hours, 980-1200°C, 1atm flowing O ₂	229
Caplan, Harvey, Cohen	Etched	100 hours, 980-1200°C, 1atm flowing O ₂	231
Gulbransen, Andrew	Mechanically polished	6 hours, 700-1100°C, 0.1 atm O ₂	232
Hagel	Ground	8 hours, 750-1100°C, 0.1atm O ₂	245
Mortimer, Post	Etched	1200 hours, 650-1000°C, 1 atm flowing O ₂	247
Phalnikar, Evans, Baldwin	Mechanically polished	5, 11 hours, 1000°C, 1200°C, 1 atm flowing O ₂	260
Caplan, Sproule	Etched	100 hours, 980-1200°C, 1atm flowing O ₂	264
Gulbransen, Andrew	Mechanically polished	2 hours, 700-900°C, 0.1 atm O ₂	280
Caplan, Sproule	Etched	100 hours, 980-1200°C, 1atm flowing O ₂	292
Kofstad, Lillerud	Thermally etched	70 hours, 800-1075°C, 1 atm static O ₂	297
Cotell et al	Mechanically polished	18 hours, 900°C, 1 atm O ₂ , 20 hours, 1025°C, 0.05 atm O ₂	330

order to remove any electropolishing oxide film. Thermal etching involved heating the polished sample in high vacuum in order to smooth the surface by evaporation. Volatilisation of the oxide becomes significant above 1000°C and most workers have accounted for it in some way, either by suppressing it by coating the reaction chamber with Cr_2O_3 or calculating its magnitude from the kinetics available in the literature. Only two sources (21,46) have disregarded it and both carried out their experiments before the phenomenon was discovered.

The two lowest rates in the figure were calculated from thickness measurements of a monocrystalline oxide film found on an etched sample (25,26). The rate of growth is too large for lattice diffusion to account for and there are no grain boundaries in the oxide for transport. This implies that, like the monocrystalline oxide reported by Przybylski and Yurek (62), the oxide has grown by dislocation pipe diffusion. Przybylski and Yurek's result (62), that this growth mechanism gives growth rates an order of magnitude below that of grain boundary diffusion, seems to be borne out by these results. The difference between the two lines is probably due to errors associated with the statistics of measuring thickness. The data from Gulbransen and Andrew (21) is given as three lines as plotted in their paper. They used this apparent change in mechanism to postulate a relationship with the vapour pressure of chromium at high temperature. Their results are not confirmed directly by any of the other workers and volatilisation was not accounted for.

Of the other authors who investigated the oxidation of chromium, some did not provide sufficient data to gain values of k_p (47,71). Skeldon, Calvert and Lees (46), oxidising at one temperature to investigate the growth mechanism, provide some points which are plotted in the figure and seem to fit the rest of the data. Mills (72) produced a large number of results that seemed to fit non-parabolic kinetics and thus rate constants are not available for comparison. Widmer, Yukawa and Grant (22) used an interrupted oxidation technique to gain a rate constant but substantial spalling occurred, rendering their results useless for kinetic studies.

The types of chromium used for the oxidation experiments with their differing purities, the different surface preparations and the different oxidation conditions used by the various workers make comparison difficult. Even in cases where, for example, identical surface preparations have been used, other parameters in the oxidation process have been different, leading to a lack of consensus as to the best conditions to use.

There are no obvious relationships between any of the parameters given and either the magnitudes of the rate constants or the activation energies. Some authors (25,26,29) noted that electropolished surfaces oxidised more rapidly than other surfaces and attributed this to a smaller grain size in the oxide film. The graph of the oxidation kinetics does not bear this out. This lack of a relationship leads to the

assumption that, either these relationships do not exist or that they are overridden by a more major effect. Although the amount of oxide deformation will depend upon the factors mentioned above, the absolute mass of the oxide formed during break-away may vary considerably even on samples that have been oxidised under nominally identical conditions. This can be seen in the data produced by Caplan, Harvey and Cohen (25) and by Caplan and Sproule (26) where nominally identical conditions have been used but the kinetic data are different. This also leads to the conclusion that probably the most reliable parabolic rate constant is that determined by Hussey, Mitchell and Graham (24), as the oxide that grew in the measurement of the rate constants was compact, undeformed and adherent to the metal surface.

The majority of work on the oxidation of chromium has been carried out on thick films and very few workers have studied the behaviour of thin films (37,45,73). A review of the theory and experimental evidence for this regime is given by Atkinson (45). The Wagner theory of oxidation only covers the behaviour of thick films, the behaviour of thin films is more complex; thin films, generally, are less than approximately 20 nanometres thick (45). The transition to parabolic kinetics was found to occur for films on chromium at a thickness of around 6 nanometres below 400°C and at around 16 nanometres at 600°C. Oxidation kinetics in the thin film region have been covered by Cabrera and Mott who proposed that electrons tunnel through the oxide film and ionise the adsorbed oxygen atoms. The uniform electric field set up pulls the diffusing ion species through the film, thereby causing thickening. The transfer of ions is the rate-controlling step and leads to logarithmic kinetics if the activation energy for ion migration is a function of film thickness, as is usually the case (45).

Mitchell, Hussey and Graham (73) used sequential $^{16}\text{O}_2/^{18}\text{O}_2$ oxidation at 700°C and Hope and Richie, quoted by Atkinson (45), used electrical marker experiments to study the movement of ions in thin films; both deduced that chromium ions were the only mobile species in the oxide film. The electrical marker experiments also indicated that ionic or electronic transport was rate controlling. Young and Cohen (37) studied the growth kinetics of chromium oxide in the thin film region and found good agreement with the Cabrera-Mott theory.

1.5 The Reactive Element Effect

Early in this century it was noted that additions of rare earth elements to nickel-chromium heating elements produced large increases in lifetime under thermal cycling conditions. This was due to a much improved adhesion of the protective Cr_2O_3 scale. Later it was realised that other oxygen-active elements had the same effect and other benefits were noted, the major benefit being a significant reduction in

the growth rate of the scale. Alloying was not alone in producing the effect, surface coatings which converted to oxides at high temperatures gave the same results as did additions of the oxygen-active elements in the form of oxide particles. The reactive element effect, as it has become known, has been the subject of many papers. The work up to 1980 has been reviewed comprehensively by Whittle and Stringer (1) and the main effects noted are: a reduction in oxide growth rate of an order of magnitude or more, an increased adhesion of the scale and a change from growth at the oxide/gas interface to growth at the oxide/metal interface. This latter occurs only at higher levels of reactive element. There have been two other recent reviews of the reactive element effect. The first is a general review by Moon (74) and the second is a review of the effect of implanting yttrium into chromium by Przybylski and Yurek (62).

The elements found to have the greatest effect are yttrium, cerium and lanthanum (75). The reactive element effect is enhanced if the elements are implanted into the surface of the metal or their oxides are present as a dispersed phase or a surface coating (74). There is believed to be a saturation limit, above which additions bring no further gain (76). Generally, the minimum amount of reactive element needed to bring about a change in the growth rate is: for implantation, 1×10^{17} ions cm^{-2} at 300keV implantation energy giving a distribution of 150 nanometres depth and a maximum concentration of 21wt% at 65 nanometres (77); for dispersed oxides a concentration of about 2vol% (78); for alloying additives about 0.1at% reactive element (32). The benefits of a reactive element addition, thought to be due to reactive element ions being active in the scale (74), only appear to occur at temperatures above one third of the oxide melting point, possibly because, below this temperature, there are not sufficient reactive element ions in the scale due to a drop in the solubility of the reactive element in the oxide (74). The reactive element has its greatest effect when distributed uniformly across the surface of the substrate. This can be best achieved by ion implantation or by coating the reactive element onto the surface. This has the added advantage of lowering the total amount of reactive element needed to bring about the desired protective behaviour (74).

The mechanisms whereby the reactive elements have their effect are still under investigation. The rate reduction is thought to be due to the change in the growth mechanism from outward cation diffusion to inward anion diffusion (79), along grain boundaries, which is thought to be due to the reactive element blocking the cation fast diffusion paths (74) either by their physical size (80,81) or by the formation of defect complexes (82). Although figure 1.4.1 shows the rate of oxygen diffusion along fast diffusion paths being similar to that for chromium along grain boundaries, Hussey, Mitchell and Graham (24) have shown that the total flux of oxygen ions is orders of magnitude lower than that for chromium, thus reducing the rate of oxide formation. The change in growth mechanism has been noted for

reactive-element-containing chromium (83) and the reactive element has been found to segregate to the oxide grain boundaries in this case.

Mechanisms for the improvement of scale adhesion are many and varied and Whittle and Stringer (1) provide a comprehensive discussion of the main theories. The theories include: promotion of chemical bonding across the metal/oxide interface (84,85), and scavenging of impurities that could weaken interfacial bonding (86). The suppression of cation diffusion could reduce porosity and loss of interfacial contact (74,87). The build-up of compressive stress that leads to oxide deformation is thought to be due to oxygen ions diffusing into the scale and subsequent oxide growth within the scale; if cations were not diffusing outwards, the anions would diffuse all the way to the oxide/metal interface and the compressive stress would no longer form. Enhancement of scale plasticity could prevent spalling (74) and a smaller grain size in the oxides formed on reactive-element-containing metals could increase stress relaxation by increasing creep rates. Keying of the oxide to the substrate could prevent decohesion and the provision of vacancy sinks could also prevent the loss of interfacial contact (1). Of these, the most relevant to Cr_2O_3 forming on pure chromium are probably the chemical bonding theory, the impurity scavenging theory and the cation diffusion suppression theory (74). There is no real evidence that the lack of adhesion for chromia scales on pure chromium is due to vacancy coalescence at the metal/oxide interface, enhanced scale plasticity would just allow the scales to buckle to a larger extent than normal and oxide pegs are almost never seen. There is also evidence to suggest that reactive elements do not enhance scale plasticity (88).

There have been very few studies of the effects of reactive elements on the oxidation of pure chromium. Hagel (27) oxidised chromium containing 1wt% Y and found no reduction of the growth rate and there was no improvement in the adherence of the oxide film. Cotell, Przybylski and Yurek (32) compared the oxidation behaviour of pure chromium with a Cr-0.04wt%Y alloy and found that the rate of oxidation dropped by a factor of six although the direction of growth did not change. They ascribed this to a decrease in the flux of cations along grain boundaries. Cotell, Yurek, Hussey, Mitchell and Graham (79,83) studied the effect of implanting pure chromium with yttrium at dose rates of 1×10^{15} and 2×10^{16} ions cm^{-2} . They found that the segregation of yttrium ions to the grain boundaries in the oxide reduced the cation flux, raising the rate of anion transport above that for cation transport for the higher dose samples. When anion transport dominated, the anions diffused along oxide grain boundaries as would be expected from the relative rates of grain boundary and volume diffusion given in figure 1.4.1.

2 EXPERIMENTAL

2.1 Material.

The chromium to be used in this investigation was bought by the industrial sponsors of this project: AEA Technology at Harwell, Oxfordshire. It was supplied by Goodfellow Metals as sheets of electrolytic chromium 10cm x 10cm x 0.5mm which were then spark cut into coupons 1cm x 1cm x 0.5mm. Metal from two separate batches of production were obtained; metal from batch A was used for studying the oxidation of the unimplanted metal and batch B was implanted with either chromium or cerium. Samples from each of the two batches were analysed by mass spectrometry at the NRC, Canada and the results are given in table 5. The high oxygen content and the low level of metallic impurities, excepting tin and antimony, were expected from previous analyses of electrolytic chromium (29,67). The levels of tin and antimony had not been previously reported in studies of the oxidation of electrolytic chromium. The major source of the metallic impurities is the chromic acid used in the electrolyte (6), the tin and antimony contamination will arise from the anodes used in the electrolyte bath.

2.2 Annealing treatments.

The electrolytic chromium was subjected to three sets of heat treatments, detailed in table 6. The first, carried out at Imperial College, consisted of annealing in argon at 1050°C for 1 hour and 24 hours in order to close the microcracks found in the metal. Coupons of the as-received material were wrapped in molybdenum foil, sealed in silica tubes under an argon atmosphere, annealed in a tube furnace for 1 hour or 24 hours and then analysed using transmission electron microscopy. The results of this analysis removed the necessity for further investigation of the samples by either light or scanning electron microscopy.

The second and third sets of heat treatments were carried out at Harwell. The second set was designed to study the development of the metal microstructure under the influence of a hydrogen atmosphere. Accordingly, coupons of untreated electrolytic chromium were annealed at 600°C, 800°C and 1000°C for 24 hours in an atmosphere of hydrogen gas at a pressure of 10^5 Pa. Other coupons, as a control, were annealed under the same conditions but in a vacuum of $2 \cdot 10^{-9}$ Pa. This was carried out in a special vacuum furnace.

Having analysed these samples using transmission electron microscopy, it was decided to carry out a third and final set of heat treatments. These were each of 3 hours in duration for reasons of safety at the higher temperatures involved. The

Table 5

A table showing the analyses of the two batches of electrolytic chromium as-received. This is a mass spectrometric analysis carried out at NRC, Canada and the concentrations are in parts per million by mass.

Composition in ppm by mass

	Batch A	Batch B
Cr	balance	
O	1100	1500
N	1.8	2.7
Si	0.7	0.53
S	83	86
Cl	28	43
Fe	5.2	5.6
Ni	0.064	0.076
Cu	8.7	9.2
Sn	20	74
Sb	280	710
Other	21.5	36.5

Table 6

A table giving the heat treatments carried out on the electrolytic chromium as-received. The pressures of the argon atmosphere used was 10^5Pa , the hydrogen atmosphere 10^5Pa and the vacuum was 10^{-9}Pa . The treatments at the temperatures marked with an asterisk were also followed, in some cases, by a second heat treatment consisting of 1 hour at 500°C in a vacuum of 10^{-9}Pa .

Temperature °C	Time	Atmosphere
1050	1 hour	Argon
1050	24 hours	Argon
600	24 hours	Vacuum
600	24 hours	Hydrogen
800	24 hours	Vacuum
800	24 hours	Hydrogen
1000	24 hours	Vacuum
1000	24 hours	Hydrogen
1000 [*]	3 hours	Hydrogen
1100	3 hours	Hydrogen
1200	3 hours	Vacuum
1200 [*]	3 hours	Hydrogen
1250	3 hours	Hydrogen
1300 [*]	3 hours	Hydrogen
1400 [*]	3 hours	Hydrogen
1500 [*]	3 hours	Hydrogen

* were also treated for 1 hour at 500 °C in a vacuum in some cases.

coupons were annealed in 10^5 Pa pressure of hydrogen at temperatures of: 1000°C , 1200°C , 1300°C , 1400°C and 1500°C and at 1200°C in a vacuum of $2 \cdot 10^{-9}$ Pa. Some of the hydrogen-annealed coupons received a second heat treatment consisting of 1 hour at 500°C in a vacuum of $2 \cdot 10^{-9}$ Pa in order to ensure the removal of dissolved hydrogen. Subsequently, additional heat treatments in hydrogen were carried out. These were of 3 hours duration at temperatures of 1100°C and 1250°C . This third set of heat treatments permitted a thorough determination of the behaviour of the metal microstructure under the reducing atmosphere. Using the results of these sets of heat treatments it was decided to anneal all of the metal for oxidation for 3 hours at 1500°C in 10^5 Pa of hydrogen and then for 1 hour at 500°C in a vacuum of $2 \cdot 10^{-9}$ Pa; this material shall be referred to as standard-annealed chromium.

2.3 Ion implantation

Coupons of standard-annealed chromium were polished using diamond particles of sizes from 14 down to 1 micrometre. These were then implanted in the Cockcroft-Walton ion implanter at the Harwell Laboratory. The coupons were implanted with Ce^+ ions at an energy of 150KeV at a dose of $2 \cdot 10^{16}$ ions/ cm^2 . Other coupons were implanted with Cr^+ ions at an energy of 70KeV at a dose of $2 \cdot 10^{16}$ ions/ cm^2 in order to determine whether the implantation process had any effect on the oxidation of the chromium.

2.4 Preparation of bulk samples

Coupons of the standard-annealed electrolytic chromium to be examined using light microscopy or scanning electron microscopy were either electropolished to produce a deformation-free surface or mechanically polished. This also applied to discs that were to be oxidised. The mechanical polishing was carried out using two different methods. Coupons polished at Imperial College were first ground on 1200 grade SiC paper with a water lubricant and then polished using a suspension of 2 micrometre alumina particles in distilled water. This caused the grains of the metal to be etched due to the grain orientation dependent wear rate but grinding the coupons on SiC paper prior to polishing enabled the grain etching to be reduced to a minimum. The coupons were held on a steel block approximately 2cm x 2cm x 2cm in size using a thermoplastic resin. Alumina particles were used in the polishing in order to prevent the substantial particle pick-up found with diamond particles. Those samples prepared at Harwell were ground and polished using solely diamond particles, starting with 14 micrometre size particles and reducing to 1 micrometre particles. Their concern in the investigation was with longer time oxidation and they avoided SiC

paper and alumina particles as preventing Si and Al contamination of the surface was a higher priority.

Electropolishing of the surfaces was carried out using a 10% perchloric acid / 90% methanol solution in a stainless steel beaker. The solution was continuously stirred using a magnetic stirrer and cooled to -30°C by placing the beaker in a bath of cold methanol, ensuring a constant temperature. An electropolishing voltage of 20V was used with the sample as anode and the metal beaker as cathode. Large coupons of the chromium were gripped by their edges using steel tweezers and the whole surface of the tweezers plus coupon, except for the surface to be electropolished, was protected from attack by coating with Lacomit Varnish lacquer. Discs of the chromium that were to be electropolished prior to oxidation were held in a different manner. The discs were too small, when held by tweezers, to be coated with lacquer leaving one surface free of the lacquer, due to the surface tension of the lacquer. Instead, several strands of nichrome wire 10 cm long were twisted together and one end of the resulting thick wire was attached to the back of the discs using a conducting paint. This was far more easily coated with lacquer.

The samples were placed in the polishing solution and current allowed to flow. After around 5 - 10 seconds a dark brown stain would start to flow from the surface and the polishing would be stopped. The sample would be washed in methanol and polished for a further 5 - 10 seconds. This would be repeated and, after the third wash, the sample would be placed in a bath of acetone to remove the lacquer. The electropolishing procedure would remove around 5 micrometres of material from the surface of the sample.

2.5 Light Microscopy

The light microscopy of the oxidised and unoxidised specimens was carried out using a Vickers M41 Photoplan microscope. The samples were viewed in reflection using unpolarised light. The other main technique used was the Nomarski interference technique. This gave increased surface contrast, highlighting variations in surface level. A beam of polarised light is split and recombines when reflected from the surface of the sample; the path difference between the two rays is adjusted so that the main surface level gives destructive interference of the two rays and, therefore, any parts of the sample that are at different heights have different interference conditions giving different contrast.

2.6 Scanning Electron Microscopy

Two scanning electron microscopes were used in this investigation. A JEOL JSM T-220A was used for the main secondary electron imaging utilising its ability to handle large samples and to tilt to angles of up to 90°. For the back-scattered electron imaging a JEOL JSM T-200 microscope with a KE Developments Ltd. separable quadrant detector was used. This microscope was also used for qualitative energy dispersive X-ray spectroscopy.

2.7 Grain size and particle number density

The method whereby a mean grain diameter was determined was taken from reference 89. A circle of known circumference was inscribed on a micrograph showing the grain structure of the material and the number of grain boundaries that intersected this circle was counted. Dividing the circumference by the number of boundaries gave the mean grain diameter for that circle. The circle diameter was chosen to be approximately two-thirds of the size of the micrograph so that several circles could be used on each micrograph. The final mean grain diameter was found from the total length of circle circumference divided by the total number of grain boundaries; the sample means from each circle that contributed to the final figure were used to determine a standard deviation and this gave the standard error in the mean grain diameter for the material.

The particle number density on a plane for each of the annealed coupons was taken from back-scattered electron micrographs of the electropolished surfaces of the relevant metal. The smooth surface was assumed to be planar and care was taken to distinguish between pits in the surface where particles had intersected the surface and holes beneath the surface that were revealed by the depth of penetration of the electron beam. For a given micrograph the number of pits in the surface was counted and this was divided by the area of the micrograph to give a number of pits in unit area, taken here to be 1 square micrometre. It was assumed that the pits were produced solely by particles in the surface being attacked by the polishing solution and dropping out.

2.8 Transmission Electron Microscopy

Various transmission electron microscopes were used in this investigation. Most of the general microscopy was carried out using a Phillips EM301 and a JEOL 120CX TEMSCAN at an accelerating voltage of 100KeV. The environmental cell work was carried out using an AEI EM7 1MeV electron microscope. For analysis of

thick oxides where greater penetration was needed combined with a facility for quantitative X-ray energy dispersive spectroscopy, a JEOL 2000FX operating at 200KeV was used. The STEM analysis was carried out at Harwell by J.M. Titchmarsh using a VG HB501 STEM with a field emission gun.

2.9 Preparation of TEM samples

Coupons of the metal to be analysed were first ground on both sides to a thickness of approximately 200 - 300 micrometres using 1200 grit SiC paper with a water lubricant. They were then affixed to a brass block and 3mm diameter discs spark eroded from the coupons. Usually six discs could be obtained from a 1cm square coupon. The discs were ground further until approximately 150 micrometres thick and the final thinning to electron transparency was carried out by electropolishing. A Struers Tenupol II jet polishing unit was used; jets of electrolyte simultaneously electropolishing two concave faces from either side of the disc. The electrolyte used was a 10% perchloric acid / 90% methanol solution cooled to -30°C ; a medium flow rate of electrolyte being used with an electropolishing voltage of 30V. The discs were thinned until they perforated, the moment of perforation being detected by a light beam / photocell arrangement. In practice the photocell was generally too unreliable to guarantee that the polishing would be stopped exactly at the moment of perforation and far better results were gained by removing the photocell and using visual examination to detect the first mote of light through the foil. The thin discs were then washed carefully in methanol and distilled water. This thinning procedure gave a sample from approximately the centre of the metal.

As well as electropolishing the discs to electron transparency, the discs could be thinned by ion bombardment, should electropolishing be deemed unfavourable. In this case the discs were ground to 100 micrometres thickness and a concave dimple produced in each face to facilitate the thinning process. The dimples were produced using a Dimpler™ model D500 manufactured by VCR, San Francisco. This consisted of a precisely counterbalanced grinding wheel of 1cm diameter rotating about a horizontal axis through its centre, being loaded vertically down onto the specimen by a small mass. The disc was attached to the specimen stage using a thermoplastic resin, an artificial version of Lakeside cement, and the stage rotated about a vertical axis through its centre. A slurry of 3 micrometre diamond particles was used. The specimen was first dimpled on one side then on the other until the thickness between the two concave faces was of the order of 30 - 40 micrometres. If dimpling was continued past this point, grain boundary cracking of the metal through the thickness occurred. A rotation rate of 40 rpm. was used with a loading of 20 grammes.

Final thinning was carried out in a dual beam ion mill; in this case a GATAN model 600 using argon ions accelerated to 6kV. The ion beams were set at an angle of 20° to the plane until perforation occurred, after which the sample received another hour at 8°. The ion beam milling generally took between 20 and 40 hours of continuous milling to produce an electron transparent specimen.

As well as analysing the centre of the chromium the surface of the metal was of great interest, especially when there was an oxide film whose structure needed to be determined. In order to study a prepared surface using TEM the samples needed to be thinned from one side only so as to preserve the surface structure; this process will be referred to as back-polishing. Both of the methods mentioned above were used successfully with only slight modifications. In order to protect the coupons during grinding they were attached to metal blocks using the thermoplastic resin detailed above. This prevented damage to the surface and the resin could subsequently be completely dissolved in acetone.

Thinning from one side only, during the electropolishing stage, was simply a matter of disconnecting the electrode from the side nearest to the surface of interest and protecting that surface from attack by coating it with a protective lacquer. The probability of obtaining a large amount of electron transparent area was increased by firstly decreasing the thickness of the disc prior to electropolishing to around 100 micrometres; secondly by dimpling the face to be jet polished so as to provide a form for the jet and also to reduce polishing time and, lastly, by ensuring that the layer of lacquer was sufficiently thin so that the moment of perforation could be detected easily. The electropolishing needed to be stopped as soon as the disc perforated because, not only did the amount of electron transparent area decrease significantly after perforation, but the surface of the metal that was protected by the lacquer could also be destroyed. The lacquer used in this investigation was Lacomit Varnish and as this dissolved readily in acetone, acetone could also be used as a thinner for the lacquer. The discs were coated immediately prior to jet polishing and allowed to dry. After perforation, the discs were washed in methanol as usual and then placed in a bath of acetone to soak off the lacquer. The liquid was not agitated during this time so as not to destroy the thin area of the disc. Once the lacquer had visibly dissolved, the disc was transferred to a clean bath of acetone and left for some time; the disc was not allowed to dry during transfer as this reduced the chances of removing the last traces of the lacquer.

Back-polishing in a ion beam thinner was carried out by only using one beam of ions. The discs were a maximum of 100 micrometres thick but were only dimpled on one side. Care was taken in dimpling as the metal would bulge on the surface of interest if the loading mass was too high. After perforation, the unthinned surface was found to be covered with a thin layer of deposited material. This was removed

carefully using the ion beams at a high angle for a very short time and the removal was monitored every 30 seconds using a light microscope to ensure that the surface was not damaged.

2.10 TEM Techniques

The majority of the microscopy consisted of bright field imaging and selected area diffraction for microstructural characterisation. For identification of smaller particles, microdiffraction was used. This consisted of focusing the beam onto the particles to be identified, using a small spot size and condenser aperture to produce a fine beam in the SA magnification imaging mode, before changing to diffraction mode. If possible, when photographing diffraction patterns, standard diffraction patterns from Cr or Cr_2O_3 were also recorded under the same conditions so that the camera constant could be determined precisely for each diffraction pattern. As well as normal TEM imaging, STEM imaging together with secondary electron imaging in the JEOL 120CX was used to gain information about the oxide films. X-ray energy dispersive spectroscopy, both qualitative and quantitative, was carried out on the oxide films to determine impurity levels and concentrations of Ce; both point analysis using a Link Systems AN10000 analytical system and STEM area analysis using a Link Systems 290 analytical system were employed.

2.11 Microdensitometry

A microdensitometer was used to determine distances on some diffraction pattern negatives so that the spacings of the spots on the diffraction pattern could be found precisely. The negative was sandwiched between two flat sheets of glass and a light beam focussed onto the negative. Using a slit/photocell arrangement the intensity of light transmitted through the negative was plotted. A motor drive allowed the light to be moved in a straight line across the negative and the distribution of transmitted intensity versus distance could be plotted precisely. Spots on the negative appeared opaque so they were registered as drops in intensity which, by inverting the plot, were converted into peaks. The spots were most opaque at their centres allowing the centres of the spots to be located precisely. Traces across the central spot were used. As the spots on the pattern were arranged symmetrically about the central peak, distances between two peaks could be determined and then halved to derive the lattice spacing. This took away the necessity of finding the centre of the central spot which was generally so opaque that it went off scale. A scale that showed all of the central spot would have been too large to register the smaller peaks of interest.

2.12 X-ray Analysis

The X-ray analysis of specimens carried out at Imperial College was conducted using a Phillips PW1710 X-ray spectrometer with a Cu $K\alpha$ X-ray source, calibrated using a silicon {111} standard.

2.13 SIMS

The SIMS analysis was carried out at Imperial College using equipment made available by Dr. J.A. Kilner and operated by Mr. R.J. Chater. The instrument used was a SIMS Quadrupole instrument manufactured by Atomika, Munich with a beam of Xe^+ ions from a hot filament, gas source used at normal incidence. For surface profiling a beam current of 30nA was used whereas for depth profiling a beam current of 200nA was used. The beam was rastered over an area on the sample of up to 1mm x 1mm but was electronically gated to detect signal from the central 6% of the area to avoid the walls of the crater. For the native oxide profile this was 250 x 250 micrometres and for the other profiles, an area of 150 x 150 micrometres. The ion species detected were $^{16}\text{O}^+$, $^{16}\text{O}^-$, $^{52}\text{Cr}^+$, $^{140}\text{Ce}^+$ and $^{52}\text{Cr}^{16}\text{O}^+$. In order to provide a compensating electron flux while depth profiling, an electron flood gun was used simultaneously with the ion beam. This gun sent a 30 μA current of electrons into an area 3mm in diameter centred on the crater. Sputter rates were calibrated using standards of Cr, Cr_2O_3 and CeO_2 under similar conditions. For the profiles of the native oxide films, the yield of oxygen ions was plotted against depth. On the unimplanted metal, the $^{52}\text{Cr}^+$ and the $^{52}\text{Cr}^{16}\text{O}^+$ species were also detected in order to determine the position of the metal/oxide interface precisely and, as these were positive ions, the positive oxygen ion had to be detected. For the implanted specimens, it was decided to detect the species with a higher yield, that is the negative ion.

2.14 The Gas Reaction Cell

The gas reaction cell is an environmental cell that could be incorporated into an AEI 1MeV EM7 electron microscope to allow the direct observation of the interaction between a TEM sample and various gases. In this investigation the cell was used in conjunction with a special heating stage to study the oxidation of thin foils of chromium by pure oxygen at low pressure. A schematic diagram of the cell is given in figure 2.1. The cell was situated between the two objective pole pieces, just above the objective aperture assembly, with the locating cylinder fitting inside the

upper objective pole piece to align the cell along the central axis of the microscope. The cell consisted of two chambers, both pierced by 100 micrometre diameter apertures to allow the electron beam through the cell. Reaction between the gas and the sample occurred in the inner chamber and the outer chamber protected the rest of the microscope from the gas.

The gas was fed from a cylinder via a short length of plastic tubing to a needle valve. A pressure gauge attached to the valve gave the gas pressure on the cell side of the valve. The valve controlled the flow of gas into the inner chamber and around the sample holder. Gas filled the space between the pole pieces in order to provide a large volume of gas so that a constant pressure in the cell would be maintained; the whole volume was isolated from the microscope vacuum by O-ring seals except at the two apertures. These apertures led into the outer chamber of the cell which was constantly evacuated by a rotary pump so as to protect the column vacuum from gas leaking through the outer apertures; a pirani gauge measured the pressure on this side of the cell. The column vacuum could also be monitored simultaneously via a penning gauge so that gas leaks through the apertures could be detected.

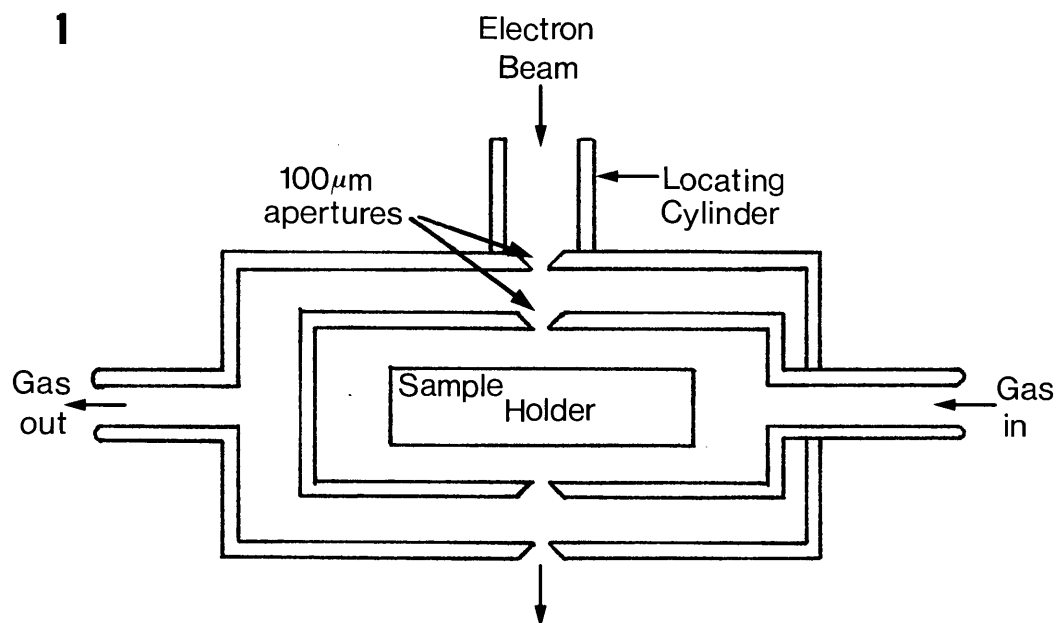
A schematic diagram of the heating stage used for the oxidation experiments is given in figure 2.1.2. The stage was a single tilt stage and as the space available inside the cell was limited, the sample could only be tilted through angles of about 10° . The current through the heating stage was provided by a constant current source, adjustable to give currents of between 0 - 2A. The temperature of the sample was measured by a thermocouple attached to the heating crucible. The crucible was mounted on two small bars to minimise heat loss through conduction to the sample holder. A clamping ring held the sample into the crucible. In operation there was an a.c. signal from the thermocouple's electronic display superimposed upon the objective lens current, which caused the image quality to deteriorate significantly. This could be avoided by switching off the display but this prevented measurement of the temperature. During the period when the sample was reaching temperature, significant movement of the sample occurred, preventing photography. Video recording of the image was tried but did not give sufficient image quality.

Another problem was contamination of the sample by carbonaceous material prior to oxidation. The contamination came from three sources: the specimen, the interior of the cell and from the gas feed pipes. Contamination from the specimen was very rarely a major effect as care was taken to avoid using dirty specimens. A sample was oxidised at the start of every session to remove the contaminants from the interior of the cell and the gas feed pipes were shortened to as small a length as possible, which reduced the effect. The residual contamination could not be eliminated.

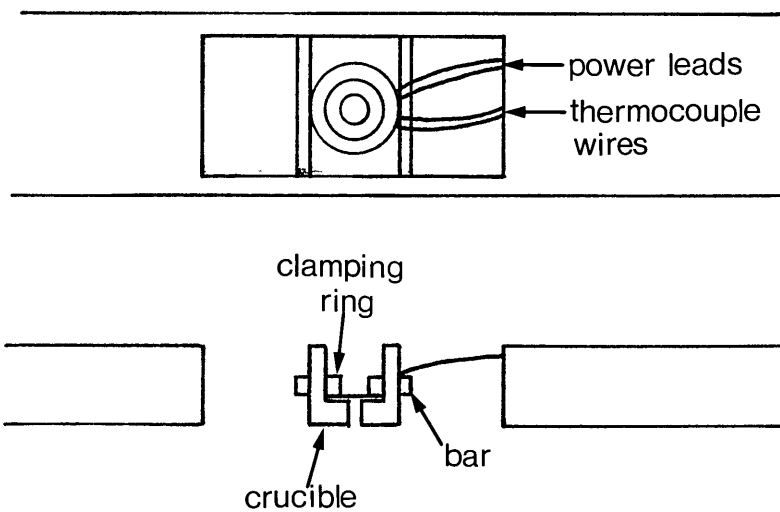
Figure 2.1

Schematic diagrams of the gas reaction cell and the heating stage used in the oxidation experiments carried out in the 1 MeV electron microscope. This figure is not to scale.

1



2



The sample was loaded into the heating stage and then into the microscope. Gas was allowed to flow into the cell at a rate controlled by the needle valve and the pressure was left to come to equilibrium. After some time, the current was turned on and set to the desired value. The sample took a finite length of time to reach the desired temperature and a graph of temperature indicated by the thermocouple near the sample plotted against the time after switching on the current is given in figure 2.2 for a desired temperature of 900°C. It should be noted that the desired temperature was only achieved after around 25 seconds. If a period of oxidation of one or two minutes was to be used then the sample would spend a large proportion of its time at the desired temperature and there would be sufficient time for the oxidation process to be observed. This was used to study the more developed oxide structures.

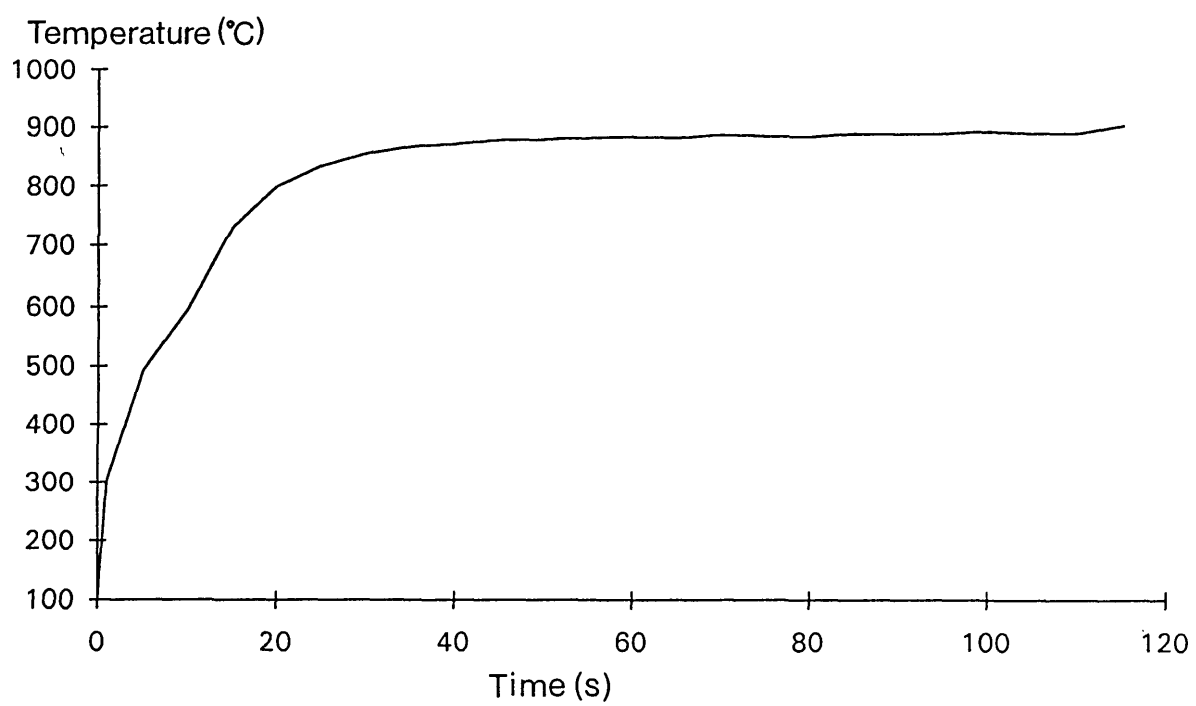
The purpose of the investigation was also to study the initial periods of oxidation and, at temperatures of 700°C and above, the length of time needed for the temperature to reach the desired value would be too long; the scale would have developed. Oxidation times of a few seconds were needed, but if times of less than 20 seconds were used then the sample would not have reached the desired temperature and temperatures above 700°C could not be reached. It was decided, in these cases, to set the current to a value that would give the desired temperature at equilibrium and use oxidation times of ten seconds. The temperature indicated after this period was usually around 650°C. Both the temperature reached by the sample and the time of oxidation were recorded. In the short oxidation time cases, the temperature will be reported as temperatures up to that reached after 10 seconds. In the case of longer times, the equilibrium temperature will be given. After the desired length of time, the current was switched off. The samples were left to cool and were then either analysed in the microscope or, more frequently, were removed for analysis in another electron microscope.

2.15 Short Term Oxidation

Samples of electrolytic chromium were oxidised in order to investigate the structure of the oxide film using transmission electron microscopy and so to compare the films grown on implanted and on unimplanted surfaces. The study was meant to complement the environmental cell work and to take it one stage further. The oxide films needed to be sufficiently thick so that they exhibited the characteristics of the thick films but not so thick that sample preparation for microscopy became arduous. Oxidation periods of several minutes at 750°C, 850°C and 950°C were used; longer times of oxidation were used in the parallel investigation at Harwell which also included thermogravimetric analysis. Temperatures below 1000°C were used so that

Figure 2.2

A graph of temperature measured by the thermocouple attached to the heating stage plotted against time after raising the current through the crucible to the desired level. This is for a cell oxygen pressure of 250 Pa.



the volatilisation of Cr_2O_3 would not be significant. The samples were oxidised in a purpose-built rig, described in the next section.

2.16 The Oxidation Rig

The apparatus used to oxidise the samples in this investigation was a modified thermogravimetric apparatus with a CI Electronics Ltd. Mark 2 vacuum microbalance head and a vertical tube furnace. The apparatus is shown in figure 2.3. The sample was placed on a wire tray suspended by a silica chain from one arm of the microbalance. The sample tray was constructed from nichrome wire and then oxidised to form a layer of chromium oxide on its surface so that the tray would not interfere with the specimen being oxidised. The chain hung down through two concentric silica tubes, the inner of which guided the gas onto the sample and then out of the rig up the outer tube. The outer tube came in two parts, separated by a seal, and the lower part of the tube could be removed at the seal to allow access to the sample tray. A water jacket surrounded the outer tube above the seal, to isolate the microbalance head from the heat of the furnace. A platinum/platinum10%rhodium thermocouple hung near to the sample tray and exited the tubes via another seal. The lower half of the apparatus could be surrounded by a vertical tube furnace that could be moved up and down on guide rails and was counterbalanced so that it did not fall. Two stops were fixed to the guide rails so that when the furnace was raised to the stops, the sample tray was in the hot zone of the furnace.

Gas came from two cylinders, high purity argon and high purity oxygen, fixed near the rig. The gas was fed via two valves, through a junction piece and then a length of tube into a vial of magnesium perchlorate powder that would dry the gas. A filter of silica wool in another vial prevented the powder being blown further through the system. Another tube fed the gas into the oxidation rig. On exiting the rig, the gas passed through a flowmeter and was then bubbled through silicone oil to keep the gas pressure in the rig constant and to prevent back diffusion. A flowrate of 600cc/minute of oxygen was used.

The heating rate of the sample in the rig was determined and a graph of temperature plotted against time from the moment the furnace was raised is given in figure 2.4. It can be seen that the temperature reaches its maximum after 10 minutes but, in practice, it was decided not to wait that long before starting the oxidation. There would be traces of oxygen in the gas stream regardless of the precautions taken and so the heat-up period was kept as short as possible. A gettering system whereby the gas was passed over hot titanium turnings to remove oxygen from the argon was constructed but was not used, due to the need for a rapid transition between the argon flow and the oxygen flow and also because of the risk of pure oxygen entering the

Figure 2.3

A schematic diagram of the oxidation rig used including a flow chart of the gas feed system. The figure is not to scale.

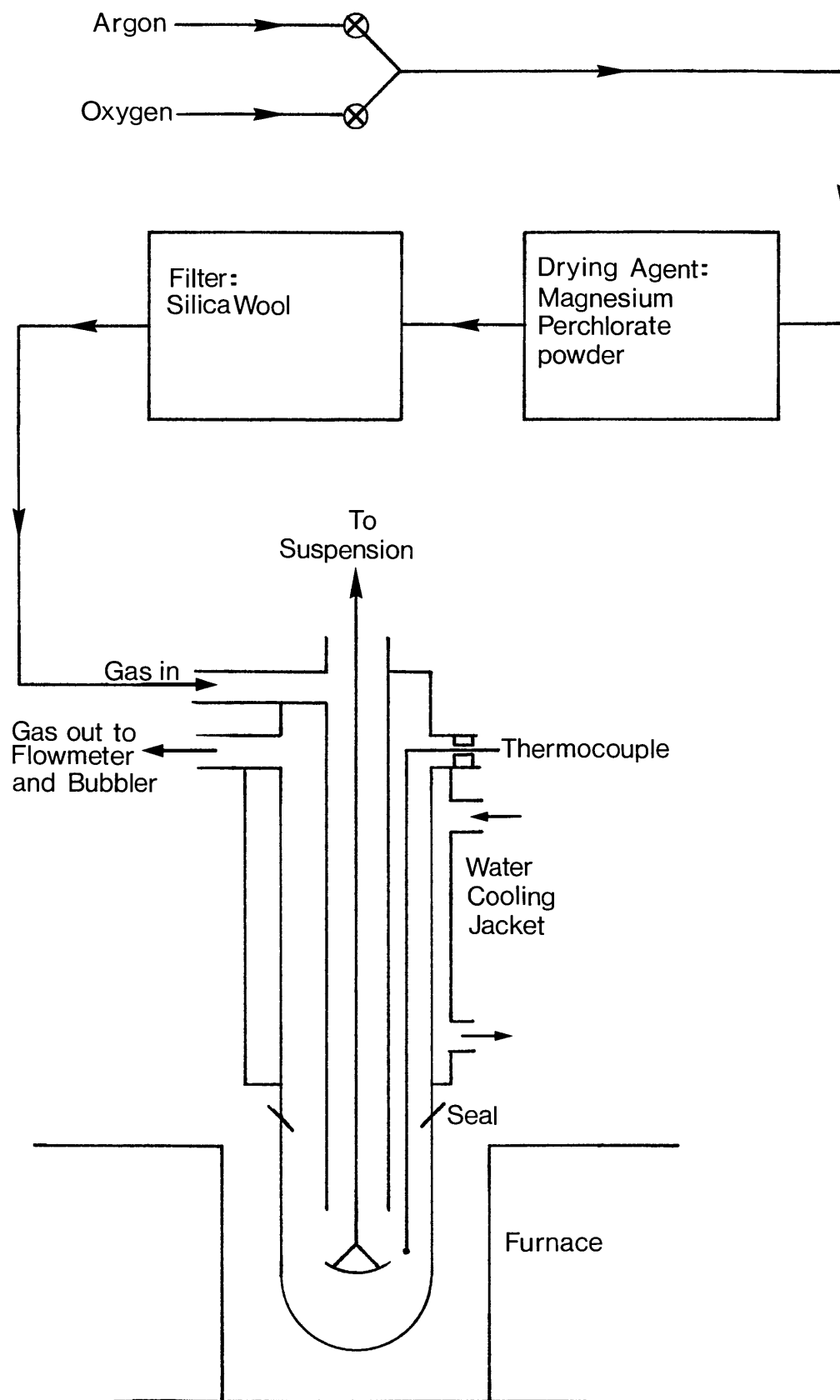
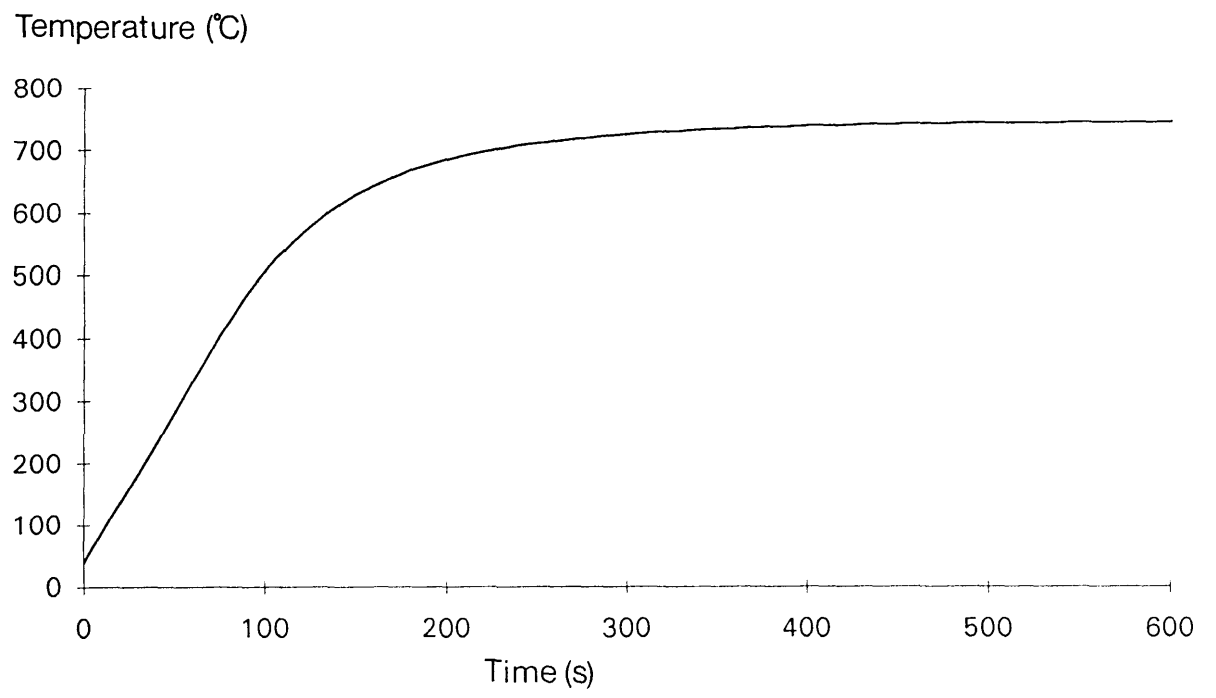


Figure 2.4

A graph of temperature measured by a thermocouple next to the sample holder in the oxidation rig plotted against time after the furnace was raised into position. This is for a gas flow of 600 cm^3 per minute and a required temperature of 750°C .



gettering system. A compromise heating period of six minutes was used. The temperature rise during oxidation would have little effect as the weight gain of the sample was not being measured.

2.17 Preparation of samples for oxidation

Coupons of standard-annealed electrolytic chromium were ground to a thickness of 200 - 300 micrometres using 1200 grit SiC paper with a water lubricant and six discs, 3 mm in diameter were spark eroded from each coupon. The discs were then either ground to approximately 100 micrometres in thickness and mechanically polished using a suspension of 2 micrometre alumina particles in distilled water or electropolished in the manner mentioned previously. There were two reasons for oxidising 3 mm discs rather than the 1 cm square coupons: firstly the oxidised samples were to be back-thinned for examination of the oxide film in the TEM and so the less that had to be done to the oxidised samples, the more likely that the oxide film would stay intact. Secondly there would be six times as many samples for oxidation. Tests on discs and coupons showed that the oxide films on disc specimens would be representative of the oxidation behaviour of bulk specimens. At corners and edges of bulk specimens the stress state of the oxide is different than in the centre of the specimens and there is a pinning effect on the oxide; the affected region extends for a small distance into the sample and this might override the normal oxidation behaviour of small samples. No modification of the oxidation behaviour was seen on mechanically polished samples; on the electropolished discs there was a region around the edge of the disc, approximately 200 micrometres wide, where the morphology of the oxide buckling differed from that in the centre of the disc, although the differences varied from disc to disc.

After mechanical polishing/electropolishing, the discs were left to soak for some time to remove the resin/lacquer used in their preparation. They were then cleaned using an ultra-sonic bath containing: firstly distilled water, then absolute alcohol and, finally, Inhibisol. The solvents were chosen so that each dissolved away that previously used, the Inhibisol should completely vapourise, leaving a clean metal surface. If the samples were not immediately oxidised, as was occasionally the case, then they received a further wash in Inhibisol immediately prior to oxidation. The discs were cleaned individually and carried to the oxidation rig in separate gelatine capsules.

2.18 Oxidation Procedure

The oxidation experiments in each set were usually carried out in one session with the samples being oxidised consecutively. While the furnace was being brought up to temperature, the rig was flushed out with high purity argon. This took approximately 20 minutes. The first disc to be put in to the rig would be left, at temperature, in the flowing argon for 10 minutes in order to rid the system of any remaining oxygen. After the furnace had been lowered and the rig had cooled sufficiently, it was opened and the disc replaced with a fresh sample. The rig would be re-sealed and the furnace raised so that the sample was in the hot zone of the furnace. Argon would be kept flowing continuously throughout this entire process. The sample was left to reach the operating temperature for six minutes. After this time the argon valve would be closed and oxygen, at a fixed, constant flowrate, would be let in to the system by opening the oxygen valve. The timing of the oxidation started from the moment when the valve was opened to the moment it was closed and the argon flow re-established. The furnace would then be immediately lowered. The rig took 10 minutes to cool sufficiently for it to be opened and the next sample inserted. If the temperature of the furnace needed to be changed, then argon was kept flowing through the system while the new temperature was achieved.

The oxidised specimens were examined using light microscopy as well as scanning and transmission electron microscopy.

3 RESULTS

3.1 Microstructural Characterisation

Before any oxidation experiments could be carried out the microstructure of the electrolytic chromium had to be investigated and, where necessary, altered to provide a suitable substrate for oxidation. The metal in its bulk form was characterised first.

The coupons of electrolytic chromium as-received were bright in appearance with a rough surface but, when mechanically polished, the surface took on a milky appearance. Figure 3.1.1.1 shows a light micrograph of the mechanically polished surface of a coupon of the untreated electrodeposited chromium using Nomarski interference contrast to highlight surface variations. When the coupon was electropolished, the network of microcracks contained in the material was revealed, figure 3.1.1.2. The cracks are randomly distributed throughout the metal and generally run vertically, that is: parallel to the direction of deposition of the metal. There are no cracks whose plane lies parallel to the plane of the coupon implying that the cracks were due to a uniform stress in the plane of the coupon that had no component perpendicular to that plane. The mean spacing of the cracks in the surface of the sample in figure 3.1.1.2 is 16 micrometres whereas that in figure 3.1.1.1 is 45 micrometres. The two micrographs of the cracked surfaces, figures 3.1.1.1 and 3.1.1.2, show differing amounts of cracking; this is due, in part, to the metal on the surface of the mechanically polished coupon, figure 3.1.1.1, having been smeared by the polishing procedure, concealing some of the cracks. This smearing is indicated by the larger cracks appearing discontinuous due to partial covering. The electropolished sample probably overestimates the number of cracks intersecting the surface of the coupon because the electropolishing solution may, through preferential attack, reveal cracks that would normally be covered.

Transmission electron microscopy, figure 3.1.1.3, revealed the internal microstructure of the metal, showing it to be highly microcrystalline - the mean grain diameter is (43 ± 2) nanometres. Electron transparent areas were rather difficult to produce from samples of the untreated metal as the specimens would break up along the lines of the microcracks running through the metal, leaving only occasional areas of thick matrix to be studied. A selected area diffraction pattern with its rings indexed is given in figure 3.1.1.4. This pattern consists solely of reflections corresponding to a $\langle 111 \rangle$ chromium zone axis normal to the coupon surface. The rings imply a free rotation of orientations around this axis.

This preference is repeated in the X-ray diffractometer spectra in figure 3.1.2. These spectra were taken from the electrolytic chromium in an untreated state and

Figure 3.1.1

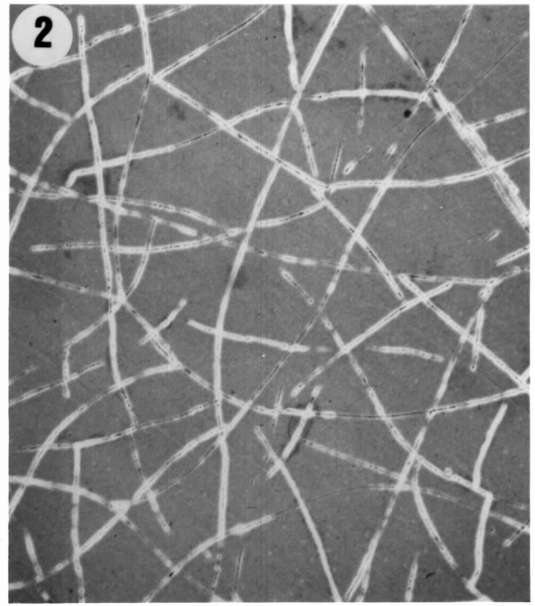
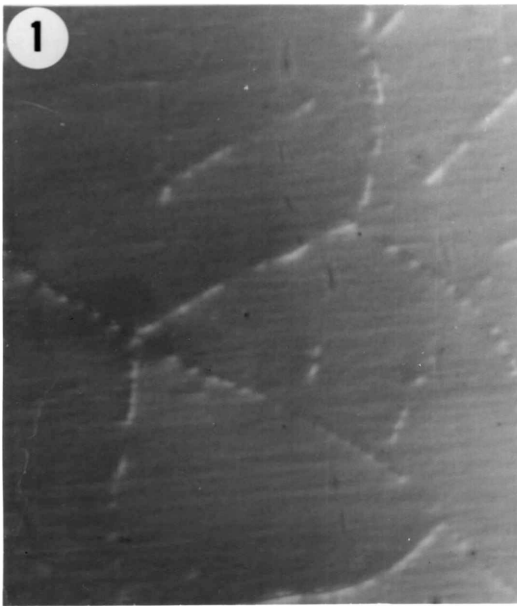
A figure showing the microstructure of the electrolytically deposited chromium prior to the annealing treatments.

3.1.1.1 Light micrograph of a mechanically polished surface of a coupon of the electrolytically deposited chromium using Nomarski interference contrast to highlight the appearance of the crack network on the surface of the sample.

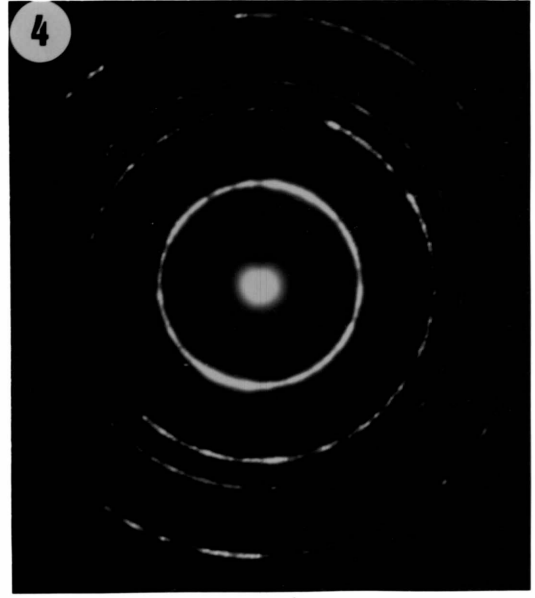
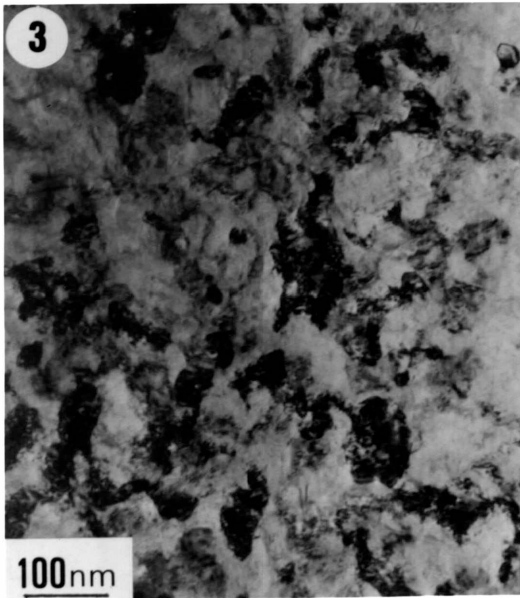
3.1.1.2 A scanning electron micrograph of a coupon of the electrolytic chromium. The surface has been electropolished in order to reveal the crack network. A secondary electron image.

3.1.1.3 A transmission electron micrograph of the electrolytic chromium showing the very fine grain size.

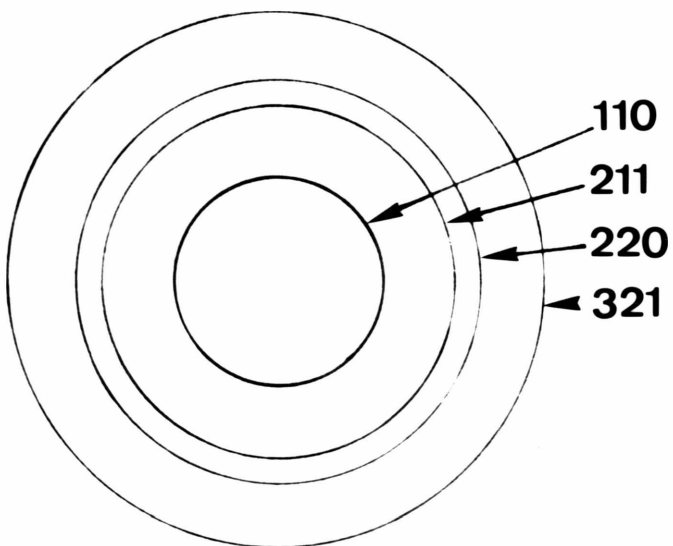
3.1.1.4 A selected area diffraction pattern from the electrolytic chromium. The aperture selected an area of the sample of diameter 2.7 micrometres; sampling so many grains that the reflections form rings. The rings are indexed in the adjacent diagram.



50 μm



$rd = 2.75 \text{ cm}\text{\AA}$



after annealing for 3 hours in 1 atmosphere hydrogen at 1500°C using the same conditions so the traces are comparable. Figure 3.1.2.1 shows the trace from the untreated chromium. This spectrum shows a {222} chromium peak far larger than the other peaks and, when compared with the {222} peak in the post-annealing spectrum, the peak is seen to be broadened implying a microcrystalline structure with a high degree of inherent strain. The {220} and {310} peaks are missing from this trace. The peaks just to the right of the {222} peak and the {110} peak were not identified, but they do not correspond to lattice spacings from either the chromium or to the chromium (III) oxide structure. The spectrum in figure 3.1.2.2 is taken from electrodeposited chromium after annealing for 3 hours in 1 atmosphere hydrogen at 1500°C. The peaks are sharper, the main peaks are higher and all of the chromium peaks are present. The {222} peak still dominates but the {110} and the {211} peaks have become stronger.

Figures 3.1.2.3 and 3.1.2.4 are {110} pole figures taken from untreated electrodeposited chromium and from electrodeposited chromium annealed for 3 hours in hydrogen at 1500°C. These figures were taken normal to the surface of each specimen and show two different levels of texture. The total diffracted intensity is found for each pole figure and is divided over the whole pole figure to give the random pole intensity for the figure. The density of poles in each part of the figure is then represented by contour lines: each contour line being a multiple of the random pole intensity. The pole figure from the untreated chromium, figure 3.1.2.3, shows only contours of 1 x random indicating a very weak texture; whereas that in figure 3.1.2.4 shows areas of high pole density, indicated by contours of 4 x random, distributed in two rings around the centre of the figure. This indicates a large degree of texture and comparing this distribution of poles with standard {110} pole figures gives the centre orientation, and thus the direction normal to the surface of the metal, as $\langle 111 \rangle$. This supports the evidence of the X-ray diffraction traces and the selected area electron diffraction patterns.

Figure 3.1.3 shows transmission electron micrographs of the microstructures found in electrolytic chromium after the first and second series of heat treatments. The heat treatments were carried out in three different atmospheres: argon, hydrogen and in a vacuum of $2 \cdot 10^{-9}$ Pa. The chromium annealed for 1 hour in argon at 1050°C, figure 3.1.3.1, was found to contain a uniform dispersion of small particles, around 10 - 50 nanometres in size. There were also lines of larger particles ranging in size from 50 - 500 nanometres such as the line indicated in figure 3.1.3.1. The chromium annealed for 24 hour at 1050°C in argon also contained lines of large particles; these, however, were generally much larger, most being in the range 100 - 1000 nanometres. The dispersion of fine particles was completely missing and the grain size of the metal had increased.

Figure 3.1.2

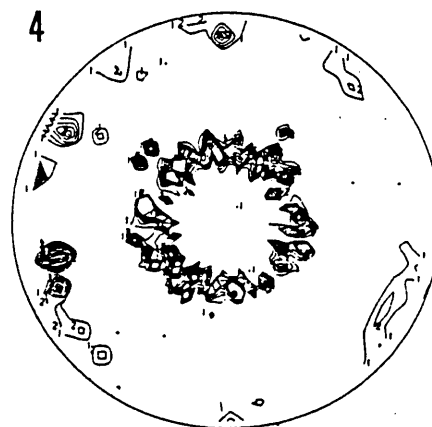
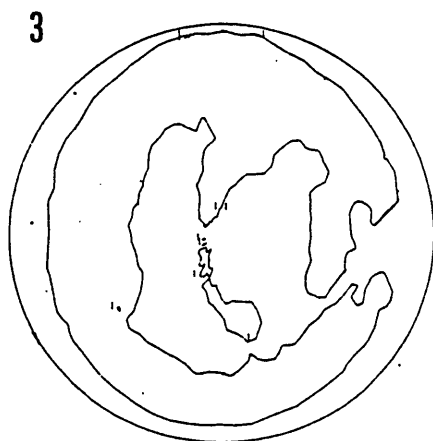
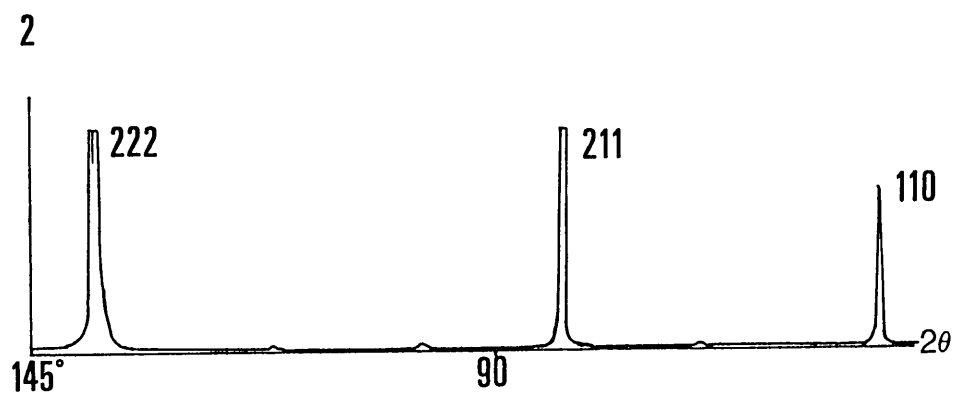
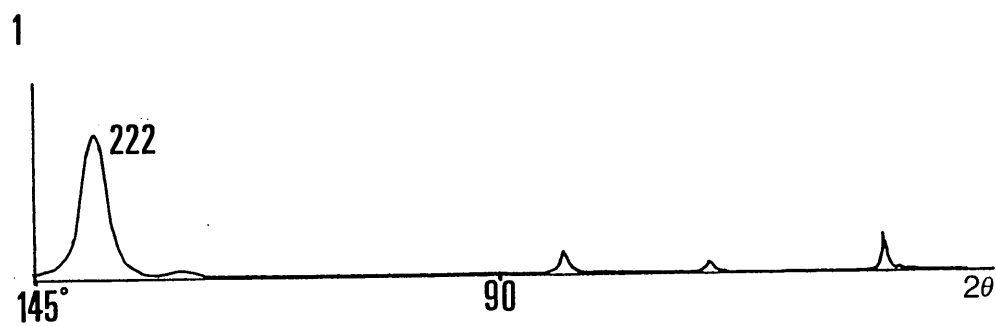
X-ray analysis, using diffractometry and pole figures, of electrolytic chromium in the untreated state and after annealing for 3 hours at 1500°C in hydrogen. The diffractometer traces show the texture and the broadening of the major {222} peak due to strain and small grain size in the untreated metal and the effects on both of annealing. The {110} pole figures show the texture in the two materials.

3.1.2.1 An X-ray diffractometer spectrum from untreated electrolytic chromium.

3.1.2.2 An X-ray diffractometer spectrum from electrolytic chromium annealed for 3 hours at 1500°C in hydrogen. This spectrum was gained using the same conditions as that for 3.1.2.1.

3.1.2.3 {110} pole figure from untreated electrolytic chromium. The lines are contours of pole density.

3.1.2.4 {110} pole figure from electrolytic chromium annealed for 3 hours at 1500°C in hydrogen. This figure was acquired using the same conditions as that for 3.1.2.3.



Although the dispersion of small particles was uniform there were areas, adjacent to some grain boundaries and alongside the lines of larger particles, that were denuded of the smaller particles. Such areas can be seen in figure 3.1.3.1. It was assumed that the particles were Cr_2O_3 ; the literature (6) and subsequent selected area diffraction of the particles confirmed this.

The second series of anneals show very little change from the findings already mentioned although they shed more light on the processes involved. Figures 3.1.3.3 and 3.1.3.4 show samples of the chromium annealed at 600°C for 24 hours. The dispersion of small particles is obvious in both samples. The conglomeration of spots indicated by the arrow in figure 3.1.3.3 is contamination from the electropolishing solution. Lines of larger particles are not visible in these specimens because, in the electron transparent areas near the edges of the foils produced, the lines were preferentially attacked by the polishing solution leaving lines of holes occasionally bridged by metal as in figure 3.1.3.4. As with the untreated samples this causes most of the electron transparent areas to drop off leaving very little to study.

The samples annealed at 800°C for 24 hours, figures 3.1.3.5 and 3.1.3.6, suffered less from their preparation although there was still a tendency for the metal to crack along the lines of larger particles. The size of the small particles does not vary between the 1050°C , 1 hour; the 600°C , 24 hour and the 800°C , 24 hour annealed samples; however, the larger particles in the 800°C samples show a smaller variation in size than those in the 1050°C sample as can be seen in figure 3.1.3.5. Regions depleted of particles can also be seen in figures 3.1.3.5 and 3.1.3.6 alongside the lines of large particles. Also noticeable in these figures is the pinning effect of the lines of large particles on the grain boundaries.

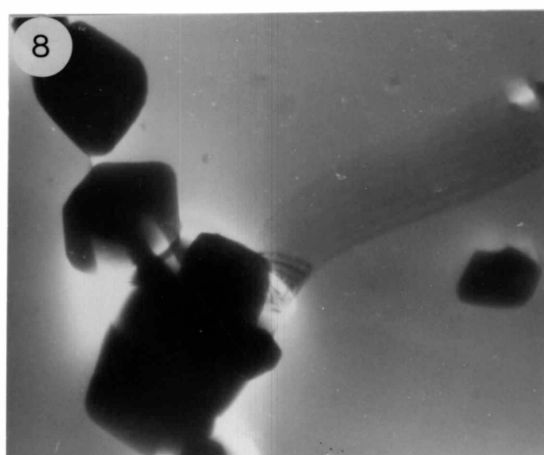
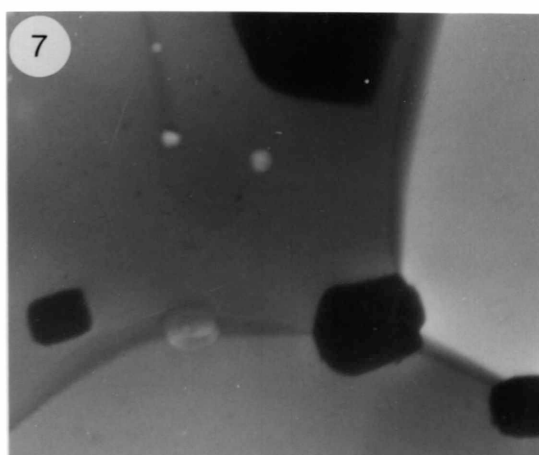
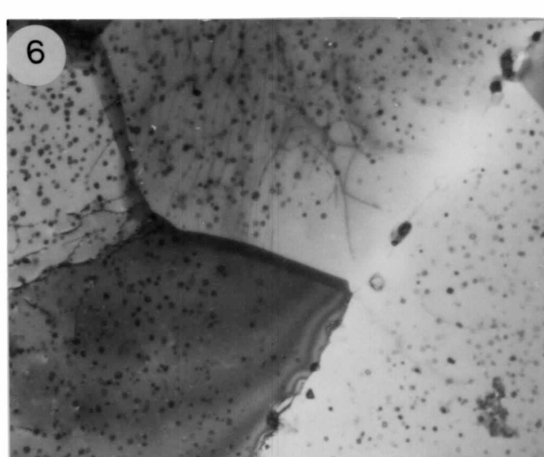
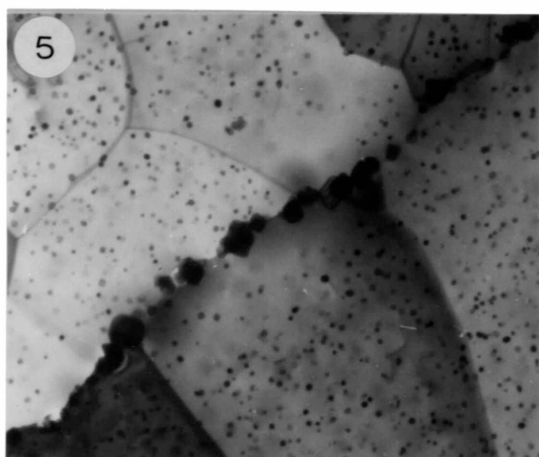
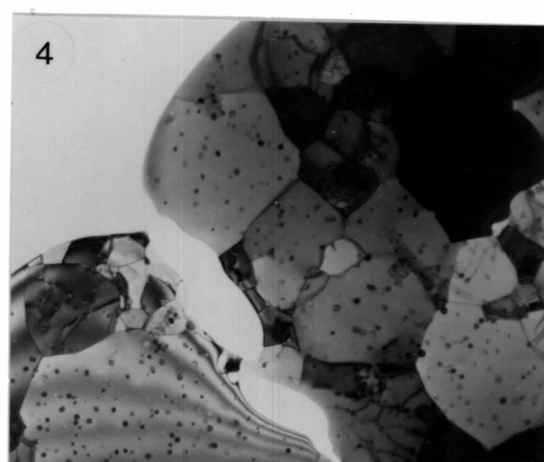
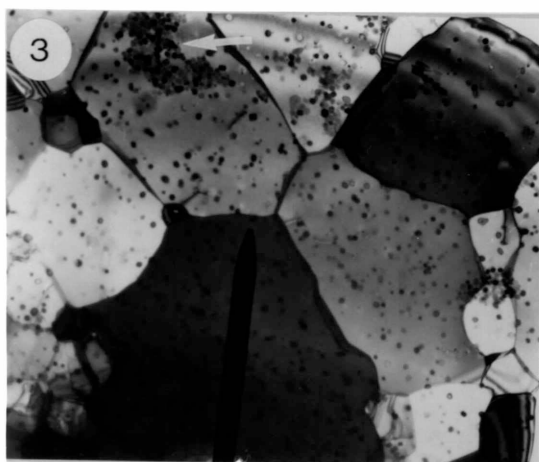
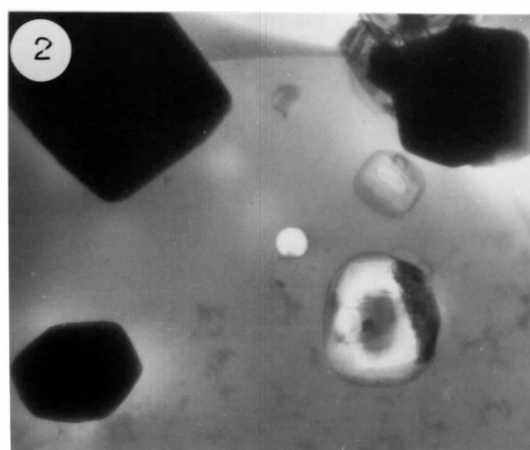
Figures 3.1.3.7 and 3.1.3.8 show the microstructure of the 1000°C , 24 hour annealed specimens. These, as one would expect, are very similar to the 1050°C , 24 hour annealed specimen. Large particles still form lines through the metal, although these have less of a pinning effect on the grain boundaries of the metal. A few small particles exist, albeit in the centre of grains and usually 5 micrometres or more from the lines of particles. The main results from this series of heat treatments are that: for treatments below 24 hours at 1050°C , the atmosphere of the treatments seems to make no difference to the microstructure; the microstructure develops from a fine dispersion of particles with lines of larger particles and a small grain size, to lines of more widely spaced large particles and a large grain size and finally the cracks heal, probably by a sintering process.

The third series of heat treatments are illustrated in figure 3.1.4. Figure 3.1.4.1 shows the microstructure of chromium annealed at 1000°C for 3 hours in 1 atmosphere pressure of hydrogen. The dispersion of small particles is still evident but with wide particle-free regions around the grain boundaries. The larger particles

Figure 3.1.3

Transmission electron micrographs of the electrolytic chromium after the first and second series of heat treatments showing the development of the microstructure and contrasting the three annealing atmospheres.

- 3.1.3.1 Electrolytic chromium annealed in high purity argon for 1 hour at 1050°C.
- 3.1.3.2 Electrolytic chromium annealed in high purity argon for 24 hours at 1050°C.
- 3.1.3.3 Electrolytic chromium annealed in a vacuum of $2 \cdot 10^{-9}$ Pa. for 24 hours at 600°C.
- 3.1.3.4 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 24 hours at 600°C.
- 3.1.3.5 Electrolytic chromium annealed in a vacuum of $2 \cdot 10^{-9}$ Pa. for 24 hours at 800°C.
- 3.1.3.6 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 24 hours at 800°C.
- 3.1.3.7 Electrolytic chromium annealed in a vacuum of $2 \cdot 10^{-9}$ Pa. for 24 hours at 1000°C.
- 3.1.3.8 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 24 hours at 1000°C.



1 μm

show only a small variation in size and this value falls somewhere between the sizes of those in the 800°C, 24 hour and the 1000°C, 24 hour heat treatments. There is still evidence of grain boundary pinning by the particles. Figure 3.1.4.2 is from chromium treated for 3 hours in hydrogen at 1100°C. The small particles have disappeared leaving only lines of more widely spaced large particles. The particles have grown and the variation in size is more pronounced; they also no longer have a large pinning effect on the grain boundaries in the material. This sample was a coupon from batch B, table 5, whereas the others studied were from batch A; the main difference between the two batches is the higher oxygen content of batch B and this is unlikely to cause major differences in the general behaviour of the metal's microstructure under heat treatment.

Metal treated for 3 hours at 1200°C in a vacuum has large relatively isolated particles, figure 3.1.4.3. Sufficiently few were observed by transmission electron microscopy that statements about their average size cannot be made, although the particle in the figure is larger than most particles previously observed. In contrast, the metal annealed for 3 hours at 1200°C in hydrogen, figure 3.1.4.4, has numerous particles. There are still traces of the dispersion of small particles and the lines of larger particles contain far more particles than for the 1000°C, 3 hour sample. In general the particles in the 1200°C, hydrogen-annealed sample are smaller than those in the 1000°C, hydrogen-annealed sample.

For the 1300°C, 3 hour, hydrogen-annealed sample, the particles are few and far between, figure 3.1.4.5. Those that remain are 0.5 - 1 micrometres in size, usually at the low end of this range. The 1500°C, 3 hour, hydrogen-annealed sample is shown in figure 3.1.4.6. Particles were never found in this material using transmission electron microscopy. A subsequent anneal of 1 hour at 500°C in a vacuum of 2.10^{-9} Pa does not have a detectable effect on the microstructures detailed above.

Figures 3.1.4.7 and 3.1.4.8 show a dark field micrograph and a selected area diffraction pattern of one of the large particles found in the heat treated samples. The diffraction pattern is indexed, giving it as a Cr_2O_3 $[\bar{3}211]$ zone axis; the extra spot indicated on the diffraction pattern is a chromium $\{110\}$ reflection. The dark field micrograph was taken from the $(02\bar{2}\bar{2})$ reflection.

The treated chromium from the third series of anneals was electropolished to reveal the grain structure. Figure 3.1.5 shows scanning electron micrographs of the surfaces of these samples imaged using back-scattered electrons. The grains, revealed here by channelling contrast vary considerably in size. A graph of grain size plotted against temperature is given in figure 3.1.6. Also visible in each of the micrographs are pits in the surface of the metal. It is assumed that these pits are produced by large oxide particles being preferentially attacked by the polishing solution and dropping

Figure 3.1.4

Transmission electron micrographs of the electrolytic chromium after the third series of heat treatments showing the further development of the microstructure of the metal.

3.1.4.1 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1000°C.

3.1.4.2 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1100°C.

3.1.4.3 Electrolytic chromium annealed in a vacuum of $2 \cdot 10^{-9}$ Pa. for 3 hours at 1200°C.

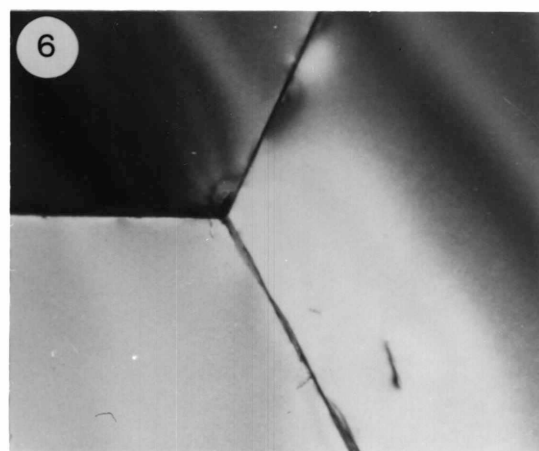
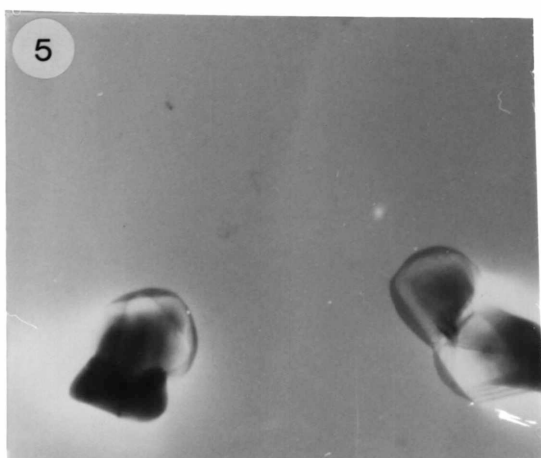
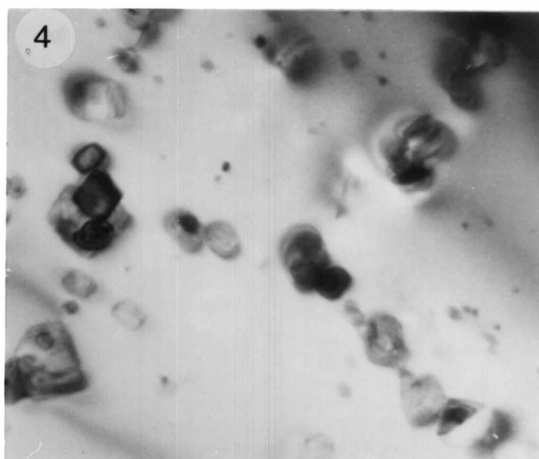
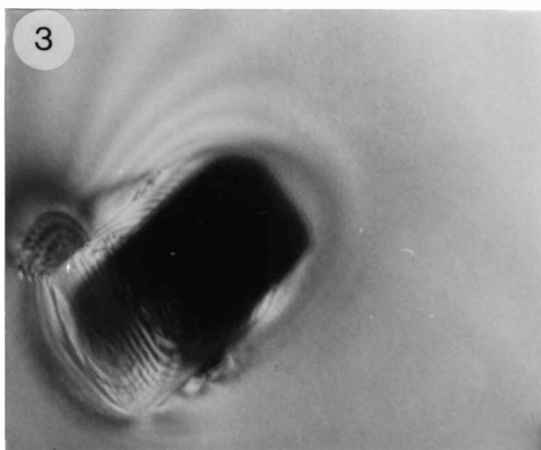
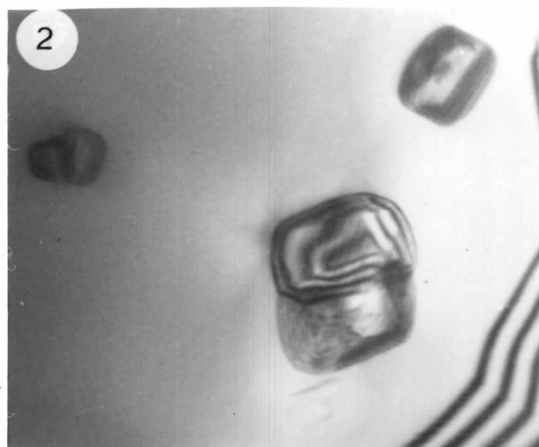
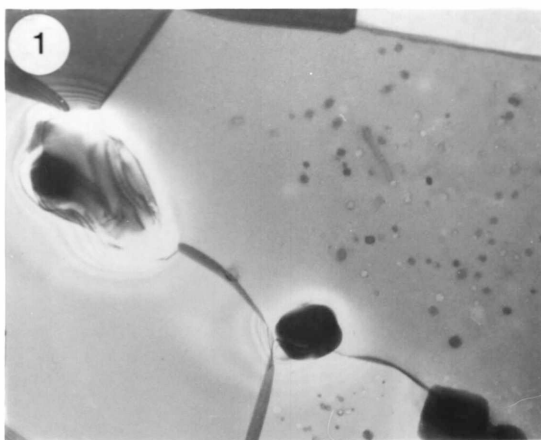
3.1.4.4 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1200°C.

3.1.4.5 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1300°C.

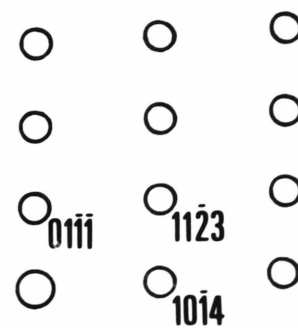
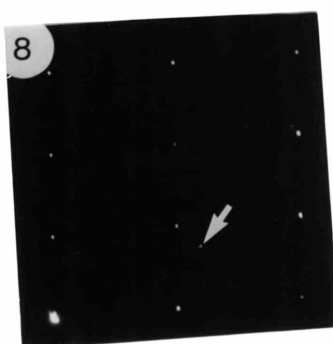
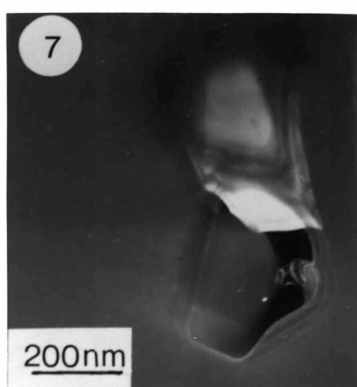
3.1.4.6 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1500°C.

3.1.4.7 Dark field micrograph of a particle from the matrix of the 1100°C, 3 hour, hydrogen annealed metal. The dark field image was taken from the $(02\bar{2}\bar{2})$ reflection.

3.1.4.8 Selected area diffraction pattern from the particle in figure 3.1.4.7; indexed in the adjacent diagram. The pattern is a $\langle \bar{3}211 \rangle$ Cr_2O_3 zone axis. Indicated by an arrow is a $\text{Cr } \{110\}$ reflection from the matrix.



1 μm



out. If the majority of the pits had been produced by etching or some other process then their numbers would not be expected to decrease with increasing temperature of heat treatment as they do in this figure.

The lines of large particles revealed by the electropolishing can be most easily seen on the 1000°C, 3 hour sample, figure 3.1.5.1. It should be noticed that the network of lines of particles is similar to the crack network in the untreated sample. The lines of particles are less well defined in figure 3.1.5.2, the sample annealed at 1100°C for 3 hours in hydrogen. Whilst the grains in the 1000°C sample are smaller than the spacings of the lines of particles, in the 1100°C sample they are equal to, or greater than, this spacing implying that the pinning effect of the lines of particles has diminished greatly. For samples treated at temperatures above 1100°C, the particles are isolated rather than in obvious lines and there is evidence of abnormal grain growth. This is shown by the occurrence of several grains that are much larger than the others in the metal. Figures 3.1.5.3 and 3.1.5.4 make the effects of the treatment atmospheres obvious. The sample annealed at 1200°C in a vacuum, figure 3.1.5.3, has large particles and large grains while that annealed in hydrogen at the same temperature has more numerous, smaller particles and a smaller grain size. The contrast between these two figures also shows that the particles must still be retarding grain growth as the mean grain diameter for the hydrogen-annealed sample is lower than that for the vacuum-annealed sample at the same temperature. Above 1200°C for hydrogen-annealed material the particles become smaller, although not particularly less numerous, and the grains become larger. This is illustrated in figures 3.1.5.5 and 3.1.5.6: the 1300°C and 1500°C hydrogen-annealed samples. The particle number density on the 1300°C sample is $2 \times 10^9 \text{m}^{-2}$, on the 1400°C sample it is $3 \times 10^9 \text{m}^{-2}$ and on the 1500°C sample $2 \times 10^9 \text{m}^{-2}$.

Figure 3.1.6 shows graphs of data taken from the micrographs of the electropolished samples of hydrogen-annealed chromium. The grain size of each sample is plotted in figure 3.1.6.1, against the temperature at which it was annealed; similarly, the number of particles per unit area on the electropolished surface is plotted in figure 3.1.6.2, against the temperature of the anneal. The grain size was determined for the 24 hour heat treatments as well as for the 3 hour heat treatments; the 24 hour results were taken from transmission electron micrographs and the 3 hour results from back-scattered electron images. Figure 3.1.6.1 shows a sudden increase in grain size above 1500K; this is evident in figure 3.1.5, where the grains become obviously larger above 1200°C. The grain size of the coupon from batch B, annealed at 1100°C for 3 hours in hydrogen, appear to fit reasonably with the other data and its larger value can be ascribed to the existence of abnormally large grains in the metal. The standard errors in each of the points in figure 3.1.6.1 are too small to register on the graph but it must be noted that these error bars are standard errors in the sample

Figure 3.1.5

Scanning electron micrographs of the electropolished surfaces of the electrolytic chromium after the third series of heat treatments showing the variation in grain size of the metal and also the changing particle distribution. Back-scattered electron images.

3.1.5.1 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1000°C.

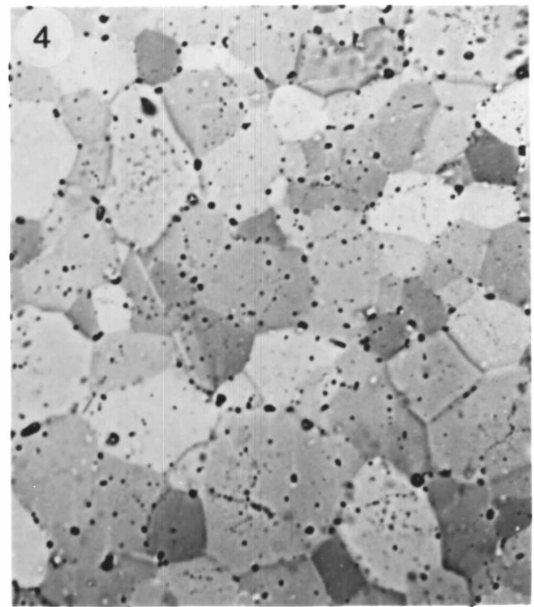
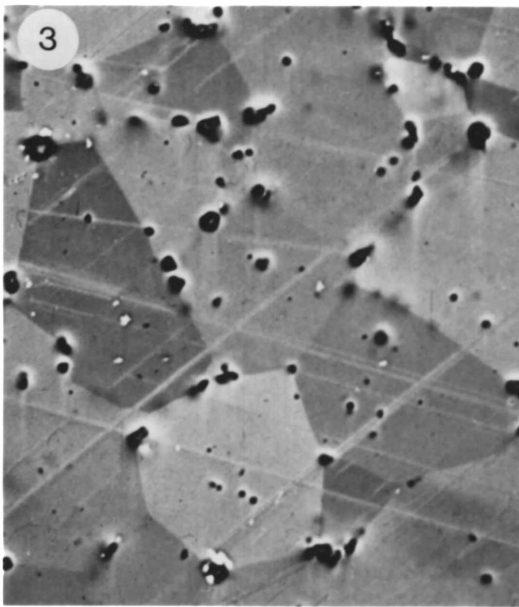
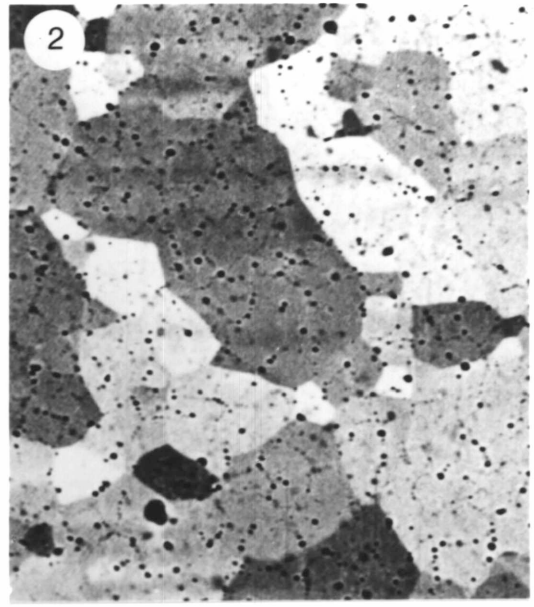
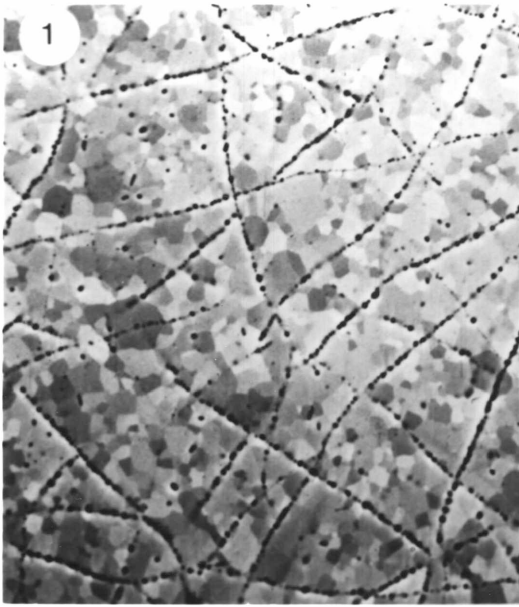
3.1.5.2 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1100°C.

3.1.5.3 Electrolytic chromium annealed in a vacuum of $2 \cdot 10^{-9}$ Pa. for 3 hours at 1200°C.

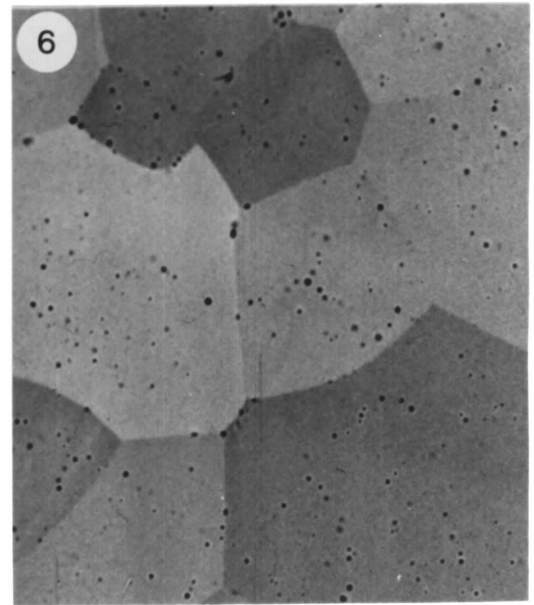
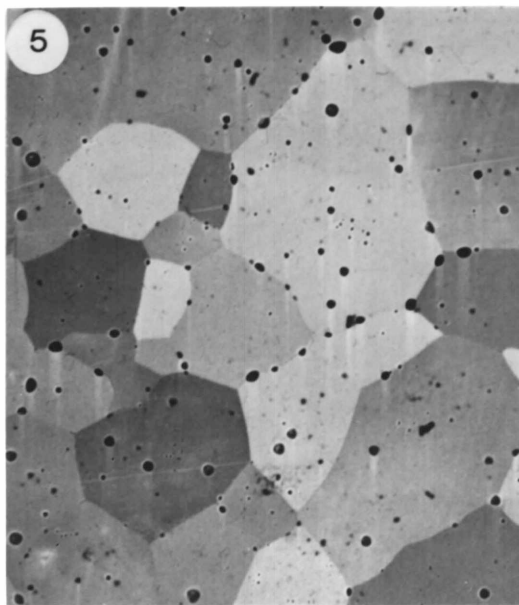
3.1.5.4 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1200°C.

3.1.5.5 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1300°C.

3.1.5.6 Electrolytic chromium annealed in 1 atmosphere of hydrogen for 3 hours at 1500°C.



25 μ m



100 μ m

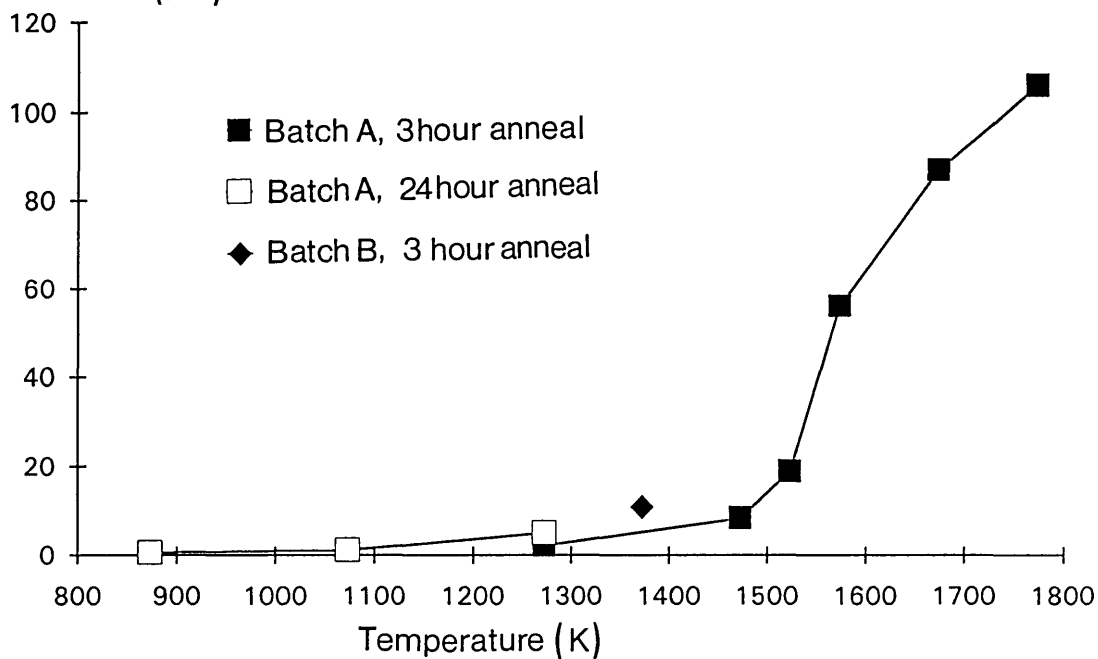
Figure 3.1.6

Graphs of grain size versus annealing temperature and particle number density versus temperature for coupons of electrolytic chromium annealed in hydrogen. The compositions of batches A and B are given in table 5.

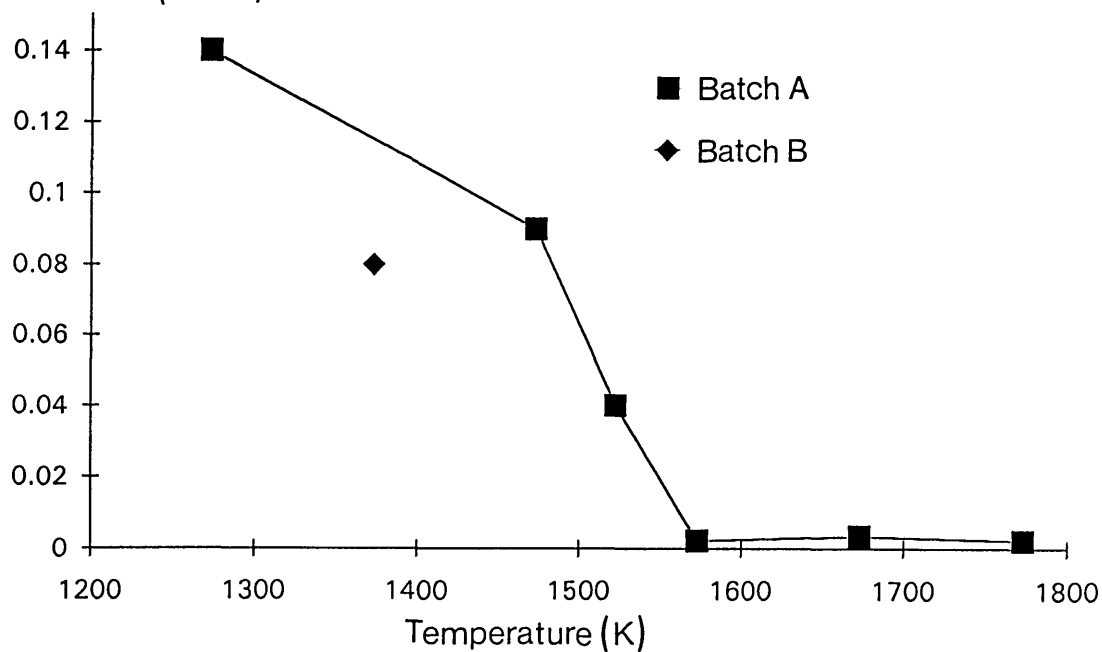
3.1.6.1 Plot of grain size versus annealing temperature for samples of chromium from batch A annealed for 24 hours and for 3 hours and for a sample from batch B annealed for 3 hours at 1100°C.

3.1.6.2 Plot of the number density of particles on the electropolished surfaces of coupons of hydrogen-chromium versus annealing temperature. The coupons were annealed for 3 hours.

1

Mean grain
diameter (μm)

2

Number of
particles per
unit area (μm^{-2})

mean for each temperature and are not necessarily representative of the population mean.

Figure 3.1.6.2 is not as conclusive as figure 3.1.6.1 but there is a sustained drop in the particle number density on the surfaces of samples annealed at temperatures above 1500K. This is, again, evident in the micrographs in figure 3.1.5. Once again, the error bars for the points are too small to register on the figure and the qualification, detailed above, that each point is only a sample mean, also holds.

Table 7 gives the results of mass spectrometric analysis of coupons of electrolytic chromium after various heat treatments with the analysis for batch A of the untreated metal given for comparison. The mass spectrometry was carried out by NRC, Canada. The oxygen levels can be seen to drop dramatically above 1200°C. The two 1200°C heat treatments have no obvious effect on the absolute abundance of oxygen in the metal, only on its distribution through the metal. The sulphur content has been reduced significantly by the 1200°C heat treatments, regardless of the atmosphere used. The copper and nickel levels change due to contamination from the furnaces used for heat treatment. Two furnaces were used: one for hydrogen atmospheres and one for heat treatments in a vacuum. The former gave significant copper contamination and the latter, significant nickel contamination. The abundances of the other elements are unchanged by the heat treatments with the exception of silicon. This shows an increased abundance in the standard-annealed sample. From table 7 the abundance of antimony appears to double but this is only due to fluctuations in the abundance of antimony in the as-deposited metal, table 5.

3.2 Surface Characterisation

Having characterised the bulk of the metal, the surface of the standard-annealed chromium was then investigated. Figure 3.2.1 shows light micrographs of the surfaces of the standard-annealed chromium, both implanted and unimplanted, in a mechanically polished condition. Figure 3.2.1.1 is unimplanted, standard-annealed chromium that has been ground on SiC paper to 1200 grade and then polished using alumina particles with a mean size of 2 micrometres, as a suspension in water. The micrograph uses the Nomarski interference technique to highlight surface variations. Visible are scratches due to the polishing and also pits in the surface. The pits appear to be raised above the surface but this is an optical illusion caused by the interference technique; the pits are approximately 1 micrometre in size, taking into consideration the enlarging effect on the apparent size of the pits of the contrast being used. The grain structure has been etched during the polishing procedure because the long nap of the cloth used causes differential wear of the grains.

Table 7

A table giving the analyses of the electrolytic chromium after heat treatment under the conditions stated. The analyses were carried out at NRC, Canada by mass spectrometry and are given in parts per million by mass.

Composition in ppm by mass.

	Un- treated.	1200 C, 3 hours, vacuum.	1200 C, 3 hours, hydrogen.	1500 C, 3 hours, hydrogen.
Cr		balance		
O	1100	1700	1300	4.8
N	1.8	3.8	4.0	2.6
Si	0.7	0.9	0.85	3.2
S	83	5.5	12	3.8
Cl	28	48	38	62
Fe	5.2	5.9	2.9	6.7
Ni	0.064	57	0.22	0.78
Cu	8.7	52	280	340
Sn	20	15	14	17
Sb	280	610	430	600
Other	21.5	33.7	29.0	33.4

Figure 3.2.1.2 shows a light micrograph of an unimplanted coupon that has been ground and polished using only diamond particles. This has scratches that are more obvious than those in the previous figure and there appear to be far more pits on the surface of the sample in figure 3.2.1.2 than that in figure 3.2.1.1. The pits range in size from approximately 0.5 micrometres up to 2 micrometres. If the number of pits per unit area is calculated for each of the first four micrographs in the figure, assuming that each of the black spots is a pit then a comparison can be made with the particle number density found after electropolishing the surface, from figure 3.1.5.6. The pits on the surface of the electropolished sample have been assumed to be the locations of Cr_2O_3 particles prior to electropolishing. The results are presented in table 8:

Figure	Number Density/ m^{-2}
3.2.1.1	2.1E9
3.2.1.2	8.9E9
3.2.1.3	1.0E10
3.2.1.4	3.8E9
3.1.5.6	2.2E9

Table 8: Number of particles per unit area in the figures given.

It can be seen that the alumina polished sample has approximately the same pit number density as the electropolished sample whereas the diamond polished sample has approximately four times as many pits in unit area.

The coupons in figures 3.2.1.3 and 3.2.1.4 have been mechanically polished using diamond to a finish of 1 micrometre particle size and have then been implanted with Cr^+ ions in figure 3.2.1.3 and Ce^+ ions in figure 3.2.1.4. The two micrographs were taken using the Nomarski interference technique and reveal a surface similar to those unimplanted specimens that were also polished using diamond particles. There are two types of pit visible on these samples: small, particle-like pits 1-2 micrometres in size and larger indentations approximately 6 micrometres in size. The larger indentations are more numerous on the implanted specimens than on the unimplanted specimens and a number of them appear to lie along lines of scratches such as that indicated by the arrow; the number density of the small pits on both specimens is larger than for the electropolished sample, with the chromium-implanted sample having a similar value to the unimplanted specimen, but there are generally fewer on the cerium-implanted specimens. In figures 3.2.1.5 and 3.2.1.6 the surfaces are imaged using a scanning electron microscope. The back-scattered electron micrograph of the surface of the unimplanted, alumina polished sample, figure

Figure 3.2.1

Light micrographs of the surfaces of implanted and unimplanted standard-annealed chromium after mechanical polishing. The 50 micrometre marker refers to figures 3.2.1.1, 3.2.1.3 and 3.2.1.4; the 25 micrometre marker refers to figures 3.2.1.5 and 3.2.1.6.

3.2.1.1 Unimplanted chromium polished with alumina particles and imaged using the Nomarski interference technique to show the etching of the grain structure.

3.2.1.2 Unimplanted chromium polished with diamond particles.

3.2.1.3 Chromium polished with diamond and then implanted with Cr^+ ions, imaged using the Nomarski interference technique to show the lack of grain etching and revealing the large indentations among the smaller particles.

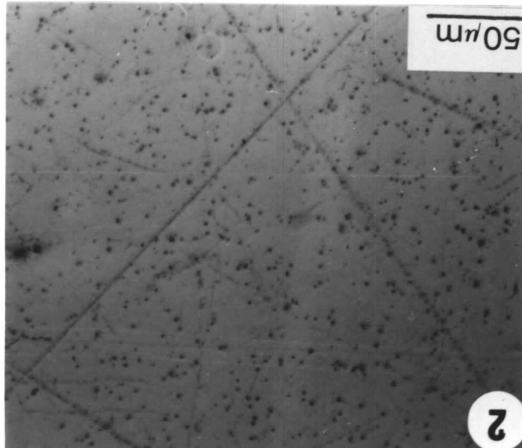
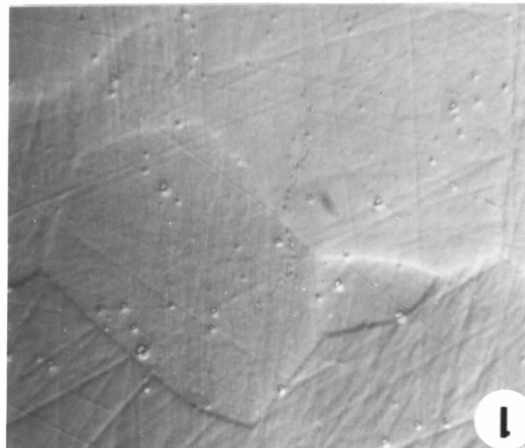
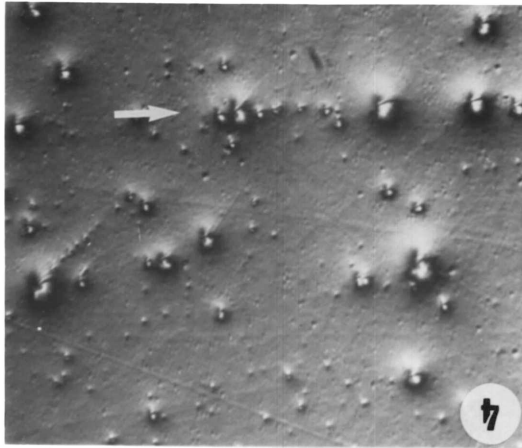
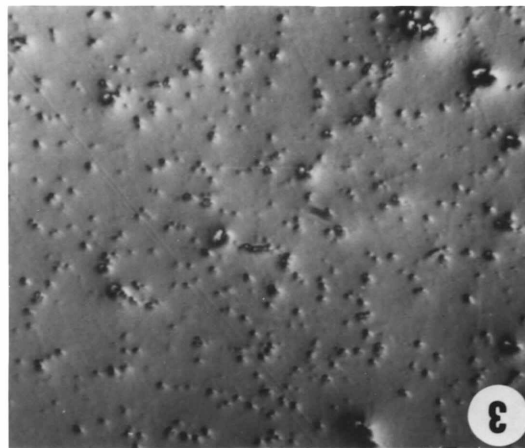
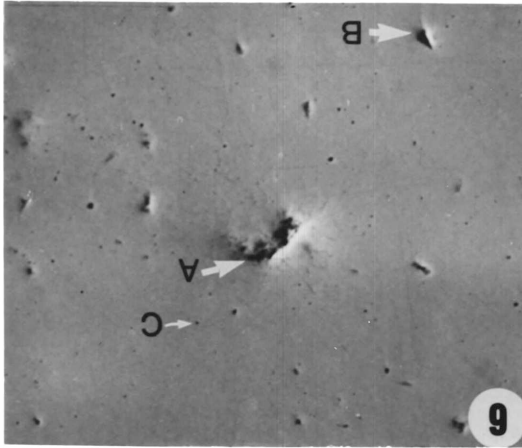
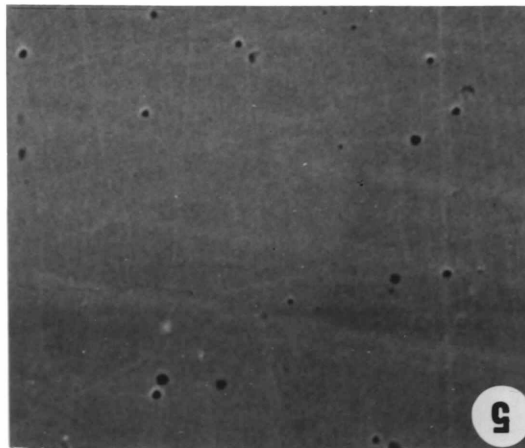
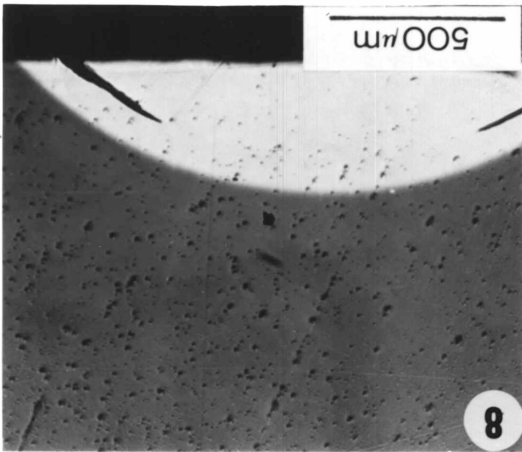
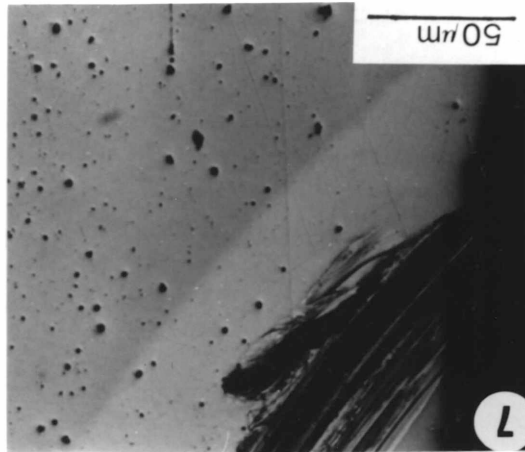
3.2.1.4 Chromium polished with diamond and then implanted with Ce^+ ions, imaged using the Nomarski interference technique. The small particles and the large indentations are both visible; some of the indentations lie on a scratch line (indicated by the arrow).

3.2.1.5 Scanning electron micrograph of the surface of unimplanted chromium polished using alumina particles showing the holes left by the particles. A back-scattered electron image.

3.2.1.6 Scanning electron micrograph of the diamond-polished surface of an implanted specimen showing a large indentation (A), the holes left by the smaller particles (B) and the 50 nanometre voids (C). A secondary electron image.

3.2.1.7 A micrograph showing the contrast between the tarnished surface of a Cr-implanted specimen and the area protected by the retaining clip. The surface of the metal was polished using diamond particles prior to implantation.

3.2.1.8 A micrograph showing the contrast between the tarnished surface of a Ce-implanted specimen and the area protected by the retaining clip. The film on this sample is much darker than that on figure 3.2.1.7. The surface of the metal was polished using diamond particles prior to implantation.



3.2.1.5, shows pits, probably left by particles having been pulled out during the polishing process. These pits are approximately 1 micrometre in size. Any grain contrast similar to that seen on electropolished samples, for example figure 3.1.5, has been lost due to surface deformation from the polishing. The secondary electron micrograph of the cerium-implanted specimen in figure 3.2.1.6 shows a large indentation (A), 7 micrometres in size, surrounded by smaller pits, such as (B), 1-2 micrometres in size and also some very small pits (C) that are smaller than 0.2 micrometres. All of the samples shown in figure 3.2.1 have pits that are around 1 micrometre in size; the diamond polished samples have larger indentations of around 6 micrometres and the cerium-implanted sample has very small pits that are less than 0.2 micrometres in size.

Apart from the different sizes of pits on the samples the implanted specimens differed in another, more visually striking, manner. The coupons implanted with cerium have a golden-brown film on each polished surface and some of the chromium-implanted coupons have a similar film that is lighter in colour. The coupons of standard-annealed chromium are held in place in the implanter by small retaining clips and small crescents of untarnished metal attest to the fact that these areas have been protected by the clips. These abrupt changes from dark gold-brown film to bright metal enable the film to be photographed, figures 3.2.1.7 and 3.2.1.8. They also enable films to be detected on samples where the film is invisible to the unaided eye. The film is only apparent on some of the chromium-implanted samples with this extra means of identification and gives at most only a faint discolouration to the surface. The majority of the cerium-implanted samples had a dark gold-brown colouration to their surfaces and all had an obvious film; the film was not necessarily uniform, varying smoothly across the coupons and being more intense on some coupons than on others. It was found that the film could not be removed by soaking in standard solvents but, if the surface was coated in a protective lacquer and briefly electropolished, then the film and lacquer could be floated off in acetone provided that the sample was kept wet. The removed film could then be treated in the same way as a stripped carbon replica and deposited on a 3 mm copper grid and analysed in a transmission electron microscope. When this was attempted, the film was unfortunately destroyed in the deposition procedure and there were not sufficient samples to pursue this line of enquiry.

Figure 3.2.2 shows transmission electron micrographs of back-polished specimens of both implanted and unimplanted standard-annealed chromium and illustrates the surface structure of these specimens. The samples in this figure have been thinned both by electropolishing and by ion thinning. Figure 3.2.2.1 is not a back-polished sample but a normal TEM sample that has been ion thinned. Comparing this figure with a similar specimen that was thinned by electropolishing,

Figure 3.2.2

Transmission electron micrographs of back-thinned specimens of implanted and unimplanted chromium produced by electropolishing and by ion thinning. The micrographs show the appearance and structure of the surfaces of the samples after mechanical polishing.

3.2.2.1 Unimplanted chromium ion-thinned to reveal the damage introduced into the sample by ion thinning. The sample has not been back-thinned but possesses the typical speckled appearance of the ion thinned sample.

3.2.2.2 A sample back-thinned by electropolishing showing the network of surface scratches revealed by the back-thinning. The sample is a Cr-implanted specimen.

3.2.2.3 A sample back-thinned by ion bombardment showing the dislocation network produced by the deformation associated with mechanical polishing. The contrast reveals fine surface scratches such as the one indicated by the arrows. The sample is chromium from another source but the microstructure shown is typical of the standard-annealed chromium.

3.2.2.4 The surface structure of Cr-implanted chromium revealed by back-thinning. Visible are subgrains (A) and small voids (B). The sample was ion thinned.

3.2.2.5 A sample of Cr-implanted chromium back-thinned by electropolishing showing the subgrains and the lack of a major dislocation network.

3.2.2.6 A sample of Ce-implanted chromium back-thinned by electropolishing showing the particles trapped in the surface (A), the voids (B) and the film over the sample (C).

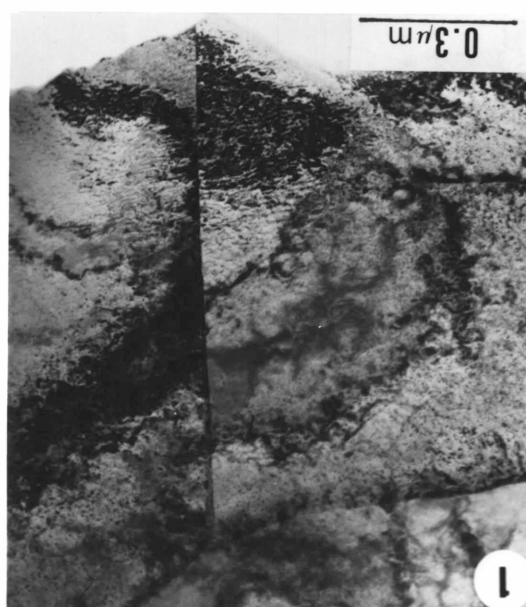
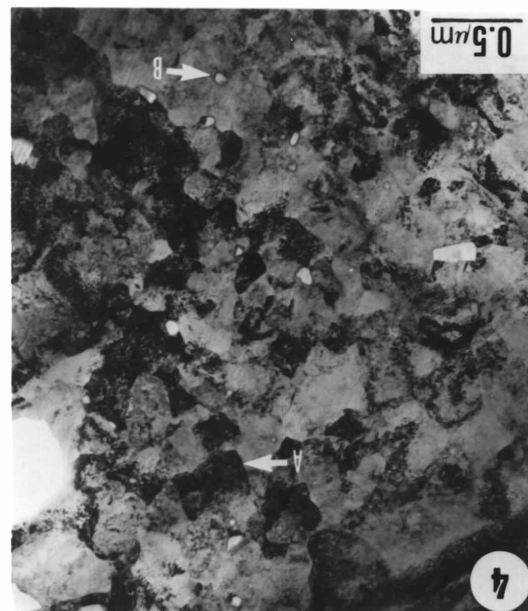
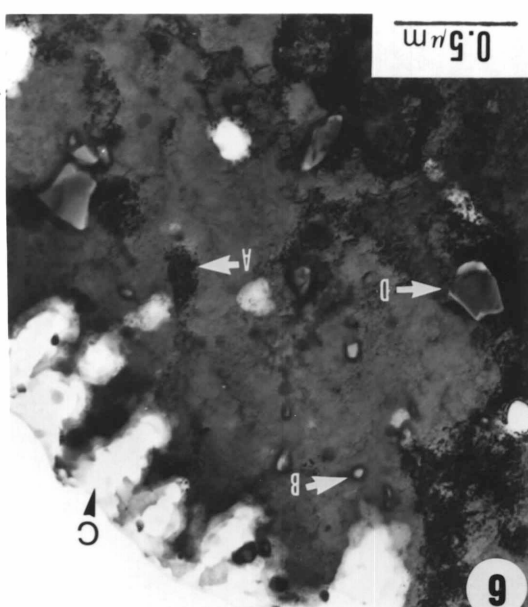
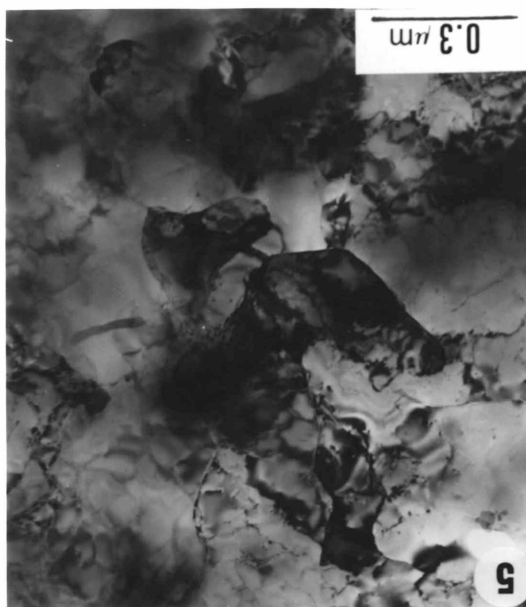


figure 3.1.4.6, it is possible to identify the damage caused to the specimen by ion thinning. This is necessary when the effects of two types of ion bombardment: the implantation effects and those from the ion thinning, are superimposed and need to be de-convoluted. The major effect of the ion thinning is to introduce point defect clusters into the surface of the sample giving the sample a speckled appearance. Figure 3.2.2.2 is a low magnification micrograph of a back-polished specimen showing how scratches on the surface of the metal are revealed by the back-polishing. Dislocation tangles associated with this deformation can be seen in figure 3.2.2.3 and, again, the dislocation network reveals the effects of the finer scratches such as that indicated in the figure by the arrows. The metal from which this micrograph is taken is pure chromium from another source but the deformation morphology that it exhibits is typical of that in the standard-annealed chromium used in this investigation. The only unimplanted metal samples that were examined specifically to determine the structure of their surfaces were those polished using alumina .

Figure 3.2.2.4 shows the surface structure of standard-annealed chromium implanted with chromium ions. The metal has a large number of subgrains (A) of approximately 0.2 micrometres in size and does not show the large number of dislocations seen in the unimplanted material. Also visible in this figure are small voids of around 50 nanometres in size (B). The sample has been produced by ion thinning and has the characteristic speckled appearance mentioned above. A sample of the same material that has been electropolished is shown at higher magnification in figure 3.2.2.5. This shows the subgrains in the metal and also the relative lack of intrasubgranular dislocations. The size of the subgrains in this figure is approximately 0.3 micrometres.

The structure of chromium implanted with cerium is shown in figure 3.2.2.6. This sample has been electropolished. There are a few areas that appear to be subgrains (A) around 200 nanometres in size but these are not common. Also visible in this figure are small voids (B), 30nanometres in diameter, like those seen in the chromium-implanted metal, as well as 0.2 micrometre particles (D). These particles are also present in the chromium-implanted metal. Point defect clusters and dislocations are more common in the metal than for the electropolished chromium-implanted specimen. At the edge of the foil, in some places, is an amorphous film (C). This film is only seen in those parts of the specimen where the true surface of the metal is retained; those places where the region near the surface has been exposed but the true surface has been destroyed by the electropolishing process never have this film. The film appears either as a thin membrane hung between fingers of metal, figure 3.2.2.6, or as a thicker film with a straight edge. In this latter case, the film does not usually follow the edge of the thin area; this could be due to the film folding over onto itself.

Figure 3.2.3

Diffraction patterns taken from the back-thinned specimens in figure 3.2.2, revealing the existence of surface oxide on the ion thinned samples.

3.2.3.1 Selected area diffraction pattern taken from the area shown in figure 3.2.2.1 showing the main chromium pattern together with some oxide reflections. The diffraction pattern is indexed in the adjacent diagram giving a Cr $\langle 111 \rangle$ zone axis and a Cr_2O_3 $\langle 1\bar{1}01 \rangle$ zone axis. The diffraction aperture selected an area 2.5 micrometres in diameter on the surface of the sample.

3.2.3.2 Selected area diffraction pattern from the area in figure 3.2.2.4. The two bright rings correspond to the chromium $\{110\}$ and $\{211\}$ respectively; between them is a ring corresponding to the Cr_2O_3 $\{30\bar{3}0\}$ reflection. Indicated by the arrow is a set of six ring arcs corresponding to the Cr_2O_3 $\{11\bar{2}0\}$ reflection. The diffraction aperture selected an area 8.3 micrometres in diameter on the surface of the sample.

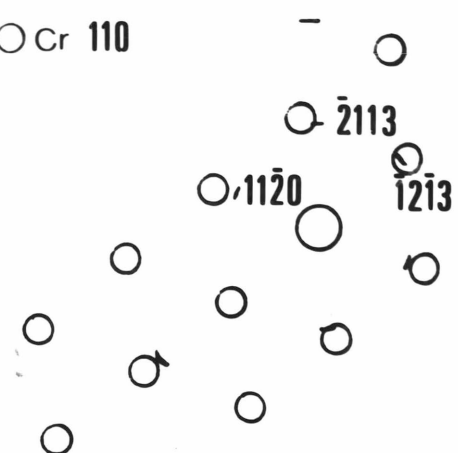
3.2.3.3 Selected area diffraction pattern from a Cr-implanted specimen back-thinned by electropolishing. The spots are indexed in the adjacent diagram; the diffraction pattern consists only of chromium reflections and belongs to a Cr $\langle 111 \rangle$ zone axis. The diffraction aperture selected an area 2.5 micrometres in diameter on the surface of the sample.

3.2.3.4 Selected area diffraction pattern from a Ce-implanted specimen back-thinned by electropolishing. The spots are indexed in the adjacent diagram; the diffraction pattern belongs to a Cr $\langle 111 \rangle$ zone axis. The diffraction aperture selected an area 2.5 micrometres in diameter on the surface of the sample

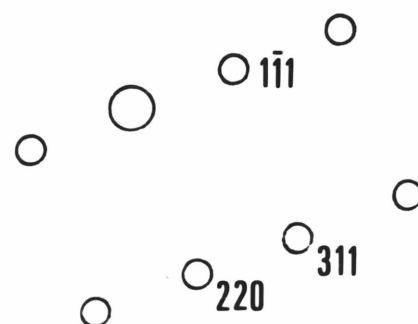
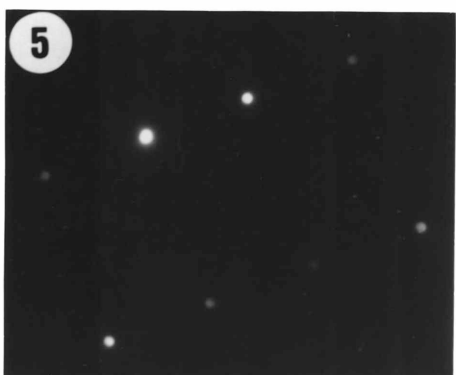
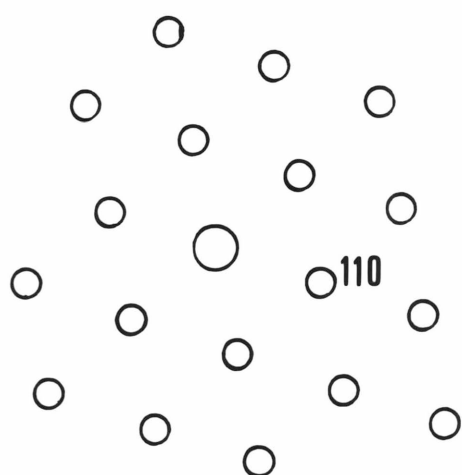
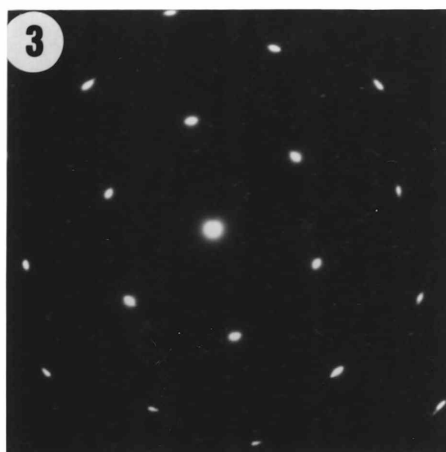
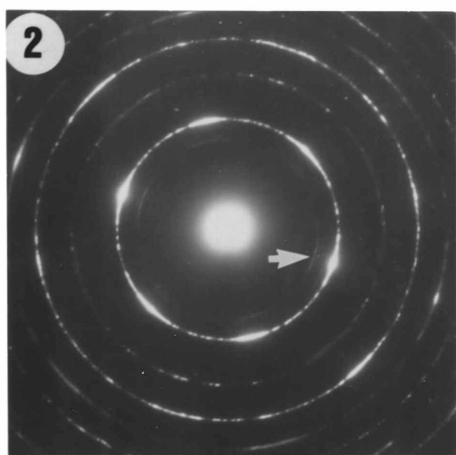
3.2.3.5 Microdiffraction pattern from a particle similar to those in figure 3.2.2.6. The diffraction pattern is indexed in the adjacent diagram and is a C (diamond) $\langle \bar{1}12 \rangle$ zone axis.



○ Cr 110



rd = 2.99 cm Å



Selected area diffraction patterns of the samples reveal more information, figure 3.2.3. Figure 3.2.3.1 shows a selected area diffraction pattern from the ion thinned chromium sample shown in figure 3.2.2.1. The major spots correspond to Cr $\{110\}$ reflections and make up a Cr $\langle 111 \rangle$ zone axis pattern slightly tilted away from the zone axis. There are, however, some smaller spots that correspond to oxide reflections. These oxide reflections can be indexed as indicated in the diagram adjacent to the figure and they form a Cr_2O_3 $\langle 1\bar{1}01 \rangle$ zone axis pattern. Other spots on the micrograph are double diffraction spots produced by the brightest $\{110\}$ reflection. Figure 3.2.3.2 is a selected area diffraction pattern from a large area of figure 3.2.2.4. The two brightest rings are made up of Cr $\{110\}$ and Cr $\{211\}$ reflections respectively; there are also oxide reflections: a ring corresponding to the Cr_2O_3 $\{30\bar{3}0\}$ reflection between the two bright Cr rings and, indicated by the arrow, a set of six ring arcs corresponding to the Cr_2O_3 $\{11\bar{2}0\}$ reflection. Both of these diffraction patterns are from ion thinned samples and both contain oxide reflections; selected area diffraction patterns from electropolished specimens of unimplanted standard-annealed chromium and, figures 3.2.3.3 and 3.2.3.4, standard-annealed chromium implanted with chromium and cerium respectively do not contain any reflections other than the standard chromium spots. The diffraction patterns in figures 3.2.3.3 and 3.2.3.4 are the same pattern, shown in the adjacent diagram. The spots correspond to a Cr $\langle 111 \rangle$ zone axis pattern; the diffraction pattern from the chromium-implanted sample, figure 3.2.3.3, has single spots, though, whereas the diffraction pattern from the cerium-implanted sample, figure 3.2.3.4, contains spots rotated with respect to each other whilst having the same spacing indicating that subgrains are present. In figure 3.2.3.2 the chromium rings are almost complete indicating a large number of grains in the selected area and a complete range of grain orientations around the fibre axis. This would argue that there were large misorientations between some neighbouring grains and the description of the microstructure as containing subgrains is no longer valid in these cases.

The selected area diffraction pattern in figure 3.2.3.3, of a supposedly similar microstructure, shows two or three grains rotated only a few degrees with respect to each other; these can be described as subgrains. The number of subgrains that give rise to diffraction spots will depend on the specimen orientation. These diffraction patterns were taken with the foil plane perpendicular to the beam, not necessarily at the angle of tilt that would reveal the largest number of subgrains. A larger selected area in the diffraction pattern in figure 3.2.3.3 may have revealed the full range of grain orientations, in a similar manner to figure 3.2.3.2, the few that were selected may not have been representative of the microstructure of the sample. Recrystallisation may have occurred in this sample during implantation, explaining the

wide range of orientations in figure 3.2.3.2, or possibly even during the ion-thinning process; it is impossible, though to come to any conclusion without further evidence.

The microdiffraction pattern in figure 3.2.3.5 is taken from a particle similar to those in figure 3.2.2.6. This diffraction pattern and two others taken from the same particle at different angles of specimen tilt enable the particle to be identified. All three of the diffraction patterns fit the diamond cubic structure and the spacings of the spots corresponds with the lattice spacings for diamond; the particles can be identified, therefore, as diamond particles. The diffraction pattern given here and indexed in the adjacent diagram is from the C (diamond) $\langle \bar{1}12 \rangle$ zone axis.

Profiles of the native oxide films on implanted and unimplanted standard-annealed chromium produced by SIMS are given in figure 3.2.4. Figure 3.2.4.1 shows the thickness of the native oxide films on the untreated electrolytic metal and on the standard-annealed chromium. The profiles are graphs of abundance of $^{16}\text{O}^+$ ions plotted against depth into the sample and show the thickness of the native oxide films on both samples to be around 2 nanometres; the interface between metal and oxide on the untreated sample is sharp whereas that on the heat-treated sample appears to be spread over a further 2 nanometres. The variation in the heights of the peaks is not significant. On the cerium-implanted specimens, figure 3.2.4.2, there is a brown tarnish on the surface of the samples. The profiles in this figure are from a sample where the tarnish varied from dark brown at one edge of the sample to invisible at the other edge and the areas of analysis were in the dark region and in the "untarnished" region at the opposite edge of the sample. The secondary ions detected to construct these depth profiles were $^{16}\text{O}^-$ ions and the traces have been shifted so that their metal/oxide interface regions coincide, giving a better idea of their relative thicknesses. The thickness of the oxide film in the tarnished region is seen to be 2 nanometres thicker than that in the "untarnished" region.

Depth profiles of the implanted cerium ions in the standard-annealed chromium are given in figure 3.2.5; figure 3.2.5.1 shows the surface profiles of chromium and cerium while figure 3.2.5.2 shows the whole profile of the cerium implantation. The surface oxide as measured by the $^{68}\text{CrO}^+$ signal is seen to be around 20 nanometres thick. The presence of oxygen in this region enhances the yield of the other ion species by an unknown factor due to chemical interactions between the oxygen and the ion species. These interactions do not occur if oxygen is not present and will vary between ion species. If the abundance of cerium in the material is small then the yield of chromium ions should be constant with depth but at a higher level in the oxide than in the metal due to the presence of oxygen. Thus, taking the cerium trace relative to the chromium trace and assuming the chromium abundance to be constant, it can be seen that the cerium abundance is low at the oxide/gas interface and rises to a peak at the oxide/metal interface. The relative

Figure 3.2.4

SIMS depth profiles of the native oxide film on implanted and unimplanted chromium showing the variation with depth of the abundance of the $^{16}\text{O}^+$ and $^{16}\text{O}^-$ ions.

3.2.4.1 $^{16}\text{O}^+$ profiles of the surface layer on as-received electrolytic chromium and on standard-annealed chromium.

3.2.4.2 $^{16}\text{O}^-$ profiles of the surface layer on a sample of Ce-implanted standard-annealed chromium. The sample had a brown tarnish that varied in thickness across its width and the profiles are from an area of thick tarnish and from an area where there was apparently no tarnish.

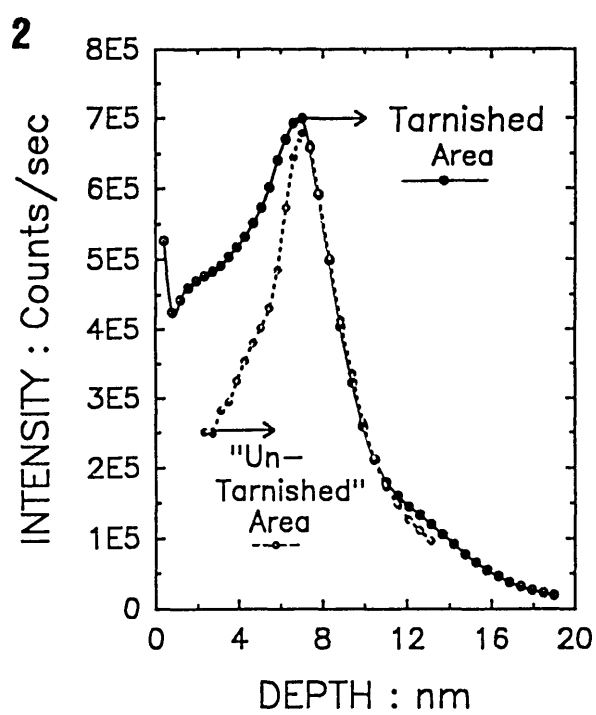
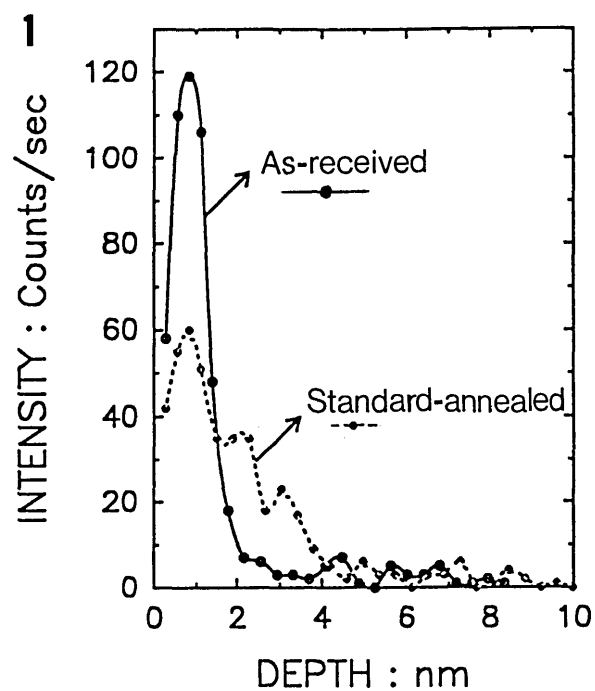
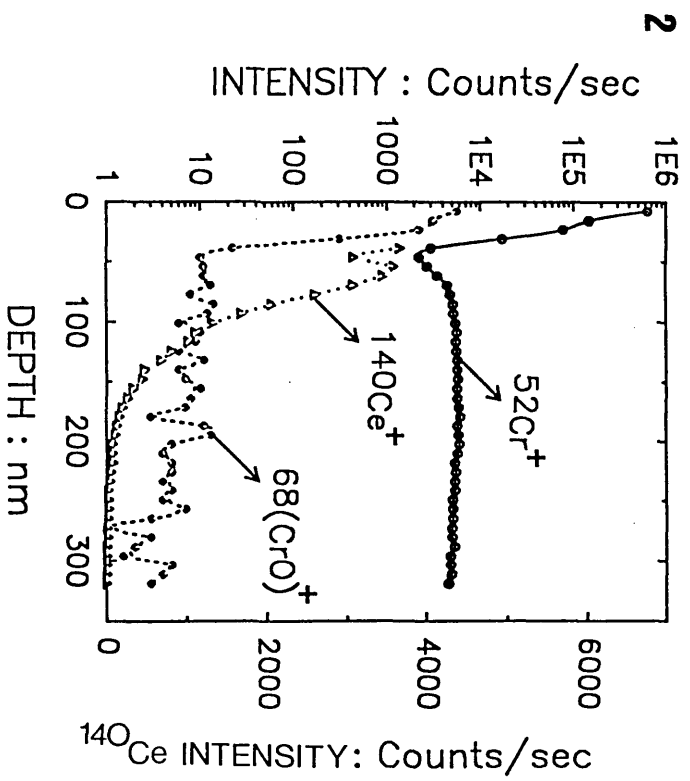
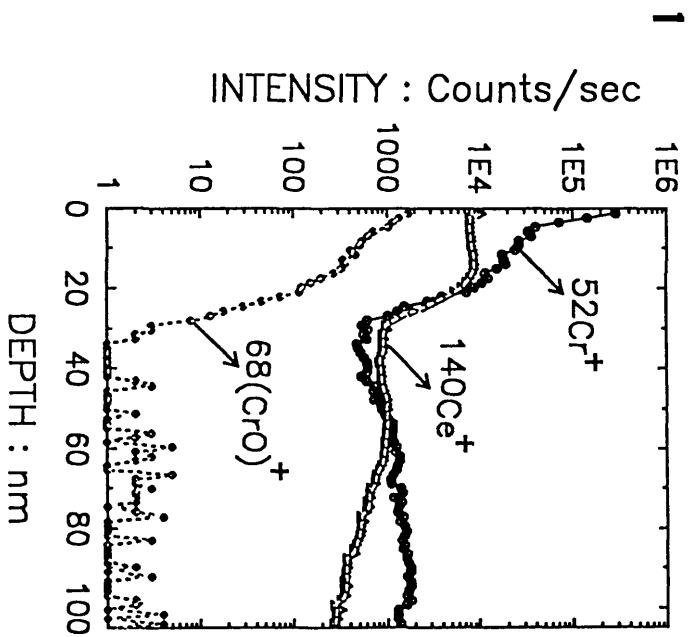


Figure 3.2.5

SIMS depth profiles showing the distribution of the implanted cerium ions through the surface layer of a sample of Ce-implanted standard-annealed chromium.

3.2.5.1 Profile of the surface layer including the native oxide film. The drop in the $^{52}\text{Cr}^+$ and the $^{140}\text{Ce}^+$ shows the metal/oxide interface.

3.2.5.2 Depth profile showing the entire cerium distribution. It should be noted that the $^{140}\text{Ce}^+$ signal is plotted on the scale to the right rather than that on the left axis.



sputtering yields of chromium and cerium are not known precisely for these conditions and the magnitudes of the signals may not be accurate. That the cerium trace exceeds the chromium trace in magnitude, indicates a large proportion of cerium in the metal. So, in figure 3.2.5.1, the cerium distribution cannot be deduced by assuming that the chromium yield is constant. Oxygen, however, is no longer present and the sputtering yields will now only be governed by physical processes which implies that the relative heights of the cerium and chromium traces should give an indication of the abundances of each element with depth. Thus, as shown in figure 3.2.5.2, the cerium has another peak at around 50 nanometres depth from the surface. The chromium trace dips to one third of its bulk value at around this depth and then rises further into the metal. This fact, together with the observation that the chromium and cerium traces cross with roughly equal, if opposite, slopes suggests that the matrix concentration of the cerium, at its peak, is a significant fraction of the matrix composition, even as high as 50%. The majority of the cerium will be situated in the matrix. The error bars on the yields, above 100 counts/second, will be approximately the size of the points. It should be noted that, in figure 3.2.5.2, the $^{140}\text{Ce}^+$ trace is plotted on the scale at the right not the logarithmic scale on the left. This enables the depth of the implant to be assigned a value of between 100 and 150 nanometres.

3.3 Oxidation in the Gas Reaction Cell

Thin foils of chromium were oxidised in the gas reaction cell of a 1 MeV transmission electron microscope in order to study the initial oxidation behaviour of the metal in both the implanted and unimplanted state. Normal transmission electron microscopy specimens as well as back-thinned specimens were used.

Figure 3.3.1.1 shows a typical specimen after oxidation in the gas reaction cell. This sample was oxidised for two minutes at 780°C in 250 Pa pressure of oxygen. The micrograph shows a plan view through the metal foil and the oxide films on its top and bottom surfaces, with the metal edge visible, indicated by the arrow. A schematic diagram of the foil edge is given in figure 3.3.2 showing how the foil changes during oxidation. Figure 3.3.2.1 shows the foil in cross-section prior to oxidation and figure 3.3.2.2 shows the foil after oxidation. The oxide takes up more volume and thus the edge extends forwards. The metal gets thinner as it oxidises and, being wedge-shaped, this implies that the edge of the metal will appear to retreat from the foil edge. In the transmission electron microscope, figure 3.3.2.2 will appear in plan as shown in figure 3.3.2.3. The rate of oxidation could, in principle, be estimated during oxidation by the speed at which the edge of the metal appears to retreat. This speed would also vary with the sample thickness and with the wedge

Figure 3.3.1

Transmission electron micrographs of specimens oxidised in the gas reaction cell.

3.3.1.1 Specimen of standard-annealed chromium oxidised for two minutes at 780°C in an oxygen pressure of 250 Pa. The oxide structure is typical of films found on foils oxidised using similar conditions to these. The arrow indicates the edge of the metal.

3.3.1.2 Selected area diffraction pattern from the area in figure 3.3.1.1. The diffraction pattern is indexed in the diagram below; the spots form a chromium $\langle 111 \rangle$ zone axis pattern and the rings are from a Cr_2O_3 $\langle 0001 \rangle$ zone axis.

3.3.1.3 Another selected area diffraction pattern containing the two oxide rings found in figure 4.3.1.2, indexed in the diagram below. The spots form a chromium $\langle 111 \rangle$ zone axis pattern.

3.3.1.4 Bright field micrograph of a specimen of electrolytic chromium annealed for 3 hours in hydrogen at 1100°C taken prior to oxidation.

3.3.1.5 Bright field micrograph of the same area as figure 3.3.1.4 taken after oxidation for 10 seconds at temperatures up to 650°C in an oxygen pressure of 250 Pa.

3.3.1.6 Bright field micrograph of the same sample as figure 3.3.1.5 after oxidation but from an area not previously photographed.

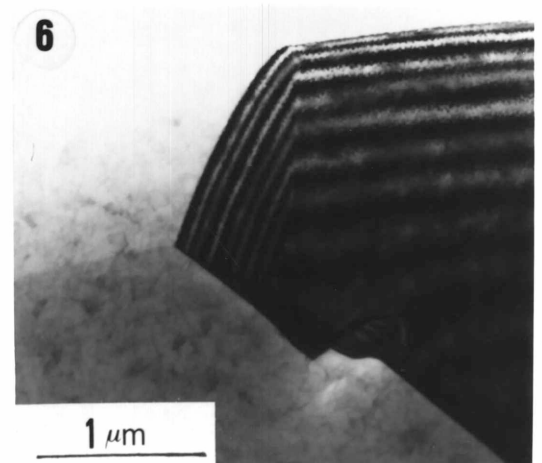
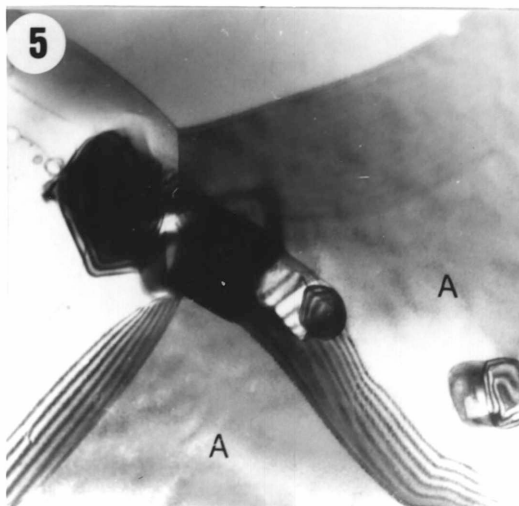
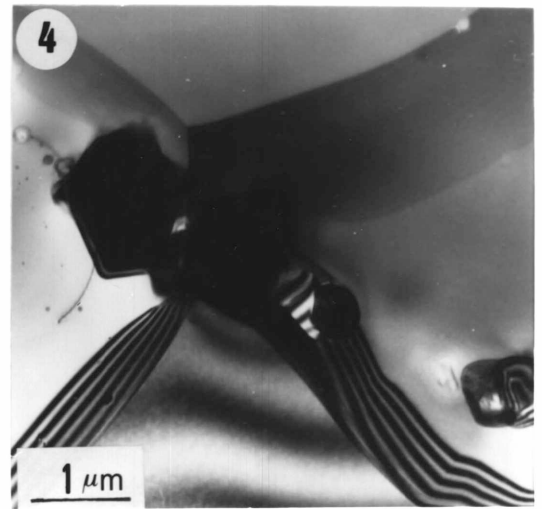
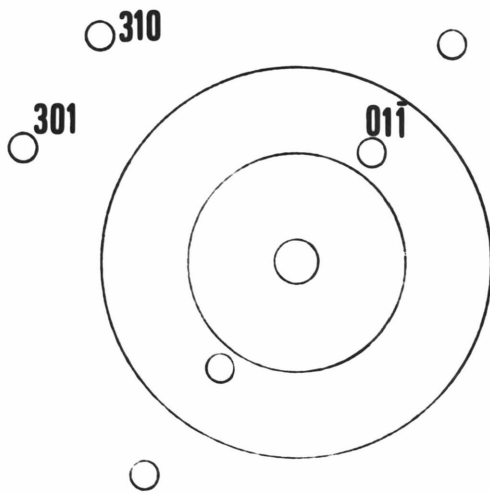
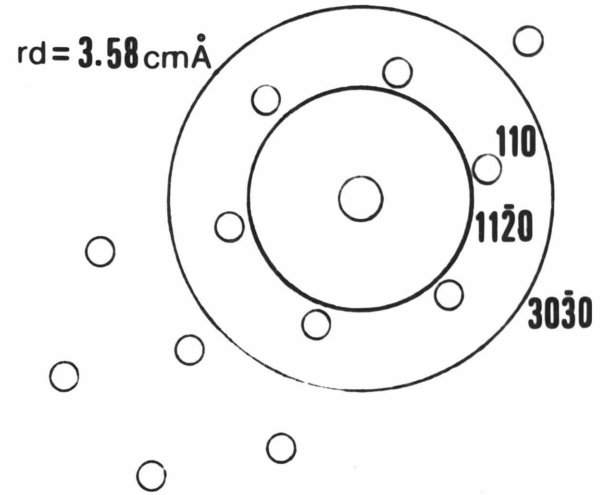
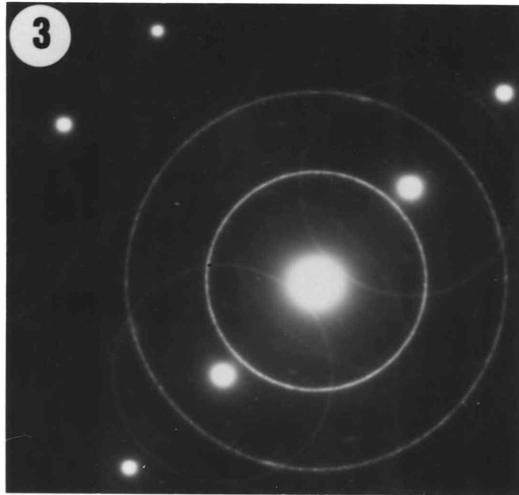
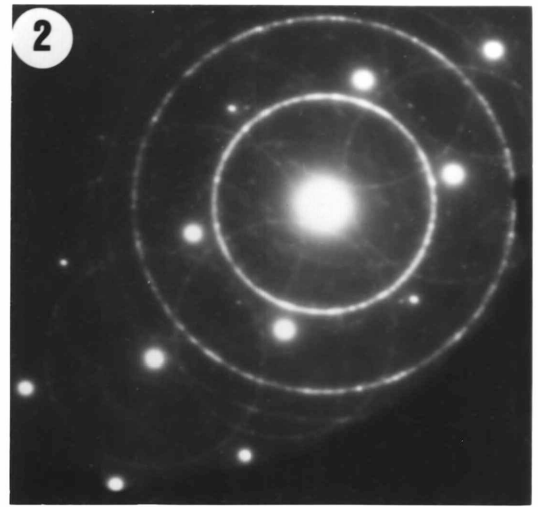
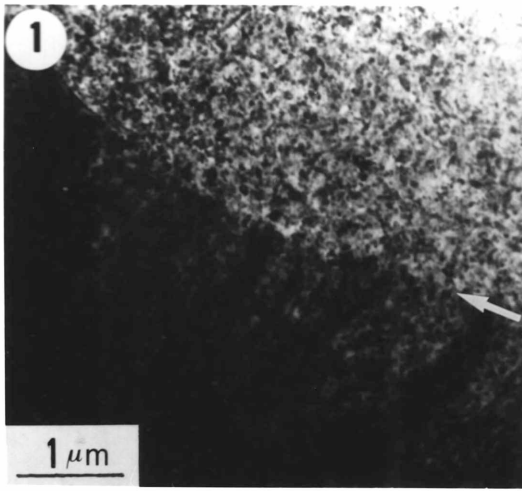


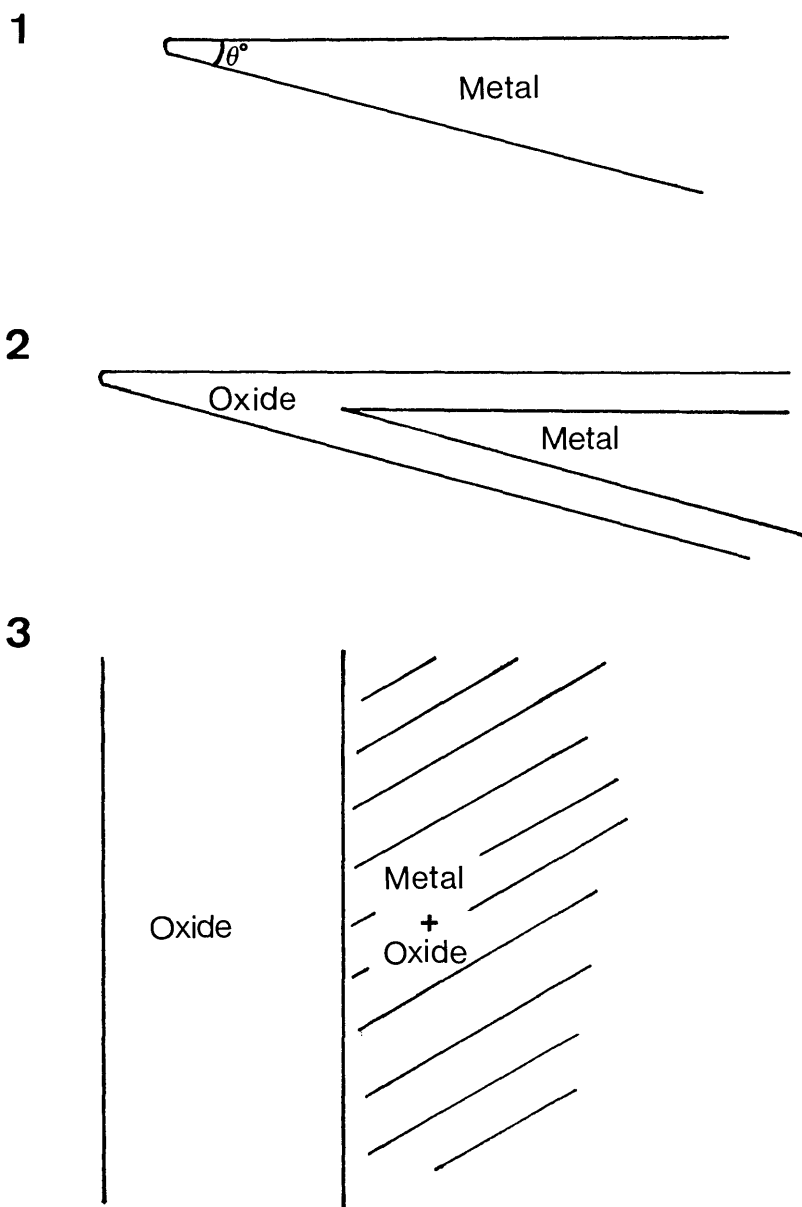
Figure 3.3.2

Schematic diagram of a metal foil before and after oxidation in the gas reaction cell showing the general morphology of oxidation.

3.3.2.1 Cross-section of the metal foil before oxidation. The wedge angle θ of the foil is indicated.

3.3.2.2 Cross-section of the foil after oxidation showing how the metal edge retreats from the foil edge.

3.3.2.3 Plan view of figure 3.3.2.2 showing how the oxidised foil appears in the transmission electron microscope.



angle θ . At temperatures below around 600°C this retreat was imperceptible while above 800°C it was extremely rapid. The grain size of the oxide film is between 50 - 100 nanometres.

A selected area diffraction pattern from the area of metal and oxide in figure 3.3.1.1 is given in figure 3.3.1.2. The diffraction pattern consists of a set of spots corresponding to the chromium $\langle 111 \rangle$ zone axis and two rings corresponding to Cr_2O_3 reflections. The inner ring is made up of Cr_2O_3 $\{11\bar{2}0\}$ reflections and the outer ring of Cr_2O_3 $\{30\bar{3}0\}$ reflections. No other oxide rings are present. If the two reflections are assumed to form a zone axis pattern then the zone axis can be calculated to be $\langle 0001 \rangle$. This combination of Cr_2O_3 $\langle 0001 \rangle$ and Cr $\langle 111 \rangle$ is ubiquitous; the metal is textured with the $\langle 111 \rangle$ direction perpendicular to the surface as found here. The two oxide rings were also found associated with other chromium orientations such as that in figure 3.3.1.3. Here, the spots form a $[\bar{1}33]$ zone axis. Although this is a rarely observed orientation, it is unlikely to be due to the foil having bent away from being perpendicular to the beam as the foil edge was unbroken and thus self-supporting.

If the sample in the gas reaction cell was examined prior to oxidation, the oxidation behaviour of the examined area changed. This is illustrated in figures 3.3.1.4 to 3.3.1.6. Figure 3.3.1.4 shows a sample of electrolytic chromium annealed for 3 hours in hydrogen at 1100°C prior to oxidation. This area was only exposed to the electron beam for a few seconds - long enough to photograph the area. After oxidising for 10 seconds at temperatures to 650°C, a standard oxidation condition, the area was re-photographed, figure 3.3.1.5, and compared with a previously unexamined area on the same sample, figure 3.3.1.6. In figure 3.3.1.5 the oxide appears on two of the grains (A) as a slight shading in the contrast levels and as a granularity of the surface. In figure 3.3.1.6 the oxide can be seen as a granularity in the strongly diffracting grain and as the variations in the contrast on the other grains. The oxide film is at a later stage of development in the latter micrograph than in the former implying that irradiation-induced contamination of the sample has reduced the amount of oxidation over this short time period. Damage to the sample due to the electron beam was not seen. If the beam was held in one place for some time, the only visible effect would be a build-up of a contamination spot on the sample.

Samples were also oxidised at higher and lower gas pressures than 250 Pa. Figure 3.3.3.1 shows a specimen of electrolytic chromium annealed for 3 hours in hydrogen at 1200°C, oxidised in the gas reaction cell for 2 minutes at 770°C in a gas pressure of 4000 Pa oxygen. The oxide is thicker than was seen on samples oxidised for similar times and temperatures but at lower gas pressure. The oxide appears to have penetrated the grain boundaries of the metal more quickly than the grain interiors, for example where indicated by the arrow. Alternatively, this may just be

Figure 3.3.3

Transmission electron micrographs of foils oxidised in the gas reaction cell at oxygen pressures other than 250 Pa.

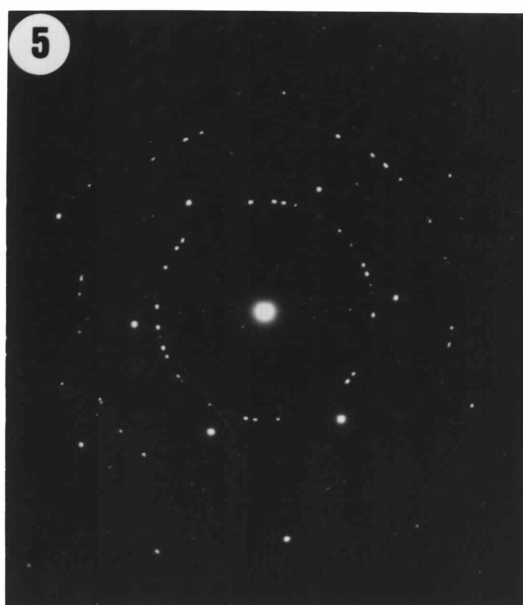
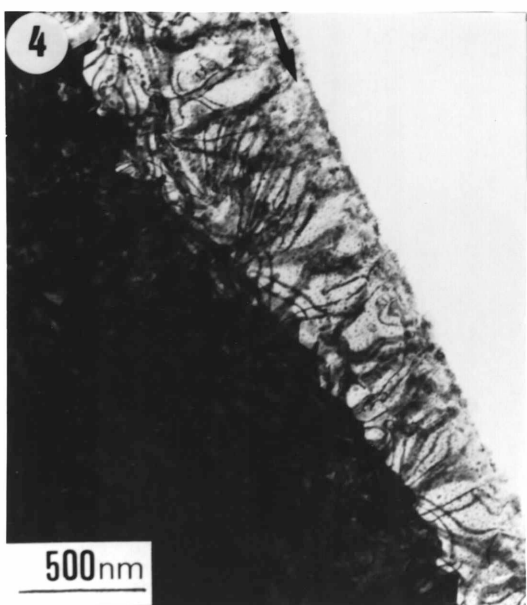
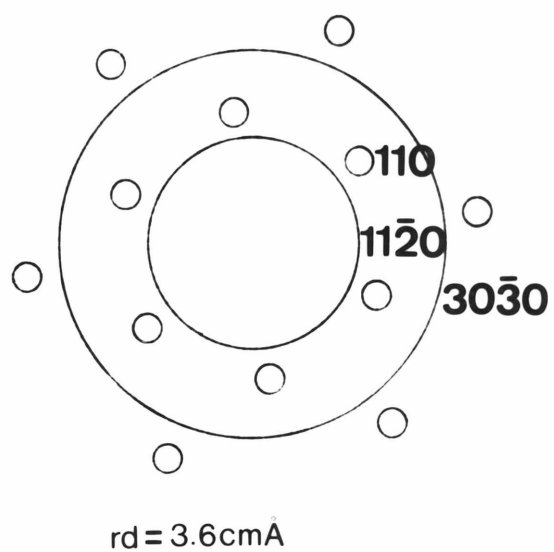
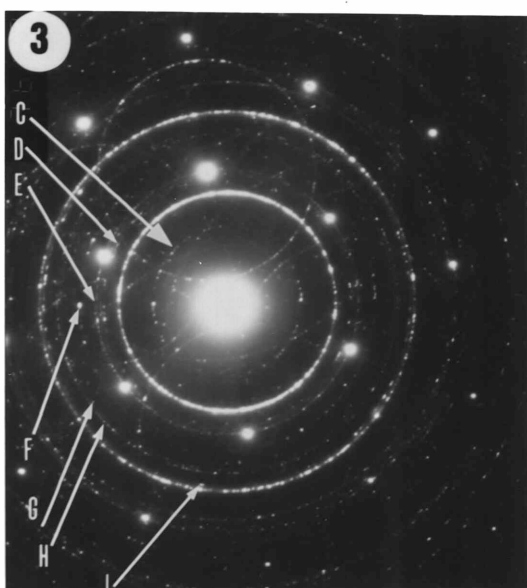
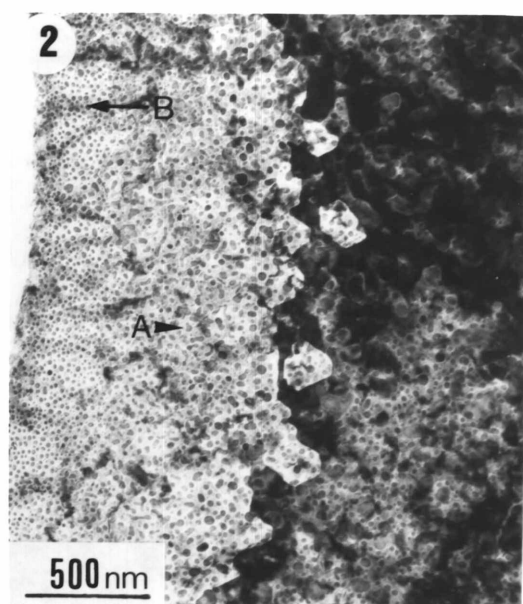
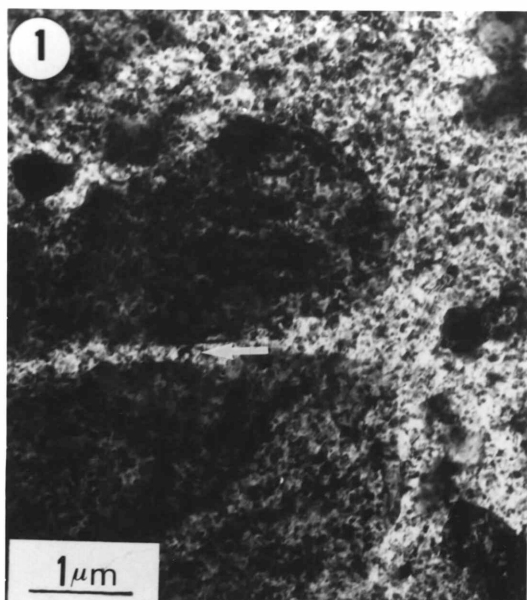
3.3.3.1 Specimen of electrolytic chromium annealed for 3 hours in hydrogen at 1200°C oxidised for 2 minutes at 770°C in an oxygen pressure of 4000 Pa.

3.3.3.2 Standard-annealed specimen oxidised for 20 seconds at temperatures up to 850°C with no gas flow showing penetration and facetting of the metal edge by the oxide film.

3.3.3.3 Selected area diffraction pattern from the sample in figure 3.5.3.2, indexed in the adjacent diagram. The spots form a chromium $\langle 111 \rangle$ zone axis and the oxide rings are from a Cr_2O_3 $\langle 0001 \rangle$ zone axis.

3.3.3.4 Bright field micrograph of a specimen of chromium annealed for 3 hours in hydrogen at 1200°C, oxidised for 30 seconds at 800°C with no gas flow.

3.3.3.5 Selected area diffraction pattern from the oxide film in figure 3.3.3.4. The diffraction pattern takes the indexing from the diagram above; the oxide rings are now discrete spots due to the large grain size of the oxide.



because the boundary areas were thinner than the surrounding area, due to attack by the electropolishing solution during the specimen preparation procedure but this was never seen on other samples. Evidence of this sort of preferential oxidation at grain boundaries was contradictory and infrequent and was never seen at dislocations. The grain size of the oxide film is around 50 nanometres.

Two samples were oxidised with no gas flowing, just using the oxygen present in the cell and between the pole pieces. The level of contaminants would be likely to be lower than normal as they could not be replenished from the gas feed system. Figure 3.3.3.2 shows a standard-annealed specimen oxidised for 20 seconds at temperatures up to 850°C with no gas flow. The edge of the metal is not continuous as in the general case, but is penetrated and faceted. The metal grain is oriented with $\langle 111 \rangle$ parallel to the beam and normal to the sample surface as is seen in the selected area diffraction pattern of the area, given in figure 3.3.3.3. The facets are oriented so that their straight edges are parallel to the $\{110\}$ planes in the metal and are only seen on grains that are oriented with $\langle 111 \rangle$ normal to the foil surface. Penetration of the metal by the oxide behind the main metal edge is probably due to the slight variations in the thickness of the original metal foil combined with a smaller wedge angle θ , figure 3.3.2. The oxide in figure 3.3.3.2 contains many particle-like features (A), around 10 - 40 nanometres in size. These only appeared on the two samples oxidised with no gas flow. There are also faint, darker, wavy lines in the oxide (B) indicating that the oxide may be wrinkled at its edge.

The selected area diffraction pattern of the area, figure 3.3.3.3, shows again the combination of $\langle 111 \rangle$ Cr with $\langle 0001 \rangle$ Cr_2O_3 and the adjacent diagram gives the indices of the major rings and spots. Apart from the double diffraction rings, there are also some fainter rings that are not indexed in the diagram. These are, from the centre: $\{10\bar{1}2\}$ (C), $\{11\bar{2}3\}$ (D), $\{20\bar{2}2\}$ (E), $\{20\bar{2}4\}$ (F), $\{12\bar{3}0\}$ (G), $\{10\bar{1}8\}$ / $\{12\bar{3}2\}$ (H) and $\{12\bar{3}4\}$ (I). The $\{10\bar{1}8\}$ ring has a spacing of 0.1581 nanometres and the $\{12\bar{3}2\}$ ring has a spacing of 0.1579 nanometres making them indistinguishable. The presence of these other rings imply that there are orientations other than $\langle 0001 \rangle$ present.

The other sample oxidised with no gas flowing is shown in figure 3.3.3.4. This is a specimen of 1200°C, 3 hour, hydrogen-annealed chromium, oxidised for 30 seconds at 800°C. The metal edge can be seen to be faceted but not penetrated, the grain is oriented with $\langle 111 \rangle$ normal to the foil surface and the oxide has the particle-like features seen in figure 3.3.3.2, albeit smaller, being less than 10 nanometres in size. The grain size of this oxide film is obviously larger than the other oxides due to the presence of sets of bend contours in each grain; the grain size is approximately 400 nanometres. The bend contours also indicate that the oxide is wrinkled. The receding metal edge will leave behind two oxide layers connected at

the foil edge but otherwise separated. This is visible on figure 3.3.3.4; the thin strip where the two films are joined at the foil edge appears granular and is indicated by the arrow. The upper and lower oxide layers behind this strip will be relatively unconstrained which will enable them to wrinkle under an applied stress. A selected area diffraction pattern of the area is given in figure 3.3.3.5 which takes the indexing shown in the diagram above it. This is, again, the combination of $\langle 111 \rangle$ Cr and $\langle 0001 \rangle$ Cr_2O_3 except that the oxide rings are now sets of discrete spots. This is due to the much increased grain size of the oxide. There are no other oxide reflections visible on the diffraction pattern; the faint spots are double diffraction spots.

The back-polished discs were oxidised for a short period only, in order to try to determine the initial stages of the oxide growth. Figure 3.3.4 shows a standard-annealed specimen, back-thinned by electropolishing and then oxidised for 10 seconds in 250 Pa oxygen pressure at temperatures up to 650°C . The oxidised sample had areas of oxide overhanging the metal edge; a bright field transmission electron micrograph of one is given in figure 3.3.4.1. The oxide has strong diffraction contrast and appears to be covered in tiny specks. A selected area diffraction pattern from the oxide is given in figure 3.3.4.2 and indexed in the adjacent diagram. A high resolution dark field micrograph was taken from the spot ringed in the diagram; the dark field micrograph is shown in figure 3.3.4.3. The grain size of the oxide measured from the dark field micrograph is larger than would be expected from previous specimens, being between 100 and 200 nanometres. The large grain size gives rise to discrete spots appearing in the diffraction pattern rather than rings; the diffraction pattern has an $\langle 0001 \rangle$ zone axis. Figure 3.3.4.4 is a secondary electron image of another area of overhanging oxide from the same specimen taken using a scanning transmission electron microscope. The surface visible is the mechanically polished surface to which the sample was back-thinned. The oxide has cracked and there are areas where the film has spalled, revealing the metal. Such an area (A) appears to have specks of oxide on the surface implying a degree of re-oxidation after spallation of the film. There is nothing apparent on the micrograph to explain the small specks on the oxide in figure 3.3.4.1. The large particle visible near the edge is probably Cr_2O_3 but its origin is unknown. Just visible is a pair of slight humps 100 nanometres in size (B) in the oxide film and also the outline of the oxide on the underside of the specimen (C).

Samples of standard-annealed chromium implanted with chromium ions, back-thinned by electropolishing, were oxidised in the gas reaction cell and are shown in figure 3.3.5. A specimen oxidised for 10 seconds at temperatures up to 650°C at an oxygen pressure of 250 Pa is shown in figure 3.3.5.1. The metal edge is seen to be penetrated but, despite the area being oriented close to $\langle 111 \rangle$ normal to the surface, there is no obvious facetting. There is a slight tendency for the rounded holes to take

Figure 3.3.4

Electron micrographs of a sample of standard-annealed chromium, back-thinned by electropolishing and oxidised for 10 seconds at temperatures up to 650°C in an oxygen pressure of 250 Pa, showing the structure of the oxide film on the mechanically polished surface.

3.3.4.1 Bright field micrograph of some overhanging oxide showing the oxide grain structure.

3.3.4.2 Selected area diffraction pattern from the oxide film in figure 3.3.4.1, indexed in the diagram below. The oxide spots form a Cr_2O_3 $\langle 0001 \rangle$ zone axis pattern.

3.3.4.3 Dark field micrograph of the oxide film in figure 3.3.4.1 imaged using the spot ringed in the diagram. The grain structure can be seen more easily.

3.3.4.4 Secondary electron image of a similar oxide film from the same sample imaged using the scanning transmission electron microscope.

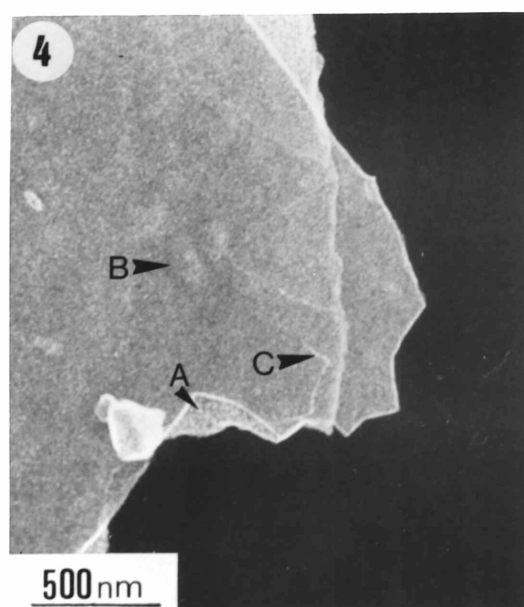
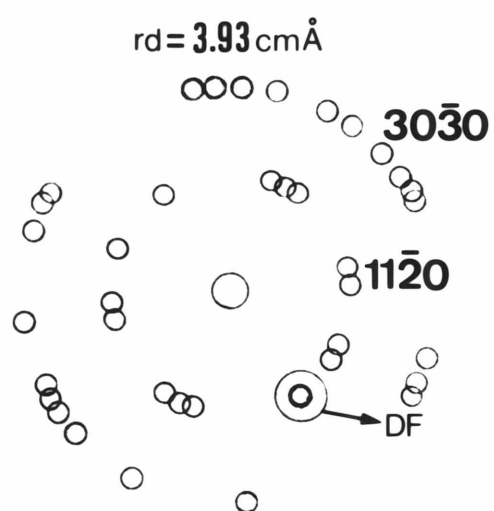
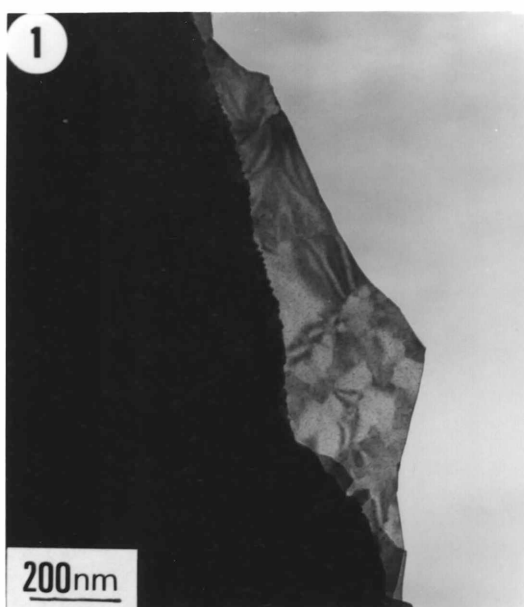


Figure 3.3.5

Electron micrographs of specimens of chromium-implanted chromium oxidised in the gas reaction cell.

3.3.5.1 Bright field micrograph of a specimen oxidised for 10 seconds at temperatures up to 650°C in an oxygen pressure of 250 Pa showing penetration of the metal edge.

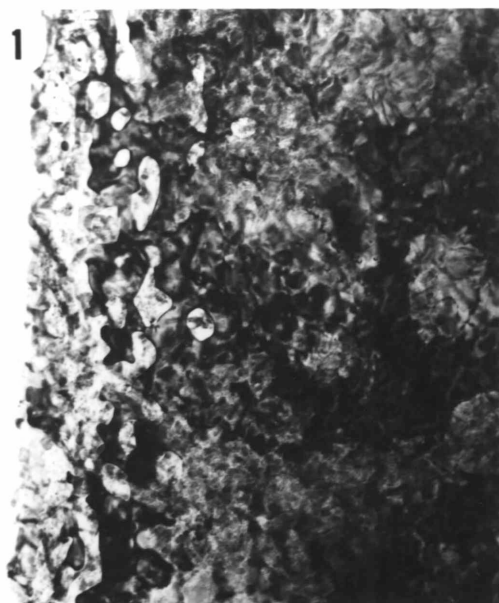
3.3.5.2 Selected area diffraction pattern of the area in figure 3.3.5.1. The two ring arcs are the Cr_2O_3 $\{11\bar{2}0\}$ and $\{30\bar{3}0\}$ reflections; the spots form a partial chromium $\langle 111 \rangle$ zone axis pattern.

3.3.5.3 Bright field micrograph of a specimen oxidised for 20 seconds at temperatures up to 850°C in an oxygen pressure of 400 Pa.

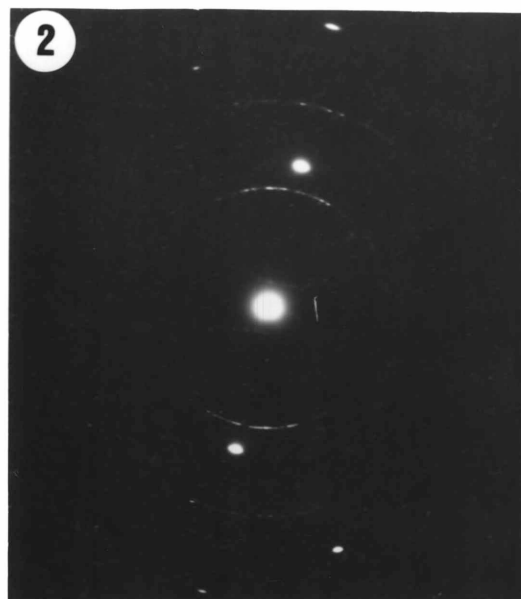
3.3.5.4 Selected area diffraction pattern of the area in figure 3.3.5.3. The diffraction pattern consists of two rings of oxide reflections corresponding to the Cr_2O_3 $\{11\bar{2}0\}$ and $\{30\bar{3}0\}$ and a pair of ring arcs corresponding to the chromium $\{110\}$ reflections.

3.3.5.5 Secondary electron image of an oxide film on a sample oxidised for 10 seconds at temperatures up to 650°C in an oxygen pressure of 250 Pa showing nodules and wrinkles in the film.

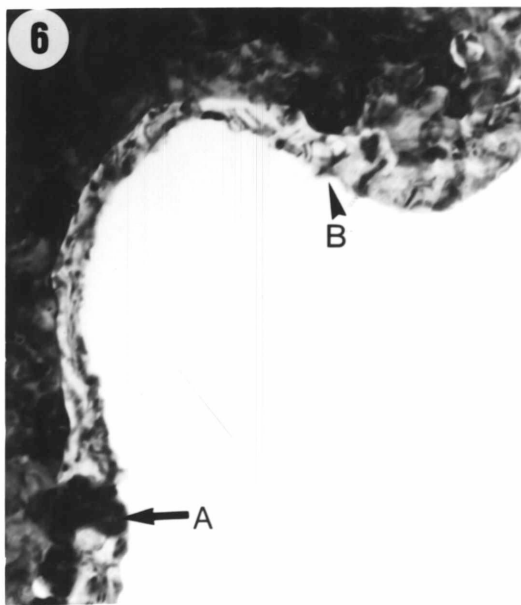
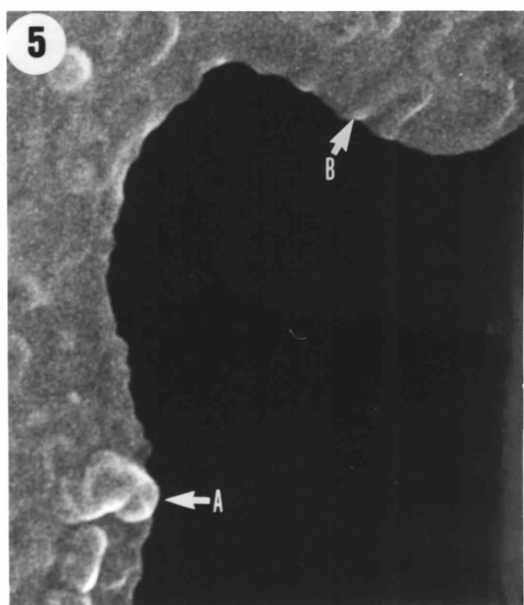
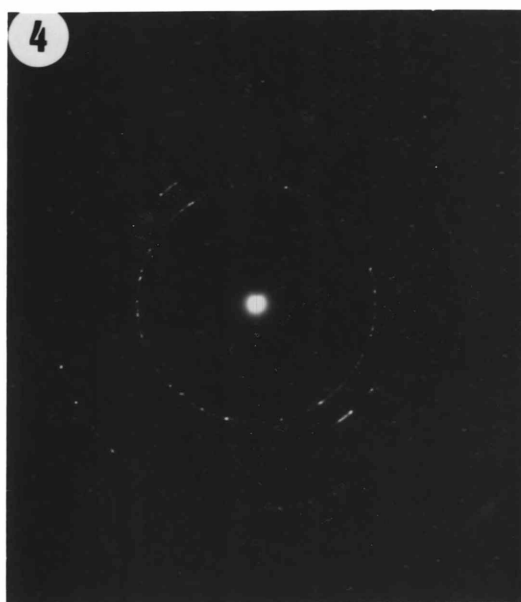
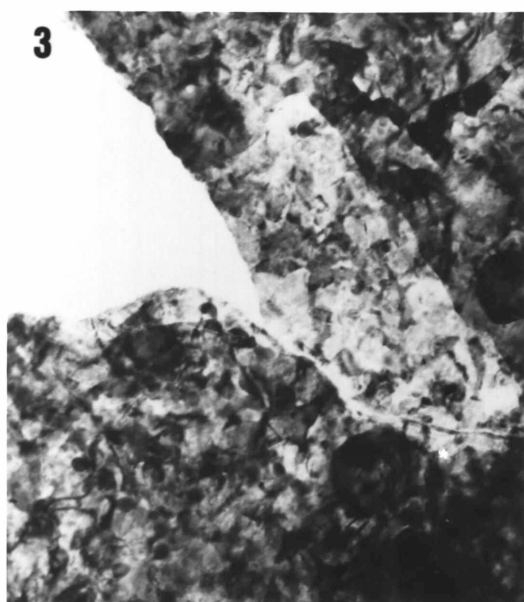
3.3.5.6 Transmission electron micrograph of the area in figure 3.3.5.5 showing the contrast from features seen in that figure and allowing the position of the metal edge to be determined.



200 nm



rd = 3.93 cmÅ



up similar shapes to those seen in figure 3.3.3.2 but this is not consistent from hole to hole. The oxide, where visible, appears thicker than that in figure 3.3.4 and has a grain size of approximately 50 nanometres; it has neither cracked nor spalled. A selected area diffraction pattern of the area is given in figure 3.3.5.2. This has the ubiquitous two oxide rings, here only as arcs, corresponding to $\{11\bar{2}0\}$ and $\{30\bar{3}0\}$, together with a partial chromium $\langle 111 \rangle$ zone axis pattern.

Figure 3.3.5.3 is a bright field transmission electron micrograph of a specimen of chromium-implanted chromium oxidised for 20 seconds at temperatures up to 800°C in an oxygen pressure of 400 Pa. The metal edge is smooth and the oxide appears thicker than the previous sample, figure 3.3.5.1. The grain size of this oxide film is perhaps larger than that in figure 3.3.5.1 but it is difficult to measure precisely. The selected area diffraction pattern from the area shown is given in figure 3.3.5.4. This consists of the two oxide rings and a pair of short arcs corresponding to the chromium $\{110\}$ reflection.

A secondary electron image of an oxide film grown on chromium-implanted chromium, oxidised for 10 seconds at temperatures up to 650°C in an oxygen pressure of 250 Pa is given in figure 3.3.5.5. The surface shown is the top surface of the sample, back to which the sample was thinned. Nodules (A) and wrinkles (B) in the oxide film are quite clearly seen. These are approximately 100 nanometres in size. This micrograph was taken in the scanning transmission electron microscope; a transmission electron micrograph of the same area is given in figure 3.3.5.6. The nodule (A) can be clearly seen, as can diffraction contrast from the wrinkles (B). The structure of the oxide seen in figure 3.3.5.5 bears no relationship to the position of the metal edge seen in figure 3.3.5.6; the metal edge is smooth.

The cerium-implanted specimens oxidised in the gas reaction cell are shown in figure 3.3.6 and 3.3.7; those specimens oxidised for short lengths of time are shown in figure 3.3.6. Figure 3.3.6.1 shows part of a specimen oxidised in 250Pa oxygen pressure for 10 seconds at temperatures up to 630°C. The sample has a film covering its surface (A), in some cases the film appears to be doubled (B). The metal foil was back-thinned by electropolishing and this appears to have been carried out at too low a temperature as the metal near the edge of the foil has a colander-like structure, with etched holes caused by local overheating due to a too-viscous electrolyte and the formation of bubbles at the metal/electrolyte interface. The film covers this colander structure extending past the metal edge and the film over each hole has a concentric hole (C). Islands of metal (D) also appear in the film near the main metal edge and the film has small laths of oxide (E) scattered over its surface.

The doubling of the film can be explained by the film folding over on to itself as shown in figure 3.3.6.2, a secondary electron image taken in the scanning transmission electron microscope. A selected area diffraction pattern of the film is

Figure 3.3.6

Electron micrographs of specimens of cerium-implanted chromium, oxidised in the gas reaction cell.

3.3.6.1 Bright field micrograph of the film on a sample oxidised for 10 seconds at temperatures up to 630°C in an oxygen pressure of 250 Pa.

3.3.6.2 Secondary electron image of the edge of the film on the sample shown in figure 3.3.6.1 showing how it folds over.

3.3.6.3 Selected area diffraction pattern from the film in figure 3.3.6.1, consisting of oxide reflections arrayed in rings on a background of two broad rings from an amorphous source.

3.3.6.4 Bright field micrograph of the film on a sample oxidised for 10 seconds at temperatures up to 640°C in an oxygen pressure of 250 Pa.

3.3.6.5 Selected area diffraction pattern from the film in figure 3.3.6.4, consisting of rings of oxide reflections, indexed in the adjacent diagram, on a background of two broad rings from an amorphous source. A ring corresponding to the CeO_2 {111} reflection is also present in the diffraction pattern.

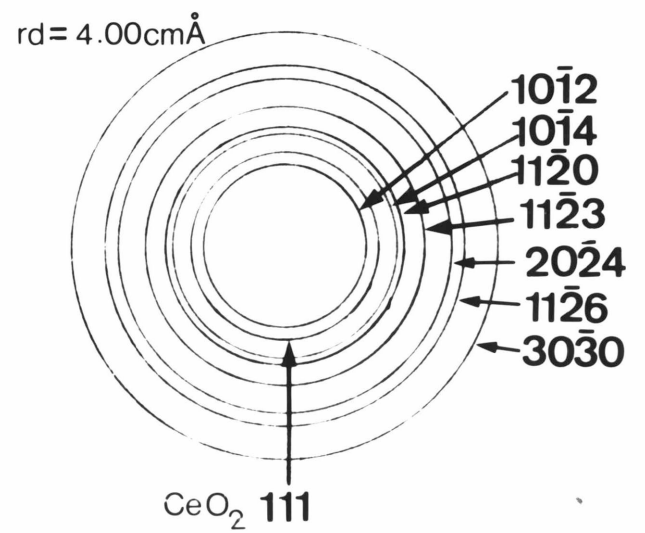
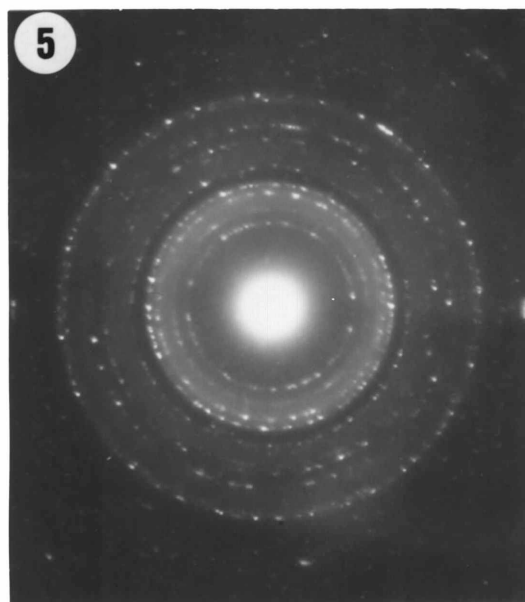
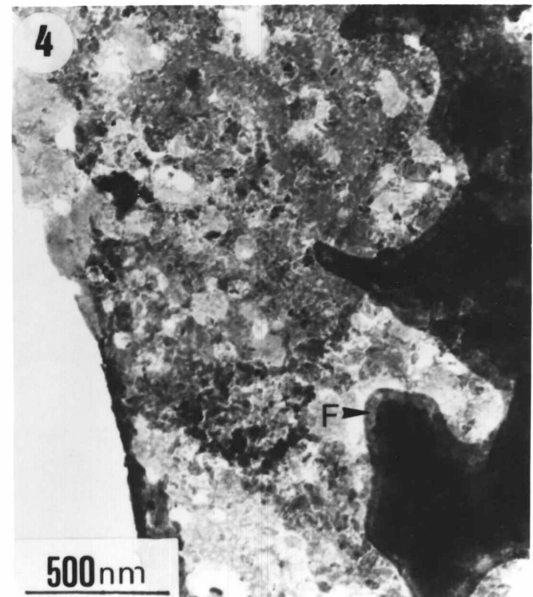
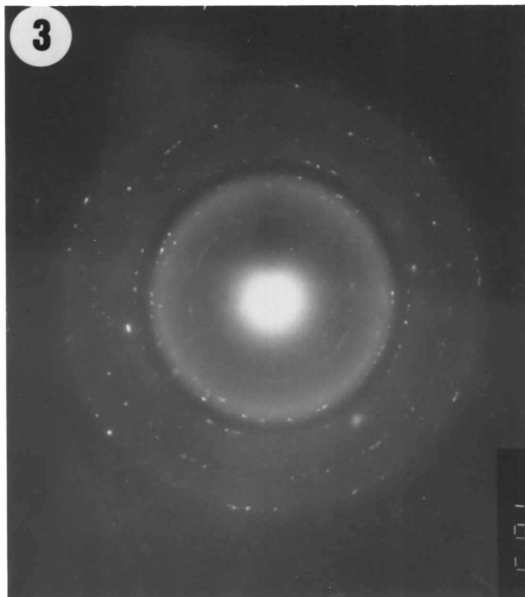
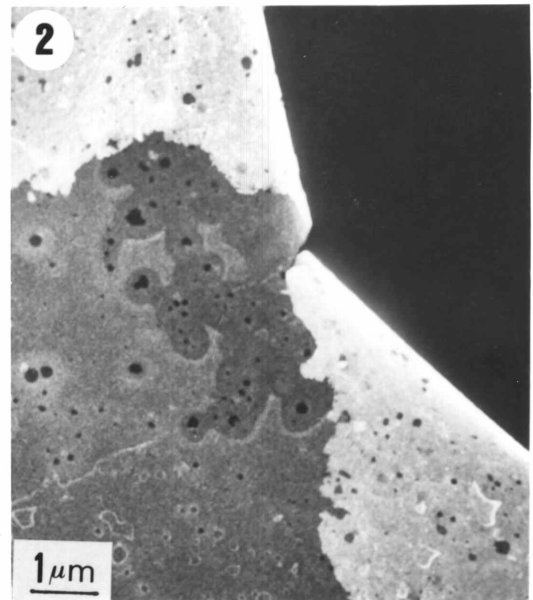
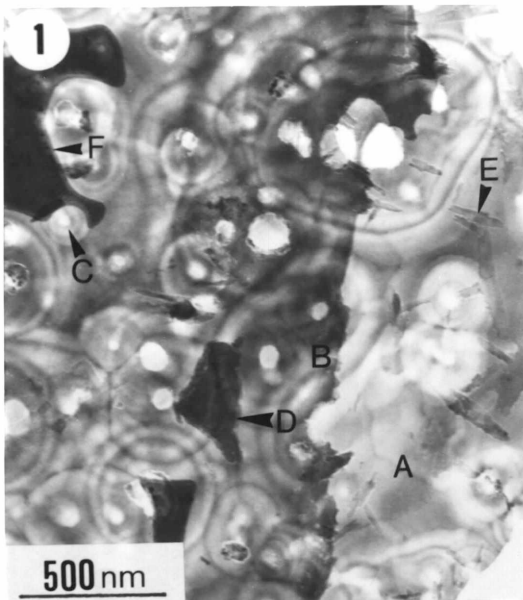


Figure 3.3.7

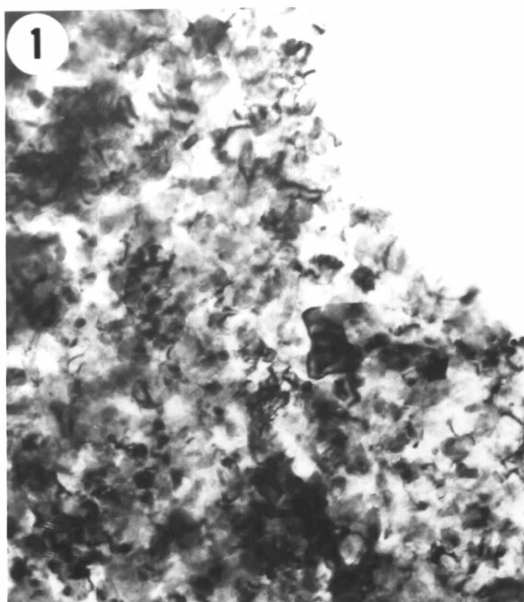
Transmission electron micrographs from samples of cerium-implanted chromium oxidised in the gas reaction cell for longer periods of time.

3.3.7.1 Bright field micrograph of the oxide film on a sample oxidised for 1 minute at 780°C in an oxygen pressure of 2000 Pa.

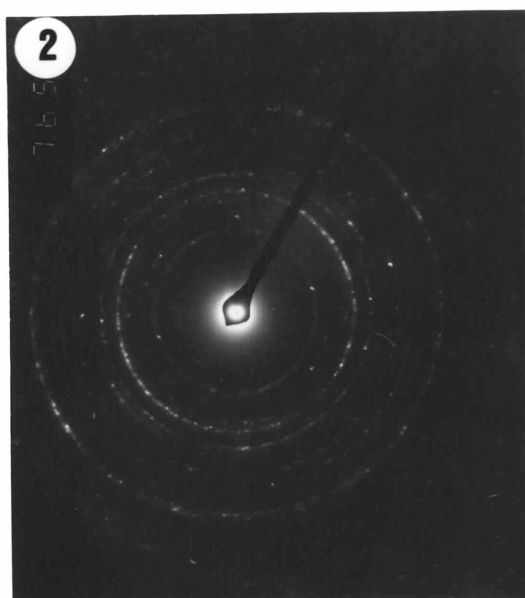
3.3.7.2 Selected area diffraction pattern from the area shown in figure 3.3.7.1, indexed in the diagram below. The diffraction pattern contains a ring corresponding to the CeO_2 {111} reflection among the rings of Cr_2O_3 reflections.

3.3.7.3 Bright field micrograph of the oxide film on a sample oxidised for 30 seconds at 860°C in an oxygen pressure of 250 Pa.

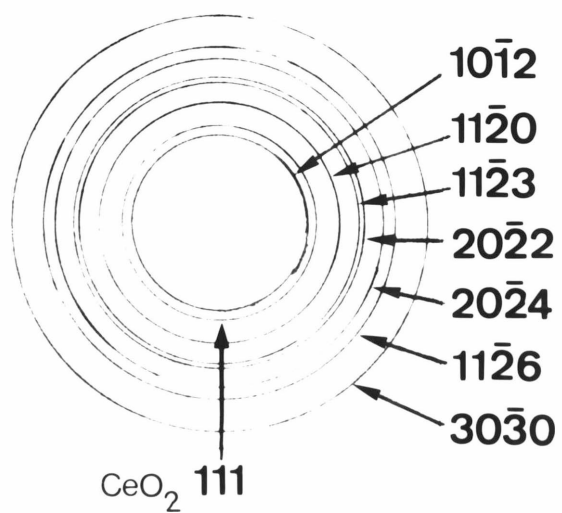
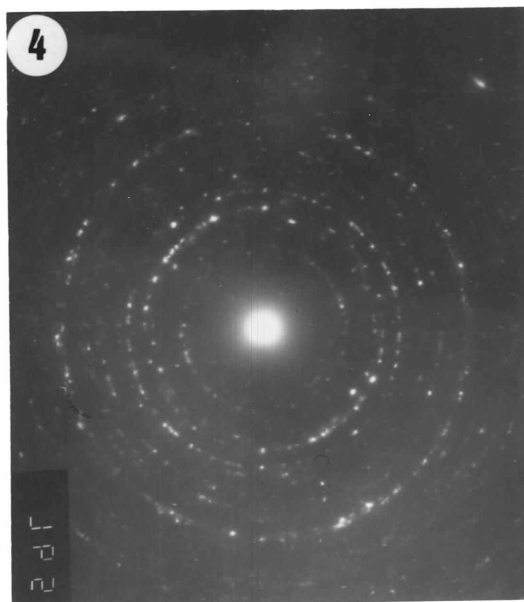
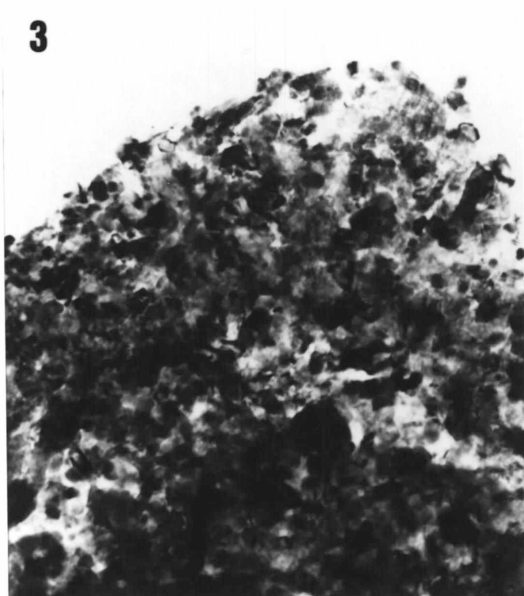
3.3.7.4 Selected area diffraction pattern from the area shown in figure 3.3.7.3, indexed in the diagram below. The diffraction pattern contains a faint ring corresponding to the CeO_2 {111} reflection among the rings of Cr_2O_3 reflections.



200nm



$rd=3.92\text{cm}\text{\AA}$



given in figure 3.3.6.3. This consists of oxide spots arrayed around rings and a background intensity consisting of two broad rings. The oxide spots are reflections from the laths in figure 3.3.6.1 and come from rings indexed in the diagram below. The broad rings cannot be identified but they must arise from an amorphous source. This source is most likely to be the film itself.

The specimen in figure 3.3.6.4 was oxidised for 10 seconds at temperatures up to 640°C in an oxygen pressure of 250 Pa and also has the colander-like metal structure and a film covering its surface, doubled over in places. The film here appears more evidently crystalline although the selected area diffraction pattern from the film, figure 3.3.6.5, still has the microcrystalline background, albeit with far more oxide reflections. The diffraction pattern is indexed in the adjacent diagram. The metal areas both in this figure and in figure 3.3.6.1 have evidence of oxidation of their lower surfaces in a thin band of oxide around the metal (F). The selected area diffraction patterns of the two films differ in one other feature. The diffraction pattern in figure 3.3.6.5 has a ring corresponding to the CeO_2 {111} reflection while that in figure 3.3.6.3 does not.

Figure 3.3.7 shows transmission electron micrographs of oxidised foils of cerium-implanted chromium; figure 3.3.7.1 is an oxide film from a specimen oxidised for 1 minute at 780°C in an oxygen pressure of 2000Pa. The grain structure has developed and has an approximate grain size of 50 nanometres. A selected area diffraction pattern is given in figure 3.3.7.2 and indexed in the diagram below. The diffraction pattern shows the two main rings corresponding to the {11 $\bar{2}$ 0} and {30 $\bar{3}$ 0} reflections and also rings corresponding to other Cr_2O_3 reflections whose intensities are more equal to the main rings than has been seen previously showing that the initial texture is greatly reduced. The diffraction pattern also has a set of spots corresponding to the CeO_2 {111} reflections.

Figure 3.3.7.3 is of a specimen oxidised for 30 seconds at 860°C in an oxygen pressure of 250 Pa. The grain size of this oxide film is smaller than of that in figure 3.3.7.1 especially near the edge; the grain size is estimated to be around 30 nanometres. The selected area diffraction pattern from the sample, given in figure 3.3.7.4, takes the same indexing as that in figure 3.3.7.2 and also shows a faint ring of spots corresponding to the CeO_2 {111} reflection.

3.4 Oxidation in the Oxidation Rig

Discs of chromium 3 millimetres in diameter were oxidised in the oxidation rig at temperatures between 750°C and 950°C for periods of a few minutes in order to study the oxide films formed on their surfaces after short times. This was meant to continue the gas reaction cell work to thicker oxide films and to give a more macroscopic view of the initial oxidation period.

Figure 3.4.1.1 shows the oxide film produced on a mechanically polished specimen of standard-annealed chromium after oxidation for 1 minute at 950°C. When examined in reflection using the light microscope the oxide film appears light grey and transparent with areas of a more yellow colouration; this mottling can be seen in the micrograph. The sample is covered with star-shaped convolutions (A) 25 micrometres in diameter and nodules (B) 5 micrometres in diameter as indicated in the figure and between these features the oxide film is adherent. The other black features (C) are pits in the surface. There are a few areas where the film bulges from the surface contained within an area of lighter coloured oxide, the boundaries of which are three smooth lines that bear a strong resemblance to metal grain boundaries. The oxide also appears speckled with fine black dots.

The mechanically polished sample oxidised for 3 minutes at 950°C, figure 3.4.1.2, has a flat, adherent oxide film that appears dark brown in the light microscope. The film is far more granular in appearance than the previous sample but the film contains only a few convolutions, shown in the micrograph (D). There are some pits in the surface of the oxide (E) and some circular areas where the oxide has either spalled or is thinner (F).

Figure 3.4.1.3 is a scanning electron micrograph of the sample shown in figure 3.4.1.1 taken at an angle of 45° to the vertical to reveal the surface relief. The star-shaped convolutions (A), the pits in the oxide (C) and the bulged oxide (G) can be seen. This sample was back-thinned for transmission electron microscopy before being examined in the scanning electron microscope; the bulge in the top right of the micrograph (H) is assumed to be a product of the thinning process as it occurs next to the hole and the cracks around the base of the bulge do not appear around the other bulge. Also visible on this micrograph are small white speckles which are whiskers growing from the surface of the oxide. Figure 3.4.1.4 is a light micrograph of a mechanically polished sample oxidised for 5 minutes at 950°C. The oxide on this sample is opaque and very dark. The bulging of the oxide is more frequent and there are also ridges of buckled oxide (I) evident.

A sample of mechanically polished standard-annealed chromium oxidised for 1 minute at 850°C is shown in figure 3.4.1.5. When viewed in reflection using a light microscope the oxide film appears bright green and transparent except for the buckled

Figure 3.4.1

A figure showing the oxide films grown on mechanically polished discs of standard-annealed chromium oxidised in the oxidation rig in 1 atmosphere of flowing oxygen. The marker below the first two figures applies to figures 3.4.1.1, 2, 4 and 5.

3.4.1.1 A light micrograph of standard-annealed chromium oxidised for 1 minute at 950°C.

3.4.1.2 A light micrograph of standard-annealed chromium oxidised for 3 minutes at 950°C showing the general adherence of the oxide to the metal.

3.4.1.3 A scanning electron micrograph of standard-annealed chromium oxidised for 1 minute at 950°C. The sample is tilted at an angle of 45° to the vertical to show surface relief. The sample has been back-thinned and the large bulge at the top right (H) was caused by this thinning procedure.

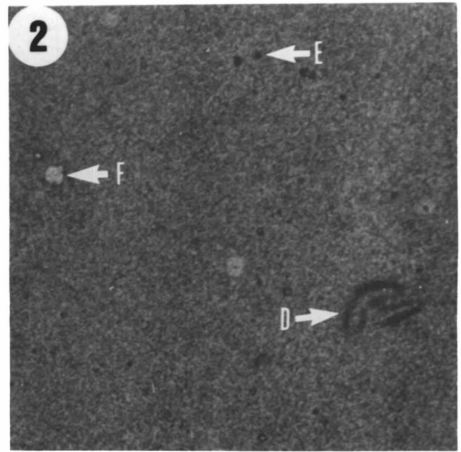
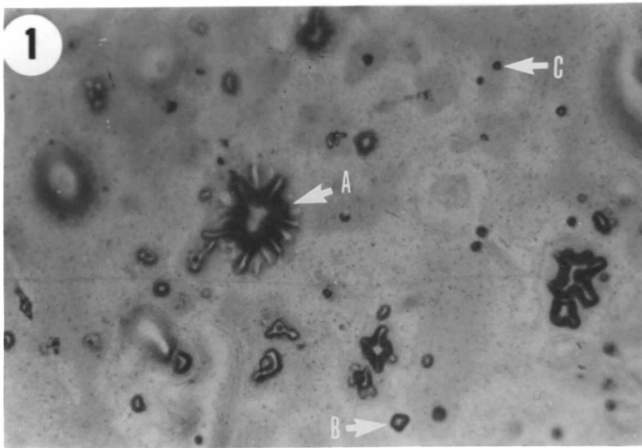
3.4.1.4 A light micrograph of standard-annealed chromium oxidised for 5 minutes at 950°C showing ridge-like buckled oxide (I). This oxide film was opaque.

3.4.1.5 A light micrograph of standard-annealed chromium oxidised for 1 minute at 850°C showing more general buckling of the oxide (J).

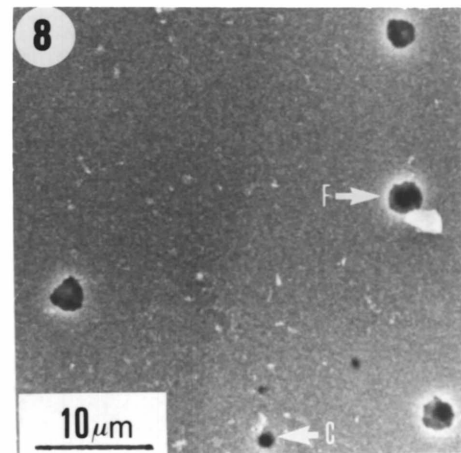
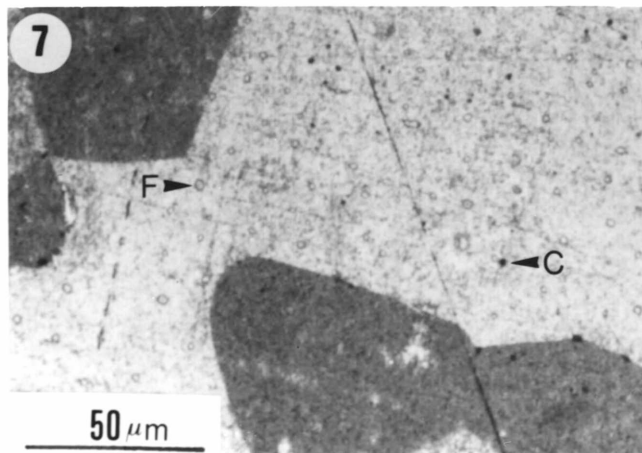
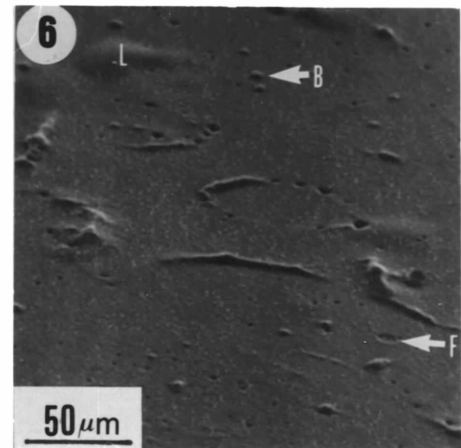
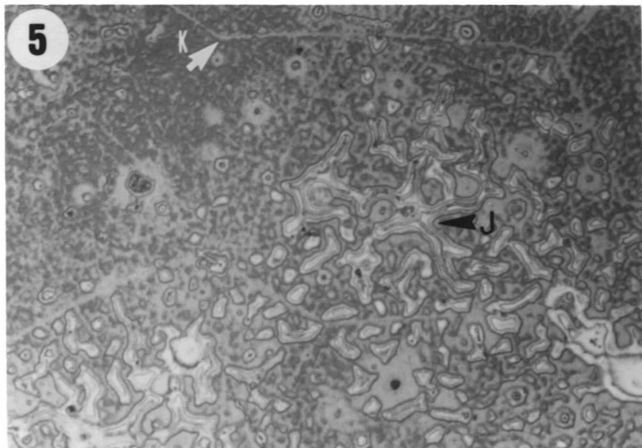
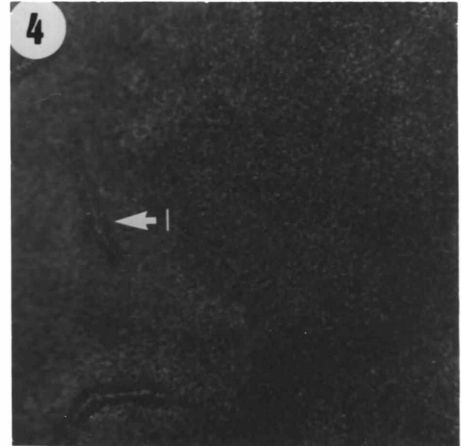
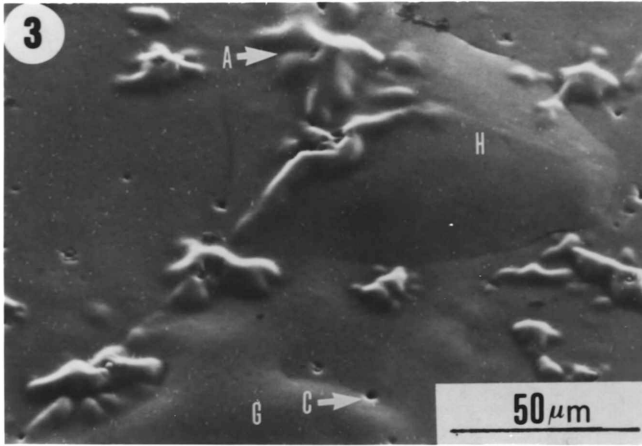
3.4.1.6 A scanning electron micrograph of standard-annealed chromium oxidised for 5 minutes at 950°C. The sample is tilted at an angle of 65° to the vertical.

3.4.1.7 A light micrograph of standard-annealed chromium oxidised for 5 minutes at 850°C showing the dependence of the oxide thickness on the orientation of the metal grains.

3.4.1.8 A scanning electron micrograph of standard-annealed chromium oxidised for 5 minutes at 850°C.



50 μ m



areas (J) which are white. The adherent areas are a mixture of a yellow-green and green with some red and have a stippled appearance, the green oxide appearing darker in the micrograph. Lines in the oxide (K) conform to the geometry of the metal grain boundaries; the oxide in these lines being yellow-green. The strong colour is an interference effect, produced by interference between light reflected from the top of the oxide and from the metal surface. The wavelength at which destructive interference is maximum determines the colour seen. The convolutions are finger-like rather than star-shaped, 5 micrometres wide and have occasionally spalled. Pits in the oxide are also present together with circles of thinner or spalled oxide.

Figure 3.4.1.6 is a scanning electron micrograph of the sample in figure 3.4.1.4 taken at an angle of 65° to the vertical. The ridges of buckled oxide can be seen together with pits in the oxide film. Areas of bulged oxide (L) become more evident as do nodules on the surface (B). Visible on this micrograph are whiskers on the surface of the oxide and also a circle of spalled or thinner oxide (F). The ridges of oxide appear to lie along the metal grain boundaries.

A sample of mechanically polished standard-annealed chromium oxidised for 5 minutes at 850°C is shown in figure 3.4.1.7. This light micrograph shows areas of oxide on the sample that have different interference colours. The main light areas of the micrograph are yellow-green, the dark areas in the bottom right are green with red stippling and the dark areas in the top left are blue with green stippling. These areas have the same geometry as the underlying metal grain structure and appear to show a dependence of the oxide thickness, as measured by interference colour, on the metal grain orientation. Visible in the light areas are circles of spalled oxide (F) 2 micrometres in diameter, some of which have central spots, and pits in the oxide (C) 1 micrometre in diameter. The pits are visible all over the sample and the circles are also generally spread; the circles, however, were most numerous in the yellow-green oxide and did not appear in the green/red oxide. If the oxidised sample is compared with light micrographs of the sample taken prior to oxidation then the dark pits in the surface of the oxide match in position with the pits in the surface of the unoxidised specimen. Virtually none of the spalled circles coincide with these pits. A scanning electron micrograph, figure 3.4.1.8, show the circles of spalled oxide (F), some of which have pits at their centres, and pits in the oxide unassociated with oxide spallation (C).

Two specimens of mechanically polished, standard-annealed chromium oxidised for 10 minutes at 750°C are shown in the light micrographs in figures 3.4.2.1 and 3.4.2.2. The first has large areas of buckled oxide that has spalled together with areas of unspalled convolutions. These convolutions are of the form both of the ridge like structures thought to be associated with the metal grain boundaries and of the star-shaped buckles found on other mechanically polished

Figure 3.4.2

Light and scanning electron micrographs of discs of electrolytic chromium oxidised in the oxidation rig in 1 atmosphere flowing oxygen at various times and temperatures. The 50 micrometre marker applies to all of the figure except 3.4.2.3.

3.4.2.1 A light micrograph of standard-annealed chromium oxidised for 10 minutes at 750°C showing oxide buckles that have spalled and circles of thinner oxide distributed in the adherent oxide.

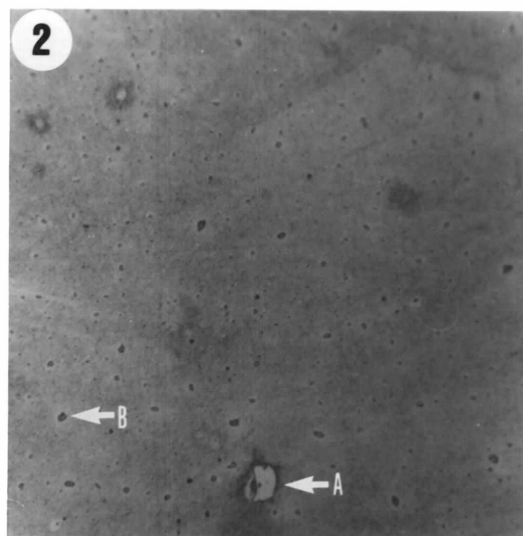
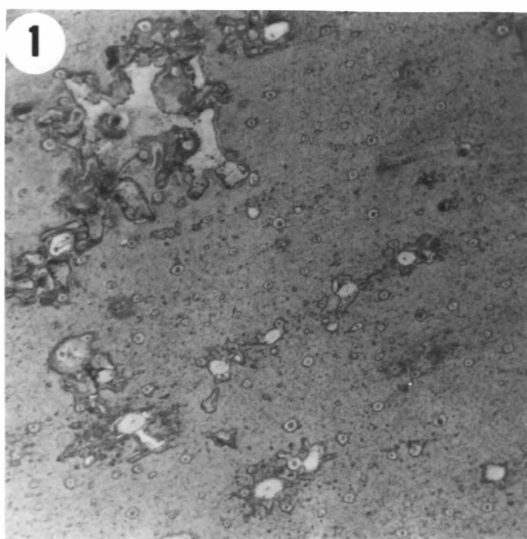
3.4.2.2 A light micrograph of another disc of standard-annealed chromium oxidised for 10 minutes at 750°C to be compared with figure 3.4.2.1.

3.4.2.3 A scanning electron micrograph of the sample in figure 3.3.2.1 taken at an angle of 65° from the vertical to show surface relief.

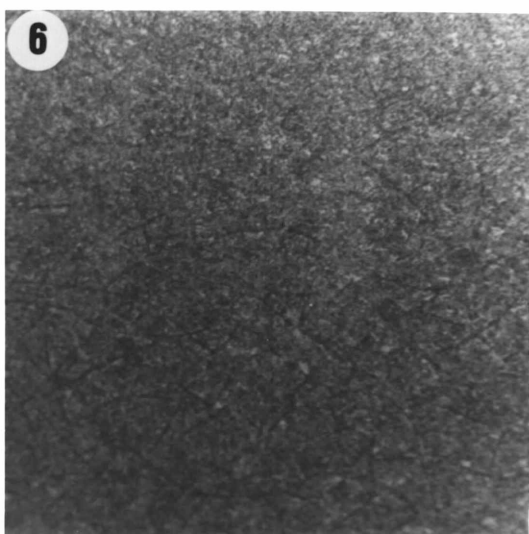
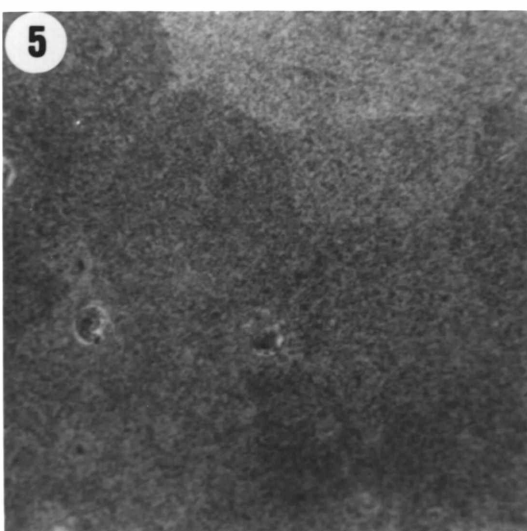
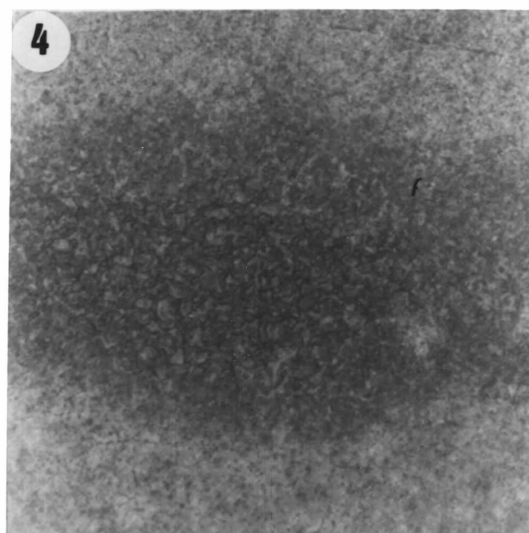
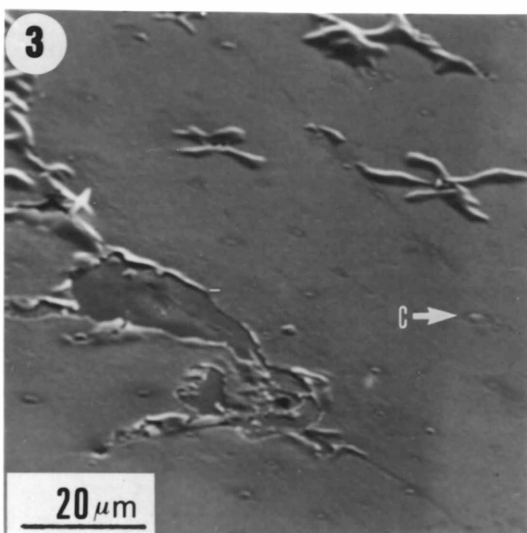
3.4.2.4 A light micrograph of a mechanically polished sample of electrolytic chromium annealed for 3 hours at 1000°C in hydrogen, oxidised for 3 minutes at 850°C showing a large area of buckled oxide found in the centre of an otherwise perfectly adherent scale.

3.4.2.5 A light micrograph of standard-annealed chromium oxidised for 15 minutes at 850°C showing the dependence of the oxide thickness on metal grain orientation.

3.4.2.6 A light micrograph of a mechanically polished sample of electrolytic chromium annealed for 3 hours at 1000°C in hydrogen, oxidised for 3 minutes at 950°C; shown as a comparison with the sample of standard-annealed chromium oxidised under the same conditions. The pits in the surface of the metal can be seen through the oxide as a network of lines.



50 μ m



specimens. The oxide is transparent and its thickness gives rise to yellow-green interference colours, in some areas stippled with green. The film also has a granular appearance and is covered with circular areas of thinner or spalled oxide 4 micrometres in diameter. These circles all seem to possess a central speck of darker material.

The sample in figure 3.4.2.2, in contrast, has an adherent oxide film that gives rise to a yellow interference colour. The film appears almost uniform in thickness except for a slight dependence on the metal grain orientation that shades the oxide more orange than yellow. There are a few areas of spallation such as (A) and the surface is covered with specks of blue colouration (B) 1 micrometre in size. These specks are distributed in the same fashion as the pits on the unoxidised metal but it cannot be stated whether they match in position.

Figure 3.4.2.3 is a scanning electron micrograph of the sample in figure 3.4.2.1 taken at an angle of 65° to the vertical. The star-shaped buckled oxide with an area of spallation can be seen together with some pits in the surface. Also visible (C) are circles of thinner oxide with central nodules; these are thought to be the circular features seen on the light micrograph. Comparison with the spalled area where the oxide edge is visible, shows that the circles are not areas of recently spalled oxide.

A specimen of chromium annealed for 1000°C in hydrogen for 3 hours and oxidised for 3 minutes at 850°C is shown in the light micrograph in figure 3.4.2.4. This has a perfectly adherent oxide scale except for an irregularly shaped area of buckled, thicker oxide in its centre, shown here in the micrograph. The buckled areas have occasionally spalled and are similar in shape to those shown in figure 3.4.3.6, from an electropolished surface.

Figure 3.4.2.5 is a sample of mechanically polished, standard-annealed chromium oxidised for 15 minutes at 850°C . It possesses an adherent oxide film that is dark brown in colour when viewed in a light microscope except for some areas, shown in the figure, where there is evidence of metal-grain-orientation-dependent oxide thickness. These are generally lighter in colour and some have a green stippling. Figure 3.4.2.6 shows a sample of 1000°C , 3 hour, hydrogen-annealed chromium, oxidised for 3 minutes at 950°C . This sample also has an adherent oxide film that gives rise to a brown interference colour. The pits in the surface of the metal can be seen through the oxide as a faint network of black lines, but they have had no obvious effect on the oxide growth.

Figures 3.4.3.1 and 3.4.3.2 are from the same area of an electropolished sample of standard-annealed chromium oxidised at 850°C for 4 minutes. The scanning electron micrograph, figure 3.4.3.2, shows the convolutions in the oxide film and pits in the surface. One of the convolutions can be seen to be cracked at its

Figure 3.4.3

A figure showing the oxide scales grown on electropolished surfaces of standard-annealed chromium and on chromium annealed for 3 hours at 1000°C in hydrogen. The 50 micrometre marker applies to figures 3.4.3.1, 2 and 3.

3.4.3.1 A light micrograph of a standard-annealed chromium sample oxidised for 4 minutes at 850°C showing the large finger-like buckles typically found in oxide grown on electropolished surfaces.

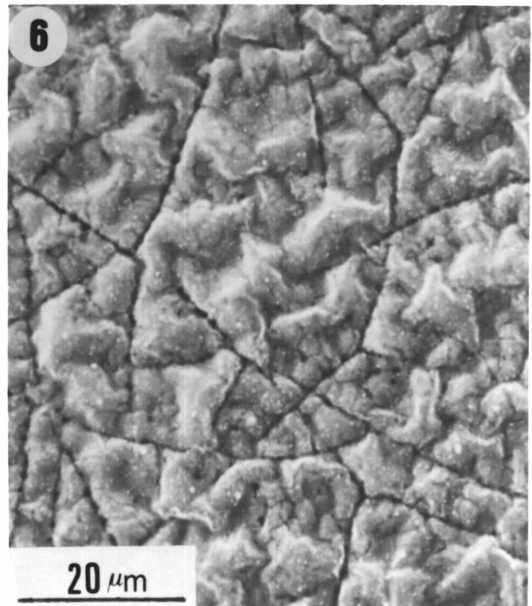
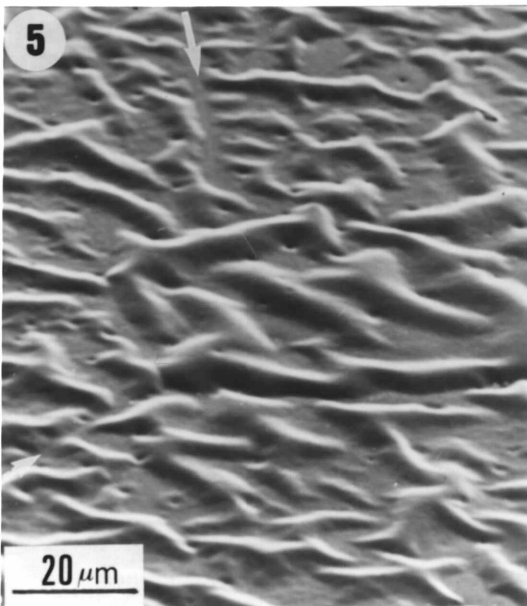
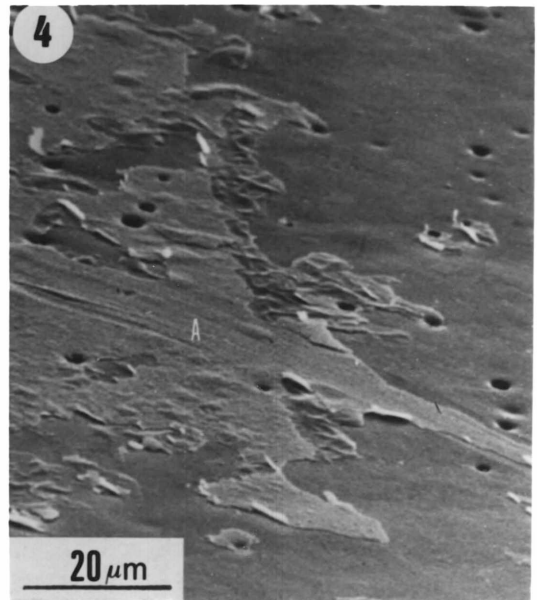
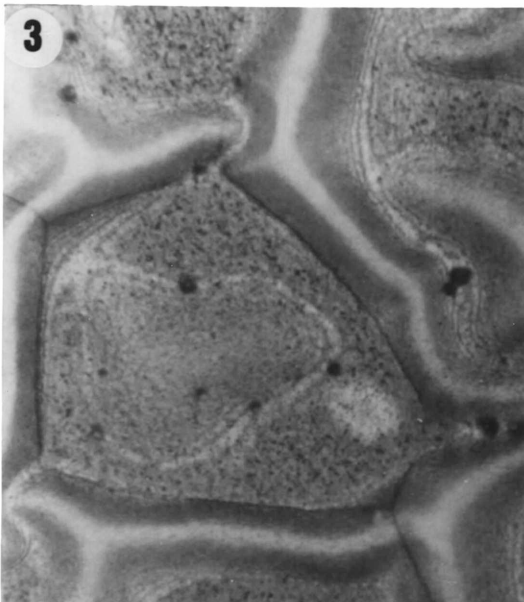
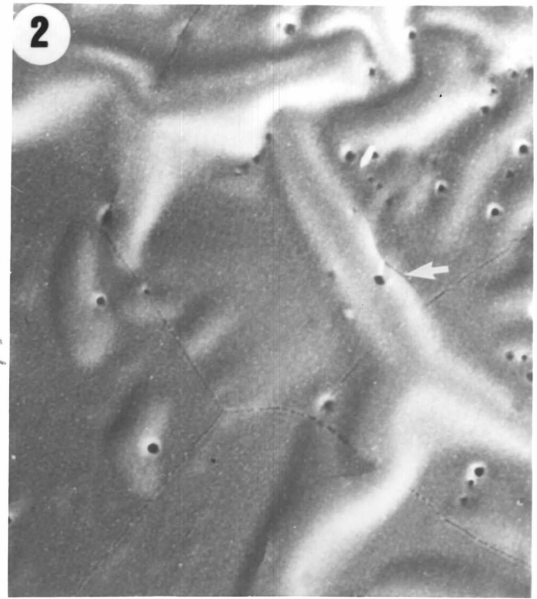
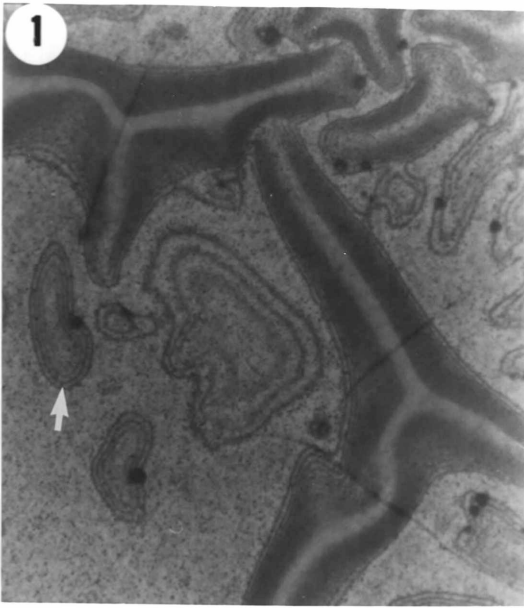
3.4.3.2 A scanning electron micrograph of the area shown in figure 3.4.3.1. Comparing this micrograph with the light micrograph of the area enables the features to be identified.

3.4.3.3 A light micrograph of a standard-annealed chromium sample oxidised for 3 minutes at 950°C showing how the buckling of the oxide film can be affected by the metal grain boundaries and by the pits in the surface of the metal.

3.4.3.4 A scanning electron micrograph of an electropolished sample of standard-annealed chromium oxidised for 30 minutes at 700°C, taken at an angle of 70° from the vertical so that the surface features can be seen in relief. The oxide has been mechanically stripped from parts of the surface.

3.4.3.5 A scanning electron micrograph of a standard-annealed chromium sample oxidised for 4 minutes at 850°C taken at an angle of 65° to the vertical. The effect of the metal grain boundaries is illustrated by the channel of adherent oxide indicated by the arrow.

3.4.3.6 A scanning electron micrograph of electrolytic chromium annealed for 3 hours at 1000°C in hydrogen, oxidised for 3 minutes at 750°C showing how the buckled oxide film conforms to the lines of pits in the surface of the metal.



base, indicated by the arrow, and there are other lines on the surface that appear also to be cracks but the lines disappear when they meet the large buckles. Comparison with the light micrograph, figure 3.4.3.1, shows the same lines running through the buckles implying that the lines are on the surface of the sample and that the oxide is transparent; borne out by the appearance of interference colours when viewed in reflection using a light microscope. The lines on the surface are probably metal grain boundaries. The pits in the surface appear as black spots on the light micrograph and the convolutions appear to have contour lines. These contour lines are formed by destructive interference between light reflected from the surface of the metal and from the lower surface of the oxide film in a manner similar to Newton's rings. The scanning electron micrograph of the area enables the connection between these contour lines and the buckled oxide to be made and the light micrographs of oxidised samples can be used to detect areas where decohesion of the oxide has occurred but cannot be seen in the electron microscope. It is possible to use these interference lines to estimate the separation between the oxide film and the metal surface. For light of wavelength λ and for a distance t between the metal surface and the underside of the oxide, the m th dark line indicating destructive interference will be given by:

$$2t = m\lambda$$

$$21$$

So, if it is assumed that the tungsten-halogen lamp in the light microscope gave yellow light of wavelength 520 nanometres, then each black contour line is equivalent to around 250 nanometres change in height. If the convolutions on this specimen are compared with those seen in figure 3.4.1.5, the convolutions on the mechanically polished specimen can be seen to be around 0.5 micrometres high and those on this electropolished sample, figure 3.4.3.1, are greater than 2 micrometres high; after the fourth contour line the lines become impossible to resolve which means that the convolutions could be much higher than 2 micrometres. Their widths also reflect this: the convolutions in this figure are 20 micrometres wide and those on the mechanically polished surface were 5 micrometres wide. If the slopes of the sides of the smaller convolutions, such as that indicated in figure 3.4.3.1, are calculated then it is found that the convolutions on the electropolished surface and on the mechanically polished surface both have slopes of around 0.2. This slope also corresponds to the initial slope of the larger convolutions on the electropolished samples. The granular appearance of the oxide film is more noticeable on the light micrograph than on the scanning electron micrograph.

Figure 3.4.3.3 shows a micrograph from a specimen of standard-annealed chromium electropolished and then oxidised at 950°C for 3 minutes. It shows oxide convolutions, pits in the oxide surface and what are thought to be metal grain

boundaries. The buckled oxide appears to be pinned by the grain boundaries, being steeper on the boundary side than on the other side; there is also a slight pinning effect on the flat bulge in the centre of the micrograph from the pits surrounding it. This is not evident in figure 3.4.3.1 where the convolutions run perpendicular to the metal grain boundaries. Visible on a scanning electron micrograph of the sample are small particles or whiskers on the surface of the oxide. These are only generally present on the adherent areas of oxide and could give the oxide its granular appearance when viewed in the light microscope. Another electropolished sample, oxidised for 30 minutes at 700°C, is shown in the scanning electron micrograph in figure 3.4.3.4, taken at an angle of 70° to the vertical. Most of the oxide scale has been stripped from the surface of this sample but the micrograph shows a more adherent area of oxide that remains almost intact (A). The oxide film has had more time to develop and consists of two, and in some cases three, separate layers: a smooth outer layer, a convoluted middle layer and a thin, flat layer next to the metal surface. The pits in the surface of the specimen, formed during the electropolishing process, can be seen in the exposed surface and also in the adherent oxide. These pits seem to act as pinning sites with the oxide growing in their interiors holding the oxide film down onto the surface of the sample.

Figure 3.4.3.5 shows a mechanically polished sample whose oxide film bears a strong resemblance to the scales grown on electropolished surfaces. The convoluted film covers most of the surface of the disc and the area shown in the figure illustrates the apparent dependence of the film morphology on the underlying grain structure. The buckles inside the area of the small metal grain are larger and more of the oxide has lifted off the metal; the area appears to be isolated from the surrounding area by a channel of adherent oxide thought to coincide with the metal grain boundary. Parts of the channels leading away from the area can be seen, indicated by the arrows. This apparent increase in oxide film adherence along metal grain boundaries is far more widespread on mechanically polished samples showing this type of oxide buckling than on electropolished samples. Some of the pits in the surface of the oxide seem to be raised above the level of the adherent oxide implying that any pinning effect that they may have is transitory.

The pinning effect of pits in the surface of specimens is taken to its extreme with oxide films grown on the electropolished surfaces of chromium annealed for 3 hours at 1000°C where the surface is covered with a network of lines of pits. Figure 3.4.3.6 shows such a sample oxidised at 750°C for 3 minutes and the effect is obvious. The buckles are very small, even relative to the mechanically polished samples, and are generally confined by the lines of pits to the point of being nodules. Some of the smaller convolutions can be seen to be cracked along their ridges and the thickness of the oxide is comparable with films grown at higher temperatures.

Figure 3.4.4 shows specimens of Chromium-implanted standard-annealed chromium oxidised at 850°C and 950°C. The sample shown in the light micrograph in figure 3.4.4.1 is Chromium-implanted chromium oxidised for 5 minutes at 950°C. The oxide film is dark brown when viewed in a light microscope and is covered in nodules (A) 5 micrometres in diameter and the occasional ridge-like convolution (B). The film has a granular appearance and there are a few circles of thinner oxide (C). Figure 3.4.4.2 shows a sample of Chromium-implanted chromium oxidised for 1 minute at 950°C. The oxide film has a bright green interference colour with some blue areas and is buckled. Pits in the surface can be seen around the convolutions and the convolutions appear different to those on other samples. Whereas the convolutions on the unimplanted samples were smooth and the transition from flat oxide to buckled oxide was concave when seen from above, these convolutions seem to be more abrupt, the convolutions seeming to be entirely convex. The convolutions are approximately 10 micrometres in width. Some of the buckled oxide has spalled.

The two figures 3.4.4.3 and 3.4.4.4 are from a sample oxidised for 5 minutes at 850°C. The scanning electron micrograph, figure 3.4.4.3, is taken at an angle of 45° to the vertical and the pits in the surface of the sample can be seen together with the areas of thicker oxide. The white particles in the centre of the micrograph are dust particles. The light micrograph, figure 3.4.4.4 is from the same area and the black spots on the surface match with the pits visible in the scanning electron micrograph. If both micrographs are matched with a light micrograph of the area taken prior to oxidation then the pits can be matched with the pits on the surface of the unoxidised specimen. The oxide film gives an orange-red interference colour with some red stippling; this is visible as the darker areas of the light micrograph. This area was from the edge of the sample; the oxide colouration became red with orange stippling towards the centre of the sample. The sample of chromium-implanted standard-annealed chromium oxidised at 850°C for 1 minute, not shown here, has a flat, adherent oxide film like that in figure 3.4.4.4 and gives rise to mainly a yellow interference colour with blue stippled areas.

The oxidised cerium-implanted samples are shown in figure 3.4.5. Figure 3.4.5.1 is a light micrograph of a cerium-implanted standard-annealed sample oxidised for 5 minutes at 950°C. It has a light brown colouration with areas of dark brown as seen in the micrograph. Pits can also be seen in the surface of the sample. The oxide film is flat and fully adherent with no spallation. A sample oxidised for 10 minutes at 850°C is shown in figure 3.4.5.2. It also has pits in its surface. The film gave a dark orange interference colour and, as can be seen in the micrograph, there were lines of lighter orange that seemed to have the same geometry as the metal grain structure. This effect was not seen on another sample of cerium-implanted chromium oxidised for 10 minutes at 850°C.

Figure 3.4.4

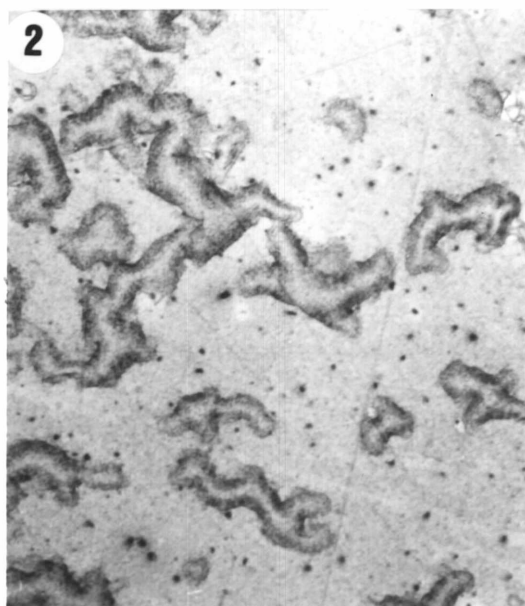
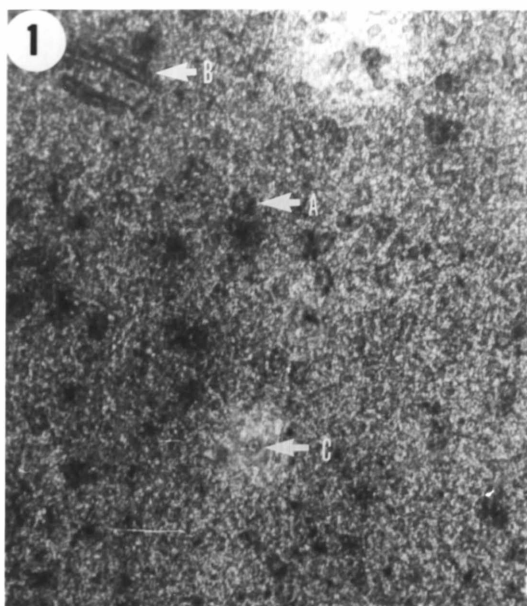
A figure showing the oxide films grown on mechanically polished discs of standard-annealed, Cr-implanted chromium, oxidised in the oxidation rig in 1 atmosphere of flowing oxygen.

3.4.4.1 A light micrograph of a Cr-implanted specimen oxidised for 5 minutes at 950°C.

3.4.4.2 A light micrograph of a Cr-implanted specimen oxidised for 1 minute at 950°C showing the buckled oxide film on the sample together with pits in the surface.

3.4.4.3 A scanning electron micrograph of a Cr-implanted specimen oxidised for 5 minutes at 850°C taken at an angle of 45° to the vertical showing the pits in the surface of the oxide. The two white particles are dust particles.

3.4.4.4 A light micrograph of a Cr-implanted specimen oxidised for 5 minutes at 850°C showing the area in figure 3.4.4.3. The pits in the surface can be seen as well as areas of thicker oxide.



100 μ m

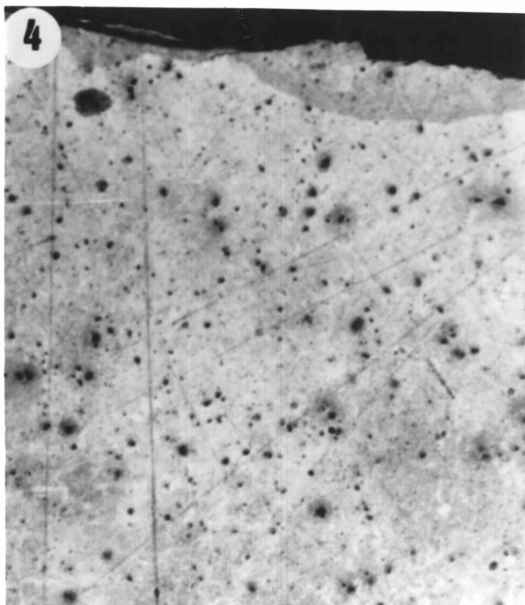
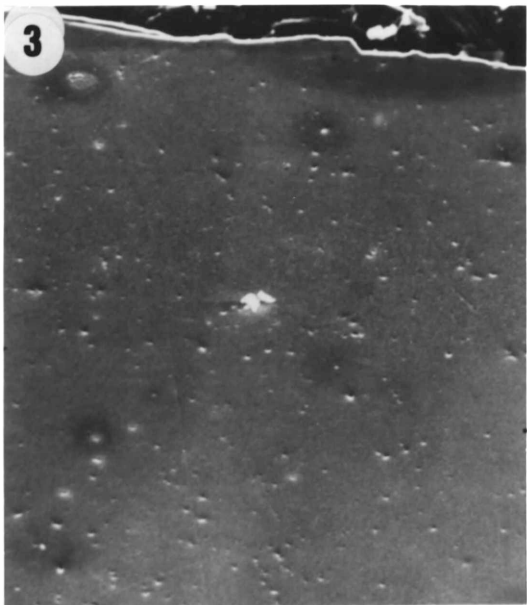


Figure 3.4.5

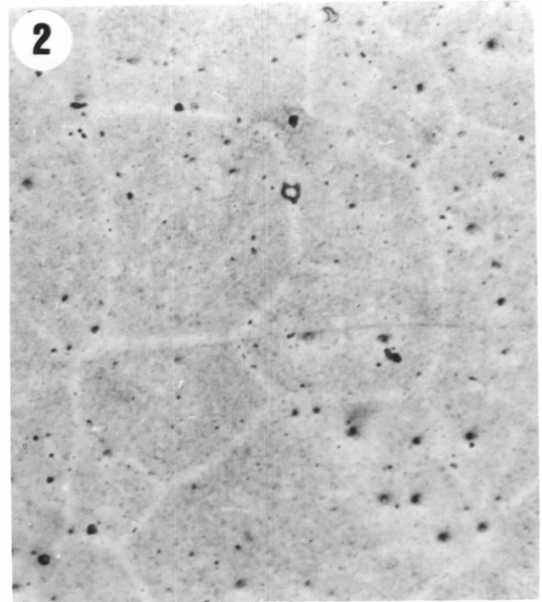
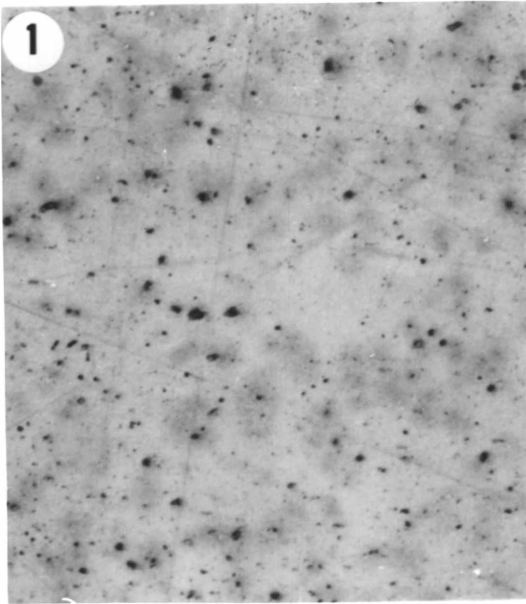
A figure showing the oxide films grown on mechanically polished discs of standard-annealed, Ce-implanted chromium, oxidised in the oxidation rig in 1 atmosphere of flowing oxygen.

3.4.5.1 A light micrograph of a Ce-implanted specimen oxidised for 5 minutes at 950°C showing the pits in the oxide film and the mottling of the specimen due to varying oxide thickness.

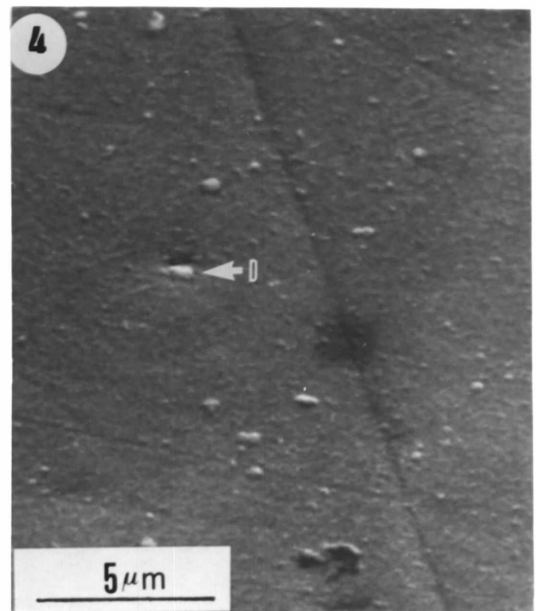
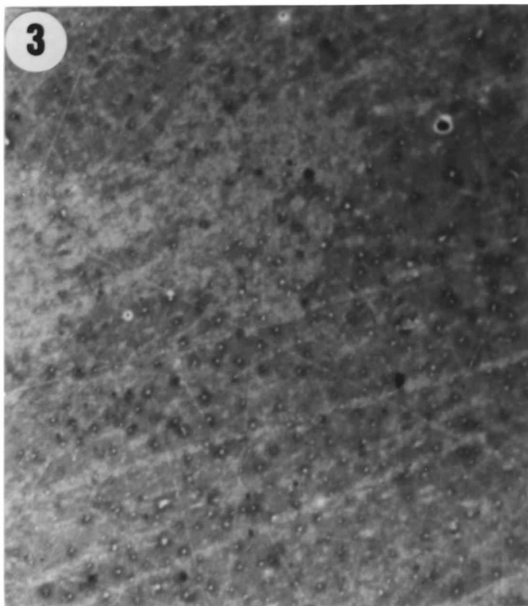
3.4.5.2 A light micrograph of a Ce-implanted specimen oxidised for 10 minutes at 850°C showing lines of thinner oxide at what appear to be metal grain boundaries.

3.4.5.3 A light micrograph of a Ce-implanted specimen oxidised for 1 minute at 950°C showing the dependence of the oxide thickness on metal grain orientation.

3.4.5.4 A scanning electron micrograph of a Ce-implanted specimen oxidised for 1 minute at 950°C taken at an angle of 45° to the vertical.



100 μm



The two micrographs in figures 3.4.5.3 and 3.4.5.4 are from the sample of cerium-implanted chromium oxidised at 950°C for 1 minute. Figure 3.4.5.3 is a light micrograph showing the slight dependence of the oxide thickness on the metal grain orientation together with the white specks scattered over the surface. The oxide film gave a blue interference colour which varied from light blue to dark blue. The scanning electron micrograph, figure 3.4.5.4, is taken at an angle of 45° to the vertical and shows the oxide to be covered with small nodules 0.5 micrometres in diameter. One of the nodules (A) appears to be adjacent to a pit in the surface. The other oxidation conditions used: 850°C for 1 minute and 5 minutes, are not shown here as their oxide morphologies are no different from that seen on the sample in figure 3.4.5.3. The interference colours observed when they are examined in the light microscope are: light blue for the 850°C, 1 minute sample and, for the 850°C, 5 minutes sample, dark blue with dark red stippling.

3.5 Examination of the Oxide Scale Structure

The micrographs in figure 3.5.1 are secondary electron images and scanning transmission electron micrographs of identical areas of standard-annealed chromium oxidised in the oxidation rig. Figures 3.5.1.1 and 3.5.1.2 are from the same area of a sample oxidised at 750°C for 10 minutes. The secondary electron image, figure 3.5.1.1, shows a buckle in the oxide film near to the edge of the back-polished foil; the top of the buckle is indicated by the arrows. The surface of the oxide is seen to be rough with oxide whiskers 100 nanometres in size (A) growing from its surface. The scanning transmission electron micrograph of the same area shows very little else, due to the thickness of the sample here, except for the relative contrast between the different parts of the buckle. The sides of the buckle appear dark, which is to be expected as the oxide film is tilted towards the vertical and the electrons have a greater thickness of oxide to penetrate; the top surface of the buckle has a similar contrast level to the oxide to either side of the buckle implying that the oxide at the top of the buckle is not significantly thicker than at either side, presumably where the oxide film contacts the metal. It is not known whether there is metal under the oxide films shown in figure 3.5.1 but, given their apparent thickness, it is likely.

Figures 3.5.1.3 to 3.5.1.6 are from a sample oxidised at 950°C for 1 minute and show a star-shaped buckle and the oxide film around it. In plan, figure 3.5.1.3, the main buckle (B) and a smaller subsidiary buckle (C) can be seen. There are also what appear to be two nodules 3 micrometres in size (D) and also oxide whiskers: the small white specks. The scanning transmission electron micrograph, figure 3.5.1.4, reveals more detail. Using the contrast variations noted above, many more subsidiary convolutions can be seen, such as in the area around (E). The main, raised, part of

Figure 3.5.1

Buckled oxide films imaged using the secondary electron mode and the scanning transmission electron imaging mode of a JEOL 120CX TEMSCAN. The same area was imaged using different techniques to reveal more information than could be gained from one technique alone.

3.5.1.1 Secondary electron image of a sample oxidised for 10 minutes at 750°C

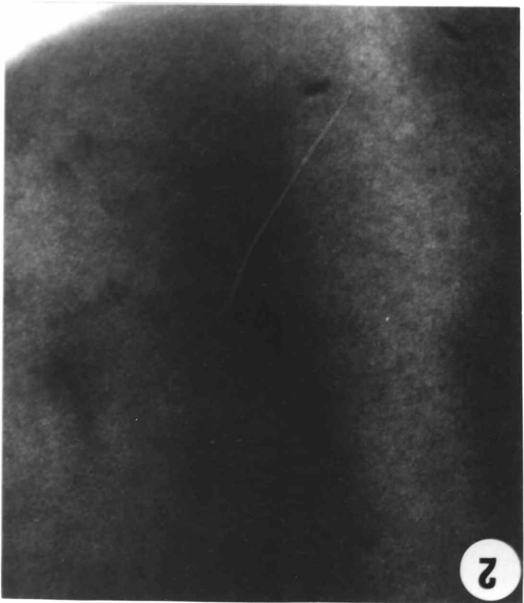
3.5.1.2 Scanning transmission electron micrograph of the area seen in figure 3.5.1.1

3.5.1.3 Secondary electron image of a sample oxidised for 1 minute at 950°C

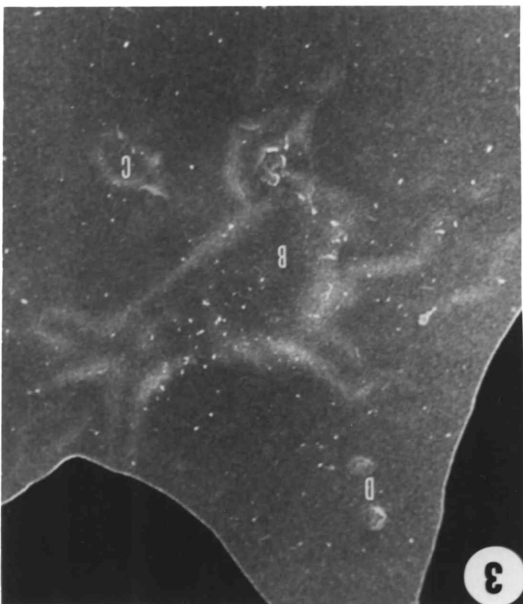
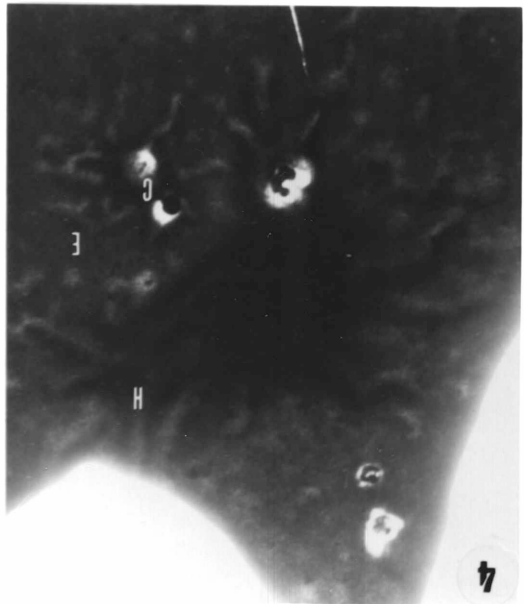
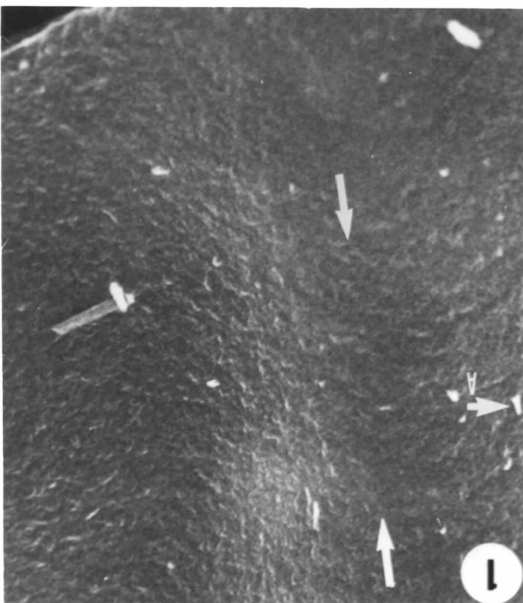
3.5.1.4 Scanning transmission electron micrograph of the area seen in figure 3.5.1.3

3.5.1.5 Secondary electron image of the area seen in figure 3.5.1.3 taken at an angle of 45° to the vertical.

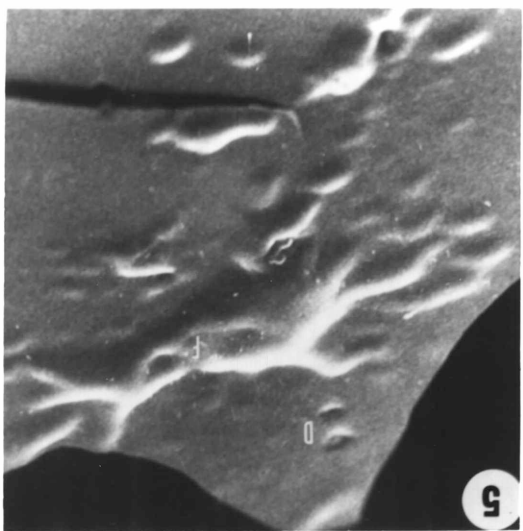
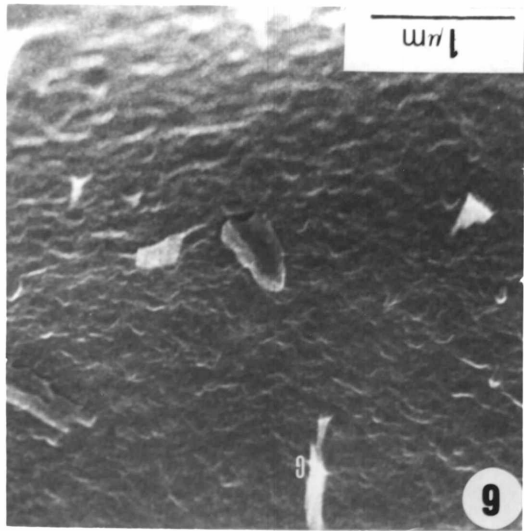
3.5.1.6 Secondary electron image of the oxide surface at the base of the large buckle in figure 3.5.1.5.



1 μ m



20 μ m



the large convolution (B) is much darker than the rest of the oxide and the tops of the convolutions appear brighter than the surrounding adherent scale. The area of buckled oxide at (H) in figure 3.5.1.4 has a different contrast distribution than elsewhere on the same figure. The regions immediately adjacent on either side of the dark lines that indicate the sides of the convolution are brighter than the areas further away from the convolution. These bright regions have a contrast level equal to that of the top of the convolution

It is not possible to tell whether the very bright parts of the micrographs, such as (C), are very thin parts of the oxide film or whether there is a metal sheet under the oxide that has been penetrated at these points. The bright areas also appear to have particles associated with them which, in the case of (C) and (D), do not appear on the secondary electron image; implying that they are underneath the oxide. This could be possible if the particles are embedded in the metal sheet which would then have been penetrated in the thinning process due to preferential attack at the particle/metal interface.

A secondary electron image of the area but taken tilted at an angle of 45° to the vertical is given in figure 3.5.1.5. The smaller areas of non-adherence revealed in figure 3.5.1.4 can be seen due to the increase in surface relief brought about by tilting the sample. Areas that are bright on top are convolutions whereas features such those at (D), that have bright rims at their bottom edges, are revealed to be depressions in the oxide surface. The features at (C) appear to be pits in the surface of the film for similar reasons. More detail on the surface of the main convolution becomes evident, such as the two dents at (F). Figure 3.5.1.6 is a higher magnification secondary electron image of the base of the main buckle. Oxide whiskers (G) can be seen and the surface of the oxide is again found to be rough. The size of the asperities is approximately 100 nanometres.

Samples of electrolytic chromium oxidised in the oxidation rig were back-thinned by electropolishing to reveal the structure of their oxide films. Figures 3.5.2 to 3.5.6 show transmission electron micrographs of the structure of these oxide films. The samples all possessed mechanically polished surfaces except for the sample of 1000°C , 3 hour hydrogen-annealed chromium oxidised for 3 minutes at 950°C which was electropolished. In some cases, the oxides have been further thinned by ion bombardment to achieve electron transparency.

The oxide film formed on a sample of standard-annealed chromium oxidised at 750°C for 10 minutes is shown in figure 3.5.2.1. The oxide grains can be clearly seen; the grains are mainly equi-axed and have a mean grain diameter of (55 ± 5) nanometres. The darker area with black specks is a region with underlying metal; the sample has been ion thinned and the specks are point defect clusters in the metal. Figure 3.5.2.2 shows oxide from a sample of standard-annealed chromium oxidised

Figure 3.5.2

A comparison of the oxides grown on chromium as a function of temperature and time. Transmission electron micrographs showing the relative grain sizes of the oxides. The scale marker applies to all micrographs in this figure; the arrows indicate large oxide grains forming a second layer of oxide.

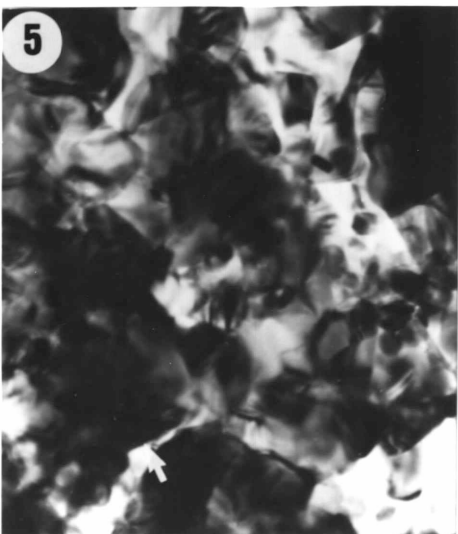
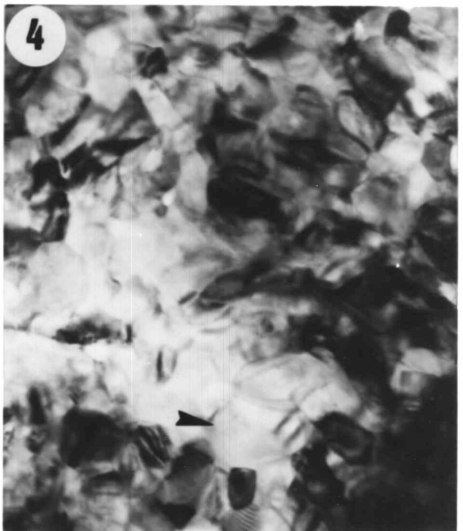
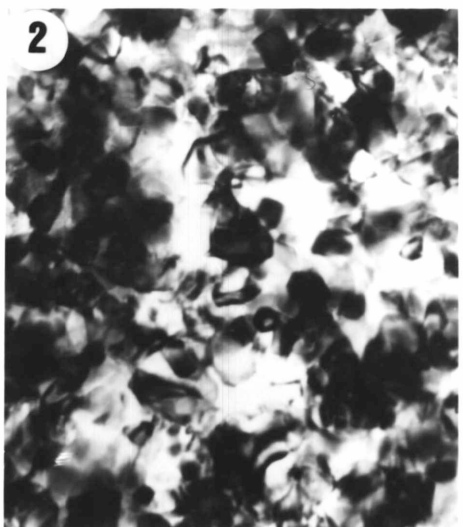
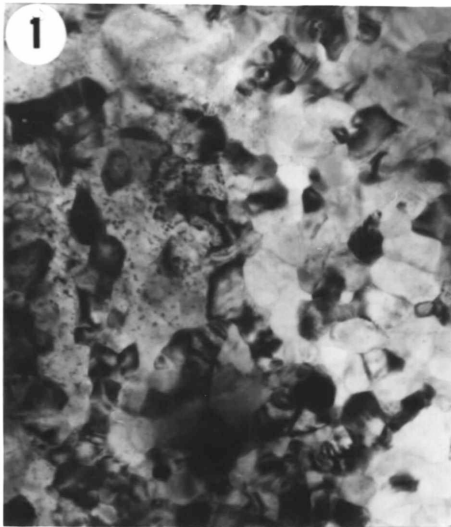
3.5.2.1 Standard-annealed chromium oxidised for 10 minutes at 750°C.

3.5.2.2 Standard-annealed chromium oxidised for 1 minute at 850°C.

3.5.2.3 Standard-annealed chromium oxidised for 15 minutes at 850°C.

3.5.2.4 Standard-annealed chromium oxidised for 3 minutes at 950°C.

3.5.2.5 Chromium annealed in hydrogen for 3 hours at 1000°C then oxidised for 5 minutes at 850°C.



200 nm

for 1 minute at 850°C. This, too, has equi-axed grains and the film has a mean grain diameter of (48 ± 5) nanometres.

After longer periods of oxidation, a second layer of larger grains grows on top of the first layer. This causes a greater variation in the grain size. While the grains in the first layer appear to be restricted to a maximum size of between 50 - 60 nanometres, the grains in the second layer seem to be unrestricted in their growth. An oxide film from a sample of standard-annealed chromium oxidised for 15 minutes at 850°C is shown in figure 3.5.2.3 with a typical large grain indicated by the arrow. The grains are equi-axed and have a mean grain diameter of (75 ± 15) nanometres.

At higher temperatures, the second layer forms more quickly. Figure 3.5.2.4 shows an oxide film formed on a standard-annealed sample after oxidation at 950°C for 3 minutes. This film has a mean grain diameter of (66 ± 12) nanometres; a large, second layer, grain is indicated by the arrow.

Oxide films formed on samples of electrolytic chromium annealed at 1000°C for 3 hours in hydrogen exhibited an earlier appearance of the second layer. Figure 3.5.2.5 shows an oxide film formed after 5 minutes at 850°C. This has a mean grain diameter of (100 ± 20) nanometres and shows a greater variation in the size of its grains. A second layer oxide grain is indicated by the arrow. This sample has been ion-thinned to ensure electron transparency and, as material has been removed from the surfaces of the oxide film, the second layer may not be obvious. It is only revealed by the variation in the sizes of the grains.

Figure 3.5.3 shows oxide films formed on the surfaces of implanted specimens. The oxide film formed on a chromium-implanted sample oxidised for 1 minute at 850°C is shown in figure 3.5.3.1. This is a continuous layer of equi-axed grains with a mean grain size of (60 ± 5) nanometres. There are one or two larger grains evident, for example that grain indicated by the arrow. This oxide layer bears a strong resemblance to that formed on the standard-annealed sample oxidised for 1 minute at 850°C, figure 3.5.2.2.

Figure 3.5.3.2 shows the oxide film on a cerium-implanted specimen oxidised for 1 minute at 850°C. The reduced grain size of the oxide film is obvious; the film has a mean grain diameter of (25 ± 5) nanometres. The oxide forms a single, continuous layer. An oxide film formed on a cerium-implanted specimen after 5 minutes at 850°C is shown in figure 3.5.3.3. This is still a single, continuous layer of equi-axed grains despite the occasional larger grain such as that indicated. The mean grain diameter of this film is (55 ± 6) nanometres. Similarly, after 10 minutes at 850°C, figure 3.5.3.4, the oxide appears to be a single layer but the large grains are more frequent. The variation in the grain size is not large; the mean grain diameter of this oxide film is (60 ± 5) nanometres. The darker band to the left of the figure is the underlying metal. It is not possible, from a visual examination of these

Figure 3.5.3

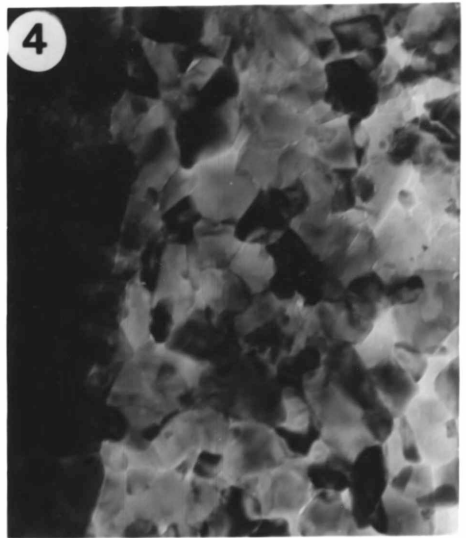
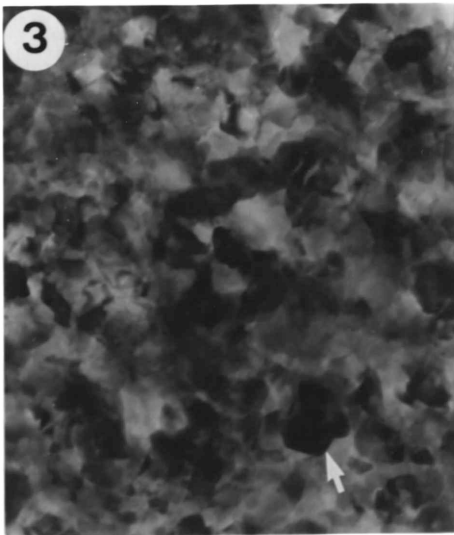
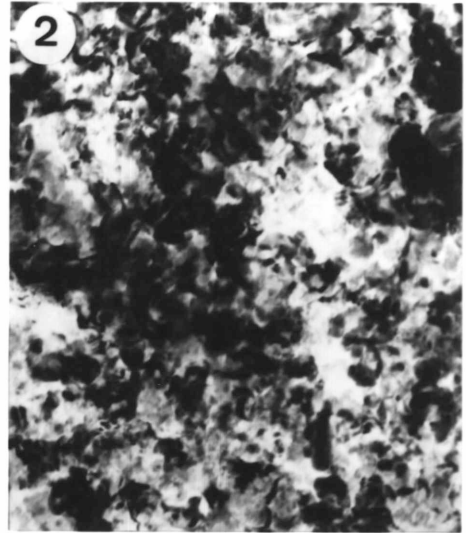
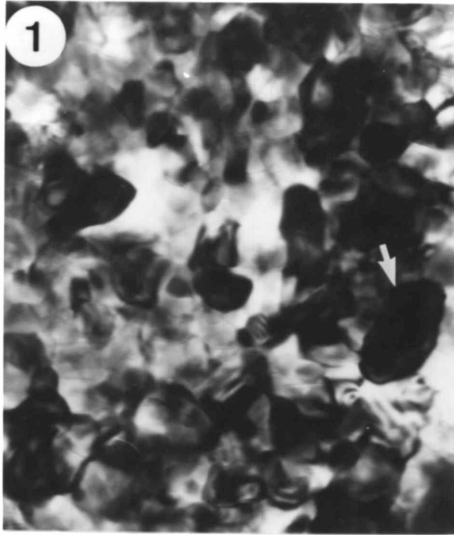
A comparison of the oxides grown on standard-annealed chromium as a function of ion-implantation, temperature and time. Transmission electron micrographs showing the relative grain sizes of the oxides. The scale marker applies to all micrographs in this figure; the arrows indicate large oxide grains forming a second layer of oxide.

3.5.3.1 Standard-annealed chromium implanted with chromium ions then oxidised for 1 minute at 850°C.

3.5.3.2 Standard-annealed chromium implanted with cerium ions then oxidised for 1 minute at 850°C.

3.5.3.3 Standard-annealed chromium implanted with cerium ions then oxidised for 5 minutes at 850°C.

3.5.3.4 Standard-annealed chromium implanted with cerium ions then oxidised for 10 minutes at 850°C. The dark band on the left side of the micrograph is the underlying metal.



200nm

oxide films, to determine whether there are any cerium-containing particles in the oxide scales.

A complete table of the mean grain diameters of the oxide scales observed is given in table 9; some of these are presented in graphical form in figure 3.5.4. The scales on the unimplanted standard-annealed coupons have mean grain diameters that slowly increase with time and temperature, as would be expected. The mean grain diameters of the higher temperature oxidation samples have larger standard deviations implying a larger variation in the sizes of the grains in the oxide scale. This is the appearance of the second layer of larger grains that are apparently unrestricted in their growth. The unimplanted coupons annealed for 3 hours at 1000°C in hydrogen have scales whose mean grain diameters also increase in size. The oxide scales on the implanted specimens, both chromium- and cerium-implanted, show an increase in mean grain diameter with time and temperature, with the chromium-implanted samples having scales whose standard deviations increase whereas the standard deviations in the mean grain diameters of the scales on the cerium-implanted coupons do not increase. This implies no substantial appearance of a second layer of large grains on the cerium-implanted samples.

The graphs in figure 3.5.4 are isothermal plots of the mean grain diameter of the oxide scales grown on the different specimens against time; the error bars are the standard deviations in the mean. Figure 3.5.4.1 is the graph for 850°C and shows most of the grain diameters lying approximately around the line of the unimplanted standard-annealed samples. The only exceptions are the cerium-implanted specimen oxidised for 1 minute at 850°C whose mean grain diameter is lower than expected from the graph and the specimen of 1000°C, 3 hour, hydrogen-annealed chromium oxidised for 5 minutes at 850°C which is much higher. The similar graph for specimens oxidised at 950°C, figure 3.5.4.2, shows the oxide on the unimplanted standard-annealed sample having a smaller mean grain diameter than the chromium-implanted samples or the 1000°C, 3 hour, hydrogen-annealed chromium sample. The surface of the 1000°C, 3 hour, hydrogen-annealed chromium was electropolished, in contrast to the other samples which possessed mechanically polished surfaces.

Figure 3.5.5 shows selected area diffraction patterns from oxide films grown on unimplanted standard-annealed chromium taken from areas such as those in figure 3.5.5.1. Figure 3.5.5.1 shows a diffraction pattern from an area of oxide and metal on a sample oxidised for 10 minutes at 750°C. The bright spots form a chromium $\langle 111 \rangle$ zone axis pattern while the interrupted ring of spots (A) inside the six chromium spots corresponds to the $\{11\bar{2}0\}$ Cr_2O_3 lattice spacing. A second, fainter ring (B) corresponds to the $\{30\bar{3}0\}$ Cr_2O_3 lattice spacing. Together, these two oxide reflections make up the Cr_2O_3 $\langle 0001 \rangle$ zone axis that was ubiquitous on samples

Table 9

A table of the mean grain diameters of oxides formed on chromium. The mean grain diameters were measured from transmission electron micrographs of back-thinned samples oxidised under the conditions given in the table.

Sample	Temperature of oxidation °C	Time of oxidation minutes	Mean grain diameter nm.	Standard deviation nm.
Unimplanted, standard- annealed chromium	750	10	55	5
	850	1	48	5
	850	15	75	15
	950	3	66	12
1000°C, 3 hours, hydrogen- annealed chromium	850	3	60	5
	850	5	100	20
	950	3	100	5
Chromium- implanted chromium	850	1	60	5
	950	1	85	7
	950	5	105	10
Cerium- implanted chromium	850	1	25	5
	850	5	55	6
	850	10	60	5

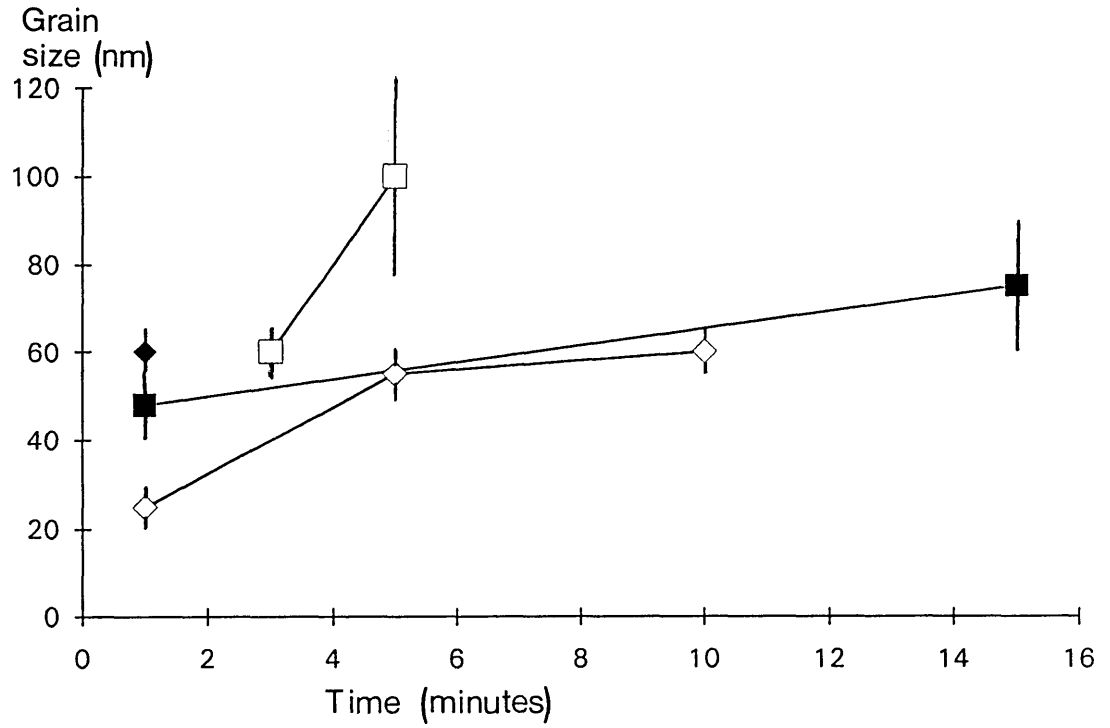
Figure 3.5.4

Graphs of mean grain diameter plotted against time of oxidation at 850°C and 950°C for samples of chromium oxidised in the oxidation rig and back-thinned to reveal their oxide structure. Mean grain diameters were taken from transmission electron micrographs of the oxide scales.

3.5.4.1 Graph of mean grain diameter against time for samples oxidised at 850°C

3.5.4.2 Graph of mean grain diameter against time for samples oxidised at 950°C

1



- Standard-annealed
- 1000°C, 3 hour, hydrogen-annealed
- ◆ Chromium-implanted
- ◇ Cerium-implanted

2

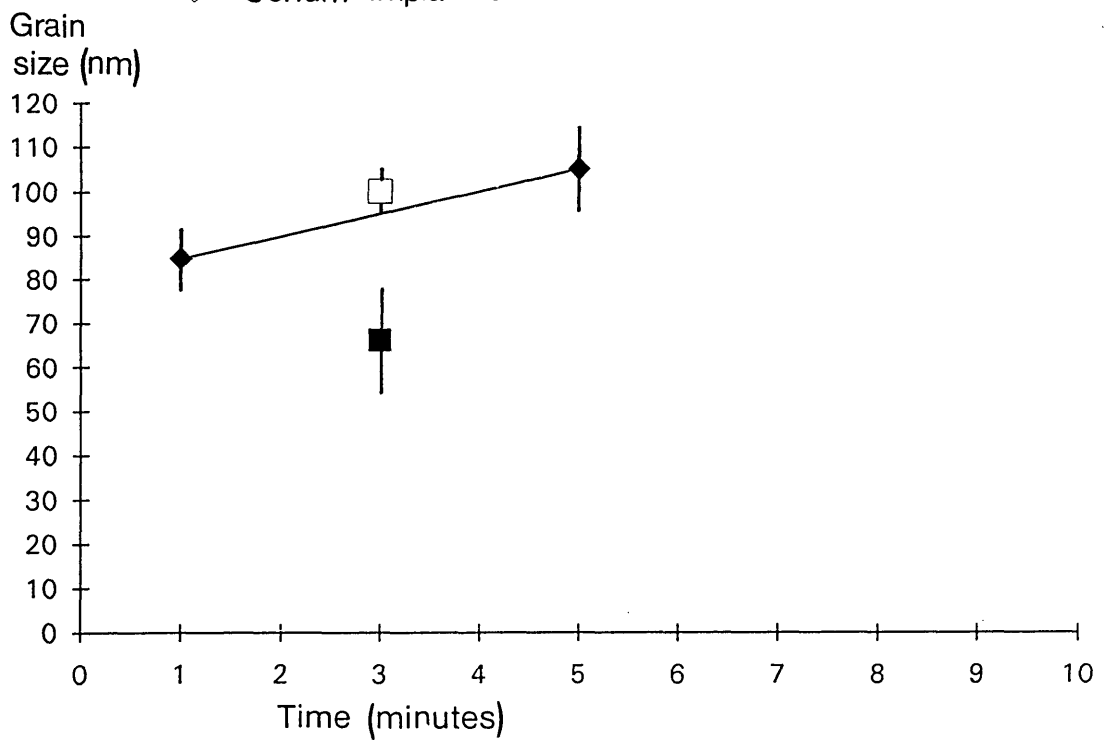


Figure 3.5.5

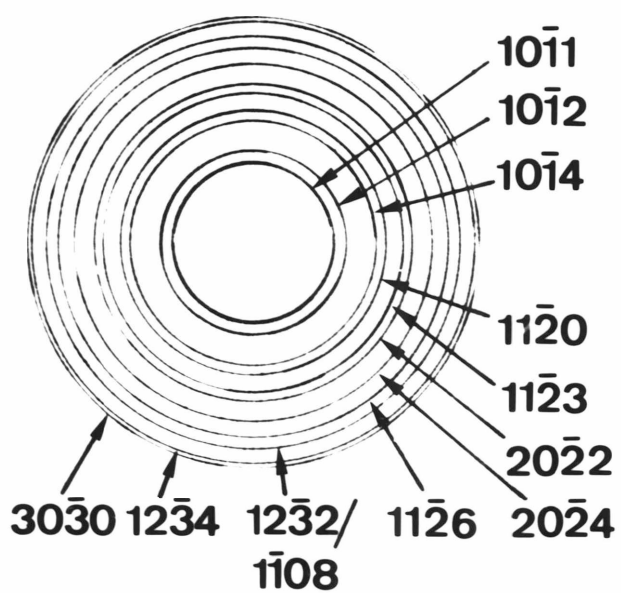
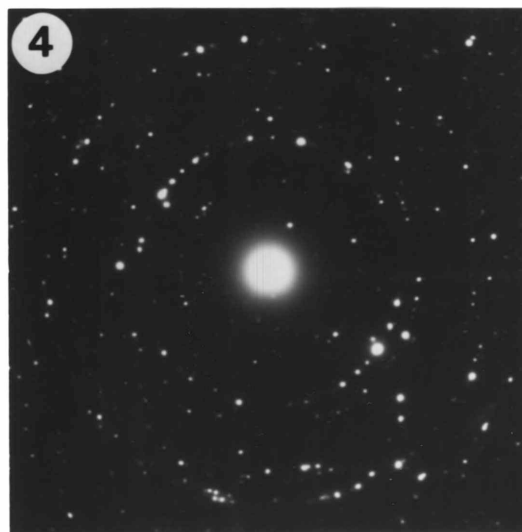
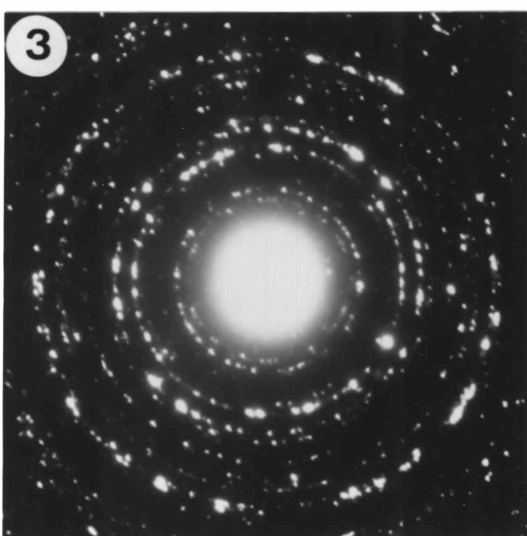
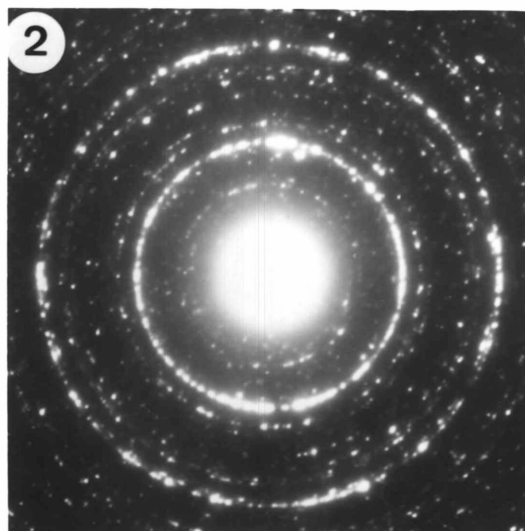
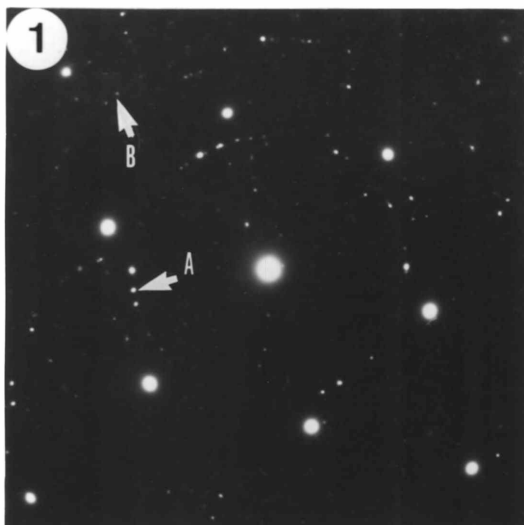
Selected area diffraction patterns from the oxides in figure 3.5.2 comparing the orientations of the initial oxide layers on each sample and showing the loss of the preference for the oxide to grow with $\langle 0001 \rangle$ parallel to the direction of growth. The scale given applies to all diffraction patterns in this figure.

3.5.5.1 Standard-annealed chromium oxidised for 10 minutes at 750°C. The bright spots form a chromium $\langle 111 \rangle$ zone axis pattern and the rings are the Cr_2O_3 $\{11\bar{2}0\}$ (A) and $\{30\bar{3}0\}$ (B) reflections. The diffraction aperture selects an area in the sample 0.6 micrometres in diameter.

3.5.5.2 Standard-annealed chromium oxidised for 1 minute at 850°C. The oxide rings are indexed in the diagram below. The diffraction aperture selects an area 2.5 micrometres in diameter.

3.5.5.3 Standard-annealed chromium oxidised for 15 minutes at 850°C. The rings are indexed in the diagram below. The diffraction aperture selects an area 2.5 micrometres in diameter.

3.5.5.4 Chromium annealed for 3 hours at 1000°C in hydrogen then oxidised for 3 minutes at 850°C. The rings are indexed in the diagram below. The diffraction aperture selects an area 2.5 micrometres in diameter.



$$rd = 4.39 \text{ cm}\text{\AA}$$

oxidised in the gas reaction cell. The other spots in the diffraction pattern are double diffraction spots.

The diffraction pattern from an oxide film formed at 850°C after 1 minute is shown in figure 3.5.5.2. This has the two main oxide rings corresponding to the $\{11\bar{2}0\}$ and the $\{30\bar{3}0\}$ reflections but also, at a lower intensity, other reflections indexed in the diagram below. This implies that: while the $\langle 0001 \rangle$ orientation is still strong, it is not the only orientation present. The diffraction pattern in figure 3.5.5.3, from oxide formed after 15 minutes at 850°C, shows the end of the process. The other orientations have grown so strong that the reflections are now similar in intensity and the initial texture is lost. This is also seen in figure 3.5.5.4 which shows a selected area diffraction pattern from the oxide scale grown on a sample of chromium annealed for 3 hours at 1000°C in hydrogen then oxidised for 3 minutes at 850°C. The spots in the diffraction pattern are of similar intensity indicating a loss of the initial texture.

Selected area diffraction patterns from oxide films formed on implanted specimens are shown in figure 3.5.6. Figure 3.5.6.1 is taken from an oxide film formed at 850°C after 1 minute oxidation. The only well developed ring of spots corresponds to the $\{11\bar{2}0\}$ Cr_2O_3 reflection implying that the $\langle 0001 \rangle$ orientation is more frequent. The other spots are equal in intensity to those in the ring implying that the preference for $\langle 0001 \rangle$ has been almost lost. For films oxidised for 5 minutes at 950°C, figure 3.5.6.2, each of the rings indexed in the diagram below is present at a similar intensity implying that the initial preference for $\langle 0001 \rangle$ has been completely lost.

The cerium-implanted samples show a similar trend. The oxide film formed on a cerium-implanted sample after 1 minute at 850°C is shown in figure 3.5.6.3. This has only the two initial oxide rings, showing a strong preference for $\langle 0001 \rangle$ normal to the surface. The oxide film formed after 5 minutes at 850°C, figure 3.5.6.4, shows no preference, the rings being of similar intensity. This figure, unlike figure 3.5.6.3, has a spot corresponding to the CeO_2 $\{111\}$ reflection, indicated by the arrow. Figure 3.5.6.5 is from an oxide film grown on a cerium-implanted sample that was oxidised for 10 minutes at 850°C. This again shows a lack of preference for a particular orientation. There is a pair of spots, one of which is indicated, that corresponds to the CeCrO_3 $\{200\}$ reflection; there are no CeO_2 spots.

The order in which the major Cr_2O_3 rings appear on the diffraction patterns seems not to vary from sample to sample. The first two rings to appear are the $\{11\bar{2}0\}$ and the $\{30\bar{3}0\}$. The $\{10\bar{1}2\}$ and $\{11\bar{2}3\}$ are the next to appear followed by the $\{10\bar{1}1\}$, $\{10\bar{1}4\}$, $\{20\bar{2}2\}$, $\{20\bar{2}4\}$, $\{11\bar{2}6\}$, $\{1\bar{1}08\}/\{12\bar{3}2\}$ and the $\{12\bar{3}4\}$ reflections. These then strengthen in intensity until they are similar to the primary rings. The $\{0006\}$ reflection does not appear on any of the diffraction patterns.

Figure 3.5.6

Selected area diffraction patterns from the oxides in figure 3.5.3 comparing the orientations of the initial oxide layers on each of the samples and showing the loss of the preference for the oxide to grow with $\langle 0001 \rangle$ parallel to the direction of growth. The scale given applies to all diffraction patterns in this figure.

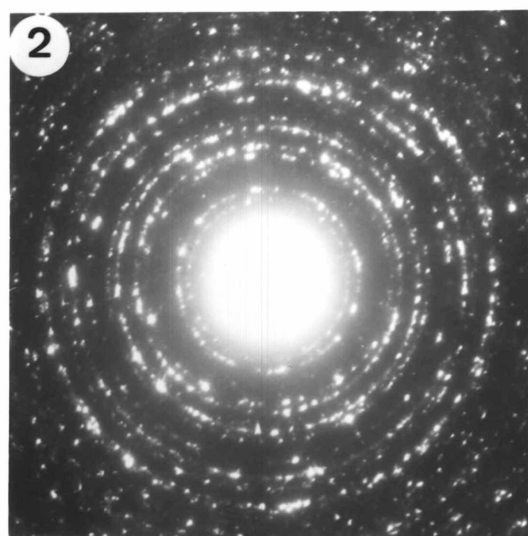
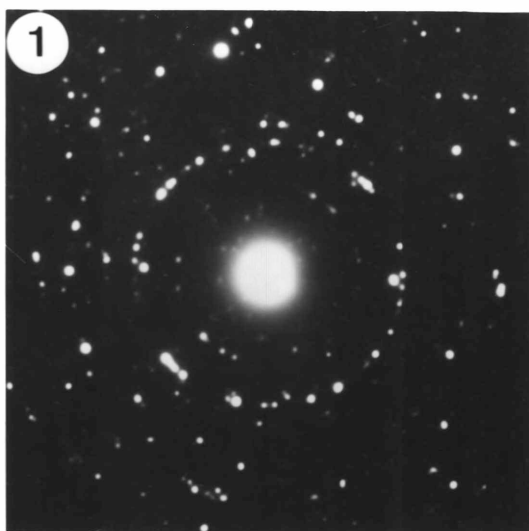
3.5.6.1 Standard-annealed chromium implanted with chromium ions then oxidised for 1 minute at 850°C. The spots belong to the Cr_2O_3 rings indexed in the diagram below. The diffraction aperture selects an area 0.6 micrometres in diameter.

3.5.6.2 Standard-annealed chromium implanted with chromium ions then oxidised for 5 minutes at 950°C. The spots belong to the Cr_2O_3 rings indexed in the diagram below. The diffraction aperture selects an area 2.5 micrometres in diameter.

3.5.6.3 Standard annealed chromium implanted with cerium ions then oxidised for 1 minute at 850°C. The rings belong to the Cr_2O_3 $\{11\bar{2}0\}$ and $\{30\bar{3}0\}$ reflections. The diffraction aperture selects an area 0.83 micrometres in diameter.

3.5.6.4 Standard-annealed chromium implanted with cerium ions then oxidised for 5 minutes at 850°C. The spots belong to the Cr_2O_3 rings indexed in the diagram below. The diffraction aperture selects an area 0.6 micrometres in diameter. The arrow indicates a $\{111\}$ CeO_2 reflection.

3.5.6.5 Standard-annealed chromium implanted with cerium ions then oxidised for 10 minutes at 850°C. The spots belong to the Cr_2O_3 rings indexed in the diagram below. The diffraction aperture selects an area 0.6 micrometres in diameter. The arrow indicates a CeCrO_3 $\{200\}$ reflection.



$rd = 4.35 \text{ cm}\text{\AA}$

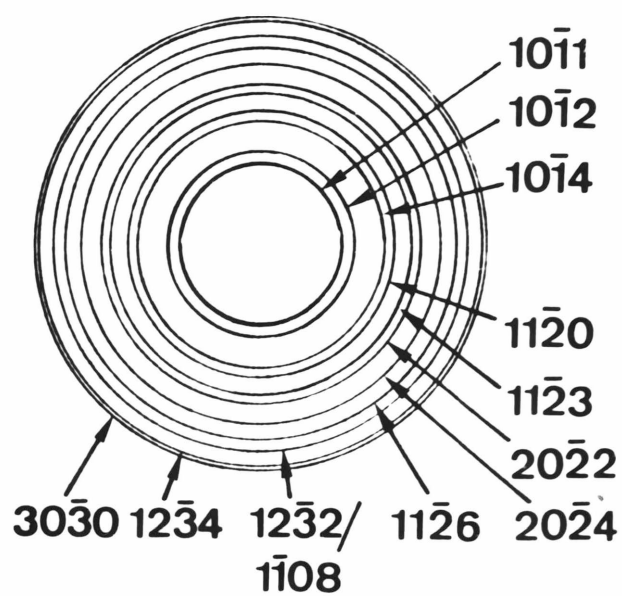
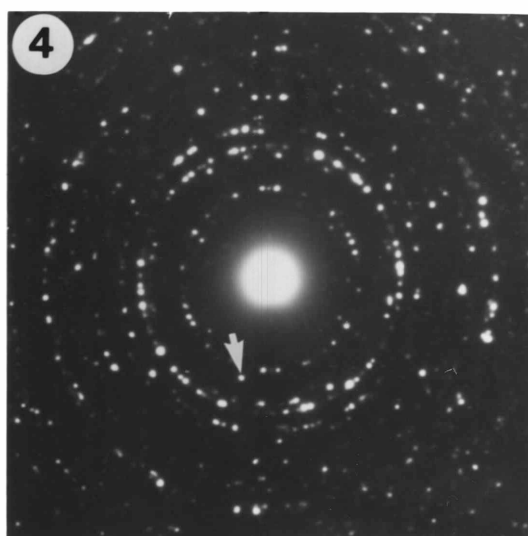
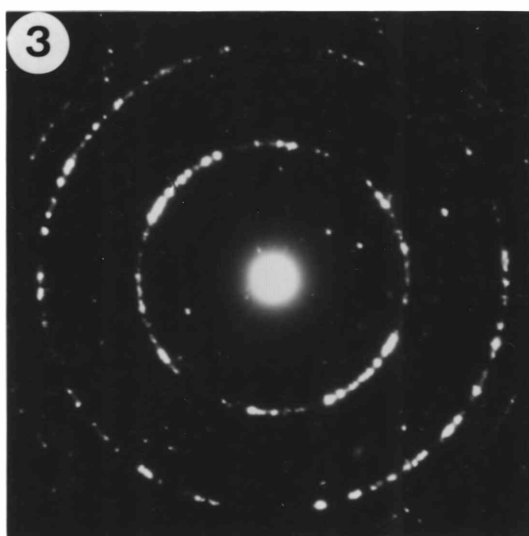


Figure 3.5.7 shows areas of cerium-implanted specimens used to acquire chemical analyses of the metal and oxide. The cerium-implanted coupons were covered with a brown film which was determined, using SIMS, to be an oxide film containing cerium, figure 3.2.4. This film could influence the oxidation behaviour of the metal significantly. When the coupons were back-thinned to the film-covered surface, figure 3.2.2.6, areas of the sample were seen to be covered by a thin membrane of amorphous material while other areas on the sample with a similar microstructure did not have this membrane. Figure 3.5.7.1 is from a different area of the sample and shows this membrane of material covering the metal. The selected area diffraction pattern, figure 3.5.7.2, shows a chromium $\langle 111 \rangle$ zone axis pattern and a very faint ring which is indicated by an arrow.

After oxidation in the gas reaction cell, the back-thinned cerium-implanted samples were found to be covered by a film of material. Two such samples possessing films of different appearance, together with their selected area diffraction patterns, are shown in figures 3.5.7.3 to 3.5.7.7. Figure 3.5.7.3 shows the oxidised metal-colander structure with the film, after oxidation in the gas reaction cell for 10 seconds at temperatures up to 630°C in an oxygen pressure of 250Pa; this was also illustrated in figure 3.3.6.1. The selected area diffraction pattern, figure 3.5.7.4, is from the film and shows Cr_2O_3 reflections on an amorphous background. The sample oxidised for 10 seconds at temperatures up to 640°C in an oxygen pressure of 250Pa is shown in figure 3.5.7.5; the oxidised metal colander structure with the covering film can be seen. The selected area diffraction pattern from the metal, figure 3.5.7.6, shows a spot pattern corresponding to the chromium $\langle 111 \rangle$ zone axis pattern and two bright rings corresponding to the $\{11\bar{2}0\}$ (inner ring) and the $\{30\bar{3}0\}$ (outer ring) Cr_2O_3 reflections. The selected area diffraction pattern from the film, figure 3.5.7.7, shows Cr_2O_3 reflections on an amorphous background together with a ring corresponding to the CeO_2 $\{111\}$ reflection, indicated. The two large arrows on this figure indicate the line along which the microdensitometer trace in figure 3.5.8.1 was taken.

A sample of cerium-implanted chromium oxidised in the oxidation rig for 5 minutes at 850°C and then back-polished to reveal the oxide structure is shown in figure 3.5.8.8. The area (A) is oxide with an underlying metal sheet, area (B) is only oxide. A selected area diffraction pattern from area (A) is given in figure 3.5.8.9. This has four spots corresponding to the chromium $\{110\}$ reflection and a pair of spots corresponding to the CeCrO_3 $\{200\}$ reflection, one of which is indicated by the small arrow. The other spots on the diffraction pattern are Cr_2O_3 reflections. The two large arrows indicate the line along which the microdensitometer trace in figure 3.5.8.2, used to identify the CeCrO_3 reflection, was taken.

Figure 3.5.7

Bright field transmission electron micrographs of cerium-implanted, standard-annealed chromium specimens, oxidised under different conditions, showing the areas used for quantitative energy dispersive X-ray spectroscopic analysis with their associated selected area diffraction patterns.

3.5.7.1 Unoxidised specimen of cerium-implanted chromium showing the membrane seen on some parts of the specimen.

3.5.7.2 Selected area diffraction pattern from the area shown in figure 3.5.7.1. The major spots are chromium $\{110\}$ reflections.

3.5.7.3 Specimen oxidised in the gas reaction cell for 10 seconds at temperatures up to 630°C .

3.5.7.4 Selected area diffraction pattern from the area shown in figure 3.5.7.3 containing oxide reflections on an amorphous background.

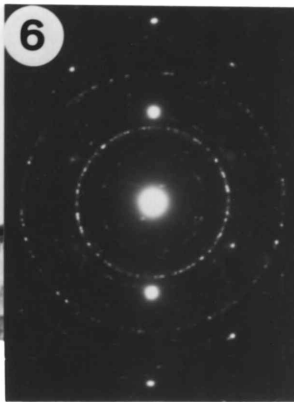
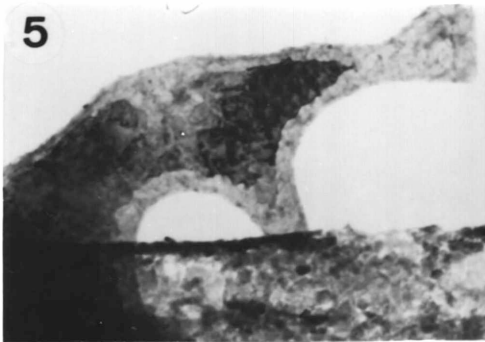
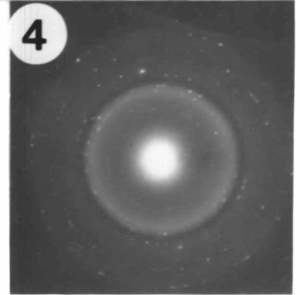
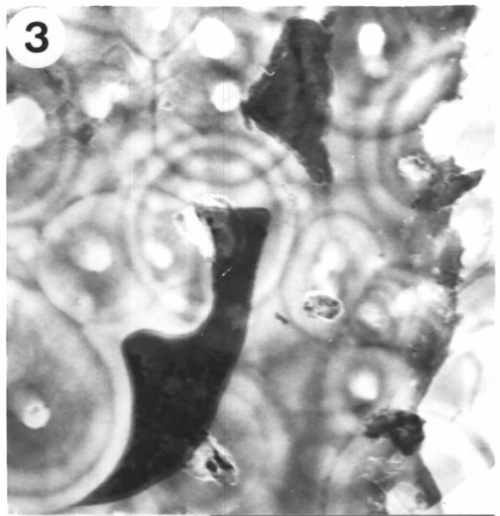
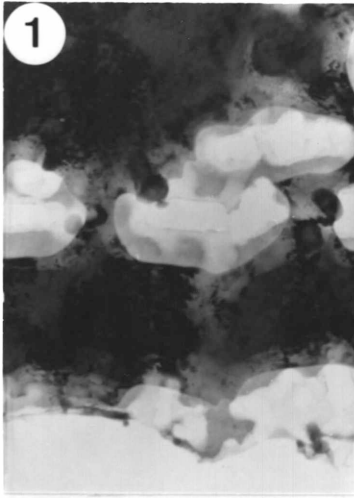
3.5.7.5 Specimen oxidised in the gas reaction cell for 10 seconds at temperatures up to 640°C .

3.5.7.6 Selected area diffraction pattern from the area indicated in figure 3.5.7.5. The two major rings are due to the $\{11\bar{2}0\}$ and the $\{30\bar{3}0\}$ oxide reflections; the spots are from the chromium $\langle 111 \rangle$ zone axis pattern.

3.5.7.7 Selected area diffraction pattern from the area indicated in figure 3.5.7.5. The small arrow indicates the ring of spots with a spacing corresponding to that for $\{111\}$ CeO_2 ; the two larger arrows giving the line along which the microdensitometer trace in figure 3.5.8.1 was taken. The other spots are Cr_2O_3 reflections on an amorphous background.

3.5.7.8 Specimen oxidised for 5 minutes at 850°C in the oxidation rig. Area (A) is oxide with an underlying metal sheet and (B) is oxide only.

3.5.7.9 Selected area diffraction pattern from the area in figure 3.5.7.8. The two larger arrows show the line along which the microdensitometer trace given in figure 3.5.8.2 was taken with the small arrow indicating the spot with a spacing corresponding to the $\{200\}$ CeCrO_3 reflection.



rd = **2.45** cmÅ

500 nm

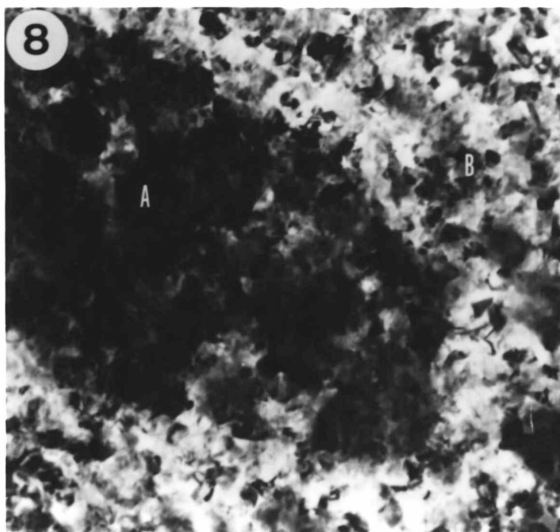


Figure 3.5.8 shows microdensitometer traces taken from along the lines indicated in the diffraction patterns, figures 3.5.7.7 and 3.5.7.9. The first trace shows peaks corresponding to Cr_2O_3 reflections, allowing a scale to be determined, together with a strong CeO_2 peak, also indicated in figure 3.5.7.7. As the traces are recorded along a diameter of the rings on the diffraction pattern, the traces should be symmetrical about the central 000 peak. Precise measurements of the distance a reflection is from the central spot can thus be gained by halving the distance between the two symmetrical peaks corresponding to the particular reflection. Scale and resolution allow spacings to be determined to 0.001 nanometres. For the CeO_2 peak this is not necessary as there is no other peak close but with figure 3.5.8.2, the CeCrO_3 {200} peak at 0.274 nanometres needs to be differentiated from the CeO_2 peak at 0.271 nanometres and the Cr_2O_3 peak at 0.267 nanometres. This is not necessarily possible from a print of the diffraction pattern as there will be some error in determining the centre of the spots. The spot at 0.274 nanometres is indicated by the small arrow in figure 3.5.7.9. The scale in figure 3.5.8.2 can be gained from the four chromium spots whose spacings are known to a precision of more than 0.001 nanometres. The subsidiary peaks near the central peak in figure 3.5.8.2 are from double diffraction spots.

Energy dispersive X-ray spectra taken from areas of the cerium-implanted samples are shown in figure 3.5.9. The peaks that should appear in the spectra are the chromium $\text{K}\alpha$ and $\text{K}\beta$ peaks at 5400eV and 5900eV and the cerium $\text{L}\alpha$ at 4800eV. Figures 3.5.9.1 and 3.5.9.2 were taken from different areas of the same specimen of back-thinned cerium-implanted chromium; figure 3.5.9.1 was taken from the area of membrane-covered metal shown in figure 3.5.9.1 whilst figure 3.5.9.2 was taken from another area that had the same dislocation structure but no membrane. The most important difference between the two spectra is the appearance of a cerium peak in the spectrum from the membrane-covered area and the absence of a cerium peak in the spectrum from the area with no membrane. Figure 3.5.9.1 shows a small calcium peak, figure 3.5.9.2, a small chlorine peak and they both have small copper peaks.

A spectrum taken from the area of metal, oxide and film shown in figure 3.5.7.3 is given in figure 3.5.9.3 and shows only chromium peaks and a cerium peak. This is contrasted with the spectrum in figure 3.5.9.4, taken from part of the film-covered area in figure 3.5.7.5, which also has a small calcium peak as well as the chromium and cerium peaks. The area from which the latter spectrum was taken contained no metal. The area of metal and oxide (A) in figure 3.5.7.8 yields the spectrum given in figure 3.5.9.5 which also has a small calcium peak together with the chromium and cerium peaks and two copper peaks.

Figure 3.5.8

Microdensitometer traces taken from along the lines indicated in figures 3.5.7.7 and 3.5.7.9 respectively showing peaks corresponding to the spots on the diffraction patterns and giving the indexed planes relating to the spacings of the spots. The peaks are symmetrical about the central 000 peak.

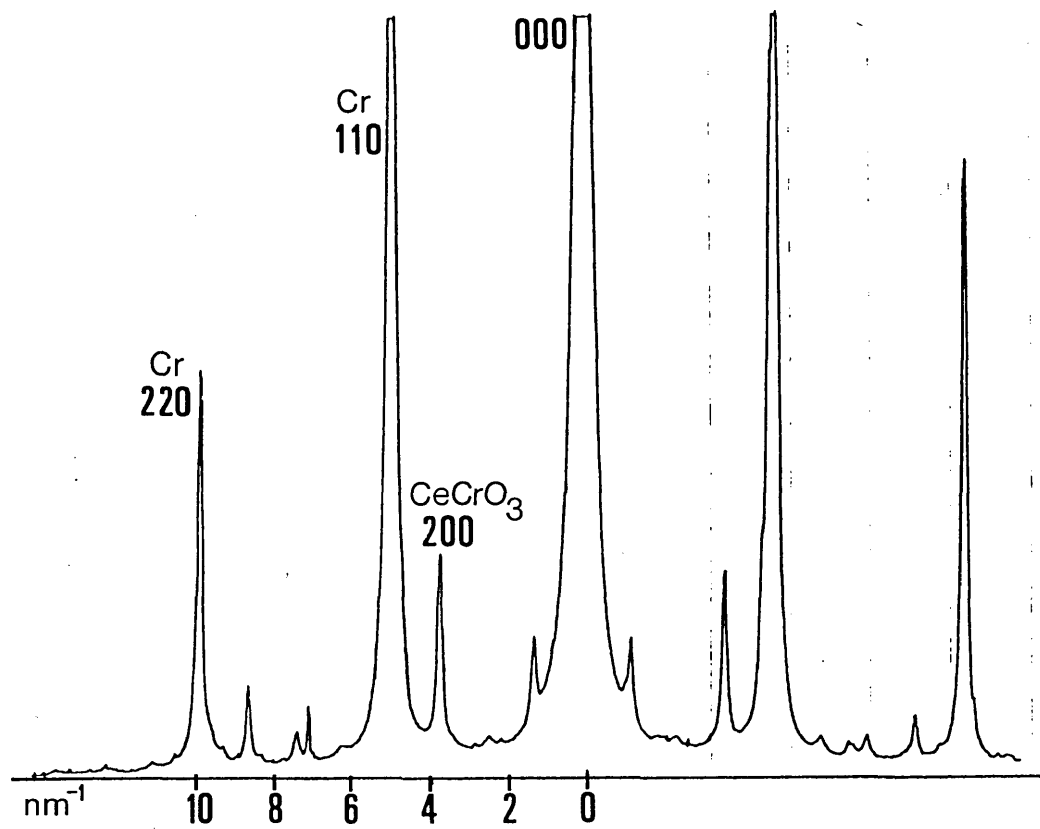
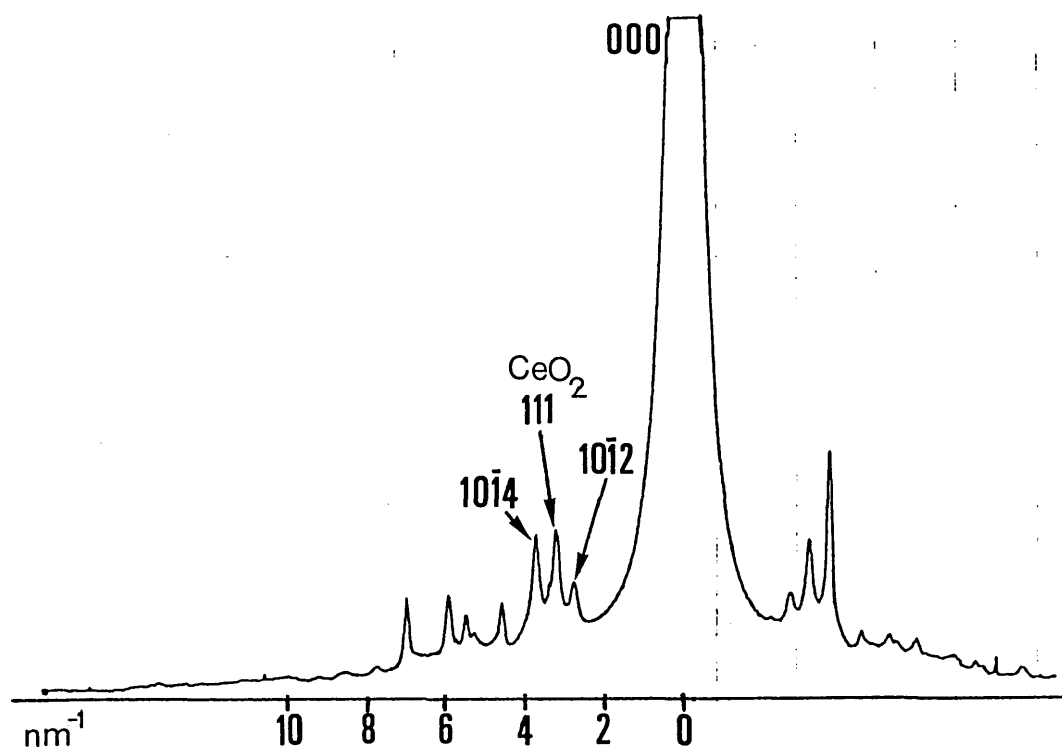


Figure 3.5.9

Spectra from the energy dispersive X-ray analyser for analyses taken from cerium-implanted chromium oxidised under different conditions showing the elements found in the oxides at a concentration of greater than 0.3% by atomic fraction.

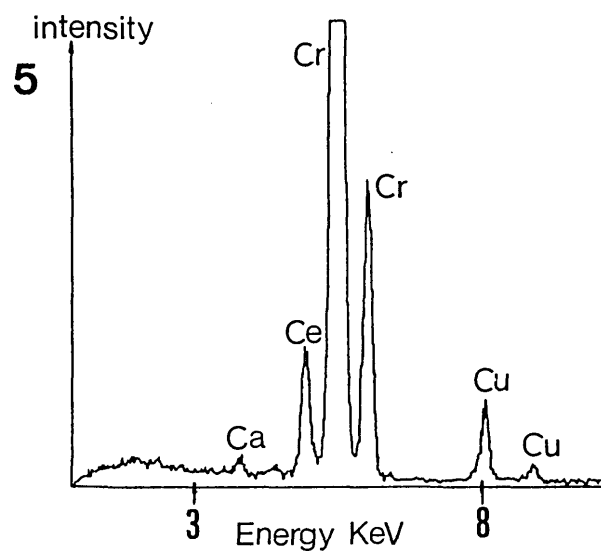
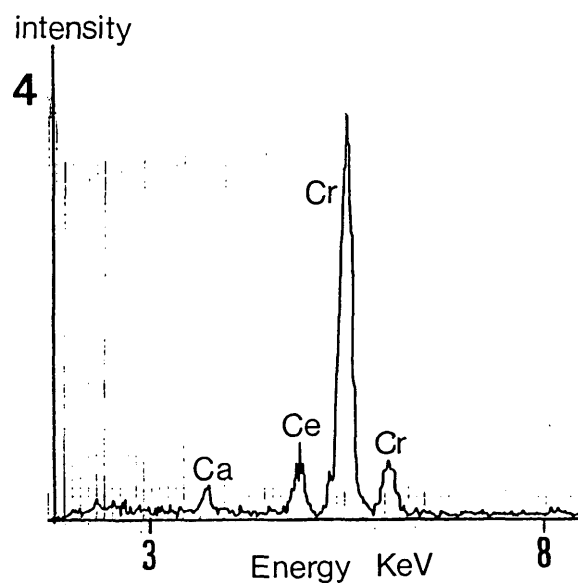
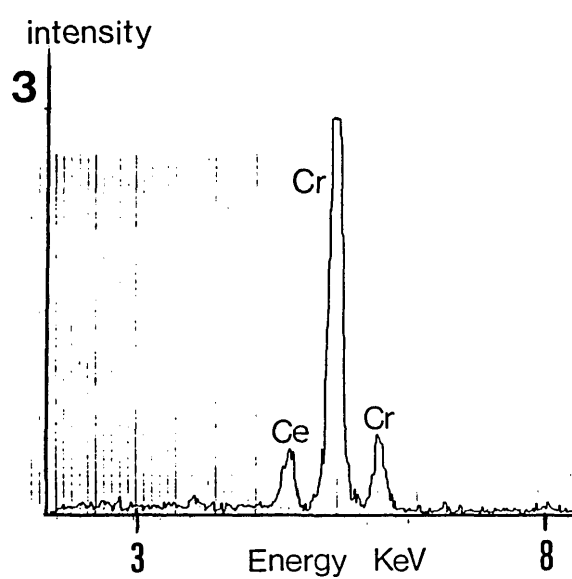
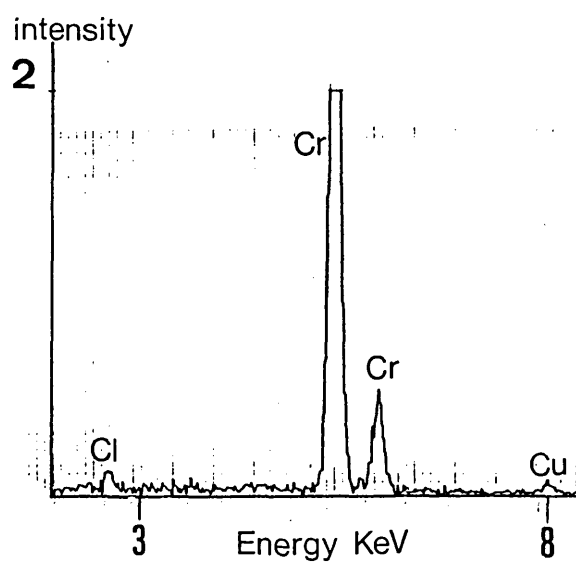
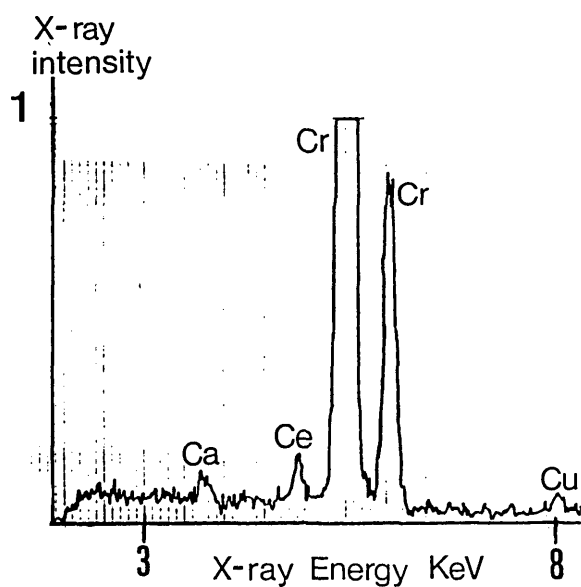
3.5.9.1 Spectrum taken from the whole area in figure 3.5.7.1 including both membrane and metal. Acquisition time 400 seconds.

3.5.9.2 Spectrum taken from the same sample as that in figure 3.5.7.1 but from an area of that sample that had the same structure but no membrane. Acquisition time 400 seconds.

3.5.9.3 Spectrum taken from the area of metal and oxide shown in figure 3.5.7.3 with an acquisition time of 400 seconds.

3.5.9.4 Spectrum gained from the area of oxide in figure 3.5.7.5 from which the diffraction pattern in figure 3.5.7.7 is taken. Acquisition time 500 seconds.

3.5.9.5 Spectrum taken from the area of metal and oxide shown in figure 3.5.7.8 with an acquisition time of 300 seconds.



Also of note are the relative heights of the cerium peaks and the chromium K β peaks on the spectra in the figure. In figures 3.5.9.3 and 3.5.9.4 the size of the cerium peak is roughly equivalent to the chromium K β peak whereas in 3.5.9.5 the cerium peak is smaller and the cerium peak in figure 3.5.9.1 is much smaller than the chromium K β peaks in the relevant spectra.

The results of quantitative point analyses using the energy dispersive X-ray spectroscopy system on the JEOL 2000FX transmission electron microscope are given in table 10. Elements with atomic numbers lower than 11 (sodium), including oxygen, were not included in the analysis. The oxide was known to be Cr₂O₃ from electron diffraction and the oxygen content from any other oxides could not, due to absorption of the oxygen X-rays by the Cr₂O₃, have been determined accurately. Furthermore, due to the presence of chromium throughout the scale, it would not have been possible to distinguish between any CeCrO₃ particles and CeO₂ particles found as neither could have been isolated from the oxide grains. The analyses were carried out on a number of samples. The arithmetic mean of the compositions was taken in order to reduce statistical variations in the compositions and the variety of different samples ensured good coverage of the materials analysed. Analyses in which elements other than chromium and cerium appeared were excluded from this averaging process and are quoted in the table.

The oxides formed on unimplanted chromium samples comprised only chromium oxide, except for two samples. One of these oxide scales also contained small amounts of silicon and chlorine at a composition level of around 0.5 - 1% and the other contained approximately 0.5% calcium. Samples of chromium-implanted material showed similar results, with the oxide films comprising only chromium oxide. The three analyses of oxide on the metal substrate all contained small amounts of silicon and calcium which, when averaged, gave abundances of approximately 0.5% each. The samples showing elements other than chromium were all oxidised in the gas reaction cell.

Analyses at points on the unoxidised cerium-implanted specimens in areas with the membrane, such as that shown in figure 3.4.6.1, where both metal and membrane were analysed simultaneously, showed only chromium and cerium with the cerium composition being approximately 2.5%. An analysis of the membrane itself gave 2% cerium and 8% silicon. This abnormally high silicon content was also seen in two analyses of the oxide scale on oxidised cerium-implanted samples. The silicon abundances here were 5% and 4% and were coupled with calcium abundances of 2.5% for both analyses and cerium abundances of 14% and 11% respectively. The other thirteen analyses carried out on the oxidised cerium-implanted specimens showed neither silicon or calcium; the analyses of the oxide only gave cerium compositions of 4% and analyses of the oxide on metal gave cerium compositions of

Table 10

A table of the quantitative energy dispersive X-ray point analyses carried out on oxidised chromium and chromium implanted with chromium or cerium. The analyses were acquired with a count time of 300 seconds. Where a mean composition has been quoted, the analyses were taken from different samples and from different areas of the same sample wherever possible. The compositions are given in atomic %. The errors are from counting statistics.

	Elemental Composition in atomic %				
	Cr	Ce	Si	Ca	Cl
Oxide on unimplanted chromium	100 $\pm$ 1	mean of 9 separate analyses			
	98 $\pm$ 1		1.0 $\pm$ 0.3		0.6 $\pm$ 0.2
Metal and oxide	99 $\pm$ 1				
	99 $\pm$ 1			0.4 $\pm$ 0.2	
Oxide on chromium-implanted chromium	100 $\pm$ 1	mean of 5 separate analyses			
Metal and oxide	99 $\pm$ 1		0.4 $\pm$ 0.2	0.4 $\pm$ 0.2	
	mean of 3 separate analyses				
Cerium-implanted chromium. Membrane	88 $\pm$ 3	2 $\pm$ 1	8.5 $\pm$ 1.7		
Metal and membrane	97 $\pm$ 1	2.5 $\pm$ 0.3			
	mean of 4 separate analyses				
Oxide	95 $\pm$ 1	3.7 $\pm$ 0.3	mean of 7 separate analyses		
	79 $\pm$ 1	14 $\pm$ 0.5	5 $\pm$ 0.5	2.4 $\pm$ 0.3	
	80 $\pm$ 1	11 $\pm$ 0.5	4 $\pm$ 0.5	2.3 $\pm$ 0.3	
Metal and oxide	93 $\pm$ 1	6.1 $\pm$ 0.2	mean of 6 separate analyses		

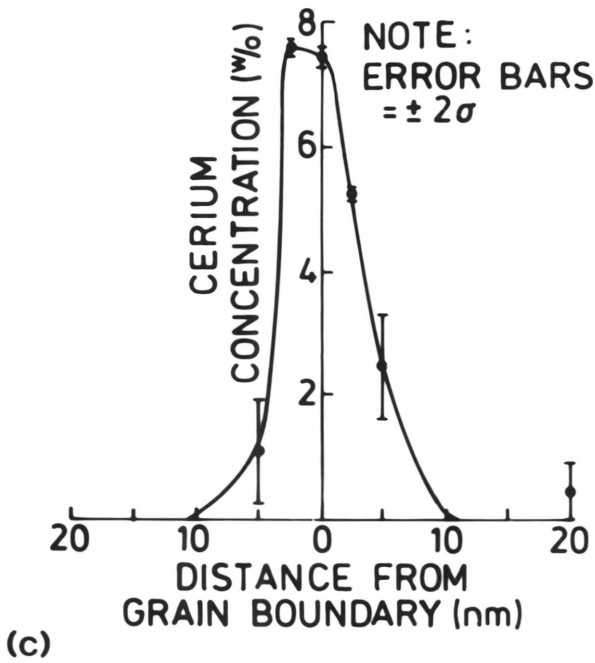
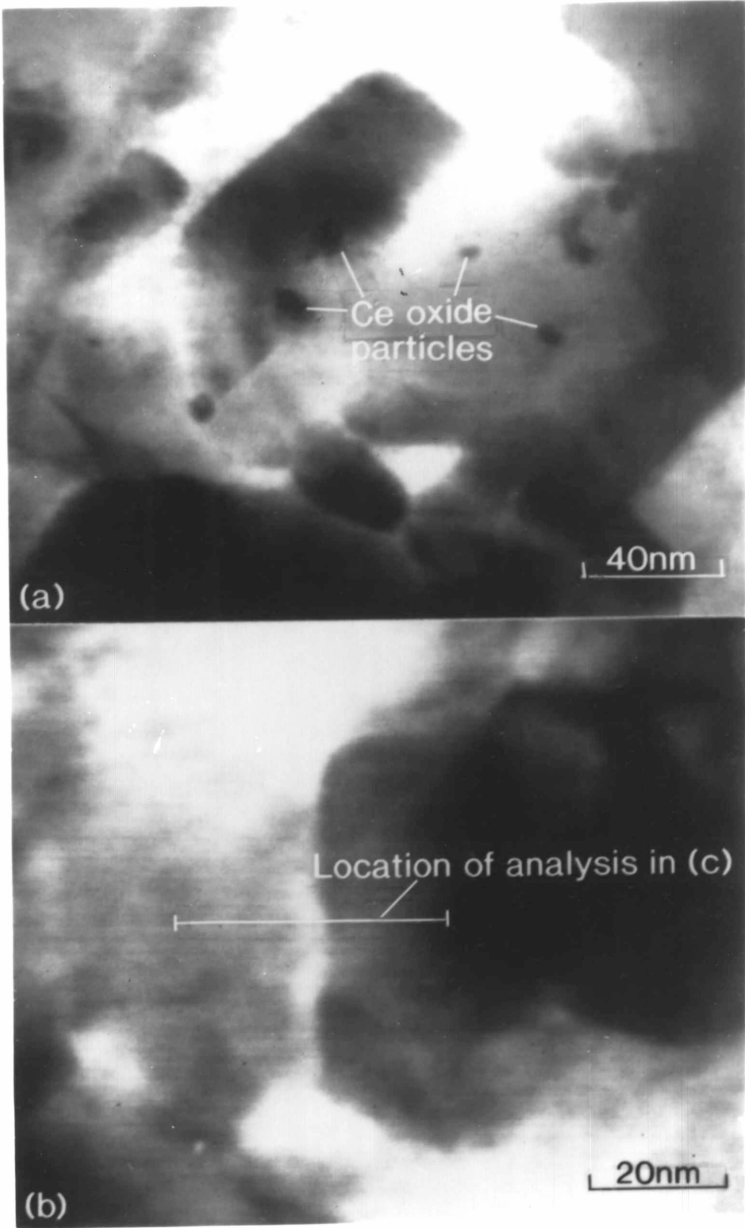
Figure 3.5.10

Scanning transmission electron micrographs of the oxide scale on a back-thinned sample of cerium-implanted chromium oxidised for 5 minutes at 850°C in the oxidation rig together with a plot of cerium concentrations across an oxide grain boundary found by high resolution microanalysis using energy dispersive X-ray spectrometry.

3.5.10(a) A scanning transmission electron micrograph of the oxide scale showing 8 nanometres sized particles that are thought to be cerium oxide.

3.5.10(b) A scanning transmission electron micrograph of the oxide scale showing the line along which the point analyses for the high resolution microanalysis were taken.

3.5.10(c) A graph of cerium concentration plotted against distance along the line in figure 3.5.10(b). The vertical axis is situated at the boundary between the two grains and the error bars are two standard deviations rather than one.



6%. The two abnormal results were from samples oxidised in the gas reaction cell as were three of the averaged results.

A sample of cerium-implanted chromium oxidised for 5 minutes at 850°C and then back-thinned by electropolishing was analysed at the Harwell Laboratory using high resolution energy dispersive spectroscopy to determine the distribution of cerium in the oxide film. The results are given in figure 3.5.10. Small particles, approximately 8 nanometres in size, were found amongst the Cr_2O_3 grains as shown in figure 3.5.10(a). These particles were found to be cerium-rich and are most likely to be cerium oxide. This is an area of the sample where the metal has been completely removed and, in such areas, electron diffraction revealed only CeO_2 and Cr_2O_3 . Figure 3.5.10(b) shows the area used to determine cerium concentrations across an oxide grain boundary. The two oxide grains can be seen clearly and the line indicates the location of the analyses carried out; the grain boundary was taken to be the edge of the right hand grain. The cerium concentrations, as measured by high resolution energy dispersive X-ray spectroscopy, are given in figure 3.5.10(c) plotted against distance from the grain boundary. A significant increase in cerium concentration is found in a 3 nanometre region to either side of the grain boundary with approximately an order of magnitude increase in cerium abundance at the boundary. Error bars of 2 standard deviations in the cerium concentrations are quoted to show the precision that can be achieved.

4 DISCUSSION

4.1 Electrolytic Chromium

The electrolytic chromium has been found to contain microcracks, to possess a $\langle 111 \rangle$ fibre texture, to contain large amounts of oxygen, to have a grain size of approximately 50 nanometres and to possess inherent strain; Sully and Brandes (6) report that the metal also contains a large amount of hydrogen, approximately 0.01% to 0.1% by weight. The hydrogen content usually occurs in a roughly constant ratio to the oxygen content by mass. The oxygen/hydrogen ratio is between 4 and 16 (6) which would imply that the hydrogen content of the electrolytic chromium studied here is between 0.01% and 0.04%. The phenomena reported above all result from the electrolytic deposition process.

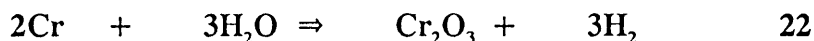
The stress that builds up in the metal is tensile and is relieved by cracking of the metal (7). This is the origin of the microcracks seen in the metal but, according to the latest review of chromium electrodeposition (7), the causes of the stress have provoked much controversy. The main causes that have been suggested are: texture effects, the structure of the electrodeposit, the inclusion of cathode film particles into the deposit, the texture and structure of the substrate, the stress in the substrate, absorption of hydrogen by the metal, absorption of hydrogen by the substrate and the oxygen content of the metal. Dennis and Such (7) suggest that the most feasible mechanism is the Gabe and West theory: growth occurs in a series of "cells" and the cathode film becomes entrapped between these cells, eventually forming continuous or semi-continuous oxide membranes. The oxide layers so produced at internal surfaces provide sites for nucleating hydrogen from dissolved atomic hydrogen and the build-up of pressure from hydrogen so produced, causes brittle cracks to be initiated. This would explain not only the oxygen and hydrogen contents, the microcracks and the inherent strain, but also the eventual distribution of the oxide particles and the small grain size.

The presence of oxide coatings on the grain surfaces would limit the size of the grains and promote a fine grain size and, upon heating, these oxide films would spheroidise at the metal grain boundaries giving the distribution of small particles seen in the metal. Calculations indicate that less than a monolayer coverage of each grain surface could account for the oxygen abundance, see Appendix. The oxide, assumed to be Cr_2O_3 , would fill up to 43% of the total interfacial volume, defined in the Appendix, assuming that the grains are spherical and that the oxide thickness at the interface is 0.25 nanometres. If the grains had a smaller volume to surface area ratio or the oxide thickness at the grain interfaces was larger, then the fraction of volume taken up by the oxide would be smaller.

This theory does not explain the long term persistence of hydrogen in the chromium. Sully and Brandes (6) report a study that discovered that the hydrogen content of a chromium electrodeposit did not change significantly over a period of 18 months at room temperature whereas cathodically treated iron and steel, in which hydrogen is contained as the atomic species on interstitial sites or as molecules adsorbed on defects, lost hydrogen over a shorter period. This argument would also apply to hydrogen in a supersaturated solid solution. They suggested that the hydrogen was more tightly bound: as hydrides or as hydrated chromium oxide. Raub and Müller (8) report that, under normal electroplating conditions, they have found that chromium hydride is not deposited; chromium hydride has not been detected in the metal in this study either. None of the authors who discuss hydrogen in electrodeposited chromium mention the conditions under which chromium hydride will form at equilibrium and no data regarding its formation can be found elsewhere.

The best explanation may be that the oxide films in the Gabe and West theory are hydrated and, for a formula of $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$, up to 12% of the hydrogen can be accounted for, see Appendix. If all of the hydrogen is accounted for by hydrated oxide, then the formula would have to be $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. This would imply that most of the interfacial grain volume would be water, which would not be consistent with the theory. The hydrated oxide theory does allow for the presence of the dissolved hydrogen that is needed for the tensile stress to be generated but does not explain the persistence of hydrogen in the metal. The amount of hydrogen needed to generate the tensile stress may be small or may be released into, and entrapped by, the cracks that relieve the stress, but there is nothing to confirm this.

Heating the metal will force any hydrogen content in solution towards its equilibrium value: a solubility of approximately 3 ppm at 400°C (90). Any water associated with hydrated oxide will oxidise the surrounding metal by the reaction:



and hydrogen will be given off in gaseous form. At equilibrium, the ratio of the partial pressures of hydrogen and water vapour is found to be 10^8 at 400°C (91) and, so, the metal will contain excess water which will drive the reaction to the right. Thus, hydrogen gas will be produced and the dramatic drop in hydrogen content above 400°C reported by Sully and Brandes (6), among others, will occur.

The spacing of the microcracks varies, in practice, between 40 micrometres and 12 micrometres (8) so the 16 micrometres crack spacing found for the electrolytic chromium examined in this study fits well with other published results. During deposition there is some preferential deposition of chromium at cracks, allowing some cracks to heal. It is possible that the difference between the two surface preparations,

being at either end of the range of ideal crack spacing, is that the electropolishing reveals cracks that have healed over whereas the mechanical polish does not. Sully and Brandes (6) report a similar phenomenon from a chromium electrodeposit having plated over cracks, one area of which has a large number of cracks intersecting the surface and another area has cracks that are almost all subcutaneous. This re-deposition can also cause a compressive stress in the surface of the metal by acting as wedges.

The orientation of the initial layers of the deposit is controlled by the substrate orientation, especially on electropolished surfaces (7,8); on these surfaces the epitaxy is very strong, even if there is a large mismatch between the lattices of the substrate and deposit. This has been reported for chromium deposited to a thickness of 20 nanometres on copper; copper is an fcc metal with a lattice spacing of 0.361 nanometres whereas chromium is a bcc metal with a lattice spacing of 0.288 nanometres (8). On mechanically polished surfaces the epitaxy is not as strong and Raub and Müller (8) found that a 20 nanometre thick deposit of chromium grew on mechanically polished copper with a fine grain size and no preferred orientation. On all surfaces, the typical orientation of the deposit will assert itself after some time, usually through re-nucleation of the complete range of possible orientations on the initial crystals. Sully and Brandes (6) report that for thick films the orientation of the deposit bore no resemblance to the substrate orientation. The typical orientation of the deposit will be that orientation which can grow most rapidly in the direction normal to the plane of deposition. For bcc metals this should be the $\langle 110 \rangle$ orientation (9) but, as this thesis, and three other authors quoted by Safranek (10), have shown, chromium has a $\langle 111 \rangle$ fibre texture. That is: the $\{111\}$ plane can be deposited more rapidly than any other chromium plane. Safranek (10) also reports electrodeposits of chromium as having grain sizes of around 100 nanometres; this is similar in magnitude to the grain size found in the electrolytic chromium examined in this thesis.

Hume-Rothery and Wyllie (92) investigated the variation of preferred orientation with electrodeposition conditions and found that: as the temperature of the electrolyte bath increased, so did the brightness of the electrodeposit and that there was also a correlation between the brightness of the deposit and the degree and perfection of the $\langle 111 \rangle$ preferred orientation, with the brightest deposits having their $\langle 111 \rangle$ fibre axes most precisely aligned with the normal to the deposition plane. Furthermore, for bright deposits the very marked preferred orientation did not alter with thickness from 1 to 10 micrometres whereas, for those deposits with some randomly oriented crystals, the misalignment of the fibre axis decreased to a third of its original value when the thickness of the deposit increased from 10 to 36 micrometres. This suggests that for the deposits examined in this study, with

thicknesses of up to 500 micrometres, the degree and perfection of the preferred orientation is very good. This is also borne out by the brightness of the initial deposit.

The selected area electron diffraction pattern, figure 3.1.1.3, shows the high degree of texture present in the material as do the X-ray diffraction spectra and the second pole figure in figure 3.1.2. The texture of the as-received metal is not represented by its pole figure, which shows a very weak texture; this may be due to a combination of a slight, circularly symmetrical deviation of the $\langle 111 \rangle$ axis of the metal from the normal to the surface causing a variation in the positions of the $\langle 110 \rangle$ poles and the small grain size and inherent strain in the deposit causing broadening of the $\{222\}$ peak thus smearing out the apparent positions of the poles to a greater degree. The height of this peak relative to the others in the spectrum is characteristic of an electrodeposited sheet with a fibre texture, having $\langle 111 \rangle$ normal to the surface of the sheet (93). After heat treatment, the $\{211\}$ peak on the diffraction spectrum is much increased. This may be a result of the grain growth process, implying that grains with this orientation grow preferentially or it could be that the overall lower number of grains has made this orientation proportionally more frequent.

4.2 Microstructural Development

Heat treatment of the as-received material at temperatures above 400°C drives off the hydrogen and causes a distribution of oxide particles to form in the metal. When examined after heat treatment at 800°C, the oxide particles had a bimodal size distribution. The smaller particles are uniformly distributed throughout the material, have an apparent spacing roughly equivalent to twice the original grain size of the metal. This would imply that the small particles were formed at grain boundaries in the first stages of grain growth. As metal grain growth has been substantial in all of the samples, this is impossible to verify especially as the particle distribution, being three dimensional, does not have an obvious grain-boundary-precipitation appearance. The size of some of these small particles is similar to the original grain size which implies that they should have been detected in the original material. As they were not, coarsening must have occurred. The distribution of the larger particles as lines through the metal implies that they have formed along the lines of the microcracks, which have subsequently closed.

The coarsening of the particles that takes place in the metal is driven by the drop in interfacial energy of the system that arises from a decrease in the total particle/matrix interface area; particles larger than the mean particle size grow while particles that are smaller than the mean particle size shrink, the rate being determined

by the sizes of the large and small particles relative to the mean particle size (94,95). The change in size of the particles is brought about by the diffusion of oxygen from the small particles to the larger particles and the diffusion of oxygen through the metal is the rate-determining step in the coarsening process. This is implied by the existence of particle-free regions alongside the lines of larger particles in those samples annealed at 800°C and 1000°C. Particle-free zones also exist alongside grain boundaries implying that grain boundaries are diffusion paths. The existence of particle-free zones implies that the rate limiting step in the process is the diffusion of oxygen to the particles; if transport across the particle/matrix interface was rate-limiting, then the particles would decrease in size uniformly throughout the metal with the smallest particles disappearing first, rather than as a function of distance from the larger particles.

Initially, the particles on the crack surfaces will coarsen by surface diffusion and those in the matrix will coarsen by grain boundary diffusion. When the cracks close and the metal grains grow, the larger particles will coarsen by grain boundary diffusion and the small particles by lattice diffusion. Eventually the grains will be so large that the particles will all coarsen by lattice diffusion. At temperatures between 400°C and 1200°C (two-thirds of the melting point of chromium), surface diffusion is more rapid than grain boundary diffusion which is, in turn, more rapid than lattice diffusion and the coarsening of the particles will occur more quickly on surfaces than on grain boundaries or in the matrix (95). At higher temperatures, the rate of lattice diffusion will begin to approach the rate of grain boundary diffusion. The oxygen diffusion rates will vary by several orders of magnitude depending upon the diffusion path taken and the relative rates will determine the microstructure of the metal after heat treatment.

Grain growth in the metal will be affected by the presence of particles in the matrix and formulae for the maximum grain size for a given particle distribution have been determined by several authors (96). In general they give the maximum grain size, D , as being:

$$D = kr/f \qquad 23$$

where r is the mean radius of the particles, f is the volume fraction of particles in the matrix and k is a constant of proportionality with a value generally between 0.1 and 1. This implies that: for a given particle distribution, a maximum grain size exists, disregarding abnormal grain growth; if the volume fraction of particles is reduced then the maximum grain size increases; if the mean radius of the particles increases, then the maximum grain size will increase.

There are three stages in the coarsening process, governed by the diffusion processes that occur in each. Firstly there is the coarsening of the particles up to the point where the cracks close; this is the regime of surface and grain boundary diffusion. Secondly there is the stage after the cracks have closed but before the grains have grown larger than the crack spacing; this is where grain boundary and lattice diffusion control coarsening. Finally there is the stage after the grains have grown sufficiently large that lattice diffusion is entirely responsible for coarsening.

The mechanism for the first stage can be explained from the microstructural results of the Gabe and West theory. Upon heating, the semi-continuous oxide membranes will spheroidise in order to reduce their surface energy and this will enable the metal grains to grow, utilising the strain energy remaining in the lattice and fine oxide particles will exist in the matrix and decorating the cracks. These particles will coarsen at different rates because those on the cracks will be coarsening via surface diffusion and those in the matrix will be coarsening via grain boundary diffusion. So, by the time the cracks have closed and surface diffusion is terminated, there will be a distribution of larger particles decorating those grain boundaries that mark the traces of the cracks and an intragranular distribution of small particles. This is illustrated by figure 3.1.3.5.

Approximate values for the mean particle size and volume fraction of each distribution can be determined from the transmission electron micrographs in figures 3.1.3 and 3.1.4; these will be sufficient to give estimates for order of magnitude calculations to determine maximum grain sizes from equation 23 but the values will not be sufficiently precise that statements regarding the value of the constant of proportionality, k , in equation 23 can be made. At temperatures up to 1200°C the oxygen content of the metal does not change and thus the volume fraction of particles will be constant. The values for each heat treatment illustrated are given in table 11. As can be seen from table 11, a small value of r/f is brought about by a low mean particle radius which depends upon there being many intragranular particles and, so, the particles that control the grain size will be the intragranular particles. The only anomalous values of r/f are those for the 800°C annealed and 1200°C hydrogen-annealed materials where the actual grain size appears to be similar to r/f rather than several times lower. The data used are not sufficiently precise to determine whether these are real deviations or just products of the errors involved. The strong texture of the metal may be mitigating the effect of the particles by making grain growth easier by the coalescence of closely crystallographically aligned grain pairs.

In the second stage of the coarsening process, the mechanism for the development of the eventual microstructure of the metal depends upon the relative sizes of the grain boundary diffusion rate and the lattice diffusion rate. A higher rate

Table 11

A table of approximate values of the mean particle radius and volume fraction for the oxide particle distributions in the figures indicated. The value of r/f calculated from the given parameters using equation 23 is compared with the actual mean grain diameter of the metal.

Figure	Heat treatment	Mean particle radius nanometres	Volume fraction	r/f micrometres	Actual grain size micrometres
4.1.3.5/6	800°C, 24 hours	9 ± 3	5.6×10^{-3}	1.6	1
4.1.3.7/8	1000°C, 24 hours	200 ± 50		36	5
4.1.4.1	1000°C, 3 hours, hydrogen	70 ± 15		12	2.5
4.1.4.2	1100°C, 3 hours, hydrogen	150 ± 50		27	10
4.1.4.3	1200°C, 3 hours, vacuum	700 ± 150	7.4×10^{-3}	95	25
4.1.4.4	1200°C, 3 hours, hydrogen	50 ± 10	5.6×10^{-3}	9	8

of diffusion will imply faster coarsening, as will a larger driving force. For the grain boundary particles, the rate of increase in size is:

$$\text{rate} = k_1 D_{gb} / R^3 \quad 24$$

whereas the rate of decrease in size for the intragranular particles is:

$$\text{rate} = k_2 D_L / r^2 \quad 25$$

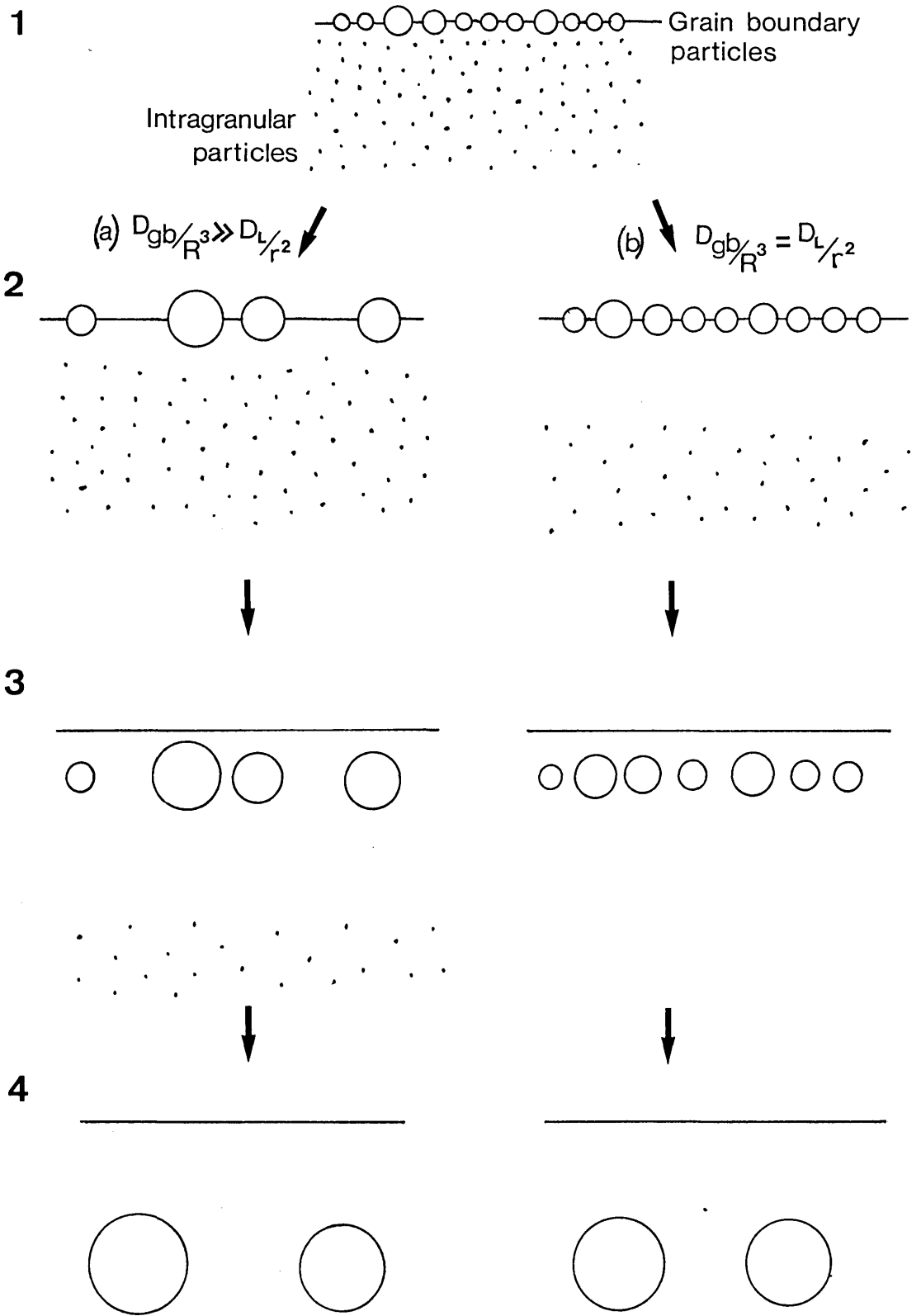
k_1 , k_2 are constants of proportionality which will be similar in magnitude, D_{gb} and D_L are the diffusion rates for grain boundary and lattice diffusion respectively, R is the mean radius of the distribution of grain boundary particles and r is the mean radius of the whole particle distribution (95). The mean radius of the intragranular particles is smaller by a factor of ten than that of the grain boundary particles but the rate of diffusion can be significantly higher for the grain boundary particles depending upon the temperature of heat treatment. There will be two regimes of coarsening, depending upon whether D_{gb}/R^3 is much greater than or is equal to D_L/r^2 .

The second stage will end when the grain size becomes larger than the mean crack spacing and the main diffusion path becomes the lattice. The average crack spacing is approximately 20 micrometres and table 11 shows that this is exceeded only by the 1200°C vacuum-annealed material, although the 1100°C annealed material approaches the value. Figure 3.1.5.2 shows that the metal grains are occasionally larger than the spacing of the lines of particles.

Figure 4.1 shows the second stage of coarsening for the two regimes mentioned above; that is: at low and high temperatures. The initial microstructure, after the cracks have closed is shown in figure 4.1.1. When $D_{gb}/R^3 \gg D_L/r^2$, the shrinkage of the intragranular particles is slow and the distribution will be effectively isolated from the coarsening process. The grain boundary particle distribution will coarsen due to differences in the sizes of particles within the distribution, figure 4.1.2. The grain boundary particle coarsening will continue until the mean size of the grain boundary particles is sufficiently large that the driving force between the two particle distributions overcomes the slow rate of lattice diffusion. The grain boundary particle distribution will then coarsen as a whole while the intragranular particles shrink, figure 4.1.3. When sufficient numbers of intragranular particles have dissolved such that the maximum grain size becomes larger than the spacing of the lines of particles, the grains will grow and the boundaries will be released from the lines of particles. The coarsening will then enter its third stage where mass transport is solely by lattice diffusion, figure 4.1.3, and will proceed to equilibrium at a rate dependent upon the rate of lattice diffusion with only the largest particles surviving.

Figure 4.1

A figure showing the two regimes of coarsening for the particles in the heat treated chromium. The microstructure of the metal evolves from the initial bimodal distribution of particles on the grain boundaries and in the intragranular regions in two different manners depending upon whether $D_{gb}/R^3 \gg D_L/r^2$ or whether $D_{gb}/R^2 \approx D_L/r^2$. R is the mean radius of the distribution of particles on the grain boundaries, r is the mean radius of the entire particle distribution, D_{gb} is the coefficient for grain boundary diffusion and D_L is the coefficient for lattice diffusion.



For the regime where $D_{gb}/R^3 \approx D_L/r^2$, the driving force for coarsening between the two distributions will be sufficient to override the coarsening within the grain boundary particle distribution and the intragranular particles will shrink and dissolve before the grain boundary particle distribution has been able to coarsen significantly, figure 4.1.2. This will cause the grains to grow and the grain boundaries to be released from the lines of particles and the coarsening process will enter its third stage. All of the particles will then coarsen or shrink by lattice diffusion only. The main difference between the mechanisms at high and low temperatures is in the size and number of grain boundary oxide particles when the grain boundaries are released.

These mechanisms can be compared to the microstructures found in the heat treated samples. The 800°C anneals correspond to figure 4.1.1, the 1000°C, 24 hour anneals correspond to a point between figures 4.1.3(a) and 4.1.4(a) and the 1200°C, 3 hour vacuum-annealed sample is beyond figure 4.1.4. If the existence of an interactive atmosphere is ignored then the 3 hour hydrogen anneals can also be fitted into the mechanisms. The microstructure of the 1000°C annealed sample corresponds to a point between figures 4.1.2(a) and 4.1.3(a) and that of the 1100°C annealed sample is similar to figure 4.1.4. The 1200°C hydrogen-annealed sample has a microstructure similar to that in figure 4.1.3(b).

Gladman (97) gives an example of an austenitic stainless steel whose fine grain size is maintained at high temperatures by the pinning effect of particles. At high temperatures, these particles will coarsen and their pinning effect will diminish until it is not sufficient to hold back grain growth. There will be a temperature at which the coarsening proceeds so rapidly that the pinning effect will be reduced sufficiently quickly so that grain growth can occur after a short time, for example one hour. In his theory of pinning, Gladman considers individual grains and gives the critical radius of the particles for the pinning of that grain as being inversely proportional to the ratio of the size of the grain under consideration and the mean grain size; that is:

$$r^* \propto \left[\frac{3}{2} - \frac{2}{Z} \right] \quad 26$$

where r^* is the mean particle size and

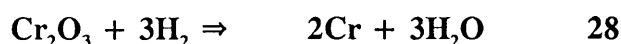
$$Z = \frac{D_0}{D} \quad 27$$

D_0 is the size of the grain under consideration and D is the mean grain size of the metal (97). This implies that the largest of the grains in the distribution will no longer be affected by the pinning force before the majority of the grains can begin to grow, that is just below the critical temperature mentioned above. These large grains

can grow substantially larger than the other grains in the distribution before the particles coarsen sufficiently that the rest of the grains are released (97). A microstructure similar to this, containing large grains amid finer grains, has been seen in the 1100°C hydrogen-annealed sample implying that this sample is in a part of the coarsening process just before a release of the constraints on growth. The constraint that is being released in this case is probably the distribution of small intragranular particles.

These mechanisms of coarsening, though, take no account for the effects of the atmosphere of the heat treatment and this is most clear in the discrepancy between the microstructures of the 1200°C vacuum-annealed and hydrogen-annealed samples. Although both samples have been heat treated for the same period of time at the same temperature, the vacuum-annealed sample is very much closer to equilibrium than the hydrogen-annealed sample. This implies that there has been a retardation of the particle coarsening due to the hydrogen atmosphere. There is also a difference between the microstructures of the 1100°C and 1200°C hydrogen-annealed samples. The 1100°C sample appears to be in the regime where grain boundary diffusion is predominant whereas the 1200°C sample appears to be in the second regime. This implies that the $D_{gb}/R^3 \approx D_L/r^2$, at around 1200°C but should not imply a drop in the rate of coarsening. The retardation of the coarsening process has only affected the grain boundary particles, the intragranular particles having almost completely disappeared. This implies that the hydrogen atmosphere is not interfering with the diffusion of oxygen through the lattice from the small particles to the large particles, neither does it appear to be inhibiting the transfer of oxygen across the matrix/particle interfaces.

The reduction of the oxide particles is given by the reaction:



with a rate constant, K , which depends upon:

$$K = [p(\text{H}_2\text{O})]^3 / [p(\text{H}_2)]^3 \quad 29$$

where $p(\text{H}_2\text{O})$ and $p(\text{H}_2)$ are the partial pressures of water vapour and hydrogen in the system. If the pressure of water vapour is higher than the equilibrium value then the reaction will be driven to the left, otherwise to the right, reducing the oxide particles. Some values for the equilibrium partial pressure of water vapour in this system are given in table 12, quoted by Sully and Brandes (6):

Temperature in °C	p(H ₂ O) in Pa
1022	40
1210	177
1300	270
1500	800

Table 12: Some values of the equilibrium partial pressure of water vapour in the Cr₂O₃/H₂ equilibrium (6).

For the hydrogen used in the heat treatment of the electrolytic chromium the ratio of hydrogen to water vapour is approximately 10^6 which gives the partial pressure of water vapour in the gas as approximately 0.1Pa. This is well below the partial pressures in table 12 implying that the reaction can proceed at these temperatures. Reference to diagrams of oxide stability (91) show that the lowest temperature at which the reaction can proceed, for this hydrogen/water vapour ratio, assuming no water is picked up between the gas cylinder and the furnace, is 600°C. The reaction will occur by oxygen diffusion from the particles' surfaces down a chemical gradient to the free surfaces of the metal where the oxygen will react with the hydrogen to form water vapour. This implies that, although the reaction may be possible, the kinetics could be so slow that the reaction does not appear to occur. The gas flow will ensure that there is no build-up of water vapour that could halt the reaction.

The coarsening and dissolution processes both involve the diffusion of oxygen and the final destination of the diffusing oxygen atoms will depend upon the driving forces for each process. That there is no noticeable drop in the oxygen content of the metal at or below 1200°C implies that the dissolution process is not occurring at these temperatures and so the driving force for dissolution must be smaller than that for coarsening. At 1200°C there is evidence that the coarsening process has been retarded by the hydrogen atmosphere. In the hydrogen-annealed sample the lines of large particles are no longer associated with the grain boundaries, grain growth having occurred. This implies that the driving force for coarsening is entirely dependent upon the difference in the sizes of the particles, rather than being affected by the path that the diffusing species takes. Thus the driving force for dissolution may be smaller than that for coarsening between the intragranular particles and the grain boundary particles but larger than the driving force for coarsening within the grain boundary particle distribution. Coarsening of the grain boundary particles has definitely occurred in the 1200°C sample as the particles are larger than the grain boundary particles in the 800°C vacuum-annealed sample; if the intragranular particles had dissolved and the grain boundary particles had not coarsened, then the grain boundary

particles should have been the same size as the grain boundary particles in the 800°C sample where no coarsening has occurred.

The processes occurring in the metal at 1200°C would then be: coarsening of the particles until the intragranular particles had disappeared followed by diffusion of oxygen from the large particles to the free surfaces, with the larger distances involved causing an undetectable loss of oxygen in the remaining time. At temperatures above 1200°C, there would be a smaller amount of coarsening and a larger flux of oxygen atoms to the free surface, with more oxygen being able to leave the metal at higher temperatures.

The process of particle dissolution and subsequent grain growth is similar to that in austenitic steels containing AlN particles. In that system, the grain size of the steel remains small under heat treatment until the steel is treated above a critical temperature, the temperature at which AlN dissolves into the matrix. The grains then coarsen rapidly (98). The temperature above which growth of the chromium grains becomes significant is 1200°C and, as has been shown, this is the temperature at which the oxide particles begin to be reduced by the hydrogen atmosphere. If the atmosphere used was inert then a similar effect would be noticed above 1000°C, the temperature at which the coarsening of the oxide particles becomes significant. For isochronous heat treatments, such as those carried out in this work, ridding the metal of oxide particles will be a matter of determining the lowest temperature at which the oxide particles are completely removed in the time available. For heat treatments of 3 hours duration, this temperature is 1500°C. Ideally the method would involve choosing a temperature just above the critical temperature, for example 1250°C, and annealing for as long a time period as is necessary to completely remove the particles. This latter option was not available in this work for reasons of safety.

4.3 Contaminants

Of the contaminants contained in the standard-annealed chromium, the most important will be those elements that affect the surface of the metal significantly. These are the oxygen in the oxide particles and those elements that will segregate to the free surfaces. The oxide particles have been discussed. Possible segregants include: sulphur, chlorine, tin and antimony; Rice and Wang found that, in iron, sulphur, tin and antimony all segregated to surfaces and would have a deleterious effect on the strengths of interfaces (99). Sulphur is well known as a surface segregant that can cause drastic weakening of interfaces through the formation, at high temperatures, of low melting point compounds. It is also indicated as a factor in the loss of scale adhesion but the potentials of tin and antimony are not as well documented. Tin and antimony are known to embrittle grain boundaries in iron (99).

and Cottrell (100) suggests that because the strengthening or weakening effect of a segregated species will be proportional to the relative cohesive energies of the matrix atoms and the segregant: tin and antimony, with low cohesive energies, will weaken interfaces. On this basis, sulphur will have a strong weakening effect on interfaces. Although the concentration of sulphur, in the bulk of the metal, has been lowered by the heat treatment from 85 ppm to 5 ppm, it is still sufficiently large to provide more than a complete monolayer coverage of the free surfaces of the metal if total segregation occurred.

The untreated electrolytic chromium is not a good substrate for studying the oxidation of chromium as its microstructure is unstable at 800°C - 1000°C, the oxidation temperatures under consideration. This will introduce an uncontrollable parameter into the oxidation process. All of the defects found in the metal are inherent in the method of production and all other untreated electrolytic chromium will possess them to some degree. Heat treatment can cure some of the problems and the standard-annealed material is the best substrate that could be produced given the constraints on time and temperature mentioned previously. It is stable at the temperatures involved and can be characterised.

4.4 Surface Characterisation

The mechanically polished surfaces are highly deformed with a dense dislocation substructure. The transmission electron micrographs of the surface indicate that this does not affect the grain size of the material prior to oxidation and so the surface grain size will be identical to that of the bulk. Recrystallisation may occur during oxidation, though, altering the grain size substantially. Pivin *et al* (101) found that the compressive stresses were larger in the surfaces of mechanically polished samples of nickel than electropolished samples.

The 1000°C, 3 hour hydrogen-annealed samples were only polished using SiC and alumina and their surfaces will be contaminated with Si, C (101) and Al. Their surfaces appear roughened by scratches from the alumina polish and undulate due to preferential wear of certain grain orientations during the alumina polishing. Pivin *et al* (101) also discovered that the mean asperity heights on the surface of samples polished using 1 micrometre size diamond particles was similar to those on electropolished samples; for samples polished with 9 micrometre size diamond particles, the mean asperity height was only slightly larger. The lines of oxide particles are exposed and most, but not necessarily all, of the particles will have been pulled out during polishing. During the annealing treatment, elements that can segregate to the metal surfaces will do so. The mechanical polishing will remove the top surface of the metal and any elements segregated there. This will reduce the

abundance of these elements in the metal and, more importantly, reduce their abundance at the free surface to be oxidised. The segregants will diffuse to the new surface during oxidation but the surface will now be the metal/oxide interface, not a free surface, and the equilibrium concentration of the segregants will be lower. The metal has a 2 nanometre thick native oxide layer.

The standard-annealed chromium mechanically polished using SiC and alumina will also have a deformed surface, roughened by scratches. The high dislocation density seen in the transmission electron micrographs illustrates the high degree of deformation that occurs in the polishing procedure. The smearing of the surface of the metal by the nap of the cloth used will be the cause of much of the deformation but any mechanical polishing process will leave deformation in the thin layer immediately under the surface. There are height variations across the surface of the sample due to preferential wear of certain grain orientations which are likely to be larger, though with a wider spacing, than on the 1000°C material, due to the larger grain size of the standard-annealed material, the mean grain diameter being 106 micrometres as opposed to 2.5 micrometres. The surfaces are contaminated with C, Si and Al from the mechanical polishing. The oxide particles, or pits where the particles have been pulled out, are present in the surface with a mean spacing of 12 micrometres, the pits being up to 2 micrometres in diameter and depth. The mechanical polishing will remove the top surface of the metal and any elements segregated there. There is a native oxide layer on the metal that the SIMS results show to be 2 nanometres thick.

For standard-annealed chromium mechanically polished using diamond particles, the surface of the metal is as severely deformed as after the alumina polish, there is roughening due to scratches but no variations in surface height. The only contamination will be from carbon and this should be to a lesser extent than the carbon contamination on the samples polished using SiC (101). As with all of the other unimplanted specimens, there will be a 2 nanometre thick native oxide layer on the surface of the metal and the mechanical polishing will have removed any elements that had segregated to the free surface.

The samples polished with diamond particles have large pit number densities, around 4 - 5 times the number density of the electropolished surface and they range in size from 7 micrometres in diameter to 0.5 micrometres. The differences in the number and size of the pits in the surfaces of the diamond and alumina polished samples in figure 3.2.1 reflect their different polishing procedures. For the calculation of particle number density from the electropolished surfaces it was assumed that all of the pits in the surfaces of those samples were originally particles. This is likely to overestimate the number of particles in the surface due to etch pitting and the number quoted in table 8 is possibly higher than the true value; it certainly

will not be too low. The features in the surface of the mechanically polished specimens, from the scanning electron micrographs in figures 3.2.1.5 and 3.2.1.6, are pits in the surface, although some may contain particles. These pits are assumed to be due to embedded particles being pulled out by the mechanical polishing. The polishing procedure is likely to cause an underestimation of the number of pits per unit area, due to the smearing of the surface brought about by the nap of the cloth used, but the value for the number density on alumina polished surfaces agrees with the value for the electropolished sample, which cannot be an underestimation. Thus the value of pit number density gained from these samples is an accurate representation for the number of pits and particles on the surface of the standard-annealed chromium. It is impossible to ascertain whether any particles have been embedded in the surface and then buried by metal being smeared over them.

The increase in the pit number density from the alumina polished samples to the diamond polished samples implies that diamond particles have embedded themselves into the surface of the metal and then have been ripped out. The pits due to oxide particles in the metal and those due to the 1 and 3 micrometre diamond particles are the same size, making it impossible to distinguish between them by size. The number of pits per unit area due to diamond particles can be calculated by subtracting the number of pits on the alumina polished samples from the total number of pits on the diamond polished samples, giving $6 \times 10^9 \text{ m}^{-2}$, but the relative numbers of diamond particles left embedded in the metal is unknown. This must be quite large, since diamond particles are found in the small sampling areas examined during transmission electron microscopy whereas the oxide particles are never seen. The diamond particles found by transmission electron microscopy are only around 0.25 micrometres in size and thus come from the smaller end of the diamond particle size distribution; the fact that they can remain in the metal may be due to their small size. The large indentations seen in the light micrographs are most probably due to the 6 micrometre diamond particles embedding into the surface and the damage caused by this not being removed by the subsequent 3 micrometre and 1 micrometre polish.

The electropolished surfaces of the hydrogen-annealed coupons are smooth and undeformed. There are pits in the surface, whose distribution and number will depend upon the heat treatment that the coupon has undergone. The two heat treatments used for oxidation purposes were the standard-annealed and the 1000°C, 3 hour hydrogen heat treatments. The 1000°C, 3 hour hydrogen-annealed samples have a mean grain diameter of 5 micrometres and lines of pits spaced approximately 16 micrometres apart. Each pit is up to 1 micrometre in diameter and depth. The majority of the grains have their {111} planes parallel to the surface of the coupon. Studies by Pivin *et al* (101) indicate that electropolishing with perchloric acid leaves the surface of the sample contaminated with chlorine; Caplan, Harvey and Cohen

(102) have found that electropolishing leaves a thin oxide layer on the surface of the metal that could be amorphous. This is not contradicted by the selected area diffraction patterns from electropolished samples, which shows neither the oxide spots nor a diffuse background from an amorphous film, implying that the oxide film is only a few nanometres thick. The electropolishing treatment will also remove the top surface of the metal and, with it, any elements that had segregated there.

The standard-annealed material was also electropolished with a perchloric acid solution has larger grains and far fewer pits. The pits are up to 3 micrometres in diameter and depth and have a mean spacing of 12 micrometres. This material will also have the thin oxide film and the contamination associated with electropolishing.

4.5 The Effects of Implantation

The implanted coupons are all diamond polished, standard-annealed chromium. The coupons implanted with chromium have similar numbers of pits in their surfaces as the unimplanted diamond polished coupons but with the 7 micrometre pits being more numerous. This implies that the implantation of chromium ions has little effect on the number density of pits seen in the surface of the diamond polished metal.

Ion implantation will introduce a large number of point defects into the metal surface and cause radiation enhanced diffusion to occur (103). This will allow dislocation movement at temperatures far lower than normal and a recovery process will occur, with the dislocations produced by the mechanical polishing forming themselves into the subgrain boundaries seen in the chromium-implanted material. The coupons will heat up, possibly to 200°C, during bombardment, which will aid diffusion processes, but not sufficiently that the dislocations can move entirely due to thermal effects. The large number of vacancies will be necessary for dislocation motion. Coalescence of vacancies will also occur, forming voids in the metal and these are seen in the transmission electron micrographs. These voids are probably also the small pits, less than 200 nanometres in size, observed in the scanning electron micrograph, figure 3.2.1.6.

The immediate surface layer of the implanted specimens should become amorphous as indicated by the Hägg rule (103). This states that if the ratio of the radius of the implanted atom to the radius of the substrate atom is greater than 0.59 then the material will become amorphous especially if the structure is "frozen in" by implanting at low temperatures. The ratio for chromium ions implanted into chromium metal is obviously 1 and, so, amorphisation of the surface will occur. This amorphisation of the surface will have an effect upon the oxidation that will occur when the samples, still hot from the implantation, become exposed to oxygen. The

dislocations and of point defects causes orientation fluctuations and, if the orientations of neighbouring grains coincide, then their grain boundaries will be eliminated (105).

The surface of the cerium-implanted samples should also be amorphous, using the Hägg rule; the ratio of the atomic radii of cerium and chromium is certainly greater than 0.59. The native oxide on the cerium implanted samples is thicker than on the surface of mechanically polished, unimplanted chromium by approximately an order of magnitude and is likely to be thicker than that on the chromium-implanted samples. The electron diffraction patterns of the implanted samples shows no oxide spots and so the oxide layer on the surface of cerium-implanted specimens must be amorphous; this is probably due to the surface being amorphous.

The cerium concentration peaks 30 nm below the surface of the metal and then extends up to 100 nm further and there is also a cerium peak in the native oxide film next to the metal/oxide interface. The dose rate used gives the most implanted material possible, any higher and as much cerium is lost due to sputtering as is implanted. This implies that the peak of the cerium concentration should be at the surface of the metal in the unoxidised state. As the peak is below the surface level, cerium must have concentrated in the oxide layer, depleting the metal immediately adjacent to the metal/ oxide interface. Cerium will oxidise preferentially over chromium and is thus likely to form a thin layer over which the rest of the native oxide can grow. The cerium could be randomly distributed through the amorphous layer or could segregate slightly at the surface in order to minimise strain energy giving a surface layer, prior to oxidation, that is rich in cerium whilst the layer below is depleted. The latter case would give rise to a cerium concentration peak in the oxide more readily than the former. This segregation is known as Gibbsian adsorption.

The thickness of the native oxide on the cerium-implanted samples does not appear to vary considerably across the sample despite there being a large change in the colour of the film. This implies that the colour is not related strongly to the film thickness. As the film is too thin for the colour to arise via interference effects, it must be due to the composition of the film, specifically from the cerium that is present in the film. In this case, the variations in colour that are seen will be due to a variation on the cerium content of the oxide. If this is so, then the thickness of the film, which is thinner in the lighter coloured areas, will be dependent on the cerium content: more cerium implies a thicker film. It will not occur the other way around: a thicker film implies more cerium, because the cerium would have been in the metal prior to oxidation.

The membrane seen in the transmission electron micrographs is thin and amorphous and there are three possibilities for its existence: it could be an artifact of the electropolishing, brought about by the interaction between the polishing solution

and the cerium-implanted metal; it could be the native oxide film alone or it could be the native oxide film with remnants of the protective lacquer on top. Of these three, the latter is the most likely. Energy dispersive X-ray spectroscopy has shown that the membrane contains cerium. For an electropolishing film to contain cerium, the protective lacquer must have been penetrated but areas where this has occurred have been found on the cerium-implanted specimens and, in every case, the areas have not been associated with a membrane nor can cerium be detected by energy dispersive X-ray spectroscopy in the penetrated areas. If no interaction with cerium has occurred, then an electropolishing artifact would only be due to an interaction between the solution and the chromium metal and the membrane should have been present on other, non-cerium-containing, specimens. In this case it would not contain cerium.

4.6 Initial Oxidation

The oxide film that forms on the samples oxidised in the gas reaction cell grows initially with the basal plane of the oxide unit cell parallel to the surface of the metal and possesses a fibre texture with $\langle 0001 \rangle$ normal to the surface of the metal. The basal plane of the oxide lattice has the highest packing of oxygen atoms and both the chromium and oxygen atoms are arranged with hexagonal symmetry. The metal is highly textured and the majority of its surface is made up of chromium $\{111\}$ planes in which the atoms have a threefold symmetry. This would imply that the two lattices could have an orientation relationship that causes the oxide to grow with a fibre texture. If the atom positions in the oxide plane and in the chromium plane are calculated and then compared, numerous points where the two lattices coincide closely can be found. Origins are taken at atoms in the oxygen and chromium sublattices of the oxide and other in the metal lattice at sites where the chromium and oxygen atoms would wish to be sited. The origin in the chromium sublattice is then matched with the origin in the metal lattice where a chromium atom would wish to be sited and the points where other chromium atoms in the oxide sublattice coincide with similar sites in the metal lattice are determined. This procedure is repeated for the oxygen atoms.

If the oxide lattice was oriented so that these atom positions coincided, then the energy of the interface would be lower than if the lattices were completely mismatched. The points of coincidence are well separated, approximately five chromium lattice spacings from the origin, implying that the coherency of the interface is low and, so, any energy drop is small. Thus the orientation relationship between the $\{0001\}$ basal plane of the oxide and the $\{111\}$ plane of the metal must be based on the large number of possible orientations that would bring about energy savings and, with so many orientations to choose from, a fibre texture is inevitable. This may not occur if some of the coincidences are more favourable than the others;

in which case, given an apparently random distribution of orientations around the fibre axis, there must be a mechanism whereby these more favourable orientations are suppressed.

It is possible that the oxide may grow naturally with its basal plane parallel to the metal surface regardless of the metal orientation. This cannot be disproved here as all of the metal surface orientations discovered by electron diffraction have been either the $\{111\}$ plane or have had a distorted hexagonal symmetry such as the $\{\bar{1}33\}$ plane. Hussey, Mitchell and Graham (24) report an orientation relationship for initial oxide layers of $[1\bar{1}0] \text{ Cr}_2\text{O}_3 // [011] \text{ Cr}$ with the oxide grains having a fibre texture of $[110]$ normal to the surface. In the lattice planes perpendicular to these directions the chromium atoms are arranged in rectangular symmetry which seems to imply that the symmetry of the surface metal atoms has a stronger influence on initial oxide orientation than oxygen close packing arrangements. The existence of a fibre texture implies only weak matching between the oxide and metal lattice points in a similar way to the orientation relationship noted above.

The oxide film on the unimplanted sample in figure 3.3.1.1 has become continuous and has a grain size of between 50 and 100 nanometres. Several statements regarding the nucleation of this oxide film can be made. The mean spacing of the nuclei cannot be larger than the mean grain size of the oxide and is unlikely to be much smaller. The oxide nuclei, after forming, will have expanded sideways until they met adjacent nuclei and, unless the adjacent nuclei were of exactly similar orientation, a grain boundary will form between the two, making separate oxide grains. The chance of this happening on a sample where, according to the electron diffraction pattern from the oxide film, the initial orientations of the oxide nuclei are likely to be randomly distributed around the fibre axis, is slight. At 800°C , less than one third of the melting point of the oxide, very little grain growth will occur in the oxide and, after a few minutes at these temperatures, the effect will be negligible. The oxide grains appear not to vary considerably in size which implies that the oxide nuclei were distributed uniformly across the surface of the metal.

Certain of the samples oxidised in the gas reaction cell were oxidised at different oxygen pressures. Two samples oxidised under otherwise similar conditions are shown in figures 3.3.1.1 and 3.3.3.1 with the former being oxidised in 250Pa of oxygen and the latter in 4000Pa of oxygen. The rate constant for oxide growth on chromium has been found to be independent of oxygen partial pressure as discussed in section 1.4 and, so, the amount of oxidation should be similar on these two samples. The oxide film on the sample in figure 3.3.3.1 appears to be thicker than that shown in figure 3.3.1.1 but, lacking precise thickness measurements, nothing definite can be deduced from these two samples regarding the effects of oxygen partial pressure. The extent of the penetration of the oxide down the metal grain boundaries, only seen on

the sample in figure 3.3.3.1, will be due to the combination of the oxidation conditions and the sample used. Preferential nucleation should occur at grain boundaries as they are sites of higher free energy and each side of the boundary will act as a surface for oxidation. As the boundary widens due to the removal of metal by diffusion to the oxide surface, the oxide will be able to penetrate further down the boundary. This preferential attack has only become obvious because this sample has a large number of grain boundaries, due to its small grain size, and because the oxide is thicker than on other samples where the grain boundaries have been studied. Preferential attack will also occur at the interfaces between the oxide particles and the matrix for similar reasons.

The faceting of the edges of the metal grains is unsurprising for grains that have low order orientations parallel to the surfaces as a flat surface will have a lower energy. In the areas where the metal has been penetrated, the two oxide films will be separated and the sides of the hole will become free surfaces. Surface diffusion is more rapid than grain boundary diffusion at these temperatures and will have a lower activation energy and the free energy drop brought about by the change from a disordered surface to a flat surface will drive mass transport via surface diffusion. The planes that the surfaces will transform into will be those of lowest free energy, that is the most closely packed (106). The $\{110\}$ planes are the most closely packed of the planes in the body centred cubic lattice and, being perpendicular to the foil and parallel to the newly created surfaces, are the most likely to be formed by surface diffusion. The penetration of the foil behind the main edge will be due either to preferential oxidation or to variations in the thickness of the metal. There is no evidence for the latter and no obvious features in the metal that would give rise to the former, there being very few dislocations in the metal.

The particle-like features may be nuclei for the oxide grains that give rise to the other orientations seen in the electron diffraction patterns but no dark field work was carried out to confirm this. The wrinkling of the oxide film will be brought about by the constraints at the edge of the foil. The oxide film is pinned at either end of the area shown and, as the compressive growth stress forces the oxide film to expand beyond the foil edge, the curvature of the edge will cause a lateral stress to exist in the film, parallel to the edge, which will cause the oxide to wrinkle. The magnitude of this lateral stress will not be very large as the curvature of the edge is not great.

The existence of large oxide grains, of the order of 400 nanometres, on the sample shown in figure 3.3.3.4 appears to be a freak event for electropolished samples oxidised in the gas reaction cell yet the back-thinned, mechanically polished samples, such as that in figure 3.3.4.1, all have oxide films with grain sizes that are larger than those on the electropolished samples. These large grains could arise either

from larger oxide nuclei spacings or from a more frequent coalescence of the growing nuclei; grain growth will be negligible at these temperatures. There was no difference in the preparation procedure for this electropolished sample relative to the others and so no reason for the spacing of the oxide nuclei to change; the mechanically polished samples could have more widely spaced nuclei but there should be more sites for nucleation than on the electropolished surfaces, the surface being rougher and having a higher dislocation density. It is more likely that coalescence of the oxide nuclei has occurred.

The general preference for the oxide grains to grow with their basal planes parallel to the metal $\{111\}$ planes is a synthesis of a large number of specific orientation relationships, all of similar strengths; the strength of the relationship being the magnitude of the energy saving that occurs if the two materials were joined according to the orientation relationship. Some of these orientation relationships will result in larger energy savings than others, though, even if it is only by a small amount and, in a perfect interface, these stronger relationships would predominate. In this case of epitaxy between the oxide film and the metal surface, all of the nuclei should grow with the same orientation, enabling coalescence of the grains to occur and resulting in a large oxide grain size. If the stronger orientation relationships were weakened, though, the orientations of neighbouring nuclei need not be similar and coalescence would be unlikely, resulting in a small grain size.

For oxidised samples that do not have a large oxide grain size, there must be some factor that reduces the driving force for epitaxy. The main factor that weakens the driving force for epitaxy at an interface is contamination by adsorbed atomic species or molecules or by segregants. The abundance of segregants in the metal should not vary between samples annealed at temperatures above 1200°C and, because the variation in the grain size of the oxide seen on the samples used is quite large, this implies that segregants are not the major interface weakeners. The variation in the strength of the orientation relationships, as measured by the oxide grain size, indicates that the contamination of the surface of the metal varies from sample to sample. As the samples were cleaned individually prior to oxidation this is possible. The contamination, though, appears not to be able to destroy the preference for the oxide to grow with its $\{0001\}$ plane parallel to the metal $\{111\}$ plane completely, only weaken the strengths of specific relationships.

The scanning electron micrograph of the oxide film on the back-thinned sample in figure 3.3.4 shows that it is thin and generally flat. The two humps indicate that, even at this early stage, the oxide film is beginning to decohere. The small specks visible in the transmission micrograph, but not in the scanning micrograph, could be tiny whiskers that were not resolved in the latter image although identification from the transmission electron micrograph is difficult because the film is

being seen in transmission from above; it is assumed that they are present in the area photographed as the two micrographs, figures 3.3.4.1 and 3.3.4.4, are from different areas of the same sample. Spallation of the oxide film has occurred; the area of re-oxidation indicates that spallation occurred immediately on cooling. Very little oxide has formed, implying that the temperature at which the oxidation has taken place is lower than that at which the main oxide film formed; the sample will cool in approximately the same time that it took to heat up which, in this case, is the period of the oxidation. If the film had spalled when cold, no oxide would have been visible.

The cold work introduced into the surface of the mechanically polished specimens does not appear to be altering the growth morphology of the oxide although there may be some effect on the growth rate as reported (107) for nickel. This cannot be confirmed. The large numbers of dislocations in the surface of the mechanically polished specimens could have an effect on the epitaxy between the oxide and metal but this does not appear to have occurred. No investigations were carried out on mechanically polished samples that had been annealed to remove the cold work and, so, the maximum possible size of initial oxide grains on mechanically polished samples cannot be stated.

The samples of chromium-implanted chromium oxidised in the gas reaction cell are very similar to the samples of unimplanted chromium. The oxide has a similar grain size and is seen to be wrinkled. The existence of circular nodules in the film implies that the stress in the oxide film is uniform in all directions in the plane of the oxide. This will not be brought about by shape constraints during cooling, as the wrinkles might have been, as shape constraints would give rise to directional stresses. The orientation of the oxide grains produces a fibre texture with the Cr_2O_3 $\langle 0001 \rangle$ parallel to the Cr $\langle 111 \rangle$. If only the strongest of the many orientation relationships that make up this general preference were operating, then coalescence of neighbouring nuclei would cause the oxide grains to grow to the size of the underlying metal grains. This would still produce a fibre texture in the oxide on a macroscopic scale as the grains in the chromium-implanted metal are arranged in a fibre texture. The oxide grains are smaller than the metal grains, implying that more than one of the orientation relationships between oxide and metal is operating. The areas where the metal foil is penetrated behind the main interface are rounded rather than faceted as in the unimplanted metal. This is probably due to distortions in the lattice caused by dislocations and point defects.

The oxidation of the cerium-implanted chromium foils in the gas reaction cell is governed by the film on the surface of the specimens. This comprises the native oxide film and, possibly, the residues of the protective lacquer. The lacquer should be removed completely by the acetone that was used to clean the foils but there may

have been a slight residue left. The two samples in figures 3.3.6.1 and 3.3.6.4 were produced in nominally identical manners and were oxidised under similar conditions. The widespread crystallinity of the film on the sample in figure 3.3.6.4 shows that the native oxide film has crystallised but there is still an amorphous background apparent on its electron diffraction pattern. The film on the sample in figure 3.3.6.1 is crystalline to a much lesser degree and its electron diffraction pattern has an amorphous background. The sample in figure 3.3.6.4 been oxidised at a slightly higher temperature than the sample in figure 3.3.6.1 and should have a greater degree of crystallinity in the film on its surface but the difference should be small; certainly not as large as the difference between these two samples. This would argue that the native oxide films on both samples had crystallised to the same extent but that there was far less of the oxide film left after thinning on the sample in figure 3.3.6.1. This will explain why the former sample contained CeO_2 whereas the latter did not. This would imply that the amorphous background on the diffraction pattern was from another source and the most likely source is the protective lacquer. On metallic surfaces, when there has been a residue of lacquer left by insufficient cleaning, the lacquer generally breaks up and becomes entrapped locally (108). The amorphous film on the oxidised gas reaction cell samples appears to be continuous. The surface of the cerium-implanted samples, when the lacquer is applied, is covered with an amorphous oxide layer and the lacquer may bond more strongly with this and stay intact. Indeed, the native oxide layer has been found to bond more strongly to the lacquer than to the metal surface after electropolishing. Eventually the lacquer would burn off if subjected to further oxidation.

The electron diffraction patterns in figures 3.3.6 and 3.3.6 show that the native oxide in the areas of the film that are not in contact with the metal surface crystallises with a large range of orientations. The nuclei will have formed in the amorphous film without external influence and the oxide does not grow with a fibre texture. This argues that the fibre texture is caused by the interaction between the oxide and the metal surface.

After longer periods of oxidation, the amorphous background on the diffraction patterns disappears and the oxide grains take on an appearance similar to those formed on other materials. The grain size is similar to, or smaller than, the grain sizes of the other films; the smaller grain size is probably due to the crystallising film having more closely spaced nuclei than an oxidising metal surface. The electron diffraction patterns show that, when in contact with the metal surface, the oxide film on the cerium-implanted metal grows with the same crystallographic relationship that is found on the unimplanted specimens.

4.7 Oxide Thickness

The interference colours seen in the light microscope can be used to derive an approximate value for the thickness of the oxide films for which they occur. The colours are produced by the interference of light reflected from the upper surface of the oxide and from the metal surface, for adherent oxide, and are the result of one frequency being removed from the visible spectrum. The phenomenon is discussed by Evans (109), who gives a list of the colours usually seen, given in table 13. Light is incident vertically onto the surface of the oxide, which is flat, and destructive interference will occur when the path difference between the rays reflected from the two surfaces is equal to half of a wavelength. The phase change on reflection is nominally identical for the two surfaces. Thus, destructive interference occurs for:

$$2nt = \left(m + \frac{1}{2}\right)\lambda \quad 30$$

where n is the refractive index of the oxide, m is an integer and λ is the wavelength of the light. The thickness of the oxide can be calculated by determining which wavelength of light has suffered destructive interference, from the resulting colour, and then applying equation with the requisite value of m . For example, from table 13, a mauve colour is produced by the destructive interference of the yellow wavelength of white light and, according to the table given, this must be a first order interference, that is m equal to one. If the wavelength that suffers destructive interference is in the infra-red or ultraviolet, then no interference colour will be seen; the oxide will take on its own colour.

A graph of the range of oxide thicknesses at which destructive interference occurs, for each value of m , is given in figure 4.2. The silvery hiatus is due to the large gap in oxide thicknesses between 75 and 120 nanometres where there is no destructive interference of light in the visible range. In this gap, constructive interference of light can occur and could give rise to colours by an enhanced intensity of the wavelength at which constructive interference occurs. Evans does not mention any colours seen in the silvery hiatus, so the contribution from constructive interference cannot be major. As the oxide thickness rises, more than one interference condition will be satisfied by a specific thickness and the oxide will appear a colour that is a composite of the different interference colours, usually shades of green or brown. For the thickest oxides, the film will become opaque, probably appearing grey before full opacity is achieved.

A table of the colours seen on each of the specimens examined by light microscopy is given in table 14 together with the proposed oxide thicknesses. The oxide thicknesses given here can only be approximate values as the technique is crude

Table 13

A table giving the colours of oxide films of increasing thickness due to the destructive interference of one or more of the wavelengths in the visible spectrum. The colour of the wavelength suffering destructive interference is correlated with the colour of oxide film that this gives rise to for each order of interference (109).

Colour removed	Interference colour	m
Blue	Yellow	0
Green	Orange	0
Yellow	Mauve	0
Red	Blue	0
	Silvery hiatus	
Blue	Yellow	1
Green	Red	1
Yellow	Blue	1
Red, Blue	Green	1,2
Blue	Yellow	2
Green	Red	2
Red, Blue	Green	2,3
Green, Blue	Red or Brown	3,4

Figure 4.2

A figure showing the thicknesses of oxide films that give rise to interference colours using equation 30. The lines are calculated from the wavelengths in the visible region of the electromagnetic spectrum for each order of destructive interference and give a connection between thickness and colour. Indicated for each order of interference are the colours that suffer destructive interference at specific oxide thicknesses.

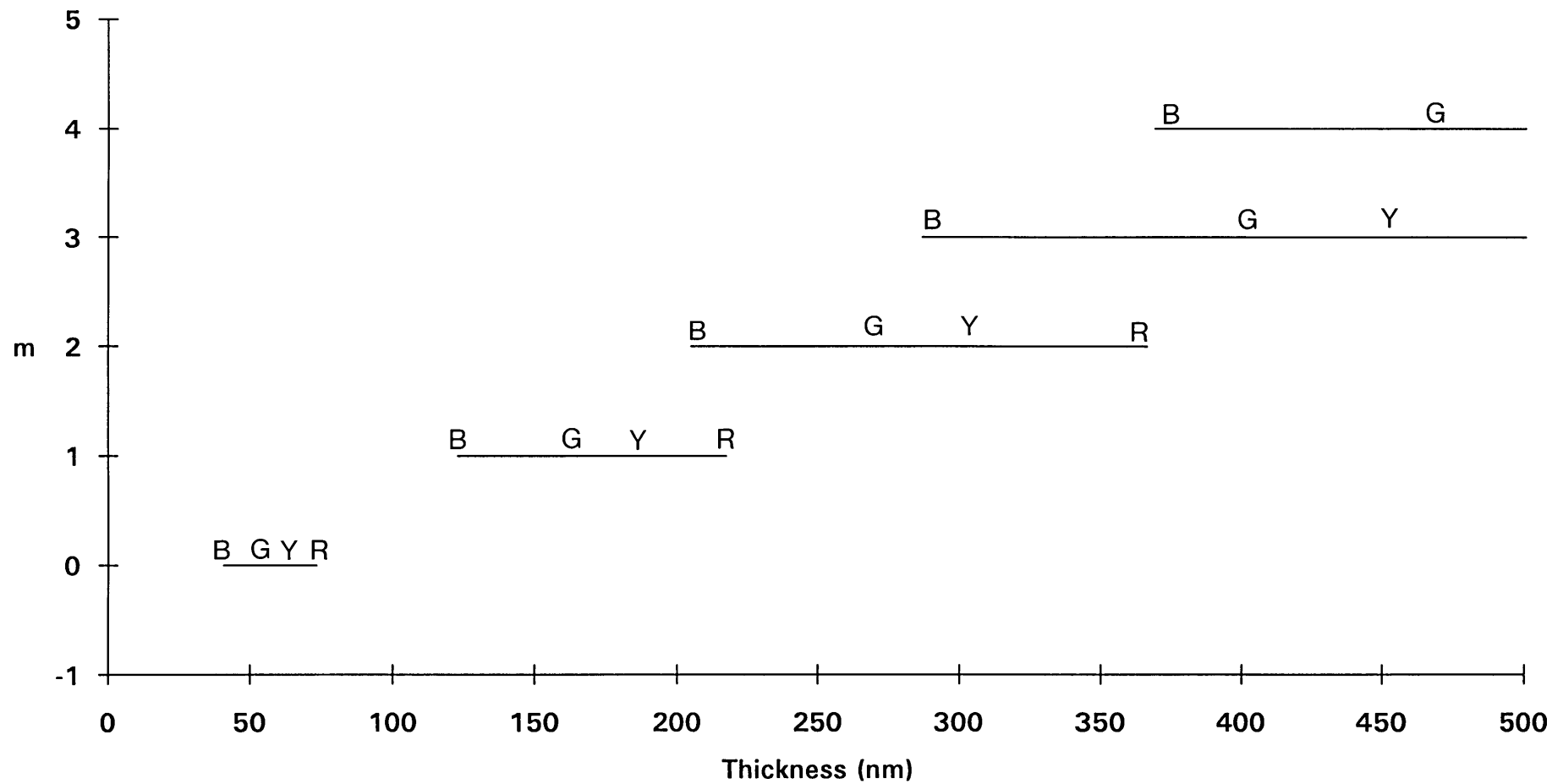


Table 14

A table of the interference colours seen on the samples oxidised in the oxidation rig and the proposed thicknesses that they correspond to. The thicknesses are calculated by correlating the colours in table 13 with the thicknesses in figure 4.2.

Temperature in °C	Time in minutes	Colour observed in light microscope	Thickness in nm.
Unimplanted			
750	10	Yellow, green	220 - 250
850	1	Green, yellow, red	220 - 250
850	5	Yellow, red, blue, green	220 - 250
850	15	Brown, green	> 450
950	1	Grey	> 450
950	3	Dark brown	> 450
950	5	Opaque	> 450
Cr-implanted			
850	1	Yellow, blue	160
850	5	Orange, red	260
950	1	Green, blue	220
950	5	Dark brown	> 450
Ce-implanted			
850	1	Blue	70
850	5	Blue, red	170
850	10	Self-coloured, grey	> 450, 100?
950	1	Blue	180
950	5	Light orange/brown	> 450

and fairly uncertain. For the unimplanted specimens, the yellow/green combination appears only for one thickness, around 230 nanometres, and the extra colours seen on other oxide films will be the colours nearest to this thickness. It is simple to assign a thickness condition to the brown and opaque oxide films, that they must be thicker than the point at which three conditions overlap, but to be more exact than this requires a better knowledge of the optical properties of chromia than is available at present. The grey colour of the 950°C, 1 minute sample is either due to the silvery hiatus or to the oxide becoming opaque. The silvery hiatus occurs for oxide films of thicknesses between 70 and 120 nanometres. At maximum, this is half of the thickness of the 850°C, 1 minute sample and, if the 950°C, 1 minute sample were this thickness, it would imply an extremely large variation in the oxide growth rate. The grey colour must, thus, be due to the oxide becoming opaque. As with the brown colour, the thickness of this sample can only be given as greater than 450 nanometres.

The chromium-implanted specimens can be assigned colours in a similar manner. The 850°C, 1 minute sample is mainly yellow with blue stippling; the stippling is likely to be thicker than the main oxide film and, so, the oxide is assigned a thickness of around 160 nanometres. The orange/red combination on the 850°C, 5 minute sample is likely to be from the lower of the two possible orders, the thickness then would be equivalent to that on the unimplanted sample oxidised under the same conditions. It is slightly more difficult to assign thicknesses to the cerium-implanted specimens. Two of the samples have blue interference colours and, as there are two possible thicknesses at which blue occurs, the sample oxidised at 850°C is assumed to have a thinner oxide film than the sample oxidised at 950°C, giving the former a film thickness of 70 nanometres and the latter a film thickness of 180 nanometres. The red/blue oxide film on the 850°C, 5 minute oxidised sample is probably due to the second order condition. As with the brown and grey films on the other specimens, the only comment that can be made regarding the brown and grey films on the cerium-implanted specimens is that they are thicker than 450 nanometres. It is possible that the grey film on the 850°C, 10 minute oxidised sample is due to the thickness of the oxide corresponding to the silvery hiatus; the 850°C, 1 minute specimen is thinner than this thickness and the 850°C, 5 minute sample is not very much thicker than the 120 nanometres that corresponds to the maximum of the silvery hiatus.

The unimplanted specimens show a distinct separation in their thicknesses, half of the specimens being around 250 nanometres thick and the others being greater than 450 nanometres thick. No comment can be made regarding the relative thicknesses of the thicker oxide films but there should be a larger variation in the thicknesses of the thinner set. According to the Wagner theory of scale growth, the 850°C, 5 minute

sample should have an oxide film that is $\sqrt{5}$ times as thick as the film on the 850°C, 1 minute sample; this is obviously not so. This implies, either a large error in the measurement technique, that is the interference colours, or a large variation in the rate of growth of the adherent oxide films. Although the absolute values of the thicknesses as measured by the interference technique will not be very accurate, the relative values should be accurate, which implies that the parabolic rate constant can vary by at least a factor of two for these short time periods. This should not be surprising given the variation found by previous workers, illustrated in figure 1.4.2, although less variation would have been expected from adherent scales. This variation is not as obvious for the implanted specimens where more variation is seen although the increase in thickness between the chromium-implanted specimens oxidised at 850°C for 5 and 10 minutes is far more than the $\sqrt{2}$ factor that would have been expected. This much increased thickness is a reason for suspecting that the grey film on the 850°C, 10 minute sample is actually due to the silvery hiatus.

Comparing the implanted specimens with the unimplanted specimens, it is seen that the chromium-implanted specimens are generally thinner than their unimplanted counterparts, with the exception of the 850°C, 5 minute specimen. The cerium-implanted specimens are thinner than both, with the exception of the 850°C, 10 minute specimen, and the 850°C, 1 minute specimen is very much thinner, possibly reflecting the fact that its initial oxide layer was amorphous and would take some time to crystallise. If the grey film on the 850°C, 10 minute sample were due to the silvery hiatus, then all of the oxide films on the cerium-implanted samples could be said to be thinner than the films on the other samples. After longer times, after the cerium should have had its slowing effect on the oxide growth rate, the oxide film on the cerium-implanted sample is seen to be thinner than that on the unimplanted sample oxidised under similar conditions. It is possibly not a great deal thinner than the oxide film on the equivalent chromium-implanted sample, both films on the implanted specimens being brown, but the brown of the cerium-implanted sample is lighter and more orange, as would be expected for a thinner film.

The thicknesses of the oxide films as calculated from their colours, table 14, can be compared with the mean grain size of the oxide grains in each film, table 9. It can be seen that the films are thicker than the mean grain diameter of the oxide grains implying that the films are more than one grain thick. The oxide films also appear to be split into two thickness ranges: those over 200 nanometres thick and those over 400 nanometres thick. Those over 400 nanometres thick are also the oxide films in which the large oxide grains appear, with the exception of the 850°C, 10 minute oxidised cerium-implanted sample. This is consistent with the idea that the initial oxide film forms and grows with oxide grains approximately 50 nanometres in size. This first layer will be more than one grain thick. There is then growth of a second

layer of grains that are much larger than those in the first layer, seemingly unconstrained in their growth; this causes the increased thickness apparent in some of the samples and gives a reason for the large jump in film thickness.

On all samples but the cerium-implanted chromium, the initial oxide layer establishes a grain size of around 50 nanometres very rapidly. It would seem that this then stabilises while the second layer of grains grows more freely. This may be due to the pinning effect on the grain boundaries of the large outward flux of cations that supplies the oxide-gas interface with material. Any increase in the grain size of the oxide closest to the metal interface will mean a decrease in the number of grain boundaries and, assuming that the boundaries were saturated with respect to the cation flux, a decrease in the flux of metal ions. Transverse sections of oxide formed after longer times show the initial oxide layer formed on pure chromium as reaching a size of 100 - 200 nm (79,110). implying that the grains nearest the oxide/metal interface eventually grow to the size of those in the second layer.

4.8 Oxide Adherence

The oxide films formed on mechanically polished samples of standard-annealed chromium are generally adherent after short periods of oxidation but every sample shows some signs of buckling or spallation of the oxide scale. The buckling of the oxide scale occurs during oxidation, rather than on cooling, as is shown by the multiple oxide layers that form on some samples. The method whereby buckles in the oxide film form is shown in figure 4.3, after Evans, Crumley and Demaray (42). A prerequisite for buckling is an interfacial separation larger than a critical radius; figure 4.3.1 shows the situation when the interfacial separation, radius r , is smaller than this critical size. The compressive stress is lateral only and there are neither normal nor shear stresses at the interface to cause the separation to grow. If the surface of the metal were convex rather than flat, then there would be a normal component of the stress and, thus, a driving force for growth of the separation. If the radius of the separation were to be larger than the critical radius, then the film would fail by buckling as shown in figure 4.3.2.

The critical radius for buckling, c , is given by Evans, Crumley and Demaray (42) as:

$$c^2 > \left[\frac{kEt^2}{12\sigma(1-\nu)^2} \right] \quad 31$$

where k is a constant approximately equal to 14.7, E is the Youngs Modulus of the oxide film, t is the thickness of the oxide film, ν is Poisson's Ratio for the oxide film and σ is the compressive stress in the oxide film. Thin films are more likely to buckle

Figure 4.3

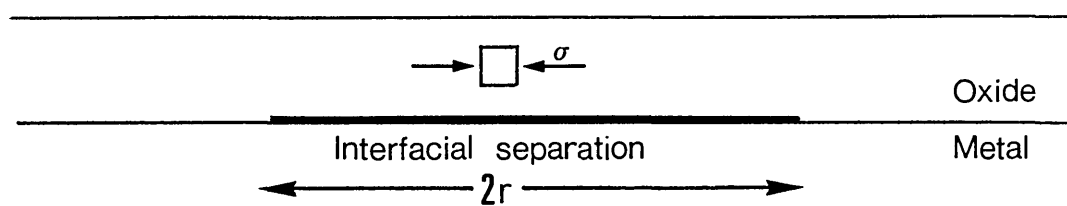
A figure showing the oxide film that forms on chromium and defining the interfacial separation prior to and after buckling. Also shown is the film buckling at a buried particle.

4.3.1 The oxide film prior to buckling showing the lateral compressive stress in the film and the interfacial separation.

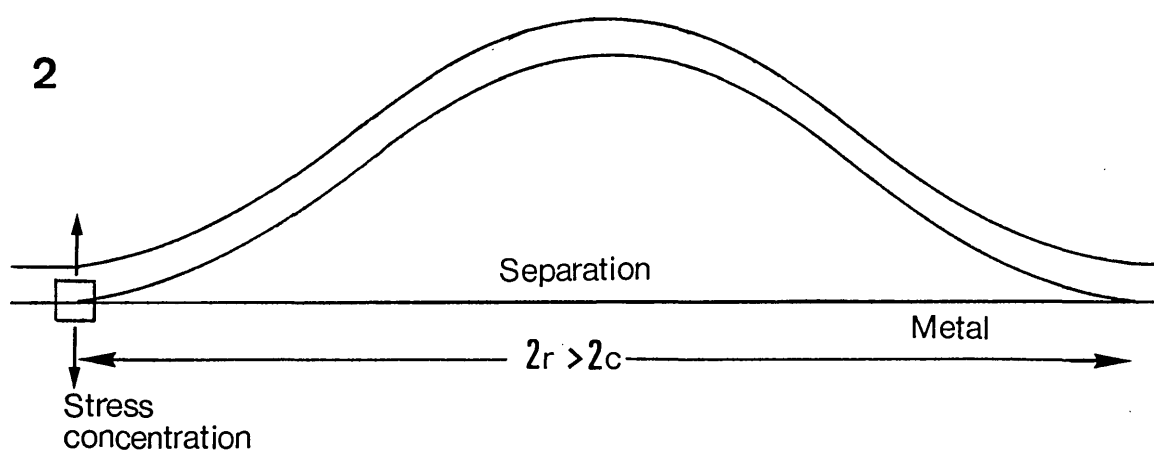
4.3.2 The oxide film after buckling showing the interfacial separation and the stress concentration normal to the surface.

4.3.3 The method whereby a buried particle can induce sufficient separation at the metal/oxide interface that the film buckles in the presence of a lateral compressive stress.

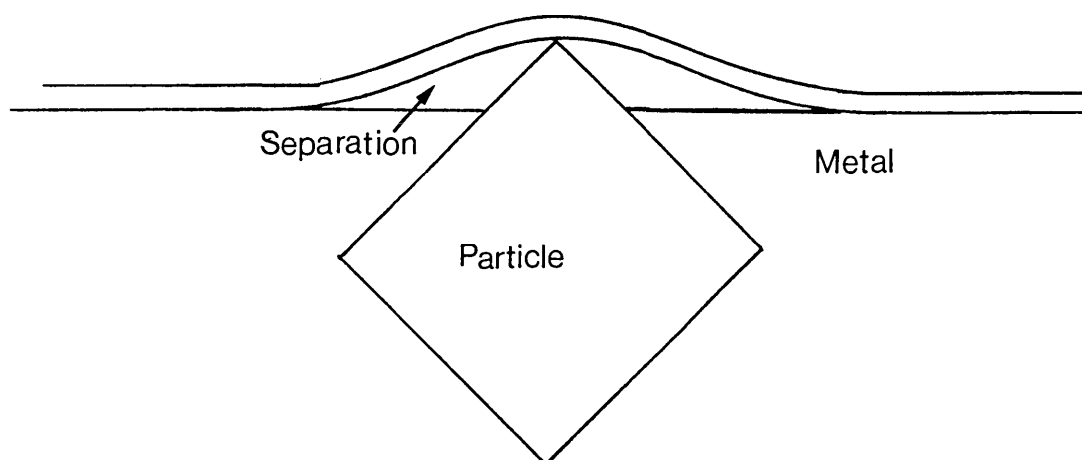
1



2



3



for a given stress than thick films as the critical radius is smaller. Creep buckling can initiate at lower stresses than elastic buckling but this has not been quantified (41).

For chromia, Stout, Gerberich, Lin and Lii (3) give $E=293\text{GPa}$ at room temperature and the compressive stress not due to thermal expansion, here assumed to be the growth stress, as approximately 3GPa . Robertson and Manning (43) give $\nu=0.29$ and the yield stress of chromia as 5GPa . As the buckling occurs at high temperature, the value for Young's Modulus will be lower. The temperature dependence of E is not known but, if the dependence of the shear modulus is used as a rough approximation, a value for E of 254GPa is gained. The temperature dependence of the shear modulus is given by Ashby (111). This gives equation 31 as

$$c > 14t \quad 32$$

For oxide films of approximately 220 nanometres thickness, buckling has already occurred which implies that the radii of separation of the buckles, r , could have been lower than 2 micrometres. Buckling relieves the lateral compressive stress in the oxide film but increases the driving force for growth of the interfacial separation due to the stress concentration that now exists at the crack tip. The oxide film is thick, so the upper surface of the buckled oxide film will be under a slight tensile stress which could lead to an increase in the compressive stress if microcracks formed.

Having buckled, with a constantly increasing compressive stress, the area of deformed oxide film will expand either laterally by further cracking of the interface, if the interface is uniformly weak, or vertically if the interface is only weak in isolated patches and the interface crack will not grow. The strain rate during the initial buckling and the following continual deformation will be slow and the major relaxation mechanism will probably be Coble creep, unless the oxide film cracks. The grain sizes of the films are very small and grain boundary diffusion is rapid at these temperatures. The only problem that may arise is that, in the area of the scale where most relaxation is needed, that is at the point where the oxide film meets the metal surface, the flux of chromium ions in the relaxation mechanism will be counter to the flux of chromium ions involved in the oxidation process. For very thin oxide films, where the film is at most two grains thick, deformation may occur by grain boundary sliding. Very little is known about the deformation behaviour of very thin oxide films and this is only speculation. Vertical expansion will lead inevitably to through-scale cracking as the scale thickens and as the curvature required for failure drops.

There is evidence for cracking of the oxide films on electropolished surfaces from the multiple oxide layers seen in figure 3.4.3.4 but the oxide layers on mechanically polished surfaces can be seen to be single layered, from the area that has

spalled in figure 3.4.2.3. From the thickness of the initial oxide layer on the sample in figure 3.4.3.4, the through-scale cracking has not occurred immediately on buckling. This could be explained if the strain rate due to the growth stress experienced by the oxide film after buckling was larger for electropolished samples than for mechanically polished samples, due to a higher growth rate on the electropolished samples. This would also imply that the relaxation mechanisms operating in the oxide films are only just coping with the strain rate experienced by the oxide films on the mechanically polished specimens.

On cooling, the buckled oxide will encounter stresses at far higher strain rates than previously and brittle cracking will probably occur at the points on the buckle where the stress concentration is highest, that is where the radius of curvature of the oxide film is the smallest (42). Evans and Cannon (41) discuss the mechanism whereby buckled oxide spalls and conclude that spalling is due to the interfacial crack being deflected to the surface of the oxide film in a mode II failure. They go on to give two conditions that should be satisfied before spalling occurs. The first is that the initial crack radius, r , should be sufficient for buckling, equation 32, and the second is that the rate of strain energy release, G , should exceed the fracture resistance, G_c , of the film. G is given by:

$$G = \frac{\sigma^2 t (1 - \alpha)}{E(1 + \nu)} \quad 33$$

where α is a constant, equal to 0.39 for Cr_2O_3 . They also give a critical radius, c' , above which they say that the stress intensity factor, K_{II} , becomes negative and spalling is predicted:

$$c' = 1.9t(E/\sigma)^{1/2} \quad 34$$

The magnitude of the stress experienced on cooling has been calculated by Stout, Gerberich, Lin and Lii (3) and is not much greater than the measured growth stress (3). Examination of the short term oxidation samples indicates that spallation has occurred consistently at the point where the buckled oxide meets the metal surface which implies that the mode of failure of the buckled oxide is that discussed by Evans and Cannon (41).

The equations given above can be used to determine the stress experienced by the buckled oxide. The largest stress will have been experienced by the buckled oxide that has spalled. The circles of spalled oxide have a mean radius of approximately 2 micrometres and the mean thickness of the oxide films in which they are seen is approximately 220 nanometres. This gives a compressive stress in the film, from equation 34, of approximately 3GPa, which is lower than the yield stress for chromia,

but stress concentration at the crack tip will probably raise the actual stress above the yield stress. There is no value of G available for chromia, but the value for alumina should not be very different; it may be slightly higher as the Young's Modulus for alumina is higher than that for chromia. Alumina has a G value of 20Jm^{-2} (112) which gives a stress on buckling, from equation 33, of 8.5GPa . This is much higher than the value derived from equation 34. which implies that the value of G for chromia may be less than that for alumina.

Robertson and Manning (43) derived the yield stress for chromia by scaling the value for alumina, which they derived from the Vickers Hardness value for alumina. The yield stress for alumina gained by Robertson and Manning (43) was 6.5GPa ; this is to be compared to a value for the yield stress of alumina quoted by Anderson, Leaver, Rawlings and Alexander (113) of 11.3GPa . The yield stress of chromia therefore may be higher than that given above and, thus, the stress concentration at the crack tip may also be higher.

Stout, Gerberich, Lin and Lii (3) calculated the stress due to the mismatch in the thermal expansivities of chromium and chromia to be approximately 1GPa which gives the growth stress to be approximately 2GPa for the spalled oxide. This is lower than the mean value determined by Stout, Gerberich, Lin and Lii (3) but is within the range of their variation in the overall stress. The buckled oxide may have spalled because it could no longer relieve the growth stress by growing outwards. The nodules are small, much nearer in width to the thickness of the oxide film than the larger buckles, and are surrounded by adherent oxide which constrains them to grow vertically. This would imply either that those buckles that did not spall had relieved the growth stress sufficiently that the extra stress caused by the thermal expansion mismatch did not take them beyond the yield stress after the stress concentration at the crack tip had been included or that the stress concentration was not as great for those convolutions.

Very little of the buckled oxide has spalled, which implies that the stress generated during cooling is only just sufficient to cause through-scale cracking in the buckles that are the most constrained, for these thicknesses of oxide. The largest constraints are found on buckles with the steepest sides, that is those convolutions that have grown proportionally more in the vertical direction than laterally. These will be in areas where the oxide surrounding the buckle is most adherent. This will explain why the largest numbers of circles of spalled oxide are found on the 850°C , 5 minute oxidised sample. The buckled oxide films on the electropolished samples have been found to have similar initial slopes to the unspalled buckled oxide on the mechanically polished samples and they have probably managed to relieve the majority of the compressive stress.

As already mentioned, buckling requires an initial separation between oxide and metal and the origin of this separation is in some doubt. The analyses of buckling (41-44) assume the existence of an interfacial separation, often without much comment as to its origin. One method put forward is that the separation forms by the coalescence of vacancies at ledges (41); this requires a normal tensile stress if an interfacial crack is to develop and there is not sufficient information to determine whether this is a viable mechanism. Particles in the surface provide excellent sites for buckling as shown in figure 4.3.3. The oxide film will not bond strongly to the particle and, thus, both an interfacial separation and a normal component of the stress are provided. This may imply that the oxide film will buckle at particles before buckling at smoother areas of the metal surface where these are not in evidence. In order to provide the interfacial separation, the particles must be buried, probably during polishing, so that they are revealed as the metal recedes during oxidation. The particles are approximately 2 micrometres in diameter, determined from the size of the pits, and, thus, the largest thickness of oxide that could initiate buckling for this critical radius is 70 nanometres. This is feasible as oxide ridges have been seen in oxide 12 nanometres thick (37). If the oxide film is sufficiently rigid to buckle at this thickness, then the critical radius could be as small as 200 nanometres. This, however, is still too large to be accounted for by features on an atomic scale such as dislocations and ledges.

Evans, Crumley and Demaray (42) suggest that vacancies will not coalesce at interfaces but that the separation could be caused by voids produced at sites of residual tension. These are usually found in areas where the metal surface undulates. The surface of the mechanically polished chromium does not undulate to a large extent but the magnitude required for void formation is not known. They also suggest that asperities might be sources of interface crack nucleation, in a similar manner to the mechanism explained above for particles. In general, the discussions on the sources of interfacial separation are defeated by the lack of data as to the behaviour of thin oxide films and very little more can be said regarding the nucleation of buckles without further information.

The sources of the interfacial separations that give rise to convolutions seen on the oxidised chromium surfaces other than the nodules are not obvious. Apart from particles, which must initiate buckling, and pits, which do not, there are very few other surface features that are sufficiently large to provide a separation larger than the critical radius. Ridges appear to have been initiated at grain boundaries in figure 3.4.1.6, although this is no guarantee that the grain boundary was responsible for their initiation. In figure 3.4.2.3 an area of buckled oxide has spalled revealing a grain boundary and the remaining buckled oxide appears to follow the grain boundary. The large buckled area at the near end of the boundary appears to have

been initiated by the particle in its centre and the grain boundary may just have been a line of weakness that the interfacial crack could follow. There are areas of buckled oxide on samples, such as that shown in figure 3.4.1.5, that are transparent and do not have a visible initiator. This may indicate that vacancy condensation has occurred but there is no evidence of void formation beneath any of the spalled areas. The buckle initiator may be concealed by a second oxide film formed after through-scale cracking of the buckled oxide film. The sources of buckle initiation are worthy of investigation because, if the initiators could be suppressed or removed, then buckling would not occur.

The morphology of the buckling is quite varied on the mechanically polished samples. The various forms that appear: the intragranular star-shaped convolution, the grain boundary ridge, the small nodule, the intragranular finger-like buckle, the occasional area of more general non-adherence where the oxide film has bulged, fall into two categories: those associated with major non-adherence and those associated with limited non-adherence of the oxide film. For example the star-shaped buckles on the 950°C, 1 minute sample are isolated and infrequent, implying that they are the product of a rare decohesion of the oxide film; they are never seen in large groups. The intragranular finger-like buckles on the 850°C, 1 minute sample are either joined or are close and appear frequently implying that the decohesion is more general; they are never seen in isolation.

The distribution of the oxide features associated with the more adherent oxide films are intimately linked to the features that initiated them. Unfortunately, these are generally hidden by the oxide. The areas of spallation reveal the surface of the metal but the mechanisms for buckle initiation can still be ambiguous as has already been mentioned. The circles on the 850°C, 5 minute sample appear to have pits or particles at their centres which do not correspond with features in the surface of the metal prior to oxidation; there are only a very few circles of spalled oxide that do coincide with features that were on the surface prior to oxidation. These new features are probably particles; no voids have been found in the surface layer of the unimplanted material by transmission electron microscopy implying that revealed pits would be unlikely. If the revealed features are particles, then this would link the circles of spalled oxide to particles in the surface, implying that the features that were on the original surface, that coincided with circles of spalled oxide, must also be particles. This would agree with their very low frequency of occurrence. Nodules like those seen on the 950°C, 1 minute oxidised sample are likely to be the precursors of the circles of spalled oxide.

The fact that the circles of spalled oxide are only slightly larger than the features that initiated them implies that the buckled oxide that formed above the features prior to spallation did not spread. This implies that the oxide films around

the features must have been strongly adherent to the metal. The nodules seen on the 950°C, 1 minute oxidised sample appear to have very steep sides implying that the oxide surrounding them is adherent. Thus the only direction for the growth of the nodules would be vertically, explaining why, on other samples, they have all spalled when other buckled areas have not.

In the areas where the oxide is flat there is often non-uniform growth associated with different metal grains. This is best illustrated on the 850°C, 5 minute oxidised sample where the oxide film is almost completely adherent. The variation of oxide thickness with underlying grain orientation, indicated by this behaviour, implies that the epitaxy between the oxide and metal is strong. If there was no strong link between oxide and metal, the metal could not affect the oxide growth to such a large extent. This will be an example of the oxide/metal interface at its strongest and the lack of decohesion implies that the cases of non-adherent oxide films are due to the weakening of a fundamentally strong interface. The mechanical polishing technique used to produce the samples that showed good oxide adherence was identical to those that showed a certain degree of non-adherence, implying that the effect of any segregated species was minimal. This may be because they were removed by the polishing procedure. During long term oxidation, re-segregation at a lower surface concentration, may occur. This will lead to weakening of the metal/oxide interface, possibly even leading to decohesion of adherent oxide films, but this will be on a longer timescale than is being considered in this study.

The distribution of the finger-like convolutions associated with general non-adherence differs from the distribution of the other type of convolutions. The latter type appear uniformly across the surface of the sample whereas the former occur in patches. The patches are irregular in shape and size which leads to the conclusion that they are associated with surface contamination rather than the microstructure of the metal surface which would give more geometrically shaped areas. The fact that the patches are both large and irregular, with only low convolutions having been formed, implies that the interface has been weakened sufficiently by the contamination for the interfacial crack that initiated the buckling to run with only a small driving force and that the weakening of the interface only extends as far as the contaminated area. The contamination is likely to have occurred during or after the cleaning process.

The convolutions on the oxidised electropolished surfaces are larger versions of the finger-like convolutions seen on the mechanically polished surfaces, that are associated with general decohesion. This decohesion is similar to that seen on electropolished surfaces by previous authors and implies that the metal/oxide interface is significantly weaker than that on the mechanically polished surfaces that do not have this type of convolution. The increased size of the convolutions on the electropolished samples may be due to the growth rate of the oxide being higher, as

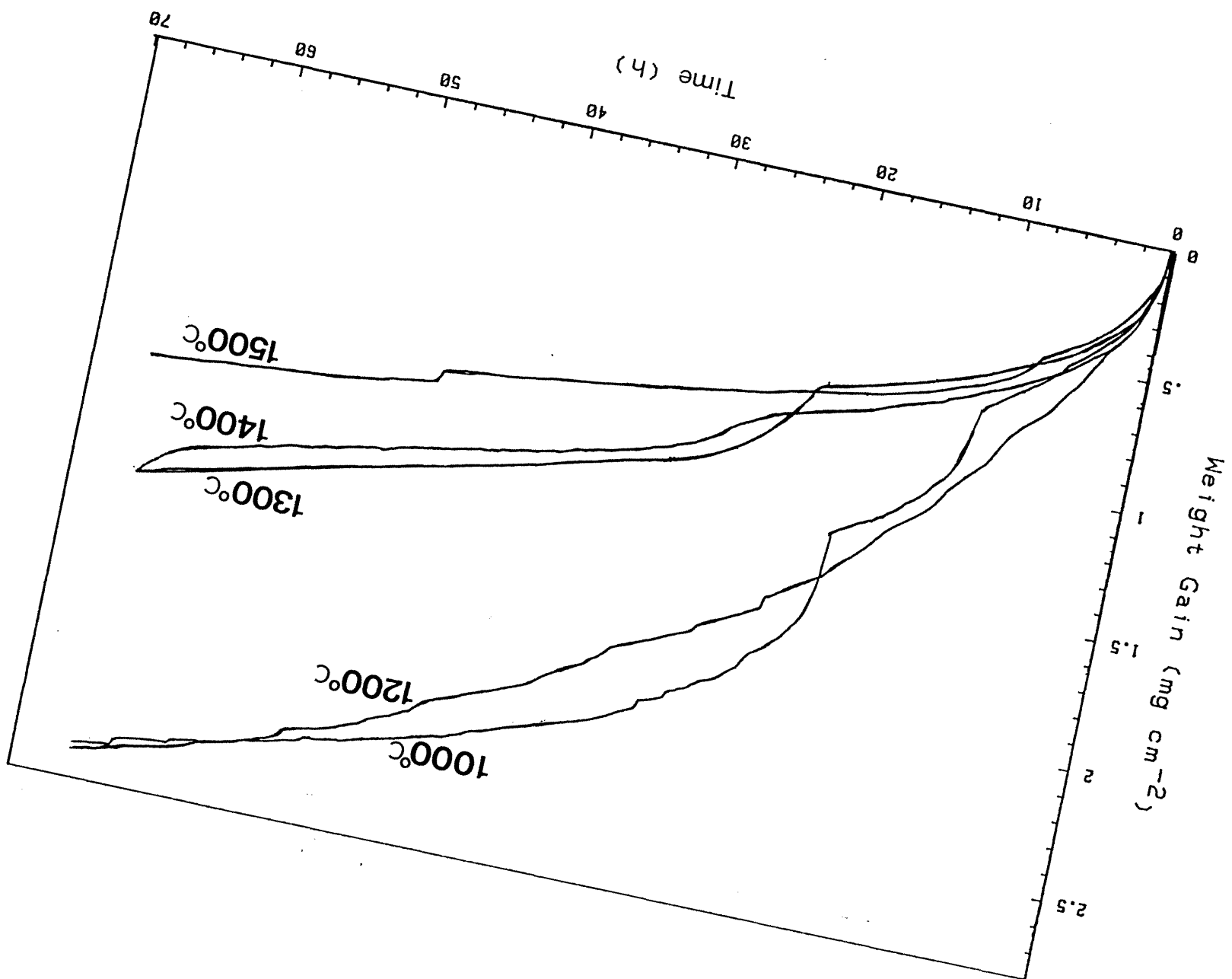
proposed by Lillerud and Kofstad. The extent of the contamination must be larger than on the mechanically polished surfaces since the decohesion extends across the whole surface and not just in patches. The major contaminant is likely to be chlorine from the electropolishing solution; there is no major source of sulphur in the electropolishing process. This implies that interfacial weakening can occur from non-metallic elements other than sulphur and stresses the importance of surface cleanliness. In some cases the grain boundaries and pits are providing keying sites and preventing the spread of the convolutions, most obvious on the 1000°C sample but this keying has only a limited duration as shown by the pits in the oxide on standard-annealed samples that have been raised by the oxide film lifting from underneath. That the interfacial crack that spreads the buckling of the film can travel along such a curved interface as exists in the interior of a pit implies that the interface is very weak indeed.

The 1000°C samples, mechanically polished with alumina, generally have flat oxide films, implying that the defects in the surface of the metal are not sufficient to cause decohesion at these short times. In this material the oxide particles, that are thought to initiate buckling in the standard-annealed metal, are arranged as lines of particles. They are possibly more vulnerable to pull-out in this arrangement than if they were isolated, as in the standard-annealed metal, because, in the line, each particle is only separated by a thin metal sheet and is, therefore, not as well embedded. The sample oxidised for 3 minutes at 850°C has a patch of convoluted oxide in its centre which has spalled to some extent. This is similar to the patches of non-adherent oxide on the standard-annealed material implying that non-adherence is associated with surface contamination. The oxide is also thicker, implying that convoluted oxide films grow more rapidly than undeformed films.

Oxidation for longer periods of time is likely to magnify the differences between the surfaces of the specimens. Figure 4.4 gives the results of oxidation experiments, carried out at Harwell, on coupons heat treated in each of the 3 hour hydrogen-anneal conditions; the reproducibility of these results was good. The coupons were oxidised for 66 hours in 1 atmosphere pressure of flowing oxygen at 850°C. The surfaces of each coupon were mechanically polished using diamond to a minimum particle size of 1 micrometre. The weight gain curves show a distinct difference between the coupons annealed above 1200°C and those annealed below 1200°C; apart from the differences in the absolute weight gains, the coupons annealed above 1200°C showed far less break-away oxidation, indicated by sharp increases in the curves, both in terms of major scale breakdown and the minor breakdowns indicated by the roughness of the curves. This would imply that the coupons annealed above 1200°C had far fewer crack initiation sites and that their metal/oxide interfaces were stronger. That is, the differences in the two sets of weight gain curves are

Figure 4.4

Graphs of weight gain versus time for coupons of electrolytic chromium that have had 3 hour heat treatments in hydrogen at the temperatures indicated. The coupons were oxidised for 66 hours in 1 atmosphere flowing oxygen at 850°C at the Harwell Laboratory.



probably due to the lower numbers of particles in the surface of the coupons annealed at the higher temperatures and possibly to their lower inherent contaminant levels. The 1200°C hydrogen-annealed metal contains as much sulphur as the 1500°C hydrogen-annealed metal implying that segregated species are possibly not as important as the oxide particles in causing increased oxidation.

Except for an apparent increase in the adherence of the thinnest oxide films, the oxide films on the chromium-implanted metal show little difference to the films on unimplanted samples. Although none of the unimplanted samples oxidised were polished using diamond, the lack of difference between the chromium-implanted and the unimplanted metal implies that there would be little difference between the oxidation behaviour of the diamond and the alumina polished samples after short periods of oxidation. It can also be stated that the physical effects of implantation such as the amorphisation of the surface and the subgrain formation have no effect upon the oxidation after short periods.

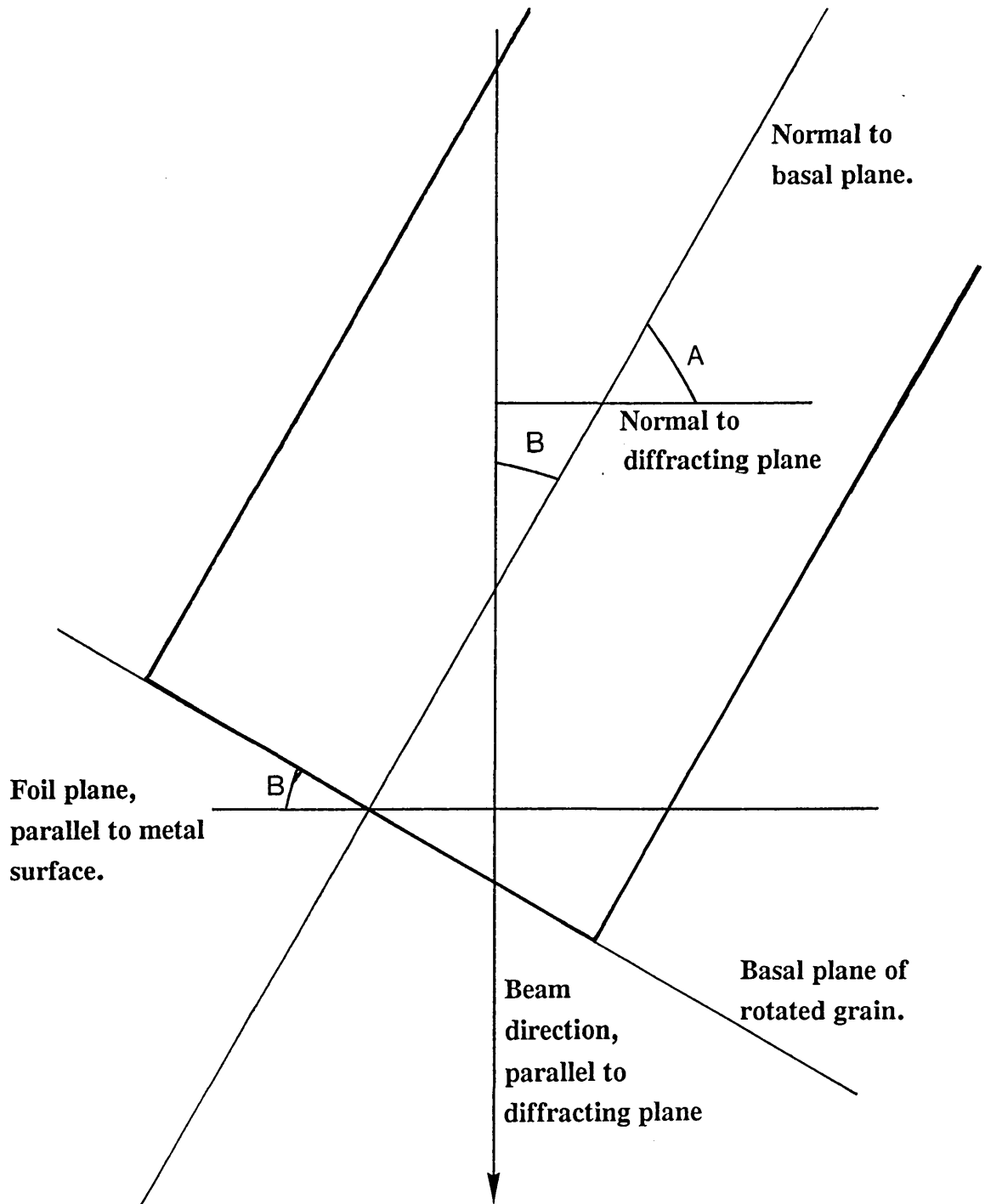
The major difference between the oxide films on the cerium-implanted metal and those on other samples is the complete adherence of the cerium-containing film. Although the chromium-implanted specimens had large areas of adherent oxide, there were nodules or ridges on most of the specimens; the cerium-implanted metal has none of these. This can be attributed entirely to the presence of cerium in the surface layer. The major cause of non-adherence appears to be contamination on the surface of the metal prior to oxidation which implies that the main role of the cerium would be negating the weakening effect of the contamination and ensuring that the radii of the separations surrounding particles in the surface stay below the critical radius for buckling. Whether this negation of the weakening is due to scavenging of the contaminants, to the cerium strengthening the metal/oxide interface bond or a combination of the two mechanisms cannot be determined.

4.9 Oxide Grain Orientations

From the short term oxidation studies it is seen that the initial preference for $\langle 0001 \rangle$ oxide normal to the surface appears in the early stages of growth on all of the substrates studied. As the oxide film develops and thickens and oxide grains nucleate and grow on the metal, this preference diminishes and the whole range of oxide orientations starts to appear. The appearance of each of the different oxide reflections can be correlated, to a certain extent, with their divergence from $\langle 0001 \rangle$. A plane (hkil) that gives rise to a diffraction spot will be virtually parallel to the beam direction and the normal to the diffracting plane will be perpendicular to the beam direction. The geometry is given in figure 4.5. For each of the diffracting

Figure 4.5

A figure showing the geometry of a diffracting grain tilted away from $\langle 0001 \rangle$ normal to the surface of the metal, giving the angles used in determining the angle through which the grain has tilted. The diffracting plane is assumed to be parallel to the beam. The angle between the normal to the diffracting plane and $\langle 0001 \rangle$, A , is found; the angle, B , that the basal plane of the diffracting grain makes with the foil plane is $90^\circ - A$.



planes, the angle A, between their normals and the normal to the {0001} basal plane can be found using equation 35 (114):

$$\cos(A) = \frac{h\sqrt{3}(a/c)}{2\{h^2 + k^2 + (3/4)l^2(a/c)^2\}^{1/2}} \quad 35$$

where a and c are the lattice parameters for Cr_2O_3 . This can be seen to be equal to $90^\circ - B$ where B is the angle to which the grain has tilted away from having $\langle 0001 \rangle$ perpendicular to the surface of the metal. A table of the angles A and B for each of the diffracting planes is given below; the first two planes appear before the others.

Diffracting Plane (hkil)	A	B
{10 $\bar{1}$ 2}	57.7°	32.3°
{11 $\bar{2}$ 3}	61.3°	28.7°
{10 $\bar{1}$ 1}	72.5°	17.5°
{10 $\bar{1}$ 4}	38.4°	51.6°
{11 $\bar{2}$ 6}	42.4°	47.6°
{12 $\bar{3}$ 2}	76.6°	13.4°
{10 $\bar{1}$ 8}	21.6°	68.4°
{12 $\bar{3}$ 4}	64.5°	25.5°

Table 15: A table giving the angles between the normals to the planes that give rise to diffraction spots and the normal to {0001} in order to determine the angle away from {0001} parallel to the metal surface through which the diffracting grain has rotated.

The maximum angle through which the basal plane has tilted is 68° if the ring at 0.158 nanometres is the {1 $\bar{1}$ 08} plane rather than the {12 $\bar{3}$ 2}. Otherwise the maximum angle is 52° , the angle between the normals of the {0001} plane and the {10 $\bar{1}$ 4} plane. The {0006} reflection does not appear on any of the diffraction patterns implying that the crystal is never completely tilted on its side. This is a measure of the influence that the initial preference for $\langle 0001 \rangle$ parallel to $\langle 111 \rangle$ has on the development of the oxide scale structure. As more grains form on the surface of the oxide, the rest of the oxide orientations will be found.

4.10 Energy Dispersive X-ray Spectroscopy

The quantitative analysis of thin foils assumes that the material is sufficiently thin that the effects of absorption and fluorescence are negligible. The absolute thickness at which this holds will vary from sample to sample depending on the elemental composition. For thick samples, though, the effects of absorption and

fluorescence will increase and only an approximation to the composition will be found in the analysis. In the case of chromium and Cr_2O_3 containing trace impurities and implanted cerium, absorption of the trace element X-rays in the bulk of the material will reduce the apparent level of the trace elements in the bulk whilst at the same time making any surface elements, whose X-rays do not suffer absorption, seem relatively more abundant; this is illustrated in figure 4.6. Fluorescence of the cerium by the chromium K X-rays will occur but is unlikely to give a major contribution to the apparent abundance of cerium.

In the oxidised samples, the thickness of the areas analysed is large in most cases so the absorption of X-rays could be significant. The thickness in this case is being estimated from the electron transparency of similar substances and is a relative thickness between the samples. If two samples of oxidised metal were examined consecutively, under nominally identical conditions of beam current and accelerating voltage, a sample 200 nanometres thick would appear darker than a sample that was 100 nanometres thick. On the spectra in figure 3.9.5, the relative heights of the cerium $\text{L}\alpha$ and chromium $\text{K}\beta$ differ from specimen to specimen with the lowest cerium peaks in the spectra from the thickest samples. This could be due to the abundance of cerium in the thicker samples being lower or it could imply that the measured cerium concentration is being reduced by absorption in the thick samples. Those elements that are assumed to be contaminants from the production process would be situated on the surfaces of the foils. This would lead to their abundance being overestimated due to lack of absorption and also due to possible fluorescence by the chromium X-rays.

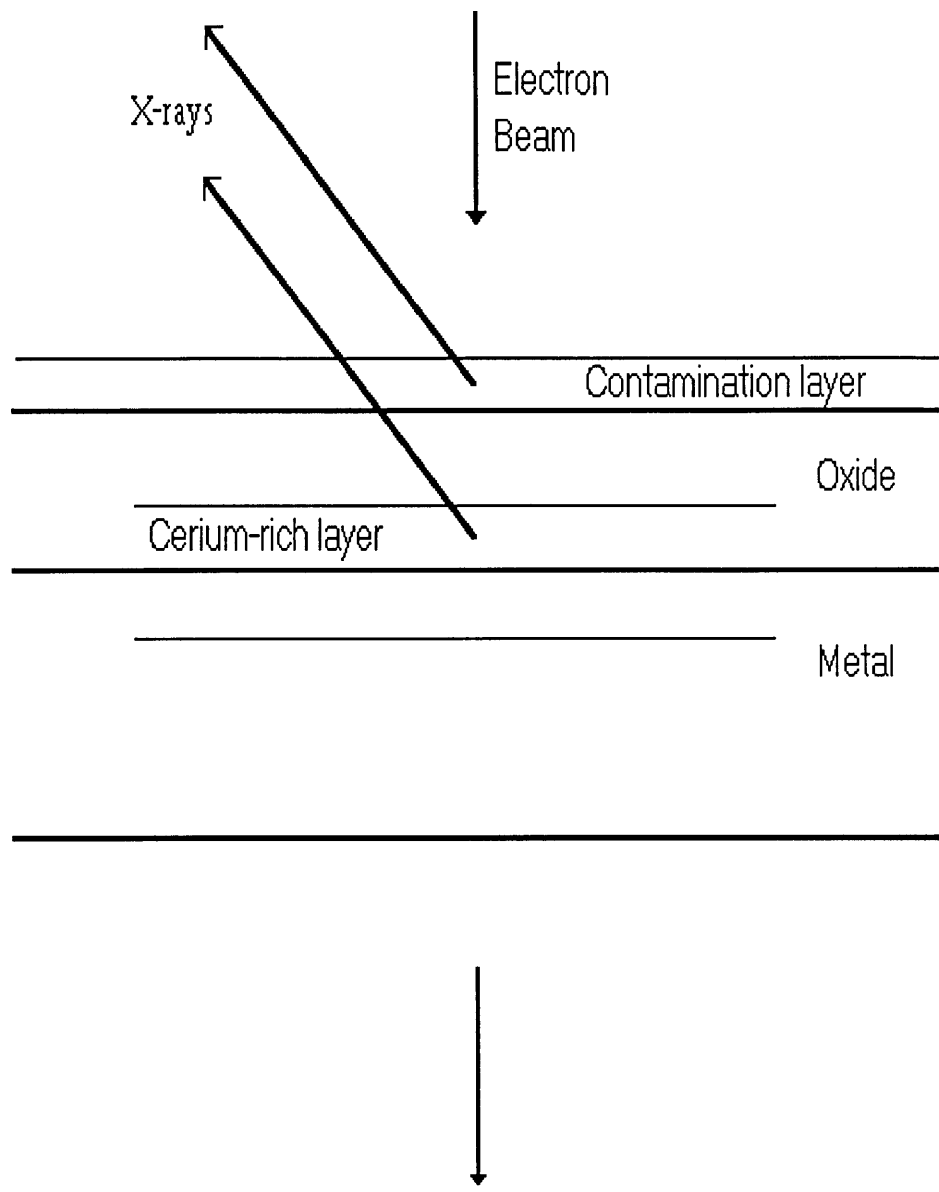
The oxide films on the samples implanted with chromium are no different in their compositions to those on the unimplanted samples. Any elements that segregated to the surface of the coupons during the heat treatments may have been mixed up in the surface layer during the implantation and thus found their way into the oxide film. If this has occurred, then the segregated species are at too low a concentration in the oxide to be detected. Apart from the expected cerium content, the compositions of the oxide scales on the cerium-implanted specimens are similar to those on the unimplanted chromium.

4.11 The Oxidation of Cerium-implanted Chromium

The implantation of cerium into chromium causes an amorphous oxide layer to form on the surface of the coupons. On heating, the layer will crystallise and the crystals will grow. The first cerium compound to form is CeO_2 and this is located in the oxide layer. CeCrO_3 is associated with the metal on samples that have been oxidised for longer periods but there is no evidence for its formation at earlier times.

Figure 4.6

A figure showing how absorption of X-rays in a thick sample can distort the relative abundances, as measured by energy dispersive X-ray spectroscopy, of elements found in the bulk of a sample and on the upper surface of the sample.



There is no Ce/Cr/O phase diagram but the Y_2O_3 - Cr_2O_3 phase diagram (115) shows that, for small concentrations of Y_2O_3 , only $YCrO_3$ should exist at equilibrium. Since yttrium and cerium both form this perovskite phase, it may be possible to predict that the CeO_2 should convert completely to $CeCrO_3$ equilibrium. The experimental evidence suggests that, either this assumption is false or that equilibrium has not been reached after 5 minutes oxidation at $850^\circ C$. The implantation procedure should ensure that the cerium is well mixed with the chromium and subsequent oxidation should convert the components of the amorphous layer rapidly to their equilibrium forms.

In the oxide on the $850^\circ C$, 5 minute oxidised cerium-implanted sample, electron diffraction shows the existence of only Cr_2O_3 and CeO_2 and energy dispersive X-ray spectroscopy reveals cerium rich particles, implying that the cerium-rich particles are CeO_2 . The particles are distributed in a similar manner to the Y_2O_3 particles reported by Cotell *et al* (79) for an oxidised Y-implanted chromium sample and to the CeO_2 particles in the oxide formed on the surface of an Fe-Cr alloy reported by Downham *et al* (110).

Downham *et al* (110) reported that the coating of a 40 nanometre thick layer of CeO_2 on an Fe-Cr alloy is equivalent to implanting with 1×10^{16} Ce ions/cm² and 2×10^{16} Y ions/cm² and that this produced the change in growth mode from cation to anion diffusion control. This implies that the implantation of 2×10^{16} Ce ions/cm² should also change the growth mode. Cotell *et al* (79) noted that implantation of 2×10^{16} Y ions/cm² produced an oxide grain boundary coverage of approximately 10% of a monolayer for a maximum grain boundary concentration of Y of 1.2%. The maximum concentration of cerium detected on the grain boundaries in the oxide formed after 5 minutes oxidation at $850^\circ C$ was 7% so the grain boundary coverage should be a much larger fraction of a monolayer. Almost no cerium could be detected inside the oxide grains on this sample which corresponds with the distribution of Y reported by Cotell *et al* (79).

The cause of the segregation may be one of several mechanisms (62) including electrostatic and dipole interactions between the cerium ions and the grain boundary and the reduction in chemical bond energy upon segregation. Przybylski and Yurek (62) give the most likely cause for yttrium, though, as the driving force due to misfit in the matrix, which is proportional to the difference in the ionic radii of the solute ion and the host ion. The radius of the Cr^{3+} ion is 63 picometres and the radius of the Y^{3+} ion is 89 picometres which would imply a large driving force. The driving force for segregation would be even larger for the Ce^{4+} ion whose radius is 92 picometres suggesting that the segregation of cerium at the grain boundaries will be strain-induced.

The short term oxidation of the cerium-implanted metal will result in an initial layer of crystallising Cr_2O_3 and CeO_2 that reaches a stable grain size of around 50 nanometres at a longer time than for equivalent unimplanted specimens. The cerium that is in the metal will be converted to CeCrO_3 in the metal surface and cerium ions will segregate to the oxide grain boundaries. The cerium does not provide its protective capability immediately, only after a short period. This is possibly due to the large numbers of grain boundaries in the oxide layer immediately after crystallisation of the amorphous native oxide. Once the oxide grains have grown sufficiently large such that the average grain boundary concentration is larger than that required for the reactive element effect to operate, the protective potential of the cerium will be realised and the growth rate of the scale will decrease. The large abundance of cerium in the immediate surface region will allow the rapid neutralisation of surface contaminants such as sulphur and chlorine immediately oxidation starts.

5 CONCLUSIONS

As-deposited electrolytic chromium is not a good substrate for the study of the oxidation behaviour of pure chromium as it is highly microcrystalline with large oxygen and hydrogen contents, is textured, has a high degree of inherent strain and contains a substantial crack network.

Heat treatment of the electrolytic chromium at temperatures above 600°C causes the oxygen to be incorporated into the metal as a bimodal distribution of oxide particles. The larger particles decorate the traces of the cracks, which heal, and the small particles form a uniform distribution in the interiors of the grains. The larger particles then coarsen at the expense of the smaller particles, the process being controlled by the diffusion of oxygen through the metal; coarsening in an inert atmosphere becomes significant above 1000°C. When annealed in hydrogen, the oxide particles are slowly reduced by the atmosphere, this process becoming significant at temperatures above 1200°C.

A heat treatment of 3 hours at 1500°C in 1 atmosphere flowing hydrogen followed by 1 hour in a vacuum of 2×10^{-9} Pa at 500°C can convert this undesirable substrate into one that is eminently suitable, removing almost all of the oxide particles from the metal. The metal is left with a large grain size and a substantial $\langle 111 \rangle$ fibre texture. It may be possible to produce a heat treatment that results in a smaller grain size by using a lower temperature than has been used in this study.

The unimplanted, mechanically polished surfaces of the chromium annealed using the above heat treatment are highly deformed, contain pits of up to 2 micrometres in size and with a mean spacing of 12 micrometres and some oxide particles and have native oxide films approximately 2 nanometres thick.

The ion implantation of cerium causes an amorphous native oxide film approximately 20 nanometres thick to be formed on the surface of the samples. The cerium is implanted to a depth of between 100 and 150 nanometres from the surface with its peak at a depth of approximately 50 nanometres. The maximum concentration of cerium is thought to be above 5%.

The oxide films on unimplanted chromium substrates have been found to form with an initial grain size of between 50 and 400 nanometres. The film grows with a strong preference for its $\{0001\}$ to be parallel to the $\{111\}$ plane in the metal surface. As the metal is highly textured with a $\langle 111 \rangle$ fibre axis, the $\{111\}$ metal plane is parallel to the metal surface and the oxide film takes up a fibre texture with

$\langle 0001 \rangle$ normal to the metal surface. The largest oxide grain sizes are thought to be found where this preference is strongest.

The preference for $\{0001\}$ in the oxide film to be parallel to $\{111\}$ in the metal is not broken by the implantation of ions into the surface of the metal.

The thick amorphous native oxide film on the cerium-implanted metal crystallises in the first stages of oxidation and does not reach a grain size similar to the grain size of the oxide films on the unimplanted metal for some time. The cerium in the oxide film is present as CeO_2 . CeCrO_3 is found to form after several minutes oxidation at 850°C .

The presence of cerium causes the oxide films on the cerium-implanted chromium to be thinner than on equivalent unimplanted samples.

The oxide films that form on the mechanically polished surfaces of unimplanted chromium after oxidation for short periods of time at temperatures between 750°C and 950°C are generally adherent, although most have areas where the film has become non-adherent and has buckled. The extent of the buckling varies from sample to sample indicating that the lack of adherence is not due to any property of the metal but is specific to the sample. The metal/oxide interface is normally strong; surface contamination by non-metallic elements is thought to be the major cause of decohesion. The decohesion is thought to be initiated at particles buried in the surface of the metal. The extent of the buckling on electropolished surfaces is much greater than on mechanically polished surfaces.

The physical effects of the implantation process appear to have had very little effect on the adherence of the oxide films after short periods of oxidation. Implantation of cerium causes the oxide film to become completely adherent. This is thought to be due to the cerium negating the weakening effect that surface contamination has on the metal/oxide interface.

The grain size of the oxide films that forms initially on the unimplanted metal samples is approximately 50 nanometres; after some time a second layer of larger grains forms on the first layer. The grains in this second layer appear to be unconstrained as to their maximum size.

The preference for the oxide to grow with its $\{0001\}$ plane parallel to the $\{111\}$ metal plane is also apparent in the initial oxide films on unimplanted samples after short periods of oxidation. Oxide grains that grow on top of the initial film tend to have a more random orientation.

The physical effects of implantation did not affect the grain size or the orientations of the grains in the initial oxide film significantly. The samples of cerium-implanted chromium had an initial grain size that was much smaller than that for the unimplanted chromium. This is due to the amorphous film on the cerium-implanted metal crystallising with a smaller mean nucleus spacing. The initial preference of the oxide to grow with its {0001} plane parallel to the metal {111} plane is unaffected by the presence of cerium.

Cerium is found to segregate to grain boundaries in the oxide and the amount of cerium at the boundaries should cause a change in the growth direction of the oxide from outward transport of cations to an inward transport of anions.

6 Suggestions for further work

A full study of the coarsening kinetics of the oxide particles in the metal could determine precisely how the size distribution of the particles changes with time at temperatures around 1200°C. This would enable a heat treatment, at a lower temperature than 1500°C, to be devised that would cause the oxide particles to be reduced without leaving the metal with a very large grain size. The distribution of particles in the metal, once the cracks have healed, appears sufficiently uniform that it could be used to study the coarsening process itself, values for the grain boundary and volume diffusion coefficients of oxygen in chromium could be determined. The process of grain growth under the influence of coarsening particles could also be fully investigated using this material. The purity of the metal is a great advantage in this regard.

No single study has completely characterised all of the parameters that make up the physical structure and chemical states of a surface to be oxidised. Having determined that adherent oxide can form on the surface of annealed electrolytic chromium, the surface prior to oxidation should be characterised fully so that the effects of varying each parameter can be investigated. Techniques for measuring such parameters as roughness and abundance of surface contaminants exist so that, for example, the effects on the oxidation process of the surface roughness and the carbon contamination induced by mechanically polishing with diamond particles could be decoupled. Quantification of the effects of each parameter is needed so that the major parameters can be identified.

Far more work is needed on the mechanical properties of thin oxide films, to identify whether the values of, for example, Young's Modulus and Poisson's Ratio are different from the bulk values. Equations exist for the elastic behaviour of buckled thin plates and, if the shapes of the buckled oxide, on samples such as those illustrated in this thesis, could be measured, values for these quantities, and others, could be inferred.

The diffusion rates of chromium along fast diffusion paths and through the lattice should be determined in a growing oxide film. It may be possible to do this by depositing a layer of a tracer, such as ^{51}Cr , on the metal surface prior to oxidation and using SIMS to determine how this diffuses during growth, possibly combining this with an oxygen tracer to differentiate between oxidation periods. The distribution of p-type and n-type oxide in a growing oxide film also needs to be determined.

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Acknowledgements

I should like to thank Dr. H.M. Flower for all his advice, assistance and support over the last few years, Mr. G.W. Briers for his invaluable technical assistance and all of the members of the EM Group, particularly Douglas Arrell, for helping the years that I have spent at Imperial College pass so quickly. Thanks go to Professor D.W. Pashley for providing the laboratory facilities.

Many thanks to Dr. M.J. Bennett and to Dr. A.T. Tuson and Dr. D.P. Moon for the help and advice they have given to me. I should also like to thank AEA Technology at Harwell for their financial assistance via the CASE award scheme and for allowing me to present some relevant data collected at Harwell.

Finally, thanks to SERC for funding the project and for providing me with sufficient funds on which to live.

APPENDIX

Calculation of the maximum volume of Cr_2O_3 in the as-deposited metal.

The volume of a typical coupon is $5 \times 10^{-8} \text{m}^3$, the density of chromium is 7190Kg m^{-3} and so the mass of a typical coupon is $3.6 \times 10^{-4} \text{Kg}$.

Thus the number of moles of chromium in the coupon = 6.9×10^{-3} moles and the number of atoms of chromium in the coupon = 4.2×10^{21}

The average abundance of oxygen, by mass, in the coupons = 1500ppm

The minimum abundance of hydrogen, by mass, in the coupons = 0.01%.

In atomic %, the abundance of oxygen = 0.5% and the minimum abundance of hydrogen = 0.5%

Thus number of oxygen atoms in coupon = 2×10^{19} and the minimum number of hydrogen atoms = 2×10^{19}

In one formula unit of Cr_2O_3 there are 3 oxygen atoms, the molar volume of Cr_2O_3 is $2.9 \times 10^{-5} \text{m}^3$ and so one formula unit of Cr_2O_3 has a volume of $4.8 \times 10^{-29} \text{m}^3$.

Thus total oxide volume = $3.2 \times 10^{-10} \text{m}^3$

Grain interface volume

For a polycrystalline material, the total area of the grain boundaries within the material will be half the sum of the surfaces of each individual grain. If there is a species located at the grain boundaries that has a finite thickness, then the grain interface volume will be the product of the thickness that the species takes up at the interface and the total area of interface. The minimum grain interface volume arises when the grain surface area is minimised, that is when the grains are spherical.

Radius of grains = 25 nanometres so the surface area of one grain = $7.9 \times 10^{-15} \text{m}^2$ and the volume of one grain = $6.5 \times 10^{-23} \text{m}^3$.

Thus the number of grains in the volume of the coupon = 7.7×10^{14}

Total grain surface area = 6m^2 and the total interface area = 3m^2 .

The least thickness of oxide that will form is 1/6 of the c spacing = $2.5 \times 10^{-10} \text{m}$ and so the minimum grain interface volume for spherical grains = $7.5 \times 10^{-10} \text{m}^3$.

For cubical grains, the same calculation can be carried out and gives a minimum grain interfacial volume of $2 \times 10^{-9} \text{m}^3$.

Therefore, the oxide volume contained in the coupon is sufficient to fill 43% of the grain interfacial volume to a thickness of 1/6 of the oxide c spacing if the grains are assumed to be spherical, or 16% if the grains are assumed to be cubes.

If the oxide is hydrated then the calculation can be modified. The hydrated oxide will be assumed to have the formula $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This has 2 hydrogen and 4 oxygen atoms

in each formula unit. The volume of each formula unit can be calculated by assuming that the water will take up a volume equal to a large fraction of its volume in the liquid state.

The volume of H_2O formula unit in the liquid state = $3 \times 10^{-29} \text{m}^3$ so assume that the hydrated oxide takes up a volume of $7 \times 10^{-29} \text{m}^3$.

As the number of oxygen atoms in each formula unit is 4 and there are 2×10^{19} oxygen atoms in the coupon then the number of hydrated oxide units will be 5×10^{18} , which will take up a volume of $3.5 \times 10^{-10} \text{m}^3$.

This is 45% of the total grain interfacial volume if the grains are assumed to be spherical and 17% if the grains are assumed to be cubes.

This also implies that there are at least 1×10^{19} hydrogen atoms unaccounted for.