Effects of Grain Boundary and Triple Line Structures on Carbide Precipitation in Type 304L Stainless Steel

By

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A thesis submitted in accordance with the requirements for the degree of Master of Applied Science, in the Department of Metallurgy & Materials Science, University of Toronto

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ABSTRACT

Type 304L stainless steel samples, solution treated and annealed at different sensitization temperatures, were used to investigate the correlation between carbide precipitation and grain boundary (GB) and triple line (TL) structure. The Orientation Imaging Microscopy (OIM™) technique was employed in measuring the crystallographic parameters of the samples. Grain boundaries were characterized using (1) the coincident site lattice/displacement shift complete (CSL/DSC) model, and (2) the coincident axial direction/plane matching (CAD/PM) model. In addition, the Brandon criterion and the Palumbo-Aust criterion were used to obtain the allowable deviation from the exact CSL misorientations. The models used to characterize triple lines were (1) Bollmann’s disclination model, (2) the Palumbo-Aust CAD model, (3) the CSL/GB model and (4) the CAD/GB model.

Using the CSL/DSC model, it was found that more than 90% of special GBs (Σ≤29) and only about 20% of general GBs exhibited immunity to carbide precipitation. The upper limit of the low angle boundary for this material was found to be between 10° and 15°. GB carbide precipitation showed no correlation with the CAD/PM model. For Bollmann’s disclination model, the percentage of special TLs (I-lines) immune to carbide precipitation, increased from 35% to 80%, when the heat treatment approached the ideal selective condition, while more than 80% of general TLs (U-lines) exhibited susceptibility to carbide precipitation regardless of the sensitization conditions. Carbide precipitation was observed in all general TLs characterized by the CAD/GB model. No clear correlation between precipitation and triple line structure as per the CSL/GB and CAD models was found.
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List of Acronyms

EBSD Electron Back Scattered Diffraction
SGBD Secondary Grain Boundary Dislocation
OIM Orientation Imaging Microscopy
TL / GB Triple Line / Grain Boundary
CSL / DSC Coincident Site Lattice / Displacement Shift Complete
CAD / PM Coincident Axial Direction / Plane Matching
NNR Nearest Neighbor Relation
SS Stainless Steel
GBCD Grain Boundary Character Distribution

List of Symbols

A Orientation matrix of a grain
M Misorientation matrix of a GB
R_a, R_b and R_c Rotation matrices describing GB misorientations
N_a, N_b and N_c Matrices describing GB misorientations in terms of the nearest-neighbor relation
θ [uvw] Angle-axis pair description of GB misorientation, where [uvw] is the Miller index of the axis and θ is the rotation angle around it
Σ Volume ratio of the CSL unit cell to that of the lattice unit cell
Π Equal to h^2 + k^2 + l^2, where [hkl] are the Miller indices of the plane normal common to two or three adjoining grains
ϕ_1, ϕ_2 and ϕ_3 Euler angles in Bunge’s notation
Chapter 1    Introduction

Most metallic materials used in engineering applications are composed of grains separated by grain boundaries. Hall [1951] and Petch [1953] demonstrated the well-known effect of grain boundaries on bulk mechanical properties in steels: a linear relationship between the flow-stress and reciprocal square-root of grain size. Earlier, Hargreaves and Hills [1929] proposed that different structures could exist for different grain boundaries in metals. These structure differences could lead to different grain boundary properties, such as their energy [Aust and Chalmers, 1952]. A breakthrough in grain boundary structure studies was made after Kronberg and Wilson [1949] indicated the importance of the concept of a coincident site lattice (CSL), whereby at certain crystallographic misorientations a three-dimensional lattice could be constructed with lattice points common to both adjacent grains. One of the earliest studies based on the CSL model [Aust and Rutter, 1959] showed that grain boundaries associated with CSL may display less susceptibility to impurity segregation and higher mobility. Many studies [e.g. Chadwick and Smith, 1976; Erb et al., 1982] demonstrated that boundaries associated with CSLs possess low energy and high resistance to intergranular corrosion.

To take advantage of the beneficial properties (e.g. reduced susceptibility to interfacial segregation and corrosion) possessed by CSL boundaries, Watanabe [1984] introduced the concept ‘grain boundary design and control’, in which he proposed that the bulk properties of materials could be improved by controlling the grain boundary structure distribution. Many recent studies have demonstrated the feasibility of this concept [e.g., Palumbo et al., 1997, 1998].
To explain the observation of intrinsic dislocations in boundaries which were outside the range commonly accepted by a CSL description, the coincident axial direction (CAD)/plane matching (PM) theory was introduced. The basic concept of the CAD/PM model is that a set of low index atomic planes from each of the adjoining grains may be only slightly misaligned across a boundary. These relatively densely packed planes may relax to form a region of perfect plane matching across the boundary [Pumphrey, 1972, Loberg and Norden, 1976]. In contrast to the CSL model, not much work has been done to correlate the CAD/PM boundary structure with properties.

Early studies on the properties of nano-crystalline materials (grain size ≤ 100 nm) found that their bulk behavior could not be entirely predicted and interpreted from ‘grain boundary’ content considerations. This may be due to the omission of another important intercrystalline element, the triple lines, where three grain boundaries meet. Wang et al. [1997] found that room temperature creep of nanocrystalline nickel electrodeposites is controlled by the grain boundary sliding mechanism and the contribution to the total creep strain due to diffusion along the intercrystalline components (e.g., GBs and TLs) becomes significant only at small grain sizes (< 20 nm). The presence of triple lines has also been found to influence material properties in conventional polycrystalline materials such as diffusion induced grain boundary migration (DIGM) and recrystallization [Hackney, 1988], grain boundary sliding [Miura et al., 1988], intergranular corrosion [Palumbo and Aust, 1988]. Rabukhin [1986] has shown that a polycrystalline wire with triple lines always displays higher ductility and lower strength than a wire without triple lines (bamboo grain structure). With the dramatic increase of the volume fraction as the grain size
decreases into nanometer range [Palumbo et al., 1990], the effect of triple lines on nanocrystalline materials is expected to be significant. The models used in characterizing triple lines are based on similar ideas as for grain boundary models. Details will be given in Section 2.2.

Carbide precipitation in austenitic stainless steels is a well-studied phenomenon [Aborn and Bain, 1931; Kinzel, 1952; Stickler and Vinckier, 1963; Aust, 1969; Cihal, 1984 and Bruemmer, 1989]. However, little work has been done to correlate this phenomenon with the structures of grain boundaries and triple lines. In light of this and the previous studies, the objective of this work is to determine the correlation between (1) carbide precipitation and grain boundary structures, and (2) carbide precipitation and triple line structures in Type 304L stainless steel.

The following is the organization of this thesis. Chapter 2 gives background information and an overview on carbide precipitation in Type 304L stainless steel, grain boundary models and triple line models. Chapter 3 describes the experimental procedures and orientation imaging microscopy (OIM™), the technique used in this study to measure the crystallographic parameters associated with grain boundaries and triple lines. Chapter 4 presents the results and discussion of this work. The conclusions are presented in Chapter 5, and recommendations for future work are given in Chapter 6.
Chapter 2  Literature Review

§ 2.1  Grain Boundaries

A grain boundary (GB) can be regarded as the region where two crystals, differing only in orientation, are in contact with each other [Gleiter and Chalmers, 1972]. There are eight degrees of freedom, three microscopic and five macroscopic, describing a pair of grains joining at a grain boundary. The three microscopic degrees of freedom refer to atomic-level translations of the two grains at the boundary. These translations, both parallel and perpendicular to the boundary surface, act so as to minimize the grain boundary energy. Since they are not measurable using standard techniques (e.g. EBSD-electron back scattered diffraction), they are usually not considered in GB studies [Randle, 1996].

Among the five macroscopic degrees of freedom, three characterize completely the misorientation between the two adjacent grains at a grain boundary; the other two describe the orientation of the grain boundary plane.

2.1.1 Representation of Grain Boundary Misorientation

The crystallographic structure associated with the GB is often referred to as its geometry. Most commonly GB geometry is approached from the standpoint of the misorientation of the two adjoining lattices since this is a relatively easy parameter to measure; three macroscopic degrees
of freedom define the misorientation. The orientations of two contiguous grains, $A_1$ and $A_2$, are measured relative to the same reference system using a standard technique such as electron back scattered diffraction (EBSD) [see section 3.2.1]. The misorientation $M$ between two grains is then given by

$$M = A_2 * A_1^{-1}$$

(2.1)

Often the misorientation is expressed as a $3 \times 3$ matrix which has the advantage of mathematical manipulation although it overdefines the misorientation since nine numbers are used to define three degrees of freedom. The angle-axis pair, i.e. $\theta[u \ v \ w]$, is the more economical expression of misorientation, where $[u \ v \ w]$ is the index of the invariant direction of the transformation (rotation axis) and $\theta$ is the rotation angle. The conversion between the two expressions is given elsewhere [Grimmer, 1974, Mykura, 1979].

2.1.2 The CSL/DSC Model

As a result of a study of secondary recrystallization in copper, Kronberg and Wilson [1949] first proposed the concept of coincident site lattice (CSL) boundaries. The CSL is a three-dimensional lattice constructed with lattice points common to both adjoining crystals at certain misorientations. The volume ratio of the unit cell of the CSL to that of the crystal is described by the parameter $\Sigma$, which can also be considered the reciprocal density of CSL points. Figure 2.1 is a schematic representation of the CSL geometry for a $\Sigma 5$ interface formed by a $36.87^\circ [100]$ misorientation of two adjoining lattices. Although all grain boundaries can be represented by an appropriate CSL description if $\Sigma$ is allowed to approach infinite values [Warrington, 1979], $\Sigma$ may achieve very high values of questionable physical significance. Watanabe [1985] suggested the
upper limit for 'special 'properties associated with the low \( \Sigma \) CSL boundaries to be \( \Sigma 29 \), which appears to be in agreement with experimental observations [Shvindlerman and Straumal, 1985; Aust et al., 1993].

![Schematic representation of the CSL geometry for a \( \Sigma 5 \) interface formed by a 36.87° [100] misorientation of two adjoining lattices [Aust, 1994]](image)

**Figure 2.1** Schematic representation of the CSL geometry for a \( \Sigma 5 \) interface formed by a 36.87° [100] misorientation of two adjoining lattices [Aust. 1994]

### 2.1.2.1 The DSC Lattice

The CSL model would be of limited interest if grain boundary specific characteristics were only observed for exact CSL misorientations. In fact, many properties of special grain boundaries are preserved for small angle deviations from the precise CSL misorientations. Thus the requirement for CSL analysis in polycrystals is to identify all misorientations which are 'close to' CSLs (up to a predetermined \( \Sigma \) value, say 29) in terms of an angular deviation. These small angular deviations from exact low \( \Sigma \) CSL misorientations can be described as being accommodated by translations of
one lattice relative to the other, conserving the periodicity of the exact CSL [Grimmer et al., 1974]. The resulting dislocations are termed ‘secondary grain boundary dislocations’ (SGBDs). The Burgers vectors of the SGBDs comprise the Displacement Shift Complete (DSC) lattice (Figure 2.2) [Bollmann, 1970]. The DSC lattice is only dependent on the misorientation of the two adjoining lattices, and can be considered the reciprocal lattice of the CSL [Grimmer, 1974] with a unit cell volume proportional to $\Sigma^{-1}$ [Grimmer et al., 1974].

Figure 2.2   CSL-DSC description of a grain boundary deviating from the exact $\Sigma5$ interface [Aust, 1994]
2.1.2.2 Allowable Deviations from Exact CSL Misorientations

The maximum allowable deviation, \( \Delta \theta_m \), beyond which the special properties of a grain boundary are lost, equates in physical terms to the maximum conservation of the CSL by secondary dislocations.

Several semi-empirical criteria have been proposed to estimate \( \Delta \theta_m \). All of them are extrapolations of the well-known Read and Shockley [1950] relation which links the dislocation spacing \( d \) in the low angle boundary with Burgers vector \( b \) and the angular misorientation \( \theta_{\text{low}} \):

\[
\theta_{\text{low}} = \frac{b}{d} \tag{2.2}
\]

Unlike low angle boundaries where the deviation is accommodated by primary lattice dislocations, i.e. \( b \) is a lattice translation vector, the deviation from a CSL misorientation is accommodated by DSC lattice dislocations, i.e. \( b_{\text{DSC}} \) is a translation vector of the DSC lattice [Warrington et al., 1974, Bollmann, 1974, Ishida et al., 1974]. Hence,

\[
\Delta \theta_m = \frac{b_{\text{DSC}}}{d} \tag{2.3}
\]

Pumphrey [1976] expected that \( d \) should be in the order of the boundary periodicity \( p \), i.e. \( p \propto d \).

Unfortunately it is impossible to give a general expression for \( \Delta \theta_m \) as a function of \( \Sigma \) since the CSL model does not take into consideration the GB plane orientation; \( p \) and \( b_{\text{DSC}} \) depend upon the choice of the GB plane. However, the mean value of \( p \) can be considered to be proportional to the edge of the CSL cell. Since \( \Sigma \) represents the relative volume of the CSL cell, it yields

\[
p \propto d \propto \Sigma^{1/3} \tag{2.4}
\]

On the other hand, \( b_{\text{DSC}} \) is expected to be proportional to the mean edge of the DSC cell; the volume of the DSC cell is proportional to \( \Sigma^{-1} \). Thus,
\( b_{\text{DSC}} \propto \Sigma^{-1/3} \)  

(2.5)

It follows that

\[ \Delta \theta_m = \theta_0 \Sigma^{-2/3} \]  

(2.6)

where \( \theta_0 \) is a constant independent of the misorientation [Deschamps et al., 1987]. If the validity limit of Read-Shockley model is taken, as \( \theta_0 = 15^\circ \), it follows that \( \Delta \theta_m = 15^\circ \) for a \( \Sigma 1 \) (low angle) grain boundary.

The criterion can be adjusted according to the GB conditions. For a \(<100>\) twist GB, \( p \propto \Sigma^{1/2} \) and \( b_{\text{DSC}} \propto \Sigma^{-1/2} \) since \( b_{\text{DSC}} \) lies in a boundary plane perpendicular to a \(<100>\) misorientation axis. Hence

\[ \Delta \theta_m = \theta_0 \Sigma^{-1} \]  

(2.7)

as was first proposed by Ishida and McLean [1973]. The universally adopted Brandon criterion [Brandon, 1966], i.e.

\[ \Delta \theta_m = \theta_0 \Sigma^{1/2} \]  

(2.8)

was the result of taking only the boundary periodicity, i.e. \( p \propto \Sigma^{1/2} \) into account.

As demonstrated by Grimmer, Bollmann and Warrington [1974], \( b_{\text{DSC}} \) can break down into three components such that two of them vary as \( \Sigma^{-1/2} \); the third is independent of \( \Sigma \) and varies only as the interplanar spacing along the rotation axis. Thus, \( p \propto \Sigma^{1/3} \) and \( b_{\text{DSC}} \propto \Sigma^{-1/2} \) which gives

\[ \Delta \theta_m = \theta_0 \Sigma^{-5/6} \]  

(2.9)

This criterion was proposed by Palumbo and Aust [1990b] and proved to be the most consistent with experimental observations [Pan et al., 1996, Palumbo et al., 1998]. Figure 2.3 correlates
these four criteria with the observation of intergranular corrosion of 99.999% pure polycrystalline Ni in 2N H₂SO₄. The experimental points represent the maximum deviation Δθₘ for GBs with respect to intergranular corrosion. All GBs below these points were found to be immune to intergranular corrosion; all GBs above these points were susceptible to intergranular corrosion. It is obvious that the criterion with the best fit of experimental data is the Palumbo-Aust criterion, i.e. Δθₘ = θ₀ Σ⁻⁵/₆.

Figure 2.3  Maximum deviation angle (Δθ) from any exact CSL (Σ) in 99.999% Ni displaying selective immunity to intergranular corrosion in 2N H₂SO₄ [Palumbo and Aust, 1990b]
2.1.3 The Coincident Axial Direction (CAD)/Plane Matching (PM) Model

It has been proposed by Pumphrey [1972, 1976] that when a set of low index atom planes are only slightly misaligned across a boundary, these planes can relax to form regions of perfect matching.

![Diagram showing plane matching](image)

Figure 2.4 The accommodation of the misorientation of a set of low index planes for (a) tilt and (b) twist misfit [Loberg and Norden, 1973]

Figure 2.4 shows how a set of low index planes may match by accommodating edge and screw dislocations in a tilt and a twist GB, respectively. The idea of planar matching (PM) can alternatively but equivalently be considered from the standpoint of the deviation from parallelism of the plane stack normals, rather than the misorientations across the planes themselves. Thus, the angular deviation from the axis of misorientation, \( l \), between two adjacent grains gives a measure of the deviation from exact matching of plane stacks which are nearly normal to \( l \) in both grains.
This approach to boundary structure is termed the coincident axial direction (CAD) model [Randle et al., 1988]. Such boundaries can be described by a \( \Pi \) value with

\[
\Pi = h^2 + k^2 + l^2
\]

where \([h \, k \, l]\) are the Miller indices of \( l \), i.e. the coincident axial direction.

The CAD/PM model was proposed to account for the observation of intrinsic GB dislocations at GBs far from coincident relationships, yet having Burgers vector equal to those of lattice dislocations [Palumbo and Aust, 1990a]. The model can be considered the one-dimensional limit of the three dimensional CSL. Warrington et al. [1974] have demonstrated that as \( \Sigma \) becomes large, two of the three Burgers vectors, \( b_1 \) and \( b_2 \), defined by the DSC, which vary as \( \Sigma^{-1/2} \), vanish; the third, \( b_3 \) being independent of the \( \Sigma \) value and only affected by the interplanar spacing in the direction of CAD, remains. Ishida and McLean [1977] have shown that the \( \Sigma=31 \) CSL for f.c.c has \( b_1 / b = 0.18 \approx \Sigma^{-1/2} \) while \( b_3 / b = 0.82 \), where \( b \) is the Burgers vector of primary dislocations in a low angle boundary.

The maximum angular deviation from an exact CAD grain boundary can be deduced in a manner analogous to the procedure for CSLs. Because \( b_3 \) approaches the interplanar spacing due to the increase of \( \Sigma \) value, the Burgers vector of SGBDs in a CAD boundary, \( b_{CAD} \) is given by

\[
b_{CAD} = b_3 = a \, \Pi^{1/2}
\]

where \( a \) is the lattice parameter. On the other hand, \( b_1 \) and \( b_2 \) are the Burgers vectors defined by the DSC, and vary as \( b \, \Sigma^{-1/2} \) with large \( \Sigma \) values. Thus, the Burgers vector of SGBDs for a CSL, \( b_{DSC} \), is given by

12
\[ b_{\text{DSC}} = b_1 = b_2 = b \Sigma^{-1/2} \]  

(2.12)

According to Equation 2.2, the maximum deviations from an exact CAD and CSL boundary are proportional to the boundary Burgers vectors, \( b_{\text{CAD}} \) and \( b_{\text{DSC}} \), respectively. It yields

\[ \frac{\Delta \theta_{\text{CAD}}}{\Delta \theta_m} = \frac{b_{\text{CAD}}}{b_{\text{DSC}}} = a \Pi^{-1/2} / b \Sigma^{-1/2} \]  

(2.13)

where \( \Delta \theta_{\text{CAD}} \) and \( \Delta \theta_m \) are the CAD and CSL deviation limits, respectively. By substituting the Brandon criterion for \( \Delta \theta_m \), the maximum angular deviation for a CAD is

\[ \Delta \theta_{\text{CAD}} = \theta_0 (a/b) \Pi^{-1/2} \]  

(2.14)

where \( \theta_0 \) is the angular limit for a low angle GB (15°). For face-centered-cubic (f.c.c.) materials, the appropriate value of \( a/b \) is 1.35 [Warrington et al., 1975].

§ 2.2 Triple Lines

Triple lines (TLs), or triple junctions, are intersection lines of three grain boundaries. When boundaries meet together in polycrystalline materials, there is a connectivity among them which means that the misorientations from adjoining grains around a triple line are not independent. The connectivity relationship among three adjoining grains is given by

\[ R_c R_b R_a = I \]  

(2.15)

where \( R_a \), \( R_b \) and \( R_c \) are the rotation matrices describing the misorientations between adjoining grains and \( I \) is the identity matrix [Randle, 1993]. Four models used to characterize the triple line are presented in the following sections.
2.2.1 Bollmann's Disclination Model

This model classifies triple lines into two categories: triple lines where the dislocation balance is satisfied, and triple lines where it is not. The former is called I-line; the latter is called U-line. Clarebrough and Forwood [1987] analyzed an I-line by transmission electron microscopy (TEM) and found that a dislocation balance occurred at the triple line.

In order to calculate the dislocation structure of a boundary between two adjoining grains by means of the O-lattice method [Bollmann 1972, 1982], an expression is needed which represents the nearest-neighbor relation (NNR), the minimum displacement between the two adjoining grains. The NNR yields the dislocation network with the widest possible dislocation spacing and, hence, the lowest energy. The dislocation balance of the so determined boundary networks is always satisfied. This means that, within the boundary between two perfect crystals, no dislocations are created or lost and Frank’s node condition is satisfied in every dislocation node (Bollmann, 1989). Nonetheless, the dislocation balance of the so determined dislocation networks around a triple line does not always occur.

The general idea of the model is schematically shown in Figure 2.5. The rotation matrices \( R_a \), \( R_b \) and \( R_c \) are the conventional representations of grain boundaries between grains 1 and 2, grains 2 and 3 and between grains 3 and 1, respectively; they are obtained directly from the experimental measurements and usually do not represent the NNR. Using these representations of GBs, the sequence around the triple line always leads to the identity matrix.

\[
T = R_c \cdot R_b \cdot R_a = I
\]  

(2.16)
To solve this problem, the boundary representations $R_a$, $R_b$, and $R_c$ have to be converted into the NNR representations, $N_a$, $N_b$, and $N_c$, respectively. Thus, the unit cell representations of grains 1, 2, and 3 are converted into $X_1$, $X_2$, and $X_3$ through unimodular transformation $U_a$, $U_b$, and $U_c$. 

Figure 2.5  Schematic illustration of Bollmann's disclination model
respectively to obtain the NNR between adjoining grains. Consequently, the sequence around the triple line becomes,

\[ T = N_e \cdot N_b \cdot N_a = U_e \cdot U_b \cdot U_a \] (2.17)

If \( T \) equals to identity, the triple line is classified as I-line; otherwise it is classified as U-line. The details for determining the NNR are given elsewhere [Bollmann, 1988]. \( T \) is a tensor of rank 2, a 3x3 matrix. Thus, triple lines in polycrystals can be interpreted as disclinations owing to the fact that a disclination is an oriented line associated with a tensor of rank 2, usually a rotation, while a dislocation is an oriented line with the Burgers vector, a translation with a tensor of rank 1 attributed to it [Kléman, 1980, Bollmann, 1984, 1988, 1990, Müllner, 1999].

An example of triple lines as U-line and I-line in a cubic system is shown in Figure 2.6. The rotation axes for both triple lines are [100]. The rotation sequence (grain 1-2-3-1) of the I-line describing misorientations between adjoining grains is 30°-15°-15°=0° (Figure 2.6 (a)); that of the U-line is 30°+30°+30°=90° (Figure 2.6 (b)). In the case of the I-line, the net rotation sequence is 0°, which means that the rotation (-15°) from grain 3 back to grain 1 leads to the orientation exactly the same as that of grain 1. No dislocation is created or lost after the sequence, or in other words, the dislocation balance is satisfied. However, the net rotation sequence in the U-line is 90°, which means that the final rotation (30°) from grain 3 back to grain 1 leads to an orientation 90° different from that of grain 1. Therefore, there is a virtual boundary (v.b.) within grain 1. Since a 90° rotation is a symmetrical operation, this virtual boundary cannot be observed, but it is a means of 'book-keeping', identifying that the dislocation balance is not satisfied in the triple line. This imbalance results in line tension, thus high energy in the U-line, leading to susceptibility to degradations such as corrosion and cracking [Bollmann, 1984, 1989, 1991].
(a) I-line with the rotation sequence 30°-15°-15° around [100] axis

(b) U-line with the rotation sequence 30°+30°+30° around [100]

Figure 2.6 Example of (a) I-line and (b) U-line in a cubic system with the rotation sequence from grain 1 to 2 to 3 and back to 1 [Bollmann, 1984]
2.2.2 The Palumbo-Aust CAD Model

This model was proposed by Palumbo and Aust [1990a] to consider the periodicities which may exist when (a) the dislocation balance of adjoining GBs cannot occur (i.e., Bollmann's U-lines), and (b) adjoining interfaces cannot be described by a low \( \Sigma \) CSL relationship. This is the extension of the CAD/PM grain boundary model. When the atomic planes with low index \( \{h k l\} \) are only slightly misaligned across the three adjoining lattices, these planes can relax to form regions of perfect matching, upon which is superimposed an array of intrinsic dislocations, and a one-dimensional periodicity proportional to the interplanar spacing \( (d_{hk\bar{l}}) \) is achieved along the triple line (Figure 2.7). Likewise, such triple lines can be described by a \( \Pi \) value with

\[
\Pi = h^2 + k^2 + l^2
\]  

(2.18)

where \( \{h k l\} \) is the index of the CAD. If several low index axes common to three grains (CAD) are possible, the one with the lowest \( \Pi \) value will be chosen.

The angular deviation limit for a CAD triple line is given by

\[
\Delta \theta_{\text{CAD}} = \theta_0 (a/b) \Pi^{1/2}
\]  

(2.19)

where \( \theta_0 \) is the angular limit for a low angle GB (15°), \( a \) is the lattice parameter and \( b \) is the Burgers vector of primary dislocations in a low angle GB. For f.c.c. materials, the appropriate value of \( a/b \) is 1.35 [Warrington et al., 1975].
Figure 2.7  Schematic representation of the continuity of a set of low index planes with the plane normal \([hkl]\), the coincident axial direction (CAD), across a triple line [Palumbo and Aust, 1990a].

2.2.3 The CSL/GB Model

This is the extension of the CSL model. Since the triple line is the line where three boundaries meet, Doni et al. [1988] proposed that triple lines can be defined by the CSL classification of the three adjoining boundaries. Triple lines can then be classified into four groups: a) lines with three CSL boundaries, b) lines with two CSL and one random boundaries, c) lines with one CSL and two random boundaries and d) lines with three random boundaries [Kurzydlowski, et al., 1993]. Triple lines in group a) may be called CSL or special triple lines; those in group d) may be called random triple lines. In the case of groups b) and c), they may be called mixed triple lines.
In the case of CSL or special triple lines, the geometric restriction of a triple line results in the following relationship of $\Sigma$ values among the three adjoining grains:

$$\Sigma_3 = \Sigma_2 \cdot \Sigma_1$$  \hspace{1cm} (2.20)

or

$$\Sigma_3 = \frac{\Sigma_2}{\Sigma_1}$$  \hspace{1cm} (2.21)

if $\Sigma_2$ and $\Sigma_1$ have a common factor. Here $\Sigma_1$, $\Sigma_2$ and $\Sigma_3$ refer to the $\Sigma$ values of GB 1, 2 and 3, respectively [Palumbo et al, 1992, Randle, 1994].

2.2.4 The CAD/GB Model

In this work, a new model was introduced to explore triple lines. The idea of this model is the same as that of the CSL/GB model. The only difference is that the adjoining GBs around a triple line were characterized by the CAD/PM grain boundary model. Likewise triple lines are classified into four groups: a) lines with three CAD boundaries, b) lines with two CAD and one random boundaries, c) lines with one CAD and two random boundaries and d) lines with three random boundaries. Triple lines in group a) may be called special triple lines; those in group d) may be called random triple lines. In the case of group b) and c), they may be called mixed CAD triple lines.
§ 2.3 Intergranular carbide precipitation in Type 304L stainless steel (SS)

Carbide precipitation occurs readily in the 300 series stainless steels due to the low solid solubility of carbon. Rapid cooling from high temperature will trap an excess or supersaturated amount of carbon, which can then precipitate during lower temperature annealing. Experimental measurements on extracted carbides in 300 series stainless steels have shown that the dominant carbide is the f.c.c chromium-rich M_{23}C_6 [Cihal and Jezek, 1964; Leonard, 1969]. The precipitation of M_{23}C_6 carbides on grain boundaries promotes the development of an adjacent region depleted in chromium. Depletion occurs in a temperature range where carbides are thermodynamically stable and chromium diffusion is sufficiently rapid for carbide nucleation and growth in a finite time frame. The chromium depletion results in susceptibility to intergranular corrosion [Bain et al., 1933].

Carbide precipitation in the 300 series stainless steels depends highly on the heat treatments. In their studies, Aust et al. [1966, 1968,1969] found that there is no carbide precipitation at grain boundaries in Type 304 SS after a solution heat treatment, i.e. 2 hour at 1050°C and water quenched, and the amount and morphology of carbide precipitates can be controlled by subsequent heat treatments. A typical method of describing heat treatment effects on carbide precipitation is by a time-temperature-precipitation (TTP) diagram. Figure 2.8 is a TTP diagram, illustrating precipitation behavior and showing susceptibility of various grain boundaries to carbide precipitation in Type 304 SS [Stickler et al., 1961].
Figure 2.8  Time-Temperature-Precipitation curves for carbides in Type 304 SS [Stickler and Vinckier, 1961].

Grain boundary structure is an important factor in carbide precipitation. Previous studies have shown that boundary properties such as corrosion, mobility, diffusivity and resistivity are highly dependent on the boundary structure in general [e.g. Aust et al, 1993, 1996; Palumbo et al. 1990b, 1995, 1998]. Therefore, it is expected that there is likely a correlation between carbide precipitation and grain boundary structure for boundaries other than coherent and incoherent twin boundaries (Figure 2.8). Furthermore, triple lines have been shown to have unique structure [e.g. Bollmann, 1988; Doni et al., 1988; Palumbo and Aust, 1989]. This fact leads to the expectation that there would also be a correlation between carbide precipitation and triple line structure.
Chapter 3 Experimental Procedure

§ 3.1 Experimental Strategy

Selectivity is the key issue in correlating carbide precipitation with GB and TL structures in the present work. Thus, the design of the experiments was focused on how to promote selective carbide precipitation along grain boundaries and triple lines. In principle, the lower the carbon content, the more selective the carbide precipitation in austenitic stainless steels. Owing to the fact that Type 304L SS has lower carbon content than Type 304 SS, the former was chosen to be the material used in the present work, although the latter was much more thoroughly studied in terms of carbide precipitation [e.g. Stickler and Vinckier, 1961; Aust et al., 1966]. The nominal chemical composition of these two materials is listed in Table 1. They are almost the same except the carbon content. Therefore, the results of previous studies for Type 304 SS were used as a guidance in designing the experiments in the present work.

It is important to obtain GBs and TLs free of carbides before the precipitation treatments. Aust et al. [1966] demonstrated that no carbide was observed at GBs in Type 304 SS after annealing at 1050 °C for two hours followed by water quenching. The carbide precipitates in Type 304L SS are likely to dissolve into the matrix under the same condition because of the lower carbon content. Therefore, this condition was taken as the solution treatment for Type 304L SS in the present work.
With the guidance of the time-temperature-precipitation curve for Type 304 SS (Figure 2.8), the precipitation treatments in the present work were designed in a hope that varying amounts of carbide precipitates with different degrees of selectivity would be obtained in different samples. This difference in the precipitate amount would give the possibility to explore the structure-property correlation in terms of selectivity.

Table 1: Nominal chemical composition (wt. %) of Type 304 SS and Type 304L SS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 304L SS</td>
<td>≤0.03</td>
<td>18.0-20.0</td>
<td>8.0-12.0</td>
<td>≤1.00</td>
<td>≤2.00</td>
<td>≤0.045</td>
<td>≤0.03</td>
<td>Bal.</td>
</tr>
<tr>
<td>Type 304 SS</td>
<td>≤0.07</td>
<td>18.0-20.0</td>
<td>8.0-10.5</td>
<td>≤1.00</td>
<td>≤2.00</td>
<td>≤0.045</td>
<td>≤0.03</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

§ 3.2 Sample Preparation

The material used in this work is commercial Type 304L stainless steel (SS). Samples were cut from bulk Type 304L SS with a size about 6 × 6 × 2 (mm³). All samples were first solution treated, i.e., annealed at 1050 °C for two hours followed by water quenching to eliminate residual carbides in the GBs and triple lines. Some of the samples were then given different sensitization heat treatments to induce varying amounts of carbide precipitation at GBs and triple lines. Thus, there are two groups of samples: those only with solution treatment (Table 2) and those with solution and sensitization treatment (Table 3). The samples in the former group were used to examine the effect of the solution treatment on the intergranular corrosion, while the samples in
the latter group were for investigating the carbide precipitation at GBs and triple lines. All the heat treatments were conducted in argon atmosphere.

Table 2: The samples only with solution treatment (ST)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ST1</th>
<th>ST2</th>
<th>ST3</th>
<th>ST4</th>
<th>ST5</th>
<th>ST6</th>
<th>ST7</th>
<th>ST8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treatment</td>
<td>2 hrs @ 1050° C and WQ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: The samples with solution and sensitization treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Step1</th>
<th>Step 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 hrs @ 1050° C and WQ</td>
<td>30 minutes @800° C and WQ</td>
</tr>
<tr>
<td>2</td>
<td>2 hrs @ 1050° C and WQ</td>
<td>20 minutes @800° C and WQ</td>
</tr>
<tr>
<td>3</td>
<td>2 hrs @ 1050° C and WQ</td>
<td>10 minutes @780° C and WQ</td>
</tr>
</tbody>
</table>

After heat treatment, samples were ground using silicon carbide grinding paper from 400 up to 2400 grade. They were then mechanically polished using alumina with a particle size of 3 μm to 0.05 μm. The polished surfaces were then cleaned using ethanol to eliminate residual alumina particles. Subsequently, the samples were electro-polished to obtain a deformation-free surface.

The samples only with solution treatment were etched under different conditions to examine the effect of carbide dissolution on the intergranular pitting (Table 4). For the samples with solution and sensitization treatments, the etching condition was chosen because under this condition, a selective pitting occurred at GBs and triple lines and pitting sizes were easy to observe. Also the surface condition of the samples after etching under this condition was good enough to give strong diffraction pattern, which is important in the subsequent orientation measurement (Table 5). The composition of the solutions used for electro-polishing and etching throughout the experiments were
for electro-polishing: 5% (volume) percholic acid (70%) + 95% pure ethanol [Kurban, 1999];
for electro-etching: oxalic acid : water = 1(g) : 10(ml) [ASM, 1985].

Table 4: Polishing and etching parameters of the samples with solution treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>ST1</th>
<th>ST2</th>
<th>ST3</th>
<th>ST4</th>
<th>ST5</th>
<th>ST6</th>
<th>ST7</th>
<th>ST8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polishing current density (A/cm²)</td>
<td>2.3</td>
<td>2.27</td>
<td>2.41</td>
<td>2.31</td>
<td>2.49</td>
<td>2.28</td>
<td>2.51</td>
<td>2.19</td>
</tr>
<tr>
<td>Polishing time and temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45 sec @-20 ºC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Etching voltage (V)</td>
<td>3.6</td>
<td>3.6</td>
<td>6</td>
<td>12</td>
<td>18</td>
<td>24</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>Etching time at room temperature (s)</td>
<td>60</td>
<td>120</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 5: Polishing and etching parameters of the samples with solution and sensitization treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electro-polishing</th>
<th>Electro-etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.25 A/cm², 45 sec @-20 ºC</td>
<td>3.6 V, 60sec @25 ºC</td>
</tr>
<tr>
<td>2</td>
<td>2.4 A/cm², 45 sec @-20 ºC</td>
<td>3.6 V, 60sec @25 ºC</td>
</tr>
<tr>
<td>3</td>
<td>2.35 A/cm², 45 sec @-20 ºC</td>
<td>3.6 V, 60sec @25 ºC</td>
</tr>
</tbody>
</table>
§ 3.3 Analysis of Crystallographic Orientations

3.2.1 The Electron Back Scattered Diffraction (EBSD) Patterns

Grain orientations were obtained from analysis of EBSD patterns, using the Orientation Imaging Microscopy (OIM\textsuperscript{TM}) technique. When a electron beam hits a specimen, a large number of scattered electrons are generated, some of which interact elastically with the atomic planes in the crystal in all directions. There are always some scattered electrons which satisfy Bragg’s condition given by

\[ 2d_{hkl} \sin \theta_B = n\lambda \]  \hspace{1cm} (3.1)

where \( d_{hkl} \) is the interplanar spacing for a family of planes, \{hkl\}, \( \lambda \) is the electron wavelength, n is the order of the reflection, and \( \theta_B \) is Bragg’s angle. In addition to the elastic scattering, many electrons are scattered inelastically and give rise to a diffuse background in a diffraction pattern.

When Bragg’s condition is satisfied, electrons are diffracted through the Bragg’s angle, forming two cones called Kossel cones from a single set of planes as shown in Figure 3.1. If a flat surface such as a phosphor screen is placed to intercept the diffracted beams, the two conic sections will appear as a band of two lines known as Kikuchi lines. Since the Bragg angles are very small (typically about 0.5°) as a result of the short wavelength used, the sections appear as sets of parallel lines rather than parabolae on a flat detector. Hence each pair of Kikuchi lines represents a single set of planes in the crystal [Randle, 1992].
The complete Kikuchi pattern is the interaction of the scattered electron beam with all the planes in the crystal (Figure 3.2). By analyzing the Kikuchi pattern, the orientation of the crystal can be determined.

Figure 3.1 Diagram showing the diffracted electrons form Kossel cones centered at P on the diffraction planes (William and Carter, 1996)
3.2.2 Orientation Imaging Microscopy (OIM\textsuperscript{TM}) System

Through generating, analyzing and indexing Kikuchi patterns, OIM\textsuperscript{TM} [TSL, 1996] is capable of automatically measuring orientations of individual grains in an area of interest on a sample and plotting the crystallographic map matching the area. The OIM\textsuperscript{TM} system is composed of a scanning electron microscope (SEM), a low light camera on which a phosphor screen is attached, a camera control unit (CCU), a TV monitor, and a computer to index the EBSD patterns (Figure 3.3).
Figure 3.3 Typical set-up for an OIM system
The sample stage for OIM\textsuperscript{TM} is tilted by 70° to minimize the electron absorption into the lattice, and therefore maximize the amount of scattered electrons into the direction where they are detected. The geometry of sample arrangement with respect to incident electron beam and detector in the OIM\textsuperscript{TM} system is shown in Figure 3.4.

Figure 3.4 OIM system geometry: the relative position of electron beam, detector and sample holder
The Kikuchi patterns are formed on the phosphor screen and captured by the fiber optically linked low light camera. The camera sends the signals to the CCU where it provides video output to the TV monitor for adjusting the pattern quality, and to the computer for indexing the pattern by built-in OIM™ software.

During the automated scan, the system moves the electron beam automatically point by point at a given step size (depending on the grain size) in the area of interest on the sample. At each point, the computer captures and indexes the pattern thereby storing the crystallographic data and the corresponding location. Upon the completion of the scan, the OIM™ software allows the stored data to be presented in many different ways such as pole figures and orientation image map. Figure 3.5 shows (a) a SEM micrograph and (b) the corresponding orientation image map.

3.2.3 Mathematical Considerations in the OIM™

The software in OIM™, written by TSL Co., gives a grain orientation in terms of three Euler angles, \( \varphi_1 \), \( \varphi_2 \) and \( \varphi_3 \), using Bunge's notation [TSL, 1996]. However, for the mathematical manipulation, it is convenient to express the grain orientations as 3x3 matrices, of which the physical meaning may be described as a rotation to bring the crystal axes into parallelism with the sample axes, e.g., the set of Rolling Direction-Transverse Direction-Normal Direction (RD-TD-ND) [see Figure 3.4 and 3.6]. For materials with a cubic crystal structure, the crystal axes are the set of [100]-[010]-[001]. Their geometrical relation is shown schematically in Figure 3.6.
Figure 3.5  SEM micrograph and the corresponding OIM map of Sample 2
Figure 3.6  Schematic illustration of sample axes (RD, TD, ND) and crystal axes ([100],[010], [001]) [Kim, 1999]
Figure 3.7 illustrates schematically the operation to convert an orientation representation from the Euler angles (Bunge’s notation) into a 3x3 matrix. \( \varphi_1 \) is the angle through which the coordinates are rotated along the \( Z \) (001) axis of the crystal axes (system space 1), leading to the matrix \( g_1 \):

\[
g_1 = \begin{pmatrix} \cos \varphi_1 & \sin \varphi_1 & 0 \\ -\sin \varphi_1 & \cos \varphi_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]  

(3.2)

\( \varphi_2 \) is the rotation angle along the \( X' \) axis of the transformed axes (system space 2), leading to the matrix \( g_2 \):

\[
g_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \varphi_2 & \sin \varphi_2 \\ 0 & -\sin \varphi_2 & \cos \varphi_2 \end{pmatrix}
\]  

(3.3)

Likewise, \( \varphi_3 \) is the rotation angle along the \( Z'' \) axis of the transformed axes (system space 3), leading to the sample axes. The corresponding rotation matrix \( g_3 \) is:

\[
g_3 = \begin{pmatrix} \cos \varphi_3 & \sin \varphi_3 & 0 \\ -\sin \varphi_3 & \cos \varphi_3 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]  

(3.4)
Figure 3.7  The Bunge's notation of Euler angles ($\varphi_1, \varphi_2, \varphi_3$) and the rotation operations from the crystal axes to sample axes: $R = g_3 \ast g_2 \ast g_1$
Therefore, the grain orientation

\[
R = g_3 \times g_2 \times g_1 = \begin{pmatrix}
R_{11} & R_{12} & R_{13} \\
R_{21} & R_{22} & R_{23} \\
R_{31} & R_{32} & R_{33}
\end{pmatrix}
\] (3.5)

which is a rotation matrix describing a rotation from the crystal axes to the sample axes. The three column vectors in \( R \), \([R_{11} \ R_{21} \ R_{31}]\), \([R_{12} \ R_{22} \ R_{32}]\) and \([R_{13} \ R_{23} \ R_{33}]\) are the indices of the three crystal axes [100], [010] and [001], respectively in reference to the sample axes.

### 3.2.4 Identification of GBs and TLs

Prior to the OIM analysis, the surface areas of interest were marked using microhardness indentations so that they could be identified quickly in the SEM. The boundaries and triple lines were identified and individualized with numbers by matching the SEM micrographs with the OIM maps (Figure 3.5). A GB was thought to be susceptible to carbide precipitation if more than two pits were observed along the GB. This is simply because there are background pits caused by material imperfections (see Figure 4.1).

Since only the CSL model of GB is incorporated in the current OIM™ software, the raw data of the grain orientations had to be collected for the other models such as CAD/PM model and all models for triple lines. To collect data of grain orientations around a triple line, the sequence should be always anti-clockwise from grain 1 to grain 3 so as to keep a right-hand coordinate system (e.g., Figure 2.6).
Chapter 4  Results and Discussion

§ 4.1  Intergranular Pitting and Carbide Precipitation

Figure 4.1 shows a typical microstructure of an electro-etched sample after the solution heat treatment, i.e. 2hr@1050°C followed by water quenching. The prevailing structure along GBs is the step structure, an indication of the immunity to intergranular attack. There are some pits at the GBs and triple lines, but also pits are inside the grains in Figure 4.1. They are probably randomly distributed pits at some imperfections. Such a kind of microstructure was observed in all solution treated samples under the different etching conditions with the etching time and voltages ranging from 60 to 120 seconds and 3.6 to 36 volts, respectively. On the other hand, all three sensitized samples displayed selective intergranular pitting after being etched in the oxalic acid. Figure 4.2 shows a typical microstructure of this selective intergranular pitting. One can see that some GBs experienced intergranular pitting; others did not. The selectivity was also shown at triple lines.

Since very little intergranular pitting was observed in the solution treated samples (Figure 4.1), whereas a lot of intergranular pitting occurred in the sensitized samples (Figure 4.2), it can be assumed that the mechanism of the intergranular pitting in this work is chromium depletion caused by the chromium-rich carbide precipitates as shown in previous studies [e.g. Aust, 1969]. Thus, the intergranular pitting in this work can be equivalently described as carbide precipitation.
Figure 4.1 Typical SEM micrograph of the etched samples in solution treated conditions
Figure 4.2  Typical microstructure for the sensitized samples in this work: pitting selectivity of grain boundaries (GB) and triple lines (TL)
§ 4.2 Analysis of Data For Various Grain Boundary Models

4.2.1 The CSL/DSC Model

Figure 4.3 presents the correlation between the CSL/DSC model and pitting behavior, using both Brandon criterion (a) and Palumbo-Aust criterion (b) as the allowable deviation from the exact CSL values. For low angle GBs, the deviation upper angular limit was explored by dividing them into two groups: the first with the deviation angle $\theta \leq 10^\circ$ and the second with $10^\circ < \theta \leq 15^\circ$. Carbide precipitation happened exclusively in the second group. This suggests that $15^\circ$ may be too high as the deviation upper angular limit for low angle GBs in this material. The more appropriate value may lie between $10^\circ$ and $15^\circ$.

For high angle GBs, the fraction of special GBs ($\Sigma 3-29$) showing immunity to carbide precipitation is 0.97, 0.91, and 0.96 using Palumbo-Aust criterion, and 0.82, 0.76, and 0.9 using Brandon criterion for samples 1, 2 and 3, respectively. Here, special GBs were classified up to $\Sigma 29$. For the random GBs, that fraction ranges from 0.16 to 0.24 for all samples, using both criteria.

This indicates that all the sensitization heat treatments are in the proper selective region for the GB structure since all the samples displayed a clear selectivity between special and random GBs using both criteria. The Palumbo-Aust criterion shows a better fit with the experimental data than the Brandon criterion, in agreement with previous studies [Pan et al., 1996, Palumbo et al, 1998].
Figure 4.3: Fraction of GBS characterized by the CSE/DSC model with (a) Brandon and (b) Palumbo-Aust criterion, showing immunity to phing in samples 1, 2, and 3.
Table 6 gives the fraction of special GBs showing immunity to intergranular pitting according to their specific $\Sigma$ values. The corresponding significant figures are given in the bracket below the fractions. The graphic presentation of Table 6 is shown in Figure 4.4 and 4.5.

Table 6: Fraction of GBs characterized by the CSL/DSC model, showing immunity to intergranular pitting

<table>
<thead>
<tr>
<th>$\Sigma$ Value</th>
<th>Fraction of GBs immune to pitting using Brandon Criterion</th>
<th>Fraction of GBs immune to pitting using Palumbo-Aust Criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>$\Sigma 1 (0 \leq \Sigma \leq 10)$</td>
<td>1 (5/5)</td>
<td>1 (9/9)</td>
</tr>
<tr>
<td>$\Sigma 1$ *</td>
<td>0.2 (1/5)</td>
<td>0.63 (10/16)</td>
</tr>
<tr>
<td>$\Sigma 3$</td>
<td>0.9 (35/39)</td>
<td>0.88 (57/65)</td>
</tr>
<tr>
<td>$\Sigma 7$</td>
<td>0 (0/3)</td>
<td>0 (0/5)</td>
</tr>
<tr>
<td>$\Sigma 9$</td>
<td>1 (3/3)</td>
<td>1 (3/3)</td>
</tr>
<tr>
<td>$\Sigma 11$</td>
<td>*</td>
<td>0 (0/2)</td>
</tr>
<tr>
<td>$\Sigma 13$</td>
<td>*</td>
<td>0.33 (1/3)</td>
</tr>
<tr>
<td>$\Sigma 15$</td>
<td>*</td>
<td>0.5 (1/2)</td>
</tr>
<tr>
<td>$\Sigma 17$</td>
<td>1 (2/2)</td>
<td>1 (1/1)</td>
</tr>
<tr>
<td>$\Sigma 21$</td>
<td>*</td>
<td>0 (0/1)</td>
</tr>
<tr>
<td>$\Sigma 23$</td>
<td>0 (0/1)</td>
<td>*</td>
</tr>
<tr>
<td>$\Sigma 25$</td>
<td>0 (0/1)</td>
<td>0.5 (1/2)</td>
</tr>
<tr>
<td>$\Sigma 27$</td>
<td>*</td>
<td>0.67 (2/3)</td>
</tr>
<tr>
<td>$\Sigma 3-29$</td>
<td>0.82 (40/49)</td>
<td>0.76 (66/87)</td>
</tr>
<tr>
<td>Random</td>
<td>0.23 (36/155)</td>
<td>0.23 (39/172)</td>
</tr>
</tbody>
</table>

Total number of GBs investigated: 576

*not observed
Figure 4.4 Fraction of GBs with specific Σ values by Brandon criterion, showing immunity to pitting in samples 1, 2 and 3.
Figure 4.5  Fraction of GBs with specific Σ values by Palumbo-Aust criterion, showing immunity to pitting in samples 1, 2 and 3
That some special GBs did not show resistance may be due to the fact that the model does not define the position of the actual GB plane, which can be important in GB properties [Randle, 1994]. A good example for the role of GB plane is the twin boundary. Carbide precipitation usually does not occur at coherent twin boundaries but quite frequently at incoherent twin boundaries [Figure 4.6], although both are Σ3 boundaries. Such a phenomenon was also observed by Trillo and Murr [1998,1999] in their studies of carbide precipitation in Type 304 SS and by Bennett and Pickering [1987] in correlating sensitization behavior of stainless steel with GB structure.

The fraction of Σ3 and Σ9 GBs is predominant within special high angle GBs (Σ3-29) in the Type 304L SS of this work: 0.98 (i.e. 128 out of 131 special GBs) and 0.81 (i.e. 136 out of 167 special GBs) for Palumbo-Aust and Brandon criterion, respectively. The total number of special GBs (Σ3-29) using Palumbo-Aust criterion (i.e. 131) is less than using Brandon criterion (i.e. 167). However, Palumbo-Aust criterion gives higher fraction of Σ3 and Σ9 GBs within special GBs since the more restrictive nature of this criterion excludes almost all special GBs with Σ values, according to Brandon criterion, other than Σ3 and Σ9 (see Table 6). On the other hand, the fraction of Σ3 and Σ9 GBs showing immunity to carbide precipitation is as high as 0.96 (i.e. 123 out of 128 GBs) and 0.89 (i.e. 121 out of 136 GBs) for Palumbo-Aust and Brandon criterion, respectively. This fact supports the idea of a ‘twin-limited microstructure’ as a ultimate strategy for grain boundary engineering (GBETM), where thermomechanical-type processing could produce a microstructure having a CSL distribution consisting entirely of ‘twin related variants’ (Σ3n) (where n=1,2) and possibly some low-angle boundaries (Σ1 GB) [Palumbo et al., 1992].
Figure 4.6  Typical selective pitting behavior of the coherent twin boundaries (CTW) and incoherent twin boundaries (ICTW) in 304L stainless steel of this work
4.2.2 The CAD/PM Model

Figure 4.7 presents the correlation between the CAD/PM model and pitting behavior. The fraction of special GBs showing immunity to carbide precipitation is 0.46, 0.47, 0.47, whereas that of random GBs is 0.15, 0.3, and 0.42 for Sample 1, 2, and 3, respectively. Here, special GBs were classified up to $\Gamma=20$. Although such characterized special GBs do have higher resistance to carbide precipitation, the model did not effectively differentiate special GBs from random GBs in this case.

![Figure 4.7](image)

Figure 4.7 Fraction of GBs characterized by the CAD/PM model, showing immunity to pitting in samples 1, 2 and 3
Table 7 gives the fraction of the special and random GBs characterized by this model, showing immunity to intergranular pitting. The corresponding significant figures are given in the bracket below the fractions. It is interesting to note that using the CAD/PM model, most grain boundaries are special GBs (up to $\Pi=20$) with the fraction of 0.75, 0.80 and 0.85 for samples 1, 2 and 3, respectively (Table 8). Warrington et al. [1975] have calculated the fraction of the special GBs in a randomly oriented f.c.c. polycrystal using the CAD/PM model. According to their calculation the fraction of the special GBs (up to $\Pi=24$) is 0.73. Randle and Ralph [1988] studied the coverage for special GBs using the CAD/PM model. They observed the fraction of the special GBs (up to $\Pi=24$) ranges from 0.63 to 0.76 in different materials with different treatments. All the studies so far show that GBs are highly likely to be characterized as special GBs using the CAD/PM model. This is probably the reason why the model failed to correlate the property of carbide precipitation with GB structure.

Table 7: Fraction of GBs characterized by the CAD/PM model, showing immunity to intergranular pitting

<table>
<thead>
<tr>
<th>GB character</th>
<th>Fraction of GBs immune to pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>Special GBs ($\Pi \leq 20$)</td>
<td>0.46 (74/160)</td>
</tr>
<tr>
<td>Random GBs</td>
<td>0.15 (8/54)</td>
</tr>
<tr>
<td>Total number of GBs investigated:</td>
<td>576</td>
</tr>
</tbody>
</table>


Table 8: Grain boundary character distribution by the CAD/PM model

<table>
<thead>
<tr>
<th>GB character</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Special GBs</td>
<td>0.75 (160/214)</td>
<td>0.80 (227/284)</td>
<td>0.85 (66/78)</td>
</tr>
<tr>
<td>Random GBs</td>
<td>0.25 (54/214)</td>
<td>0.20 (57/284)</td>
<td>0.15 (12/78)</td>
</tr>
</tbody>
</table>

Total number of GBs investigated: 576

§ 4.3 Analysis of Data For Various Triple Line Models

4.3.1 Bollmann’s Disclination Model

Figure 4.8 shows the fraction of I-lines and U-lines in the samples displaying immunity to pitting. In the case of I-lines, the fraction of immunity to carbide precipitation increases from 0.35 in Sample 1 and 0.5 in Sample 2 to 0.8 in Sample 3, whereas that of U-lines is 0.1, 0.11 and 0.19 for samples 1, 2 and 3, respectively.

I-lines are special triple lines with a balanced dislocation network. Thus they are expected to show special properties, such as resistance to carbide precipitation. On the other hand, the structure-property correlation, especially for triple lines, can only be justified when the related phenomenon lies in the appropriate selective region. Beyond this region, it is difficult to make a reliable conclusion. According to the precipitation treatments, it is expected that there are various degrees of carbide precipitation in the three samples with the most in Sample 1 and the least in
Sample 3. In general, the less the carbide precipitation, the higher the selectivity, thus the better correlation between structure and properties. Hence, the structure-property correlation is expected to become better from Sample 1 to 3. This is exactly shown in Figure 4.8. In Sample 3 with the highest selectivity, the fraction of immunity to carbide precipitation of I-lines is as high as 0.8.

Figure 4.8 Fraction of I-lines and U-lines, showing immunity to pitting in samples 1, 2 and 3
According to the model, U-lines are triple lines with line tension, thus high energy. Carbide precipitation is expected to happen preferentially at U-lines. An obvious support for this prediction can be seen in Figure 4.8. In all three samples, the fraction of U-lines showing carbide precipitation (pitting) ranges from 0.81 to 0.9, regardless of the sensitization treatment. Table 9 gives the fraction of the TLs characterized by this model, showing immunity to intergranular pitting. The corresponding significant figures are given in the bracket below the fractions.

Table 9: Fraction of TLs characterized by Bollmann’s disclination model, showing immunity to intergranular pitting

<table>
<thead>
<tr>
<th>TL character</th>
<th>Fraction of TLs immune to pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>I-line</td>
<td>0.35</td>
</tr>
<tr>
<td>(27/77)</td>
<td></td>
</tr>
<tr>
<td>U-line</td>
<td>0.1</td>
</tr>
<tr>
<td>(24/247)</td>
<td></td>
</tr>
</tbody>
</table>

Total number of TLs investigated: 513

This result is in accordance with the observation of Palumbo and Aust [1989]. In their study of corrosion in high purity nickel, they found that the pit initiation starts exclusively at U-lines. When the destabilization potential was increased, the pit initiation occurred at other sites, generally in the order of I-lines, GBs and crystal matrix. Thus a selective condition is essential to observe distinct characteristics of triple lines as well as of GBs.
Figure 4.9  Fraction of triple lines characterized by the CAD model, showing immunity to pitting in samples 1, 2 and 3

4.3.2  The Palumbo-Aust CAD Model

Figure 4.9 gives the correlation between the CAD model on triple lines and the pitting behavior. Those triple lines whose $\Pi$ values are smaller than or equal to 20 were classified as special triple lines, while the others were classified as random triple lines. The fraction of the special triple lines showing immunity to carbide precipitation is 0.13, 0.2 and 0.29 for samples 1, 2 and 3, respectively, while that of random triple lines is 0.16, 0.22 and 0.28 for samples 1, 2 and 3, respectively.
The fraction of the special triple lines showing immunity increases as the degree of carbide precipitating decreases. Nonetheless, the random triple lines behave almost the same way. It seems that this model does not differentiate the special triple lines effectively from the random lines in the case of the carbide precipitation in this material. It may result from the fact that the model requires only one dimensional order, i.e. the periodicity along the CAD, for the triple lines to be classified as special; this may leave the structural difference between the random and special not big enough to distinguish from each other in the case of carbide precipitation.

In his work to correlate the triple line structure with the presence (or absence) of bismuth at triple lines in copper substrate, Fortier [1996] found that classifying special triple lines up to $\Pi=8$ instead of $\Pi=24$ would increase the fraction of special lines showing absence of bismuth, the special property, from 0.27 to 0.56. In the present work, the fraction of the immunity to pitting of the special triple lines up to $\Pi=8$ would be 0.132, 0.2, and 0.286 for samples 1, 2 and 3, respectively. Compared with those up to $\Pi=20$, it does not change much since in all three samples the $\Pi=3$-8 triple lines are predominant in the triple line character distribution up to $\Pi=20$. Therefore, the upper limit of $\Pi$ value in classifying special triple lines seems not to be an important factor in the correlation between the model and carbide precipitation in the samples. Table 10 gives the fraction of the TLs characterized by this model, showing immunity to intergranular pitting. The corresponding significant figures are given in the bracket below the fractions.
Table 10: Fraction of TLs characterized by the Palumbo-Aust CAD model, showing immunity to intergranular pitting

<table>
<thead>
<tr>
<th>TL character</th>
<th>Fraction of TLs immune to pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>Special TLs (Π ≤ 20)</td>
<td>0.13 (5/40)</td>
</tr>
<tr>
<td>Random TLs</td>
<td>0.16 (46/284)</td>
</tr>
<tr>
<td>Total number of TLs investigated:</td>
<td>513</td>
</tr>
</tbody>
</table>

4.3.3 The CSL/GB Model

The correlation between the CSL/GB model and triple line pitting behavior is shown in Figure 4.10. The two criteria, Brandon (BR) and Palumbo-Aust (PA) criteria, were used for allowable deviation from the exact CSL GBs. BR0, 1, 2, 3 and PA0, 1, 2, 3 are the triple lines with 0, 1, 2 and 3 special GBs around them using the BA and PA criteria, respectively. Special GBs were classified up to Σ29.

In his computer simulation of triple lines, Fortier et al. [1995, 1997] found that the higher the number of low Σ GBs around a triple line, the greater its probability to be a I-line. To some extent, this is reflected in Figure 4.10. In samples 1 and 3, BR0 and PA0 triple lines are susceptible to carbide precipitation, whereas BR3 and PA3 triple lines—with the exception that no PA3 triple lines were observed in Sample 3—show the highest fraction of triple lines with pitting immunity. However, triple lines in Sample 2 show no clear-cut tendency. In this sample, the fraction of immune triple lines of BR0 and BR1 type is 0.2 and 0.23, respectively. For BR2 and BR3 triple...
Figure 4.10 Fraction of triple lines characterized by the CSL/GB model, showing immunity to pitting in samples 1, 2 and 3.
lines, the values are 0.18 and 0.22, respectively. The tendency is similar when using the PA criterion; the fractions for PA0, 1, 2 and 3 triple lines in this sample are 0.19, 0.23, 0.14 and 0.25, respectively. As a result, the CSL/GB model for triple lines is not consistent in correlating the structure with the carbide precipitation in this material. Table 11 gives the fraction of the TLs characterized by this model, showing immunity to triple line pitting. The corresponding significant figures are given in the bracket below the fractions.

Table 11: Fraction of TLs characterized by the CSL/GB model, showing immunity to intergranular pitting

<table>
<thead>
<tr>
<th>TL character</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR0</td>
<td>0.08</td>
<td>0.2</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>(9/112)</td>
<td>(6/30)</td>
<td>(4/18)</td>
</tr>
<tr>
<td>BR1</td>
<td>0.18</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>(29/160)</td>
<td>(13/56)</td>
<td>(11/41)</td>
</tr>
<tr>
<td>BR2</td>
<td>0.23</td>
<td>0.18</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>(9/40)</td>
<td>(4/22)</td>
<td>(3/9)</td>
</tr>
<tr>
<td>BR3</td>
<td>0.33</td>
<td>0.22</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>(4/12)</td>
<td>(2/9)</td>
<td>(2/4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TL character</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA0</td>
<td>0.06</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>(10/159)</td>
<td>(7/37)</td>
<td>(4/22)</td>
</tr>
<tr>
<td>PA1</td>
<td>0.25</td>
<td>0.23</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>(36/146)</td>
<td>(15/65)</td>
<td>(12/40)</td>
</tr>
<tr>
<td>PA2</td>
<td>0.24</td>
<td>0.14</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>(4/17)</td>
<td>(1/7)</td>
<td>(4/10)</td>
</tr>
<tr>
<td>PA3</td>
<td>0.5</td>
<td>0.25</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>(1/2)</td>
<td>(2/8)</td>
<td></td>
</tr>
</tbody>
</table>

Total number of TLs investigated: 513

*not observed
4.3.4 The CAD/GB Model

Figure 4.11 shows the correlation between the CAD/GB model and triple line pitting. CAD 0, 1, 2 and 3 are the triple lines with 0, 1, 2 and 3 special GBs around them, respectively; special GBs were classified up to $\Pi=20$ while the other GBs were classified as random. None of the triple lines with three random GBs around them (CAD0) showed immunity to carbide precipitation. For the triple lines with one (CAD1), two (CAD2) and three (CAD3) special GBs, no clear tendency was observed. Again one dimension periodicity may be not enough for the structure to show some special properties such as resistance to carbide precipitation. However, this model successfully sorted out the random triple lines (CAD0). Table 12 gives the fraction of the TLs characterized by this model, showing immunity to triple line pitting. The corresponding significant figures are listed in the bracket below the fractions.

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD0</td>
<td>0 (0/7)</td>
<td>0 (0/1)</td>
</tr>
<tr>
<td>CAD1</td>
<td>0.12 (5/43)</td>
<td>0.18 (3/17)</td>
</tr>
<tr>
<td>CAD2</td>
<td>0.17 (20/121)</td>
<td>0.22 (11/51)</td>
</tr>
<tr>
<td>CAD3</td>
<td>0.18 (27/153)</td>
<td>0.23 (11/48)</td>
</tr>
<tr>
<td><strong>Total number of TLs investigated:</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.11 Fraction of triple lines characterized by the CAD/GB model, showing immunity to pitting in samples 1, 2 and 3

4.3.5 Further Discussion on Bollmann's Disclination Model

Although there is experimental evidence for the physical validity of Bollmann’s disclination model, i.e. the classification of triple lines into I-line and U-line [Clarebrough and Forwood,
1987; Palumbo and Aust, 1989], there has been a debate as to whether U-lines exist at all. Priester and Yu [1994] observed a Σ3-Σ3-Σ9 type triple line using high resolution microscopy. According to their calculation, it was a U-line; however they found that the nodal balance of dislocation occurred at this triple line, the physical character of an I-line. As a result, they questioned the physical significance of the distinction between I-lines and U-lines. Later, Palumbo and Aust [1996] pointed out that the calculation performed by Priester and Yu on the triple line was in error. The correct calculation showed that this Σ3-Σ3-Σ9 type triple line was actually an I-line. In fact, this direct observation provides further support for the basic concepts of Bollmann's disclination model.

The model was questioned again by Dimitrakopulos et al. [1996] from the theoretical point of view. The focused point in their argument is the validity of choosing a nearest-neighbor-relation (NNR), the cornerstone in Bollmann's disclination model, in describing GB misorientations. They argued that all descriptions of a given interface (GB) were equivalent and consistent with a physical bicrystal. A particular description (e.g. the NNR, corresponding to the widest spaced dislocation network) may be more convenient, but not more meaningful. When GBs meet at a triple line, it was important to describe GB misorientations in a consistent manner. The NNR is obtained by an unimodular transformation, which would introduce inconsistency in describing GB misorientations at a triple line. Therefore, choosing NNR was neither necessary nor valid as a criterion for selection of GB misorientation descriptions at a triple line. Without NNR, the sequence around a triple line always leads to the identity matrix as discussed in section 2.2.1. Thus, they concluded that all triple lines were I-lines in Bollmann's terminology.
Recently, Müllner [1999] pointed out that small angle tilt boundaries are made up by walls of edge dislocations with the smallest possible dislocation content [Read and Shockely, 1950] and, thus, correspond to the NNR. In describing a virtual multiple junction line (e.g., a triple line), there are two approaches: 1) Bollmann's disclination approach, in which the choice of the NNR is crucial as a criterion of selecting GB misorientation descriptions, and 2) the conventional elasticity approach (rotational Volterra cuts, Volterra disclinations). Through a thought experiment, Müllner demonstrated that the Bollmann disclination, U-line, is a real crystallographic defect with the dislocation network corresponding to the NNR, and is physically different from the Volterra disclination (an elastic defect) in the second approach. Moreover, the Bollmann disclination (U-line) can only be identified by the first approach. The method used by Dimitrakopulos et al. [1996] in their work is the second approach (rotational Volterra cuts, Volterra disclination) and, hence, can not identify the distinction between U-lines and I-lines.
Chapter 5  Conclusions

§ 5.1  Grain Boundaries

1. With respect to sensitivity to carbide precipitation, the conventional upper limit of low angle boundary, 15°, is too high for Type 304L SS. The appropriate value appears to be somewhere between 10° –15°.

2. The CSL/DSC model gives a clear and consistent correlation between the GB structure and carbide precipitation in Type 304L SS. Using this model, more than 90% of the special GBs (Σ3-29) are immune, and about 80% of the random GBs are susceptible to carbide precipitation.

3. In the CSL/DSC model, the Palumbo-Aust criterion gives a better fit for the experimental data than Brandon’s criterion. A special GB is more likely to show immunity to carbide precipitation, using the Palumbo-Aust criterion.

4. The CAD/PM model gives no clear correlation between carbide precipitation and grain boundary structure.
§ 5.2 Triple lines

1. Bollmann's disclination model gives the best fit for the experimental observations. The percentage of I-lines immune to the carbide precipitation can be as high as 80% if the samples are annealed in the proper selective region. The percentage of U-lines immune to the carbide precipitation is always below 20% in all conditions.

2. If the triple lines are ranked according to their degree of order, the CAD/GB model is effective in correlating the structure of the lowest degree of order with the carbide precipitation; all the triple lines characterized as random experienced carbide precipitation. However, such correlation was not found for the triple lines with some higher degree of order.

3. The CAD and CSL/GB models gave no clear correlation between structure and carbide precipitation.
Chapter 6 Recommendations for Future Research

- Bollmann's disclination model on triple lines appears to be a successful one to characterize triple lines. However, one of the drawbacks is that no deviation is taken into account in characterization. In fact, there is always discrepancy between a real orientation and a measured one. For example, the accuracy of experimentally measured Euler angles is in the order of $\pm 0.75^\circ$ for a given grain in the OIM™ system at University of Toronto. Since the character of a triple line is highly sensitive to the orientations of the three adjoining grains in this model, the effect of deviation needs to be incorporated into the model.

- Triple lines are expected to be much more significant in nanocrystalline materials owing to the fact that their volume fraction increases enormously as the grain size decreases into the nanometer range (<100 nm). Understanding the effect of grain size on the character distribution of triple lines may give insight into the unique behavior of nanocrystalline materials.

- Other alloy systems and/or other properties need to be involved to further test the validity of the triple line models.
References


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42. Ishida, Y. and McLean, M., (1973), Phil. Mag., 27, 1125.
48. Kurban, M., 1999, Personal talk


