SEGREGATION AT GRAIN BOUNDARIES IN SENSITISED A.I.S.I 316 STAINLESS STEEL

by

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Analytical electron microscopy (AEM) has been used to examine the relationship between grain boundary structure and the segregation of chromium in a sensitised AISI 316 stainless steel. Fifty grain boundaries have been analysed, the majority of which had an ubiquitous coverage of chromium-rich carbides.

There was a threefold difference in full width half maximum (FWHM) of the measured chromium concentration profiles. This variation has been interpreted in terms of varying long-range stress fields created by different combinations of structural unit that accommodate the various misorientations. Due to the narrowness of their profiles, it is believed that the $\Sigma=3, 11, 13a, 13b$ and probably the 29a boundaries are favoured, using the structural unit classification of grain boundary structure. The $\Sigma=9$ boundary is non-favoured. Approximately 20% of the boundaries conformed to $\Sigma<49$ orientations, the majority of which behaved like random high-angle grain boundaries. All boundaries analysed had a misorientation angle exceeding 20°. There was no correlation between FWHM and grain boundary chromium concentration.

Additionally, it is not pre-requisite for the boundary plane to be close to $\{111\}$ for a chromium carbide to nucleate. There is also no correlation between the boundary normal and either the FWHM of the chromium concentration profile or the grain boundary chromium concentration.

These results support the chromium depletion model of sensitisation and the structural unit representation of grain boundary structure.
I like work: it fascinates me.
I can sit and look at it for hours.
I love to keep it by me: the idea of getting rid of it nearly breaks my heart.

Jerome K. Jerome, "Three Men in a Boat".
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Abstract

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Chapter 1

INTRODUCTION.

Austenitic stainless steels have been used extensively in the construction industry since they are relatively inexpensive, have excellent mechanical properties and corrosion resistance and are readily fabricated into large structural assemblies designed to have a high structural integrity (Toboada and Frank, 1978).

The choice of materials and fabrication processes for electrical power generation have to satisfy three main criteria. They have to (in order of importance) be reliable, cheap and have the capacity to resist high temperatures and stresses (Wyatt, 1971). In this light, austenitic stainless steels seem an ideal proposition and accordingly have found application as superheater/reheater tubing and steam pipes in current power generating plant and have been chosen for the coolant piping in the next generation of boiling water reactors (BWR) (Kass et al, 1980).

However, they have one major drawback. Under certain conditions these materials are susceptible to stress-corrosion cracking (both transgranular and intergranular) that may result in failure of the component affected. Indeed, several significant austenitic pipe cracking incidents due to this have been reported in recent years (Kekkonen, 1985). This phenomenon arises from a combination of high tensile stresses and corrosive environments acting synergistically to penetrate the protective oxide and proceed through the material at a relatively rapid rate.
This work is concerned with intergranular stress corrosion cracking of AISI 316 austenitic stainless steel. In addition to the above mentioned factors concerning stress corrosion cracking, a "sensitised" microstructure is also required which results from the intergranular precipitation of chromium rich carbides after certain heat treatments. Chromium is the element responsible for creating the passive oxide film that provides corrosion resistance in austenitic stainless steels. On formation of a carbide at the grain boundary the adjacent matrix is depleted of chromium to a level below that required for passivity, usually 12-13wt%. This condition can be generated during welding, in which the heat affected zone (HAZ) is held in the critical temperature range for a very short time promoting the nucleation of carbides at the grain boundaries. If the welded component is operated in this state, even at temperatures below the normal sensitisation range, the previously nucleated carbides can grow while the low temperature (300-400°C) prevents further nucleation and greatly impedes chromium diffusion. After extended periods of time (i.e. 10yrs), this situation can produce intergranular stress corrosion cracking if the material is subjected to a corrosive environment.

This problem of sensitisation has been well known for many years and three commonly employed remedial measures can be taken to prevent it occurring (Bennett and Pickering, 1988). These are avoidance of the critical temperature range for carbide formation, reduction of carbon levels and addition of carbide stabilising elements (Ti and Nb). However, as each of these remedies require tight control of each material processing and/or fabrication step, sensitisation is still a major industrial concern. As a result,
experimental and theoretical research continues on this major topic.

It is intended to analyse the chromium concentration distribution around grain boundaries using STEM-EDX, determine the boundary misorientation and plane and then correlate the segregation characteristics of chromium to the boundary crystallography. Hopefully, this will provide more insight into the structure of grain boundaries and extend support for one of the existing grain boundary models. Additionally, any further remedial measures that can be utilised to prevent sensitisation, as a result of this work, will be discussed.
Chapter 2

THEORIES OF SENSITISATION.

2.1. Introduction.

Austenitic stainless steels generally have excellent corrosion resistance when rapidly cooled from the solution anneal temperature of ~1100°C. However, if an unstabilised austenitic stainless steel (i.e. without Ti or Nb additions) is slowly cooled from the solution anneal temperature or is reheated in the temperature range 500-800°C (Joshi and Stein, 1972, Briant et al, 1982, Mulford et al, 1983), the corrosion resistance breaks down due to the formation of a sensitised microstructure. In this sensitised condition the steels are susceptible to intergranular corrosion. Many models have been proposed to explain this phenomenon and these can be divided into two main categories:

1. chromium depletion theories;

2. electrochemical theories.

In the following section a brief review of the theoretical and experimental studies that have been undertaken is presented.
2.2. Chromium Depletion Theories.

Strauss et al, (1930) originally proposed that intergranular corrosion could be explained by the depletion of chromium in the areas adjacent to grain boundaries. This was supported by Bain et al, (1933) who reported that the 18%Cr/8%Ni type austenitic stainless steels are susceptible to intergranular corrosion after heat treatment in the temperature range 500-800°C.

The time-temperature transient associated with welding is capable of inducing this effect, producing narrow regions on either side of the weld which become prone to this form of attack when exposed to a corrosive environment. The fact that the zones appear on either side of the weld indicates that an intermediate temperature is responsible for the loss of corrosion resistance. The time at temperature determines the severity of intergranular attack. This severity can be determined by the modified Strauss test which is the standard test for detecting intergranular corrosion in austenitic alloys (Streicher, 1978). Electropolished samples are wrapped with copper wire, placed in a beaker and surrounded with copper shot. They are then immersed in an aqueous solution of CuSO₄/H₂SO₄. The solution is then boiled for three days, after which the samples are bent into a U shape and examined for corrosion. The electrochemical potential of the test is -330mV_SHE, at which Fe-Cr binary alloys containing greater than 13wt%Cr will not be attacked whereas those containing less chromium will be badly corroded.
The mechanism of sensitisation is attributed to the formation of chromium-rich carbides at the grain boundaries. Heating in the critical temperature range provides sufficient thermal energy for carbon to diffuse to the grain boundaries where it combines with chromium to form a carbide. Carbon, having a higher diffusivity in austenite than chromium, migrates from a greater distance creating a wider concentration profile than chromium. This is shown in Fig 2.2.1.

After a prolonged heat treatment at a temperature in the sensitising range, the sensitised material can recover its corrosion resistance. The carbon having migrated from greater distances than the chromium, will eventually create such a shallow concentration profile that the propensity for diffusion to the grain boundary will decrease and eventually cease at some minimum finite value. Hence, chromium can diffuse into the narrow depleted zone adjacent to the grain boundary and restore the critical concentration required to provide a passive film. This is known as self-healing and is shown in Fig 2.2.2.

Methods of prevention of intergranular corrosion are also discussed by Bain. Reduction of the carbon content to the solubility limit of 0.02wt% would essentially eliminate sensitisation altogether as the carbon could remain in solid solution rather than segregate. Additionally, titanium can be added to stabilise the alloys. Titanium has a greater affinity for carbon than chromium and preferentially forms carbides, leaving the chromium in solid solution where the full benefit of its corrosion resistance properties can be realised.

In conclusion, intergranular corrosion was attributed to
Fig 2.2.1. Idealised diagram showing probable carbon and chromium distribution in the vicinity of a carbide particle.
Fig 2.2.2. Idealised diagram showing probable carbon and chromium distribution approaching equilibrium to restore grain boundary corrosion resistance.
chromium depletion in the vicinity of grain boundaries and the recovery of corrosion resistance explained by the removal of carbon from a wide zone about the grain boundary and of chromium from a narrow zone.

Stawström and Hillert, (1969) derived a diffusion controlled reaction model covering all stages of the sensitisation process in which the chromium concentration in the steel adjacent to the grain boundary carbide could be calculated. It was assumed that this chromium content could be thermodynamically determined by the alloy-carbon-M\(_{23}C_6\) local equilibrium. The more usual assumption however was that the chromium content in the vicinity of the carbide particle was negligible and that variation in the degree of sensitivity resulted from changes in particle morphology or distribution along the boundary (Electrochemical theories) and not from variation in chromium composition. It was also assumed that grain boundary diffusivity at typical sensitising temperatures would be fast enough to produce no variation in chromium composition along the boundary between carbide particles.

From the model, the width \(m\), of the zone where the chromium content is less than 13at\%, was calculated such that:

\[
m = 2 \sqrt{\frac{0.13 - x^{1}_{Cr}}{x^{0}_{Cr} - x^{1}_{Cr}}} \left( \frac{0.13 - x^{1}_{Cr}}{x^{0}_{Cr} - x^{1}_{Cr}} \right)
\]
where $D =$ diffusion coefficient for Cr in $\gamma$ iron

$t =$ time

$x_1^i =$ Cr content at the carbide interface at the beginning of precipitation

$x_0^o =$ Cr content of the steel.

Hence, the time of annealing to produce a depleted zone with less than 13at\% chromium and of a certain width could be calculated. Good agreement between experimental and calculated data was attained using a zone width of 200Å.

It was concluded that the chromium depleted zone theory of Bain could explain the effect of annealing on intergranular corrosion. It was also stipulated that for a steel to become sensitive, a zone containing less than 13at\% chromium and greater than 200Å in width must be created.

The concept of self-healing was also discussed. During prolonged annealing, as the carbide particles continue to grow, the carbon content of the material and consequently the carbon activity will decrease. This in turn allows the chromium to diffuse into the depleted zone without being engulfed in the carbide. Hence, the chromium concentration in the depleted zone will increase.

Additionally, the diffusion coefficient of chromium in austenite at low temperatures, $D_o$, was evaluated to be 0.08 cm$^2$/s. The activation energy, $Q$, was found to be 58500 cal/mol.

Tedmon et al, (1971) presented a model conceptually similar to that of Stawström and Hillert to interpret intergranular sensitivity of stainless steels but which differed considerably in
detail and results. Chromium concentration profiles both normal to and along the grain boundaries between carbides were calculated. It was shown that the grain boundary chromium concentration between carbides is not uniform as assumed by Stawström and Hillert but that large gradients exist between carbides which affect the corrosion behaviour significantly.

Initially, the minimum chromium content, which occurs at the boundary/carbide interface, was calculated from the reaction:

\[ 23\text{Cr} + 6\text{C} \leftrightarrow \text{Cr}_{23}\text{C}_6 \]

The equilibrium constant is given by

\[ K = \frac{1}{(\gamma_{\text{Cr}}X_{\text{Cr}})^{23}(\gamma_{\text{C}}X_{\text{C}})^6} \]

where \( \gamma_{\text{Cr}} \) = activity coefficient of chromium
\( \gamma_{\text{C}} \) = activity coefficient of carbon
\( X_{\text{Cr}} \) = chromium concentration
\( X_{\text{C}} \) = carbon concentration.

Unit activity was assumed for the carbide.

Having attained the chromium concentration at the grain boundary in equilibrium with the carbide, the chromium concentration along the grain boundary was calculated and found to vary considerably with distance from the carbide. Chromium concentration gradients normal to the boundary were also calculated. The results were then confirmed experimentally using corrosion tests.
It was concluded that at the lower sensitising temperatures, grain boundary diffusion is sufficiently rapid to create a reasonably uniform chromium depletion along the boundary. At higher temperatures, due to the lower ratio of grain boundary to bulk diffusion, a patchy type of corrosion behaviour is encountered. The results indicate that it is the minimum chromium content that primarily controls the degree of sensitivity with the carbide morphology playing a secondary role.

Fullman, (1982) proposed a method of incorporating elements other than iron, chromium, nickel and carbon into the thermodynamic models of sensitisation. He utilised the work of Cihal, (1970) who introduced the concept of effective chromium and carbon contents. For example, an effective chromium content may be defined as

$$Cr^* = Cr(\%) + 1.42 \text{ Mo}(\%)$$

reflecting the observation that a 1% increase in molybdenum is as effective as a 1 to 2% increase in chromium in suppressing sensitisation and an effective carbon content may be defined as

$$C^* = C(\%) + 0.002 [ \text{ Ni}(\%) - 10 ].$$

Equivalent susceptibility to stress corrosion cracking is expected for alloys with equal values of

$$K = Cr^* - 100C^*.$$
Additionally, if the effective chromium content is greater than 13 to 13.8, the material will be immune to attack in the Strauss test. Hence, a high value of Cr* and a low value of C* are desired. A steel with 10% nickel is taken as a reference case. Chromium equivalency parameters were calculated estimating the relative effects of various elements on the activity of carbon and on the stability of M_{23}C_{6} carbide. The parameters express the relative changes in the concentration of chromium and other elements for equivalent expected susceptibility to intergranular corrosion and agree well with experimental results. The thermodynamic information was based on Fe-Cr-Ni-M-C interactions and the chromium depletion model of sensitisation. It was not intended to propose a new model for sensitisation, but apply current theory to provide explicit quantitative predictions on the effects of composition changes.

The model proposed that if two austenitic stainless steel compositions have the same chromium concentration in equilibrium with an M_{23}C_{6} carbide at a temperature in the sensitising range, then they will have equal susceptibility to intergranular stress corrosion cracking. Hence, no specific chromium depletion width or concentration profile between carbides was hypothesised as a criterion for susceptibility, as was the case with earlier models. In addition, the model did not attempt to provide predictions of stress, corrosive environment and sensitisation time and temperature that will cause cracking.
2.3. Electrochemical Theories.

Stickler and Vinckier, (1961) postulated that the chromium depletion model proposed by Bain et al could not explain various observations made by themselves and other investigators. For example, extrapolation of corrosion data by Bain et al suggests that complete recovery from intergranular susceptibility will occur after annealing at 650°C for 1500 hr. On the other hand, extrapolation of data by Bendure et al suggests that only 45% of the total carbon will be precipitated after this heat treatment. Consequently, it is difficult to explain why, at a particular sensitising temperature, a chromium depleted zone is created initially due to carbide precipitation, but at a later stage the chromium is replenished in the depleted zone although precipitation is still continuing at an appreciable rate.

Furthermore, after prolonged annealing in the sensitising range, austenitic steels transform partially to martensite on cooling to room temperature. This is confirmed by the Schaeffler diagram, (Schaeffler, 1949), in which a reduction in the chromium concentration in Fe-Cr-Ni alloys increases the propensity of martensite formation. However, the regions of maximum martensite formation do not coincide with the areas where maximum susceptibility to intergranular corrosion occurs (i.e. adjacent to the grain boundaries).

These observations indicate that the major factor influencing intergranular corrosion of these alloys is not that of chromium depletion. Hence an alternative mechanism was proposed based on experimental findings.
Two factors were stated as controlling the intergranular corrosion process:

1. the local attack around carbides;

2. the penetration along grain boundaries.

The local attack around the \((\text{Cr,Fe})_{23}\text{C}_6\) carbides is controlled by an electrochemical reaction between the more noble carbide and the adjacent matrix. This reaction may be influenced by residual stresses around the particles.

The penetration along grain boundaries is controlled solely by the morphology of the carbides precipitated on the boundary. If the carbides are interconnected along the boundary then the electrochemical reaction can proceed entirely along the boundary. The more boundaries interconnecting with carbides of this morphology the greater will be the intergranular penetration. This is illustrated in Fig 2.3.1.

At the lower sensitising temperatures, 480-650\(^\circ\)C, an interconnecting sheet of carbides is precipitated along the boundaries and hence penetration can occur readily into the material. This is shown in Fig 2.3.1A. At the intermediate sensitising temperatures, 730-815\(^\circ\)C, the continuous path of interconnected precipitates is replaced by individual carbide particles which become more widely spaced the higher the temperature. This is reflected in a reduction in the penetration of the intergranular corrosion, Fig 2.3.1B.

Additionally, the slight recovery of the metal from
Fig 2.3.1. Mechanism of intergranular corrosion in austenitic stainless steel.
susceptibility to intergranular attack after long sensitising heat treatments can be explained by a change in the carbide morphology. As the time at temperature is increased through the sensitising range, the morphology changes from an interconnecting sheet of thin flakes to a geometric array of coarser particles which disrupts the continuous corrosion path required for maximum penetration.

Aust et al, (1966) reported that the morphology of carbides produced after a sensitising heat treatment could not be entirely responsible for the resultant intergranular corrosion because this form of corrosion was found to occur after non-sensitising heat treatments with no detectable carbide precipitation. Evidence was presented using measurements of microhardness across a boundary showing that solute segregation had occurred to the boundary. This segregant, it was proposed, could create the electrochemical cell required to produce anodic dissolution of the adjacent matrix. The intergranular corrosion tendency could then be alleviated by a heat treatment which would prevent the formation of continuous solute-rich regions near grain boundaries. For example, the continuous solute rich regions formed on solution heat treating and quenching could be effectively reduced by a further heat treatment in which separate carbides are precipitated at the grain boundaries. This is depicted in Fig 2.3.2.

In Fig 2.3.2A, after a solution anneal followed by a quench, solute is enriched along the grain boundaries forming a continuous corrosion cell and hence a high probability of deep penetration into the material if subjected to a corrosive medium. If the material is given a further anneal between 500-600°C, a continuous
Fig 2.3.2. Schematic illustration of local changes in microstructure and composition near grain boundaries for different heat treatments.
path of grain boundary carbides is produced for classical intergranular corrosion in a sensitised material, as shown in Fig 2.3.2B. However, if the material is heat treated between 800-900°C and quenched, isolated carbides are formed on the grain boundaries as shown in Fig 2.3.2C. These carbides are believed to incorporate solute impurities from the grain boundary on their formation and hence create a discontinuous penetration path. Indeed, when subjected to a corrosive solution of HNO₃ + Cr⁶⁺, the structure shown in Fig 2.3.2C has the greatest corrosion resistance followed by 2.3.2A and then 2.3.2B (Aust et al, 1967). Also a low corrosion rate would be produced if the material was of high purity on the basis of this model (Fig 2.3.2D). Hence, it was concluded that intergranular corrosion of Type 304 material was not related solely to the carbide morphology as had been stipulated by Stickler and Vinckier (1961), because the same phenomenon was found to occur in carbide-free material. A simple model was proposed indicating that the mechanism of intergranular corrosion was associated alternatively with the presence of continuous grain boundary paths of either second phase or solute segregated regions. On this basis, the intergranular corrosion rate could be markedly reduced by the formation of a discontinuous second phase at the grain boundaries if it incorporated the majority of solute sited in the grain boundary regions. Additionally, if high purity stainless steel is utilised then there is no excess grain boundary hardening and no evidence of intergranular corrosion.
2.4. Summary.

As mentioned previously, the several theories proposed to explain the phenomenon of sensitisation can be classed into two main types:

1. chromium depletion theories;

2. electrochemical theories.

Gellings and de Jongh, (1967) provided support for the chromium depletion theory by carrying out corrosion tests which showed that the oxidation rate at high temperatures was greater along the grain boundaries due to the precipitation of chromium rich carbide which thus lowers the chromium content of the alloy at these areas. This increased oxidation rate was predicted by the chromium depletion theory but could not be explained by the electrochemical theory. Sinigaglia et al, (1982) applied the Stawström and Hillert model, which used the chromium depletion theory as its basis, to predict carbide precipitation kinetics together with the onset and termination of sensitisation. Experimental and theoretical results regarding carbide precipitation showed good agreement, but some discrepancies arose concerning desensitisation times. The Stawström and Hillert model predicted non-sensitising conditions while the modified Strauss test showed a sensitised state, causing the authors to question the reliability of the model in predicting sensitisation and self-healing times. Briant et al, (1982) and Mulford et al, (1983)
provided further experimental evidence for the chromium depletion theory employing both corrosion tests and analytical electron microscopy. They also stated that other variables have a significant effect on sensitisation and can be divided into two categories:

1. variables which alter the thermodynamics and/or kinetics of carbide formation at grain boundaries for example, cold work, the presence of martensite, grain size and the addition of elements which significantly alter the chromium and carbon activities in the alloy or which on segregating to the grain boundary retard carbide nucleation or growth;

2. variables which change the corrosion behaviour of the material independently such as the enhancement in corrosivity of stainless steels in very oxidising conditions due to the presence of phosphorus (Joshi and Stein, 1972).

The chromium concentration profile normal to the grain boundary was measured using analytical electron microscopy (AEM) providing quantitative evidence of chromium depletion and thus reinforcing the chromium depletion theory. It was also found that nitrogen retards the nucleation and/or growth of carbides at grain boundaries and hence increases the time necessary for sensitisation. The nitrogen segregates to the grain boundary and hinders carbide precipitation (Briant, 1987). Molybdenum increases the ease at which passivation occurs in these steels, thus increasing the amount of chromium depletion required to produce
detectable sensitisation. In combination, nitrogen and molybdenum retard sensitisation more effectively by acting synergistically to disrupt carbide nucleation and/or growth. Additionally, Hall and Briant, (1984), using AEM, measured grain boundary chromium concentrations and significant depletion was detected at carbide-matrix interfaces and along grain boundaries between carbides. The profiles were compared with profiles calculated from thermodynamic models and good agreement was found.

Mozhi et al, (1986) utilised the thermodynamic models proposed by Stawström and Hillert, (1969), Tedmon et al, (1971), and Fullman, (1982) to incorporate the effect of nitrogen on sensitisation behaviour as it was found that nitrogen retards sensitisation. AEM results and calculations based on these models indicated that nitrogen increases the chromium concentration on the grain boundaries, thereby retarding the growth of carbides. Additionally, time-temperature-sensitisation (TTS) curves were also calculated using the nitrogen-incorporated model and found to agree well with experimental results.

Bruemmer and Charlot, (1986) compared existing theories of sensitisation to the measurement of the chromium concentration in equilibrium with the growing carbide as a function of temperature. The results are shown in Fig 2.4.1. The variation between prediction and measurement utilising the different models is quite apparent. They modified the relationship between chromium activity and concentration using experimentally determined results which improved the fit of theoretical to experimental data. It is evident that existing theories overestimate chromium minimums above 800°C and underestimate them below ~600°C although
Fig 2.4.1. Comparison of measured and predicted chromium minimums as a function of annealing temperature.
qualitative agreement between the various theories was found. It was also determined experimentally, having been verified theoretically, that the minimum grain boundary chromium concentration increases with increasing annealing temperature, as does the profile width.

Further support for the chromium depletion theory was provided by Butler and Burke, (1986) using AEM to measure chromium concentration profiles normal to the boundary. The experimental solute profiles were compared with those predicted from the Stawström and Hillert model. Good agreement was found after short annealing times. Also the effects of ageing time and temperature on zone width and extent of chromium depletion were consistent with the thermodynamic analysis of Tedmon. They concluded that the ageing temperature is the principle factor which controls the minimum chromium content in equilibrium with the $M_{23}C_6$ carbide.

Additional evidence showing chromium depletion about grain boundaries was supplied by Chastell et al, (1987) who showed that the concomitant precipitation of carbides and chromium depletion renders a sensitised microstructure at distances up to 3mm from a weldment fusion boundary depending on the thermal transient.

Indeed, using AEM, it is now possible to discover whether significant variations in grain boundary chromium concentration do exist between carbides on the same boundary. By analysing between carbides the concentration gradients can be measured directly. Hence, it is apparent that the assumption of a constant grain boundary concentration (Stawström and Hillert, 1969) can be investigated to determine its validity.

Support for the electrochemical theory is less widespread.
Armijo, (1967) and (1968) showed the effect of high temperature heat treatment on the intergranular corrosion rate of non-sensitised alloys in a solution of HNO$_3$ + Cr$^{6+}$. High purity stainless steel alloys were doped with controlled additions of impurity elements to determine which ones had a detrimental effect on intergranular corrosion. The samples were solution heat treated and quenched before being subjected to the corrosive environment. It was found that silicon and phosphorus segregate to grain boundaries and have a deleterious effect on the susceptibility of the alloy to intergranular corrosion in this solution. Hence, chromium depletion at the grain boundary is not responsible for the corrosion in this situation.

To completely explain the process of sensitisation, the total chemical content of the material as well as microstructural factors must be considered. This compositional effect was tackled by Fullman, (1982) using the concept of effective chromium concentrations and chromium equivalency parameters which take into account the effects of other major elements in the alloy, as discussed in Section 2.2. Significant trends in data from different samples can be seen most easily when this concept is employed.

A number of workers have examined the effects of other elements on sensitisation. Mulford et al, (1983) determined the relative effects of C, N, Mo and Mn. It was found that sensitisation times decreased significantly with decreasing C content. N, which can be added as a solid-solution strengthener in place of C, retards sensitisation by decreasing the nucleation and/or growth rate of carbides. Mo also retards sensitisation by
aiding in passivation of the steel, thus increasing the amount of chromium depletion required before cracking is observed in the Strauss test. It also reinforces the beneficial effects of nitrogen. Mn retards sensitisation by again enhancing the beneficial effects of nitrogen, but not however, to such an extent as Mo.

Ni, on the other hand, added chiefly to enhance mechanical and fabricating properties, accelerates carbide formation and increases susceptibility to sensitisation (Hänninen, 1979).

P, which is one of the most important segregants in austenitic stainless steels, has a critical effect in most oxidising media, but not however, in the Strauss test. P segregation depends on the crystallographic orientation of the grain boundary plane, being large for planes with high indices and small for planes with low indices (Suzuki et al, 1981). Enrichment of S at grain boundaries has also been detected by Briant, (1982) although its effect on sensitisation was not discussed.

Consequently, it can be seen that the effects of all elements need to be considered to allow a complete understanding of the sensitisation process.

From the preceding review it is evident that the original model proposed by Bain seems to provide qualitatively the correct explanation of sensitisation. The extent of the experimental evidence and theories which have originated from this model indicate that the phenomenon of sensitisation is indeed controlled by the precipitation of chromium carbides and resultant chromium depletion at the grain boundary. The chromium depletion theory has gained widespread acceptance because it explains the influence of
carbon and chromium content, various heat treatments and stabilising elements on sensitisation. In addition, direct experimental evidence of chromium depletion at grain boundaries has now been obtained using thin foil microanalysis. However, there are also experimental observations supporting the electrochemical models although these were obtained under different test conditions. It seems probable therefore that two completely different mechanisms are operating. Chromium depletion at the grain boundaries is dominant in slightly oxidising solutions such as the Strauss test but in highly oxidising solutions the impurity segregation phenomenon seems to be important.
3.1. Introduction.

It has long been known that the local chemical composition at interfaces such as grain boundaries can drastically influence the properties of materials (Inman and Tipler, 1963, Westbrook, 1964, Hondros and Seah, 1977). As with other imperfections in solids, grain boundaries constitute sinks at which impurities or secondary components become concentrated.

Enrichment of solute atoms at these interfaces can be due to either equilibrium or non-equilibrium segregation. If a material is held at a sufficiently high temperature to permit appreciable diffusion of solute then equilibrium segregation can occur. The driving force for this phenomenon is a reduction in the interfacial energy of the loosely packed interface regions by the absorption of solute atoms (Karlsson et al, 1988). The segregants are localised to a few atomic layers at the boundary and the total amount is usually of the order of a monolayer. The conditions required to cause equilibrium segregation have been extensively reviewed by Hondros and Seah, (1977).
A simple relationship between the degree of segregation and temperature was formulated such that

\[ \frac{c_b}{c_q} = A \exp \left( \frac{E}{kT} \right) \]

where

- \( c_b \) = segregating atom concentration on the boundary
- \( c_q \) = segregating atom concentration in the bulk
- \( A \) = constant
- \( k \) = Boltzmann’s constant
- \( T \) = absolute temperature
- \( E \) = free energy of segregation, which is the reduction in energy of the segregating atom in the segregated site e.g. a grain boundary.

This equation predicts that segregation is greater at lower temperatures and for higher free energies of segregation. The important aspect of the kinetics of segregation is not accounted for in this treatment, although this has been successfully dealt with by McLean, (1957) and Seah, (1977) with respect to the classic temper embrittlement of steel by phosphorus.

Non-equilibrium segregation, on the other hand, occurs during cooling from high temperatures. It was first noted by Westbrook, (1964) who measured a marked hardness increase at grain boundaries in a number of quenched alloys. He postulated that some unknown segregation mechanism must have been in operation since the kinetics of the grain boundary hardening could not be fully
explained in terms of equilibrium segregation.

Non-equilibrium segregation theory was first established by Aust et al, (1968) who proposed that this boundary hardening was due to the presence of solute clusters resulting from the decomposition of vacancy-solute clusters near the boundary. Since then the theory has been developed considerably by a number of investigators (Anthony, 1969 and 1975, Williams et al, 1976, Faulkner, 1981, Doig and Flewitt, 1981, Chapman and Faulkner, 1983, Doig and Flewitt, 1985, Tingdong, 1987 and 1989 and Karlsson, 1988).

These two mechanisms of segregation can be differentiated from each other by their temperature and cooling rate dependencies and by the shape of their concentration profiles. Equilibrium segregation is confined to within a few atomic layers at the boundary and the amount of segregation increases with decreasing temperature (Hondros and Seah, 1977). Non-equilibrium segregation however, produces a broader (often hundreds of nanometers wide), smooth concentration profile and the amount of segregation increases with increasing annealing temperature. Non-equilibrium segregation is also strongly cooling rate dependent with the largest amount of segregation occurring at some intermediate cooling rate, when the time has been sufficient to let vacancy-solute pairs diffuse to the grain boundaries but not let deposited solute atoms diffuse away from the boundary zone (Williams et al, 1976 and Faulkner, 1981).

From the shape of the concentration profiles measured in sensitised materials (Mulford et al, 1983, Joshi and Stein, 1972,
Bruemmer and Charlot, 1986, Butler and Burke, 1986, Chastell et al, 1987), it is postulated that non-equilibrium segregation is the dominant mechanism in depositing chromium at the grain boundaries and will therefore be discussed in more detail in the next section.

3.2. Mechanism of Non-equilibrium Segregation.

Solute enrichment and solute depletion of vacancy sources and sinks such as dislocations, grain boundaries, external surfaces and internal pores can be produced by vacancy flows during the heating, cooling or sintering of a material. It was first postulated by Anthony, (1969) that this phenomenon could explain the sensitisation of welds.

The mechanism of segregation is based on an equilibrium in which a sufficient quantity of vacancy-solute complexes exists. These three parts: solute atom I; vacancy V; and the complex C; are in equilibrium with each other such that

$$I + V \leftrightarrow C$$

If there exists a positive binding energy between a solute atom and vacancy then a vacancy-solute complex will be established (Aust et al, 1968). In the case of chromium, a positive binding energy of 0.5eV has been deduced (Doig and Flewitt, 1985) and hence complex formation is favoured.

During a high temperature anneal, an equilibrium
concentration of vacancies is generated and distributed throughout the lattice. If a positive binding energy exists, vacancy-solute coupling can occur at this temperature. On cooling a pure metal or alloy from a temperature such as this, the equilibrium vacancy concentration at that temperature will try to reduce to that of the lower temperature. This equilibrium vacancy concentration associated with the lower temperature cannot be realised during fast cooling except at highly efficient vacancy sinks such as grain boundaries and surfaces. Vacancies within diffusive range of the grain boundary will therefore try to migrate to the interface where they can be annihilated. Thus the vacancy concentration in the vicinity of the boundary will decrease. This in turn causes the complexes to dissociate into separate solute atoms and vacancies producing a decrease in the complex concentration exhibited at the boundary.

At lower temperatures, vacancy-solute coupling is enhanced as entropy effects are reduced. Consequently, in regions remote from the boundary, where no other vacancy traps are present, vacancies recombine with solute atoms to reduce the excess vacancy concentration. This produces a complex concentration gradient between the grain boundary and regions remote from it. As a result, a driving force is provided for the complexes to diffuse down the concentration gradient from the grain centres to the grain boundaries in order to equilibrate the complex concentration throughout the material and annihilate the excess vacancy concentration. This diffusion causes excessive solute atoms to concentrate in the vicinity of the grain boundary.
This can be related to the segregation of chromium to grain boundaries in a stainless steel. If the material is solutionised at 1100°C for 1hr, which is standard industrial practice, an equilibrium vacancy concentration \( c_v \), will be created which can be calculated from (Williams et al, 1976)

\[
c_v = k_v \exp \left( -\frac{E_v}{k \cdot T} \right)
\]

where \( K_v \) = entropy term = 4

\( E_v \) = vacancy formation energy = 1.3eV (Doig et al, 1985)

\( k \) = Boltzmann's constant

\( T \) = temperature = 1373K

This results in 0.007% or 70ppm vacancies being present. An AISI 316 austenitic stainless steel contains ~18wt% chromium. Hence, there exists an ubiquitous supply of chromium atoms and only a few vacancies. With a high solute concentration such as this, a simple one-to-one pairing of all vacancies and solute atoms is not possible because solute atoms greatly outnumber vacancies (Anthony, 1969). So for concentration profiles of the order of hundreds of nanometers to develop, either more than one chromium atom must be bound to each vacancy forming a cluster or one vacancy can help in the transportation of more than one chromium atom to the boundary.

The actual situation in a stainless steel however is further complicated due to the presence of carbon, which also segregates
to grain boundaries on cooling. The diffusivity of carbon in austenite is $\sim 10^4$ higher than that of chromium and so it probably diffuses interstitially to the grain boundary, although computer simulations have shown that if the vacancy-carbon binding energy is positive, non-equilibrium segregation of carbon could occur (Karlsson and Norden, 1988).

Chromium and carbon have a high affinity for one another and form chromium rich carbides on the grain boundary. This effectively depletes the boundary region of chromium resulting in chromium concentration gradients adjacent to the carbides.

As a result of this precipitation occurring, there will be no de-segregation which is a reverse solute diffusion process. This usually arises due to the non-equilibrium solute content at the boundary producing a concentration gradient which causes a time dependent reduction in the solute profile by reverse diffusion (Doig and Flewitt, 1981).

It is thus hypothesised that chromium accumulates at grain boundaries mainly by non-equilibrium segregation of mobile vacancy-chromium complexes diffusing down vacancy gradients. This phenomenon of non-equilibrium segregation was recognised 20 years ago, but due to the lack of measured quantitative concentration profiles, the development of a complete understanding of the underlying mechanism has been prevented (Karlsson et al, 1988).
3.3. Quantification of Segregation.

3.3.1. Introduction.

The magnitude and width of non-equilibrium segregation profiles have previously been predicted by two different approaches:

1. approximate solutions to mathematical diffusion rate equations
   e.g. (Anthony, 1969 and 1975, Williams et al, 1976, Faulkner, 1981, Doig and Flewitt, 1981);

2. computer simulations of diffusion on an atomic scale
   e.g. (Chapman and Faulkner, 1983, Bennett and Pickering, 1988).

Long range segregation can be described with no restrictions on solute contents, cooling rates etc using the former approach. However, it is not possible to obtain exact mathematical solutions for a general case where the coupling between the flows of the different species is included. Segregation within a narrow boundary zone (of the order of 100 atomic spacings) can be described in detail using the latter approach and concentration profiles can be calculated when neighbouring diffusion fields overlap. However, the computer time needed to perform the simulations places restrictions on the choice of solute content, vacancy content and width of the boundary zone.

Considering the width of the profiles generated in the
non-equilibrium segregation of chromium to grain boundaries, it is considered the former approach is of greater relevance.

3.3.2. Magnitude of Segregation.

Quantification can be effected by considering Fig 3.3.2.1 from Faulkner, (1981). The magnitude of the segregation can be measured in a number of different ways. For example, it can be estimated from the area under the curve in Fig 3.3.2.1 which would represent the amount of solute atoms transported to the boundary. Alternatively, it could be denoted by the actual weight percentage of solute detected at the boundary $c_b$, using analytical electron microscopy. Faulkner however, defined the magnitude of the effect by the ratio $c_b / c_g$. He defined the extent as the distance $x$, at which the concentration of impurity is reduced to minimal levels. However, the magnitude of the "minimal values" was not defined. Other investigators (Doig et al, 1981) have selected a value

$$\frac{c_x}{c_b} = \frac{1}{e} = 0.37,$$

assuming an exponential type concentration profile. Alternatively, the bulk value could be chosen as the minimal value. The extent of the segregation could also be represented by a full width half maximum (FWHM) criterion.

Utilising the technique developed by Faulkner, the magnitude of non-equilibrium segregation is determined assuming that only diffusion of complexes occurs. Changes in solute concentration
Fig 3.3.2.1. Magnitude and extent of non-equilibrium segregation.
produced at the boundary on cooling from temperature $T_1$ to $T_{0.5T_m}$ are indicated, where $T_1$ is the solution anneal temperature and $T_{0.5T_m}$ is half of the melting temperature. This temperature was chosen because it is assumed that very little diffusion will occur below $T_{0.5T_m}$. The concentration of complexes $c_c$, at temperature $T$, is given by Williams et al, (1981) such that

\[
c_c = k_c c_v c_i \exp \left( \frac{E_b}{kT} \right),
\]

where $k_c = \text{geometric constant}$

$c_v = \text{vacancy concentration}$

$c_i = \text{impurity concentration}$

$k = \text{Boltzmann's constant}$

$E_b = \text{vacancy-impurity binding energy}$

Also, the concentration of vacancies

\[
c_v = k_v \exp \left( \frac{-E_f}{kT} \right),
\]

where $k_v = \text{geometric constant}$

$E_f = \text{vacancy formation energy}$

Combining the above equations gives

\[
c_c = k_c k_v c_i \exp \left( \frac{E_b - E_f}{kT} \right).
\]
On cooling from $T_1$ to $T_{0.5T_m}$ in a time sufficiently short so that isolated impurity atoms cannot move, the magnitude of the segregation is given by

$$\frac{c_b}{c_g} = \exp \left( \frac{(E_b - E_f)}{kT_1} - \frac{(E_b - E_f)}{kT_{0.5T_m}} \right)$$

This equation predicts that segregation will increase as the vacancy-solute binding energy $E_b$, decreases which is clearly not correct. To compensate for this, Faulkner introduces a factor which indicates absolute concentrations of complexes. However, the validity of this expression is not obvious. The resultant equation, after incorporation of this factor, has the form

$$\frac{c_b}{c_g} = \exp \left( \frac{(E_b - E_f)}{kT_1} - \frac{(E_b - E_f)}{kT_{0.5T_m}} \right) \frac{E_b}{E_f}$$

This equation predicts the magnitude of non-equilibrium segregation solely resulting from the diffusion of complexes.
3.3.3. Extent of Segregation.

The extent of the effect is calculated assuming the resultant concentration profile to have the form depicted in Fig 3.3.2.1. It can be evaluated by assuming diffusion to occur isothermally for sequential periods of time at temperature. Quantification is then achieved by applying the solution to Fick's second law for semi-infinite solids (Crank, 1956, Doig et al, 1981)

\[
\frac{c_x - c_q}{c_b - c_q} = \text{erf} \left( \frac{-x}{2(D_v t)^{1/2}} \right),
\]

where \(D_v\) = complex diffusion coefficient
\(c_x\) = concentration of solute at a distance \(x\) from the boundary.

This solution is applicable to diffusion in a semi-infinite solid of composition, \(c_q\), to or from an interface with constant composition, \(c_b\). A major assumption in this treatment is that of a constant boundary composition, but this is not always the case especially during short ageing times and for boundaries where the carbides are widely spaced. For a complete derivation of this formula, see Stark, (1976).

The grain boundary composition can be calculated using the method of Tedmon, (1971) and Fullman, (1982). The calculation with respect to the material employed in this investigation is shown in
Appendix I.

Knowing the boundary composition $c_b$, the bulk composition $c_q$ and heat treatment, the diffusion profiles can be calculated and compared directly with experimentally determined profiles (Thorvaldsson and Dunlop, 1983).

The spatial extent of segregation when this process is occurring can be given approximately as

$$x_v = (D_v t)^{1/2}$$

where $t =$ ageing time.
3.4. Intergranular Precipitation of Chromium-rich Carbides.

3.4.1. Nucleation and Growth.

Due to the presence of non-equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults etc, nucleation in solids is almost always heterogeneous (Porter and Easterling, 1980). If the creation of a nucleus results in the elimination of a defect, some free energy will be released thereby reducing (or even removing) the activation energy barrier for nucleation.

The driving force for precipitation is proportional to the reduction in Gibbs free energy $\Delta G$, given by

$$\Delta G = \Delta G_c + \Delta G_s + \Delta G_{st}$$

where $\Delta G_c$ is the chemical energy, $\Delta G_s$ the surface energy and $\Delta G_{st}$ the strain energy (Pumphrey, 1976). If $\Delta G$ is plotted against the size of the nucleus, the resultant curve usually passes through a maximum $\Delta G^*$, which represents a barrier to precipitate nucleation.

As a grain boundary is a pre-existing interface, $\Delta G^*$ is smaller for precipitation and if the reaction is dominated by the surface energy term, this will induce heterogeneous grain boundary precipitation rather than homogeneous precipitation in the matrix. Additionally, the precipitation nucleation rate at grain boundaries is higher than in the matrix because solute segregation
and the enhanced solute diffusivity along the grain boundaries both increase the rate at which solute atoms join any critical nucleus (Butler and Swann, 1976). Thus on reaching the grain boundary, a rapid diffusion path is provided for chromium to diffuse to intergranular precipitates which grow by the collector-plate mechanism (Aaron and Aaronson, 1968, Chastell et al, 1987, Carolan and Faulkner, 1988). This mechanism considers each grain boundary to be filled by a set of square collector plates which receive chromium from the adjacent grains and feed it to the growing carbide. This is shown schematically in Fig 3.4.1.1.

Allotriomorphs, which are crystals that nucleate at grain boundaries and grow preferentially and more or less smoothly along them, tend to form by this mechanism. The morphology of the carbides produced in sensitised material is heat treatment dependent, but for short heat treatment times the carbides tend to be of this type as shown in Fig 3.4.1.2.

Thickening of the $\text{(Fe, Cr)}_{23}\text{C}_6$ carbides is controlled by the rate of diffusion of chromium along the $\text{(Fe, Cr)}_{23}\text{C}_6 :\gamma$ boundaries comprising the broad faces of the carbides. Also, the lengthening kinetics are controlled by volume diffusion of chromium to the $\gamma$ grain boundaries, followed by grain boundary diffusion to the advancing edges of the carbide, the former being the rate controlling step (Aaron and Aaronson, 1968, Aaronson et al, 1970).

Intergranular precipitation of chromium-rich carbides occurs principally on random high-angle grain boundaries and there is a wide variation in carbide size and spacing from boundary to
Figure 3.4.1.1. Schematic diagram of the collector-plate model.
Fig 3.4.1.2. Allotriomorphs produced in sensitised material.
boundary (Stickler and Vinckier, 1961, Butler and Swann, 1976, Hall and Briant, 1984, Butler and Burke, 1986). This may be attributed to differences in the angular misorientation between the two grains (Nicholson, 1970, Hall and Briant, 1984) and will be discussed in more detail in Section 4.2. An example of this is shown in Fig 3.4.1.3.

Chromium carbides formed in sensitised material are generally semi-coherent with one austenite grain and incoherent with the other. They exhibit a cube-cube orientation relationship with austenite of the type (Butler and Burke, 1986);

\[(111)_c // (111)_\gamma; \langle110\rangle_c // \langle110\rangle_\gamma.\]

On formation, the carbides initially assume a geometric shape, with the carbide/austenite interfaces favouring \{111\} type planes. These planes are favoured as the misfit between the carbide and austenite matrix is at its lowest and a semi-coherent interface can be created. This is a low energy interface, although the mismatch between the carbide and austenite is not accommodated elastically but by a grid of interfacial dislocations (Kekkonen et al, 1985, Butler and Burke, 1986). The interface with the other grain will be a high energy interface.

Depending on the annealing temperature, grain boundary diffusion can be a rapid means of mass transport, being more effective at lower annealing temperatures as in the case of low temperature sensitisation (LTS). On annealing, the numerous small carbide nuclei rapidly deplete the grain boundary area of
Fig 3.4.1.3. Variation in carbide size and spacing from boundary to boundary.
chromium. Hence, more chromium from the adjacent matrix diffuses to the grain boundary and then along it to supply the growing carbides, creating a depleted zone in the grain boundary area of chromium. The shape and growth of the carbide are controlled by a tendency to minimize the ratio of surface to volume of the carbide particle and hence interfacial energy.

Common structural features of random high-angle grain boundaries are steps and ledges and these act as preferential sites for precipitate nucleation, resulting in non-uniform carbide precipitate distributions along the length of a grain boundary. Also, the precipitate density and morphology are affected by variations in grain boundary plane along a curved boundary (Butler and Swann, 1976) and will be discussed in more detail in Section 4.2.

The actual composition of carbides in stainless steel has been determined by Hall and Briant, (1984). It was found not to change with heat treatment time and temperature. The composition of the M portion of the $M_{23}C_6$ carbides was found to be, in weight percent, 19% Fe, 65% Cr, 3% Ni and 13% Mo. This agrees well with the findings of Weiss and Stickler, (1972).

3.4.2. Characteristics of Precipitation.

High temperature exposure of 316 austenitic stainless steel can lead to the formation of various carbides and intermetallics. The nucleation and growth characteristics, morphology and composition of these phases have been determined by Weiss and
Stickler, (1972). They determined time-temperature-precipitation (TTP) diagrams so that given a specific time-temperature transient, the expected transformations could be predicted, as shown in Fig 3.4.2.1.

The stability regions of the various phases are represented by C-curves characteristic of such precipitation reactions. This can be explained by the relative dependencies of nucleation and growth rates on increased undercooling, ΔT. At temperatures close to the solutionising temperature, the driving force for transformation is small resulting in slow nucleation and growth rates with concomitant long transformation times. When ΔT is large however, transformation is limited by slow diffusion rates. Hence, a maximum rate is obtained at intermediate temperatures. The various phases identified include $M_{23}C_6$ and the intermetallics $\kappa$, $\sigma$ and $\eta$ (Laves). At ageing temperatures below 900°C, the carbide phase forms first, while the intermetallic phases appear only after longer ageing times. From the diagram, it is evident that the only phase expected following the heat treatment employed in this work, is $M_{23}C_6$.

$M_{23}C_6$ is f.c.c. with a reported lattice parameter of 10.621Å (Andrews et al, 1971). In solution treated and aged samples, $M_{23}C_6$ precipitates successively on grain boundaries, incoherent twin boundaries, coherent twin boundaries and finally intragranularly, as shown in Fig 3.4.2.2.

The morphology of the grain boundary carbides depends on the annealing temperature and on the nature of the boundary (Stickler and Vinckier, 1961). This temperature dependency is shown in Fig
Fig 3.4.2.1. Time–temperature precipitation diagram of 316 stainless steel, solution treated at 1533K for 1.5 hr and water quenched.
Fig 3.4.2.2. Sequence of precipitation sites of chromium-rich carbides in 316L stainless steel, solution treated at 1373K.
3.4.2.3. At low sensitising temperatures, the grain boundaries are covered with sheets of thin interconnecting flakes. At intermediate temperatures, the number of boundaries covered in sheets decreases until at high sensitising temperatures, the grain boundaries are decorated with discontinuous massive dendritic particles.

The form of the carbide also depends on the misorientation of the boundary. Various dendritic and geometric forms can precipitate on grain boundaries as mentioned above. On coherent twin boundaries the carbides are equilateral thin triangles and on incoherent twin boundaries they form ribbons of connected trapezoids as shown in Fig 3.4.2.4. Some preferential thinning of the boundary region is evident in this micrograph which occurs during electropolishing and is caused by the lower chromium content of the boundary region (Hall and Briant, 1984). As a result, it can serve as a useful visual indication of the location and extent of chromium depletion. It does not affect chromium concentration profile measurement significantly and can be eliminated by altering the temperature of the electropolishing bath.
Fig 3.4.2.3. Temperature Dependency of the Morphology of Grain Boundary Carbides.
Fig 3.4.2.4. Precipitation on an incoherent twin boundary.
3.5. Measurement of Segregation.

3.5.1. Applicable Analysis Techniques.

All early techniques for measuring segregation to boundaries had one major deficiency in common. They all required a knowledge of the surface active species beforehand (Hondros and Seah, 1977). This predicament was alleviated in the late 1960's with the introduction of a range of electron-optical techniques based on a number of physical processes such as Auger electron emission, X-ray photo-electron emission, secondary ion mass spectroscopy, ion-beam scattering and field-ion microscopy with the atom probe. No one technique can satisfy simultaneously all of the desired experimental requirements but by using a combination of these techniques the important information can be obtained. The relevant techniques are considered briefly below.

The most generally applied technique up to the late 1970's for metallurgical microanalysis and simultaneous microstructural examination was electron probe microanalysis using characteristic X-ray emissions. The sample is subjected to a focused beam of electrons which promotes inner shell excitations resulting in the emission of characteristic X-rays. However, this technique has been limited by a poor spatial resolution of 1μm which has prevented any quantitative measurement of localised grain boundary compositions.
This was partially overcome by the advent of the surface specific technique of Auger electron spectroscopy (AES), which has a depth resolution approaching atomic distances and a high lateral resolution. However, to obtain the analysis, the interface must be exposed by fracturing the specimen in-situ in an ultra-high vacuum chamber. This can only be achieved if the segregant at the boundary promotes intergranular brittleness. Additionally, segregation profiles up to boundaries can only be obtained by sequential ion-sputtering which can introduce errors owing to preferential removal or redeposition of particular ion-species.

As mentioned, employment of this technique necessitates that the boundary of interest be fractured to expose its surface. In many instances this situation is acceptable. Obviously however, if one is trying to correlate segregation characteristics with grain boundary crystallography, then this method is not applicable.

Field ion microscopy with the atom probe is another applicable technique, in which a selected atom on the surface of the specimen tip, which may be located at a boundary site, is desorbed by field evaporation and projected into a mass spectrometer. Due to its near atomic spatial resolution, this technique should be capable of distinguishing the boundary sites associated with segregation. As a result, the structural and chemical details of adsorption of solutes to a grain boundary or a precipitate/matrix interface could, in principle, be mapped out.

Field desorption microscopy could also be applied to grain boundary segregation studies. An applied field is raised to peel off atoms layer by layer from the tip surface. Atoms of a chosen
mass can be used to form an image of the tip. As a result, the locality of specific atoms can be determined. The atom probe has difficulty achieving this because of field curvature at defect sites such as grain boundaries resulting in the field desorbed atoms not following exactly the same trajectories as the atoms used to produce the usual FIM image.

Another surface technique which has had limited application to grain boundary segregation is that of ion back-scattering spectroscopy (IBS). In this technique, accelerated $^{12}\text{C}^+$ ions strike a grain boundary fracture surface and penetrate into the grain interior. The lattice atoms cause back-scattering of some of these ions in such a way that, at a given scattering angle, the ion’s energies are related to the mass of the scattering atom. The sensitivity of the technique is comparable to AES if the segregated atoms are heavier than those of the matrix.

Auto-radiography has in recent years become a relatively standard analytical technique for determining the spatial distribution of boron and certain other elements in metallic systems (Finlan, 1987). During irradiation, the $^{10}\text{B}(n,\alpha)^7\text{Li}$ fission reaction occurs releasing an alpha particle which may be detected by track sensitive plastics laid on the sample surface. The spatial distribution of boron can thereby be recorded in the material. However, the most widely used technique available currently for detecting segregation at grain boundaries is scanning transmission electron microscopy (STEM) and this technique will be discussed in more detail in the next section as it was employed throughout this work.
3.5.2. Scanning Transmission Electron Microscopy (STEM).

A TEM when operated in the scanning transmission mode has the capability of forming small (~5nm) high intensity electron probes and maybe interfaced with energy dispersive X-ray spectrometers (EDS) for detecting characteristic X-ray emissions (Doig and Flewitt, 1983). On traversing a thin foil specimen, one of the primary inelastic interactions induced by a high voltage beam of electrons is that of inner shell ionisation as depicted in Fig 3.5.2.1 (Williams, 1984). On ejection of an inner shell electron the atom is left in an excited and thus unstable state. One of the ways that it can return to its stable ground state is by an electron from an outer shell falling to the vacant inner shell position and at the same time emitting an X-ray of characteristic energy (and therefore wavelength). These X-rays, whose characteristic energy is a function of the difference in electron energy levels of the atom, provide direct information about the chemistry of the electron beam-specimen interaction volume and can be detected.

The X-rays generated can be detected by EDS involving a negatively biased Si chip into which Li has been diffused and onto which a thin Au contact layer has been evaporated. The detection is performed by the action of the X-ray photons entering the Si layer creating electron-hole pairs. This charge signal is then amplified and discriminated into incident X-ray energy by multi-channel analysers on the basis of height of the charge
Fig 3.5.2.1. Schematic diagram showing the ionisation of an inner shell (k) electron by a high energy electron.
signal pulse generated.

The electron source determines the electron current density in the probe and field emission guns provide the greatest brightness, typically about three orders of magnitude higher than a LaB$_6$ thermionic filament (Finlan, 1987).

STEM is usually restricted to detecting elements of atomic number greater than 11 although when the detector is operated in the "windowless" mode, lighter elements can be detected.

The spatial resolution of the technique is dependent on the initial probe size and the amount of beam spreading that occurs due to elastic and inelastic scattering of the electrons in the thin foil. It is however orders of magnitude better than the spatial resolution attained in the electron probe microanalyser, mainly due to the thinness of the specimen being used. This beam broadening effect will be described in a later section and has particular relevance in the microanalytical examination of segregation to grain boundaries and interfaces. Due to this effect, quantitative assessment of the amount of segregant at the boundary is not possible in some cases unless the beam profile is deconvoluted from the observed segregant profile (Hall et al, 1981). This will also be discussed in more detail in Section 3.5.2.4.

One of the most significant advantages of STEM is that measured segregations can be correlated with the crystallography of the grain boundary. The high resolution imaging and diffraction capability of conventional TEM (Edington, 1975) can be used simultaneously with chemical microanalysis. Consequently, the
grain boundary crystallography can be determined and directly correlated with the measured segregation to examine the role of misorientation on elemental segregation.

3.5.2.1. Electron Beam Spreading.

The main advantage in using thin films for X-ray microanalysis is the improved spatial resolution that results as compared to analysis of bulk samples using the electron probe microanalyser. However, on passing through the specimen, the electron beam still broadens. All incident electrons on a TEM sample potentially contribute to X-ray production and those scattered to the greatest angles define the effective width of the X-ray source size and hence the spatial resolution for analysis. This situation has been modelled by Goldstein et al, (1977) who assumed that each incident electron suffered a single, elastic, large-angle Rutherford scattering event at the centre of the foil, as shown in Fig 3.5.2.2.

They derived an expression such that the beam spreading,

\[ b = 6.25 \times 10^6 \frac{Z}{E_0} \left( \frac{\rho}{A} \right)^{1/2} t^{3/2} \text{ cm} \]

where \( E_0 \) is the incident beam energy in kV, \( A \) is the atomic weight, \( Z \) is the atomic number, \( \rho \) is the density (g/cm\(^3\)) and \( t \) is the specimen thickness in cm.

Although this model is based on a simple scattering treatment, the values predicted agree remarkably well with the
Fig 3.5.2.2. Model used for beam broadening calculation.
Monte-Carlo calculations of Geiss and Kyser, (1977) and the experimental measurements of Hutchings et al, (1979). Monte Carlo calculations are based on the computation of a large number of individual electron trajectories using a random number generator to approximate path length, scattering angle etc. Although easy to implement, these calculations are very (computer) time consuming (Jones and Loretto, 1981). Additionally, Cliff and Lorimer, (1981) have tried to modify the model by incorporating the effects of plural scattering but obtained an expression identical with that predicted by Goldstein et al.

Relating this expression to the detection of a segregant at a grain boundary, it is evident that the proportion of X-ray signal obtained from the segregant will be increased by decreasing the foil thickness and incident electron probe size and increasing the electron accelerating voltage. In other words, the effective interaction volume induced in the foil will be reduced. This will in turn reduce the X-ray intensity emitted for a given electron source brightness. Thus any benefit of improved spatial resolution will be offset by decreased statistical accuracy of the recorded X-ray data (Doig et al, 1981). As a result, these factors must be considered simultaneously when conducting any analysis.

The general effect of beam broadening is principally to increase the measured grain boundary segregant concentration in sensitised material. This is because the signal is acquired from regions of a locally higher chromium concentration adjacent to the boundary which is incorporated in the interaction volume. This effect can be accounted for however by considering the electron
intensity distribution within the probe (Section 3.5.2.4).

3.5.2.2. Effect of Grain Boundary Alignment on STEM-EDS X-ray Microanalysis of Grain Boundary Segregations.

In order to obtain maximum X-ray signal from a segregant at a grain boundary, it is desirable to orient the boundary parallel to the incident electron beam. This is to ensure that as much of the resulting interaction volume (produced by electron scattering events) consists of the segregated species and not the adjacent matrix. However, the limited spatial resolution of imaging and the specific requirement of orienting the foil with respect to the X-ray detector, may result in some misalignment, $\psi$, of the boundary with respect to the electron beam (Doig and Flewitt, 1983). This is shown schematically in Fig 3.5.2.3.

This misalignment will reduce the proportion of X-rays derived from the segregant. The greater the misalignment, the lower will be the proportion derived from the segregant. Increasing the electron probe size decreases the sensitivity to boundary misalignment (Doig and Flewitt, 1983). For a point source of electrons (at the foil surface) a misalignment of $1^\circ$ reduces the measured X-ray intensity from the segregant by 50% but for a 10nm probe, a misalignment of $\sim10^\circ$ is required to produce an equivalent reduction in intensity, if the foil is 100nm thick.

In conclusion, it is essential to align the grain boundary as near parallel to the electron beam as possible before undertaking any microanalysis. This will then increase the accuracy of any
Fig 3.5.2.3. Effect of grain boundary misalignment on STEM–EDS X-ray microanalysis of grain boundary segregations.
3.5.2.3. Quantitative Microanalysis.

A significant gain in the spatial resolution of analysis can be attained if thin specimens are used as opposed to bulk specimens. Quantitative analysis of such thin sections is also easier to perform. This is because very little of the energy of the primary electrons is lost in the specimen and so the ionisation cross-section (the probability that an electron will eject a particular inner shell electron) will be constant throughout the specimen thickness (Goodhew and Chescoe, 1980). This is known as the thin film criterion. As a result of this effect, quantification is simplified because to a first approximation, X-ray absorption and fluorescence effects can be neglected. It has been shown by Cliff and Lorimer, (1975) that for thin samples (<100nm)

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

where $I_A$ and $I_B$ are the measured characteristic X-ray intensities and $C_A$ and $C_B$ are the weight fractions of any two elements A and B in the specimen. The Cliff-Lorimer factor, $k_{AB}$, is dependent on the two elements, the operating conditions, the detector response and can be calculated or determined experimentally. It does not have to be collected for all possible pairs of elements and it is
common practise to standardise all elements with respect to silicon.

Having obtained spectra, characteristic X-ray intensities can be determined in a similar fashion to those used for bulk specimens (Goodhew, 1987). The filtered least squares method (Statham, 1987) was utilised in this work in which peak shapes and positions are deduced from standard spectra and the spectrum to be analysed compared with these. As a result, the background is subtracted and overlapping peaks deconvoluted.

The limit of detectability of an element A in a matrix of element B is given by Goldstein, (1979) as

$$C_A = 3 \left( \frac{2I_C}{I_B k_{AB} C_B} \right)^{1/2}$$

where $I_C$ is the continuum background for element A. From this equation, it can be seen that the detectability decreases as the count rate or counting time increases. To increase count rate either a thicker specimen or a larger probe is required both of which cause a deterioration of the spatial resolution. As a result, absorption and fluorescence may come into play; fluorescence being a particularly important consideration in stainless steels because the major elements are close in atomic number (Cr=24, Mn=25, Fe=26, and Ni=28). In practise, detectability limits are typically of the order of 0.1 to 0.5wt% for bulk analyses in which the composition does not vary throughout the analysed volume.
3.5.2.4. Conversion of Measured Concentration Profiles to True Ones.

In order to determine the distribution of a segregant about a grain boundary, it is necessary to analyse at a succession of positions across the boundary. A true quantitative description of the resultant composition profile can only be attained by considering the precise electron intensity distribution within the thin foil interaction volume together with the true composition profile and deconvoluting the two effects (Goodhew and Chescoe, 1980, Hall et al, 1981, Doig et al, 1981, Mulford et al, 1983, Hall and Briant, 1984). This is because the incident electron probe scatters after penetrating a thin foil specimen producing a distribution of generated X-ray intensity. Doig et al, (1981) have employed this approach and developed an empirical expression for the dispersion of the electron beam within the foil.

The electron intensity distribution in a STEM electron probe on passing through a thin foil is given by

\[
I(r, t) = I_e \left[ \pi(2\sigma^2 + \beta t^3) \right]^{-1} \exp \left\{ -r^2 / (2\sigma^2 + \beta t^3) \right\}
\]

where \( \beta = (4Z/E)^2.(\rho/A).500 \), \( I_e \) is the total electron flux, \( \sigma(\text{nm}) \) is a measure of the incident electron probe size, \( Z \) and \( A \) are the mean atomic number and weight of material with density \( \rho \) and \( E(\text{V}) \) is the electron accelerating voltage.
The grain boundary segregation profile shown in Fig 3.5.2.4. can be described by

\[ C_x = C_0 \exp \left( -\frac{|x|}{w} \right) \]

where \( C_x \) is the concentration of the segregant at a distance \( x \) from the boundary, \( C_0 \) is the concentration on the boundary and \( w \) is the spatial extent of the segregation.

Combining this assumed segregation profile with the electron intensity distribution gives the X-ray signal, \( I'(0) \) from the grain boundary \((x=0)\):

\[ I'(0) = K \int_{V} C_x \cdot I(r,t) \, dV \]

where \( K \) is a constant defining the efficiency of X-ray detection, \( r^2 = x^2 + y^2 \) and \( V \) is the foil volume.

By utilising this above expression the true composition profile about a grain boundary can be determined from a measured one as shown by Doig et al, (1981). An example of this is shown in Fig 3.5.2.5, (Hall and Briant, 1984), with respect to a chromium concentration profile measured normal to a grain boundary in a 316L stainless steel aged at 650°C for 50hr. The principal effect of beam broadening in this case is to increase the observed segregant concentration to above the true value. This effect will be increased with increasing specimen thickness (Hall et al, 1981). The maximum error in grain boundary chromium concentration for the thickness range generally encountered in AEM specimens
Fig 3.5.2.4. Assumed grain boundary segregation profile.
Fig 3.5.2.5. Comparison of true and experimental concentration profiles.
(100-400nm) is 11% (Mulford et al, 1983). Hence, to a first approximation, effects due to different foil thicknesses can be ignored.

In addition, it can be seen that the measured concentration profile in this case is in good agreement with that calculated using the model and thus to a first approximation can be considered to truly reflect the segregation characteristics at the boundary. However, if the concentration profile is very narrow (as in the case of equilibrium segregation), then the effects of beam broadening are more significant resulting in a larger deviation between measured and true concentration profiles.

In the present work, a precise knowledge of the exact form of the concentration profile was not required. The profiles were accumulated from a number of boundaries with the objective of comparing them with boundary crystallography. Hence, only relative differences from boundary to boundary were required. This fact, coupled with the good agreement between measured and true profiles for thin foils of thickness compatible to AEM, permitted direct comparison of measured profiles with no need to implement the effects of electron intensity distribution within the incident beam. The effect of the broadening was however noted.

4.1.1. Introduction.

A grain boundary may be defined as a boundary that separates two crystals which differ in either crystallographic orientation, composition or dimensions of the crystal lattice or in two or all of these properties (McLean, 1957). It is a high energy region in which the atoms do not have the normal number, arrangement or separation of nearest neighbours and as an internal surface may favour the initiation of phase transformations such as precipitation (Westbrook, 1964).

Grain boundaries are usually classed as either low-angle or high-angle according to the misorientation of the crystals on either side. An arbitrary boundary can be represented by five degrees of freedom. Three are required to define the misorientation between the two crystals and the other two to define the direction of the boundary normal (Lange, 1967). Although several models have been proposed to explain grain boundary structure, none could be classed as the "ideal" model. An ideal model should provide complete information regarding the structure of the boundary and how it varies with changes in crystal parameters. It should account for the role of the structure in governing the properties of the material such as
sliding, precipitation, etc. Additionally, it must give precise information about the width of the boundary and its free energy and how the latter varies with misorientation (Maheswaran, 1982).

The original model proposed to explain grain boundary structure was proposed by Rosenhain, (1913). This amorphous cement theory postulated that "the crystals of a pure metal are surrounded and cemented together by a very thin layer of the same crystal in the amorphous condition, whose properties correspond to those of the liquid metal subjected to extreme undercooling". This was supported experimentally by the fact that at high temperatures grains slide over one another. By considering the relative temperature dependencies of crystalline and amorphous materials, this behaviour would be expected. However, this model could not explain how many boundary properties depend on the angular misorientation between the two grains and are not isotropic in the boundary plane.

In 1924, Jefferies and Archer suggested the transition lattice theory which predicted that a few layers at the boundary consist of atoms occupying compromise positions between the two lattices. They deduced that for any given misorientation a definite arrangement of atoms exists which is determined by the minimum potential energy. The downfall of this model was that it could not account for grain boundary sliding without the requirement of a very thick boundary zone and it is now known, using field-ion microscopy, that the boundary consists of only 2-3 atomic layers (Brandon et al, 1964).

Two additional theories put forward to explain sliding at
grain boundaries are the island theory of Mott, (1948) and the
diffusion structure of Ke, (1949). It was envisaged that islands
of good atomic fit existed between areas of bad atomic fit and
that these islands could slide easily. However, this assumed that
all high-angle grain boundaries were structurally similar. Also,
neither model could account quantitatively for the energy of the
boundary. It seems apparent that the concept of a boundary
consisting of regions of good atomic matching surrounded by
regions of poor atomic matching is an accurate one and indeed this
forms the basis of the currently utilised grain boundary structure
models.

The lattice dislocation model for low-angle boundaries,
originally suggested by Burgers, (1939) and Bragg, (1940) and
developed by Read and Shockley, (1950) has however won general
acceptance (Pumphrey, 1976). It describes precisely atomic
arrangement and enables boundary energy to be calculated as a
function of the angular misorientation, as will be shown in
Section 4.1.2. Additionally, it satisfactorily explains the
mechanical behaviour of low-angle boundaries.

High-angle boundary structure is, however, far less well
understood as it is rather difficult to extend the lattice
dislocation model to these boundaries. This is a consequence of
the separation between dislocations decreasing as the angular
misorientation between the grains increases. Dislocation cores
begin to overlap when the misorientation exceeds 10-15° resulting
in a loss of identity of individual defects. High-angle boundary
structure may however be described geometrically by this model but
this is of limited value when a physical description is required. One model to explain this type of boundary structure was described by Li, (1961) in which he extended the lattice dislocation model by taking into account the core energy interaction of the dislocations. However, most experimental evidence provides support for the coincidence site lattice (CSL) model which will be described in Section 4.1.3.

As models must relate the boundary structure to the crystallographic parameters, it will be shown that the lattice dislocation model for low-angle boundaries together with the coincidence site lattice model of high-angle boundaries (and its variants) are geometric in origin (i.e. they do not take into consideration the physical interaction between atoms at the interface).
4.1.2. Low-angle Boundaries.

The dislocation model developed originally by Burgers, (1939) and Bragg, (1940) can be used to describe the structure of low-angle grain boundaries. If adjacent grains have a small difference in orientation, the dislocation model emerges naturally from the crystal geometry. This can be seen by considering Fig 4.1.2.1. The two simple cubic crystals have a common cube [001] axis and their orientation difference is defined by a relative rotation through an angle $\theta$ about this axis (Fig 4.1.2.1a). If the two grains are joined to form a bicrystal (Fig 4.1.2.1b), then the misfit between the two will have to be accommodated. This is achieved by a set of regularly spaced edge dislocations in the case of a low-angle tilt boundary. If the spacing between the dislocations is denoted by $D$, then from the geometry,

$$\tan \theta = \frac{b}{D}$$

where $\theta$ = misorientation angle

$b$ = Burgers vector of the dislocation

For small $\theta$,

$$\theta = \frac{b}{D}$$

The misorientation $\theta$, depends on the spacing of the dislocations. When $\theta$ exceeds about 20°, the dislocations are so close together that they cannot be regarded as distinct (McLean, 1957). As a result, it is not possible to apply this model to high-angle
Fig 4.1.2.1. A simple grain boundary. The plane of the figure is parallel to a cube face and normal to the axis of relative rotation of the two grains.
boundaries due to the elastic strain fields at dislocation centres and dislocation interactions themselves being ignored.

A tilt boundary can be defined as a boundary in which the orientation difference between the two crystals on either side of the boundary is equal to a rotation about an axis which lies in the plane of the boundary (McLean, 1957). A twist boundary is one in which the orientation difference between the two crystals on either side of it is equivalent to a rotation about a simple crystallographic axis which is normal to the boundary. Tilt boundaries are made up of edge dislocations and twist boundaries of screw dislocations. General low-angle boundaries contain dislocations of mixed character.

The energy of low-angle boundaries can be calculated assuming they are composed of dislocations and then applying dislocation theory, such that

\[ E = E_0 \theta (A - \ln \theta) \]

where

- \( E_0 = \frac{Gb}{4\pi(1 - \nu)} \)
- \( A = 4\pi(1 - \nu) \frac{B_e}{Gb^2} \)
- \( G = \) shear modulus
- \( b = \) Burgers vector of the dislocations
- \( \nu = \) Poisson's ratio
- \( r = \) distance reached by the elastic distortion of the dislocation
- \( B_e = \) energy of the dislocation core where the distortion becomes non-linear.
$E_0$ and $A$ are only constant if the boundary direction does not change and the equation is only valid if the dislocations are regularly spaced. Comparing theoretical predictions using this equation with experimental observations on tilt boundaries yields good agreement as shown in Fig 4.1.2.2.

Additionally, using TEM, Hirsch et al (1956) correlated the directly observed dislocation density in a low-angle boundary with the boundary misorientation thus providing further experimental confirmation of this theory.

In conclusion, it is apparent that the lattice dislocation model can explain the structure of low-angle grain boundaries and can also provide accurate information regarding the relationship between boundary energy and the misorientation angle between the two crystals.
Fig 4.1.2.2. Comparison of theoretical energy of dislocation boundaries (curve) with measured energies of grain boundaries (points).
4.1.3. High-angle Boundaries.

It was concluded in an article relating grain boundary structure and energy by Goodhew in 1979, that no adequate model exists to predict either the detailed structure or the energy of a boundary given the geometrical misorientation between the crystals and this remains the unsatisfactory state of the art at the present day. Hence, experimental measurements and calculations from interatomic potential are the only weapons available to alleviate this predicament.

Models to account for boundary structure are geometric in origin and utilise the concept of a Coincidence Site Lattice (CSL). A CSL is a three dimensional superlattice on which a fraction \( \frac{1}{\Sigma} \) of the lattice points in both lattices lie (Pumphrey, 1976). The common sites of both lattices comprise a single three dimensional lattice with a larger unit cell than the single crystal lattice itself.

The coincidence lattice model was originally proposed by Kronberg and Wilson, (1949). In 1950, Read and Shockley extended their dislocation model for low-angle boundaries to account for the structure of high-angle boundaries in terms of two dislocation arrays. Brandon, (1966) combined and extended these two models such that a dense dislocation array corresponded to the coincidence boundary and a low density array to the coincidence lattice sub-boundary itself.

Fig 4.1.3.1 shows a CSL generated by a rotation of 50.5° about [110]. The reciprocal density of common lattice points \( \Sigma \), is
Fig 4.1.3.1. $\Sigma = 11$ CSL boundary in a two dimensional b.c.c bicrystal.
11. The best fit and lowest energy of the interface occurs when a plane containing a high density of coincident sites is followed, i.e. A-B or C-D. When the boundary plane is inclined to such a high density plane, it will develop a stepped path (ABCD) to maximise the proportion of good matching.

Thus the structure of a coincidence site boundary can also be interpreted in terms of regions of good fit, where the boundary follows the most densely packed coincidence lattice planes and regions of bad fit at the ledges, as implied by Mott.

It should be stressed at this point that while the density of coincidence points is only orientation dependent, the density of coincidence sites at a boundary depends on the plane of intersection of the boundary with the coincidence lattice (Brandon et al, 1964).

According to Ranganathan, (1966) a three dimensional CSL will be generated by a rotation $\theta$ about $[hkl]$ if

$$\theta = 2 \tan^{-1} \left( \frac{y}{x \sqrt{N}} \right)$$

where $x$ and $y$ are integers and

$$N = (h^2 + k^2 + l^2).$$

Also

$$\Sigma = x^2 + N y^2.$$
Obviously an infinite number of CSLs can be generated with a large $\Sigma$ and there is no good criterion for deciding how large $\Sigma$ can be without becoming meaningless. Indeed, the question of how high $\Sigma$ can become while still having a significant influence on boundary properties is in itself rather presumptuous. This assumes there does exist a correlation between $\Sigma$ and boundary energy, as all boundaries with $\Sigma$ values above this upper limit must have greater energies than those below it. This assumption however, has no foundation.

Each CSL only exists for a precise angle/axis pair misorientation and thus only a very small percentage of real boundaries would be expected to conform to this criterion. Most boundaries will lie at an angle to the most densely packed planes of the coincidence lattice. Small orientations away from these "special" boundaries can be accommodated by sets of dislocations which are known as "secondary intrinsic grain boundary dislocations". By considering how closely the dislocation cores may approach before overlap begins, it is possible to define an approximate angular deviation from an exact CSL which is acceptable. This was proposed by Brandon, (1966) to be

$$V = V_0 \Sigma^{-1/2}$$

where $V$ is the CSL angular limit and $V_0$ is the angular limit for a low-angle boundary description, which is $\sim 15^0$.

An alternative geometrical concept of a more general nature
than the CSL is that of the 0-Lattice, (Bollmann, 1970) in that actual coincidence of lattice sites is not important but the points in space about which there is no misfit (before relaxation) are plotted. This is equivalent to finding all the rotation axes about which lattice 2 could be rotated with respect to lattice 1 to achieve the same pattern. It provides a good explanation of low-angle boundaries and dislocation networks and also predicts the gradual transition of properties as the misorientation between the two crystals increases. However, the model does not show enough physical insight, and does not predict the occurrence of special boundaries.

A conceptually simpler model developed to account for linear structures observed in many boundaries is the planar matching model. In this model, only planes of atoms are considered and individual atomic locations ignored. So many boundaries will exist in which the misorientation axis is (or nearly is) a common direction in both crystals. In this case, stacks of planes may be coincident across the boundary and the boundary might therefore be one of low energy (Pumphrey, 1973). If there is a slight planar misalignment then these planes may relax to regions of perfect atomic matching in the boundary plane interspersed with regions of mismatch accommodated by arrays of intrinsic dislocations.

The difference between this model and the CSL models is that all boundaries created by rotations about a low index axis are considered as low energy as opposed to the CSL model in which only those at special misorientations are of low energy. Utilising this planar matching model it is easier to interpret electron
micrograph images of linear structures in boundaries as diffraction patterns are interpreted in terms of planes. However, lots of special misorientations are predicted making the concept of a "special" boundary itself meaningless.

Another model emphasising the periodic nature of a boundary is the structural units model (Bishop and Chalmers, 1968). This is confined to the boundary itself rather than to the three dimensional crystal and hence overcomes the objection to the CSL theory that a long range order matrix superlattice is unlikely to affect grain boundary structure. The basic concept is that grain boundaries may be described in terms of a two dimensional array of certain polyhedral units. By the periodic repetition of these units along the boundary, the boundary itself may be constructed.

Recently, Wolf, (1985) and Gleiter and co-workers, (1985) proposed two new geometric criteria for low interfacial energy. Wolf suggested that either a high planar CSL site density or large interplanar spacing would generate low boundary energy. The first criterion is specific to twist boundaries and is identical to an earlier concept (Brandon et al, 1964). It predicts minimum interfacial energy on a given lattice plane at twist angles corresponding to the "locally smallest" CSL unit-cell area. The second criterion applies to tilt boundaries and predicts energy minima for tilt angles corresponding to "locally large" interplanar spacing. However, the magnitude of the term "local" is not stated and thus the ranges of validity of these criteria are not known, making their predictive power effectively zero (Sutton and Balluffi, 1987).
Gleiter, (1985) using the rotating crystallite technique (see Section 4.1.4) found that metallic spheres rotated to relatively low energy misorientations with ionic crystal substrates during annealing. It was observed that some close packed directions and low index planes in the two phases became parallel. This could not be explained in terms of the CSL model as no CSL orientations of low \( \Sigma \) existed in the vicinity of the observed relationships. It was envisaged that these close packed atomic planes in the metallic surface could "lock-in" to the valleys between close packed planes in the adjacent ionic crystal.

In the next section, the above geometric criteria will be compared with experimental results to determine their applicability in describing grain boundary structure.
4.1.4. The Relationship Between Grain Boundary Structure and Energy.

As pointed out in the last section, it is evident using the CSL concept that a low value of $\Sigma$ is a necessary precursor to low energy (i.e. an orientation dependence exists) while the planar matching model predicts energy valleys for all rotations about low index axes. Hence, experimental evidence is required to determine the validity of these opposing predictions.

Grain boundary energy data has been attained from two main sources:

1. experimental observations based mainly on grain boundary tension measurements at triple points or from rotating crystallite experiments;

2. computed values based on theoretical atomic potentials and predicted relaxed structures.

This topic has been reviewed in the past (Pumphrey, 1976, Goodhew, 1979) and only the major observations are outlined here.

It has been shown experimentally by Hasson and Goux, (1971) that at $650^\circ$C, outside the low angle region, there is no significant variation in energy of [100] symmetrical tilt boundaries in aluminium. In the case of [110] symmetrical tilt boundaries however, deep cusps in boundary energy appear at particular misorientations which correspond to $\Sigma = 3$ and $\Sigma = 11$ CSLs. These results are shown in Fig 4.1.4.1 and showed excellent
Fig 4.1.4.1. Measured grain boundary energy for symmetric tilt boundaries in aluminium:
(a) [100] rotation axis;
(b) [110] rotation axis.

Fig 4.1.4.2. Computed grain boundary energy at 0K for symmetric tilt boundaries in aluminium:
(a) [100] rotation axis;
(b) [110] rotation axis.
agreement with computed predictions (Fig 4.1.4.2).

The fact that grain boundary energy cusps occur for $\Sigma = 3$ and $\Sigma = 11$ boundaries is expected as these boundaries ($\langle110\rangle$ in f.c.c. metals) are comprised of entirely close packed polyhedra according to Vitek et al, (1979). Thus these boundaries would be expected to have special properties such as low energy and inhibited diffusion, corrosion and segregation characteristics compared to other boundaries. However, it is not clear why these two boundaries exhibit marked cusps, while other low $\Sigma$ CSL boundaries with low index planes show no cusps. This brought into question the validity of CSL type geometric models in interpreting boundary structure.

Grain boundary energy also varies as a function of boundary inclination and this was demonstrated by Gleiter, (1970) using a $71^\circ/\langle110\rangle$ tilt boundary in an Al-0.46%Cu alloy. This is shown in Fig 4.1.4.3. Cusps in the observed energy were found to exist at inclinations which corresponded to symmetric high-coincidence tilt boundaries. For all other boundary inclinations, the boundary energy was approximately constant. However, this effect is difficult to isolate from other variables such as variation in misorientation and so the evidence is not conclusive.

Boundary energy would also be expected to decrease as a function of temperature from the Gibbs free energy equation, namely $E = H - TS$. Erb and Gleiter, (1979) demonstrated this using sintered Cu spheres in which the boundary energy at specific orientations was seen to decrease at higher temperature presumably due to a change in the structure of the boundary brought about by
Fig 4.1.4.3. Measured energy of a [110] tilt boundary as a function of the inclination.
the increased entropy. It is generally accepted that boundary energy anisotropy decreases as the temperature is raised (Fig 4.1.4.4). Further evidence for this was provided by Lojkowski et al, (1988) who found that the number of boundaries associated with energy cusps decreased with increasing temperature. They interpreted these results in terms of unlocking of locked atoms due to thermal vibrations.

Additionally, it is known that the boundary energy varies with impurity levels at the boundary (Hondros and Seah, 1979, Goodhew, 1979). There is not much experimental evidence to reinforce this fact but generally the grain boundary energy decreases as the solute level increases. There is also some evidence that the energy of boundaries with a low $\Sigma$ is less affected than that of random boundaries. The effect of impurities on boundary energy is summarised in Fig 4.1.4.5.

These experimental studies are generally carried out on specially oriented bicrystals or carefully produced interfaces with a pre-determined boundary crystallography. Emphasis should be re-directed to polycrystalline materials as the literature available concerning grain boundary crystallography studies in real engineering materials is pitifully small. Perhaps a greater insight into the more general nature of grain boundaries could then be established. Having received so much attention, results attained from symmetrical tilt and twist boundaries could rationally be used as building blocks to create a greater understanding of the polycrystalline nature of grain boundary structure which controls so many materials properties.
Fig 4.1.4.4. Effect of temperature on grain boundary energy. (a), (b) and (c) are sections of the $\gamma = f(\theta)$ surface at increasing temperatures. The number of cusps remaining decreases as the temperature rises.
Fig 4.1.4.5. Effect of alloying and segregation on grain boundary energy. (a) A section of $\gamma = f(\theta)$ containing four cusps. (b) The effect of alloying. (c) The effect of subsequent segregation.
Computational efforts to shed light on the problem involve using the Morse interatomic potential and assuming the atoms in the boundary region to be relaxed in their minimum energy positions at 0K. However, the vast majority of experimental evidence has been obtained at room temperature so direct comparison may seem invalid if the effects of temperature on entropy are considered. Nevertheless, the disordering effects of temperature on structure are expected to be either of little importance or of a relatively simple type when \( T < T_m/3 \), \( T_m \) being the melting temperature. Therefore, in many cases, structures calculated at 0K may be legitimately compared with experimental observations made at room temperature (Balluffi, 1985). Additionally, most calculations have been performed for symmetrical tilt boundaries and thus care must be taken in extrapolating to other boundaries.

Recent computer simulated atomistic studies of grain boundaries have discovered that atoms occupying coincidence sites generally do not exist in coincidence grain boundaries due to the relative rigid body translations of the grains themselves away from these coincidence positions to achieve a relaxed state (Vitek et al, 1979, Gleiter, 1982).

In addition, these atomistic studies also demonstrated that for both tilt and twist boundaries, the energy of the boundary is not directly related to either the reciprocal density of lattice sites \( \Sigma \), or the density of coincidence sites or O points in the boundary (Vitek et al, 1979). Pronounced energy differences between different coincidence boundaries do not exist except for a
small number of very low energy \( \langle 110 \rangle \) tilt boundaries. As a result, no strong dependence of grain boundary energy on structure can be expected in general. This contrasted with earlier views that good fit at coincidence sites would create a low energy boundary (Brandon et al, 1966, Bollmann, 1970). Although this implies that the CSL and O-lattice models should not be used in considerations of energy and atomic structure of boundaries, the CSL theory is critical in the construction of periodic boundaries utilised in atomistic studies and consequently is the backbone of future initiatives. In addition, due to its formal geometry, Burgers vectors of boundary dislocations are readily calculable (Goodhew, 1979). The fact that only a few \( \langle 110 \rangle \) tilt boundaries exhibited a low energy also provided evidence against the planar matching theory which predicted widespread energy dependencies for rotations about high index axes.

These results overall provided support for the structural unit model as these polyhedral configurations could be combined to accurately describe the grain boundary structure in its relaxed (minimum energy) position whereas the CSL and O lattice models failed to do this.

Consequently, it seems likely that the structural unit/grain boundary dislocation model should be applicable to all types of boundaries at low temperatures \( (T < \frac{T_m}{3}) \). Such boundaries will therefore exhibit the degrees of order characteristic of this model. Evidence favouring this has been found for a wide variety of boundaries including short and long period tilt and twist boundaries and also mixed boundaries (Balluffi, 1985). Extension
to general mixed boundaries would involve the combination of a relatively large number of different types of structural units and hence would be highly complex. Even so, they would possess characteristic structures and therefore complex types of order. In addition, it is thought that this model is applicable for most boundaries over essentially the entire temperature range.

It should be noted that in many boundaries only distorted polyhedra could be identified and there is some debate as to the maximum acceptable distortion these units can exhibit before they are no longer recognisable as one of the distinct polyhedral types compatible with this model.

However, it is evident that grain boundaries are not as amorphous as originally thought and that considerable degrees of order exist in many boundaries.

Currently, mainly low Σ special boundaries have been simulated and future work in this field will be to apply these findings to higher Σ and random grain boundaries. Indeed, if the same type of polyhedral units are found in all boundaries, this could explain why many properties of grain boundaries are similar although some orientation dependencies exist.

From the preceding brief review, it is evident that no definitive model exists which can completely describe the geometric structure and properties of high-angle grain boundaries, although with the advent of computer simulated atomistic studies, the light at the end of the tunnel is becoming brighter.

Experimental studies to date indicate that cusps are exhibited in grain boundary energy versus "some variable" plots
for specific misorientations. However, no adequate model exists to relate this physical characteristic to the two dimensional atomistic structure of the grain boundary itself. Having tested the various geometrical criteria against experimental results it is evident that too many discrepancies exist and as a result no geometric criterion for low interfacial energy can be regarded as wholly reliable. The CSL concept is helpful but the structural unit model seems more promising but at too early a stage in its development to command widespread applicability.
4.2. Segregation and Precipitation as a Function of Grain Boundary Crystallography.

One of the most striking features in any examination of grain boundaries is the wide variation in the number and distribution of precipitates from boundary to boundary. These precipitates are a direct consequence of the segregation of solute from the grain interiors to the boundary. In the case of non-equilibrium segregation, the important factor is the ability of the boundary to act as a vacancy sink (Karlsson et al, 1988). It has been shown experimentally (Balluffi, 1980) that random high-angle grain boundaries act as highly efficient vacancy sinks whereas special boundaries, such as coherent twins, do not. Thus, the amount of non-equilibrium segregation should be roughly the same at the majority of boundaries, whereas special boundaries such as coherent twins, should be devoid of, or have less, segregated solute atoms. So some boundaries act as more efficient sinks for vacancies/impurities than others, which will produce steeper concentration gradients and thus a greater driving force for segregation to the boundary. The resultant effect is shown in Fig 4.2.1.

Impurity segregation is known to reduce grain boundary energy (Butler and Swann, 1976, Hondros and Seah, 1977, Goodhew, 1979) and thus the higher the boundary energy the greater will be the propensity of segregation occurring to that boundary. The energy of planar high angle grain boundaries reduces to a minimum at specific misorientations, namely special boundaries. These
Fig 4.2.1. Variation of grain boundary precipitation in sensitised stainless steel.
boundaries exhibit a lower impurity segregation level than random grain boundaries (Gleiter, 1970), although the experimental evidence is somewhat conflicting. As a result, one would expect to see less precipitation occurring on a special boundary than on a random high-angle grain boundary (Butler and Swann, 1976). Indeed, Butler and Burke, (1986) observed no precipitation at coherent twin boundaries ($\Sigma = 3$) in a sensitised austenitic stainless steel. Limited precipitation was observed however at incoherent twin boundaries causing a very narrow chromium depleted region (<50nm) adjacent to the boundary. The most extensive precipitation was detected at random high-angle grain boundaries leading to the widest chromium depleted zones, in agreement with Weiss and Stickler, (1971). This would be expected on consideration of the relative energies of a coherent twin boundary, incoherent twin boundary and grain boundary of 19, 209 and 835 mJm$^{-2}$ (Murr, 1975) for a similar stainless 304 alloy. No mention was made of precipitation occurring on low-angle grain boundaries which would be expected as these boundaries have a lower energy than high-angle boundaries and thus a smaller driving force to attract the segregant (Watanabe et al, 1978).

In addition, boundary diffusion was determined by Achter and Smoluchowski, (1951) to be faster in high-angle grain boundaries than in low-angle grain boundaries. The depth penetration of silver along the boundaries of columnar copper in the columnar direction [100] was monitored and correlated with Mott’s conception of grain boundary structure. For low-angle grain boundaries, good lattice matching across the boundary is envisaged
which prevents intergranular diffusion being faster than volume diffusion. For high-angle grain boundaries (where the island model of Mott applies) faster diffusion occurs through the regions of large misfit, around the islands of good atomic matching. As the angle of misorientation between the grains increases so does the fraction of disordered regions, facilitating more rapid intergranular diffusion as demonstrated experimentally.

Furthermore, a cusp in intergranular diffusion was detected at an orientation corresponding to a special boundary as was expected from grain boundary structure theory.

Hence, for significant precipitation to occur, a rapid diffusion path is required to supply the growing carbide and this pre-requisite condition is only encountered in high-angle grain boundaries, in accordance with experimental observations that carbides only precipitate on these boundaries.

It is also known that carbides formed in austenitic stainless steel share an orientation relationship with the matrix (Butler and Burke, 1986). If the grain boundary exhibits this preferred orientation then precipitation will be favoured. Indeed, this is the predominant reason why the distribution of carbides is not uniform along the length of a boundary. Due to the nature of high-angle grain boundaries, they are not planar entirely along their length and thus certain regions, namely steps and ledges, will provide preferential nucleation sites (Butler and Swann, 1976). The precipitate orientation seems to be controlled by the condition that a good fit exists between precipitate and matrix atoms over planes of relatively low index (Vaughan and Silcock,
1967). Also, the grain boundary plane can change along the length of a high-angle grain boundary which can affect precipitate nucleation density.

The contact angle between the precipitate and grain boundary is dependent on the boundary energy and the orientation of the precipitate with respect to the adjoining grains (Nicholson, 1970). This angle increases as the boundary energy decreases and hence, low-angle boundaries are not favoured nucleation sites, as illustrated by Vaughan, (1968) in a study of grain boundary precipitation in an Al-4%Cu alloy. He found that equilibrium \( \theta \) only precipitated on boundaries whose misorientation was \( \approx 9^0 \), and at misorientations below this the \( \theta' \) precipitate nucleated. It was suggested that the boundary is composed of individual dislocations at misorientations \( \approx 9^0 \) such that nucleation is due primarily to elastic strain interactions as for nucleation on matrix dislocations. At misorientations \( \approx 9^0 \), as boundary energy increases, the contact angle is reduced thus favouring precipitation.

In a separate study, Clark, (1967) discovered that allotriomorphs only formed when the misorientation exceeded \( \sim 16^0 \) in an Al-Ag system, which was confirmed in the present work as all boundaries analysed had a misorientation above this value.

In an investigation of precipitation in an aged Al-Zn-Mg alloy, Unwin et al, (1969) attributed variations in precipitate morphology and density to:
1. deviations in boundary coincidence (with lower precipitate densities being shown at coincidence positions);
2. the effect of grain boundary plane.

In addition, they found that copious nucleation occurred on low-angle boundaries provided the misorientation was greater than \(-2^\circ\) (Unwin and Nicholson, 1969).

This observation may be explained by the suggestion of Pumphrey, (1973) that it is not the structural features of grain boundaries as expressed by the coincidence site theory that are important for precipitate nucleation, but the existence of a low energy precipitate/matrix interface laying parallel to the grain boundary plane. Thus, if there exists a favourable relationship between the precipitate habit plane and the grain boundary plane, then the activation barrier to nucleation is reduced, making precipitation easier. This opinion is strongly supported by both the experimental and theoretical results of Clough et al, (1974) and those of Forest and Biscondi, (1978), who concluded that the angle between the grain boundary plane and the precipitate habit plane was the controlling factor in intergranular precipitation kinetics.

Further experimental evidence providing support for the boundary plane dependency on precipitation was supplied by Park and Ardell, (1986) using an Al-Zn-Mg alloy. They found that precipitation was favoured if a crystallographic orientation relationship was established with respect to one grain, with the grain boundary orientation playing the decisive role on the
nucleation of precipitates.

However, this can not be the only controlling factor as in sensitised austenitic stainless steel the carbides and austenite share an orientation relationship with \{111\} type planes being favoured interfaces. Therefore, the coherent twin boundary seems an ideal site for copious precipitation but experimentally this is not the case. No precipitation occurs on this boundary except after prolonged heating in the sensitisation range.

Rath and Bernstein, (1971) determined the relationship between grain boundary orientation and intergranular cracking in purified iron. The results showed that cracking only occurred when the misorientation between the grains exceeded $20^0$, being independent of the boundary type and common rotation axis. This effect was interpreted in terms of the increase in areas of misfit in the grain boundary as the misorientation increases which in turn affects the ability of the boundary to absorb segregant.

Watanabe et al, (1978), in a study of the misorientation dependence of grain boundary segregation in an Fe-Si alloy, found that the Si enrichment ratio varied depending on the tilt component of grain boundary misorientation for misorientations greater than $20^0$. No segregation was detected at boundaries with a misorientation less than $20^0$, reinforcing earlier investigations. It was stipulated that the tilt component was the critical parameter as a tilt boundary has a considerably larger energy than a twist boundary. In addition, the binding energy of impurity atoms with pure tilt boundaries is higher than twist boundaries. No segregation dependence on the twist component of misorientation.
was detected.

It was also suggested that the grain boundary enrichment ratio could change locally along a curved or faceted boundary as the boundary inclination and hence energy will change altering the propensity of grain boundary segregation.

This effect of the tilt component was supported by Watanabe et al, (1980), who correlated the amount of tin segregation in an Fe-Sn alloy with the increased hardness measured at the grain boundary. The grain boundary enrichment ratio was again found to increase with increasing tilt angle.

However, in both of these studies the crystallographic orientation of the grain boundary plane was not determined. As mentioned in Section 4.1.1, both the misorientation between the crystals and the boundary plane are required to completely categorise a grain boundary.

Indeed, Suzuki et al, (1981) found no correlation between the amount of phosphorus segregation in an Fe-1wt%P alloy and the tilt component of misorientation. However, the accuracy of the misorientation determined in this work was only to within ±5°, which seems insufficient when directly correlating segregation characteristics with grain boundary structure. Even so, they managed to relate the amount of phosphorus segregation to the crystallographic orientation of the grain boundary plane. The enrichment ratio was higher for boundary planes with high indices.

This was reinforced by Bouchet and Priester, (1987) who postulated that the grain boundary plane characterised by the interplanar spacing rather than the Σ criterion is the fundamental
parameter in determining the propensity for segregation at a grain boundary. Boundaries showing the highest levels of segregation are those with the lowest $d(h,k,l)/a$ values.

The effect of grain boundary structure on sensitisation and corrosion of stainless steel has been investigated by Bennett and Pickering, (1987). They used a chemical etching technique to relate the grain boundary groove widths in sensitised specimens to boundary crystallography. However, the validity of comparing groove widths (which is obviously etching time dependent) and misorientation angle (about any axis) is not obvious. They found that sensitisation occurred more readily on grain boundaries which exhibited a low coincidence of atomic sites, corresponding to a high energy. Additionally, it was stipulated that sensitisation would not occur for grain boundary misorientations less than $14^\circ$.

A similar study using a grain boundary etching technique in an Fe-Ni-Cr alloy by Ogura et al, (1987) showed that phosphorus segregated mainly to random high-angle grain boundaries with only minimal segregation to low-angle boundaries and low $\Sigma$ boundaries. It was suggested that an essential geometric factor on an atomic scale which controls the amount of phosphorus segregation at high-angle boundaries is their atomic coherency or free volume.

From the preceding review, it is evident that it is still not clear how the misorientation and plane of the grain boundary (and in particular whether the boundary is close to a high density coincidence site position) affect precipitate nucleation resulting from the segregation of solute from the grain interior.
4.3. Grain Boundary Crystallography Determination.

4.3.1. Introduction.

As described in Section 4.1.1, the axis and angle of misorientation together with the boundary plane specify the five degrees of freedom needed to describe the overall geometry of a grain boundary.

Methods of determining axis/angle pairs fall into two main categories:
1. stereographic methods;
2. analytical methods.

The principles of these methods are outlined below.

4.3.1.1. Stereographic Methods of Axis/angle Pair Determination.

The best known method in this category is that due to Goux, (1961). However, a less widely known method, due to Ralph, (1964), is also applicable. In this latter technique, knowledge of three pairs of plane normals which have the same indices in both crystals is required. These axes are plotted in pairs on the stereogram and the great circle containing the locus of points midway between the poles obtained in each case as shown in Fig 4.3.1.1. The resultant three great circles will all intersect producing a triangle of uncertainty for the misorientation axis. The axis of misorientation 1, is taken at the centre of this triangle.
Fig 4.3.1.1. Determination of the misorientation parameters using the Ralph stereographic method.
The angle of misorientation is obtained utilising one pair of plane normals with the same indices on either side of the boundary. Two great circles are then plotted; one through each plane normal and 1. The angle of misorientation is the angle between the poles of these great circles i.e. P1 and P2.

The accuracy with which the axis of misorientation is obtained depends on the size of the triangle of uncertainty but is usually to within ±0.5°.

Stereographic methods have the advantage of being quick and straightforward and the Ralph method provides an inbuilt check of the accuracy. However, they provide a solution for only one variant of the axis/angle pair and this may not be the variant with greatest physical significance (see Section 4.3.3).

4.3.1.2. Analytical Method of Axis/angle Pair Determination.

A general mathematical analysis using matrix algebra for determining boundary misorientation was developed by Lange, (1967) for the interpretation of Laue back-reflection patterns. This was later modified and combined with computer techniques by Young et al, (1973) to interpret Kikuchi patterns.

The procedure involves considering the two crystals as three dimensional vector bases and producing a 3 x 3 rotation matrix to represent the rotation of a vector in crystal 1 to its equivalent vector in crystal 2. Three perpendicular coordinate systems are selected when indexing the Kikuchi patterns. They are the;
1. crystal frame, CF (usually the orthogonal 001 translation vectors)

2. pattern frame, PF (any convenient pole or line on the pattern)

3. reference frame, RF (invariant for both patterns).

A matrix is formulated representing the rotation of CF to PF and then another to rotate PF to RF for both patterns. A misorientation matrix representing the overall transformation of CF to RF can be obtained from which the axis/angle pair can be calculated.

Young et al, (1973) claim that for high-angle boundaries, the angle of misorientation can be calculated to within $0.1^\circ$. Hence, it is more accurate than the stereographic procedures described in Section 4.3.1 and was thus used in the present work.

4.3.2. Axis/angle Pair Determination From Rotation Matrices.

Given an orientation relation, the matrix elements for the cubic case are:

\[
\begin{align*}
R_{11} &= p_1^2 (1 - \cos \theta) + \cos \theta \\
R_{12} &= p_1 p_2 (1 - \cos \theta) - p_3 \sin \theta \\
R_{13} &= p_1 p_3 (1 - \cos \theta) + p_2 \sin \theta \\
R_{21} &= p_2 p_1 (1 - \cos \theta) + p_3 \sin \theta \\
R_{22} &= p_2^2 (1 - \cos \theta) + \cos \theta \\
R_{23} &= p_2 p_3 (1 - \cos \theta) - p_1 \sin \theta \\
R_{31} &= p_3 p_1 (1 - \cos \theta) - p_2 \sin \theta \\
R_{32} &= p_3 p_2 (1 - \cos \theta) + p_1 \sin \theta \\
R_{33} &= p_3^2 (1 - \cos \theta) + \cos \theta
\end{align*}
\]
where $P_1$, $P_2$ and $P_3$ are vector components of the rotation axis $P$, which is defined as a unit vector.

Having attained the nine elements which are direction cosines between cartesian axes in one grain with respect to those in the adjacent grain, the misorientation matrix can be formulated (Ralph, 1964) such that

$$
R = \begin{bmatrix}
R_{11} & R_{12} & R_{13} \\
R_{21} & R_{22} & R_{23} \\
R_{31} & R_{32} & R_{33}
\end{bmatrix}
$$

From this it can be demonstrated that the rotation angle $\theta$, is given by

$$
\theta = \cos^{-1}\left\{ \frac{R_{11} + R_{22} + R_{33} - 1}{2} \right\}
$$

and the direction of the rotation axis $\langle hkl \rangle$ is given by

$$
h : k : l = (R_{21} - R_{12}) : (R_{13} - R_{31}) : (R_{32} - R_{23})
$$

The relative orientation of two cubic crystals can be described in 24 different ways as the three cube axes are equivalent. When the poles of 24 rotation axes are plotted onto the stereographic projection, then one pole falls in each unit triangle. The 24 equivalent axis/angle pairs are generated by pre-multiplying the misorientation matrix with each orthogonal matrix which represents a symmetry operation in turn (Tweed,
1983). The relevant matrices have been tabulated by Karakostas et al, (1979) and Tweed, (1983). In this case, one of the 24 rotation axes will be associated with the smallest rotation angle. This axis/angle pair is by convention used to describe the orientation relationship (Omar, 1987).

4.3.3. Comparison of the Experimental Misorientation Data With Those Predicted by CSL Theory.

Having attained the axis/angle pair representation of grain boundary misorientation, it is only meaningful if this can then be used to determine the class of a boundary, e.g. low-angle, random, or special. Hence, it is necessary to determine the deviation of a particular boundary from the nearest CSL. The procedure for determining the CSL axis/angle pairs was outlined in Section 4.1.3 together with the criterion for establishing an acceptable deviation from these exact CSLs.

Randle and Ralph, (1987, 1988) chose an arbitrary cut off of $\Sigma = 49$ as the limit of validity of coincidence theory stating that energy cusps had been observed in boundaries with $\Sigma$ as high as 83. Warrington and Bufalini, (1971) and Grimmer et al, (1974) have published a complete list of CSL rotations together with the corresponding matrices for $\Sigma \leq 25$ and $\Sigma \leq 49$ respectively. Employment of rotation matrices is the most efficient way of comparing CSL and experimental boundaries.

Having formulated matrices for the experimental and CSL case, direct comparison can be made by calculation of the angular
difference between equivalent columns in each matrix. If the average of the three values is less than the CSL limit set by the Brandon criterion, then the boundary can be regarded as a special boundary.

A computer programme was developed in the process of this work to determine all 24 equivalent axis/angle pairs for a given misorientation and the one with the lowest angle compared directly with a subjectively chosen CSL boundary.

4.3.4. Boundary Normal Determination.

Once the orientation relationship between the grains has been deduced, the boundary normal has to be determined to describe the two remaining degrees of freedom needed to categorise a grain boundary. Boundary normal determination is generally subject to quite large errors unlike the misorientation analysis. Additionally, a further complication is introduced where the grain boundaries are curved causing the boundary plane to vary continuously.

The simplest method involves tilting the boundary plane vertical (i.e. parallel to the electron beam) to minimise its apparent projected width and then taking diffraction patterns from the grains on either side. The problem encountered here is deciding when the boundary is vertical and large errors can be introduced.
Another technique is that due to Young et al, (1973) who used their method of misorientation calculation as a basis for the determination of boundary normals. Boundary images at the same magnification and Kikuchi patterns of the same crystal are taken before and after a specimen tilt. This tilt can be represented by a matrix and this matrix together with the change of projected boundary image is used to calculate the boundary normal.

Two vectors lying in the plane of the boundary are selected on micrographs taken before and after the tilt. These vectors should be taken between well defined features on the boundary such as steps on extrinsic dislocations. Their x and y coordinates can be measured in the reference frame and the z coordinate calculated from the specimen tilt matrix. The cross product of these vectors defines the boundary normal.

The major drawback with this method is finding suitable features in the boundary plane and observing a significant change in their magnitude and direction within the limits of tilt available in the microscope.

In this work, the method of Young et al, (1973) was employed wherever possible as it results in a more accurate determination of the boundary normal. If however, no suitable features were found in the boundary plane, then the boundary normal was determined by tilting the plane as near parallel as possible to the electron beam.
4.3.5. Practical Aspects of Axis/angle Pair Determination.

In the previous sections some of the methods available to determine axis/angle pairs have been discussed. However, the accuracy of the calculated boundary crystallography will depend on the accuracy of accumulation of the experimental data.

Kikuchi electron diffraction was utilised in this work as the resultant patterns provide a more accurate measure of crystal orientation than spot patterns (Edington, 1975).

In the transmission electron microscope (TEM) Kikuchi patterns are most easily obtained by the use of microdiffraction with a convergent probe (Randle and Ralph, 1986). This relaxes the conditions necessary for the excitation of Kikuchi lines as compared to their generation by conventional selected-area diffraction. Consequently, this imposes fewer restrictions on crystal thickness from which accurate diffraction data can be obtained.

In practise, misorientation is more easily determined if one grain is tilted near to a zone axis or to a situation where a major Kikuchi line pair is excited. Additionally, if a low camera length is employed, enough of the reciprocal lattice section is visible to enable absolute beam direction determination. Only one pattern is then required from each grain to determine the misorientation. This is because no 180° ambiguity exists in the diffraction pattern obtained using Kikuchi lines as it does in normal selected-area mode.

A more recent technique (Voice and Faulkner, 1984) involves
tilting to low index orientations in both grains and using the difference in tilt stage readings to calculate the boundary misorientation. The accuracy of this method is increased by positioning the "rosette pattern", defined as the intersection of the bend contours, precisely on the boundary itself. This eliminates the constraints imposed in conventional microdiffraction in which it is impossible to define the exact origin of the diffraction data due to objective lens spherical aberration. Hence, a more localised and therefore more accurate misorientation analysis is practicable.
Chapter 5

EXPERIMENTAL TECHNIQUES.

5.1. Materials.

As a family, the stainless steels offer a combination of mechanical properties, corrosion resistance and heat resistance unmatched by other commercial metals. The austenitic grades represent the largest group of these steels in use, making up to 65-70% of the total for the past several years (Peckner and Bernstein, 1977). Collectively, they enjoy their dominant position because of a general high level of fabricability and corrosion resistance and because of the varied specific combinations of properties that can be obtained by different compositions within the group, providing useful material choices for a vast number of applications. Fig 5.1 illustrates the austenitic grades family tree.

Chromium is the element that makes stainless steels stainless or corrosion resistant. Stainless steels are iron-chromium alloys which contain at least 12wt% chromium as this is the level at which effective resistance to atmospheric corrosion begins. This is attributed to the formation of a passive oxide film on the surface. Other elements can be added to improve various properties. Nickel increases corrosion resistance slightly and greatly improves mechanical and fabricating properties. Molybdenum increases resistance to pitting type corrosion and also improves high temperature strength. Silicon increases oxidation resistance
Fig 5.1. Family relationships for standard austenitic stainless steels.
at high temperatures. Niobium and titanium additions stabilise carbides and reduce susceptibility to intergranular corrosion.

This work has been carried out with AISI 316 austenitic stainless steel. From the isothermal section (1000°C) of the Cr-Fe-Ni ternary system shown in Fig 5.1.1, it can be seen that this grade would be expected to contain a little ferrite. This is to prevent hot-short cracking after welding. Ferrite content in a weld deposit can be estimated by calculating equivalent chromium and nickel contents of the composition and using the Schaeffler diagram (Schaeffler, 1949) shown in Fig 5.1.2.

The AISI 316 stainless steel used had the following composition (in wt%): 0.064%C, 1.75%Mn, 0.63%Si, 0.018%P, 0.021%S, 2.40%Mo, 17.5%Cr, 11.5%Ni, the balance being Fe.

5.2. Sample Preparation.

5.2.1. Heat Treatment.

The time-temperature-precipitation diagram of 316 stainless steel most widely used to estimate heat treatment times and temperature is that of Weiss and Stickler, (1972). This is shown in Fig 3.4.2.1.

The material used was received in pipe form. It was first solution heat treated at 1100°C for 1hr in an evacuated quartz tube followed by a water quench. A series of heat treatments was then carried out to produce a chromium depleted zone of dimensions measurable to a high statistical accuracy with our particular
Fig 5.1.1. 1273K isotherm of Cr–Fe–Ni system.
Approximate boundary of austenite region for wrought materials

Carbon
Minimum value of 0.03 for all alloys except those otherwise indicated.

Nitrogen equals carbon in potency as austenite former. Nitrogen values vary from 0.05 for low chromium alloys, through 0.10 for the high chromium steels.

Silicon
Minimum value of 0.30

Fig 5.1.2. The Schaeffler diagram for estimating the microstructure of stainless steel weld metal.
microscope. The optimum treatment was found to be one of 680°C for 48hr followed by water quenching.

5.2.2. Electropolishing.

3mm discs produced by standard cutting, grinding and polishing techniques, were electropolished for analysis in the TEM using a Struers Tenupol unit. The conditions employed are listed below:

1. A solution of 5% perchloric acid: 95% methanol,
2. A voltage of 30V,
3. A fluid flow rate of 3.75,
4. A temperature range of -50 to -20°C.

5.3. Microanalysis Conditions.

A Philips EM 400T analytical electron microscope was employed for this analysis. It has the usual transmission capabilities and in addition is equipped with an energy dispersive X-ray (EDX) detector and scanning transmission capabilities. Ideally a dedicated STEM such as the Vacuum Generators HB 501 fitted with a field emission gun would have been used as it can provide extremely fine (~1nm) high intensity electron beams perfect for high spatial resolution EDX. Using a field emission electron source yields a thousandfold increase in brightness compared to a LaB₆ thermionic filament which itself is approximately five times
brighter than a conventional W filament (Finlan, 1987). The majority of this work was carried out using a LaB₆ filament although initially some analyses were undertaken with a W filament. Transferring from W to LaB₆ allowed a smaller spot size to be used (due to the increased brightness of the beam), although this had no noticeable effect on the shape of the resultant concentration profile. Microchemical analyses of grain boundary regions were performed using a focused electron probe of ~10nm diameter which was held stationary at the point of interest by the LINK Tracking Analyser facility. This programme was developed to combat specimen drift which is a major problem in the microanalytical examination of grain boundary segregations. The beam position is checked sequentially throughout the analysis and if it has deviated from its pre-programmed position is resited. This is achieved by selecting a microstructural feature of high contrast at the outset, such as a contamination spot or precipitate, which is employed as a reference point to the intended beam positions as the probe is automatically stepped across the boundary. Hence, a 2D compositional map in the vicinity of the grain boundary can be attained with relative ease. Additionally, this programme is of particular use if long collection times are required to produce statistically meaningful X-ray data.

An electron accelerating voltage of 120kV was used and the microscope operated in STEM mode. To attain maximum X-ray collection, the sample was tilted 30° towards the detector.

Boundaries for which the boundary plane was aligned as near
parallel as possible to the electron beam were chosen for analysis. Figs 5.3.1 and 5.3.2 demonstrate this point. Fig 5.3.1 shows a grain boundary oriented such that the boundary plane is misaligned by a high angle from the electron beam. This situation is useless for analysis as stated in Section 3.5.2.2. Fig 5.3.2 however, shows a grain boundary oriented ideally for microanalysis with its plane near parallel to the electron beam. Also illustrated on the micrograph is a region typical of those selected for microanalysis.

Boundaries were also preferred which lay normal to the edge of the thin foil so that all of the X-ray spectra were collected from regions of approximately the same thickness. In addition, boundaries were preferred which lay parallel to the line between the sample and X-ray detector so that fluorescence of the adjacent bulk material was not initiated.

Quantitation of the resulting spectra was achieved using the Cliff-Lorimer method (Section 3.5.2.3) in which X-ray intensity ratios are related to weight percent ratios by a single constant of proportionality, k. The k values used in this study were acquired from virtual standards.

STEM, combined with the tracking analyser, provides the ideal microanalytical tool for the determination of segregation induced concentration profiles in the vicinity of grain boundaries.

The experimental conditions used to determine the grain boundary crystallography have been outlined in Section 4.3.5.
Fig 5.3.1. Grain boundary oriented by a large angle from the electron beam.

Fig 5.3.2. Grain boundary at a small misalignment from the electron beam.
6.1. Accuracy of Alignment of a Boundary With Respect to The Electron Beam in TEM.

A.E.M is commonly used to detect segregation at grain boundaries and to determine the resultant composition profiles that develop. It is essential that the boundary is aligned as nearly parallel to the electron beam as possible in order to maximise the X-ray signal detected from the segregant at the boundary.

Consequently, a study was undertaken to determine the accuracy to which a boundary can be aligned with respect to the electron beam. A twin boundary was used as a "best-case" test as it has a known crystallographic orientation with respect to the adjacent grains. In F.C.C. materials, the coherent twin boundary lies on a {111} plane.

AISI 316 austenitic stainless steel was used in this investigation as it has a low stacking fault energy and thus a high propensity to form twins after quenching from the solution anneal temperature of 1100°C. Fifty five boundaries were analysed.

The accuracy of electron beam alignment was determined by the angular deviation of the twin boundary from the [111] after it had been tilted to minimise its apparent projected width. This is shown in Figs 6.1.1 and 6.1.2. In Fig 6.1.1 the boundary is oriented to within 0.5° of [111] and hence has a narrow projected
width. In Fig 6.1.2 however, the boundary is tilted by a high angle from the [111] and has a large projected width. The angular deviation was determined using Kikuchi electron diffraction.

It should be noted that the boundaries were aligned solely using the imaging mode and not by switching to diffraction and tilting to the required orientation, since a diffraction technique would be useless for a boundary of unknown type. Additionally, Gaussian focus was employed throughout and no defocus techniques were used to increase contrast.

The results obtained are presented in Fig 6.1.3. From the histogram it is evident that a boundary can be aligned to within 1° of its intended orientation more than 60% of the time. However, these results were acquired over a period of time and the less accurate alignments were much reduced in frequency as a significant amount of experience was accumulated. Hence, the actual percentage aligned to within 1° increased with experience.

The situation is further complicated in practice when aligning grain boundaries since they are not as regular as twins over such large distances and can also be curved. Further constraints may also be imposed in reality during segregation analysis since the specimen has generally to be tilted to an orientation which depends on the microscope/detector geometry in order to maximise X-ray collection.

In conclusion, truly planar interfaces can in general be aligned parallel to the beam to better than 1° using only image information. Greater inaccuracies will usually have to be tolerated for non planar boundaries (Laws and Goodhew, 1988).
Fig 6.1.1. Twin boundary oriented close to the electron beam direction.

Fig 6.1.2. Twin boundary misaligned by a large angle from the electron beam direction.
Fig 6.1.3. Histogram of results.
6.2. Effect of Spot Size on the Detectability of a Segregant at the Boundary.

For the analysis described in the previous section a spot size of 200nm was employed using the Philips EM400T analytical electron microscope. Spot sizes of this order of magnitude are acceptable for diffraction purposes. However, with respect to the detection of a segregant at a grain boundary this is not the case.

Consider a grain boundary which is set at a slight misalignment to the electron beam, as illustrated in Fig 6.2.1. In this case, the whole boundary volume will be incorporated in the interaction volume and the misalignment effect will be negligible as all possible X-rays will be excited from the boundary segregant. However, this situation is useless for analysis as the X-ray intensity derived from the boundary will be much lower than the intensity excited from the interaction volume and hence will probably not even be detected. As a consequence, a smaller spot size is required to detect a change in composition at the boundary. Typically a spot size of ~10nm is used in microanalysis to detect non-equilibrium segregation at grain boundaries (Hall and Briant, 1984). This will enhance the effect of boundary misalignment as illustrated in Fig 6.2.2.

In this case, not all of the boundary will be sampled and hence not all of the X-rays available will be collected, producing a lower detected signal. The overall influence of misalignment is hence to reduce the intensity of X-rays derived from the segregant at the boundary. Thus it is essential to align the boundary as
Figure 6.2.1. Application of a large spot size to the detection of a segregant at the grain boundary.
10nm

Unanalysed part of Boundary

Figure 6.2.2. Application of a small spot size to the detection of a segregant at a grain boundary.
parallel to the electron beam as possible to produce accurate X-ray microanalysis results.

This effect of spot size can be further demonstrated by considering the following hypothesis in which the boundary for analysis is assumed to be aligned parallel to the electron beam. Also, the segregant is assumed to be accumulated as a monolayer of atoms on the boundary, which is typical of equilibrium segregation and thus the most difficult to detect with confidence. This situation is represented in Fig 6.2.3.

It is possible to calculate the number of atoms emitting X-rays from the monolayer boundary volume compared to the number of atoms emitting X-rays from the entire interaction volume as a function of electron probe size \(d\), and specimen thickness \(t\).

The number of atoms in the monolayer boundary volume can be determined by considering beam spreading. For any particular material and experimental conditions, an expression can be obtained describing the extent of beam spreading using the Goldstein equation (Section 3.5.2.1).

Relating this equation to a 316 stainless steel in which \(\rho=8.0\text{g/cm}^3\), \(\Lambda=55.5\) and \(Z=27.2\), the beam spreading can be represented by

\[b = 64.54t^{3/2} \quad \text{.........(b and t in cm)}\]

for 100kV electrons.

This expression describes the spreading that occurs at any point throughout the thickness of the sample and will thus define
Figure 6.2.3. Illustration of hypothesis geometry.
the shape of the interaction volume, as shown in Fig 6.2.4. From this figure, the area of the shaded region $A_s$, will be

$$A_s = \int_{0}^{t_1} 64.54t^{3/2} \, dt$$

$$= 25.82t_1^{5/2}.$$  

The area of the rectangle

$$A_R = d \cdot t_1.$$  

Hence, the total area

$$A_T = 25.82t_1^{5/2} + d \cdot t_1.$$  

The total volume of the monolayer boundary

$$V_m = (25.82t_1^{5/2} + d \cdot t_1) \cdot d_0$$

where $d_0$ is the interatomic distance which is the assumed thickness of the boundary layer. Thus the number of atoms in the monolayer volume

$$N_m = \frac{(25.82t_1^{5/2} + d \cdot t_1) \cdot d_0}{V_a}$$

where $V_a$ is the atomic volume.
1.5 Curvature defined by \( b = 64.54t^{1.5} \)

Figure 6.2.4. Diagram illustrating the determination of the number of atoms in the boundary volume.
Also, the number of atoms in the interaction volume can be calculated in the same way. The geometry is shown in Fig 6.2.5. The interaction volume can be represented by rotating the shaded region around the t-axis.

At a point \( t_1 \) along the axis

\[
r = r_0 + \frac{b}{2} = r_0 + 32.27t^{3/2}.
\]

Thus, the interaction volume

\[
V_1 = \pi \int_0^{t_1} (r_0 + 32.27t^{3/2})^2 \, dt
\]

\[
= \pi \left[ r_0^2 t + 25.81r_0 t^{5/2} + 260.34t^4 \right]_0^{t_1}
\]

The number of atoms in the interaction volume

\[
N_1 = \frac{V_1}{V_o}
\]

Hence, the percentage signal derived from the boundary segregant as a function of specimen thickness and spot size can be determined. The results are shown in Figs 6.2.6-6.2.8 for the three different modes available using the EM400T AEM (note the change in scale of the vertical axis).

As the spot size and specimen thickness decrease, the percentage signal from the boundary increases. This is a result of
Figure 6.2.5. Geometry required to calculate the number of atoms in the interaction volume.
Fig 6.2.6. Results obtained using microprobe mode.
Fig 6.2.7. Results obtained using nanoprobe mode.

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<tr>
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Fig 6.2.8. Results obtained using STEM mode.
increased spatial resolution and demonstrates the necessity of using as small a spot size as is practicable for segregation analysis.


6.3.1. Macroscopic Observations.

Heat treating unstabilised austenitic stainless steels in the sensitising range results in the precipitation of chromium rich carbides on the grain boundaries. The distribution of these carbides is not uniform and varies significantly from boundary to boundary. This can be seen in the optical microscope as shown in Fig 6.3.1. The sample was electroetched in a solution of oxalic acid using a voltage of 15-20V; the electrode remaining on the sample for about 5 seconds. The grain boundaries have been non-uniformly attacked by the etch, some showing more severe corrosion than others. This is a result of the chromium concentration at some of these boundaries dropping below that required to provide passivity (i.e. ~13wt%). This drop in chromium concentration is a direct consequence of carbide precipitation. Indeed some boundaries exhibit a patchy type of corrosion as is shown more emphatically in Fig 6.3.2. This suggests that precipitation has only occurred at certain regions along the grain boundary. Hence, preferential nucleation sites are obviously available along the length of a grain boundary. This aspect is further demonstrated in Fig 6.3.3. At the point marked X,
Fig 6.3.1. Non uniform grain boundary precipitation in sensitised stainless steel.
Fig 6.3.2. Patchy type of corrosion along a grain boundary.
Fig 6.3.3. Non uniform corrosion along a single grain boundary.
corrosion of the grain boundary near the triple point has occurred with the remainder being unattacked. It is not obvious however, what happens to the boundary after the point X and so scanning electron microscopy (SEM) was employed in order to obtain its better spatial resolution. Fig 6.3.4 shows that precipitation can in fact stop abruptly along the length of a boundary and demonstrates the importance of boundary plane. There must be some variation in structure along the length of the boundary to produce this effect. It is evident that the boundary direction does not change significantly and thus there may be a change in angle of the boundary in the uncorroded region. This will alter the boundary plane, proving that it does influence the precipitation of chromium-rich carbides.

Another advantage of SEM is its capability of distinguishing differences in orientation between grains using the backscattering mode. An example of this is shown in Fig 6.3.5. Individual grains can be seen much more clearly and an unambiguous interpretation effected. Significant but differing amounts of corrosion have occurred on the majority of grain boundaries. This may reflect differences in misorientation (Section 4.2). For example, precipitation of chromium-rich carbides seems to be, from the present work, confined to boundaries with a misorientation greater than \( \sim 20^\circ \). Hence, the boundaries with a significant degree of precipitation are probably random high-angle grain boundaries. Grain boundaries with no precipitation are probably of the low-angle type or may be low \( \Sigma \) CSL boundaries.

Fig 6.3.5 also shows the high degree of twinning that occurs
Fig 6.3.4. Precipitation stopping abruptly on a grain boundary, emphasising the importance of grain boundary plane.
Fig 6.3.5. Evidence of differences in orientation between grains using the backscattering mode in SEM.
in this steel. These twins also help to demonstrate the effect of misorientation on precipitation. A twin is a $\Sigma=3$ CSL as mentioned in Section 6.1 and is a particularly low energy boundary. For F.C.C. materials the coherent interface is $\{111\}$ with all atoms being coincident along the plane of the boundary. As a result one would not expect significant segregation to and subsequent precipitation on these boundaries. Indeed this is the case for twin A with no precipitation observable on either interface. However, the incoherent interface does not exhibit the same degree of coincidence of atomic sites and consequently is of a higher energy. Segregation to this interface thus occurs on annealing which promotes precipitation and the resultant attack on etching. This is demonstrated by twin B.

Misorientation between the grains certainly affects precipitation as further demonstrated in Fig 6.3.6. Significant precipitation has occurred along the length of boundary C until the twin boundary intersects it thus altering the misorientation. Precipitation reoccurs when the grain boundary is reinstated back to its original orientation at the end demonstrating that the boundary needs a pre-requisite misorientation for precipitation to occur.

From this macroscopic survey it is possible to conclude that both the boundary misorientation and plane do affect the precipitation of chromium-rich carbides. The most significant amount of precipitation occurs on the grain boundaries which are deduced to be high-angle boundaries from the associated TEM work. Indeed some of these boundaries will probably correspond to CSL
Fig 6.3.6. Evidence of grain boundary misorientation affecting precipitation.
orientations. Significant precipitation was also found on incoherent twin boundaries but none on coherent twin boundaries in agreement with previous workers (Butler and Burke, 1986).

These macroscopic observations prompted a study of the microscopic properties of individual boundaries to determine the effect of boundary crystallography on segregation and this will be discussed in the following sections.

6.3.2. Chromium Concentration Distribution Along Grain Boundaries Between Carbides.

The experimental conditions employed for this analysis have been outlined in Section 5.3. To determine the chromium concentration profile, the electron beam was stepped automatically across the grain boundary using the Link Tracking Analyser facility. Spectra were collected for 200s with the beam position being checked for drift every 20s. Employment of this analyser simplified this work considerably as a 2-D chromium compositional map along the grain boundary between carbides could be collected. A rectangular grid of analysis points along the grain boundary region was pre-programmed into the analyser which was left to run automatically.

The chromium concentration variation along a grain boundary with distance from a carbide was measured in samples which had been aged at 680°C for 48hr after having been solutionised. The object of this exercise was to determine whether the measured chromium concentration profile was representative of the
"enclosed" boundary region between carbides or whether significant variations existed with distance from a carbide. Boundaries were only chosen for which the boundary plane remained parallel to the electron beam over large distances and which had only a single large carbide present in the region of interest. These turned out to be difficult criteria to satisfy with the material involved as it had a relatively high carbon content (0.062wt%) and a prolonged heat treatment was needed to produce chromium depleted zones measurable to a high statistical accuracy. Hence, there was generally an ubiquitous coverage of carbides along most boundaries making this sort of analysis impractical. Where possible however, profiles were collected between carbides; an example is shown in Fig 6.3.2.1.

The first and last profiles in this compilation were taken from positions along the boundary which incorporated the chromium-rich carbide itself. Hence, a high chromium concentration was detected at the boundary. This value will not be a true representation of the actual chromium concentration of the carbide as it may not encompass the entire interaction volume generated by the electron beam (i.e. the particle may not exist throughout the complete thickness of the foil). To determine a reliable measurement of this value carbon extraction replicas would have to be taken and the extracted precipitates analysed separately.

The actual chromium concentration at the carbide/matrix interface is also not measurable accurately using this technique due to the electron beam broadening as it penetrates the thin foil. If the beam was positioned at the interface, then
Fig 6.3.2.1. Chromium concentration profiles along a grain boundary between two carbides.
contributions to the detected X-ray signal would come from the carbide itself and the adjacent matrix, both of which have a higher chromium content than the actual interface. Thus any measured chromium concentration in this region will always be higher than the actual value.

The bulk chromium concentration is maintained up to distances of about 200nm from the grain boundary at which point the concentration begins to fall.

The profiles attained between the carbides are generally of the same form. Bulk chromium levels are sustained again up to about 200nm from the boundary. The chromium concentration begins to drop at this point reaching a value of \(~11.50\text{wt}\%\text{Cr}\) at the boundary. This grain boundary value remains fairly constant along the length of the boundary.

The grain boundary misorientation was determined as \(56.0^0/1,0.7,0.7\) which can be described as a random high-angle grain boundary. Additionally, the boundary plane was measured as \((-1.2,0.1,1.6)/(0.1,1.2,-0.6)\). This crystallography would therefore not be expected to provide the boundary itself with special properties. As the boundary concentration is fairly constant along its length, it is evident that the boundary has acted as a collector plate and supplied the neighbouring carbides with chromium due to the enhanced diffusivity along the boundary.

This interpretation is reinforced by the results shown in Fig 6.3.2.2 in which an identical analysis was undertaken but on a different grain boundary in the same sample. The same features are evident in the accumulated profiles confirming the results of the
Fig 6.3.2.2. Chromium concentration profiles along a grain boundary between two carbides.
previous analysis. The major difference is the measured value of the grain boundary chromium concentration which is significantly lower (-10wt%Cr). This may be due to the profiles being taken from regions of considerably different thickness although this should not produce the resultant discrepancy according to Mulford et al, (1983). For samples of thickness compatible to AEM, (100-400nm), the maximum error in the grain boundary chromium concentration is 11%. The disparity encountered above is outside this error limit and must be due to some real effect of the boundaries themselves.

The boundary misorientation in this case is 50.45°/1,-0.9,0.8 which again can be described as a random high-angle grain boundary and would not therefore be expected to have special properties. The boundary plane was determined as (0.3,0.2,0.9)_{1,2}. As the plane is identical in both grains, it is therefore a symmetrical boundary. This did not influence the segregation characteristics to this boundary however, as the measured concentration profiles were similar to those of other asymmetric boundaries.

This difference in grain boundary chromium concentration must reflect a difference in the atomic packing at the boundary produced by the variation in misorientation of the two boundaries. This in turn will affect the ease with which chromium can diffuse along the boundary and produce boundaries with different chromium concentrations, as will be reinforced in the next section.

The major conclusions to be drawn from these analyses are that there seems to be no significant variation in either the profile width or the minimum chromium concentration between closely spaced carbides on a specific random high-angle grain
boundary for the particular heat treatment employed in this work.

If however, the material is heat treated at 680°C for 24hr then a chromium concentration gradient is detected at the boundary as shown in Fig 6.3.2.3. In this case, the sensitisation process is at a much earlier stage and the amount of precipitation on each boundary notably less. Hence, the carbides tend to be well spaced along each boundary making analysis between them much easier. As can be seen, a steep gradient exists ranging from ~12.25wt%Cr near the carbide up to ~19wt%Cr (bulk) at a distance of ~200nm from the carbide. In profiles measured normal to the grain boundary however, for the same heat treatment, the chromium concentration rises to bulk values well within 200nm. Thus, there appears to be no significant difference between the bulk and grain boundary diffusivities as the concentration profiles are very similar. This contrasts with the usual behaviour in which chromium diffusion in the grain boundary is normally significantly faster than in the matrix causing the depletion to extend over much larger distances. The misorientation of this boundary was determined as 40.94°/1,-2.5,0.8 which conforms to a Σ=23 (40.45°/1,3,1) orientation and thus might be expected to have special properties. Indeed, diffusion of chromium along the grain boundary seems to have been inhibited in this case. If the boundary acted as an efficient vehicle for the transport of chromium then significant concentration gradients such as this would not exist. It is evident that the grain boundary is acting like the matrix in this instance.

Consequently, this detected gradient within the grain
Fig 6.3.2.3. a) Grain boundary Cr concentration profile with distance from a carbide.

b) Boundary along which profile was measured.
boundary may purely be a kinetic effect (i.e. not enough time for the chromium to diffuse appreciable distances) or may be a result of the boundary structure.

It is possible to eliminate the kinetic effect by calculating the approximate spatial extent expected for diffusion along the grain boundary. Hence the spatial extent

\[ x = \sqrt{D_b t} \]

where \( D_b \) = grain boundary diffusion coefficient

\[ = 1.87 \times 10^{-11} \text{cm}^2/\text{s} \] (Hall and Briant, 1984)

\( t \) = ageing time = 86400s.

Thus

\[ x = 12 \mu\text{m}. \]

Hence, there is ample time for chromium to diffuse over extremely large distances and consequently the effect demonstrated in this grain boundary may solely be due to its structure.

Through computer modelling of grain boundary structures, it is now known that a boundary can be represented by a periodic array of structural units (Sutton, 1988). However, only very special arrangements of compact polyhedra can fill space at a grain boundary. In general, configurations comprised wholly of compact polyhedra can not satisfy the requirements of filling space and being compatible with the adjoining grains (Sutton, 1984). With a few exceptions, most boundaries consist of compact polyhedra interspersed with other configurations which seem to be specific to the boundary concerned. These different units may provide a favourable environment for a segregating atom as will be discussed in more detail in the next section. Thus the boundary in
question may be composed of a regular array of close packed structural units of a short period which are not disordered enough to promote rapid diffusion of chromium along the boundary. Hence, the carbide will only be supplied with chromium from its immediate vicinity, producing steep concentration gradients along the length of the boundary.

The random boundaries, analysed after the longer heat treatment, may on the other hand be composed of compact polyhedra interspersed with irregular more highly distorted regions. These regions of the boundary which are not composed of compact polyhedra may create an easier diffusion path for chromium. This would thus allow more rapid depletion of the boundary enclosed between two carbides producing the resultant concentration profile characteristics exhibited.

Hence, when measuring chromium concentration profiles between carbides and normal to the boundary, the proximity to a carbide is not important for random high-angle grain boundaries and the resultant profile will be representative of the "enclosed" boundary region for the particular heat treatment employed in this work. Generally the carbides are so closely spaced that no significant variations in grain boundary chromium concentration exist.

These observations confirm the results of both Stawström and Hillert, (1969) and Tedmon et al, (1971). Stawström and Hillert assumed the grain boundary chromium concentration to be constant along the length of the boundary between carbides; a fact disputed by Tedmon et al. It seems apparent though that both sets of
workers were correct.

In addition to this structural effect, kinetics will also influence the chromium concentration gradient within the grain boundary. For short ageing times, significant chromium concentration gradients do exist. As the ageing time increases, the gradient gradually smooths out until the grain boundary chromium concentration eventually becomes constant between two carbides.

These observations are not surprising however. At the initial stages of precipitation, chromium having arrived at the grain boundary, will diffuse along it to supply the growing carbide due to the concentration gradient created by the nucleation of the precipitate itself. This process will continue as the carbide grows. Gradually the supply of carbon to the grain boundary will become exhausted producing a decrease in its activity. This will in turn permit chromium to diffuse to the boundary without being engulfed in the carbides. Eventually, chromium levels will build up on the boundary and reach a stable value. At this stage, any significant concentration gradients that were present initially along the boundary will have been smoothed out. Obviously in the extreme case, the chromium level will reach bulk values at the boundary but this would only occur after hundreds of hours at the annealing temperature.

Consequently, the concept of concentration gradients existing between carbides along a grain boundary is an accurate one for short annealing times, in agreement with Tedmon et al. For longer heat treatment times however, this gradient smooths out resulting
in a constant grain boundary chromium concentration between carbides as stipulated by Stawström and Hillert.

As demonstrated earlier however, these concentration gradients within the grain boundary may be an effect of the boundary structure. Grain boundaries conforming to a CSL orientation may have special properties due to the higher coincidence or greater ordering of atomic sites exhibited. This in turn might affect elemental diffusion and may generate concentration gradients in a boundary between carbides as discussed above.

Hence, where CSL-type boundaries are encountered this effect must be noted and compensated for by collecting a series of profiles between the carbides. Only then will it be possible to discover whether a CSL-type boundary has affected the segregation process by generating significant concentration gradients within the grain boundary.

6.3.3. Chromium Concentration Profiles Normal to the Grain Boundary Related to the Boundary Misorientation.

The experimental procedure for this analysis is identical to that described in the previous section. Having attained the profile, the next stage in this investigation was to quantify it. A full width half maximum (FWHM) criterion was considered to be the best method for this objective as will be explained below. The grain boundary misorientation and plane were also determined for each boundary analysed using the methods discussed in Section 4.3.
Figs 6.3.3.1-6.3.3.3 show representative chromium concentration profiles, together with their FWHM and boundary misorientation. The actual boundary from which the profiles were taken is also shown. Fig 6.3.3.1 shows a profile with a large width (210nm) taken from a boundary which conforms to a $\Sigma=29b (46.40^\circ/2,2,1)$ C.S.L orientation. Fig 6.3.3.2 shows a profile from a random grain boundary with a narrower width (142nm) and Fig 6.3.3.3 was measured across a grain boundary conforming to a $\Sigma=13b (27.79^\circ/1,1,1)$ C.S.L. It is interesting to note the large difference in width of the measured profiles taken from boundaries with a variety of misorientations.

The chromium value measured on the grain boundary will always be higher than the actual value. This is due to the size of the electron beam employed together with the broadening that occurs on passing through a thin film. The grain boundary itself is of the order of 2-3 atomic layers in width and the electron beam is approximately 10nm in diameter. Hence, the interaction volume created by an electron beam of this size will encompass a significant amount of matrix adjacent to the boundary which has a higher chromium content than the boundary itself. These atoms will contribute to the detected X-ray signal and hence result in a higher than actual measured grain boundary chromium concentration (i.e. the signal derived from the grain boundary itself will only be a small percentage of the total signal detected, as was determined in the hypothesis of Section 6.2). This is why this value is not an accurate reflection of the chromium segregation process. As shown in Appendix I, the chromium concentration in
Fig 6.3.3.1. a) Cr concentration profile normal to boundary 4.
b) Boundary from which profile was measured.
Fig 6.3.3.2. a) Cr concentration profile normal to boundary 27.
b) Boundary from which profile was measured.
Fig 6.3.3.3. a) Cr concentration profile normal to boundary 48.
   b) Boundary from which profile was measured.
equilibrium with the carbide at the grain boundary is 8.1 wt%.

The heat treatment employed in this work resulted in the grain boundary chromium concentration remaining roughly constant between closely spaced carbides for random high-angle boundaries as discussed in Section 6.3.2. Initially however, the actual value at the carbide interface must be lower than the value along the rest of the boundary to permit chromium to diffuse along the boundary to the carbide enabling its growth by the collector-plate mechanism. The time-temperature transient used in this investigation must have smoothed out this chromium concentration gradient along the boundary. Measurement of the exact value at the carbide/boundary interface is not possible practically due to the beam encompassing both adjacent matrix material and carbide particle itself in its interaction volume, as discussed in the last section. Hence, all measured values of grain boundary chromium concentration will be higher than the calculated value and this is shown in column 3 of Table 6.3.3.1 (ahead).

The lowest measured value is 8.67 wt% Cr and the highest 13.59 wt% Cr which is a significant difference and must reflect the different capabilities of these boundaries to supply chromium to the growing carbide. This will be a direct consequence of the boundary misorientation which induces different amounts of openness along a boundary and thus controls the ease with which elemental distribution can be achieved, as will be discussed below.

A slight contribution to these discrepancies in boundary chromium concentration may also originate from the boundary being
misaligned with respect to the electron beam. Misalignment of the boundary will increase the value measured as more of the adjacent higher chromium content matrix will contribute to the detected X-ray signal, as discussed in Section 3.5.2.2. Each boundary was however aligned as near parallel as possible to the electron beam and boundaries were only analysed if they adhered closely to this criterion. Any boundaries exhibiting a large projected width after alignment were ignored.

Indeed, the object of the analysis undertaken in Section 6.1 was to determine the accuracy with which a boundary could be aligned with respect to the electron beam. Admittedly a twin boundary was used to facilitate this work as it has a known crystallographic orientation relationship and hence diffraction techniques can be used to determine the accuracy of the alignment. It was generally possible to align the twin to within 1° of the intended orientation. Obviously alignment of a grain boundary is more difficult due to its curved nature. Additionally, there is no easy way of determining how accurately a grain boundary is aligned other than solely minimising the projected width of the boundary plane. This is because grains themselves have no fixed orientation relationship and thus a diffraction based technique to determine alignment accuracy is impractical. Also, the accuracy with which the boundary is aligned will increase with increasing specimen thickness as its projected width will be greater. However, boundaries chosen for microanalysis should ideally be selected from thin regions of the specimen to ensure a high spatial resolution. Hence, a trade-off has to be accepted, such that the
boundary is thick enough to align accurately but thin enough to achieve a reasonable spatial resolution (providing the count rate is adequate to produce statistically meaningful X-ray data).

The grain boundary would have to be misaligned by an extremely large angle to have any significant influence on this detected X-ray signal. This is shown in Fig 6.3.3.4 using the conditions applicable to this work. The boundary would have to be misaligned by \( \sim 10^\circ \) for part of it not to be included in the generated interaction volume. Only then would it affect the measured X-ray signal. However, as stated above, from the analysis conducted in Section 6.1, it was generally possible to align a twin boundary within \( 1^\circ \) of its intended orientation. This value will be slightly increased when aligning a grain boundary but not by an order of magnitude factor. Hence, it is not anticipated that misalignment effects will drastically influence the detected boundary X-ray signal.

However, due to the above mentioned effects, it was decided that the FWHM criterion would produce a more accurate reflection of the resultant profile and this can be compared directly with the boundary misorientation to determine its effect on segregation behaviour. Table 6.3.3.1 is set out in order of decreasing FWHM. Hence, the boundaries at the top of the table produce the widest concentration profiles and the ones at the bottom the narrowest. Also given in the table is the \( \Sigma \) value of any boundary close to a CSL orientation. This value represents the reciprocal density of coincident atomic sites of the two adjoining crystals. The method for determining whether a boundary conforms to a C.S.L orientation...
Fig 6.3.3.4. Schematic diagram showing the effect of boundary misalignment on the detected X-ray signal.
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<th>BOUNDARY NO</th>
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<td>10.89</td>
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<td>98</td>
<td>11.38</td>
<td>43.88°/1,0,1 (11)</td>
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<tr>
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<td>25.30°/1,-1.3,-1.1 (13b)</td>
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<td>86</td>
<td>12.18</td>
<td>60.54°/1,-1.1,-1.3 (3)</td>
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</table>
was discussed in Section 4.1.3. The results for the boundaries analysed in this work are presented in Table 6.3.3.2. The asterisk in the end column denotes that the boundary conforms to a C.S.L. orientation.

Figs 6.3.3.1-6.3.3.3 represent boundaries 4, 27 and 48 respectively.

It is evident that boundary (1) yielded a profile width three times that of boundary (50) which is a significant difference and must reflect effects of grain boundary structure. There is no correlation between the FWHM and minimum chromium concentration which was always measured on the grain boundary. As pointed out earlier however, there is still a significant difference in the highest and lowest values detected on the boundary. In addition, it is also noticeable that all of the boundaries analysed had a misorientation angle exceeding 20° and thus were all high-angle grain boundaries. Also, approximately 20% conformed to CSL orientations with Σ<49 and thus a wide variety of grain boundary structures is anticipated.

In order to explain these findings it is necessary to consider the possible grain boundary structures involved.

It has been established through computational atomistic calculations of grain boundaries that C.S.L, O lattice and planar matching models can only be used geometrically to determine relative atom positions. This is because they do not take into account the rigid body translations that occur at the boundary. Hence, it is not possible to predict boundary properties, such as segregation characteristics, using these models. The structural
<table>
<thead>
<tr>
<th>BOUNDARY NO</th>
<th>AXIS/ANGLE</th>
<th>CSL DESCRIPTION OF BOUNDARY</th>
<th>CSL LIMIT</th>
<th>ACTUAL DEVIATION FROM CSL</th>
</tr>
</thead>
</table>
| 1           | 48.83°/1,0.6,-1.7 | 50.13°/3,2,1  
\( \Sigma = 39b \) | 2.40 | 1.65 * |
| 2           | 29.13°/1,-0.4,-0.5 | 27.79°/1,1,1  
\( \Sigma = 13b \)  
26.52°/1,1,0  
\( \Sigma = 19a \) | 4.16 | 10.95 |
| 3           | 48.67°/1,-11,-4.7 | 48.19°/2,1,0  
\( \Sigma = 15 \)  
50.13°/3,2,1  
\( \Sigma = 39b \) | 3.00 | 3.15 |
| 4           | 45.20°/1,0.4,-0.9 | 46.40°/2,2,1  
\( \Sigma = 29b \) | 2.79 | 2.55 * |
| 5           | 29.70°/1,-0.1,1 | 31.59°/1,1,0  
\( \Sigma = 27a \) | 2.89 | 2.33 * |
| 6           | 34.54°/1,-1,-0.5 | 36.87°/2,2,1  
\( \Sigma = 45b \) | 2.24 | 1.69 * |
| 7           | 35.42°/1,-3,1 | 33.55°/3,1,1  
\( \Sigma = 33b \) | 2.61 | 1.56 * |
| 8           | 46.59°/1,-1.4,-0.3 | 50.13°/3,2,1  
\( \Sigma = 39b \) | 2.40 | 3.29 |
| 9           | 37.86°/1,-0.4,1 | 36.87°/2,2,1  
\( \Sigma = 45b \) | 2.24 | 2.48 |
| 10          | 44.86°/1,-1.1,0.9 | 46.82°/1,1,1  
\( \Sigma = 19b \)  
43.57°/1,1,1  
\( \Sigma = 49a \) | 3.44 | 3.83 |
| 11          | 37.67°/1,0.3,-1.2 | 38.94°/1,1,0  
\( \Sigma = 9 \) | 5.00 | 4.85 * |
<p>| 12          | 22.37°/1,2.9,2.8 | RANDOM | — | — |
| 13          | 54.79°/1,0.8,-0.7 | RANDOM | — | — |
|   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 14| 45.02°/1,3.2,-1.1 | 40.45°/3,1,1 | 3.13 | 3.71 |
|   | Σ = 23 |   |   |   |   |
| 15| 60.39°/1,0.7,-1.2 | 60.77°/3,2,2 | 2.29 | 3.73 |
|   | Σ = 43c |   |   |   |   |
| 16| 48.75°/1,1.1,-1.3 | 46.83°/1,1,1 | 3.44 | 4.69 |
|   | Σ = 19b |   |   |   |   |
|   | 50.57°/1,1,1 |   | 2.47 | 4.48 |
|   | Σ = 37c |   |   |   |   |
| 17| 50.45°/1,-0.9,0.8 | 46.83°/1,1,1 | 3.44 | 6.74 |
|   | Σ = 19b |   |   |   |   |
|   | 50.57°/1,1,1 |   | 2.47 | 3.72 |
|   | Σ = 37c |   |   |   |   |
| 18| 38.13°/1,1.3,0.6 | 36.87°/2,2,1 | 2.24 | 3.85 |
|   | Σ = 45b |   |   |   |   |
| 19| 52.16°/1,0.7,-0.7 | 50.57°/1,1,1 | 2.47 | 6.46 |
|   | Σ = 37c |   |   |   |   |
| 20| 34.47°/1,-2.5,3.3 | 36.87°/2,2,1 | 2.24 | 5.04 |
|   | Σ = 45b |   |   |   |   |
|   | 37.07°/3,3,1 |   | 2.19 | 3.69 |
|   | Σ = 47a |   |   |   |   |
| 21| 46.19°/1,-0.7,2 | 44.41°/2,1,1 | 3.27 | 4.36 |
|   | Σ = 21b |   |   |   |   |
| 22| 21.54°/1,-1.4,0.7 | 21.79°/1,1,1 | 3.27 | 5.66 |
|   | Σ = 21a |   |   |   |   |
| 23| 25.44°/1,-0.1,0.7 | 26.52°/1,1,0 | 3.44 | 4.61 |
|   | Σ = 19a |   |   |   |   |
|   | 27.91°/2,1,0 |   | 2.29 | 3.99 |
|   | Σ = 43b |   |   |   |   |
| 24| 39.52°/1,2.2,1 | 34.05°/2,1,1 | 2.54 | 4.26 |
|   | Σ = 35 |   |   |   |   |
| 25| 32.06°/1,-0.1,-1.6 | 31.59°/1,1,0 | 2.89 | 6.11 |
|   | Σ = 27a |   |   |   |   |
|   | 35.43°/2,1,0 |   | 2.89 | 3.74 |
|   | Σ = 27b |   |   |   |   |
|   | 27.91°/2,1,0 |   | 2.29 | 4.08 |
|   | Σ = 43b |   |   |   |   |</p>
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unit model, however, does account for these translations and can be used to relate boundary segregation characteristics to structure as will discussed.

It was found that certain special boundaries were composed entirely of one type of structural unit (Sutton and Vitek, 1983). These are termed "favoured" boundaries and are found to be the fundamental structural elements of longer period boundaries, termed "non-favoured" boundaries. A non-favoured boundary in the misorientation range between two successive favoured boundaries is composed of well defined mixtures of two different units, at least one of which will be the unit associated with one of the favoured boundaries. It should be emphasised that these boundaries are classified entirely according to their structure and not their energy.

The favoured boundary units composing a non-favoured boundary are inevitably distorted but will relax to minimise this distortion. It may be this relaxation that provides favoured boundaries with their structural significance as there will be local misorientation differences along a non-favoured boundary due to its different units relaxing to their ideal misorientations. This local misorientation difference is significant and produces secondary grain boundary dislocations which generate a corresponding stress field. Favoured boundaries only contain intrinsic grain boundary dislocations which are inherent in their equilibrium structure and thus do not produce long-range stress fields. Hence, non-favoured boundaries, due to their long-range stress fields are more likely to interact with lattice defects
that are further away from the boundary. This may enhance the ability of the boundary to absorb or emit vacancies due to the presence of these terminating planes (Sutton and Vitek, 1983).

It should also be noted that favoured boundaries are not always associated with the lowest values of $\Sigma$. For example, $\Sigma=27 (1,1,5)$ and $\Sigma=11 (1,1,3)$ are favoured $\langle 110 \rangle$ symmetrical tilt boundaries in aluminium and $\Sigma=9 (1,1,4)$ is not. Additionally, it is known that the same boundaries are not favoured in all metals with the same crystal structure.

The physical insights which this structural unit model provide are unclear. The relationship between area density, type and distribution of polyhedra in a grain boundary and its energy has not been evaluated. Indeed, there is very little evidence suggesting such a relationship exists (Sutton, 1984).

One of the most important aspects of this model is that the compact structural units themselves may provide a favourable environment for a segregating atom, or conversely segregation may be enhanced to regions which are not compact polyhedra. This may lead to pronounced selectivity of segregation sites. Hence, the propensity of segregation to different boundaries will be different because, in general, their densities of segregation sites will not be the same.

Additionally, only certain preferred sites can be occupied by substitutional segregants which may cause a substantial decrease in grain boundary diffusivity once segregation has occurred. This is because diffusion of segregants to unfavourable sites may require more activation energy than the equivalent motion
involving only host atoms (Sutton and Vitek, 1982).

Another concept introduced by these atomistic calculations was that of the multiplicity of structures exhibited by a boundary. This arises because the structures of some of the favoured boundaries are not unique (i.e. they can become distorted). General boundaries have a higher multiplicity of metastable structures than short period boundaries due to the possible changes in boundary plane (Wang et al, 1984) and hence are composed of a number of variously distorted structural units. These metastable structures have different energies and thus it might be expected that only the structure with lowest energy would occur at equilibrium. However, the difference in energy between the different structures is very small and it is possible that various metastable structures could occur at high temperatures and be frozen in upon quenching. Thus different structures may be found in various regions of the same boundary depending on local irregularities such as inhomogeneously distributed segregants or precipitates.

The annihilation or creation of vacancies at a boundary may also induce the transformation from one metastable structure to another. Hence, the efficiency of a boundary as a source or sink of vacancies will depend on the number of alternative metastable structures it possesses together with their energies. The extensive multiplicity of general boundaries may therefore explain their capability of acting as highly efficient sources and sinks of vacancies. Low Σ boundaries parallel to low index planes however, have a much lower multiplicity of structures and hence
would not be expected to act as such efficient sources or sinks as is observed experimentally.

Thus, both elemental segregation and the absorption and emission of vacancies can induce local transformations of the boundary structure leading to the co-existence of several different structures along the same boundary.

Having established the above possibilities created by the structural unit representation of grain boundary structure, it is now possible to explain the results attained in Table 6.3.3.1 more definitively.

Another obvious feature of this table is that most of the boundaries conforming to C.S.L orientations are grouped at its extremities, therefore exhibiting the widest and narrowest of chromium concentration profiles.

It is no surprise that the \( \Sigma=3 \) \( (60^\circ/1,1,1) \) boundary (50) has the narrowest profile width as this (twin) boundary is known to have a very low energy. It is composed entirely of a continuous sequence of the same compact structural unit and will thus not have a large associated stress field. Consequently, it will not interact readily with lattice defects or provide ideal sites for segregants. It is likely therefore, to be a favoured boundary.

In addition, the \( \Sigma=11 \) \( (50.47^\circ/1,1,0) \) boundary (46) is also known to be a low energy boundary and would be expected to have a narrow profile width due to the reasons outlined above for the \( \Sigma=3 \) boundary.

The relaxed structure of a \( \Sigma=11 \) \( (1,1,3) \), \( 50.48^\circ/[1,T,0] \) boundary in aluminium is shown in Fig 6.3.3.5. This boundary is
Fig 6.3.3.5. Relaxed Structure of $\Sigma = 11$ (113), 50.48°/[110] Boundary in Aluminium; the two capped trigonal prisms in one boundary period are indicated by broken lines.
composed entirely of close packed trigonal prisms. Care should be taken in comparing this structure with the $\Sigma=11$ boundary in this work because the experimental boundary is not a symmetrical tilt boundary with the same boundary plane and is from a different alloy system, albeit with the same crystal structure. However, the basic configurations of both boundaries will be similar. The computed boundary is a favoured boundary in the aluminium system and the important point to notice is the close-packed nature of the structure and the short period.

It is probable that this sort of structure exists for the $\Sigma=11$ experimental boundary (46) as segregation has obviously not occurred readily to this boundary judging by the associated narrow profile width. This suggests that if a boundary is composed of close-packed polyhedral units of the same type then segregation is impeded. Thus it is likely that segregation does not occur to the compact polyhedra themselves but to the disordered regions adjacent to them. This implies that there is indeed a pronounced selectivity of segregation sites.

Consequently, it seems likely that the $\Sigma=11$ boundary in this alloy is also a favoured boundary although no atomistic calculations have been performed to confirm this.

In addition, it is likely that the two $\Sigma=13$ ($27.79^\circ/1,1,1$ and $22.61^\circ/1,0,0$) boundaries (48 and 49) are also favoured for the reasons explained above. Obviously all of the boundaries will contain different structural units which will be of the same type with a short period for a specific boundary.

Further evidence for these boundaries being favoured or
special is the deep energy cusps that exist in boundary energy versus tilt angle plots for Σ=3 and Σ=11 boundaries and boundary energy versus twist angle plots for the Σ=13a boundary in aluminium (Sutton and Balluffi, 1987).

Although there is no evidence to suggest that boundaries are favoured in metals of the same crystal structure, it seems likely that the Σ=3, 11, 13a and 13b boundaries are favoured in this material due to the measured chromium concentration profiles and the atomistic calculations for aluminium.

One of the weaknesses of the C.S.L model is that all boundaries having a high coincidence of atomic sites (i.e. low Σ) do not exhibit special properties such as low energy. This point is reinforced in Table 6.3.3.1 by the relative position of the Σ=9 (38.94°/1,1,0) boundary (11). This boundary produced a chromium concentration profile with a FWHM of 182nm: a two-fold increase over the favoured boundaries. Hence, this difference must reflect a difference in the atomic packing at the boundary. Fig 6.3.3.6 shows the relaxed structure of a Σ=9 (1,1,4)\textsubscript{38.94°/1,1,0} boundary in aluminium. It is evident that the boundary is composed of two different types of structural element: one of which is the characteristic unit of the Σ=11 boundary shown in Fig 6.3.3.5. The other unit originates from the Σ=27 (1,1,5)\textsubscript{31.59°/1,1,0} boundary which is also a favoured boundary in aluminium. Thus the Σ=9 boundary must be a non-favoured boundary containing a periodic array of the fundamental structural units of the Σ=11 and Σ=27 favoured boundaries.

As pointed out above, these fundamental units of the favoured
Fig 6.3.3.6. Relaxed Structure of $\Sigma = 9 (114), 38.94^\circ/[110]$

Boundary in Aluminium.
boundaries may distort on relaxing to their minimum energy configurations to accommodate the misorientation. This will in turn initiate secondary grain boundary dislocations due to local incompatibilities, which generate a long-range stress field. Consequently, the propensity of segregation to a boundary of this type will be higher due to the increased density of terminating planes along the boundary. Hence, the vacancy-chromium complex flux from the grain interiors will be more readily accepted by these planes, allowing more rapid diffusion to the growing carbide and thus a greater depletion in the vicinity of the grain boundary itself.

It seems apparent therefore that the experimental Σ=9 boundary (11) in this material is a non-favoured boundary similar to that in the aluminium system. A wide concentration profile would thus be expected.

As stated earlier, it is invalid to assume that the same boundaries are favoured in metals with the same crystal structure. Up to this point, it seems that the boundaries in aluminium and 316 stainless steel exhibit the same characteristics. This is not always the case however, as the Σ=27 (31.59°/[1,1,0]) is a favoured boundary in aluminium. For the same to be true in stainless steel, a boundary of this type would be expected to yield a narrow profile width using the above arguments. However, the Σ=27a (31.59°/1,1,0) boundary (5) produced a wide (205nm) concentration profile. This implies that it is a non-favoured boundary and highlights the dangers in directly comparing two metals with the same crystal structure. Consequently, this
boundary must be composed of an array of different types of structural unit, similar to the Σ=9 boundary (11), resulting in a structure that yields similar segregation characteristics. The Σ=27a boundary however, may relax in such a way that the structural units are more distorted than those of the Σ=9 boundary. This may create a longer range stress field and possibly explain why it yields a wider concentration profile.

Indeed, this local distortion of the structural units on relaxation may explain why the boundaries analysed yielded significantly different profile widths. It is possible that the boundaries become more ordered from boundary (1) to boundary (50). For example, boundary (1), although conforming to a Σ=39b (50.13°/3,2,1) orientation, may be composed of a combination of units which are so distorted after relaxation that a long range stress field is created, encouraging the creation of a wide concentration profile. This stress field may diminish in size with each boundary misorientation as the table is descended. Hence, the boundaries conforming to C.S.L orientations at the beginning of the table would not be expected to have special properties and consequently produce wide concentration profiles. As a result, they are acting as if they were random high-angle grain boundaries.

This point of view is further supported by the fact the favoured boundaries in this alloy have all accumulated at the end of the table yielding the narrowest concentration profiles.

It is also possible that boundary (43), conforming to a Σ=29a (43.60°/1,0,0) orientation, is a favoured boundary. It has a
narrow profile width similar in magnitude to the other aforementioned favoured boundaries. This boundary together with the \( \Sigma=13a \) \((22.61^\circ/1,0,0)\) favoured boundary could define the limits of a misorientation range in which the boundaries between these misorientation limits are composed of a periodic combination of these fundamental structural elements. Thus any boundary between these limits will be a non-favoured boundary and composed of \( \Sigma=29a \) and \( \Sigma=13a \) structural elements. This is analogous to the \( \Sigma=27 \) and \( \Sigma=11 \) \([1,\bar{T},0]\) type symmetrical tilt boundaries in aluminium (Sutton and Vitek, 1983).

Possible examples of non-favoured boundaries within this misorientation range are boundaries \((35)\) and \((42)\). These boundaries \((25.74^\circ/1,11,-45 \) and \(34.95^\circ/1,17.7,6 \) respectively) could conform to high \( \Sigma \) \((1,0,0)\) type orientations and thus could be composed of the \( \Sigma=29a \) and \( \Sigma=13a \) fundamental units. It should be emphasised however, that the boundaries observed in this work are not symmetrical tilt boundaries although atomistic calculations on asymmetric tilt boundaries do show the same tendencies as those for symmetrical tilt boundaries (Sutton and Vitek, 1983).

Another interesting observation in Table 6.3.3.1 is the large variation in profile width created by the two \( \Sigma=29b \) boundaries \((4\) and \(39)\). This could be an example of the multiplicity of metastable structures exhibited by some boundaries. Although they both conform to the same C.S.L orientation they may have relaxed in different metastable configurations after quenching from the solutionising temperature, due to constraints imposed by the local boundary planes. This will create variations in boundary structure...
along the length of a particular grain boundary. Hence, the structural elements composing the boundary will be distorted by different degrees producing varying long range stress fields. The propensity of segregation to these sites will thus be different resulting in the different detected widths of the depleted region adjacent to the grain boundary. For this to be the case, the boundaries in question would have to be long-period boundaries so that they have a large multiplicity of metastable structures and thus a wide variety of segregation characteristics.

This may also explain why precipitation along a specific grain boundary is discontinuous and why large variations in coverage exist from boundary to boundary.

As mentioned earlier, there is no direct correlation between the FWHM of the resultant chromium concentration profile and the measured value of grain boundary chromium concentration. This is shown schematically in Fig 6.3.3.7.

The gradual decrease of FWHM on descending the table has been interpreted in terms of a decrease in the long range stress field created by the different combinations of structural unit that accommodate the various misorientations. The magnitude of this long range stress field will determine the ease with which chromium can be supplied to the grain boundary and thus will control the width of the profile.

It is also known that substitutional elements segregate to preferred sites in the boundary which can cause a decrease in grain boundary diffusivity once segregation has occurred. Thus, on arriving at a grain boundary, chromium may or may not be sited in
Fig 6.3.3.7. Graph to show correlation between FWHM and minimum chromium concentration.
a preferred site and this will control the ease with which it is
distributed to the carbide. Although the configuration of
structural units may inherently create specific long range stress
fields for non-favoured boundaries, this implies nothing about the
distributive capabilities of the individual units themselves. So
although a long range stress field may be created, producing a
concomitant wide profile, this will have no control on elemental
diffusion along the boundary once the segregant has arrived. Some
configurations will thus be more efficient in the distribution of
chromium, resulting in low measured grain boundary concentrations
and others will be preferred sites and inhibit diffusion producing
higher concentrations on the boundary. As a result, no correlation
between FWHM and grain boundary chromium concentration would be
expected on this basis.

These results are supported by the observations of Hall and
Briant, (1984). They found significant variations in measured
grain boundary chromium concentration at different boundaries in
the same sample for the same heat treatment although the profile
width remained roughly constant. However, no indications of
boundary crystallography were supplied so a correlation between
these two sets of data is impossible. In addition, they also found
variations in grain boundary chromium concentration along a
specific grain boundary, although again the boundary
crystallography was not determined.

Furthermore, Ortner and Randle, (1989) concluded that it is
impossible to categorise boundaries solely according to their
C.S.L misorientations when examining sensitisation. A more
detailed knowledge of the structural units comprising each C.S.L orientation is required to accurately relate crystallography to individual boundary properties, as shown in this work.

They also discovered that sensitisation was confined to high-angle boundaries with low-angle boundaries being unaffected, in agreement with Bennett and Pickering, (1987) and the work presented here. Consequently, an additional remedial measure to essentially eliminate sensitisation would be to align the microstructure by directional solidification to create a high degree of texture, with neighbouring grains having only a slight (\(<10^\circ\)) misorientation. If this exercise could be carried out practically on large structural assemblies, it may be commercially viable, as problems caused by sensitisation can result in plant shut-down in the power generation industry.

In the course of this investigation, two boundaries were encountered with anomalous properties, as shown in Figs 6.3.3.8 and 6.3.3.9. They exhibited no chromium depletion in the vicinity of the grain boundary or on the grain boundary itself and were determined to be random high-angle grain boundaries. Their misorientations were \(48.72^\circ/1,5,-3\) and \(38.25^\circ/1,-1,3\) respectively.

This phenomenon would be expected of low-angle grain boundaries or boundaries conforming to \(\Sigma\) orientations, especially favoured ones.

It is difficult to explain these observations in terms of the above discussion for normal high-angle boundaries. Although the boundaries cannot be represented by \(\Sigma<49\) orientations, it is obvious that the boundary structure itself must be of a special
Fig 6.3.3.8. Cr concentration profile normal to a boundary showing no Cr depletion.
Fig 6.3.3.9. Cr concentration profile normal to a boundary showing no Cr depletion.
Precipitation had occurred on these boundaries, being rather more sporadic than on the majority of analysed boundaries however. This implies that the boundary does not have a long-range stress field else precipitation would have occurred to a greater extent due to the increased propensity of segregation. Only local variations in misorientation along the length of a boundary could account for this behaviour, implying a multiplicity of structures. At certain sites, the misorientation must be favourable for the nucleation of a carbide. The supply of chromium to this precipitate must have come from its immediate vicinity as no concentration gradients were detected along the boundary. Thus the majority of the boundary is probably composed of compact polyhedra of a short period analogous to those incorporated along favoured boundaries. Indeed both of these boundaries may conform to orientations with \( \Sigma > 49 \) and also be favoured boundaries, as there is no universal criterion for determining how high \( \Sigma \) can be and still remain meaningful. However, it is still difficult to explain why there is no concentration gradient at all, either along or normal to the grain boundary, when even the low energy \( \Sigma = 3 \) incoherent twin boundary has a detectable profile.

On this basis, some of the other boundaries with narrow profile widths may also be "favoured" but with \( \Sigma > 49 \).

Finally, it is interesting to note, that even though some boundaries have been interpreted as "favoured" according to the structural unit classification of grain boundary structure, they still have grain boundary chromium concentrations less than 13wt\%.

Consequently, if subjected to the modified Strauss test, these
boundaries would still be attacked like any other high-angle grain boundary and thus in this respect, have no special properties.

6.3.4. Chromium Concentration Profiles Normal to the Grain Boundary Related to the Boundary Plane.

As mentioned in Section 4.1, the misorientation and boundary plane are both needed to completely categorise a grain boundary. Having established the relationships between the chromium concentration profile and various grain boundary misorientations, the next step in this work was to determine if any such relationships existed for the boundary plane. The boundary plane was determined at the same time as the misorientation using the methods outlined in Section 4.3.4.

Table 6.3.4.1 shows the misorientation and boundary plane of each grain boundary analysed, together with the Σ value of any boundary conforming to a C.S.L. The boundaries are ranked in the same order as in the previous section, with the FWHM of the generated chromium concentration profile decreasing on descending the table. Hence, the boundaries at the top of the table have the widest profiles and those at the bottom the narrowest.

It is known that $\mathrm{M}_{23}\mathrm{C}_6$ carbides are semi-coherent with one austenite grain, exhibiting a cube-cube orientation relationship of the form

$$(111)_c // (111)_\gamma ; <110>_c // <110>_{\gamma}$$
<table>
<thead>
<tr>
<th>BOUNDARY</th>
<th>MISORIENTATION</th>
<th>BOUNDARY NORMAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.83°/1,0.6,-1.7</td>
<td>-0.6,-0.2,-0.1/-0.3,0.1,0 (39b)</td>
</tr>
<tr>
<td>2</td>
<td>29.13°/1,-0.4,-0.5</td>
<td>0.4,0.2,0.9/0.4,0.5,0.8</td>
</tr>
<tr>
<td>3</td>
<td>48.67°/1,-10.6,-4.7</td>
<td>-0.4,-0.6,0.6/0.8,-1.4,0</td>
</tr>
<tr>
<td>4</td>
<td>45.20°/1,0.4,-0.9</td>
<td>0.2,0.3,0.9/0.4,0.4,0.8 (29b)</td>
</tr>
<tr>
<td>5</td>
<td>29.70°/1,-0.1,1.0</td>
<td>0,0.7,0.7/0.4,0.3,0.8 (27a)</td>
</tr>
<tr>
<td>6</td>
<td>34.54°/1,-1,0.5</td>
<td>1,-0.3,-0.5/0.7,2.4,-0.1 (45b)</td>
</tr>
<tr>
<td>7</td>
<td>35.42°/1,-3,1</td>
<td>1,0.7,-1/3,5.6,-2.9 (33b)</td>
</tr>
<tr>
<td>8</td>
<td>46.59°/1,-1.4,-0.3</td>
<td>0.3,0.2,1/0.6,0.5,0.6</td>
</tr>
<tr>
<td>9</td>
<td>37.86°/1,-1.4,-0.3</td>
<td>0.3,0.2,0.9/0.2,0,1</td>
</tr>
<tr>
<td>10</td>
<td>44.86°/1,-0.4,1</td>
<td>0.6,0.6,0.6/0.0,0.3,0.9</td>
</tr>
<tr>
<td>11</td>
<td>37.67°/1,0.3,-1.2</td>
<td>0.5,0.3,0.8/0.3,0.5,0.9 (9)</td>
</tr>
<tr>
<td>12</td>
<td>22.37°/1,2.9,2.8</td>
<td>0.6,0.6,0.6/0.6,0.5,0.7</td>
</tr>
<tr>
<td>13</td>
<td>54.79°/1,0.8,-0.7</td>
<td>1,0,0/0.6,0.5,0.6</td>
</tr>
<tr>
<td>14</td>
<td>45.02°/1,3.2,-1.1</td>
<td>0.7,0,0.7/0.4,0,0.9</td>
</tr>
<tr>
<td>15</td>
<td>60.39°/1,0.7,-1.2</td>
<td>0.5,0.4,0.8/0.3,0.4,0.8</td>
</tr>
<tr>
<td>16</td>
<td>48.75°/1,1.1,-1.3</td>
<td>0.3,-0.3,0.9/0.0,0.8,0.6</td>
</tr>
<tr>
<td>17</td>
<td>50.45°/1,-0.9,0.8</td>
<td>0.3,0.2,0.9/0.3,0.2,0.9</td>
</tr>
<tr>
<td>18</td>
<td>38.13°/1,1.3,0.6</td>
<td>0.5,0.4,0.8/0.3,0.6,0.8</td>
</tr>
<tr>
<td>19</td>
<td>52.16°/1,0.7,-0.7</td>
<td>-0.2,-0.5,0.3/-0.2,0.9,0.2</td>
</tr>
<tr>
<td>20</td>
<td>34.47°/1,-2.5,3.3</td>
<td>0.2,0,0.2/1,0.1,0.1</td>
</tr>
<tr>
<td>21</td>
<td>46.19°/1,0.7,-0.7</td>
<td>0.6,0.5,0.7/0.4,-0.1,0.9</td>
</tr>
<tr>
<td>22</td>
<td>21.54°/1,-1.4,0.7</td>
<td>-0.4,-0.9,0.3/-0.8,-0.7,0.8</td>
</tr>
<tr>
<td>23</td>
<td>25.44°/1,-0.1,0.7</td>
<td>0,0.8,0.6/0.5,0.2,0.9</td>
</tr>
<tr>
<td>24</td>
<td>39.52°/1,2.2,1</td>
<td>0.6,0.7,0.5/0.4,0.7,0.6</td>
</tr>
<tr>
<td>25</td>
<td>32.06°/1,-0.1,-1.6</td>
<td>0.4,0,0.9/0.3,0.2,0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>26</td>
<td>46.04°/1, -0.5, -2.7</td>
<td>0.5, 0.6, 0.7/0, 0.5, 0.9</td>
</tr>
<tr>
<td>27</td>
<td>45.60°/1, 4.9, -4.7</td>
<td>0.1, 0.3, 1/0, 0.7, 0.7</td>
</tr>
<tr>
<td>28</td>
<td>54.67°/1, -0.1, 0.9</td>
<td>0.4, 0.2, 0.9/0.2, 0.4, 0.9</td>
</tr>
<tr>
<td>29</td>
<td>47.81°/1, 0.5, -2.2</td>
<td>0.3, -0.1, 1/0.5, 0, 0.9</td>
</tr>
<tr>
<td>30</td>
<td>38.44°/1, -2.7, -4.4</td>
<td>0.4, 0.7, 0.6/0.5, 0.1, 0.9</td>
</tr>
<tr>
<td>31</td>
<td>45.77°/1, -0.4, -2.7</td>
<td>0.7, 0, 0.7/0.5, 0.7, 0.6</td>
</tr>
<tr>
<td>32</td>
<td>46.29°/1, -1.3, 4.5</td>
<td>-0.2, 0.8, 0.7/0.7, 0.5, 0.6</td>
</tr>
<tr>
<td>33</td>
<td>45.34°/1, 1.3, -2</td>
<td>0.3, 0.4, 0.8/0.7, 0.4, 0.6</td>
</tr>
<tr>
<td>34</td>
<td>46.99°/1, -1.2, 0.5</td>
<td>0, 0.3, 1/0.5, 0.3, 0.8</td>
</tr>
<tr>
<td>35</td>
<td>25.74°/1, 11, -45</td>
<td>0.6, 0.3, 0.8/0.7, 0.7, 0.7,</td>
</tr>
<tr>
<td>36</td>
<td>45.79°/1, 0.3, 0.4</td>
<td>0.3, 0.1/0.4, 0.7, 0.6</td>
</tr>
<tr>
<td>37</td>
<td>56.00°/1, 0.7, 0.7</td>
<td>-1.2, 0.1, 1.6/0.1, 1.2, -0.6</td>
</tr>
<tr>
<td>38</td>
<td>45.18°/1, -0.5, 1</td>
<td>0, 0.3, 0.9/0.4, 0.7, 0.6</td>
</tr>
<tr>
<td>39</td>
<td>48.69°/1, -1.9, -1.9</td>
<td>-0.1, 0.1, -0.2/-0.1, 0, 0.1</td>
</tr>
<tr>
<td>40</td>
<td>28.67°/1, -0.3, -0.3</td>
<td>0.5, 0, 0.9/0.4, 0.3, 0.8</td>
</tr>
<tr>
<td>41</td>
<td>56.57°/1, 4.9, 5.3</td>
<td>-0.2, 1.2, -0.6/0.8, 1.3, 0.3</td>
</tr>
<tr>
<td>42</td>
<td>34.95°/1, 17.7, 6</td>
<td>0, 0.4, 0.9/0.5, 0.4, 0.8,</td>
</tr>
<tr>
<td>43</td>
<td>44.35°/1, 0, 0</td>
<td>0.5, 0.4, 0.8/0.3, 0.5, 0.8</td>
</tr>
<tr>
<td>44</td>
<td>24.30°/1, 0.5, 0.1</td>
<td>0, 0.8, 0.6/0.5, 0.4, 0.8</td>
</tr>
<tr>
<td>45</td>
<td>34.91°/1, -0.6, 1.3</td>
<td>0.2, 0.3, 0.9/0.4, 0, 0.9</td>
</tr>
<tr>
<td>46</td>
<td>43.88°/1, 0.1</td>
<td>0.5, 0.2, 0.9/0.4, 0.7, 0.6</td>
</tr>
<tr>
<td>47</td>
<td>34.58°/1, -0.3, -0.2</td>
<td>0.3, 0.5, 0.8/0,-0.1, 1</td>
</tr>
<tr>
<td>48</td>
<td>25.30°/1, -1.3, -1.1</td>
<td>0.3, -0.1, 1/0.6, 0.3, 0.8</td>
</tr>
<tr>
<td>49</td>
<td>25.48°/1, 7.3, 0</td>
<td>0.7, 0.7/0.4, 0.9</td>
</tr>
<tr>
<td>50</td>
<td>60.54°/1, -1.1, -1.3</td>
<td>0.5, 0.4, 0.9/0.1, 0.3, 0.9</td>
</tr>
</tbody>
</table>

**TABLE 6.3.4.1 continued**
as stated in Section 3.4.1. Consequently, if the boundary plane was close to \( \{111\} \), then the activation energy for nucleation of a carbide would be reduced. This could enhance precipitation resulting in an ubiquitous coverage along the boundary.

However, it is apparent from the table that the majority of boundaries do not conform to this criterion. Hence, this cannot be the overriding factor in precipitate nucleation.

This conclusion however is rather tentative as the boundary may have migrated after the heat treatment employed in this work. Therefore, the boundary plane could originally have been close to \( \{111\} \) and aided in precipitate nucleation but after 48hrs annealing migrated away from this direction.

Despite this hypothesis, the proximity to a \( \{111\} \) can not be the main factor in the nucleation of a chromium-rich carbide due to the fact that the \( \Sigma=3 \) coherent twin boundary, which consists of a \( \{111\} \) interface, exhibits no precipitation until extremely long ageing times have been exercised.

Analysis of table 6.3.4.1 shows that there is no consistent pattern in the boundary normal on descending the table. The normals are a totally random distribution of directions. Of the fifty boundaries analysed only one boundary (17) was symmetrical. This boundary was not a C.S.L with \( \Sigma<49 \) and showed no special properties. The measured chromium concentration profile was symmetrical about the boundary as would be expected if the planes were similar on either side. On this basis, it may be expected that if a boundary exhibited one normal close to a low index axis and the other close to a high index axis, then an asymmetrical
profile would develop due to the differences in diffusivity along close packed and more open planes. A number of boundaries in the table conform to this situation, namely widely different planes on either side of the boundary, but all the profiles measured were symmetrical about the boundary itself. Thus there cannot be a significant difference in the diffusivity of chromium along different directions.

It should be pointed out that a direct comparison of boundary normal with FWHM of the generated chromium concentration profile is complicated by the fact that all of the boundaries in Table 6.3.4.1 have different misorientations. Consequently, the boundaries are not comparable with respect to some fixed misorientation. Ideally, a comparison should be made along a single curved grain boundary in which the misorientation stays the same but the boundary normal changes along the length of the boundary. Fortunately, a boundary arranged in this manner was discovered during this investigation. Additionally, it was possible to orient the boundary close to the electron beam direction so that accurate microanalysis could be undertaken at a number of different positions along the grain boundary. Hence, a direct comparison of FWHM with boundary normal was carried out for this particular boundary. The results of this investigation are shown in Table 6.3.4.2 and the boundary from where the analyses were performed is shown in Fig 6.3.4.3. Its misorientation was 56.00°/1,0.7,0.7 which can be described as a random high-angle grain boundary (i.e. it does not conform to a Σ<49 orientation). The boundary normal and chromium concentration profile were taken
<table>
<thead>
<tr>
<th>POSITION</th>
<th>BOUNDARY NORMAL</th>
<th>DEVIATION FROM (111) °</th>
<th>FWHM nm</th>
<th>BOUNDARY Cr CONC wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5,1.3,-0.8</td>
<td>22.06</td>
<td>199</td>
<td>9.74</td>
</tr>
<tr>
<td></td>
<td>-0.2,-3.2,2.0</td>
<td>33.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-1.2,0.1,1.6</td>
<td>33.00</td>
<td>139</td>
<td>9.08</td>
</tr>
<tr>
<td></td>
<td>0.1,1.2,-0.6</td>
<td>36.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-0.7,2.2,-0.8</td>
<td>26.04</td>
<td>130</td>
<td>9.94</td>
</tr>
<tr>
<td></td>
<td>-2.3,-1.0,1.0</td>
<td>31.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-1.4,-1.0,0.3</td>
<td>28.91</td>
<td>159</td>
<td>10.69</td>
</tr>
<tr>
<td></td>
<td>-0.8,0.6,-0.4</td>
<td>15.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-1.0,-0.5,0.3</td>
<td>28.63</td>
<td>142</td>
<td>11.35</td>
</tr>
<tr>
<td></td>
<td>-1.4,-0.3,0.6</td>
<td>29.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.8,-1.9,-2.1</td>
<td>32.08</td>
<td>133</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td>5.2,-5.1,0</td>
<td>34.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.3,1.9,-0.5</td>
<td>25.65</td>
<td>142</td>
<td>10.66</td>
</tr>
<tr>
<td></td>
<td>1.9,1.8,-0.2</td>
<td>31.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-0.8,0.3,-0.3</td>
<td>28.97</td>
<td>136</td>
<td>10.59</td>
</tr>
<tr>
<td></td>
<td>-1.0,0.6,-0.6</td>
<td>14.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig 6.3.4.3. Grain boundary from which the data in Table 6.3.4.2 was collected.
from eight positions along the length of the boundary. It is evident that none of the boundary normals were close to (111) even though the boundary was covered with precipitates. In addition, the deviation from (111) is significant, being over $14^\circ$ in all cases. This seems to imply that the (111) is not a favourable orientation for precipitate nucleation as it is unlikely that the boundary would have migrated over $14^\circ$ from this initial direction.

Another observation from this table is that there is no direct correlation between the boundary normal and FWHM of the chromium concentration profile. The majority of the measured profiles had a similar FWHM (135-145nm) but this did not correspond to similar boundary normals, which were again a random distribution of directions. Hence, it is apparent that the diffusivity of chromium is independent of the direction/plane along which it diffuses and thus a relationship between boundary normal and FWHM would be unexpected. Additionally, as the majority of profiles have similar FWHMs, this indicates that the chromium concentration profile itself is roughly constant along the length of a boundary and thus serves as a good representation of the boundary.

Position 1 showed a significantly higher FWHM (199nm) but this profile was taken near the grain boundary triple point and may have been affected by the stress fields of the other boundaries. As expected, there was also no correlation between the boundary normal and chromium concentration measured on the boundary. There was however a significant difference in the measured values, which ranged from 9.08 to 11.35wt%Cr, supporting
the concept of a multiplicity of structures existing along the length of an individual grain boundary, as indicated in the last section.

The overall conclusions to be drawn from this analysis are twofold. Firstly, it is not pre-requisite for the boundary plane to be close to \{111\} for a chromium-rich carbide to nucleate. Secondly, there is no correlation between the boundary normal and either the FWHM of the chromium concentration profile or the grain boundary chromium concentration.

6.4. Comparison of Experimentally Determined Concentration Profiles With Theory.

Having measured chromium concentration profiles at grain boundaries in sensitised material, it is then necessary to compare them with existing theoretical models to determine the model's accuracy. As mentioned in Section 3.3.3, the solution of Fick's second law for diffusion is applicable (Thorvaldsson and Dunlop, 1983, Butler and Burke, 1986, Bennett and Pickering, 1987).

This solution is useable since the chromium concentration is generally constant along the length of high-angle grain boundaries, as stated in Section 6.3.2. The calculation of the grain boundary chromium concentration, \( c_b \), is shown in Appendix I and was found to be 8.1wt%Cr. \( D_v \) was determined from Fullman, (1980).

Applying the model to experimentally determined profiles yields excellent agreement, as shown in Fig 6.4.1. The width of
Fig 6.4.1. Comparison of experimentally determined concentration profiles with theory.
the experimental profile is predicted extremely accurately by the model. The grain boundary value is predicted to be slightly lower in agreement with the discussion in Section 6.3.3. Consequently, the value of $D_v$ obtained from Fullman, which was applicable to an A.I.S.I 304 stainless steel, seems to also be valid for this 316 stainless steel, for this particular boundary.

The diffusivity of chromium in the vicinity of grain boundaries seems however, to be dependent on the individual grain boundary itself, according to the marked variation in FWHM of the measured chromium concentration profiles. This is a result of the different stress fields associated with different types of grain boundary and has been discussed in detail in Section 6.3.3. Hence, if the calculated profile was compared with a boundary at the extremities of Table 6.3.3.1, the fit would not be as good. This is not an error of the model but an inherent characteristic of specific grain boundaries to be more efficient sinks for vacancies/impurities than others, which produces steeper concentration gradients and thus a greater driving force for segregation to the boundary. Consequently, if $D_v$ was modified slightly to compensate for this differing propensity of segregation at individual grain boundaries, then the fit between experiment and theory would again be excellent.

In conclusion, the solution to Fick's second law for diffusion adequately defines the width of the generated chromium concentration profiles that develop in sensitised 316 stainless steel. This good agreement between experiment and theory justifies the decision made in Section 3.5.2.4, not to deconvolute the
effects of beam broadening from the measured concentration profiles. The extent of this effect for the particular material and conditions employed in this work is obviously negligible.
When sensitised A.I.S.I 316 stainless steel is viewed in the microscope, both optical and electron, it is immediately obvious that there are different amounts of precipitation on individual boundaries. A detailed analysis of fifty boundaries was carried out to discover if any relationships existed between grain boundary structure and the segregation of chromium.

It was found initially, having analysed fifty twin boundaries, that truly planar interfaces could be aligned to within 1° of the electron beam direction, using only image information. Greater inaccuracies will usually have to be tolerated for non-planar boundaries due to their curved nature. However, considering the conditions employed in this work, it is not anticipated that misalignment of grain boundaries with respect to the electron beam will have affected the detected chromium concentration profile. Consequently, the measured profile accurately represents the boundary from which it was attained.

The effect of spot size on the detectability of a segregant at the boundary was also considered and a model developed to simulate the situation. As the spot size and specimen thickness decrease, the percentage signal increases. This emphasises the importance of using as small a spot size as is practicable and a thin specimen for the microanalytical measurement of grain boundary segregations.

These initial results were of great practical significance
and greatly facilitated the subsequent segregation analyses.

When measuring chromium concentration profiles between carbides and normal to the grain boundary, the proximity to a carbide is not important for random high-angle grain boundaries and the resultant profile will be representative of the boundary, for the particular heat treatment employed in this work. Chromium concentration gradients along C.S.L boundaries have however been detected. Thus when this type of boundary is encountered, a series of profiles between carbides should be collected to discover whether the boundary structure has affected the segregation process.

There was a threefold difference in FWHM of the widest and narrowest profile measured. This variation may be interpreted in terms of varying long range stress fields created by different combinations of structural unit that accommodate the various misorientations. The magnitude of this long range stress field will determine the ease with which chromium can be supplied to the grain boundary and thus will control the width of the profile.

All boundaries analysed had a misorientation angle exceeding $20^\circ$ and thus were all high-angle grain boundaries. Additionally, the majority had an ubiquitous coverage of chromium-rich carbides.

Approximately 20% of the boundaries conformed to C.S.L orientations with $\Sigma < 49$ and of these, it is likely that the following are favoured boundaries due to the narrowness of their measured chromium concentration profiles:
1. $\Sigma=3\ (60^\circ/1,1,1)$;
2. $\Sigma=11\ (50.47^\circ/1,1,0)$;
3. $\Sigma=13a\ (27.79^\circ/1,1,1)$;
4. $\Sigma=13b\ (22.61^\circ/1,0,0)$.

It is thus likely that segregation does not occur to the compact polyhedra composing the boundaries themselves, but to the less ordered regions adjacent to them.

The $\Sigma=9\ (38.94^\circ/1,1,0)$ is a non-favoured boundary in this material, proving that not all boundaries with low $\Sigma$ have special properties.

$\Sigma=29a\ (43.60^\circ/1,0,0)$ may also be a favoured boundary as it has a narrow profile width comparable in magnitude to the other favoured boundaries. This boundary, together with the $\Sigma=13a\ (22.61^\circ/1,0,0)$ favoured boundary, could define the limits of a misorientation range in which the boundaries between these limits are composed of a periodic combination of these fundamental structural elements. Possible examples of boundaries in this range are the boundaries with misorientations of $25.74^\circ/1,11,-45$ and $34.95^\circ/1,17.7,6$.

The remaining C.S.L boundaries analysed, behaved like random high-angle grain boundaries and exhibited no special properties. Even the favoured boundaries had grain boundary chromium concentrations less than 13wt% and thus would be attacked if subjected to the modified Strauss test. Consequently, these boundaries behave analogous to non-favoured boundaries in this respect and do not therefore have special properties.

Two random high-angle grain boundaries were discovered with
no detectable chromium concentration profile, possibly emphasising that higher $\Sigma$ boundaries need to be considered.

There was no correlation between FWHM and the minimum chromium concentration, which was always measured on the grain boundary itself.

Additionally, it is not pre-requisite for the boundary plane to be close to \{111\} for a chromium rich carbide to nucleate. Secondly, there is no correlation between the boundary normal and either the FWHM of the chromium concentration profile or the grain boundary chromium concentration.

On a theoretical basis, the solution to Fick's second law for diffusion adequately defines the generated chromium concentration profile that develops in sensitised A.I.S.I 316 stainless steel. The results obtained in this work support the structural unit representation of grain boundary structure. The various widths of the generated chromium concentration profiles have been explained in terms of different arrangements of compact polyhedra yielding different boundary properties. It is likely therefore, that with further atomistic calculations on longer period boundaries, coupled with the continued acquisition of experimental profiles, that an accurate model will emerge to unequivocally describe the structure of high-angle grain boundaries.

Finally, this work has also shown that only high-angle grain boundaries, with a misorientation angle exceeding $20^\circ$, become sensitised. Consequently, producing a textured microstructure to create low-angle boundaries would essentially eliminate the problem. The economics and practicability of microstructural
alignment on large structural assemblies will have to be assessed and compared to the savings that could be made in the future, if the down-time of power generation plants is reduced, due to the elimination of sensitisation.
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Appendix I

Calculation of the Grain Boundary Chromium Concentration.

In order to determine theoretical diffusion profiles for comparison with experimental profiles, the grain boundary chromium concentration in equilibrium with the carbide has to calculated. To facilitate this, it is assumed that the carbide is Cr$_{23}$C$_6$. Hence, the equilibrium reaction can be written as

$$6C + 23Cr \leftrightarrow Cr_{23}C_6$$

resulting in an equilibrium constant

$$K_{eq} = \frac{1}{(\gamma_{Cr}[Cr])^{23}a_c^6}$$

where $\gamma_{Cr} = \text{chromium activity coefficient}$

$[Cr] = \text{chromium concentration in equilibrium with the carbide}$

$a_c = \text{activity of carbon in equilibrium with the carbide}$.

Thus

$$[Cr] = \left(\frac{1}{K_{eq} \gamma_{Cr}^{23}a_c^6}\right)^{1/23}$$

So to determine $[Cr]$, $K_{eq}$, $\gamma_{Cr}$ and $a_c$ are required.
\[ K_{eq} \] can be calculated from the work of Richardson, (1953). He wrote the equilibrium reaction as

\[
\frac{23}{6} \text{Cr} + \frac{1}{6} \text{C} = \frac{1}{6} \text{Cr}_6 \text{C}_{23}.
\]

For this reaction

\[
\Delta G_{298-1673K} = -16380 - 1.54T
\]

At 680°C,

\[
\Delta G = -17847.6 \text{ cal} = -74674.4 \text{ J}.
\]

This is the free energy change required to produce \(1/6\) mole of \(\text{Cr}_6 \text{C}_{23}\). So for one mole

\[
\Delta G = -448046.6 \text{ J/mol}
\]

To determine the equilibrium constant

\[
\Delta G = -RT \log K
\]

Thus

\[
K = \exp \left( \frac{-448046.6}{8.31 \times 953} \right) = 3.2 \times 10^{24}.
\]

The activity coefficient of chromium, \(\gamma_{\text{Cr}}\), can be found from Fullman, (1982). This value is valid for an Fe-10at%Ni, Xat%Cr alloy, where X varies from 10-20at%. Hence,

\[
\gamma_{\text{Cr}} = 3.9.
\]

The activity coefficient of carbon, \(a_c\), can be found from the formulation of Natesan and Kassner, (1973) using a Wagner series which takes into account the effects of chromium and nickel. It is assumed that the carbon activity is constant from the
carbide-matrix interface into the grain interior and that the carbon is not significantly depleted below its bulk value. Thus,

\[
\ln a_{c}^{(Fe, Cr, Ni, C)} = \ln (0.048\%C) + \left(0.525 - \frac{300}{T}\right)\%C \\
- 1.845 + \frac{5100}{T} - \left(0.021 - \frac{72.4}{T}\right)\%Ni \\
+ \left(0.248 - \frac{404}{T}\right)\%Cr \\
- \left(0.0102 - \frac{9.422}{T}\right)\%Cr^2.
\]

At 680°C and for AISI 316 stainless steel,

\[
a_c = 6.56 \times 10^{-3}.
\]

Having calculated \( K_{eq} \), \( \gamma_{Cr} \) and \( a_c \), \([Cr]\) can now be determined. Thus,

\[
[Cr] = \left(\frac{1}{3.72 \times 10^{24} \cdot 3.9^{23} \cdot (6.56 \times 10^{-3})}\right)^{1/23}
\]

\[
= 8.1\text{wt}\%.
\]