Intergranular Boron Segregation and Grain Boundary Character in Alloy 304 Austenitic Stainless Steel

by

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A thesis submitted in conformity with the requirements for the Degree of Master of Applied Science in the University of Toronto.

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Abstract

Secondary ion mass spectrometry (SIMS) and orientation imaging microscopy (OIM) were used to study the relationship between boron segregation susceptibility at grain boundaries and grain boundary structure in Alloy 304 austenitic stainless steel containing boron as a trace solute impurity.

Boron segregation was detected at grain boundaries in materials heat treated at 1000 and 1100°C and both boron segregation and carbide precipitation were detected at grain boundaries in materials heat treated at 800°C. Coherent Σ3 twin boundaries displayed high resistance to both boron segregation and carbide precipitation. Σ1 boundaries displayed some resistance to boron segregation and high resistance to carbide precipitation. Σ9 boundaries satisfying the Palumbo-Aust criterion displayed some resistance to both boron segregation and carbide precipitation. Other low-Σ boundaries and general boundaries (Σ>29) displayed low resistance to both boron segregation and carbide precipitation.
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1. Introduction

The core region of a grain boundary possesses a number of very general geometric properties since it is the transition zone between two grains, each with a highly periodic crystal structure. The coincidence site lattice (CSL) is a three-dimensional lattice that can be constructed with lattice points common to two adjoining grains at certain crystallographic misorientations (Kronberg and Wilson, 1949). The CSL is of importance to the crystallography of grain boundaries because it determines the relative periodicity of the atomic structure of a grain boundary based upon the relative misorientation of the adjoining grains. The degree of periodicity at a grain boundary is represented by the parameter $\Sigma$ (Grimmer et al., 1974), which is the inverse fraction of coincident sites (Kronberg and Wilson, 1949). All grain boundaries can be described by an appropriate CSL description if $\Sigma$ is allowed to approach infinite values (Warrington, 1979).

Numerous studies using high-purity materials have clearly shown that many grain boundary properties, including solute segregation susceptibility, are dependent upon grain boundary structure as characterized by the CSL model (see reviews by Shvindlerman and Straumal, 1985 and Palumbo and Aust, 1992). Grain boundaries characterized as low-$\Sigma$ (high-periodicity) boundaries (generally $\Sigma \leq 29$) were found to display improved physical and chemical properties as compared to general or high-$\Sigma$ (low-periodicity) boundaries (generally $\Sigma > 29$), such as increased resistance to solute segregation. For example, as shown by Gleiter (1970) in a study using zone-refined lead containing controlled amounts of solute, less solute segregation was detected at certain low-$\Sigma$ boundaries due to their higher degree of structural order and lower capacity to adsorb or accommodate solute atoms.

Based on the fact that many low-$\Sigma$ boundaries are characterized by “special” properties, Watanabe (1984) introduced the concept of “grain boundary design and control”. It was proposed that the interface-dependent bulk properties of conventional polycrystalline
materials could be improved beyond previous limitations by increasing the frequency of “special” boundaries in the grain boundary character distribution (GBCD). Today, this concept has evolved into a new field of material processing, commonly referred to as “grain boundary engineering”. As shown by Lin et al. (1995) in an example of grain boundary engineering, the frequencies of certain low-$\Sigma$ boundaries in conventional face-centered cubic (FCC) materials with a low stacking fault energy (SFE) can be significantly increased by appropriate thermomechanical treatments (Palumbo, 1996). As a result, many material properties, such as resistance to intergranular solute segregation, precipitation and corrosion, can be significantly improved. As proposed by Palumbo et al. (1992), based on energetic and crystallographic constraints associated with twinning, a GBCD consisting entirely of low-$\Sigma$ boundaries (i.e., $\Sigma 3^\alpha$ with $n = 1, 2$ and possibly $\Sigma 1$) is attainable. Such a “twin-limited” microstructure is of great practical importance, particularly with regard to the engineering of conventional polycrystalline materials for improved resistance to intergranular degradation, such as sensitization, embrittlement and corrosion, which are all associated to a certain degree with intergranular solute segregation.

Alloy 304 austenitic stainless steel is one of the most familiar and most frequently used alloys in the stainless steel family. Alloy 304 is commonly used in applications where properties, such as corrosion resistance, are important. It has long been known that the physical and chemical properties of conventional polycrystalline materials, especially austenitic stainless steels, are heavily dependent upon the local chemical composition at the grain boundaries. Two well-known examples are the sensitization of austenitic stainless steels to intergranular corrosion due to chromium depletion resulting from intergranular chromium carbide precipitation (Aborn and Bain, 1931) and intergranular corrosion of solution-treated (carbide-free) austenitic stainless steels due to intergranular solute impurity segregation (e.g., Aust, Armijo and Westbrook, 1966).
Boron is an alloying element that is commonly added to certain low-carbon steels to improve hardenability. In austenitic stainless steels, however, boron is usually present only as a trace solute impurity. It is well documented that boron has a strong tendency to segregate at grain boundaries in austenitic stainless steels, such as Alloy 304. Intergranular boron segregation in austenitic stainless steels is not a major problem, however, its study is of importance to better understand the general segregation behaviour of solute impurities in these types of materials and develop new materials that are more resistant to solute impurity segregation. The scope of this research was to study the relationship between boron segregation susceptibility at grain boundaries and grain boundary structure in commercial-purity Alloy 304 austenitic stainless steel, a FCC material with a low SFE.

The objectives of this study were to:

1. Investigate the applicability of the CSL model of grain boundary structure to boron segregation susceptibility at grain boundaries in commercial-purity Alloy 304 austenitic stainless steel.

2. Investigate the applicability of grain boundary engineering as a viable means of improving the resistance of commercial-purity Alloy 304 austenitic stainless steel to intergranular boron segregation.

Background information on grain boundary structure, grain boundary engineering, solute segregation mechanisms and second phase precipitation in steels is presented in Chapter 2. A description of the experimental equipment and procedures used in this study is presented in Chapter 3. The results from this study are presented and discussed in Chapters 4 and 5. The conclusions from this study are presented in Chapter 6. The recommendations for future work are presented in Chapter 7.
2. Literature Review

2.1. Geometric Model of Grain Boundary Structure

A grain boundary can be described by five independent crystallographic parameters (Lange, 1967). Three parameters describe the misorientation between the adjoining grains and the remaining two describe the grain boundary plane normal with respect to one of the adjoining grains. In this section the coincidence site lattice (CSL) model of grain boundary structure, a model strictly based upon the relative misorientation of the adjoining grains, is discussed.

2.1.1. Coincidence Site Lattice (CSL)

Kronberg and Wilson (1949) first introduced the concept of the CSL in describing grain boundary structures in metals. The CSL is a three-dimensional lattice that can be constructed with lattice points common to two adjoining grains at certain crystallographic misorientations. The CSL is considered the smallest common sublattice of both grains (Grimmer et al., 1974). The degree of coincidence or periodicity between adjoining grains is represented by the parameter $\Sigma$, which is the volume ratio of the CSL unit cell to that of the crystal lattice unit cell (Grimmer et al., 1974) or the inverse fraction of coincident sites (Kronberg and Wilson, 1949). All grain boundaries can be described by an appropriate CSL description if $\Sigma$ is allowed to approach infinite values (Warrington, 1979); however, $\Sigma$ may achieve very high values of questionable physical significance. Figure 2.1 shows a schematic representation of a $\Sigma 5$ CSL interface.

Numerous studies using high-purity materials have clearly shown that many grain boundary properties (e.g., energy, corrosion susceptibility and solute segregation susceptibility) are dependent upon grain boundary structure as characterized by the CSL model (see reviews by Shvindlerman and Straumal, 1985 and Palumbo and Aust, 1992).
Grain boundaries characterized as low-$\Sigma$ (high-periodicity) boundaries (generally $\Sigma \leq 29$) were found to display improved physical and chemical properties relative to general or high-$\Sigma$ (low-periodicity) boundaries (generally $\Sigma > 29$) due to their higher degree of structural order. These properties include lower energy, increased resistance to localized corrosion and increased resistance to solute segregation. Based on experimental studies concerning intergranular corrosion and fracture in polycrystalline materials, Watanabe (1985) proposed that "special" properties would not be expected of grain boundaries characterized by $\Sigma > 29$. Based on this proposal, only grain boundaries characterized by $\Sigma \leq 29$ are referred to as "special" or low-$\Sigma$ boundaries.

![Schematic representation of the CSL description of a $\Sigma 5$ interface formed by a $\theta = 36.87^\circ$ [100] misorientation of two adjoining lattices (Aust, 1994).](image)

**Fig. 2.1.** Schematic representation of the CSL description of a $\Sigma 5$ interface formed by a $\theta = 36.87^\circ$ [100] misorientation of two adjoining lattices (Aust, 1994).

2.1.2. Displacement Shift Complete (DSC) Lattice

As proposed by Chalmers and Gleiter (1971), the ability of a grain boundary to accommodate small deviations from an exact low-$\Sigma$ orientation and still maintain the presence of a periodic structure is more important than the exact locations of the coinciding atoms at the grain boundary. As shown in several transmission electron microscopy (TEM) studies of grain boundaries characterized as being close to exact low-$\Sigma$ orientations...
(e.g., Bäro, Gleiter and Hornbogen, 1968 and Schober and Balluffi, 1970), the existence of collective atomic relaxations at grain boundaries can lead to the formation of arrays of grain boundary dislocations (GBDs). In much the same way as lattice dislocations at low-angle boundaries act to preserve lattice structure, GBDs act to preserve the periodic structures of high-angle boundaries that deviate slightly from exact low-$\Sigma$ orientations (Bollmann, 1970). Such grain boundary structures can be visualized as GBDs superimposed on ideally oriented low-$\Sigma$ boundaries (Aust, 1981).

GBDs are distinct from lattice dislocations in terms of their Burgers vectors. The Burgers vectors of the GBDs represent the translation vectors of a second lattice called the displacement shift complete (DSC) lattice (Grimmer et al., 1974). The DSC lattice can be considered as the inverse lattice of the CSL (Grimmer, 1974) with a unit cell volume proportional to $\Sigma^{-1}$ (Grimmer, Bollmann and Warrington, 1974). Figure 2.2 shows a schematic representation of the CSL-DSC description of a $\Sigma 5$ interface that deviates slightly from exact $\Sigma 5$ orientation.

![Schematic representation of the CSL-DSC description of a $\Sigma 5$ interface](image)

Fig. 2.2. Schematic representation of the CSL-DSC description of a $\Sigma 5$ interface that deviates from exact $\Sigma 5$ orientation by $5^\circ$ (Aust, 1994).
2.1.3. **Geometric Criterion for Allowable Angular Deviation**

The presence of GBD structures at a grain boundary indicates that regions of "good fit" exist at the grain boundary interface and that such a grain boundary may display special properties. For a grain boundary that deviates slightly from exact low-$\Sigma$ orientation there is an angular deviation limit ($\Delta \theta_m$) above which it can be considered that the cores of the GBDs begin to overlap, thus resulting in elimination of the periodic structure of the grain boundary and any special properties it may possess. A geometric criterion for allowable angular deviation from exact low-$\Sigma$ orientation is dependent upon the characteristics of both the CSL and DSC lattices. The applicability of a geometric criterion to grain boundary properties is heavily dependent upon $\Sigma$ and $\Delta \theta$ in defining GBD structures through the relaxation associated with the CSL/DSC model.

Several geometric criteria have been proposed to define $\Delta \theta_m$ for low-$\Sigma$ boundaries (e.g., Brandon, 1966; Ishida and McLean, 1972; Deschamps et al., 1987; and Palumbo and Aust, 1990). Most geometric criteria are derived from the Read-Shockley relation (Read and Shockley, 1950), $\theta=b/d$, where $\theta$ is the misorientation angle between the adjoining grains, $b$ is the magnitude of the Burgers vector of the GBDs and $d$ is the dislocation spacing. For low-angle boundaries ($\Sigma 1$), the most commonly used angular deviation limit is 15.0° (Read and Shockley, 1950). For high-angle boundaries ($\theta>15^\circ$ and $\Sigma>1$) the most commonly used criterion is Brandon's criterion, $\Delta \theta_m$≤$15^\circ \Sigma^{-1/2}$ (Brandon, 1966). However, as shown by Palumbo and Aust (1990), a more restrictive criterion, $\Delta \theta_m$≤$15^\circ \Sigma^{-5/6}$, was found to be more consistent with theoretical and experimental observations.

As shown by Palumbo and Aust (1990) in a study of intergranular corrosion in high-purity nickel containing various sulfur concentrations, localized corrosion susceptibility at grain boundaries was found to increase with increasing sulfur content and was strongly dependent upon grain boundary structure. As shown in Figure 2.3, a limited structural field of immunity defined by $\Sigma$≤25 and $\Delta \theta_m$≤$15^\circ \Sigma^{-5/6}$ was determined. The initiation of localized
corrosion at grain boundaries was characterized by isolated pitting at the grain boundaries. Susceptibility to intergranular corrosion was attributed to a dislocation mechanism whereby corrosion resistance was dependent upon the specific distribution (i.e., density) of the GBDs and the local chemistry (i.e., local solute concentration) at the GBDs. In the absence of segregated solute, GBDs were found to act as preferential sites for localized corrosion. With increasing solute concentration, because GBDs can act as sinks for solute atoms at grain boundaries (Gleiter, 1970), the potential required to initiate corrosion at GBDs was reduced.

Fig. 2.3. Maximum angular deviation angles ($\Delta \theta$) from any low-$\Sigma$ boundary in 99.999 wt.% Ni displaying selective immunity to intergranular corrosion in 2N H$_2$SO$_4$ (Palumbo and Aust, 1990).

2.2. Grain Boundary Engineering

Grain boundary engineering expresses an approach in which conventional polycrystalline materials can be designed with improved interface-dependent bulk properties, such as improved resistance to intergranular corrosion, by the deliberate manipulation of the grain boundary network using fundamental knowledge of the structures and properties of grain boundaries. Grain boundary engineering is based on the fact that many low-$\Sigma$
boundaries are characterized by special or beneficial properties, such as increased resistance to solute segregation and localized corrosion (see reviews by Shvindlerman and Straumal, 1985 and Palumbo and Aust, 1992). Low-\(\Sigma\) boundaries occur naturally in all polycrystalline materials but at a frequency that is strongly dependent upon the processing history of the material. The objective of grain boundary engineering is to deliberately increase the frequency of low-\(\Sigma\) boundaries in conventional polycrystalline materials in order to improve bulk material properties beyond previous limitations.

The grain boundary character distribution (GBCD) of a random crystal orientation, as defined by Warrington and Boon (1975), is the set of grain boundaries generated from a random polycrystalline aggregate in which every grain orientation has an equal probability of occurrence. Based on the calculations of Warrington and Boon (1975), the total frequency of low-\(\Sigma\) boundaries defined by \(\Sigma\leq 29\) satisfying Brandon’s criterion (i.e., \(\Delta\theta_m \leq 15^\circ \Sigma^{-1/2}\)) (Brandon, 1966) expected in a random distribution is 13.62%. This value is, however, considerably lower than the low-\(\Sigma\) boundary frequency typically found in many metallic systems, including austenitic stainless steels.

By the assistance of new technologies, such as electron backscattered diffraction (EBSD) and orientation imaging microscopy (OIM), various material and processing parameters (e.g., twinning, grain size and prestrain and annealing) have been found to influence the frequency of low-\(\Sigma\) boundaries in polycrystalline materials (e.g., Watanabe, 1985 and 1986; Aust and Palumbo, 1989 and 1991; and Palumbo and Aust, 1990). As a result, new thermomechanical treatments have been developed that can significantly improve the bulk properties of common engineering materials (Palumbo, 1996). For example, as shown by Lin et al. (1995), after appropriate thermomechanical processing, an increase in the frequency of low-\(\Sigma\) boundaries in commercial-purity Alloy 600 resulted in a significant increase in the resistance of the material to sensitization (i.e., intergranular chromium carbide precipitation) and intergranular corrosion. By increasing the frequency of low-\(\Sigma\) boundaries
satisfying Brandon's criterion from 37% in the conventionally processed material to 71% in
the grain boundary engineered material intergranular corrosion resistance for both sensitized
and solution-treated (carbide-free) Alloy 600 was significantly increased.

As shown in several early studies, the introduction of low-Σ boundaries in FCC
materials is closely related to the formation of coherent Σ3 twin boundaries (e.g., Aust and
Rutter, 1960; Aust, 1961; and Ferran et al., 1963 and 1967). As shown by Aust and Rutter
(1960) in studies of grain growth in high-purity FCC metals, the formation of coherent Σ3
twin boundaries tends to result in the repeated replacement of general (high-Σ) boundaries
with more structurally ordered grain boundaries having lower Σ values. As shown in
Figure 2.4, the frequency of low-Σ boundaries in polycrystalline materials is influenced by
energetic, kinetic and geometric factors and the relative contribution of each factor is strongly
dependent upon the solute concentration in the material (Palumbo and Aust, 1990). According
to Palumbo and Aust (1990), the maximum contributions from energetic and
kinetic factors occur only within a certain solute concentration range and only the geometric
influence is independent of solute concentration.

Energetic influences are expected to be significant only at very low solute
concentrations. Selective solute segregation tends to cause a more rapid decrease in the
energy of general boundaries than low-Σ boundaries, as illustrated in Figure 2.5, which
minimizes the energetic preference for low-Σ boundaries (Sautter, Gleiter and Bäro, 1977).
In low-purity FCC materials with low SFEs, such as Alloy 304 austenitic stainless steel
(i.e., $\gamma_{\text{SFE}}$<21 ergs/cm$^2$ at 25°C) (Murr, 1975), only coherent Σ3 twin boundaries are strongly
preferred due to their extremely high degree of structural order and extremely low interfacial
energy as compared to general boundaries (i.e., $\gamma_{\text{gen}}$≈20 ergs/cm$^2$ at 1060°C compared to
$\gamma_{\text{gen}}$≈800 ergs/cm$^2$ at 1060°C) (Murr, 1975). The driving force for the formation of coherent
Σ3 twin boundaries during grain growth is a reduction in the total interfacial free energy
(Fullman and Fisher, 1951).
Fig. 2.4. The solute dependence of the primary influences governing the frequency of low-$\Sigma$ boundaries in polycrystalline materials (Palumbo and Aust, 1990).

Fig. 2.5. Grain boundary energy ($\gamma$) versus misorientation angle ($\theta$) for grain boundaries with and without solute segregation (Sautter, Gleiter and Bäro, 1977).

The maximum contributions from kinetic influences on the frequency of low-$\Sigma$ boundaries occur only at intermediate solute concentrations where low-$\Sigma$ boundaries have higher mobilities than general boundaries (Aust and Rutter, 1959 and Rutter and Aust, 1965). With further increases in solute concentration, the differences in the mobilities of low-$\Sigma$ boundaries and general boundaries are minimized and thus kinetic influences decrease.

As observed in many studies of low-purity materials, such as commercial-purity Alloy 304 austenitic stainless steel, there is a strong preference for $\Sigma 9$ and $\Sigma 27$ boundaries.
that can not be explained in terms of energetic or kinetic factors (e.g., Hasson and Goux, 1971). As proposed by Palumbo and Aust (1990), the frequencies of these particular low-$\Sigma$ boundaries are attributed primarily to geometric interactions between strongly preferred $\Sigma 3$-related boundaries (i.e., $\Sigma 3^n$ where n=1, 2 and 3). According to Palumbo and Aust (1990), only geometric contributions can be considered to be almost independent of solute concentration.

Several studies have shown that by suitable solid state processing the frequencies of certain low-$\Sigma$ boundaries in commercial-purity FCC materials with low SFEs (e.g., austenitic stainless steels and nickel-based alloys) can be increased to levels in the 70-90% range (e.g., Lin et al., 1995 and Palumbo, 1996). Such levels are significantly higher than those commonly found in conventionally processed materials. The high frequencies of low-$\Sigma$ boundaries in these low-purity materials are generated primarily through twinning events and geometric interactions between strongly preferred $\Sigma 3$-related boundaries. The frequencies of coherent $\Sigma 3$ twin boundaries and $\Sigma 3$-related boundaries are heavily dependent upon material and processing parameters, such as strain, annealing temperature and grain size (Palumbo, 1996).

The primary objective of grain boundary engineering, as it pertains to FCC materials, is to increase the frequency of coherent $\Sigma 3$ twin boundaries to their highest possible levels in order to take advantage of both their intrinsic properties and their ability to generate other low-$\Sigma$ boundaries. As proposed by Palumbo and Aust (1990), as a consequence of energetic and crystallographic constraints associated with twinning, a GBCD consisting entirely of low-$\Sigma$ boundaries (i.e., $\Sigma 3^n$ with n=1, 2 and possibly $\Sigma 1$) is attainable. Such a "twin-limited" CSL microstructure is expected to occur when the frequency of coherent $\Sigma 3$ twin boundaries approaches 2/3. Distributions having these characteristics have commonly been observed as clusters within conventional polycrystalline materials (e.g., Palumbo and Aust, 1990).
Geometric models have been proposed to evaluate the effects of low-$\Sigma$ boundary frequency on bulk intergranular cracking and corrosion susceptibility (Palumbo et al., 1991 and 1992 and Lehockey et al., 1996 and 1997). Results from these models show that only moderate increases in the frequency of low-$\Sigma$ boundaries may considerably reduce the degree of intergranular degradation in common engineering materials.

2.3. Intergranular Solute Segregation

Boron is a trace solute impurity commonly found in austenitic stainless steels, such as Alloy 304 austenitic stainless steel. It is well documented that boron has a strong tendency to segregate at grain boundaries in austenitic stainless steels. For example, Karlsson et al. (1988) using secondary ion mass spectrometry (SIMS) showed that boron segregation at grain boundaries was detectable in Alloy 316L austenitic stainless steel containing $<$1 ppm boron. Numerous studies on intergranular solute segregation in different materials have shown that solute enrichment at grain boundaries can be due to either equilibrium or non-equilibrium segregation.

2.3.1. Equilibrium Segregation

Equilibrium segregation is a reversible process whereby certain solute atoms (i.e., those with a significant binding energy to the crystal lattice) are adsorbed at loosely packed sites, such as grain boundaries, when a material is held at a sufficiently high temperature to permit appreciable diffusion of solute atoms (McLean, 1957). For solute atoms with a certain binding energy to the crystal lattice (i.e., lattice strain), at any temperature, there will be an increased concentration of that solute at grain boundaries. The amount of segregated solute at grain boundaries increases with increasing bulk solute concentration and decreasing temperature (McLean, 1957). The driving force for this segregation process is a reduction in the binding energy of the solute to the crystal lattice.
(i.e., reduction in lattice strain), which results when the solute atoms locate to a strain-free environment at sites of excess volume, such as grain boundaries. As a consequence of solute atoms segregating at grain boundaries, grain boundary free energy is reduced.

As shown in several field-ion microscopy (FIM) studies of solute segregation at grain boundaries, equilibrium segregation is generally localized to a few atomic layers at the grain boundary interface and the total amount of segregated solute is usually in the order of a monolayer (e.g., Howell et al., 1973 and 1976 and Smith et al., 1973). As shown in numerous studies, the amount of segregated solute at a grain boundary at any temperature or solute concentration is dependent upon the capacity of the grain boundary to adsorb or accommodate solute atoms. The adsorption capacity of a grain boundary is dependent upon the degree of grain boundary coherence or the amount of free volume associated with the grain boundary.

2.3.1.1. Structural Effects

Aust and Rutter (1959) and Rutter and Aust (1965) investigated the variability in grain boundary mobility in bicrystals of zone refined lead containing controlled amounts of solute (i.e., tin). Grain boundaries characterized as being close to exact low-\(\Sigma\) orientations (i.e., \(\Sigma 5\), \(\Sigma 7\), \(\Sigma 13\) and \(\Sigma 17\)) were found to have higher mobilities and lower activation energies than general (high-\(\Sigma\)) boundaries in the presence of solute atoms. Rutter and Aust (1965) proposed that the differences in mobility and activation energy between low-\(\Sigma\) boundaries and general boundaries were due to differences in the amount of interaction between solute atoms and the different grain boundary structures. In particular, they attributed the lower mobilities and higher activation energies of general boundaries to the strong interaction between solute atoms and the elastic strain fields associated with the high GBD densities at these grain boundaries on deviation from exact low-\(\Sigma\) orientations. The slower diffusion of solute atoms in the elastically strained regions led to a significant amount of drag on the moving grain boundaries (Lucke and Detert, 1957 and Cahn, 1962). The
higher mobilities and lower activation energies of ideally oriented low-$\Sigma$ boundaries were attributed to the lack of significantly large strain fields outside the core regions of these grain boundaries due to their higher degree of structural order, better atomic fit and lower GBD density. Solute atoms segregated primarily at the core regions of ideally oriented low-$\Sigma$ boundaries and, as a result, solute atoms were able to migrate with the moving grain boundaries without slowing them down significantly. As shown by Demianczuk and Aust (1975) in a further study of $\Sigma5$ boundaries in zone refined aluminum, grain boundary velocity was found to decrease and activation energy increase with increasing deviation (up to $5^\circ$) from exact $\Sigma5$ orientation (i.e., the amount of solute-grain boundary interaction was found to increase with increasing GBD density).

In the absence of solute or the presence of too much solute, however, no difference in mobility between low-$\Sigma$ boundaries and general boundaries was observed (Rutter and Aust, 1965). In the former case grain boundary velocity was limited by the rate at which solvent atoms moved across the grain boundaries. In the latter case grain boundary velocity was not controlled by the grain boundary structure but by the speed of the solute atoms diffusing in the vicinity of the grain boundaries.

Gleiter (1970) studied the effects of solute (i.e., copper) concentration on the energies of low-$\Sigma$ boundaries and general boundaries in zone refined lead. It was observed that with increasing solute concentration selective solute segregation reduced the energies of general boundaries more rapidly than the energies of low-$\Sigma$ boundaries. Gleiter (1970) attributed this effect to less solute segregation taking place at low-$\Sigma$ boundaries. This effect was illustrated schematically in Figure 2.5, where it was also shown that grain boundary segregation tended to reduce the number of low-energy (i.e., low-$\Sigma$) boundaries (i.e., cusps). The higher degree of solute segregation at general boundaries was attributed to the lack of structural order at these grain boundaries and the interaction of solute atoms with the elastic strain fields associated with the high GBD density at these grain boundaries on deviation from
exact low-$\Sigma$ orientations. Selective solute segregation at grain boundaries was expected to exist only for a limited solute concentration range (Sautter, Gleiter and Bäro, 1977). At high solute concentrations (i.e., when grain boundaries are solute saturated) segregation differences between low-$\Sigma$ boundaries would be minimal.

Roy, Erb and Gleiter (1982) investigated grain boundary embrittlement in copper induced by solute (i.e., bismuth) segregation using the sintered sphere-on-plate technique (Sautter, Gleiter and Bäro, 1977). Results showed that grain boundaries that were most resistant to embrittlement (i.e., sphere detachment during ultrasonic treatment) were those of lowest energy (i.e., presumably, including some low-$\Sigma$ boundaries). It was also found that grain boundaries became more embrittled with increasing deviation from low-energy (i.e., low-$\Sigma$) orientations. After annealing at low temperatures, a significant number of grain boundaries were found to be resistant to embrittlement, which was unexpected due to the higher degree of equilibrium segregation at the low temperatures. This effect was attributed to the presence of a significant number of low-energy (i.e., low-$\Sigma$) grain boundaries that possessed higher resistance to solute segregation at the low temperatures (Erb and Gleiter, 1979).

Briant (1983) studied the variability in the amount of solute enrichment at high-angle boundaries in phosphorus- and antimony-doped nickel-chromium steels using Auger electron spectroscopy (AES) on exposed (i.e., fractured) grain boundary surfaces. Results showed that in the alloys studied the variability that was observed was primarily within $\pm 30\%$ of an average value. Variations in solute segregation along a single grain boundary were not as great as the variation among grain boundaries. However, for a few grain boundaries much larger deviations were observed both above and below the average. After analyzing a number of sources of this variability, Briant (1983) concluded that one major source was grain boundary structure.
Guo et al. (1999) investigated the relationship between intergranular boron segregation, intergranular melting and grain boundary structure in simulated weld heat affected zones in high-purity Inconel 718 using SIMS and OIM. Intergranular melting in Inconel 718 was previously attributed to boron segregation at grain boundaries (e.g., Kelly, 1989 and Huang et al., 1996). As shown by Zhu et al. (1994), boron segregation at grain boundaries in Inconel 718 tends to lower the melting temperature of the grain boundary material. Guo et al. (1999) conducted studies on solution-treated Inconel 718 (i.e., heat treated at 1050°C and water quenched at 500°C/s) that was thermally cycled (i.e., heated to 1190-1220°C at 150°C/s, held there for 1-5 s and then air-jet cooled at 250°C/s). Boron enrichment at grain boundaries was attributed primarily to equilibrium segregation that resulted during isothermal annealing at the solution heat treatment temperature (i.e., 1050°C) prior to thermal cycling at higher temperatures (i.e., grain boundary melting temperatures).

In the work by Guo et al. (1999), a close relationship was observed between intergranular melting, intergranular boron segregation and grain boundary structure. Low-$\Sigma$ boundaries were defined by $\Sigma \leq 39$ using Brandon's criterion (i.e., $\Delta \theta_m \leq 15^\circ \Sigma^{-1/2}$) (Brandon, 1966). Only 4 out of 48 low-$\Sigma$ boundaries were found melted after thermal cycling. None of the $\Sigma 1$ (low-angle) boundaries (i.e., $5^\circ \leq \theta \leq 15^\circ$) or coherent $\Sigma 3$ twin boundaries were found melted. Other non-melted low-$\Sigma$ boundaries included one $\Sigma 15$ and one $\Sigma 23$ boundary. One of the low-$\Sigma$ boundaries found melted was a $\Sigma 31$ boundary. All 207 general boundaries ($\Sigma > 39$) were found melted.

Guo et al. (1999) attributed the high resistance of low-$\Sigma$ boundaries to melting (i.e., boron segregation) to low-$\Sigma$ boundaries having a high degree of structural order and thus a low capacity to adsorb or accommodate boron atoms. Boron enrichment was detected at melted grain boundaries and several non-melted low-$\Sigma$ boundaries. Guo et al. (1999) explained that certain low-$\Sigma$ boundaries did not melt because the amount of boron enrichment at these grain boundaries was not high enough to lower the melting temperature of the grain.
boundary material (i.e., low-Σ boundaries exhibited high resistance to boron segregation). Boron enrichment was not detected at coherent Σ3 twin boundaries. For this particular study, the use of Σ≤29 and a more restrictive criterion for low-Σ boundary characterization, such as the Palumbo-Aust criterion (i.e., Δθ_m≤15°Σ−5/6) (Palumbo and Aust, 1990), might have shown better correlation between grain boundary structure and boron segregation susceptibility.

2.3.2. Non-Equilibrium Segregation

As shown by Westbrook and Wood (1961 and 1963), microhardness measurements can be used to study the presence of local concentrations of solute at grain boundaries in a wide variety of materials. As observed by Westbrook and Aust (1963), the equilibrium segregation process could not, however, fully explain excess grain boundary hardening that was observed in a number of quenched dilute lead alloys in which the levels of apparent solute segregation extended over distances of several micrometers across grain boundaries. Figure 2.6 shows an example of excess grain boundary hardening measured in a bicrystal of zone-refined lead containing 1 ppm gold after water quenching and air cooling from 300°C. Aust (1968) observed the same phenomenon in solution-treated Alloy 304 austenitic stainless steel in which significant grain boundary hardening was observed with no evidence found by TEM of solute clusters of sizes exceeding 2.5 nm at grain boundaries. In order to explain these observations, Westbrook and Aust (1963) proposed that another segregation process was involved that develops from the kinetics of cooling from high temperatures. Aust and Westbrook (1965) and Aust et al. (1968) proposed a solute clustering model (i.e., non-equilibrium segregation process) for describing the grain boundary quench hardening phenomenon.

Non-equilibrium segregation can be described as the resulting effect of attempting to maintain local equilibrium between free solute atoms, free vacancies and vacancy-solute complexes in the vicinity of grain boundaries during temperature variations and thus
variations in equilibrium concentrations. During annealing at high temperatures an equilibrium concentration of vacancies is generated and distributed throughout the material and a certain amount of vacancy-solute binding takes place. During cooling from high temperatures, however, the equilibrium concentration of vacancies cannot be maintained except at vacancy sinks (e.g., grain boundaries, free surfaces and free dislocations), which are sites where excess vacancies can be adsorbed and easily annihilated. Since a supersaturated concentration of vacancies forms in the interiors of the grains during cooling a concentration gradient of vacancies develops near grain boundaries and, as a result, vacancies within diffusion distance of the grain boundaries migrate to the grain boundaries.

Fig. 2.6. Hardness-distance profiles near a grain boundary in a dilute lead alloy containing 1 ppm gold after water quenching from 300°C and after air cooling from 300°C (1 g load, 5 s loading time) (Aust and Westbrook, 1965).

At lower temperatures vacancy-solute interactions are enhanced, therefore, as vacancies migrate they tend to drag certain solute atoms (i.e., those with positive binding energies to vacancies) toward grain boundaries. The effective uphill diffusion of solute atoms produces a solute-rich region at the grain boundaries that is thermodynamically driven by the decrease in free energy associated with the annihilation of excess vacancies at the grain
In the vicinity of the grain boundaries, collisions between vacancy-solute complexes increase and such collisions result in the release of a certain number of vacancies from their complexes, which proceed toward grain boundaries, leaving behind less mobile clusters of solute atoms. Subsequent collisions between solute clusters and other vacancy-solute complexes result in the growth of solute cluster complexes. The size and frequency of solute cluster complexes increase as the grain boundary interface is approached. The resulting effect of this process is the enrichment of solute atoms at grain boundaries with concentration profiles across the grain boundaries resembling the shape to the hardness-distance profiles shown in Figure 2.6.

The degree of non-equilibrium segregation at grain boundaries (i.e., the amount of solute enrichment at the grain boundary interface and the width of the solute-enriched zone extending from the grain boundary interface into the grain interior) is dependent upon heat treatment procedure. As shown by Aust and Westbrook (1965), the amount of excess grain boundary hardening (i.e., degree of non-equilibrium segregation) is dependent upon the quenching temperature. Figure 2.7 shows an example of the influence of quenching temperature on the room temperature hardness of a grain and two grain boundaries in lead containing 0.65 ppm gold. Karlsson and Norden (1988) observed this effect in a study of intergranular boron segregation in Alloy 316L austenitic stainless steel containing 40 ppm boron using a combination of TEM, FIM, atom probe (AP) and imaging atom probe (IAP). Karlsson and Norden (1988) found that the amount of boron segregation at grain boundaries increased with increasing quenching temperature and boron enrichment was detected as far away as ~50 nm from the core regions of the grain boundaries. Unlike equilibrium segregation in which the amount of solute enrichment decreases with increasing temperature, the degree of non-equilibrium segregation increases with increasing temperature due to a higher concentration of quenched-in vacancies at the higher temperatures.
As shown in Figure 2.6, the degree of non-equilibrium segregation at grain boundaries is also dependent upon the cooling rate (Aust and Westbrook, 1965). As shown by Karlsson et al. (1988) in a study of intergranular boron segregation in Alloy 316L austenitic stainless steel using SIMS, the highest degree of boron segregation at grain boundaries occurred at an intermediate cooling rate (i.e., ~10°C/s). The degree of boron segregation was highest at this intermediate cooling rate because the cooling time was sufficient enough to allow vacancy-boron complexes to diffuse to grain boundaries but not allow the deposited boron atoms to diffuse away. At higher cooling rates (i.e., >10°C/s) less boron segregation was found at grain boundaries because vacancies and complexes ended up being frozen into solid solution during cooling since not enough time was allowed for their diffusion to grain boundaries. At lower cooling rates (i.e., <10°C/s) less boron segregation was found at the core regions of grain boundaries and the width of the boron-enriched zone was found to be significantly wider. These effects were attributed to the diffusion of boron
atoms away from grain boundaries after they were deposited (i.e., boron desegregation), which was driven by the large concentration gradient of boron atoms that developed between the grain boundaries and grain interiors during the initial stages of cooling.

As shown by Westbrook and Aust (1963), additional grain boundary hardening (i.e., solute segregation) followed by grain boundary softening (i.e., solute desegregation) can occur during isothermal annealing at low temperatures after rapid cooling from high temperatures. Karlsson et al. (1988) observed these effects in a study of intergranular boron segregation in Alloy 316L austenitic stainless steel using SIMS. Karlsson et al. (1988) found that the amount of boron enrichment at grain boundaries increased after a very short heat treatment at 500°C after water quenching from 1250°C. Chen et al. (1998) observed similar effects in a study of intergranular boron segregation in Inconel 718 using SIMS. Chen et al. (1998) found that the amount of boron enrichment at grain boundaries increased and then decreased with increasing annealing time at 1050°C after water quenching from 1200°C.

Solute segregation can occur during isothermal annealing after rapid cooling from high temperatures if the concentrations of vacancies and vacancy-solute complexes, created prior at high temperatures and partially annihilated during cooling (i.e., quenched in), are still greater than the equilibrium concentrations corresponding to the new annealing temperature (Westbrook and Aust, 1963; Ueno and Inoue, 1973; and He et al., 1989B). Solute segregation at grain boundaries that occurs during isothermal annealing after rapid cooling results from the annihilation of excess (i.e., quenched-in) vacancies and vacancy-solute complexes at grain boundaries during the low-temperature heat treatment. The diffusion of solute away from the grain boundaries (i.e., solute desegregation) occurs after solute segregation if the temperature and the concentration gradient of free solute atoms between the grain boundaries and grain interiors are sufficiently high and is completed once equilibrium concentrations are achieved. He et al. (1989A and 1989B) studied the segregation and desegregation of boron at grain boundaries in a boron-doped low-carbon steel containing 33 ppm boron annealed at 1000°C.
after water quenching from 1100°C using particle tracking autoradiography (PTA). They found that additional solute segregation occurred very quickly (i.e., completed after several seconds) but desegregation took considerably longer (i.e., completed after several minutes).

In addition to heat treatment procedure, the degree of non-equilibrium segregation at grain boundaries is also dependent upon the type of solute and its bulk concentration. According to Aust et al. (1968), in order for non-equilibrium segregation to occur, solute atoms must interact with vacancies. Solutes with positive binding energies to vacancies will become enriched at grain boundaries whereas solutes with weak or even negative binding energies to vacancies will not become enriched at grain boundaries and may even become depleted at grain boundaries. In addition to this criterion, solute clusters must also be stable or metastable (i.e., activity coefficient of the solute in the solvent must be >1). The degree of non-equilibrium segregation increases with increasing solute concentration (Aust et al., 1968); however, the maximum amount of solute enrichment that can occur is determined by the concentration of free vacancies available to form complexes, which is determined by the quenching temperature.

Non-equilibrium segregation can be differentiated from equilibrium segregation by the size and shape of the solute-enriched zone at the grain boundaries and its time and temperature dependencies. Unlike equilibrium segregation, which is dependent upon the capacity of the grain boundaries to adsorb solute atoms, non-equilibrium segregation is dependent upon the ability of the grain boundaries to adsorb and annihilate excess vacancies (i.e., effectiveness or efficiency of the grain boundary to act as a vacancy sink).

Most models proposed for describing the operation of grain boundaries as vacancy sinks (or sources) are based on the existence of GBDs that climb in the grain boundary plane by annihilating (or creating) vacancies (e.g., Balluffi, 1980). The operation of a grain boundary as a vacancy sink is generally expected to be a highly complex process involving a number of steps that involve the diffusion of vacancies to the grain boundary, diffusion of
vacancies in the grain boundary and vacancy annihilation at GBDs. The term vacancy sink efficiency, as it pertains to non-equilibrium segregation at grain boundaries, refers to the effectiveness of a grain boundary at annihilating excess vacancies during changes in temperature while maintaining an equilibrium concentration of vacancies in the close vicinity of the grain boundary. Highly efficient vacancy sinks lead to a significant amount of solute enrichment whereas less efficient or inoperative vacancy sinks lead to little if any solute enrichment. One major factor that affects the vacancy sink efficiency of a grain boundary is the distribution or density of GBDs at the grain boundary interface (e.g., Balluffi, 1980).

2.3.2.1. Structural Effects

There is experimental evidence that has shown that the efficiencies of grain boundaries as vacancy sinks or sources is dependent upon grain boundary structure (e.g., Balluffi, 1980). For example, Jaeger and Gleiter (1978) investigated the vacancy sink/source efficiencies of grain boundaries during diffusional creep in copper. For diffusional creep to occur in polycrystalline materials grain boundaries must act as both vacancy sinks and vacancy sources. Jaeger and Gleiter (1978) found a close relationship between grain boundary structure and vacancy sink/source efficiency. General boundaries ($\Sigma>29$) were found to act as very efficient vacancy sinks/sources under very low vacancy chemical potentials (i.e., vacancy concentration gradients). Grain boundaries characterized as close to exact low-$\Sigma$ orientations (i.e., $3\leq\Sigma\leq15$) were found to be inoperative as vacancy sinks/sources under low vacancy chemical potentials. The lower efficiency of low-$\Sigma$ boundaries as vacancy sinks/sources was attributed to the significantly lower densities of GBDs at these grain boundaries due to their higher degree of structural order and better atomic fit. Under high vacancy chemical potentials, however, low-$\Sigma$ boundaries were found to become operative as vacancy sinks/sources. The efficiency of coherent $\Sigma3$ twin boundaries, however, was found to remain significantly lower than that of general boundaries.
and other low-$\Sigma$ boundaries at high vacancy chemical potentials due to their extremely high degree of structural order and lack of GBDs.

Karlsson and Norden (1988) conducted fine scale studies on the segregation of boron at grain boundaries in Alloy 316L austenitic stainless steel using a combination of TEM, FIM, AP and IAP. Two general boundaries in a sample containing <1 ppm boron heat treated at 1250°C and cooled at 31°C/s (i.e., high vacancy concentration gradient conditions) were analyzed for boron segregation. The boron concentration at the core regions of the two general boundaries were both ~2.5 at.% and boron enrichment was detected as far away as ~20 nm from the grain boundary interfaces. A coherent $\Sigma 3$ twin boundary in a sample containing 23 ppm boron heat treated at 1250°C and cooled at 31°C/s was also analyzed for boron segregation. No significant amount of boron enrichment was detected at or near the coherent $\Sigma 3$ twin boundary. The boron concentration at the core region of the coherent $\Sigma 3$ twin boundary was determined to be ~0.015 at.% and no boron enrichment was detected in the region adjacent to the coherent $\Sigma 3$ twin boundary. The higher degree of boron segregation at the general boundary was attributed to the general boundary operating as a much more efficient vacancy sink than the coherent $\Sigma 3$ twin boundary during cooling from high temperatures due to its high GBD density.

Karlsson and Norden (1988) also analyzed a $\Sigma 1$ (low-angle) boundary in an Alloy 316L austenitic stainless steel sample containing 40 ppm boron heat treated at 1250°C and water quenched (i.e., >500°C/s). The concentration of boron at the core region of the $\Sigma 1$ boundary was determined to be ~2.5 at.% and boron enrichment was detected as far away as ~20 nm from the grain boundary interface. Boron enrichment was attributed primarily to non-equilibrium segregation. Boron enrichment at the $\Sigma 1$ boundary was not unexpected since the structure of a $\Sigma 1$ boundary is an array of primary dislocations.
2.4. Intergranular Precipitation in Steels

Precipitation of second phase particles at grain boundaries may result when temperature variations occur and the concentration of segregated solute at grain boundaries becomes supersaturated. The susceptibility of a material to intergranular precipitation is dependent upon both the solid solubility and bulk concentration of the solute in the material.

The solid solubility of carbon in austenitic stainless steel (wt.%) Fe-18Cr-9Ni is \(-0.15\) wt.% at 1100°C and \(-0.05\) wt.% at 900°C (Rosenberg and Irish, 1952). In austenitic stainless steels the predominant carbon-containing phase is \(M_2\text{C}_6\). The rate at which carbides nucleate and grow at grain boundaries is dependent upon the carbon content of the material (Bruemmer, 1986), as shown in Figure 2.8.

![Figure 2.8](image.png)

Fig. 2.8. Time-temperature-sensitization curves for various carbon contents (wt.% in Alloy 304 austenitic stainless steel. \(M_2\text{C}_6\) carbide precipitation occurs in the areas to the right of the various carbon content curves (Trillo et al., 1995). Based on data by Bruemmer (1986).

The solid solubility of boron in austenitic stainless steel (wt.%) Fe-18Cr-15Ni containing 0.002 wt.% carbon is \(~95\) ppm at 1100°C and \(~30\) ppm at 900°C (Goldschmidt, 1971). The solid solubility of boron in austenitic stainless steels tends to decrease with increasing carbon content, however, due to the effect of increased occupation of interstitial...
sites in the austenite lattice by an increased number of interstitial carbon atoms (Goldschmidt, 1971). In low-carbon austenitic stainless steels (i.e., ≤0.03 wt.% C) the predominant boron-containing phase is M₂B (i.e., pure borides) (e.g., Goldschmidt, 1971). In high-carbon austenitic stainless steels (i.e., >0.03 wt.% C) the predominant boron-containing phase is M₂₃(B,C)₆ (i.e., borocarbides) (e.g., Thomas and Henry, 1980).

Yao (1999) investigated intergranular precipitation in Alloy 304 austenitic stainless steel containing 33 ppm boron and 0.041 wt.% carbon using SIMS and TEM with energy-dispersive x-ray spectroscopy (EDS). Yao (1999) found that at temperatures above 900°C (Cr,Fe)₂B borides were the predominant boron-containing phase whereas at temperatures below 900°C (Cr,Fe)₂₃(C,B)₆ borocarbides were the predominant boron-containing phase (i.e., M₂₃(C,B)₆ borocarbides were thermodynamically more stable than M₂B borides at temperatures below 900°C).

Lundin and Richarz (1995) investigated the segregation of boron and phosphorus at carbide/matrix interfaces in a chromium steel (wt.% Fe-9Cr-0.17C containing 80 ppm boron and 70 ppm phosphorus using atom-probe field-ion microscopy (APFIM). Boron was not detected at carbide/matrix interfaces but was detected homogeneously distributed within the carbides. Phosphorus, on the other hand, was detected only in a monolayer at carbide-matrix interfaces.

2.4.1. Structural Effects

Liu et al. (1995) studied carbide (i.e., M₂₃C₆ and M₇C₃) precipitation at grain boundaries in a low-carbon nickel-based ternary alloy (wt.%) Ni-16.2Fe-18.6Cr containing 0.02 wt.% carbon using SEM and OIM. Results showed that there was a strong preference for coherent Σ3 twin boundaries and Σ3-related boundaries (i.e., Σ9 and Σ27) in the material. Liu et al. (1995) found that the size and spacing of grain boundary carbides were influenced by grain boundary structure. Carbides were smaller and more closely spaced at Σ1
(low-angle) boundaries (2°≤θ≤15°) and Σ3-related boundaries. No carbides were detected at coherent Σ3 twin boundaries but carbides were detected at incoherent Σ3 twin boundaries. Carbides were detected at other low-Σ boundaries and general (high-Σ) boundaries.

Trillo and Murr (1998 and 1999) investigated the effects of carbon content (0.011-0.07 wt.%) and grain boundary structure on carbide precipitation susceptibility at grain boundaries in Alloy 304 austenitic stainless steel heat treated at 670°C for 0.1 to 1000 hrs and water quenched using TEM and OIM. No carbides were detected at coherent Σ3 twin boundaries for all carbon contents but were detected at incoherent Σ3 twin boundaries for carbon contents >0.011 wt.%. Carbides were detected at other low-Σ boundaries and general boundaries for carbon contents >0.011 wt.% and the sizes and densities of the carbides were found to increase with increasing carbon content, annealing time and misorientation angle.

Trillo and Murr (1998) proposed that a critical interfacial free energy was required for carbide precipitation to occur in austenitic stainless steels, which was between the average interfacial free energy values of coherent Σ3 twin boundaries and incoherent Σ3 twin boundaries. As shown by Trillo et al. (1995), the rate at which carbides precipitate at grain boundaries in Alloy 304 austenitic stainless steel at any temperature is dependent upon grain boundary energy (i.e., grain boundary structure). As shown in Figure 2.9, grain boundaries with the highest interfacial energies (i.e., general boundaries) tend to precipitate carbides first, followed by incoherent Σ3 twin boundaries and then coherent Σ3 twin boundaries. The relative rates at which carbides precipitate at grain boundaries in austenitic stainless steels will vary, however, depending on the carbon content of the material (Trillo and Murr, 1998).

Zhou et al. (2000) investigated the effects of grain boundary structure on carbide precipitation in Alloy 304L austenitic stainless steel containing <0.03 wt.% carbon using SEM and OIM. Results showed that there was a strong preference for coherent Σ3 twin boundaries and Σ9 boundaries in the material. Low-Σ boundaries were characterized using Brandon's criterion and the Palumbo-Aust criterion. Results showed that carbide
precipitation susceptibility at grain boundaries was dependent upon grain boundary structure. \( \Sigma 1 \) (low-angle) boundaries were defined by \( 5^\circ \leq \theta \leq 15^\circ \). No carbides were detected at \( \Sigma 1 \) boundaries with \( \theta \) between \( 5^\circ \) and \( 10^\circ \); however, carbides were detected at a fraction of the \( \Sigma 1 \) boundaries with \( \theta \) between \( 10^\circ \) and \( 15^\circ \). Other low-\( \Sigma \) boundaries (\( 3 \leq \Sigma \leq 29 \)), primarily coherent \( \Sigma 3 \) twin boundaries and \( \Sigma 9 \) boundaries, displayed significant resistance to carbide precipitation. Carbides were detected at \(~20\%\) of the low-\( \Sigma \) boundaries satisfying Brandon's criterion and \(<10\%\) of the low-\( \Sigma \) boundaries satisfying the Palumbo-Aust criterion. Carbides were detected at \(~80\%\) of the general boundaries.

Fig. 2.9. Time-temperature-precipitation curves for various grain boundaries (having specific surface free energies shown in parentheses in ergs/cm\(^2\) at 1060°C) in Alloy 304 austenitic stainless steel containing 0.038 wt.% C. \( M_{23}C_6 \) carbide precipitation occurs in the areas to the right of each curve. The notations G, IT and CT refer to general boundaries, incoherent \( \Sigma 3 \) twin boundaries and coherent \( \Sigma 3 \) twin boundaries, respectively (Trillo et al., 1995). Based on data by Stickler and Vinckier (1961).
3. Experimental Procedures

3.1. Materials

The starting material for this study was commercial-purity Alloy 304 austenitic stainless steel with composition (wt.%) Fe-18.7Cr-8.0Ni-1.8Mn-0.2Mo-0.06C containing <30 ppm boron present as a trace solute impurity. Studies were conducted on conventionally processed (CP) and grain boundary engineered (GBE™) Alloy 304. The GBE™ material was prepared by Integran Technologies Inc. (Toronto, Canada). It was thermomechanically processed using a proprietary processing technique (Palumbo, 1996) to contain a higher frequency of low-∑ boundaries (∑≤29) satisfying Brandon’s criterion (i.e., $\Delta \theta \leq 15^\circ \sum^{-1/2}$) (Brandon, 1966) in the grain boundary character distribution (GBCD). The average grain diameters of the as-received CP and GBE™ materials were 15 and 20 μm, respectively, as determined by OIM analysis. The as-received CP and GBE™ materials measured 3 and 1 mm in thickness, respectively, and were cut into 5 mm × 5 mm pieces using a low-speed cutting wheel.

3.2. Heat Treatments

Table 3.1 shows the heat treatments used in this study. The samples were placed on a pre-heated stainless steel substrate, inserted into a pre-heated tube furnace, heat treated in a flowing argon atmosphere and then quickly removed and water quenched. The annealing times were kept short to minimize grain growth. The samples were water quenched because it is common practice to rapidly cool austenitic stainless steel alloys in liquid after heat treatment in order to keep all the carbon in solid solution. However, carbide precipitation was expected to occur in the samples heat treated at 800°C because the solid solubility of carbon in austenitic stainless steel (wt.%) Fe-18Cr-9Ni is ~0.025 wt.% at 800°C (Rosenberg and Irish, 1952) and the carbon content of the material was ~0.06 wt.%.
Table 3.1. Heat Treatments

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Annealing Time</th>
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<tbody>
<tr>
<td>1100°C</td>
<td>2 min</td>
</tr>
<tr>
<td>1000°C</td>
<td>2.5 min</td>
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<tr>
<td>800°C</td>
<td>3 min</td>
</tr>
<tr>
<td>800°C</td>
<td>10 min</td>
</tr>
<tr>
<td>800°C</td>
<td>20 min</td>
</tr>
</tbody>
</table>

(Water Quenched)

3.3. Secondary Ion Mass Spectrometry (SIMS) Analysis

The segregation of boron at grain boundaries in each sample was detected using secondary ion mass spectrometry (SIMS). SIMS is a surface analysis technique that is capable of imaging trace elements on samples by bombarding them with high-energy primary ions and mass separating and imaging secondary ions that are sputtered from their surfaces (see Secondary Ion Mass Spectrometry – Principles and Applications, Vickerman et al. (eds.), 1989). The SIMS technique can detect all elements in the periodic table including hydrogen, usually with a detection limit in the ppm range, and analyze areas measuring up to ~250 μm in diameter with a lateral resolution of ~1 μm. SIMS analysis was conducted at the Materials Technology Laboratory at Natural Resources Canada (Ottawa, Canada) using a Cameca IMS 4f SIMS equipped with digital imaging.

3.3.1. Sample Preparation for SIMS Analysis

After heat treatment, the samples were mechanically polished using 2400-grit silicon-carbide paper to remove surface contamination. After mechanical polishing, the samples were electropolished in 10 ml perchloric acid – 90 ml ethanol at −35°C using 65 V
(DC) for 1 min to remove surface scratches and surface deformation. After electropolishing, the samples were ultrasonically cleaned in ethanol.

3.3.2. Boron Imaging

The SIMS was operated in direct-ion imaging mode or ion microscope mode. Figure 3.1 shows a schematic diagram illustrating the setup of a SIMS for direct-ion imaging. O$_2^+$ ions were used as primary ions. The primary O$_2^+$ ion beam was focused onto the sample surface to a diameter of ~300 µm and maintained at a fixed intensity. Bombardment of the sample with primary O$_2^+$ ions causes the sputtering or ejection of sample material from the sample surface. Monatomic and polyatomic particles of sample material and resputtered primary ions are produced, along with electrons and photons. The secondary particles, which consist of atoms, clusters of atoms and molecular fragments, carry negative, positive and neutral charges and have a range of kinetic energies. The sputtering rate of the sample is dependent upon primary beam intensity, sample material and grain orientation.

Negatively charged secondary ions were extracted from the sample surface as they were produced and then analyzed in a double-focusing mass spectrometer system. The mass spectrometer is capable of separating the secondary ions according to their mass and energy and transmitting a mass-selected beam of secondary ions to an ion image detector without affecting the lateral distribution of the selected ions. Mass-resolved ion images were acquired digitally using a resistive anode encoder detector, which counts the arriving ions and records their positions. SIMS direct-ion images are usually circular because ion image detectors are circular.

SIMS ion images showing the distribution of boron in each sample were acquired by mass separating and imaging $^{11}$B$^{16}$O$_2^-$ molecular ions with atomic mass 43. The BO$_2^-$ ion was the secondary ion determined to produce the strongest boron signal. Figure 3.2 (a) shows an example of a SIMS boron image (i.e., BO$_2^-$ ion image) from an Alloy 304 sample. SIMS
Fig. 3.1. Schematic diagram illustrating the setup of a SIMS for direct-ion imaging.
Fig. 3.2.  (a) SIMS boron image and (b) SIMS oxygen image from an Alloy 304 sample.  
(c) SEM micrograph of the area imaged in (a) and (b) after SIMS analysis.
boron images show $\text{BO}_2^-$ ion intensities as a function of location on the sample surface. Boron signal intensity is dependent upon the local boron concentration in the sample. If the sputtering rate and sputtering time of the samples are controlled, the boron signal intensities can be used as a relative measure of the local boron concentration in the samples.

SIMS ion images showing the microstructure of the areas where boron imaging was performed were acquired by imaging resputtered oxygen ions (i.e., resputtered primary ions). SIMS oxygen images show resputtered oxygen ion intensities as a function of location on the sample surface. Figure 3.2 (b) shows a SIMS oxygen image of the same area imaged in Figure 3.2 (a). The contrast in a SIMS oxygen image results from the different grain surfaces sputtering at different rates due to differences in crystallographic orientation.

One SIMS boron image and one SIMS oxygen image were acquired from each of the 10 heat-treated samples (i.e., 5 CP and 5 GBE$^{\text{TM}}$ samples). All the samples were sputtered at the same rate using the same intensity primary $\text{O}_2^+$ ion beam. Different sputtering times were used for the different heat-treated samples in order to obtain relatively the same number of $\text{BO}_2^-$ ion counts from each sample. For boron imaging each sample heat treated at 1000 and 1100°C was sputtered for 120 s and each sample heat treated at 800°C was sputtered for 60 s. A shorter sputtering time was used for the samples heat treated at 800°C because the boron signal intensity was considerably stronger from these samples, due to an effect of the heat treatment on the distribution of boron at grain boundaries in these samples. For oxygen imaging every sample was sputtered for 120 s.

After SIMS analysis, the areas that were analyzed by SIMS were further analyzed using a scanning electron microscope (SEM). Figure 3.2 (c) shows a SEM micrograph of the sample surface imaged in Figures 3.2 (a) and (b) after SIMS analysis. Generally, lattice imperfections, either already present or introduced by surface mixing, can lead to roughness in the sputter craters that can take the form of ribbons, furrows, ridges, cones and agglomerations of cones. Polycrystalline materials tend to form rough sputter craters because
of differential sputter rates that are dependent upon grain orientation, as shown in Figure 3.2 (c).

Comparing all the SIMS boron images with SIMS oxygen images and SEM micrographs of the same areas showed that boron was enriched at many grain boundaries in each sample. The SIMS imaging technique can not be used to differentiate between equilibrium boron segregation and non-equilibrium boron segregation because it will detect boron enrichment at grain boundaries regardless of the mechanism responsible, nor can it be used to measure the actual concentration of boron at grain boundaries. However, qualitative information about the relative amount of boron enrichment at grain boundaries can be determined by studying the relative intensity of the boron signal from grain boundaries in the SIMS boron images.

3.4. Orientation Imaging Microscopy (OIM) Analysis

After SIMS analysis, grain boundary structures in each sample were characterized in terms of the CSL model using orientation imaging microscopy (OIM). OIM is a microstructural analysis technique that is capable of imaging microstructures, determining grain orientations and characterizing grain boundary structures in polycrystalline samples by imaging and analyzing electron backscattered diffraction patterns (EBSPs) generated from samples in a scanning electron microscope (SEM) (see Adams et al, 1993). The OIM technique has a spatial resolution of ~100 nm and an angular resolution of <1° and can analyze areas measuring up to ~2 cm in diameter. OIM analysis was conducted at the University of Toronto (Toronto, Canada) using a Hitachi 4500 cold field emission SEM equipped with a TexSEM OIM system.
3.4.1. Sample Preparation for OIM Analysis

After SIMS analysis, the perimeter of the sputtered area on each sample where SIMS analysis was conducted was marked by hardness indentations in order to help identify the area in the SEM. Following this, the samples were electroetched in 10 g oxalic acid – 100 ml water at +25°C using 2 V (DC) for 5 s to remove the thin oxide layer that remained on the surface of the sputtered areas after SIMS analysis. After electroetching, the samples were ultrasonically cleaned in ethanol.

3.4.2. Microstructure Mapping and Grain Boundary Characterization

The SEM was operated in low-magnification mode. Figure 3.3 shows a schematic diagram illustrating the setup of a SEM for OIM analysis. Each sample was mounted on a sample holder that was tilted at 70° to the incident electron beam to maximize the number of backscattered electrons emitted from the sample. The electron beam was focused to a spot on the sample surface. The position of the electron beam on the sample surface was automatically controlled by the OIM computer. The electron beam was sequentially positioned at preset points covering the sputtered area of the sample. Beam step sizes of 2, 2.5 or 3 μm were used, depending on the average grain size of the area being analyzed. Diffracted electrons emitted from the sample at each point were detected using a phosphor screen placed close to the sample. The EBSPs were imaged using a low-light camera, digitized and analyzed by special crystallographic software that is capable of automatically indexing EBSPs. Data that was calculated from each point and recorded included three angles defining the crystallographic orientation of the sample with respect to a set of reference directions and (x,y) coordinates indicating the location on the sample surface where the data was collected.

The recorded data was processed and displayed in the form of a map of the sample surface, called an OIM map. Figure 3.4 (a) shows an example of an OIM map from an Alloy
Fig. 3.3. Schematic diagram illustrating the setup of a SEM for OIM analysis.
304 sample acquired after SIMS analysis and Figure 3.4 (b) shows a SEM micrograph of the same area imaged in Figure 3.4 (a). Every pixel in an OIM map corresponds to one EBSP and one crystallographic orientation measurement. Lines in the OIM map separate pixels with misorientations >5.0°. Comparing the OIM map and SEM micrograph in Figure 3.4 shows that the microstructure of the sample was well reproduced in the OIM map.

Fig. 3.4. (a) OIM map from an Alloy 304 sample (with Σ3 twin boundaries indicated in thick lines). (b) SEM micrograph of the area imaged in (a).

In addition to being able to determine the locations of the grain boundaries in a sample, the OIM technique is also capable of calculating the Σ values of each grain boundary since the orientations of all the grains are known. Grain boundaries with specific Σ values can be drawn in specific colors for easy identification and the Σ values and deviation angles (ΔΘs) for all the grain boundaries can be extracted from the recorded data. Length fractions of each type of grain boundary can also be determined automatically. In this study, however, the
length and length fraction of every grain boundary was determined manually by counting and recording the number of line segments constituting each grain boundary in each OIM map.

3.5. Oxalic Acid Test

Carbide precipitation was expected to occur in the samples heat treated at 800°C because the solid solubility of carbon in austenitic stainless steel (wt.%) Fe-18Cr-9Ni is ~0.025 wt.% at 800°C (Rosenberg and Irish, 1952) and the carbon content of the material was ~0.06 wt.%. Carbide precipitation at grain boundaries in the samples heat treated at 800°C was detected after SIMS and OIM analysis using an oxalic acid test. The oxalic acid test used in this study was based on a standard ASTM test used to detect susceptibility of austenitic stainless steels to intergranular attack due to carbide precipitation (i.e., ASTM A 262-771, Practice A).

3.5.1. Carbide Precipitation Detection

After SIMS and OIM analysis, the samples were ultrasonically cleaned in ethanol to remove surface contamination. After ultrasonic cleaning, the samples were electroetched in 10 g oxalic acid – 100 ml water at 25°C using 2 V (DC) for 30 s. After electroetching, the samples were ultrasonically cleaned in ethanol.

Figure 3.5 (a) shows an example of a SEM micrograph showing the sputtered area of an Alloy 304 sample after SIMS analysis. As shown in Figure 3.5 (a), no grain boundary grooving was observed directly after SIMS analysis. Figure 3.5 (b) shows a SEM micrograph of the same area in Figure 3.5 (a) after an oxalic acid test. As shown in Figure 3.5 (b), localized corrosion at numerous grain boundaries was observed after an oxalic acid test. The corroded regions indicated the locations of the precipitated carbides.
3.6. **Grain Boundary Classifications**

3.6.1. **Boron Segregation at Grain Boundaries**

In each sample grain boundaries were classified as either susceptible to boron segregation or resistant to boron segregation. Grain boundaries were classified as susceptible to boron segregation if any boron was observed at the grain boundaries in the SIMS boron images. Grain boundaries were classified as resistant to boron segregation if no boron was observed at the grain boundaries in the SIMS boron images. In the case that precipitated carbides were detected at the grain boundary, the grain boundary segments between the carbides were analyzed for boron segregation.
3.6.2. Grain Boundary Structures

In each sample grain boundaries with $\Sigma \leq 29$ were designated as low-$\Sigma$ boundaries and grain boundaries with $\Sigma > 29$ were designated as general boundaries. Low-$\Sigma$ boundaries were classified using Brandon’s criterion (i.e., $\Delta \theta_m \leq 15^\circ \Sigma^{-1/2}$) (Brandon, 1966) and the Palumbo-Aust criterion (i.e., $\Delta \theta_m \leq 15^\circ \Sigma^{-4/5}$) (Palumbo and Aust, 1990). Table 3.2 lists the angular deviation limits ($\Delta \theta_m$) for low-$\Sigma$ boundaries as per Brandon’s criterion and the Palumbo-Aust criterion. Grain boundaries with a misorientation angle ($\theta$) between 5.0° and 15.0° were designated as $\Sigma 1$ (low-angle) boundaries. Grain boundaries with $\theta < 5.0^\circ$ were not analyzed. In this study every grain boundary that was characterized as a $\Sigma 3$ boundary was determined to have the twin orientation. Coherent $\Sigma 3$ twin boundaries were differentiated from incoherent $\Sigma 3$ twin boundaries by a visual inspection of the twin boundaries in the SEM micrographs. Coherent $\Sigma 3$ twin boundaries generally appeared long and straight whereas incoherent $\Sigma 3$ twin boundaries generally appeared shorter and less straight.

3.6.3. Carbide Precipitation at Grain Boundaries

In the samples heat treated at 800°C grain boundaries were classified as either susceptible to carbide precipitation or resistant to carbide precipitation. Grain boundaries were classified as susceptible to carbide precipitation if any localized corrosion was detected at the grain boundaries after an oxalic acid test. Grain boundaries were classified as resistant to carbide precipitation if no localized corrosion was detected at the grain boundaries after an oxalic acid test.
Table 3.2. Angular deviation limits ($\Delta \theta_m$) for low-$\Sigma$ boundaries as per Brandon's criterion and the Palumbo-Aust criterion.

<table>
<thead>
<tr>
<th>$\Sigma$ Value</th>
<th>Angular Deviation Limit ($\Delta \theta_m$)</th>
<th>Angular Deviation Limit ($\Delta \theta_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brandon's Criterion ($\Delta \theta_m \leq 15^\circ \Sigma^{-1/2}$)</td>
<td>Palumbo-Aust Criterion ($\Delta \theta_m \leq 15^\circ \Sigma^{-5/6}$)</td>
</tr>
<tr>
<td>1</td>
<td>15.00°</td>
<td>15.00°</td>
</tr>
<tr>
<td>3</td>
<td>8.66°</td>
<td>6.00°</td>
</tr>
<tr>
<td>5</td>
<td>6.71°</td>
<td>3.92°</td>
</tr>
<tr>
<td>7</td>
<td>5.67°</td>
<td>2.96°</td>
</tr>
<tr>
<td>9</td>
<td>5.00°</td>
<td>2.40°</td>
</tr>
<tr>
<td>11</td>
<td>4.52°</td>
<td>2.03°</td>
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<tr>
<td>13</td>
<td>4.16°</td>
<td>1.77°</td>
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<tr>
<td>15</td>
<td>3.87°</td>
<td>1.57°</td>
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<td>3.64°</td>
<td>1.41°</td>
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<tr>
<td>19</td>
<td>3.44°</td>
<td>1.29°</td>
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<tr>
<td>21</td>
<td>3.27°</td>
<td>1.19°</td>
</tr>
<tr>
<td>23</td>
<td>3.13°</td>
<td>1.10°</td>
</tr>
<tr>
<td>25</td>
<td>3.00°</td>
<td>1.03°</td>
</tr>
<tr>
<td>27</td>
<td>2.89°</td>
<td>0.96°</td>
</tr>
<tr>
<td>29</td>
<td>2.79°</td>
<td>0.91°</td>
</tr>
</tbody>
</table>
4. Results and Discussion I:

Grain Boundary Character Distributions (GBCDs)

4.1. OIM Maps and Pole Figures

OIM analysis was conducted on samples of the conventionally processed (CP) and grain boundary engineered (GBE™) materials in as-received condition. Figures 4.1 and 4.2 show the OIM maps from the as-received CP and GBE™ materials, respectively. Figures 4.3 and 4.4 show the intensity pole figures from the as-received CP and GBE™ materials, respectively. The intensity pole figures from both materials showed that neither material had a strong texture.

4.2. Grain Boundary Frequencies and Length Fractions

4.2.1. Brandon’s Criterion

Figure 4.5 shows the frequencies (i.e., number fractions) of low-\(\Sigma\) boundaries (\(\Sigma \leq 29\)) and general boundaries (\(\Sigma > 29\)) as per Brandon’s criterion (i.e., \(\Delta \theta \leq 15^\circ \Sigma^{-1/2}\)) (Brandon, 1966) in the as-received CP and GBE™ materials. Figure 4.6 shows the calculated frequencies of low-\(\Sigma\) and general boundaries as per Brandon’s criterion expected in a random distribution (see Appendix). The frequency of low-\(\Sigma\) boundaries was considerably higher in both as-received materials than that expected in a random distribution. The CP and GBE™ materials contained 47 and 62% low-\(\Sigma\) boundaries, respectively, as compared to 13.62% expected in a random distribution.

All the grain boundaries characterized as \(\Sigma 3\) boundaries in both as-received materials were determined to have the twin orientation. The frequency of \(\Sigma 3\) twin boundaries satisfying Brandon’s criterion was considerably higher in both as-received materials
Fig. 4.1. OIM map from as-received CP Alloy 304.
Fig. 4.2. OIM map from as-received GBE™ Alloy 304.
Fig. 4.3. Intensity pole figures from as-received CP Alloy 304.

Fig. 4.4. Intensity pole figures from as-received GBE$^\text{TM}$ Alloy 304.
Fig. 4.5. Frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion in (a) as-received CP Alloy 304 and (b) as-received GBE™ Alloy 304.

Fig. 4.6. Frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion expected in a random distribution (see Appendix).
(Figure 4.5) than that expected in a random distribution (Figure 4.6). The CP and GBE materials contained 30 and 41% \( \Sigma 3 \) twin boundaries, respectively, as compared to 1.76% expected in a random distribution. Don and Majumdar (1986) previously reported a strong preference for \( \Sigma 3 \) twin boundaries in Alloy 304. A strong preference for \( \Sigma 3 \) twin boundaries is a characteristic of face-centered cubic (FCC) materials with a low stacking fault energy (SFE), such as Alloy 304.

The frequency of \( \Sigma 1 \) (low-angle) boundaries \((5.0^\circ \leq \theta \leq 15.0^\circ)\) was slightly higher in both as-received materials (Figure 4.5) than that expected in a random distribution (Figure 4.6). The CP and GBE materials contained 4 and 3% \( \Sigma 1 \) boundaries, respectively, as compared to 2.28% expected in a random distribution. A lower frequency of \( \Sigma 1 \) boundaries was expected in the GBE material due to its higher \( \Sigma 3 \) twin boundary frequency. As shown by Makita et al. (1988), a preference for \( \Sigma 1 \) boundaries in FCC materials is generally attributed to a strong texture and, as shown by Gottstein (1984), an increase in the \( \Sigma 3 \) twin boundary frequency tends to lead to a more random texture.

The frequency of \( \Sigma 9 \) boundaries satisfying Brandon's criterion was slightly higher in the as-received CP material (Figure 4.5 (a)) than that expected in a random distribution (Figure 4.6). On the other hand, the frequency of \( \Sigma 9 \) boundaries satisfying Brandon's criterion was considerably higher in the GBE material (Figure 4.5 (b)) than in both the as-received CP material (Figure 4.5 (a)) and that expected in a random distribution (Figure 4.6). The GBE material contained 8% \( \Sigma 9 \) boundaries as compared to 2% in the CP material and 1.02% expected in a random distribution. As proposed by Palumbo and Aust (1990), a preference for \( \Sigma 9 \) boundaries in FCC materials is attributed primarily to geometric interactions between \( \Sigma 3 \) twin boundaries. The higher frequency of \( \Sigma 9 \) boundaries in the GBE material was thus likely due to the higher frequency of \( \Sigma 3 \) twin boundaries in the GBE material and a higher degree of interaction between them.
The frequency of other low-\(\Sigma\) boundaries (\(\Sigma \leq 29\) excluding \(\Sigma 1, \Sigma 3\) and \(\Sigma 9\)) satisfying Brandon's criterion was slightly higher in both as-received materials (Figure 4.5) than that expected in a random distribution (Figure 4.6). The CP and GBE\(^{\text{TM}}\) materials contained 11 and 10\% other low-\(\Sigma\) boundaries, respectively, as compared to 8.56\% expected in a random distribution. The \(\Sigma 27\) boundary was determined to be the most strongly preferred type of other low-\(\Sigma\) boundary in both materials, unlike in a random distribution in which \(\Sigma 5\) boundaries are expected to be the most strongly preferred with 1.22\% (see Appendix). The CP and GBE\(^{\text{TM}}\) materials contained 2 and 5\% \(\Sigma 27\) boundaries, respectively, as compared to 0.59\% expected in a random distribution. As proposed by Palumbo and Aust (1990), a preference for \(\Sigma 9\) and \(\Sigma 27\) boundaries is attributed primarily to geometric interactions between \(\Sigma 3\)-related boundaries (i.e., \(\Sigma 3^n\), where \(n=1\) and 2). The higher frequency of \(\Sigma 27\) boundaries in the GBE\(^{\text{TM}}\) material was likely due to the higher frequencies of \(\Sigma 3\) twin boundaries and \(\Sigma 9\) boundaries in the GBE\(^{\text{TM}}\) material and a higher degree of interaction between them.

The frequency of low-\(\Sigma\) boundaries excluding \(\Sigma 1\) and \(\Sigma 3\)-related boundaries (\(\Sigma \leq 29\) excluding \(\Sigma 1, \Sigma 3, \Sigma 9\) and \(\Sigma 27\)) satisfying Brandon's criterion was slightly higher in the as-received CP material (Figure 4.5 (a)) than that expected in a random distribution (Figure 4.6). On the other hand, the frequency of low-\(\Sigma\) boundaries excluding \(\Sigma 1\) and \(\Sigma 3\)-related boundaries satisfying Brandon's was slightly lower in the as-received GBE\(^{\text{TM}}\) material (Figure 4.5 (b)) than in both the as-received CP material (Figure 4.5 (a)) and that expected in a random distribution (Figure 4.6). The CP material contained 9\% low-\(\Sigma\) boundaries excluding \(\Sigma 1\) and \(\Sigma 3\)-related boundaries as compared to 5\% in the GBE\(^{\text{TM}}\) material and 7.97\% expected in a random distribution. A lower frequency of low-\(\Sigma\) boundaries excluding \(\Sigma 1\) and \(\Sigma 3\)-related boundaries was expected in the GBE\(^{\text{TM}}\) material due to its higher \(\Sigma 3\) twin boundary frequency. As shown by Lin et al. (1995), the frequency of
low-$\Sigma$ boundaries excluding $\Sigma1$ and $\Sigma3$-related boundaries tends to decrease with increasing $\Sigma3$ twin boundary frequency.

The frequency of general boundaries as per Brandon's criterion was considerably lower in both as-received materials (Figure 4.5) than that expected in a random distribution (Figure 4.6). The CP and GBE$^\text{TM}$ materials contained 53 and 38% general boundaries, respectively, as compared to 86.38% expected in a random distribution.

Figure 4.7 shows the length fractions of low-$\Sigma$ and general boundaries as per Brandon's criterion in the as-received CP and GBE$^\text{TM}$ materials. The length fractions of low-$\Sigma$ boundaries in the CP and GBE$^\text{TM}$ materials were 53 and 67%, respectively.

Fig. 4.7. Length fractions of low-$\Sigma$ and general boundaries as per Brandon's criterion in (a) as-received CP Alloy 304 and (b) as-received GBE$^\text{TM}$ Alloy 304.

As shown in Figure 4.7, the higher length fraction of low-$\Sigma$ boundaries satisfying Brandon's criterion in the GBE$^\text{TM}$ material was primarily due to the higher length fractions of $\Sigma3$ twin boundaries and $\Sigma9$ boundaries. The length fraction of $\Sigma3$ twin boundaries in the CP
and GBE™ materials was 39 and 52%, respectively, and the length fraction of Σ9 boundaries in the CP and GBE™ materials was 1 and 6%, respectively.

The length fraction of general boundaries as per Brandon’s criterion was considerably lower in the as-received GBE™ material (Figure 4.7 (b)) than in the as-received CP material (Figure 4.7 (a)). The length fractions of general boundaries in the CP and GBE™ materials were 47 and 33%, respectively.

4.2.2. Palumbo-Aust Criterion

Figure 4.8 shows the frequencies (i.e., number fractions) of low-Σ boundaries (Σ≤29) and general boundaries (Σ>29) as per the Palumbo-Aust criterion (i.e., Δθ≤15°Σ≤5/6) (Palumbo and Aust, 1990) in the as-received CP and GBE™ materials. Figure 4.9 shows the calculated frequencies of low-Σ and general boundaries as per the Palumbo-Aust criterion expected in a random distribution (see Appendix). The frequency of low-Σ boundaries was considerably higher in both as-received materials than that expected in a random distribution. The CP and GBE™ materials contained 35 and 53% low-Σ boundaries, respectively, as compared to 3.73% expected in a random distribution.

The frequency of Σ3 twin boundaries satisfying the Palumbo-Aust criterion was considerably higher in both as-received materials (Figure 4.8) than that expected in a random distribution (Figure 4.9). The CP and GBE™ materials contained 29 and 40% Σ3 twin boundaries, respectively, as compared to 0.59% expected in a random distribution.

The frequencies of Σ9 boundaries and other low-Σ boundaries satisfying the Palumbo-Aust criterion were slightly higher in the as-received CP material (Figure 4.8 (a)) than that expected in a random distribution (Figure 4.9). On the other hand, the frequencies of Σ9 boundaries and other low-Σ boundaries satisfying the Palumbo-Aust criterion were considerably higher in the as-received GBE™ material (Figure 4.8 (b)) than in both the as-received CP material (Figure 4.8 (a)) and that expected in a random distribution.
Fig. 4.8. Frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in (a) as-received CP Alloy 304 and (b) as-received GBE$^\text{TM}$ Alloy 304.

Fig. 4.9. Frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion expected in a random distribution (see Appendix).
The GBE™ material contained 6% $\Sigma 9$ boundaries as compared to 1% in the CP material and 0.11% expected in a random distribution and the GBE™ material contained 4% other low-$\Sigma$ boundaries as compared to 1% in the CP material and 0.75% expected in a random distribution. The $\Sigma 27$ boundary was determined to be the most strongly preferred type of other low-$\Sigma$ boundary in both materials. The CP and GBE™ materials contained 0.2 and 3.3% $\Sigma 27$ boundaries, respectively, as compared to 0.02% expected in a random distribution.

The frequency of general boundaries as per the Palumbo-Aust criterion was considerably lower in both as-received materials (Figure 4.8) than that expected in a random distribution (Figure 4.9). The CP and GBE™ materials contained 65 and 47% general boundaries, respectively, as compared to 96.27% expected in a random distribution.

Figure 4.10 shows the length fractions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in the as-received CP and GBE™ materials. The length fractions of low-$\Sigma$ boundaries in the CP and GBE™ materials were 44 and 60%, respectively.

![Fig. 4.10. Length fractions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in (a) as-received CP Alloy 304 and (b) as-received GBE™ Alloy 304.](image)
As shown in Figure 4.10, the higher length fraction of low-\(\Sigma\) boundaries satisfying the Palumbo-Aust criterion in the GBE\textsuperscript{TM} material was primarily due to higher length fractions of \(\Sigma3\) twin boundaries and \(\Sigma9\) boundaries. The length fractions of \(\Sigma3\) twin boundaries in the CP and GBE\textsuperscript{TM} materials were 38 and 51\%, respectively, and the length fractions of \(\Sigma9\) boundaries in the CP and GBE\textsuperscript{TM} materials were 1 and 5\%, respectively.

The length fraction of general boundaries as per the Palumbo-Aust criterion was considerably lower in the as-received GBE\textsuperscript{TM} material (Figure 4.10 (b)) than in the as-received CP material (Figure 4.10 (a)). The length fractions of general boundaries in the CP and GBE\textsuperscript{TM} materials were 56 and 40\%, respectively.
5. Results and Discussion II:

Boron Segregation at Grain Boundaries

5.1. SIMS Boron Images

Figures 5.1 and 5.2 show the SIMS boron images from the conventionally processed (CP) and grain boundary engineered (GBE™) samples heat treated for 2.5 min at 1000°C and 2 min at 1100°C, respectively. Comparing the SIMS boron images with SIMS oxygen images and SEM micrographs of the same areas showed that boron was enriched at grain boundaries in each sample.

Boron enrichment at grain boundaries in the CP and GBE™ samples heat treated at 1000 and 1100°C was likely due to a combination of equilibrium segregation that occurred during annealing and non-equilibrium segregation that occurred during cooling (i.e., water quenching). As shown in Figures 5.1 and 5.2, the majority of the grain boundaries in each SIMS boron image displayed relatively the same boron signal intensity, which indicated that the majority of the grain boundaries in each sample were enriched with relatively the same amount of boron. In the SIMS boron images some grain boundaries displayed considerably higher intensities than other grain boundaries. As shown by Karlsson et al. (1988), the stronger intensities at some grain boundaries were primarily due to geometric effects associated with the orientation of the grain boundary plane with respect to the sample surface and not due to any real variations in the amount of boron enrichment at the grain boundaries. As shown by Karlsson et al. (1988), the intensity of the boron signal from a grain boundary that is almost parallel to the sample surface tends to be stronger than that from a grain boundary that is more perpendicular because more grain boundary area is exposed at the former during sputtering.
Fig. 5.1. SIMS boron images from (a) CP Alloy 304 and (b) GBE$^\text{TM}$ Alloy 304 heat treated for 2.5 min at 1000°C.

Fig. 5.2. SIMS boron images from (a) CP Alloy 304 and (b) GBE$^\text{TM}$ Alloy 304 heat treated for 2 min at 1100°C.
As shown in Figure 5.1, the grain boundaries in the SIMS boron images from the CP and GBE samples heat treated at 1000°C displayed relatively the same boron signal intensity, which indicated that grain boundaries in both samples were enriched with relatively the same amount of boron. Similarly, as shown in Figure 5.2, the grain boundaries in the SIMS boron images from the CP and GBE samples heat treated at 1100°C also displayed relatively the same boron signal intensity, which indicated that grain boundaries in both samples were also enriched with relatively the same amount of boron. Comparing the SIMS boron images from the samples heat treated at 1000°C (Figure 5.1) with those from the samples heat treated at 1100°C (Figure 5.2) showed, however, that the intensities were slightly stronger from the samples heat treated at 1000°C. The stronger intensities from the samples heat treated at 1000°C indicated that the grain boundaries in these samples were enriched with a relatively higher amount of boron; this was likely due to a higher degree of equilibrium segregation that occurred during annealing at the lower temperature.

Figures 5.3 to 5.5 show the SIMS boron images from the CP and GBE samples heat treated for 3, 10 and 20 min at 800°C, respectively. SEM micrographs of the same areas after SIMS analysis showed no grain boundary grooving on each sample. SEM micrographs of the same areas after SIMS analysis and an oxalic acid test, on the other hand, showed localized corrosion at grain boundaries on each sample, which indicated the presence of precipitated carbides at grain boundaries in each sample.

Figure 5.6 (a) shows the carbide precipitation susceptibility at grain boundaries in the CP and GBE samples heat treated at 800°C. As shown in Figure 5.6 (a), carbide precipitation was detected at grain boundaries in each sample and carbide precipitation susceptibility at grain boundaries increased with increasing annealing time in both the CP and GBE samples.

Comparing the SIMS boron images from the CP and GBE samples heat treated at 800°C with SIMS oxygen images of the same areas and SEM micrographs of the same
Fig. 5.3. SIMS boron images from (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 3 min at 800°C.

Fig. 5.4. SIMS boron images from (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 10 min at 800°C.
Fig. 5.5. SIMS boron images from (a) CP Alloy 304 and (b) GBE\textsuperscript{TM} Alloy 304 heat treated for 20 min at 800°C.
Fig. 5.6. (a) Carbide precipitation susceptibility, (b) detection of boron within carbides and (c) boron segregation susceptibility at grain boundaries in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
areas after an oxalic acid test showed that boron was enriched within grain boundary carbides in each sample. Figure 5.6 (b) shows the detection of boron within carbides at grain boundaries in the CP and GBE™ samples heat treated at 800°C. Comparing Figures 5.6 (a) and (b) showed that boron displayed a strong tendency to become incorporated into precipitating carbides.

As shown in Figures 5.3 to 5.5, the majority of the carbides (i.e., the small bright spots) in the SIMS boron images from the CP and GBE™ samples heat treated at 800°C displayed relatively the same boron signal intensity, which indicated that the majority of the carbides in each sample were enriched with relatively the same amount of boron. In the SIMS boron images some carbides displayed considerably higher intensities than other carbides. The stronger intensities at some carbides were likely due to geometric effects associated with the orientation of the grain boundary plane with respect to the sample surface and not due to any real variations in the amount of boron within the carbides.

Comparing the SIMS boron images from the samples heat treated at 800°C with SIMS oxygen images of the same areas and SEM micrographs of the same areas after an oxalic acid test also showed that boron was enriched at grain boundaries in some samples. Figure 5.6 (c) shows the boron segregation susceptibility at grain boundaries in the CP and GBE™ samples heat treated at 800°C. As shown in Figure 5.6 (c), boron was enriched at grain boundaries in both the CP and GBE™ samples heat treated for 3 min at 800°C but was considerably less enriched at grain boundaries in the CP and GBE™ samples heat treated for 10 and 20 min at 800°C.

As shown in Figure 5.6, with increasing annealing time at 800°C and increasing carbide precipitation at grain boundaries boron tended to desegregate from grain boundaries and become incorporated into precipitating carbides. These results indicated that boron had a stronger affinity for carbides than for grain boundaries. Similar results were obtained by Karlsson et al. (1988) in a study of intergranular boron segregation in Alloy 316L austenitic
stainless steel containing 23 ppm boron and 0.016 wt.% carbon heat treated at 800°C and water quenched using SIMS.

Boron enrichment at grain boundaries in the CP and GBE™ samples heat treated for 3 min at 800°C was likely due to a combination of equilibrium segregation that occurred during annealing and non-equilibrium segregation that occurred during cooling (i.e., water quenching). As shown in Figure 5.3, the majority of the grain boundaries in the SIMS boron images from the CP and GBE™ samples heat treated for 3 min at 800°C displayed relatively the same boron signal intensity, which indicated that the majority of the grain boundaries in both samples were enriched with relatively the same amount of boron. In the SIMS boron images some grain boundaries displayed considerably stronger intensities than other grain boundaries. The stronger intensities at some grain boundaries were likely due to geometric effects associated with the orientation of the grain boundary plane with respect to the sample surface and not due to any real variations in the amount of boron enrichment at the grain boundaries.

Comparing the SIMS boron images from the CP and GBE™ samples heat treated for 3 min at 800°C (Figure 5.3) with those from the CP and GBE™ samples heat treated at 1000 and 1100°C (Figures 5.1 and 5.2) showed that boron signal intensities were considerably stronger from the samples heat treated at 800°C. The stronger intensities from the samples heat treated at 800°C indicated that the grain boundaries in these samples were enriched with a considerably higher amount of boron. The higher amount of boron enrichment in the samples heat treated at 800°C was likely due to a higher degree of equilibrium segregation that occurred during annealing at the lower temperature.
5.2. Grain Boundary Distributions and Frequencies

5.2.1. Brandon's Criterion

Tables 5.1 and 5.2 show the distributions of low-$\Sigma$ grain boundaries ($\Sigma \leq 29$) and general grain boundaries ($\Sigma > 29$) as per Brandon's criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{-1/2}$) (Brandon, 1966) characterized in the CP and GBE$^{\text{TM}}$ samples heat treated at 1000 and 1100$^\circ$C, respectively, using SIMS and OIM. Table 5.3 shows the distributions of low-$\Sigma$ and general boundaries as per Brandon's criterion characterized in the CP and GBE$^{\text{TM}}$ samples heat treated at 800$^\circ$C using SIMS, OIM and an oxalic acid test.

As shown in Tables 5.1 to 5.3, a larger number of grain boundaries were characterized in the heat-treated CP samples than in the heat-treated GBE$^{\text{TM}}$ samples. More grain boundaries were characterized in the CP samples because the CP samples had a slightly smaller grain size. The short heat treatments had no large effect on the grain sizes of the CP and GBE$^{\text{TM}}$ materials. As determined by OIM analysis, the average grain diameters of the heat-treated CP and GBE$^{\text{TM}}$ samples were $\sim 15$ and $\sim 20$ $\mu$m, respectively, which were about the same as those of the as-received CP and GBE$^{\text{TM}}$ materials.

Figures 5.7 and 5.8 show the frequencies (i.e., number fractions) of low-$\Sigma$ and general boundaries as per Brandon's criterion characterized in the CP and GBE$^{\text{TM}}$ samples heat treated at 1000 and 1100$^\circ$C, respectively, using SIMS and OIM. Figure 5.9 shows the frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion characterized in the CP and GBE$^{\text{TM}}$ samples heat treated at 800$^\circ$C using SIMS, OIM and an oxalic acid test. The short heat treatments had no large effect on the grain boundary character distributions (GBCDs) of the CP and GBE$^{\text{TM}}$ materials. The frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion in the heat-treated samples (Figures 5.7 to 5.9) were similar to those in the as-received materials (Figure 4.5).
Table 5.1. Distributions of low-$\Sigma$ and general boundaries as per Brandon's criterion in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 2.5 min at 1000°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General ($\Sigma &gt; 29$)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td>4</td>
<td>40</td>
<td>3</td>
<td>8 (1/8 $\Sigma 27$)</td>
<td>76</td>
<td>131</td>
</tr>
<tr>
<td>GBE\textsuperscript{TM} Alloy 304</td>
<td>2</td>
<td>37</td>
<td>5</td>
<td>6 (3/6 $\Sigma 27$)</td>
<td>34</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 5.2. Distributions of low-$\Sigma$ and general boundaries as per Brandon's criterion in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 2 min at 1100°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General ($\Sigma &gt; 29$)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td>3</td>
<td>55</td>
<td>3</td>
<td>11 (2/11 $\Sigma 27$)</td>
<td>89</td>
<td>161</td>
</tr>
<tr>
<td>GBE\textsuperscript{TM} Alloy 304</td>
<td>1</td>
<td>43</td>
<td>5</td>
<td>8 (3/8 $\Sigma 27$)</td>
<td>38</td>
<td>95</td>
</tr>
</tbody>
</table>
Table 5.3. Distributions of low-$\Sigma$ and general boundaries as per Brandon’s criterion in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800\degree C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General $(\Sigma &gt; 29)$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CP Alloy 304</td>
<td>7</td>
<td>56</td>
<td>5</td>
<td>10(^{\text{10/10 \Sigma 27}})</td>
<td>93</td>
<td>171</td>
</tr>
<tr>
<td>(a) GBE\textsuperscript{TM} Alloy 304</td>
<td>1</td>
<td>40</td>
<td>5</td>
<td>8(^{\text{4/8 \Sigma 27}})</td>
<td>37</td>
<td>91</td>
</tr>
<tr>
<td>(b) CP Alloy 304</td>
<td>4</td>
<td>42</td>
<td>4</td>
<td>7(^{\text{2/7 \Sigma 27}})</td>
<td>76</td>
<td>133</td>
</tr>
<tr>
<td>(b) GBE\textsuperscript{TM} Alloy 304</td>
<td>2</td>
<td>50</td>
<td>6</td>
<td>8(^{\text{5/8 \Sigma 27}})</td>
<td>46</td>
<td>112</td>
</tr>
<tr>
<td>(c) CP Alloy 304</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>8(^{\text{2/8 \Sigma 27}})</td>
<td>55</td>
<td>98</td>
</tr>
<tr>
<td>(c) GBE\textsuperscript{TM} Alloy 304</td>
<td>2</td>
<td>26</td>
<td>2</td>
<td>6(^{\text{3/6 \Sigma 27}})</td>
<td>25</td>
<td>61</td>
</tr>
</tbody>
</table>
Fig. 5.7. Frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion in (a) CP Alloy 304 and (b) GBE\textsuperscript{TM} Alloy 304 heat treated for 2.5 min at 1000°C.

Fig. 5.8. Frequencies of low-$\Sigma$ and general boundaries as per Brandon's criterion in (a) CP Alloy 304 and (b) GBE\textsuperscript{TM} Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.9. Frequencies of low-∑ and general boundaries as per Brandon's criterion in CP and GBE Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800°C.
5.2.2. **Palumbo-Aust Criterion**

Tables 5.4 and 5.5 show the distributions of low-$\Sigma$ grain boundaries ($\Sigma \leq 29$) and general grain boundaries ($\Sigma > 29$) as per the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{5/6}$) (Palumbo and Aust, 1990) characterized in the CP and GBE$^\text{TM}$ samples heat treated at 1000 and 1100°C, respectively, using SIMS and OIM. Table 5.6 shows the distributions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion characterized in the CP and GBE$^\text{TM}$ samples heat treated at 800°C using SIMS, OIM and an oxalic acid test.

Figures 5.10 and 5.11 show the frequencies (i.e., number fractions) of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion characterized in the CP and GBE$^\text{TM}$ samples heat treated at 1000 and 1100°C, respectively, using SIMS and OIM. Figure 5.12 shows the frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion characterized in the CP and GBE$^\text{TM}$ samples heat treated at 800°C using SIMS, OIM and an oxalic acid test. The short heat treatments had no large effect on the grain boundary character distributions (GBCDs) of the CP and GBE$^\text{TM}$ materials. The frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in the heat-treated samples (Figures 5.10 to 5.12) were similar to those in the as-received materials (Figure 4.8).
Table 5.4. Distributions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 2.5 min at 1000°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General ($\Sigma &gt; 29$)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td>4</td>
<td>38</td>
<td>2</td>
<td>2 (0/2 $\Sigma 27$)</td>
<td>85</td>
<td>131</td>
</tr>
<tr>
<td>GBE$^\text{TM}$ Alloy 304</td>
<td>2</td>
<td>36</td>
<td>5</td>
<td>3 (2/3 $\Sigma 27$)</td>
<td>38</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 5.5. Distributions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 2 min at 1100°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General ($\Sigma &gt; 29$)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td>3</td>
<td>53</td>
<td>2</td>
<td>2 (1/2 $\Sigma 27$)</td>
<td>101</td>
<td>161</td>
</tr>
<tr>
<td>GBE$^\text{TM}$ Alloy 304</td>
<td>1</td>
<td>42</td>
<td>4</td>
<td>4 (1/4 $\Sigma 27$)</td>
<td>44</td>
<td>95</td>
</tr>
</tbody>
</table>
Table 5.6. Distributions of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in CP and GBE™ Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 1$</th>
<th>$\Sigma 3$</th>
<th>$\Sigma 9$</th>
<th>Other $\Sigma \leq 29$</th>
<th>General $\Sigma &gt; 29$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>CP Alloy 304</td>
<td>7</td>
<td>55</td>
<td>2</td>
<td>$\frac{5}{2/5 \Sigma 27}$</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>GBE™ Alloy 304</td>
<td>1</td>
<td>39</td>
<td>4</td>
<td>$\frac{5}{4/5 \Sigma 27}$</td>
<td>42</td>
</tr>
<tr>
<td>(b)</td>
<td>CP Alloy 304</td>
<td>4</td>
<td>42</td>
<td>2</td>
<td>$\frac{3}{2/3 \Sigma 27}$</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>GBE™ Alloy 304</td>
<td>2</td>
<td>49</td>
<td>5</td>
<td>$\frac{5}{4/5 \Sigma 27}$</td>
<td>51</td>
</tr>
<tr>
<td>(c)</td>
<td>CP Alloy 304</td>
<td>2</td>
<td>30</td>
<td>2</td>
<td>$\frac{2}{1/2 \Sigma 27}$</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>GBE™ Alloy 304</td>
<td>2</td>
<td>23</td>
<td>2</td>
<td>$\frac{3}{2/3 \Sigma 27}$</td>
<td>31</td>
</tr>
</tbody>
</table>
Fig. 5.10. Frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in (a) CP Alloy 304 and (b) GBE$^\text{TM}$ Alloy 304 heat treated for 2.5 min at 1000°C.

Fig. 5.11. Frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in (a) CP Alloy 304 and (b) GBE$^\text{TM}$ Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.12. Frequencies of low-$\Sigma$ and general boundaries as per the Palumbo-Aust criterion in CP and GBE$^\text{TM}$ Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800°C.
5.3. $\Sigma 1$ Boundaries

Figure 5.13 shows the boron segregation susceptibility at $\Sigma 1$ (low-angle) grain boundaries ($5.0^\circ \leq \theta \leq 15.0^\circ$) and general grain boundaries ($\Sigma > 29$ and $15.0^\circ < \theta \leq 20.0^\circ$) as per Brandon's criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{-1/2}$) (Brandon, 1966) in the CP and GBE samples heat treated at 1000 and 1100°C. As shown in Figure 5.13, $\Sigma 1$ boundaries defined by the Read-Shockley limit of $\theta \leq 15.0^\circ$ (Read and Shockley, 1950) displayed some resistance to boron segregation whereas general boundaries with $\theta$ between 15.0° and 20.0° displayed no resistance to boron segregation. A misorientation angle limit between 5.0° and 15.0° defining a structural field of high resistance to boron segregation at $\Sigma 1$ boundaries was not determined. As shown in Figure 5.13, boron segregation was detected at a $\Sigma 1$ boundary with a misorientation angle as low as 7.5°.

Figure 5.14 shows the carbide precipitation susceptibility at $\Sigma 1$ boundaries ($5.0^\circ \leq \theta \leq 15.0^\circ$) and general boundaries ($\Sigma > 29$ and $15.0^\circ < \theta \leq 20.0^\circ$) as per Brandon's criterion in the CP and GBE samples heat treated at 800°C. As shown in Figure 5.14, the Read-Shockley limit of $\theta \leq 15.0^\circ$ (Read and Shockley, 1950) was determined to define a structural field of high resistance to carbide precipitation at $\Sigma 1$ boundaries. $\Sigma 1$ boundaries with $\theta \leq 15.0^\circ$ displayed high resistance to carbide precipitation whereas general boundaries with $\theta$ between 15.0° and 20.0° displayed low resistance to carbide precipitation. As shown in Figure 5.14, with increasing annealing time at 800°C $\Sigma 1$ boundaries continued to display high resistance to carbide precipitation whereas general boundaries displayed increased susceptibility to carbide precipitation.

Figure 5.15 shows the detection of boron within carbides and boron segregation susceptibility at $\Sigma 1$ boundaries ($5.0^\circ \leq \theta \leq 15.0^\circ$) and general boundaries ($\Sigma > 29$ and $15.0^\circ < \theta \leq 20.0^\circ$) as per Brandon's criterion in the CP and GBE samples heat treated at 800°C. As shown in Figure 5.15, boron was detected within carbides at general boundaries.
Fig. 5.13. Boron segregation susceptibility at $\Sigma 1$ boundaries ($5.0^\circ \leq \theta \leq 15.0^\circ$) and general boundaries ($\Sigma > 29$ and $15.0^\circ < \theta \leq 20.0^\circ$) as per Brandon's criterion in CP and GBE™ Alloy 304 heat treated at 1000 and 1100°C.
Carbide precipitation susceptibility at Σ1 boundaries (5.0° ≤ θ ≤ 15.0°) and general boundaries (Σ ≥ 29 and 15.0° < θ ≤ 20.0°) as per Brandon's criterion in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
Fig. 5.15. Detection of boron within carbides and boron segregation susceptibility at $\Sigma 1$ boundaries ($5.0^\circ \leq \theta \leq 15.0^\circ$) and general boundaries ($\Sigma > 29$ and $15.0^\circ < \theta \leq 20.0^\circ$) as per Brandon's criterion in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
Comparing Figures 5.14 and 5.15 showed that boron had a strong affinity for carbides at general boundaries.

As shown in Figure 5.15, boron segregation was detected at some \( \Sigma 1 \) boundaries and all general boundaries in the samples heat treated for 3 min at 800°C but was not detected at \( \Sigma 1 \) and general boundaries in the samples heat treated for 10 and 20 min at 800°C. As shown in Figure 5.15, with increasing annealing time at 800°C boron desegregated from both \( \Sigma 1 \) and general boundaries and became incorporated into carbides.

As shown in Figure 5.15, \( \Sigma 1 \) boundaries in the samples heat treated for 3 min at 800°C displayed some resistance to boron segregation whereas general boundaries in the same samples displayed no resistance to boron segregation. A misorientation angle limit between 5.0° and 15.0° defining a structural field of high resistance to boron segregation at \( \Sigma 1 \) boundaries was not determined. As shown in Figure 5.15, boron segregation was detected at a \( \Sigma 1 \) boundary with a misorientation angle as low as 6.4°.

Figures 5.16 to 5.18 show SIMS boron images illustrating the resistance and susceptibility of \( \Sigma 1 \) boundaries to boron segregation in the samples heat treated at 1000 and 1100°C. Figures 5.19 to 5.21 show SIMS boron images illustrating the resistance of \( \Sigma 1 \) boundaries to carbide precipitation and the resistance and susceptibility of \( \Sigma 1 \) boundaries to boron segregation in the samples heat treated at 800°C. The resistance of \( \Sigma 1 \) boundaries to both boron segregation and carbide precipitation was likely due to their highly ordered structures, which are close to that of a single crystal (i.e., arrays of primary dislocations).
Fig. 5.16. SIMS boron image showing no boron segregation at two $\Sigma 1$ boundaries ($\theta=8.0^\circ$ and $\theta=11.1^\circ$) in CP Alloy 304 heat treated for 2.5 min at 1000°C.
Fig. 5.17. SIMS boron image showing boron segregation at a $\Sigma 1$ boundary ($\theta=9.5^\circ$) and no boron segregation at a $\Sigma 1$ boundary ($\theta=12.9^\circ$) in GBE$^{TM}$ Alloy 304 heat treated for 2.5 min at 1000°C.
Fig. 5.18. SIMS boron image showing no boron segregation at a $\Sigma 1$ boundary ($\theta=6.5^\circ$) in CP Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.19. SEM micrograph showing no localized corrosion (i.e., no carbide precipitation) at three $\Sigma 1$ boundaries ($\theta=5.9^\circ$, $\theta=6.4^\circ$ and $\theta=10.4^\circ$) in CP Alloy 304 heat treated for 3 min at 800°C. SIMS boron image showing boron segregation at the 6.4$^\circ$ $\Sigma 1$ boundary and no boron segregation at the 5.9$^\circ$ and 10.4$^\circ$ $\Sigma 1$ boundaries.
Fig. 5.20. SEM micrograph showing no localized corrosion (i.e., no carbide precipitation) at a Σ1 boundary (θ=6.7°) in GBE™ Alloy 304 heat treated for 10 min at 800°C. SIMS boron image showing no boron segregation at the 6.7° Σ1 boundary.
Fig. 5.21. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at a general boundary ($\Sigma>29$ and $\theta=17.2^\circ$) and no localized corrosion (i.e., no carbide precipitation) at two $\Sigma 1$ boundaries ($\theta=10.2^\circ$ and $\theta=13.8^\circ$) in CP Alloy 304 heat treated for 20 min at 800°C. SIMS boron image showing boron within carbides at the 17.2° general boundary and no boron segregation at the 10.2° and 13.8° $\Sigma 1$ boundaries.
5.4. \( \Sigma 3 \) Boundaries

All the grain boundaries characterized as \( \Sigma 3 \) boundaries in the CP and GBE\textsuperscript{TM} samples heat treated at 1000, 1100 and 800°C were determined to have the twin orientation. The majority (i.e., ~95%) of the \( \Sigma 3 \) twin boundaries characterized in each sample were determined to have an angular deviation (\( \Delta \theta \)) \( \leq 2.0^\circ \). A total of 419 \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion (i.e., \( \Delta \theta \leq 8.7^\circ \)) (Brandon, 1966) were characterized in the 10 heat-treated samples (see Tables 5.1 to 5.3). 399 of the 419 \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \leq 2.0^\circ \) and 20 of the 419 \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \) between 4.6° and 8.7°. No \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \) between 2.0° and 4.6°.

In the CP and GBE\textsuperscript{TM} samples heat treated at 1000 and 1100°C 175 coherent \( \Sigma 3 \) twin boundaries and 66 incoherent \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion were characterized. 164 of the 175 coherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \leq 2.0^\circ \) and 11 of the 175 coherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \) between 4.6° and 8.7°. All 66 incoherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \leq 2.0^\circ \).

Table 5.7 shows the boron segregation susceptibility at coherent \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion (i.e., \( 6.0^\circ < \Delta \theta \leq 8.7^\circ \)) (Brandon, 1966 and Palumbo and Aust, 1990) in the CP and GBE\textsuperscript{TM} samples heat treated at 1000 and 1100°C. As shown in Table 5.7, coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \) between 6.0° and 8.7° displayed high resistance to boron segregation.

Table 5.8 shows the boron segregation susceptibility at coherent and incoherent \( \Sigma 3 \) twin boundaries satisfying the Palumbo-Aust criterion (i.e., \( \Delta \theta \leq 6.0^\circ \)) (Palumbo and Aust, 1990) in the CP and GBE\textsuperscript{TM} samples heat treated at 1000 and 1100°C. As shown in Table 5.8, both coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \leq 6.0^\circ \) and incoherent \( \Sigma 3 \) twin boundaries displayed high resistance to boron segregation.

In the CP and GBE\textsuperscript{TM} samples heat treated at 800°C 244 coherent \( \Sigma 3 \) twin boundaries and 40 incoherent \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion were
Table 5.7. Boron segregation susceptibility at coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $6.0^\circ<\Delta\theta\leq 8.7^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated at 1000 and 1100°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($6.0^\circ&lt;\Delta\theta\leq 8.7^\circ$)</th>
<th>CP Alloy 304</th>
<th>2.5 min at 1000°C</th>
<th>2 min at 1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 2/2</td>
<td>Not Detected at 2/2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8. Boron segregation susceptibility at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion (i.e., $\Delta\theta\leq 6.0^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated at 1000 and 1100°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($\Delta\theta\leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>2.5 min at 1000°C</th>
<th>2 min at 1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 38/38</td>
<td>Not Detected at 53/53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| GBE$^\text{TM}$ Alloy 304 | Not Detected at 36/36 | Not Detected at 42/42 |

<table>
<thead>
<tr>
<th>Incoherent $\Sigma 3$ Twin Boundaries ($\Delta\theta\leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>2.5 min at 1000°C</th>
<th>2 min at 1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 7/7</td>
<td>Not Detected at 13/13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| GBE$^\text{TM}$ Alloy 304 | Not Detected at 19/19 | Not Detected at 27/27 |
characterized. 235 of the 244 coherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \leq 2.0^\circ \) and 9 of the 244 coherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \) between 4.6\(^\circ\) and 8.7\(^\circ\). All 40 incoherent \( \Sigma 3 \) twin boundaries were found with \( \Delta \theta \leq 2.0^\circ \).

Table 5.9 shows the carbide precipitation susceptibility at coherent \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and GBE\(^\text{TM} \) samples heat treated at 800\(^\circ\)C. As shown in Table 5.9, carbide precipitation was not detected at coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \) between 6.0\(^\circ\) and 8.7\(^\circ\) in the samples heat treated for 3 min at 800\(^\circ\)C but was detected at those in the samples heat treated for 10 and 20 min at 800\(^\circ\)C. In the samples heat treated for 10 and 20 min at 800\(^\circ\)C coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \) between 6.0\(^\circ\) and 8.7\(^\circ\) displayed no resistance to carbide precipitation.

Table 5.10 shows the carbide precipitation susceptibility at coherent and incoherent \( \Sigma 3 \) twin boundaries satisfying the Palumbo-Aust criterion in the CP and GBE\(^\text{TM} \) samples heat treated at 800\(^\circ\)C. As shown in Table 5.10, carbide precipitation was not detected at coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \leq 6.0^\circ \) in the samples heat treated for 3 min at 800\(^\circ\)C but was detected at some of those in the samples heat treated for 10 and 20 min at 800\(^\circ\)C. In the samples heat treated for 10 and 20 min at 800\(^\circ\)C coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \leq 6.0^\circ \) displayed high resistance to carbide precipitation. The two coherent \( \Sigma 3 \) twin boundaries found susceptible to carbide precipitation were determined to have \( \Delta \theta \) between 5.3\(^\circ\) and 6.0\(^\circ\). Carbide precipitation was not detected at any of the coherent \( \Sigma 3 \) twin boundaries with \( \Delta \theta \leq 2.0^\circ \).

As shown in Table 5.10, carbide precipitation was not detected at incoherent \( \Sigma 3 \) twin boundaries satisfying the Palumbo-Aust criterion in the samples heat treated for 3 and 10 min at 800\(^\circ\)C but was detected at those in the samples heat treated for 20 min at 800\(^\circ\)C. In the samples heat treated for 20 min at 800\(^\circ\)C incoherent \( \Sigma 3 \) twin boundaries displayed no resistance to carbide precipitation.

Table 5.11 shows the detection of boron within carbides at coherent \( \Sigma 3 \) twin boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and
Table 5.9. Carbide precipitation susceptibility at coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $6.0^\circ<\Delta \theta \leq 8.7^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($6.0^\circ&lt;\Delta \theta \leq 8.7^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 1/1</td>
<td>None Found</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10. Carbide precipitation susceptibility at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 6.0^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 55/55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Not Detected at 39/39</td>
<td>Not Detected at 49/49</td>
<td>Not Detected at 23/23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incoherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 5/5</td>
<td>Not Detected at 4/4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Not Detected at 13/13</td>
<td>Not Detected at 9/9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.11. Detection of boron within carbides at coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $6.0^\circ < \Delta \theta \leq 8.7^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($6.0^\circ \leq \Delta \theta \leq 8.7^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 1/1</td>
<td>None Found</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.12. Detection of boron within carbides at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 6.0^\circ$) in CP and GBE$^\text{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 55/55</td>
<td>Not Detected at 56/56</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incoherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>CP Alloy 304</th>
<th>3 min at 800°C</th>
<th>10 min at 800°C</th>
<th>20 min at 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Detected at 13/13</td>
<td>Not Detected at 23/23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| GB$^\text{TM}$ Alloy 304 | Not Detected at 1/1 | Not Detected at 9/9 | Not Detected at 23/23 | Not Detected at 23/23 |
GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Table 5.11, boron was detected within carbides at coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 6.0° and 8.7°. Comparing Tables 5.9 and 5.11 showed that boron had a strong affinity for carbides at coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 6.0° and 8.7°.

Table 5.12 shows the detection of boron within carbides at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Table 5.12, boron was detected within carbides at coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 6.0°$ and incoherent $\Sigma 3$ twin boundaries. Comparing Tables 5.10 and 5.12 showed that boron had a strong affinity for carbides at coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 6.0°$ and incoherent $\Sigma 3$ twin boundaries.

Table 5.13 shows the boron segregation susceptibility at coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Table 5.13, boron segregation was detected at coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 6.0° and 8.7° in the samples heat treated for 3 min at 800°C but was not detected at those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 6.0° and 8.7° displayed no resistance to boron segregation. Comparing Tables 5.11 and 5.13 showed that with increasing annealing time at 800°C boron desegregated from coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 6.0° and 8.7° and became incorporated into carbides.

Table 5.14 shows the boron segregation susceptibility at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Table 5.14, boron segregation was detected at some of the coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 6.0°$ in the samples heat treated for 3 min at 800°C but was not detected at those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 6.0°$ displayed high resistance to boron segregation. The one coherent $\Sigma 3$ twin boundary found susceptible
Table 5.13. Boron segregation susceptibility at coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $6.0^\circ < \Delta \theta \leq 8.7^\circ$) in CP and GBE$^{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800$^\circ$C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($6.0^\circ &lt; \Delta \theta \leq 8.7^\circ$)</th>
<th>3 min at 800$^\circ$C</th>
<th>10 min at 800$^\circ$C</th>
<th>20 min at 800$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td></td>
<td>None Found</td>
<td></td>
</tr>
<tr>
<td>GBE$^{TM}$ Alloy 304</td>
<td>Not Detected at 1/1</td>
<td>Not Detected at 3/3</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.14. Boron segregation susceptibility at coherent and incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 6.0^\circ$) in CP and GBE$^{TM}$ Alloy 304 heat treated for 3, 10 and 20 min at 800$^\circ$C.

<table>
<thead>
<tr>
<th>Coherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>3 min at 800$^\circ$C</th>
<th>10 min at 800$^\circ$C</th>
<th>20 min at 800$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td></td>
<td>Not Detected at 42/42</td>
<td>Not Detected at 30/30</td>
</tr>
<tr>
<td>GBE$^{TM}$ Alloy 304</td>
<td>Not Detected at 39/39</td>
<td>Not Detected at 49/49</td>
<td>Not Detected at 23/23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incoherent $\Sigma 3$ Twin Boundaries ($\Delta \theta \leq 6.0^\circ$)</th>
<th>3 min at 800$^\circ$C</th>
<th>10 min at 800$^\circ$C</th>
<th>20 min at 800$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Alloy 304</td>
<td></td>
<td>Not Detected at 4/4</td>
<td>Not Detected at 5/5</td>
</tr>
<tr>
<td>GBE$^{TM}$ Alloy 304</td>
<td>Not Detected at 9/9</td>
<td>Not Detected at 4/4</td>
<td></td>
</tr>
</tbody>
</table>
to boron segregation was determined to have $\Delta \theta = 5.5^\circ$. Boron segregation was not detected at any of the coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 2.0^\circ$. Comparing Tables 5.12 and 5.14 showed that with increasing annealing time at 800°C boron desegregated from coherent $\Sigma 3$ twin boundaries with $\Delta \theta \leq 6.0^\circ$ and became incorporated into carbides.

As shown in Table 5.14, boron segregation was detected at incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion in the samples heat treated for 3 min at 800°C but was not detected at those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C incoherent $\Sigma 3$ twin boundaries displayed no resistance to boron segregation. Comparing Tables 5.12 and 5.14 showed that with increasing annealing time at 800°C boron desegregated from incoherent $\Sigma 3$ twin boundaries and became incorporated into carbides.

Figures 5.22 and 5.23 show SIMS boron images illustrating the resistance of coherent and incoherent $\Sigma 3$ twin boundaries to boron segregation in the samples heat treated at 1000 and 1100°C. Figures 5.24 and 5.25 show SIMS boron images illustrating the resistance of coherent $\Sigma 3$ twin boundaries to carbide precipitation and boron segregation and the susceptibility of incoherent $\Sigma 3$ twin boundaries to carbide precipitation and boron segregation in the samples heat treated at 800°C. The resistance of coherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion to both boron segregation and carbide precipitation was likely due to their unique twinned structure, which is highly ordered and free of secondary grain boundary dislocations. The susceptibility of incoherent $\Sigma 3$ twin boundaries to both boron segregation and carbide precipitation illustrates the effect of variations in the grain boundary plane on grain boundary properties. Coherent and incoherent $\Sigma 3$ twin boundaries share the same misorientation but differ from one another by the crystallographic orientation of the grain boundary plane. The susceptibility of coherent $\Sigma 3$ twin boundaries with $\Delta \theta$ between 4.6° and 8.6° to both boron segregation and carbide precipitation was likely due to their high secondary grain boundary dislocation densities resulting from their high angular deviations from exact $\Sigma 3$ twin orientation.
Fig. 5.22. SIMS boron image showing no boron segregation at several coherent $\Sigma 3$ twin boundaries (CT) ($\Delta \theta \leq 2.0^\circ$) and incoherent $\Sigma 3$ twin boundaries (IT) ($\Delta \theta \leq 2.0^\circ$) satisfying the Palumbo-Aust criterion in GBE$^\text{TM}$ Alloy 304 heat treated for 2.5 min at 1000$^\circ$C.
Fig. 5.23. SIMS boron image showing no boron segregation at several coherent $\Sigma 3$ twin boundaries (CT) ($\Delta \theta \leq 2.0^\circ$) and incoherent $\Sigma 3$ twin boundaries (IT) ($\Delta \theta \leq 2.0^\circ$) satisfying the Palumbo-Aust criterion and no boron segregation at a coherent $\Sigma 3$ twin boundary satisfying Brandon's criterion but not the Palumbo-Aust criterion (HT) ($\Delta \theta = 8.3^\circ$) in CP Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.24. SEM micrograph showing no localized corrosion (i.e., no carbide precipitation) at several coherent $\Sigma 3$ twin boundaries (CT) ($\Delta \theta \leq 2.0^\circ$) and incoherent $\Sigma 3$ twin boundaries (IT) ($\Delta \theta \leq 2.0^\circ$) satisfying the Palumbo-Aust criterion in GBE™ Alloy 304 heat treated for 3 min at 800°C. SIMS boron image showing boron segregation at the incoherent $\Sigma 3$ twin boundaries and no boron segregation at the coherent $\Sigma 3$ twin boundaries.
Fig. 5.25. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at an incoherent $\Sigma 3$ twin boundary (IT) ($\Delta \theta \leq 2.0^\circ$) satisfying the Palumbo-Aust criterion and no localized corrosion (i.e., no carbide precipitation) at several coherent $\Sigma 3$ twin boundaries (CT) ($\Delta \theta \leq 2.0^\circ$) satisfying the Palumbo-Aust criterion in CP Alloy 304 heat treated for 20 min at 800°C. SIMS boron image showing boron within carbides at the incoherent $\Sigma 3$ twin boundary and no boron segregation at the coherent $\Sigma 3$ twin boundaries.
5.5. \(\Sigma 9\) Boundaries

In the CP and GBE\textsuperscript{TM} samples heat treated at 1000, 1100 and 800°C a total of 41 \(\Sigma 9\) boundaries satisfying Brandon's criterion (i.e., \(\Delta \theta \leq 5.0^\circ\)) (Brandon, 1966) were characterized (see Tables 5.1 to 5.3). 11 of the 41 \(\Sigma 9\) boundaries were found satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., \(2.4^\circ < \Delta \theta \leq 5.0^\circ\)) (Brandon, 1966 and Palumbo and Aust, 1990) and 30 of the 41 \(\Sigma 9\) boundaries were found satisfying the Palumbo-Aust criterion (i.e., \(\Delta \theta \leq 2.4^\circ\)) (Palumbo and Aust, 1990). All 30 \(\Sigma 9\) boundaries satisfying the Palumbo-Aust criterion were found with \(\Delta \theta \leq 1.2^\circ\). No \(\Sigma 9\) boundaries were found with \(\Delta \theta\) between 1.2\(^\circ\) and 2.4\(^\circ\).

Figure 5.26 shows the boron segregation susceptibility at \(\Sigma 9\) boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion in the CP and GBE\textsuperscript{TM} samples heat treated at 1000 and 1100°C. As shown in Figure 5.26, \(\Sigma 9\) boundaries with \(\Delta \theta\) between 2.4\(^\circ\) and 5.0\(^\circ\) displayed no resistance to boron segregation.

Figure 5.27 shows the boron segregation susceptibility at \(\Sigma 9\) boundaries satisfying the Palumbo-Aust criterion in the CP and GBE\textsuperscript{TM} samples heat treated at 1000 and 1100°C. As shown in Figure 5.27, \(\Sigma 9\) boundaries with \(\Delta \theta \leq 2.4^\circ\) displayed some resistance to boron segregation. Those \(\Sigma 9\) boundaries found resistant to boron segregation were determined to have \(\Delta \theta \leq 0.9^\circ\).

Figure 5.28 shows the carbide precipitation susceptibility at \(\Sigma 9\) boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion in the CP and GBE\textsuperscript{TM} samples heat treated at 800°C. As shown in Figure 5.28, \(\Sigma 9\) boundaries with \(\Delta \theta\) between 2.4\(^\circ\) and 5.0\(^\circ\) displayed low resistance to carbide precipitation.

Figure 5.29 shows the carbide precipitation susceptibility at \(\Sigma 9\) boundaries satisfying the Palumbo-Aust criterion in the CP and GBE\textsuperscript{TM} samples heat treated at 800°C. As shown in Figure 5.29, \(\Sigma 9\) boundaries with \(\Delta \theta \leq 2.4^\circ\) displayed some resistance to carbide precipitation. With increasing annealing time at 800°C \(\Sigma 9\) boundaries with \(\Delta \theta \leq 2.4^\circ\)
Fig. 5.26. Boron segregation susceptibility at Σ9 boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., 2.40°<Δθ≤5.00°) in CP and GBE™ Alloy 304 heat treated at 1000 and 1100°C.

Fig. 5.27. Boron segregation susceptibility at Σ9 boundaries satisfying the Palumbo-Aust criterion (i.e., Δθ≤2.40°) in CP and GBE™ Alloy 304 heat treated at 1000 and 1100°C.
Fig. 5.28. Carbide precipitation susceptibility at \( \Sigma 9 \) boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., \( 2.40^\circ < \Delta \theta \leq 5.00^\circ \)) in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 3, 10 and 20 min at 800\(^\circ\)C.

Fig. 5.29. Carbide precipitation susceptibility at \( \Sigma 9 \) boundaries satisfying the Palumbo-Aust criterion (i.e., \( \Delta \theta \leq 2.40^\circ \)) in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 3, 10 and 20 min at 800\(^\circ\)C.
continued to display some resistance to carbide precipitation. Those $\Sigma 9$ boundaries found resistant to boron segregation were determined to have $\Delta \theta \leq 0.9^\circ$.

Figure 5.30 shows the detection of boron within carbides and boron segregation susceptibility at $\Sigma 9$ boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Figure 5.30, boron was detected within carbides at $\Sigma 9$ boundaries with $\Delta \theta$ between 2.4° and 5.0°. Comparing Figures 5.28 and 5.30 showed that boron had a strong affinity for carbides at $\Sigma 9$ boundaries with $\Delta \theta$ between 2.4° and 5.0°.

As shown in Figure 5.30, boron segregation was detected at $\Sigma 9$ boundaries with $\Delta \theta$ between 2.4° and 5.0° in the samples heat treated for 3 min at 800°C but was detected at only one of those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C $\Sigma 9$ boundaries with $\Delta \theta$ between 2.4° and 5.0° displayed no resistance to boron segregation.

Figure 5.31 shows the detection of boron within carbides and boron segregation susceptibility at $\Sigma 9$ boundaries satisfying the Palumbo-Aust criterion in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Figure 5.31, boron was detected within carbides at $\Sigma 9$ boundaries with $\Delta \theta \leq 2.4^\circ$. Comparing Figures 5.29 and 5.31 showed that boron had a strong affinity for carbides at $\Sigma 9$ boundaries with $\Delta \theta \leq 2.4^\circ$.

As shown in Figure 5.31, boron segregation was detected at 2 of the 6 $\Sigma 9$ boundaries with $\Delta \theta \leq 2.4^\circ$ in the samples heat treated for 3 min at 800°C but was not detected at those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C $\Sigma 9$ boundaries with $\Delta \theta \leq 2.4^\circ$ displayed some resistance to boron segregation. Those $\Sigma 9$ boundaries found resistant to boron segregation were determined to have $\Delta \theta \leq 0.9^\circ$. As shown in Figure 5.31, with increasing annealing time at 800°C boron desegregated from $\Sigma 9$ boundaries with $\Delta \theta \leq 2.4^\circ$ and became incorporated into carbides.
Fig. 5.30. Detection of boron within carbides and boron segregation susceptibility at \( \Sigma 9 \) boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., \( 2.40^\circ < \Delta \theta \leq 5.00^\circ \)) in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

Fig. 5.31. Detection of boron within carbides and boron segregation susceptibility at \( \Sigma 9 \) boundaries satisfying the Palumbo-Aust criterion (i.e., \( \Delta \theta \leq 2.40^\circ \)) in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
Figures 5.32 to 5.35 show SIMS boron images illustrating the resistance and susceptibility of Σ9 boundaries (among other low-Σ boundaries to be discussed in Section 5.6.) to boron segregation in the samples heat treated at 1000 and 1100°C. Figures 5.36 to 5.38 show SIMS boron images illustrating the resistance and susceptibility of Σ9 boundaries (among other low-Σ boundaries to be discussed in Section 5.6.) to carbide precipitation and boron segregation in the samples heat treated at 800°C. The resistance of Σ9 boundaries satisfying the Palumbo-Aust criterion to both boron segregation and carbide precipitation was likely due to their low secondary grain boundary dislocation densities resulting from their low deviations from exact Σ9 orientation. The susceptibility of some Σ9 boundaries satisfying the Palumbo-Aust criterion to boron segregation and carbide precipitation was likely due to the effect of variations in the grain boundary plane on the distributions of the secondary grain boundary dislocations. The susceptibility of Σ9 boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion to both boron segregation and carbide precipitation was likely due to their high secondary grain boundary dislocation densities resulting from their high deviations from exact Σ9 orientation.
Fig. 5.32. SIMS boron image showing boron segregation at two low-\(\Sigma\) boundaries (\(\Sigma_{11} (\Delta\theta=2.8^\circ)\) and \(\Sigma_{23} (\Delta\theta=2.3^\circ)\)) satisfying Brandon's criterion but not the Palumbo-Aust criterion and no boron segregation at a \(\Sigma_{9}\) boundary (\(\Delta\theta=0.8^\circ\)) satisfying the Palumbo-Aust criterion (P-A) in CP Alloy 304 heat treated for 2.5 min at 1000°C.
Fig. 5.33. SIMS boron image showing boron segregation at two low-$\Sigma$ boundaries ($\Sigma11$ ($\Delta\theta=2.4^\circ$) and $\Sigma27$ ($\Delta\theta=1.0^\circ$)) satisfying Brandon's criterion but not the Palumbo-Aust criterion, boron segregation at three $\Sigma9$ boundaries (clockwise from bottom-left, $\Delta\theta=0.5^\circ$, $\Delta\theta=1.0^\circ$ and $\Delta\theta=0.4^\circ$) satisfying the Palumbo-Aust criterion (P-A) and no boron segregation at a $\Sigma9$ boundary (center-right, $\Delta\theta=0.7^\circ$) satisfying the Palumbo-Aust criterion (P-A) in GBE$^{\text{TM}}$ Alloy 304 heat treated for 2.5 min at 1000$^\circ$C.
Fig. 5.34. SIMS boron image showing boron segregation at two low-Σ boundaries (Σ15 ($\Delta \theta = 2.1^\circ$) and Σ23 ($\Delta \theta = 2.5^\circ$)) satisfying Brandon's criterion but not the Palumbo-Aust criterion and no boron segregation at a Σ9 boundary ($\Delta \theta = 0.4^\circ$) satisfying the Palumbo-Aust criterion (P-A) in CP Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.35. SIMS boron image showing boron segregation at two low-$\Sigma$ boundaries ($\Sigma21$ ($\Delta\theta=1.3^\circ$) and $\Sigma27$ ($\Delta\theta=1.0^\circ$)) satisfying Brandon's criterion but not the Palumbo-Aust criterion, boron segregation at two $\Sigma7$ boundaries (left to right, $\Delta\theta=1.1^\circ$ and $\Delta\theta=1.9^\circ$) satisfying the Palumbo-Aust criterion and no boron segregation at a $\Sigma9$ boundary ($\Delta\theta=0.8^\circ$) satisfying the Palumbo-Aust criterion in GBE$^{\text{TM}}$ Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.36. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at two $\Sigma 27$ boundaries (left-to-right, $\Delta \theta = 0.8^\circ$ and $\Delta \theta = 0.7^\circ$) satisfying the Palumbo-Aust criterion (P-A), no localized corrosion (i.e., no carbide precipitation) at two $\Sigma 9$ boundaries (left-to-right, $\Delta \theta = 0.7^\circ$ and $\Delta \theta = 0.9^\circ$) satisfying the Palumbo-Aust criterion (P-A) and no localized corrosion at a $\Sigma 23$ boundary ($\Delta \theta = 1.8^\circ$) satisfying Brandon's criterion but not the Palumbo-Aust criterion in GBE™ Alloy 304 heat treated for 10 min at 800°C. SIMS boron image showing boron within carbides at the two $\Sigma 27$ boundaries and no boron segregation at the $\Sigma 23$ boundary and the two $\Sigma 9$ boundaries.
Fig. 5.37. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at two \( \Sigma 27 \) boundaries (left-to-right, \( \Delta \theta = 0.5^\circ \) and \( \Delta \theta = 0.6^\circ \)) satisfying the Palumbo-Aust criterion (P-A) and localized corrosion at a \( \Sigma 9 \) boundary (\( \Delta \theta = 2.6^\circ \)) and a \( \Sigma 27 \) boundary (\( \Delta \theta = 2.4^\circ \)) satisfying Brandon’s criterion but not the Palumbo-Aust criterion in GBE\textsuperscript{TM} Alloy 304 heat treated for 10 min at 800°C. SIMS boron image showing boron within carbides at the \( \Sigma 9 \) boundary and the three \( \Sigma 27 \) boundaries.
Fig. 5.38. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at a \( \Sigma 9 \) boundary \( (\Delta \theta=0.7^\circ) \) satisfying the Palumbo-Aust criterion (P-A) and no localized corrosion (i.e., no carbide precipitation) at a \( \Sigma 27 \) boundary \( (\Delta \theta=1.4^\circ) \) satisfying Brandon's criterion but not the Palumbo-Aust criterion in CP Alloy 304 heat treated for 20 min at 800°C. SIMS boron image showing boron within carbides at the \( \Sigma 9 \) boundary and no boron segregation at the \( \Sigma 27 \) boundary.
In the CP and GBE samples heat treated at 1000, 1100 and 800°C a total of 80 other low-\(\Sigma\) boundaries (\(\Sigma \leq 29\) excluding \(\Sigma 1, \Sigma 3\) and \(\Sigma 9\)) satisfying Brandon’s criterion (i.e., \(\Delta \theta \leq 15^\circ \Sigma^{\frac{3}{2}}\)) (Brandon, 1966) were characterized (see Tables 5.1 to 5.3). 46 of the 80 other low-\(\Sigma\) boundaries were found satisfying Brandon’s criterion but not the Palumbo-Aust criterion (i.e., \(15^\circ \Sigma^{\frac{5}{6}} < \Delta \theta \leq 15^\circ \Sigma^{\frac{1}{2}}\)) (Brandon, 1966 and Palumbo and Aust, 1990) and 34 of the 80 other low-\(\Sigma\) boundaries were found satisfying the Palumbo-Aust criterion (i.e., \(\Delta \theta \leq 15^\circ \Sigma^{\frac{5}{6}}\)) (Palumbo and Aust, 1990). All of the other low-\(\Sigma\) boundaries excluding \(\Sigma 27\) boundaries satisfying the Palumbo-Aust criterion were found with \(\Delta \theta \geq 1.0^\circ\). All \(\Sigma 27\) boundaries satisfying the Palumbo-Aust criterion were found with \(\Delta \theta \leq 0.8^\circ\).

Figure 5.39 shows the boron segregation susceptibility at other low-\(\Sigma\) boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and GBE samples heat treated at 1000 and 1100°C. As shown in Figure 5.39, other low-\(\Sigma\) boundaries with \(\Delta \theta\) between \(15^\circ \Sigma^{\frac{5}{6}}\) and \(15^\circ \Sigma^{\frac{1}{2}}\) displayed no resistance to boron segregation.

Figure 5.40 shows the boron segregation susceptibility at other low-\(\Sigma\) boundaries satisfying the Palumbo-Aust criterion in the CP and GBE samples heat treated at 1000 and 1100°C. As shown in Figure 5.40, other low-\(\Sigma\) boundaries with \(\Delta \theta \leq 15^\circ \Sigma^{\frac{5}{6}}\) displayed no resistance to boron segregation.

Figure 5.41 shows the carbide precipitation susceptibility at other low-\(\Sigma\) boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and GBE samples heat treated at 800°C. As shown in Figure 5.41, other low-\(\Sigma\) boundaries with \(\Delta \theta\) between \(15^\circ \Sigma^{\frac{5}{6}}\) and \(15^\circ \Sigma^{\frac{1}{2}}\) displayed low resistance to carbide precipitation. With increasing annealing time at 800°C other low-\(\Sigma\) boundaries with \(\Delta \theta\) between \(15^\circ \Sigma^{\frac{5}{6}}\) and \(15^\circ \Sigma^{\frac{1}{2}}\) displayed increased susceptibility to carbide precipitation.

Figure 5.42 shows the carbide precipitation susceptibility at other low-\(\Sigma\) boundaries satisfying the Palumbo-Aust criterion in the CP and GBE samples heat treated...
Fig. 5.39. Boron segregation susceptibility at other low-$\Sigma$ boundaries ($\Sigma \leq 29$ excluding $\Sigma 1$, $\Sigma 3$ and $\Sigma 9$) satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $15^\circ \Sigma^{-5/6} < \Delta \theta \leq 15^\circ \Sigma^{-1/2}$) in CP and GBE$^{\text{TM}}$ Alloy 304 heat treated at 1000 and 1100$^\circ$C.

Fig. 5.40. Boron segregation susceptibility at other low-$\Sigma$ boundaries ($\Sigma \leq 29$ excluding $\Sigma 1$, $\Sigma 3$ and $\Sigma 9$) satisfying the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{-5/6}$) in CP and GBE$^{\text{TM}}$ Alloy 304 heat treated at 1000 and 1100$^\circ$C.
Fig. 5.41. Carbide precipitation susceptibility at other low-Σ boundaries (Σ≤29 excluding Σ1, Σ3 and Σ9) satisfying Brandon’s criterion but not the Palumbo-Aust criterion (i.e., 15°≤Δθ≤15°Σ^{-1/2}) in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

Fig. 5.42. Carbide precipitation susceptibility at other low-Σ boundaries (Σ≤29 excluding Σ1, Σ3 and Σ9) satisfying the Palumbo-Aust criterion (i.e., Δθ≤15°Σ^{-5/6}) in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
at 800°C. As shown in Figure 5.42, other low-Σ boundaries with Δθ ≤ 15°Σ-5/6 displayed low resistance to carbide precipitation. With increasing annealing time at 800°C other low-Σ boundaries with Δθ ≤ 15°Σ-5/6 displayed increased susceptibility to carbide precipitation.

Figure 5.43 shows the detection of boron within carbides and boron segregation susceptibility at other low-Σ boundaries satisfying Brandon’s criterion but not the Palumbo-Aust criterion in the CP and GBE™ samples heat treated at 800°C. As shown in Figure 5.43, boron was detected within carbides at other low-Σ boundaries with Δθ between 15°Σ-5/6 and 15°Σ-1/2. Comparing Figures 5.41 and 5.43 showed that boron had a strong affinity for carbides at other low-Σ boundaries with Δθ between 15°Σ-5/6 and 15°Σ-1/2.

As shown in Figure 5.43, boron segregation was detected at other low-Σ boundaries with Δθ between 15°Σ-5/6 and 15°Σ-1/2 in the samples heat treated for 3 min at 800°C but was detected at only one of those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C other low-Σ boundaries with Δθ between 15°Σ-5/6 and 15°Σ-1/2 displayed no resistance to boron segregation. As shown in Figure 5.43, with increasing annealing time at 800°C boron desegregated from other low-Σ boundaries with Δθ between 15°Σ-5/6 and 15°Σ-1/2 and became incorporated into carbides.

Figure 5.44 shows the detection of boron within carbides and boron segregation susceptibility at other low-Σ boundaries satisfying the Palumbo-Aust criterion in the CP and GBE™ samples heat treated at 800°C. As shown in Figure 5.44, boron was detected within carbides at other low-Σ boundaries with Δθ ≤ 15°Σ-5/6. Comparing Figures 5.42 and 5.44 showed that boron had a strong affinity for carbides at other low-Σ boundaries with Δθ ≤ 15°Σ-5/6.

As shown in Figure 5.44, boron segregation was detected at other low-Σ boundaries with Δθ ≤ 15°Σ-5/6 in the samples heat treated for 3 min at 800°C but was detected at only one of those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C other low-Σ boundaries with Δθ ≤ 15°Σ-5/6 displayed no
Fig. 5.43. Detection of boron within carbides and boron segregation susceptibility at other low-Σ boundaries (Σ≤29 excluding Σ1, Σ3 and Σ9) satisfying Brandon's criterion but not the Palumbo-Aust criterion (i.e., $15°\Sigma^{5/6} < \Delta \theta \leq 15°\Sigma^{-1/2}$) in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.

Fig. 5.44. Detection of boron within carbides and boron segregation susceptibility at other low-Σ boundaries (Σ≤29 excluding Σ1, Σ3 and Σ9) satisfying the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 15°\Sigma^{5/6}$) in CP and GBE™ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
resistance to boron segregation. As shown in Figure 5.44, with increasing annealing time at 800°C boron desegregated from other low-$\Sigma$ boundaries with $\Delta\theta \leq 15^\circ \Sigma^{-5/6}$ and became incorporated into carbides.

Figures 5.32 to 5.35 show SIMS boron images illustrating the susceptibility of other low-$\Sigma$ boundaries (among $\Sigma$9 boundaries discussed in Section 5.5.) to boron segregation in the samples heat treated at 1000 and 1100°C. Figures 5.36 to 5.38 show SIMS boron images illustrating the susceptibility of other low-$\Sigma$ boundaries (among other $\Sigma$9 boundaries discussed in Section 5.5.) to carbide precipitation and boron segregation in the samples heat treated at 800°C. The susceptibility of other low-$\Sigma$ boundaries excluding $\Sigma$27 boundaries with $\Delta\theta \leq 0.8^\circ$ to both boron segregation and carbide precipitation was likely due to their high secondary grain boundary dislocation densities resulting from their high deviations from exact low-$\Sigma$ orientations. The susceptibility of $\Sigma$27 boundaries with $\Delta\theta \leq 0.8^\circ$ to both boron segregation and carbide precipitation tends to indicate that a $\Sigma$ value of 27 is likely too high for grain boundaries to display significant resistance to boron segregation and carbide precipitation.
5.7. General Boundaries ($\Sigma>29$)

Figure 5.45 shows the boron segregation susceptibility at general boundaries ($\Sigma>29$) in the CP and GBE$^\text{TM}$ samples heat treated at 1000 and 1100°C. As shown in Figure 5.45, general boundaries displayed no resistance to boron segregation.

Figure 5.46 shows the carbide precipitation susceptibility, detection of boron within carbides and boron segregation susceptibility at general boundaries in the CP and GBE$^\text{TM}$ samples heat treated at 800°C. As shown in Figure 5.46 (a), general boundaries displayed low resistance to carbide precipitation. With increasing annealing time at 800°C general boundaries displayed increased susceptibility to carbide precipitation.

As shown in Figure 5.46 (b), boron was detected within carbides at general boundaries. Comparing Figures 5.46 (a) and (b) showed that boron had a strong affinity for carbides at general boundaries.

As shown in Figure 5.46 (c), boron segregation was detected at general boundaries in the samples heat treated for 3 min at 800°C but was detected at considerably less of those in the samples heat treated for 10 and 20 min at 800°C. In the samples heat treated for 3 min at 800°C general boundaries displayed low resistance to boron segregation.

Figures 5.47 and 5.48 show SIMS boron images illustrating the susceptibility of general boundaries to boron segregation in the samples heat treated at 1000 and 1100°C. Figures 5.49 and 5.50 show SIMS boron images illustrating the susceptibility and resistance of general boundaries to carbide precipitation and boron segregation in the samples heat treated at 800°C. The susceptibility of general boundaries to both boron segregation and carbide precipitation was likely due to their disordered structures and high secondary grain boundary dislocation densities resulting from their high deviations from exact low-$\Sigma$ orientations.
Fig. 5.45. Boron segregation susceptibility at general boundaries (Σ>29) in CP and GBE™ Alloy 304 heat treated at 1000 and 1100°C.
Fig. 5.46. (a) Carbide precipitation susceptibility, (b) detection of boron within carbides and (c) boron segregation susceptibility at general boundaries ($\Sigma$>29) in CP and GBE$^{\text{TM}}$ Alloy 304 heat treated for 3, 10 and 20 min at 800°C.
Fig. 5.47. SIMS boron image showing boron segregation at several general boundaries ($\Sigma>29$) in GBE™ Alloy 304 heat treated for 2.5 min at 1000°C.
Fig. 5.48. SIMS boron image showing boron segregation at several general boundaries ($\Sigma > 29$) in CP Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.49. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at four general boundaries ($\Sigma>29$) and no localized corrosion (i.e., no carbide precipitation) at a general boundary (*) in GBE\textsuperscript{TM} Alloy 304 heat treated for 10 min at 800°C. SIMS boron image showing boron within carbides at the four general boundaries displaying susceptibility to carbide precipitation and no boron segregation at the general boundary displaying resistance to carbide precipitation.
Fig. 5.50. SEM micrograph showing localized corrosion (i.e., carbide precipitation) at three general boundaries (Σ>29) and no localized corrosion (i.e., no carbide precipitation) at two general boundaries (⋆) in CP Alloy 304 heat treated for 20 min at 800°C. SIMS boron image showing boron within carbides at the three general boundaries displaying susceptibility to carbide precipitation and no boron segregation at the two general boundaries displaying resistance to carbide precipitation.
Figures 5.51 and 5.52 show the frequencies (i.e., number fractions) of grain boundaries displaying resistance to boron segregation in the CP and GBE™ samples heat treated at 1000 and 1100°C, respectively. As shown in Figures 5.51 and 5.52, the GBE™ samples contained a higher frequency of grain boundaries displaying resistance to boron segregation than the CP samples. In the samples heat treated at 1000°C the GBE™ sample contained 48% grain boundaries resistant to boron segregation as compared to 34% in the CP sample. Similarly, in the samples heat treated at 1100°C the GBE™ sample contained 49% grain boundaries resistant to boron segregation as compared to 36% in the CP sample.

Figures 5.53 and 5.54 show the length fractions of grain boundaries displaying resistance to boron segregation in the CP and GBE™ samples heat treated at 1000 and 1100°C, respectively. As shown in Figures 5.53 and 5.54, the GBE™ samples contained a considerably higher length fraction of grain boundaries displaying resistance to boron segregation than the CP samples. In the samples heat treated at 1000°C the GBE™ sample contained a 59% length fraction of grain boundaries resistant to boron segregation as compared to 43% in the CP sample. Similarly, in the samples heat treated at 1100°C the GBE™ sample contained a 62% length fraction of grain boundaries resistant to boron segregation as compared to 45% in the CP sample.

Figure 5.55 shows the frequencies of grain boundaries displaying resistance to carbide precipitation in the CP and GBE™ samples heat treated at 800°C. As shown in Figure 5.55, with increasing annealing time at 800°C carbide precipitation susceptibility at grain boundaries increased in both the CP and GBE™ samples. The highest amount of carbide precipitation at grain boundaries occurred in the samples heat treated for 20 min at 800°C. In the samples heat treated for 20 min at 800°C the GBE™ sample contained a higher frequency of grain boundaries displaying resistance to carbide precipitation than the CP
Fig. 5.51. Frequencies of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 2.5 min at 1000°C.

Fig. 5.52. Frequencies of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 2 min at 1100°C.
Fig. 5.53. Length fractions of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE\textsuperscript{TM} Alloy 304 heat treated for 2.5 min at 1000\textdegree C.

Fig. 5.54. Length fractions of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE\textsuperscript{TM} Alloy 304 heat treated for 2 min at 1100\textdegree C.
Fig. 5.55. Frequencies of grain boundaries displaying resistance to carbide precipitation in CP and GBE™ Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800°C.
The GBE sample contained 49% grain boundaries resistant to carbide precipitation as compared to 38% in the CP sample.

Figure 5.56 shows the length fractions of grain boundaries displaying resistance to carbide precipitation in the CP and GBE samples heat treated at 800°C. As shown in Figure 5.56, the highest amount of carbide precipitation at grain boundaries occurred in the samples heat treated for 20 min at 800°C. In the samples heat treated for 20 min at 800°C the GBE sample contained a 61% length fraction of grain boundaries resistant to carbide precipitation as compared to 47% in the CP sample.

Boron segregation was detected at grain boundaries in the samples heat treated for 3 min at 800°C but was detected at considerably fewer grain boundaries in the samples heat treated for 10 and 20 min at 800°C. Figure 5.57 shows the frequencies of grain boundaries displaying resistance to boron segregation in the CP and GBE samples heat treated for 3 min at 800°C. As shown in Figure 5.57, the GBE sample contained a higher frequency of grain boundaries displaying resistance to boron segregation than the CP sample. In the samples heat treated 3 min at 800°C the GBE sample contained 47% grain boundaries resistant to boron segregation as compared to 37% in the CP sample.

Figure 5.58 shows the length fractions of grain boundaries displaying resistance to boron segregation in the CP and GBE samples heat treated for 3 min at 800°C. As shown in Figure 5.58, the GBE sample contained a considerably higher length fraction of grain boundaries displaying resistance to boron segregation than the CP sample. In the samples heat treated for 3 min at 800°C the GBE sample contained a 57% length fraction of grain boundaries resistant to boron segregation as compared to 46% in the CP sample.

The higher resistance of the GBE samples to both intergranular boron segregation and intergranular carbide precipitation was likely due to the higher frequencies and higher length fractions of coherent $\Sigma 3$ twin boundaries and $\Sigma 9$ boundaries satisfying the Palumbo-Aust criterion in the grain boundary character distribution.
Fig. 5.56. Length fractions of grain boundaries displaying resistance to carbide precipitation in CP and GBE\textsuperscript{TM} Alloy 304 heat treated for (a) 3 min, (b) 10 min and (c) 20 min at 800\degree C.
Fig. 5.57. Frequencies of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 3 min at 800°C.

(a) □ = No Boron Segregation Detected
    ■ = Boron Segregation Detected

(b) 37% (63/171)

Fig. 5.58. Length fractions of grain boundaries displaying resistance to boron segregation in (a) CP Alloy 304 and (b) GBE™ Alloy 304 heat treated for 3 min at 800°C.

(a) □ = No Boron Segregation Detected
    ■ = Boron Segregation Detected

(b) 46%

(b) 57%
6. Conclusions

6.1. Grain Boundary Character Distributions (GBCDs) (Chapter 4.)

1. The frequencies (i.e., number fractions) of low-Σ boundaries (Σ ≤ 29) satisfying Brandon’s criterion (i.e., Δθ ≤ 15°Σ−1/2) in conventionally processed (CP) and grain boundary engineered (GBE™) Alloy 304 in as-received condition were determined to be 47 and 62%, respectively. The as-received CP material contained 4% Σ1, 30% Σ3, 2% Σ9 and 11% other low-Σ boundaries satisfying Brandon’s criterion. The as-received GBE™ material contained 3% Σ1, 41% Σ3, 8% Σ9 and 10% other low-Σ boundaries satisfying Brandon’s criterion.

2. The frequencies of low-Σ boundaries satisfying the Palumbo-Aust criterion (i.e., Δθ ≤ 15°Σ−5/6) in as-received CP and GBE™ Alloy 304 were determined to be 35 and 53%, respectively. The as-received CP material contained 4% Σ1, 29% Σ3, 1% Σ9 and 1% other low-Σ boundaries satisfying the Palumbo-Aust criterion. The as-received GBE™ material contained 3% Σ1, 40% Σ3, 6% Σ9 and 4% other low-Σ boundaries satisfying the Palumbo-Aust criterion.

6.2. Boron Segregation at Grain Boundaries (Chapter 5.)

1. In both the CP and GBE™ samples heat treated at 1000 and 1100°C:

(a) Boron segregation was detected at grain boundaries.

(b) Σ1 (low-angle) boundaries (5.0° ≤ θ ≤ 15.0°) displayed some resistance to boron segregation.

(c) Coherent Σ3 twin boundaries satisfying Brandon’s criterion with Δθ ≤ 8.3° displayed high resistance to boron segregation. Incoherent Σ3 twin boundaries satisfying the Palumbo-Aust criterion with Δθ ≤ 2.0° displayed high resistance to boron segregation.
(d) $\Sigma 9$ boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion with $\Delta \theta$ between 2.4° and 5.0° displayed no resistance to boron segregation. $\Sigma 9$ boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 2.4^\circ$ displayed some resistance to boron segregation. Those $\Sigma 9$ boundaries found resistant to boron segregation were determined to have $\Delta \theta \leq 0.9^\circ$.

(e) Other low-$\Sigma$ boundaries ($\Sigma \leq 29$ excluding $\Sigma 1$, $\Sigma 3$ and $\Sigma 9$) satisfying Brandon's criterion but not the Palumbo-Aust criterion with $\Delta \theta$ between $15^\circ \Sigma^{-5/6}$ and $15^\circ \Sigma^{-1/2}$ and other low-$\Sigma$ boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 15^\circ \Sigma^{-5/6}$ displayed no resistance to boron segregation.

(f) General boundaries ($\Sigma > 29$) displayed no resistance to boron segregation.

2. In both the CP and GBE™ samples heat treated at 800°C:

(a) Carbide precipitation was detected at grain boundaries.

(b) With increasing annealing time at 800°C carbide precipitation susceptibility at grain boundaries increased and boron tended to desegregate from grain boundaries and become incorporated into carbides.

(c) $\Sigma 1$ boundaries displayed some resistance to boron segregation and high resistance to carbide precipitation.

(d) Coherent $\Sigma 3$ twin boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion with $\Delta \theta$ between 6.0° and 8.6° and coherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta$ between 4.6° and 6.0° displayed low resistance to both boron segregation and carbide precipitation. Coherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 2.0^\circ$ displayed high resistance to both boron segregation and carbide precipitation. Incoherent $\Sigma 3$ twin boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 2.0^\circ$
displayed no resistance to boron segregation and low resistance to carbide precipitation.

(e) $\Sigma 9$ boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion with $\Delta \theta$ between 2.4° and 5.0° displayed low resistance to both boron segregation and carbide precipitation. $\Sigma 9$ boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 2.4^\circ$ displayed some resistance to both boron segregation and carbide precipitation. Those $\Sigma 9$ boundaries found resistant to both boron segregation and carbide precipitation were determined to have $\Delta \theta \leq 0.9^\circ$.

(g) Other low-$\Sigma$ boundaries satisfying Brandon's criterion but not the Palumbo-Aust criterion with $\Delta \theta$ between $15^\circ \Sigma^{-5/6}$ and $15^\circ \Sigma^{-1/2}$ and other low-$\Sigma$ boundaries satisfying the Palumbo-Aust criterion with $\Delta \theta \leq 15^\circ \Sigma^{-5/6}$ displayed low resistance to both boron segregation and carbide precipitation.

(h) General boundaries displayed low resistance to both boron segregation and carbide precipitation.

3. GBE™ Alloy 304 displayed higher resistance to both intergranular boron segregation and intergranular carbide precipitation than CP Alloy 304. The higher resistance of the GBE™ material to both intergranular boron segregation and intergranular carbide precipitation was likely due to the higher frequencies of low-$\Sigma$ boundaries in the grain boundary character distribution, primarily coherent $\Sigma 3$ twin boundaries and $\Sigma 9$ boundaries satisfying the Palumbo-Aust criterion.
7. Recommendations For Future Work

Recommendations for future work include:

1. Investigating the effects of variables such as bulk boron concentration and bulk carbon concentration on the boron segregation susceptibility at grain boundaries in Alloy 304.

2. Conducting similar SIMS and OIM studies on other related materials such as nickel-based alloys.
Appendix

Warrington and Boon (1975) demonstrated that the random probability of occurrence (p) for any CSL grain boundary can be determined through consideration of (1) the number of equivalent rotations (n) leading to the same CSL (i.e., multiplicity) and (2) the angular deviation limit (Δθ) imposed on the CSL. The number of equivalent rotations (n) is given by,

\[ n = 24w, \]

(1)

where w is the number of distinct crystallographic forms for each CSL. Table A shows the n values for Σ=1 to 29 derived from the tabulated data of Mykura (1979). As shown in Table A, the multiplicity of CSL boundaries tends to increase with increasing Σ value.

Table A. Multiplicity of CSLs (n) from Σ=1 to 29 (Mykura, 1979).

<table>
<thead>
<tr>
<th>Σ Value</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
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<table>
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<tr>
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<tr>
<td>27</td>
<td>864</td>
</tr>
<tr>
<td>29</td>
<td>720</td>
</tr>
</tbody>
</table>

Warrington and Boon (1975) showed that the probability of a boundary lying within an angular deviation limit of Δθ (rad) from any given CSL can be determined by considering the radial density distribution resulting from spheres of radius Δθ(CSL range)
and $180^\circ$(total distribution). The probability ($P$) of a boundary lying within an angular radius of $\Delta \theta$ is given by

$$P = \frac{(\Delta \theta - \sin \Delta \theta)}{\pi}. \quad (2)$$

The random probability of occurrence ($p$) for any CSL is thus given by,

$$p = nP. \quad (3)$$

Using this analysis and an approximation of Brandon's criterion (i.e., $\Delta \theta \leq 0.25 \Sigma^{-1/2}$ rad) Warrington and Boon (1975) calculated the probabilities of CSLs in the range of $\Sigma=1$ to 25. In this study the probabilities of CSLs were recalculated using the actual form of Brandon's criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{-1/2}$) and the Palumbo-Aust criterion (i.e., $\Delta \theta \leq 15^\circ \Sigma^{-5/6}$) and extended to $\Sigma=29$. Table B shows the probabilities of CSLs in the range of $\Sigma=1$ to 29 using Brandon's criterion and the Palumbo-Aust criterion.

Table B. Random probability ($p$) for specific CSLs in the range of $\Sigma=1$ to 29 using Brandon's criterion and the Palumbo-Aust criterion.

<table>
<thead>
<tr>
<th>$\Sigma$ Value</th>
<th>Brandon</th>
<th>Palumbo-Aust</th>
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<tbody>
<tr>
<td>1</td>
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<td>2.28</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
<td>15</td>
<td>0.94</td>
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References


Bruemmer S.M., Corrosion, 42, 1 (1986), 27.


Ishida Y. and M. McLean, Phil. Mag., 27 (1973), 1125.


