Grain Boundary Studies in Ordered Intermetallic Compound Ni₃Al

by

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(ABSTRACT)

Theoretical and experimental studies of grain boundary structures were carried out to understand the grain boundary properties of Ni3Al.

Using various techniques of transmission electron microscopy, the geometry of grain boundaries was determined from a number of grain boundaries to obtain a distribution of grain boundary types in Ni3Al. Five macroscopic parameters, including a misorientation between two grains and a grain boundary plane orientation, were considered in the grain boundary type. A distribution of grain boundary types in ductile Ni3Al contained more low Σ boundaries than brittle Ni3Al. In a distribution of grain boundary plane orientations, the trend of having high density plane of coincident sites was maintained on low Σ boundaries up to Σ = 9 and random orientations of grain boundary planes became dominant after Σ = 11. In ductile Ni3Al, grain boundary accommodations of dislocations in the vicinity of grain boundaries were found, which were not shown in brittle Ni3Al. Using CBED techniques, symmetry information of a single crystal was obtained. However, an extension to bicrystals was not successful.

In order to study the possible disordering and segregation near grain boundaries, two different atomistic computer simulations, namely, molecular statics simulation and two-dimensional lattice gas model, were carried out. Both results showed a similar trend of disordering near the grain boundary regardless of grain boundary composition and atomic interaction energy assumptions. However, segregation behavior near grain boundaries showed strong influences from grain boundary compositions and atomic interaction energy assumptions.
To my Family
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Chapter 1

Introduction

1.1 Overview

Grain boundaries, the interface between crystals of the same phase but with different orientations, have been known as an important part in controlling the properties of engineering solids. Since metals and ceramics are used in polycrystalline forms with few exceptions, grain boundaries between crystals have marked effects on a variety of properties of solids [1]. The structure and behavior of grain boundaries, thus, has been a very active area of interest for a long time. Major developments in the grain boundary properties have taken place over the last few decades and these efforts have been focused on the atomic structure of grain boundaries as well as processing technologies to control grain boundary properties.
Recently, the grain boundary of ordered intermetallic compounds, such as Ni₃Al, Ni₃Si, Al₃Ti etc., has been studied intensively after a breakthrough of Ni₃Al by utilizing it in polycrystalline forms since intermetallic compounds have long been known as intrinsically brittle materials in polycrystalline forms. The success in Ni₃Al provoked a large research effort on intermetallic compounds. In general, materials properties of intermetallic compounds and ordered alloys are regarded as being intermediate between metals and ceramics. Some intermetallic compounds have significant characteristics regarding the mechanical properties. Particularly, mechanical properties at high temperature are very attractive as new structural alloys since the intermetallic compounds occasionally show an increase in flow strength with increasing temperature and excellent corrosion and creep resistance [2]. It has been, however, known that the intermetallic compounds are commonly very brittle in polycrystalline forms. Therefore, they have not been fabricated into useful shapes and also have been apart from practical uses. The brittleness of the intermetallic compounds is caused by strong tendencies to cleave at grain boundaries.

In the case of Ni₃Al, it is now well established that introduction of small amount of impurity atoms can drastically improve the ductility of polycrystalline intermetallic compounds. This is contrary to the case of pure metals which generally exhibit brittle intergranular fracture by adding impurities. One of the most important achievement in the development of intermetallic compounds is the work by Aoki and Izumi [3] who have found that the grain boundary embrittlement of Ni₃Al (L₁₂ Structure) is improved significantly by an addition of Boron and about 30% elongation can be attained in an arc-melted Ni₃Al sample. Similar experimental results have also been obtained using samples by thermomechanical processing and rapid solidification. In particular, Liu and co-workers [4] have found that boron increases the ductility only in Ni-rich Ni₃Al samples; the best ductility is achieved in samples with 24 atomic percent Al. The success in Ni₃Al triggered a large research effort in the understanding of the reasons for this behavior. From the beginning, the problem was recognized to be very complex and requiring a study from various standpoints, from a basic electronic structure study to dislocation studies and grain boundary plastic behavior.
There have been many suggestions and observations concerning the brittle-ductile transition of fracture modes in polycrystalline Ni$_3$Al by adding small amount of Boron in the off-stoichiometric alloy (24% Al). Schulson, Baker, and Horton [5] proposed that the region near the grain boundary is co-segregated by Boron and extra Ni atoms and expected this region to be disordered and behave like a FCC material. They found the dislocation rearrangement and accommodation near grain boundaries and suggested that dislocation transmission across the grain boundary could occur more easily if the region in the vicinity of a grain boundary was disordered. However they had no direct evidence for the existence of such disordering. Mackenzie, Vaudin and Sass [6] observed that boundaries in Boron doped Ni$_3$Al contained dislocations with the a/2<110> Burgers vector. The possible explanations for the presence of a/2<110>-type dislocations is that the Ni$_3$Al is disordered in the vicinity of the interface, resulting in a thin layer of FCC structure at the boundary, and the dislocation then have the expected FCC Burgers vector. They also showed experimental evidence of a disordered region near a grain boundary using high resolution electron microscopy [7]. Other suggestions in disordering are the atom-probe field ion microscopy observations [8] and analytical electron microscopy results [9] which showed that the boundary region is Ni-rich and deviations from the average alloy composition is up to 5 atomic % Ni. They suggested that the enrichment of Ni atoms near grain boundaries disordered the atomic arrangement and resulted in compositional disorder in the vicinity of grain boundaries.

On the other hand, Watanabe et al [10] reported that brittleness of polycrystalline materials depends on the distribution of grain boundary types. They suggested that there is a correlation between the distribution of boundary types in terms of $\Sigma$ values and the strength of materials. Here, the $\Sigma$ is a ratio between the coincident site lattice (CSL) volume and the volume of the base lattice. Experimental evidence showed that crack propagation follows along random boundaries instead of coincident boundaries or low angle boundaries. Farkas et al [11] also investigated the $\Sigma$ distributions of both brittle and ductile Ni$_3$Al and showed more low $\Sigma$ coincident boundaries and low angle boundaries in ductile Ni$_3$Al using back scattered channelling patterns of SEM. On the other hand, Mackenzie et al [12] performed
the same study and showed that there is no significant difference in Σ distribution. The differences in those two studies seem to reflect different thermal histories of samples, criteria used for a special boundary, and accuracy of methods used to determine the rotation angle and axis and following Σ values. However, recent atomistic studies of grain boundaries showed that the grain boundary structure depends not only on the Σ values but also on grain boundary plane orientations [13,14]. Thus, there is a strong doubt about whether Σ distribution can be related to fracture modes directly without considering the practical definition of the random grain boundaries since grain boundary plane orientations are also very important in the cohesion and structure of the grain boundary.

In a theoretical study of a grain boundary using the embedded atom potentials, Foiles [15] showed that there is a chemically disordered region near Σ = 5 grain boundaries in undoped Ni3Al using Monte Carlo simulation. Using variable sphere model, Farkas et al [16] suggested that the extreme brittleness of ordered intermetallic compounds, particularly Ni3Al, could be understood by considering its size difference of constituent atoms. They proposed that the size ratio can be used to predict the grain boundary property since the grain boundary of a compound with a large size ratio would be less dense than that of small ratio and is appeared to be weak. Another interpretation on ductilization of L12 materials was reported by Vitek et al [12] based on Molecular Statics simulation. They interpreted the brittleness of ordered intermetallic compounds was caused by the amount of distortion involved in grain boundaries. The physical reason for these distortions is the strong tendency for ordering, imposed by the potentials used to describe atomic interactions. They found that the amount of distortion occurred in the grain boundary of L12 type materials could be diminished by considering off-stoichiometric alloy.

The present work is a part of the large effort in understanding the particular behavior of grain boundaries in ordered alloys. Particularly, the grain boundary structure of ordered intermetallic compound Ni3Al was investigated to obtain the reason for ductilization of Ni3Al in polycrystalline forms. The study of grain boundaries in this dissertation classified broadly
as two categories. The first part is the study of grain boundary structures and geometries using transmission electron microscope. Secondly, atomic structures of grain boundaries were studied using atomistic computer simulations.

In the first part, grain boundary geometries of Ni$_3$Al were studied to obtain statistical distributions of grain boundary types including Σ distribution and information of grain boundary plane orientation using TEM. The energy associated with each grain boundary is different according to the grain boundary type. Thus the distribution of the grain boundary type is believed to be related to the mechanical behavior of the material although the distribution is sensitive to the thermal history of the sample, particularly, in case of Σ = 3 twin boundaries. The distribution of grain boundary types in ductile Ni$_3$Al obtained in this work was compared to the distribution of brittle Ni$_3$Al measured by Hanada et al [17]. Besides the Σ distribution of the grain boundary, the grain boundary plane orientation for each Σ was also investigated to study the validity of special Σ boundaries in real materials and the effectiveness of Σ distribution in terms of grain boundary energies.

During the TEM experiment, we also paid attention to the dislocation behavior near grain boundaries since the grain boundary accommodation of slip was also believed to be a very important factor to control the grain boundary brittleness. In the computer simulation works, two different methods were employed to calculate the structure of grain boundaries. Using Molecular Statics atomistic computer simulation, grain boundary segregation and disordering phenomena were studied by creating antisite defects. The segregation behavior and disordering phenomena was also studied using two-dimensional lattice gas model which allowed the temperature effect in grain boundary behaviors using the cluster variation method.
1.2 Format of this Dissertation

The chapters in this dissertation are organized in the form of research papers with more details when needed. The publications resulting from this work and the corresponding chapters are listed below.

"Determination of the grain boundary geometry using TEM", in preparation.


1.3 References


Chapter 2


2.1 Introduction

It has long been known that the structure and energy of a grain boundary depends on the crystal misorientation between two adjacent grains and on the orientation of a particular interface plane adopted by the boundary [1,2]. Several geometrical models have been proposed to account for the occurrence of particular misorientations and boundary planes which are associated with a low energy grain boundary structure [3]. Recently, the coincident site lattice representation of grain boundary structures has become dominant as a basis for grain boundary models [4,5]. The C.S.L. boundaries have special properties and are often associated with low
energies.

The collection and analysis of experimental data on the misorientation and grain boundary plane normal has not received as much attention as has the development of theoretical boundary models. Most of the experimental approaches to support these models are obtained from studies on specially prepared and oriented bicrystals except several recent studies [6-11]. The absence of data from polycrystalline forms reflects the labor of producing accurate crystallographic results.

This chapter describes an efficient way of collecting and analyzing the geometrical information of grain boundaries from polycrystals, including Σ and grain boundary plane orientations. The geometry of a grain boundary is determined by employing conventional TEM techniques. A procedure to assign a Σ value to a grain boundary involves the calculation of the misorientation matrix from the orientation information of two crystals across a grain boundary. For the grain boundary plane orientation, traditional trace analysis was used. Using the statistical distributions of grain boundary geometries collected from polycrystals, a possible relation between fracture modes and distributions of grain boundary types will be discussed. This is possible because the grain boundary geometry is related to the energy of the grain boundary which is associated with the cohesive energy of the grain boundary. It is based on the fact that the crack path during fracture is expected to proceed along grain boundaries of lower cohesive energies and results in intergranular fracture. Besides the investigation of grain boundary distributions, dislocation behaviors near grain boundary were studied since the dislocation behavior near grain boundaries is also believed as a very important factor to understand the mechanical behavior of materials. This is because dislocation pile-ups at grain boundaries induce the intergranular fracture.

The application of convergent beam techniques is also described in this chapter. The CBED techniques have been known as a useful tool in determining the precise thickness of a thin foil, crystal orientations and the symmetry information of the material [11-14]. The techniques and its application will be introduced in this chapter. In particular, the procedure of determining the point group and the space group of single crystals will be described in detail with some discussion on possible applications to bicrystal symmetries.
2.2 Experimental Techniques

2.2.1 Specimen preparation

The material studied was ductile off-stoichiometric Ni$_3$Al provided by Oak Ridge National Laboratories in the form of a drop-casted bulk material. The material studied is a Nickel Aluminide with the chemical composition of 24 at. % Al / 76 at. % Ni with 500ppm B. The samples were vacuum annealed at 1050$^\circ$ for 6 hours. The purpose of annealing was to reduce the defect density and control the average grain size of the material. The average grain size of the material after annealing was about 5.4 $\mu m$ in diameter.

In order to process in the electrochemical polisher, the specimen was prepared as 3 mm diameter disks using spark cutter in order to prevent the mechanical distortion during preparation of TEM samples. A final thinning procedure was done by twin-jet electrochemical polisher, in which two jets of a polishing fluid are directed on both sides of the disk. Fig. 2.1 shows the schematic diagram of twin-jet polisher by Tenupol. A light sensor in the polisher automatically stops the thinning process when perforation occurs in the sample. The area around the hole should then be thin enough to permit electron transmission. The chemical composition of the electrochemical solution was 70 vol. % CH$_3$OH + 30 vol. % HNO$_3$. The optimum current during polishing for Ni$_3$Al, with the dimension about 0.05mm thickness and 3mm diameter, was 220mA at 8 V. In order to maintain the same condition for both surfaces of the specimen, the specimen was rotated several times during polishing. The flow rate of the solution to the surface of the specimen was carefully controlled to prevent the bending of the thin edges of the hole created at the final moment of the thinning procedure. The flow rate of the solution was also a very important factor to prevent oxide formation in the surface of the sample since the turbulent flow of the solution would develop air bubbles. Additional information on the most favorable conditions for preparing the TEM specimen can be found in references [15,16].
Fig. 2.1 A schematic diagram of twin-jet polisher by Tenupol.
2.2.2 Electron Microscopes

Two different electron microscopes, JEOL 200CX and Philip EM420, were used in the studies of the geometrical analysis of grain boundaries and the symmetry interpretation of the structure of Ni3Al. Both electron microscopes were basically the same in terms of operations. However, each electron microscope has its own special features such as the differences in the spot size control and the maximum acceleration voltages available.

JEOL 200CX was mainly used for obtaining the images of the grain boundaries. The electron microscope has 200 KeV capacity as an acceleration voltage. Thus it was much easier to obtain the images of the defects in the relatively thick area of the specimen with high spatial resolution than Philips EM420 which has 120 KeV of the maximum acceleration capacity. With 200 KeV, the specimen thickness of about 2000 Å could be managed with clear images. On the other hand, the electron microscope was not designed for the convergent beam electron diffraction applications, even though it has four different settings for the spot size control. The spot sizes were too large to find a strain free area of even with the smallest spot size available.

For convergent beam electron diffraction (hereafter CBED) applications, the Philips EM420 was used. This electron microscope has 6 settings for the beam spot size control in both micro probe and nano probe modes. Therefore, Philips EM420 was more convenient than the JEOL 200CX to obtain clear CBED patterns even in deformed specimens. The strength of the first condenser lens controls the beam spot size and this is achieved by using the spot size knob. Position 6 gives the smallest spot size. However, with very small spot sizes the amount of the signal generated may not be sufficient and hence a spot size of 4 (~ 0.1 μm) was generally used for the CBED applications except for the case of highly deformed specimens.

In order to generate the Kikuchi patterns to obtain crystal orientation information, a convergent type (small convergence angle) beam of relatively large spot size (~ 0.5 μm)
was used. Generally the beam spot size 3 from both electron microscopes was good enough to have clear patterns. Therefore, the JEOL 200CX electron microscope was used to obtain images and orientation information of crystals and the Philips EM420 for CBED applications.

2.2.3 Electron Diffraction Theory

2.2.3.1 Kikuchi Patterns

Kikuchi patterns occur if a selected area diffraction pattern is taken from a single crystal region of the specimen provided the specimen is reasonably thick and has a low defect density. They define the sense of tilting more accurately than spot patterns [17]. The main feature of the geometry of the Kikuchi pattern can be understood by making use of a simplified treatment. The Kikuchi lines in the pattern are considered to arise from the diffraction of electrons that have been previously inelastically scattered by the specimen. These inelastically scattered electrons are present in most spot electron diffraction patterns both as diffused halos around the transmitted and strongly diffracted spots and as an overall faint back ground intensity.

A geometrical description of the occurrence of Kikuchi lines is illustrated in Fig. 2.2(a). A thin single crystal specimen is oriented such that the Bragg law is not satisfied for the incident beam compared with the pair of (h k l) planes. Then, some electrons change directions slightly by an inelastic scattering event occurs at O so that inelastically scattered electrons satisfy the Bragg law in plane XY (Fig. 2.2 a). As a result, instead of contributing to the intense halo around the transmitted beam, it is diffracted away towards the low background intensity region well removed from the transmitted beam down the path OBC in Fig. 2.2(a). This results in a local reduction in background intensity near the transmitted beam and an increase in a region far from it. Fewer electrons will be inelastically scattered through the large angle to be diffracted back into the region near the transmitted beam following the path OAD because only
Fig. 2.2 Geometrical descriptions of Kikuchi lines from inelastically scattered electrons (a) and the reflection of these electrons by crystal planes to form Kikuchi cones on the Ewald sphere (b).
a few are scattered into OA in the first place. When all possible incident directions into the (h k l) planes are considered, and the three dimensional distribution of the inelastic scattering events is included, the diffraction process can produce cones of radiation centered on the specimen, see Fig. 2.2(a). These Kikuchi cones may be considered in relation to the Ewald sphere construction. The result is shown in Fig. 2.2(b). It may be seen that the cones intersect the Ewald sphere in hyperbolae with such large radii that they are almost straight lines, one brighter than background and one darker than the background. Since the diffraction pattern in the electron microscope is a magnified picture of the surface of the Ewald sphere, the Kikuchi lines are visible as parallel bright and dark pairs in the diffraction pattern.

Kikuchi patterns are very important in electron microscopy because the position of Kikuchi lines in the diffraction pattern is a more sensitive measure of the crystal orientation than spot patterns. The reason for this may be seen by considering the movement of the Kikuchi lines over the surface of the Ewald sphere if the specimen is tilted slightly. The cones of radiation behave as if directly attached to the specimen. Thus the Kikuchi line pair swings about the Ewald sphere radius $1/\lambda$ and moves rapidly across the surface of the Ewald sphere. On the other hand, in the case of using spot patterns, the reciprocal lattice only tilts about its origin, that is about a radius $\bar{g} = \left( \frac{1}{2\pi} \right) \cdot \left( \frac{1}{\lambda} \right)$, which is almost undetectable with slight tilting.

2.2.3.2 *Convergent Beam Electron Diffraction*

Convergent beam electron diffraction techniques have been known for many years, being originally developed by Kossel and Mollensdtedt (1939). The techniques are straightforward and have many applications. A ray diagram illustrating the formation of a CBED pattern is shown in Fig. 2.3 and it is clear from this diagram that the diameter of the diffraction maxima (discs) is defined by the beam convergence angle $\alpha$. The discs of intensity which are formed in the screen contain the information about specimen thickness, orientation, and symmetries of the specimen. Much of this information is sensitive to small changes of the specimen thickness and orientation. A typical CBED pattern from [001] zone axis is shown
Fig. 2.3 A ray diagram illustrating the formation of the CBED pattern.
Fig. 2.4 CBED patterns taken from [001] zone axis of Ni3Al. (a) is the whole pattern with ZOLZ and FOLZ patterns and (b) is the magnified view of central area of (a).
in Fig. 2.4. Fig. 2.4 (a) shows a pattern of zero order Laue zone (ZOLZ) as disks and first order Laue zone (FOLZ) as a outer ring. Fig. 2.4 (B) is the magnified CBED disks in the central area of the Fig. 2.4 (a). The information available in CBED patterns can be classified in three classes.

a) Precise crystal orientation determination

The determination of a crystal orientation can be executed very accurately if convergent beam electron diffraction (CBED) techniques are available [18]. The electron beam direction with respect to a crystal can be determined within the error range of 0.05 ° using CBED. The angle of convergence must be large enough in order to obtain a large field of view including high order Laue zones. The Kikuchi lines are much clearer in the CBED pattern as compared to normal selected area diffraction patterns (SAD). This is primarily caused by the fact that the sampled volume in CBED (minimum probe size ≈ 50 nm) is much smaller than in SAD. Accordingly, the contrast of the Kikuchi lines is less smeared out by strain, bending of the crystals, or defects. Secondly, elastically scattered electrons also contribute to the Kikuchi lines, since the angle of convergence is larger than the Bragg angle of many planes parallel to the incident beam direction. The application of the CBED techniques to determine the precise orientation of a crystal is illustrated in the section 2.5.1.

b) Foil thickness measurement

With the variation in the intensity of strongly diffracted beams, fringes within discs can be used to determine the thickness of the specific area of the sample very accurately [19]. From the two beam dynamical theory of electron diffraction, the intensity of the diffracted beam at the bottom of a foil is given by;
\[ I = \left( \frac{\pi}{\xi_g} \right)^2 \frac{\sin^2(\pi t s_{eff})}{(\pi t s_{eff})^2} \]  

(2.1)

where \( \xi_g \) is the extinction distance for the operative reflection, \( s_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^2}} \), and \( s \) is the deviation from the Bragg condition. Thus the position of the minima is given by the condition \( t s_{eff} \) = integers, therefore;

\[ t^2 \left( s_i^2 + \frac{1}{\xi_g^2} \right) = n_i^2 \]  

(2.2)

where \( s_i \) is the deviation of the \( i \)th minimum from the exact Bragg condition. Equation 2.2 can be rearranged in the form;

\[ \left( \frac{s_i}{n_i} \right)^2 = -\left( \frac{1}{n_i} \right)^2 \left( \frac{1}{\xi_g} \right)^2 + \frac{1}{t^2} \]  

(2.3)

The plotting \( (s_i/n_i)^2 \) against \( (1/n_i)^2 \) gives the thickness \( t \) since \( 1/t^2 \) is the intercept on the \( (s_i/n_i)^2 \) axis. The slope of the straight lines gives \( (1/\xi_g)^2 \) and hence \( \xi_g \). In order to plot \( (s_i/n_i) \), values of \( s_i \), which are the measures of the deviation from exact Bragg condition, are needed and these are obtained by the equation below [19];

\[ s_i = \frac{\lambda}{d^2} \left( \frac{L_i}{L_o} \right) \]  

(2.4)

where \( \lambda \) is the wavelength of the incident beam, \( d \) is the spacing of the reflection planes, \( L_o \) is the distance measured from the center of the diffracted beam profile to the center of the transmitted beam, and \( L_i \) is the distance from the center of the diffracted beam profile to \( i \)th minima.
c) Symmetry determination

Using CBED techniques, the symmetries of crystals such as the point groups and most of the space groups can be determined from CBED patterns which reveal the three dimensional crystallographic information [12,20,21]. There are several unique features of electron diffraction. First, because of the strong dynamical scattering of electrons, Friedel's law fails and 32 crystal point groups are not reduced to the 11 Laue groups. Instead, there exist direct relationships between the point groups and the 31 possible diffraction groups of CBED patterns obtained under the normal incidence of electrons down to the high symmetry crystal axes in planar, non-deformed specimens. The second advantage of the electron diffraction is that it can be carried out using small regions of the specimens. Thirdly, given the three dimensional information available in a single CBED pattern, it is also possible to make use of double diffraction effects to elucidate the space group of the specimen. This is possible when the kinematically forbidden reflection is present due to double diffractions [12,22]. Lines of the zero intensity in these forbidden reflections are owing to the dynamical effects. The lines may be interpreted directly in terms of the presence of certain symmetry elements thus permitting the unambiguous space group determination. According to Tanaka [21], 191 space groups can be determined without ambiguity from total 230 space groups considering forbidden reflections in the discs of CBED patterns.

2.2.4 Analysis of the Grain Boundary Geometry.

There have been many investigations on general bicrystals, such as two adjacent grains, twins or two neighboring phases to study the orientation relationship between the two crystals and the atomic configuration at the boundary. In order to determine the grain boundary structure geometrically, we need to consider nine parameters [23]. Five "macroscopic" parameters, which can be determined experimentally by using conventional techniques of
TEM, define: 1) The orientation relationship from both crystals (three parameters), 2) The orientation of the grain boundary plane (two parameters). Moreover, four "microscopic" parameters define two translations; two parameters for rigid body translation of one crystal with respect to the other and two parameters for the sequential periodicity of the boundary plane. Geometrical analysis using conventional TEM is limited to determine the five macroscopic parameters. Usually, the orientation relationship in bccrystals is expressed in terms of an axis/angle pair, and is described by a rotation matrix. Geometrically, due to the symmetry of the cubic system, there are 24 different but equivalent descriptions of the relationship.

2.2.4.1 Methods available for the analysis of the grain boundary geometry.

Two basic approaches exist for the determination of axis/angle pairs from diffraction patterns. Firstly, an analytical approach by Young et al [24] characterizes the misorientation information by a 3 X 3 matrix whose columns representing the direction cosine of grain 1 referred to grain 2 using Kikuchi patterns from each grain. The procedure involves the selection of three orthogonal coordinate systems, such as a crystal frame, a pattern frame, and a reference frame to obtain a rotation matrix between two crystals. The second approach which can be used to yield misorientation data relies on standard stereographic procedures [25]. Using two or three pairs of diffraction patterns, this method is based on the fact that the pattern zone axes in both grains should be parallel, from which it follows that the axis of the misorientation lies on a zone which is equidistant from the pattern zones. This zone is, then, represented on the stereogram as the great circle which bisects the great circle through the two pattern zones.

In the present study a schematic way of determining the misorientation information from a bccrystal with grain boundary plane normal was designed. The method is basically the same as the analytical method formulating a rotation matrix [5]. However, the confusion from constructing 3 different frames is avoided by tilting the specimen at the eucentric position.
The method is convenient for data collected from a large number of boundaries and quite easy to perform. It is more precise than the stereographical method in the sense that the stereographical method has an inaccuracy in plotting the poles and in manipulating the stereogram.

### 2.2.4.2 Determination of the Grain Boundary Geometry.

The whole procedure of determining the grain boundary geometry starts with the precise orientation information of single crystals. Then, using the orientation information from both crystals across the grain boundary, the relative misorientation of the bicrystal can be determined by constructing a matrix. The matrix gives the information of the rotation axis and angle. As a final step, the orientation of grain boundary planes will be determined by trace analysis.

#### a) Precise Orientation Determination of a Single Crystal.

Accurate determination of a crystal orientation can be done from a CBED pattern of a crystal using the three pole solution. The three pole solution requires three non-parallel Kikuchi lines to obtain an incident beam direction, B, unambiguously from a pattern [17]. Three such pairs are shown in the Fig. 2.5(a). The dashed lines are the traces of the intersection of the \(hkl\) planes producing the Kikuchi lines with the Ewald sphere. Therefore, the points A, B, C correspond to the zone axis of the intersection in the reflecting planes, see Fig. 2.5(b).

In order to index a Kikuchi pattern and determine the precise foil orientation, the spacings of each Kikuchi pair are needed. If the crystal is cubic, then, the spacing of each Kikuchi line \(D\) is inversely proportional to the d-spacing of the particular \(hkl\) plane \(d\), and \(D_1d_1 = \lambda L, \ D_2d_2 = \lambda L, \ D_3d_3 = \lambda L\), where \(\lambda\) is the wavelength of the electron for a certain voltage of the TEM and \(L\) is the effective camera length. From the measured spacings of \(D_1, D_2, D_3\), and their ratios, the tentative indices of Kikuchi lines can be assigned from the table of d-spacings. The correctness of the index assignment can be checked by measuring the angles \(\phi_1, \phi_2, \phi_3\) which are the angle between two non-parallel Kikuchi lines and comparing the calculated values.
Fig. 2.5 (a) Three pairs of Kikuchi lines for the three pole solution, dotted lines are projections of reflecting planes intersect at A,B,C. (b) The projection of the responsible reflecting planes relative to the specimen.
The general procedure, described above, is time consuming and particularly inappropriate for a large number of repetitive jobs. Especially, the procedure of consulting the tables of d-spacings to find a tentative value of (h k l) is extremely tedious and almost impossible for high index Kikuchi lines for the ordered structure like Ni3Al because of superlattice Kikuchi lines. In order to overcome the difficulty, a montaged Kikuchi map for Ni3Al was constructed, see Fig. 2.6. The Kikuchi map was indexed using K-plot program [26]. The K-plot program is very useful and versatile. It can produce computer generated diffraction patterns like Kikuchi patterns and spot patterns according to the accelerating voltage, camera length, lattice parameter, and crystal structure of the material. For cubic crystals a complete map can be obtained within the triangle defined by [001], [011], and [111] poles. Once the Kikuchi map is constructed, a Kikuchi pattern from a single crystal can be easily indexed by comparing to the map.

When the three poles are indexed, the beam direction, B, can be obtained analytically. If the indices of B are $[uvw]$ and $[p_1q_1r_1], [p_2q_2r_2], [p_3q_3r_3]$ are the indices of the poles A, B, C, the beam direction $[uvw]$ can be determined by solving three simultaneous equations [17].

\[
\cos \theta_1 = \frac{u p_1 + v q_1 + w r_1}{\sqrt{u^2 + v^2 + w^2} \sqrt{p_1^2 + q_1^2 + r_1^2}} \quad (2.5)
\]

\[
\cos \theta_2 = \frac{u p_2 + v q_2 + w r_2}{\sqrt{u^2 + v^2 + w^2} \sqrt{p_2^2 + q_2^2 + r_2^2}} \quad (2.6)
\]

\[
\cos \theta_3 = \frac{u p_3 + v q_3 + w r_3}{\sqrt{u^2 + v^2 + w^2} \sqrt{p_3^2 + q_3^2 + r_3^2}} \quad (2.7)
\]

The angles $\theta_1, \theta_2, \theta_3$ are the angles OO'A, OO'B, OO'C in Fig. 2.5. These angles can be calculated by employing the calibration factor K rather than calculated from the effective camera length which may involve errors.
Fig. 2.6 A montaged Kikuchi map of Ni$_3$Al (L1$_2$ ordered structure) at 200 Kv. The computer generated Kikuchi map using K-plot program is shown in the upper right corner. Three low index Kikuchi poles [001], [011], [111] are compared with SAD spot patterns which show the superlattice spots.
\[ K_1 = \frac{\angle AO'B}{D_{\bar{A}\bar{O}}}, K_2 = \frac{\angle BO'C}{D_{\bar{B}\bar{C}}}, K_3 = \frac{\angle CO'A}{D_{\bar{C}\bar{A}}} \]  

(2.8)

\[ K_{\text{average}} = \frac{K_1 + K_2 + K_3}{3} \]  

(2.9)

Therefore,

\[ \theta_1 = K_{\text{average}} \cdot D_{\bar{A}\bar{O}} \]  

(2.10)

\[ \theta_2 = K_{\text{average}} \cdot D_{\bar{B}\bar{O}} \]  

(2.11)

\[ \theta_3 = K_{\text{average}} \cdot D_{\bar{C}\bar{O}} \]  

(2.12)

As a summary, the procedure to index a Kikuchi pattern is as follows;  

i) Index three poles using the Kikuchi map.  

ii) Measure the distances \( \overline{AB}, \overline{BC}, \overline{CA}, \overline{AO}, \overline{BO}, \overline{CO} \).  

iii) Calculate the calibration factor from ii)  

iv) Calculate the angle \( \theta_1, \theta_2, \theta_3 \) using average calibration factor.  

v) Solve three simultaneous equations (2.5), (2.6), (2.7) to obtain the indices of the incident beam axis \([u \, v \, w]\).  

b) **Determination of the Grain Boundary Misorientation.**

A brief description of the procedure to obtain the information of the grain boundary misorientation is now presented. In general, the grain boundary misorientation can be expressed in terms of the rotation axis and angle which can be derived from the rotation matrix. The rotation matrix characterizes the misorientation by 3 X 3 matrix whose columns represent the direction cosine of grain 1 referred to grain 2. In order to obtain a rotation matrix experimentally, at least two pairs of Kikuchi patterns are needed. The procedure to obtain a rotation matrix is as follows;
i) Determine the crystal orientations from both grains using Kikuchi patterns, 
\((h'_1 k'_1 l'_1), (h''_1 k''_1 l''_1)\).

ii) Tilt the specimen.

iii) Determine the crystal orientations from both grains of the tilted specimen using Kikuchi patterns, 
\((h'_2 k'_2 l'_2), (h''_2 k''_2 l''_2)\).

iv) Calculate the third axes from each grain by cross product the orientations before tilt and after tilt from the same grain;

\[
(h'_3 k'_3 l'_3) = (h'_1 k'_1 l'_1) \times (h'_2 k'_2 l'_2) \quad (2.13)
\]

\[
(h''_3 k''_3 l''_3) = (h''_1 k''_1 l''_1) \times (h''_2 k''_2 l''_2) \quad (2.14)
\]

v) Construct the rotation matrix from the crystal orientation information above and the simple matrix formulation as follows;

\[
[M]_i [R] = [M]_i 
\]

where \([M]_i, [M]_ii\), and \([R]\) are 3 X 3 matrices. By rearranging the equation (2.15);

\[
[R] = [M]_i [M]_ii^{-1} \quad (2.16)
\]

therefore, the full formulation of a rotation matrix can be described as follows;

\[
\begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix} = \begin{pmatrix}
  h_1 & k_1 & l_1 \\
  h_2 & k_2 & l_2 \\
  h_3 & k_3 & l_3
\end{pmatrix} \begin{pmatrix}
  h_1 & k_1 & l_1 \\
  h_2 & k_2 & l_2 \\
  h_3 & k_3 & l_3
\end{pmatrix}^{-1}
\]

\[
(a_{11} + a_{22} + a_{33} - 1) \quad (2.17)
\]

where the column vectors of the rotation matrix \([R]\) represents the direction cosines between the Cartesian axes from both grains across the boundary.

vi) Calculate the rotation angle from the equation below;

\[
\theta = \alpha \cos \left( \frac{a_{11} + a_{22} + a_{33} - 1}{2} \right) \quad (2.18)
\]

vii) Calculate the rotation axis \([HKL]\) from the equation below;
\[ H = a_{32} - a_{23} \]
\[ K = a_{13} - a_{31} \]
\[ L = a_{21} - a_{12} \]  

(2.19)

However, the equation (2.19) is not valid when the rotation angle is 180°. When the rotation angle is 180°, the formulation above will give a rotation axis as [000], which is not reasonable indices. The rotation axis of this case can be obtained using the grain boundary geometry of 180° rotation, i.e., the rotation axis can be obtained directly from the sum of the two crystal orientations from both grains.

The relative orientation of two cubic crystals can be described in 24 different ways, since a right-handed orthogonal coordinate system with axes <100> type directions of a cubic lattice can be chosen in 24 different ways corresponding to the symmetry operation of the point group 432. Thus, a table which has 24 equivalent rotation axis/angle with rotation matrix was prepared for each Σ value up to Σ = 49 based on C.S.L. theory. Table 2.1 shows parts of the table which is tabulated according to ascending order of Σ values (a) and ascending order of rotation angle (b) [27].

The Σ determination from the experimentally calculated rotation matrix can be performed by comparing 24 equivalent rotation angle/axis pair with the value of rotation angle/axis from exact Σ based on C.S.L. theory. Usually, a search for a Σ begins with the lowest or 180° rotation angle by comparing the rotation axis from experimental and theoretical values. If there is a similarity between the experimental and theoretical axis/angle values, a tentative Σ value is assumed. Then, the rest 23 rotation axis/angle pairs are compared to exact rotation axis/angle pairs based on C.S.L. theory to verify the tentative Σ values.

c) Criteria for deviations from CSL misorientations.

The CSL theory would be of very limited applicability if the special structures occurred only at exact CSL misorientations. In fact, there is much evidence that the special properties
Table 2.1 Parts of the table which lists the complete set of 24 rotation angle/axis pairs for each cubic CSL orientation up to $\Sigma = 49$ [27]. (a) Ascending order of $\Sigma$ values. (b) Ascending order of rotation angles.

(a)

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may persist for deviations from special misorientations [28]. It was first suggested by Read and Shockley that when there is such a deviation, a low energy interface may be maintained by an array of dislocations similar to those in a low angle grain boundary [29]. The effect of a network is to condense the mismatch onto lines of misfit. In terms of the structural unit model, it can be understood as the superimposition of a dislocation array on a CSL grain boundary, which is equivalent to adding periodically, a unit characteristics of a different CSL. As the deviation increases, the spacing between dislocations decreases. Eventually, the cores overlap and the dislocations lose their identities. Therefore, the criteria for deviation from CSL misorientations will be discussed in this section. The consideration will be given to the calculation of the actual deviation of experimentally obtained grain boundary orientations from exact CSL orientations and the allowable maximum deviation at which such dislocations have physical existence.

i) Deviations from CSL orientations.

The method to estimate the deviation from the CSL misorientation for any bicrystal whose misorientation is close to a CSL relationship is still controversial. There are two methods which are generally used. One is a method by Kokawa [30] and the other is an analytical approach by Bleris et al [31]. Kokawa calculated the deviation angle as a function of two components, the deviation of a rotation angle and the deviation of a rotation axis. On the other hand, the analytical method compared the matrices from the experiment and the exact CSL to obtain the deviation. The analytical method results in same values of deviations from 24 equivalent axis/angle expressions. However, a method by Kokawa, which has been accepted as a traditional method, generates different deviations from each axis/angle expression out of 24 equivalent expressions. Therefore the analytical method should be used to determine the actual deviation from the exact CSL orientation. The analytical method uses matrices from the experiment and the exact CSL. Let's assume $M_e$, the actual rotation matrix from a real bicrystal, and $M_C$, a CSL misorientation matrix. According to the standard procedure of the matrix calculation, the matrix which expresses the deviation is; $M_d = M_e(M_C)^{-1}$, where $(M_C)^{-1}$ is the inverse of $M_C$. Then the deviation angle $\Delta \theta_d$ is deduced from the trace of $M_d$:

31
\[ \Delta \theta_d = \alpha \cos \left[ \frac{1}{2} \left( \sum_{i=1}^{3} S_{ii} - 1 \right) \right] \]  

(2.20)

The choice of the method to calculate the deviation from the CSL orientation does influence the statistical distribution of grain boundaries in the polycrystal. Variations of deviations according to 24 equivalent matrices on both methods is shown in Table 2.2 for a \( \Sigma = 3 \) grain boundary. From the table it is obvious that the method by Kokawa is not adequate to determine unequivocally whether the grain boundary maintains the specialness or not.

**ii) The maximum allowable deviation. (Criteria for specialness)**

There is a considerable experimental evidence for special boundaries retaining their ordered relatively low energy structures at misorientations deviating from those giving geometric matching. Before the proportion of special boundaries in a random polycrystal can be determined, a criterion for the maximum allowable deviation at which a boundary remains special must be adopted. The maximum deviation of a boundary from a special misorientation is given by [29]:

\[ \Delta \theta_c = \frac{b}{d_{\text{min}}} \]  

(2.21)

where \( b \) is the dislocation Burgers vector and \( d_{\text{min}} \) is the closest allowed spacing of the dislocations which should be of the order of the boundary periodicity \( p \). It is very difficult to give a general expression for \( \Delta \theta_c \) as a function of \( \Sigma \). For a given CSL, \( p \) varies with the boundary plane, and the allowed Burgers vectors can vary in size. Not all the \( p \) and \( b \) values have the same \( \Sigma \) dependence. However, the mean value of \( p \) varies as \( \Sigma^{1/3} \) and the mean value of \( b \) varies as \( \Sigma^{-1/3} \) since the volume of the CSL unit cell varies as \( \Sigma^{-1} \) and the volume of the unit cell of the Burgers vectors varies as \( \Sigma^{-1} \) [32]. Hence
Table 2.2  Comparison of two methods to calculate the deviation angle in a $\Sigma = 3$ grain boundary. It shows twenty four variations of deviation angles according to Kokawa's method [30] and a fixed deviation angle from the analytical method [31].

<table>
<thead>
<tr>
<th>Angle/axis (CSL)</th>
<th>Angle/axis (experiment)</th>
<th>$\Delta \theta_\delta$(Kokawa)</th>
<th>$\Delta \theta_\delta$(Bleris)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/1,1,-1</td>
<td>59.9/-1.019,-1.046,-0.921</td>
<td>0.113</td>
<td>1.047</td>
</tr>
<tr>
<td>60/1,1,1</td>
<td>60.1/1.049,0.922,1.018</td>
<td>0.103</td>
<td>1.047</td>
</tr>
<tr>
<td>70.53/0,1,-1</td>
<td>73.6/0.019,1.356,-1.358</td>
<td>3.073</td>
<td>1.047</td>
</tr>
<tr>
<td>70.53/-1,0,1</td>
<td>69.7/-1.329,0.087,1.325</td>
<td>0.831</td>
<td>1.047</td>
</tr>
<tr>
<td>70.53/-1,1,0</td>
<td>68.6/1.318,-1.328,0.068</td>
<td>1.93</td>
<td>1.047</td>
</tr>
<tr>
<td>109.47/-1,1,0</td>
<td>111.7/-1.288,1.348,0.003</td>
<td>2.23</td>
<td>1.047</td>
</tr>
<tr>
<td>109.47/0,1,-1</td>
<td>106.5/0.002,-1.348,1.366</td>
<td>2.21</td>
<td>1.047</td>
</tr>
<tr>
<td>109.47/1,0,-1</td>
<td>110.6/1.288,0.001,-1.366</td>
<td>1.131</td>
<td>1.047</td>
</tr>
<tr>
<td>131.81/1,0,2</td>
<td>129.6/0.709,0.008,1.358</td>
<td>2.21</td>
<td>1.047</td>
</tr>
<tr>
<td>131.81/0,2,1</td>
<td>132.9/0.031,1.318,0.622</td>
<td>1.09</td>
<td>1.047</td>
</tr>
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<td>1.047</td>
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<td>1.461</td>
<td>1.047</td>
</tr>
<tr>
<td>131.81/0,-1,-2</td>
<td>132.2/0.040,-0.641,-1.325</td>
<td>0.391</td>
<td>1.047</td>
</tr>
<tr>
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<td>129.7/-0.709,-1.356,0.011</td>
<td>2.11</td>
<td>1.047</td>
</tr>
<tr>
<td>146.44/-1,1,3</td>
<td>145.6/-0.320,0.368,1.018</td>
<td>0.84</td>
<td>1.047</td>
</tr>
<tr>
<td>146.44/1,-3,-1</td>
<td>148.9/0.320,-0.922,0.328</td>
<td>2.46</td>
<td>1.047</td>
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<tr>
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<td>145.6/-0.320,0.368,-1.018</td>
<td>0.84</td>
<td>1.047</td>
</tr>
<tr>
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<td>145.9/1.019,-0.318,0.366</td>
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<td>1.047</td>
</tr>
<tr>
<td>146.44/1,3,-1</td>
<td>144.8/0.329,1.046,-0.366</td>
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<td>1.047</td>
</tr>
<tr>
<td>180.00/1,-2,1</td>
<td>177.2/0.682,-1.345,0.645</td>
<td>2.8</td>
<td>1.047</td>
</tr>
<tr>
<td>180.00/2,-1,-1</td>
<td>179.8/1.277,-0.685,-0.674</td>
<td>0.202</td>
<td>1.047</td>
</tr>
<tr>
<td>180.00/1,1,-2</td>
<td>177.5/0.318,0.345,-0.645</td>
<td>2.5</td>
<td>1.047</td>
</tr>
<tr>
<td>180.00/1,1,1</td>
<td>179.2/0.673,0.643,0.636</td>
<td>0.816</td>
<td>1.047</td>
</tr>
</tbody>
</table>
\[ \Delta \theta_c = \theta_o \Sigma^{-2/3} \]  

(2.22)

where \( \theta_o \) is constant for all CSLs and is the maximum deviation angle for low angle grain boundaries. In the special case of CSL Burgers vectors lying in a boundary plane perpendicular to a \(<100>\) misorientation axis, \( p \) varies as \( \Sigma^{1/2} \) and \( b \) varies as \( \Sigma^{-1/2} \). Hence,

\[ \Delta \theta_c = \theta_o \Sigma^{-1} \]  

(2.23)

An equation of this form was first proposed by Ishida and Mclean [33]. However, Brandon's criterion, which has been used by many researchers, considered the boundary periodicity only in the special case of a boundary plane perpendicular to a \(<100>\) misorientation axis [34]. The Brandon's criterion follows that

\[ \Delta \theta_c = \theta_o \Sigma^{-1/2} \]  

(2.24)

The criterion can be adjusted to specific grain boundaries, as considered by Ishida and Mclean for \(<100>\) twist grain boundaries or based on the periodicity of the grain boundary alone, as considered by Brandon. Whatever the choice of \( \Sigma \) dependence is, the constant \( \theta_o \) has to be fixed. It was suggested that the \( \theta_o \) can be a valid limit of the Read and Shockley model \((\Delta \theta_c = 15^\circ \text{ for } \Sigma = 1)\), which gives \( \theta_o = 15^\circ \). Later it was proposed by Ishida and Mclean [33] to set \( \theta_o = 8^\circ \), as a consequence of the experimental results. The experiment was to find a maximum deviation angle at which discrete grain boundary dislocations could be shown. However, the experiment was based on conventional TEM observations which were dependent upon the performance of the microscope and the observation technique. Fig. 2.7 shows discrete grain boundary dislocations in a \( \Sigma = 5 \{012\} \) grain boundary in Ni3Al with the deviation of 0.8° from the CSL orientation. Finally, recent observations obtained using HREM [35] have evidenced discrete dislocations as high as 15° and the most realistic criterion for the maximum deviation from CSL orientations including \( \theta_o = 15^\circ \) is
Fig. 2.7 Discrete grain boundary misfit dislocations in a $\Sigma = 5 \{012\}$ grain boundary in Ni$_3$Al. Spacings between misfit dislocations are about 190 Å.
\[ \Delta \theta_c = 15\Sigma^{-2/3} \]  

(2.25)

It is believed that the choice of a criterion for the maximum deviation \( \Delta \theta_c \) also influences the statistical distribution of the grain boundaries in the material. The maximum deviation angles according to the different criteria are listed for low \( \Sigma \)s:

<table>
<thead>
<tr>
<th>Criteria</th>
<th>( \Sigma = 1 )</th>
<th>( \Sigma = 3 )</th>
<th>( \Sigma = 5 )</th>
<th>( \Sigma = 7 )</th>
<th>( \Sigma = 9 )</th>
<th>( \Sigma = 11 )</th>
<th>( \Sigma = 13 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \theta_c = 15\Sigma^{-2/3} ) [32]</td>
<td>15</td>
<td>7.2</td>
<td>5.1</td>
<td>4.1</td>
<td>3.5</td>
<td>3.0</td>
<td>2.71</td>
</tr>
<tr>
<td>( \Delta \theta_c = 8\Sigma^{-1} ) [33]</td>
<td>8</td>
<td>2.6</td>
<td>1.6</td>
<td>1.1</td>
<td>0.89</td>
<td>0.27</td>
<td>0.61</td>
</tr>
<tr>
<td>( \Delta \theta_c = 15\Sigma^{-1/2} ) [34]</td>
<td>15</td>
<td>8.6</td>
<td>6.7</td>
<td>5.7</td>
<td>5.0</td>
<td>4.52</td>
<td>4.16</td>
</tr>
</tbody>
</table>

There is no criterion which is applicable to all the possible geometries of the grain boundaries. However, the equation 2.25 seems more realistic for general boundaries than others.

d) Determination of the grain boundary plane orientation.

The grain boundary plane normal can be determined in several different ways. The simplest situation is the case when the grain boundary plane can be oriented to an edge-on geometry for both before tilt and after tilt. Then the grain boundary plane normal can be directly calculated by cross product of two crystal orientations. Although this procedure is simple, it is not possible to apply this method to highly inclined grain boundary planes because of the limitation of the specimen tilting device of TEM. Secondly, the grain boundary normal can be obtained using the dislocation line direction which is contained in the boundary plane, and the direction of the grain boundary trace [36]. In order to determine a dislocation line
direction, at least three different beam directions are needed with slight tilts. This procedure
takes too much time to determine the dislocation line direction. In addition, it is not applicable
when there is no grain boundary dislocations contained in the grain boundary plane.

The more general way of determining the grain boundary plane normal is the con-
ventional trace analysis with the information of the specimen thickness at the grain boundary
[36]. The determination of the specimen thickness can be done by counting fringes from grain
boundary planes or using a convergent beam technique. The former method depends on the
number of fringes according to the thickness of the sample. The extinction distance, $\xi_g$, of
the fringes depends on both the operative reflection and the deviation from the exact Bragg
position. The value of $\xi_g$ at $s = 0$ may be calculated from the relationship;

$$\xi_g = \frac{\pi \Omega \cos \theta}{\lambda f(\theta)}$$

(2.26)

where $f(\theta)$ is the atomic scattering amplitude, $\theta$ is the Bragg angle, $\Omega$ is the volume
of the unit cell, and $\lambda$ is the electron wave length. The typical values of $\xi_g$ for Ni$_3$Al of the
various operative reflections at 100 Kv are calculated in table 2.3. The values in the table have
an accuracy of $\pm 5\%$ because of the inaccuracies in $f(\theta)$ [31].

A technique of CBED to determine the thickness of the sample also uses an equation
derived from the two beam dynamical theory of the electron diffraction. Details about this
method are given in section 2.3.2. This technique enables us to determine the specimen
thickness with an accuracy of better than $\pm 2\%$ [18]. This method using CBED is highly rec-
ommended to determine the accurate specimen thickness and easy to perform. On the other
hand, the CBED technique cannot be applied to an area which is highly defective since the
intensity variations of the fringes inside the CBED disks will be smeared by the diffused
scattering.
Table 2.3 Typical values of extinction distances (\( \xi_g \)) in ordered compound Ni\(_3\)Al, L\(_{12}\) structure) at 100Kv.

<table>
<thead>
<tr>
<th>Reflection (g)</th>
<th>Type of reflection</th>
<th>( \xi_g (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>S</td>
<td>3362</td>
</tr>
<tr>
<td>1 1 0</td>
<td>S</td>
<td>3205</td>
</tr>
<tr>
<td>1 1 1</td>
<td>F</td>
<td>369</td>
</tr>
<tr>
<td>2 0 0</td>
<td>F</td>
<td>425</td>
</tr>
<tr>
<td>2 1 0</td>
<td>S</td>
<td>3501</td>
</tr>
<tr>
<td>2 1 1</td>
<td>S</td>
<td>3680</td>
</tr>
<tr>
<td>2 2 0</td>
<td>F</td>
<td>632</td>
</tr>
<tr>
<td>3 0 0</td>
<td>S</td>
<td>4346</td>
</tr>
<tr>
<td>3 1 1</td>
<td>F</td>
<td>770</td>
</tr>
<tr>
<td>3 3 1</td>
<td>F</td>
<td>1160</td>
</tr>
<tr>
<td>4 2 0</td>
<td>F</td>
<td>1211</td>
</tr>
<tr>
<td>4 2 2</td>
<td>F</td>
<td>1422</td>
</tr>
<tr>
<td>5 1 1</td>
<td>F</td>
<td>1592</td>
</tr>
</tbody>
</table>

S: superlattice reflection.
F: fundamental reflection.
In the investigation of the grain boundary normal, four different methods were used and the selection of the method depended on the circumstances of the specific grain boundary. The most frequent use of the method to determine the grain boundary plane normals was the full trace analysis considering the specimen thickness using the fringe counting method or the CBED technique.

2.2.5 Symmetry Determination of the Crystal.

The symmetry determination of a crystal using CBED techniques can be done in two steps. The first step is the point group determination and the second step is the space group determination since screw axes and glide planes cause well defined features that can be recognized in the patterns.

2.2.5.1 Point Group Determination

The point group of a crystal is determined from a relationship between 31 diffraction symmetries and 32 point groups [12,20]. The diffraction symmetries were obtained from electron diffraction experiments and the 32 point groups are from real structural symmetries.

A pattern from a zone axis, particularly a prominent zone axis of high symmetry like [001], [011], or [111], can contain up to four pieces of symmetry information. Those are as follows;

i) Bright field symmetry, (BF).

ii) Projection symmetry in the bright field without 3-D effects.

iii) The symmetry of the whole pattern, (WP).

iv) The projection "whole pattern" symmetry without 3-D effects.

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where information of i) can be obtained from Higher Order Laue Zone (HOLZ) lines inside the central bright field disc, ii) from bright field fringes, iii) from considering whole pattern fully, and iv) from only zero layer disks without HOLZ effects. A table can be used for convenience;

<table>
<thead>
<tr>
<th></th>
<th>Bright Field</th>
<th>Whole Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Symmetry</td>
<td>i)</td>
<td>iii)</td>
</tr>
<tr>
<td>Projection Symmetry</td>
<td>ii)</td>
<td>iv)</td>
</tr>
</tbody>
</table>

After constructing a table from the symmetry information in a CBED pattern, the diffraction group of the pattern can be found from the relations between diffraction groups and four different information in the matrix above using Table 2.4. Then a tentative point group of the material can be determined by consulting the relationships between the diffraction groups and the crystal point groups in Table 2.5 [37]. If there exist ambiguity in determining an exact point group, it can be removed by following one of the procedures;

i) Use knowledge about the unit cell of the material.

ii) Obtain further information at the same zone axis to reduce the number of possible diffraction groups, that is, use additional informations from dark and ±G patterns.

iii) Go to another zone axis to determine diffraction group, then consult Table 2.6, which shows relationships between point groups and diffraction groups for different zone axes.
Table 2.4 Relation between diffraction groups and four different symmetry information from a CBED pattern [37].

<table>
<thead>
<tr>
<th>diffraction group</th>
<th>bright field</th>
<th>whole pattern</th>
<th>projection diffusion group</th>
<th>projection diffusion group</th>
<th>bright field</th>
<th>whole pattern</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>21R</td>
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</tr>
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<td>61R</td>
<td>61R</td>
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<td>61R</td>
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<td>6</td>
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<td>6mm1R</td>
<td>6mm</td>
<td>6</td>
</tr>
<tr>
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<td>6mm</td>
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<td>6mm1R</td>
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41
Table 2.5 Relation between diffraction groups and crystal point groups [14].

<table>
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<th>Diffraction Groups</th>
<th>Relation between the diffraction groups and the crystal point groups</th>
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<td>2mm</td>
<td>x</td>
</tr>
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<td>2m_R</td>
<td>x</td>
</tr>
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<td>21_R</td>
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<tr>
<td>2_R</td>
<td>x</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>x</td>
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Point Groups: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.
Table 2.6 Relation between zone axis symmetries and point groups [14].

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<td>2mm1a</td>
<td>2/mm</td>
<td>2/a</td>
</tr>
<tr>
<td>4mm</td>
<td>3m</td>
<td>4/m/a</td>
<td>m1a</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td>422</td>
<td>3/m</td>
<td>4/m/a</td>
<td>2ma/m</td>
<td>m</td>
<td>m</td>
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</table>

<table>
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<td>2/a</td>
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<tr>
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<td>3</td>
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<td>2/a</td>
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<td>m</td>
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<th>(62)</th>
</tr>
</thead>
<tbody>
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<td>2/m1a</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>m</td>
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<table>
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<th>(62)</th>
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</thead>
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<tr>
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<td>2/m1a</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>m</td>
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</tbody>
</table>

<table>
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<th>(62)</th>
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<tbody>
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<td>m4mm</td>
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<td>2/m1a</td>
<td>2/m</td>
</tr>
<tr>
<td>4mm</td>
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<td>m1a</td>
<td>m</td>
</tr>
<tr>
<td>4mm</td>
<td>2/m</td>
<td>2ma/m</td>
<td>m</td>
</tr>
<tr>
<td>422</td>
<td>2/m</td>
<td>2ma/m</td>
<td>2ma</td>
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</table>

<table>
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<tr>
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<th>(62)</th>
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<tbody>
<tr>
<td>4/m</td>
<td>4</td>
<td>m</td>
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<tr>
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<th>(62)</th>
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</thead>
<tbody>
<tr>
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<tr>
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<td>m1a</td>
</tr>
<tr>
<td>222</td>
<td>2/m</td>
<td>2ma/m</td>
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<table>
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<tbody>
<tr>
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<td>2/m1a</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>m</td>
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<table>
<thead>
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<tbody>
<tr>
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<td>1</td>
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</tbody>
</table>
2.2.5.2 Space Group Determination

In order to determine the space group, it is necessary to identify forbidden reflections. When a crystal has a screw axis or glide planes, forbidden reflections occur in the approximation of kinematical diffraction [12,21]. When dynamical diffraction takes place, such reflections are allowed to have finite intensity. However, the extinction of intensity is still caused for certain directions of the incident beam by the dynamical diffraction effect. This extinction appears as dark lines in CBED discs, and is called dynamic extinction lines or Gjønnes-Moodie (GM) lines after their study [38].

The existence of such lines indicates that the electron beam is incident on the crystal either parallel to a glide plane or perpendicular to a screw axis. The line of absence has a number of characteristics which may be used to distinguish it from accidental lines of absence occurring in similar positions. The characteristics are as follows [12]:

(i) Alternate reflections along a systematic line in a given layer must all show the characteristic line of absence.
(ii) The lines of absence become narrower as the specimen thickness increases.
(iii) The absences occur for all thickness and all microscope operating voltages.
(iv) Forbidden reflections can be confirmed by tilting. If they are indeed forbidden reflections, they will be disappeared by tilting.

The mechanism of producing forbidden reflections in CBED patterns can be found in the references [20,21,38]. The detailed procedure of determining space group of the material is illustrated in the reference [21]. The reference contains tables for dynamic extinctions. The tables list all expected GM lines for various incident beam directions of all the space groups. Using the table, the unambiguous determination of space group of a material can be done from the series of the zone axis patterns. Table 2.7 shows GM line rules for glide planes and 2\text{1} screw axis. Subscripts 2 and 3 in the table represent the dimensions in which the interaction occurs. The 'A' in the table means a black line along the major direction in the pattern and 'B' means the black line which is perpendicular to 'A'. Therefore A_3 can be seen as a mirror images refer to the major direction inside a disk.
Table 2.7 GM line rules for glide planes and 2\textsubscript{1} screw axis in a parallel-sided specimen [21].

<table>
<thead>
<tr>
<th>Symmetry elements of parallel-sided specimen</th>
<th>Orientation to specimen surface</th>
<th>GM lines in 2-D (ZOLZ) interaction</th>
<th>GM lines in 3-D (HOLZ) interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glide planes</td>
<td>Perpendicular: ( g )</td>
<td>( A_2 ) and ( B_2 )</td>
<td>( A_3 )</td>
</tr>
<tr>
<td>Glide planes</td>
<td>Parallel: ( g' )</td>
<td>----</td>
<td>( A_3 ) and ( B_3 )</td>
</tr>
<tr>
<td>Twofold screw axis</td>
<td>perpendicular: ( 2_1 )</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Twofold screw axis</td>
<td>Parallel: ( 2'_1 )</td>
<td>( A_2 ) and ( B_2 )</td>
<td>( B_3 )</td>
</tr>
</tbody>
</table>
As an example, for the cubic system of point group m3m, four different zone axis CBED patterns are needed such as CBED patterns from zone axes of [100], [110], [0kl] and [hkl] as shown in Table 2.8. If there are glide planes or screw axes, the patterns will reveal the GM lines. Finally, the space group of the material can be named with the knowledge of a lattice type. The lattice type can be deduced by projecting the lattice of reflections in each of the HOLZ's onto the zero-layer mesh.

2.2.5.3 Bicrystal symmetry determination.

Convergent beam electron diffraction is a well-known technique for determining the point and space group symmetry of single crystals. Recently an extension to the determination of bicrystal symmetry has been proposed [39,40]. The correlation between bicrystal symmetries and CBED pattern symmetries of bicrystals can be used to obtain useful information on the state of translation existing at a boundary in a bicrystal. It has been shown that the bicrystal symmetry is best classified by one of the 58 possible dichromatic point groups obtained from the interpenetrating pattern of the lattices from both crystals [41]. However a full symmetry requires space group determination from a bicrystal. Concerning the grain boundary structure, the full bicrystal symmetry may be important since specific rigid body translations can lead to the occurrence of ordinary or colored screw axes and/or glide planes in the bicrystal space group. Currently bicrystal symmetry determination has been restricted to the determination of point group from an analysis of the symmetry of CBED patterns. Experimental results on bicrystal point group determination show difficulties for the case of general bicrystals and have been limited to artificially made bicrystals with simple grain boundary geometries such as horizontal twin boundaries and vertical twin boundaries [42]. This is because general boundaries normally contain imperfect region by elastic strain field near the grain boundaries so that bicrystal CBED patterns are not clear to deduce symmetry information. In order to avoid these diffuse scattering of electrons in the grain boundary, a specimen should be annealed more carefully to reduce imperfections near grain boundaries. Also, a cooling stage specimen holder is highly recommended to avoid the thermal diffuse scattering and to enhance the clearness of the CBED pattern.
Table 2.8 GM line rules to identify the space group from the point group m3m [21].

<table>
<thead>
<tr>
<th>Incident beam direction</th>
<th>([100]) cyclic</th>
<th>([110]) cyclic</th>
<th>([\bar{h}a0]) cyclic</th>
<th>([\bar{h}hb]) cyclic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>221 Pm3m</td>
<td>P4/m32/m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>222 P43m</td>
<td>P4/n32/m</td>
<td>00(\bar{t}) n0 o0 m0</td>
<td>A3</td>
<td>00(\bar{t}) n0</td>
</tr>
<tr>
<td>223 Pm3m</td>
<td>P4/n32/m</td>
<td>00(\bar{t}) n0</td>
<td>A3</td>
<td></td>
</tr>
<tr>
<td>224 Pm3m</td>
<td>P4/n32/m</td>
<td>00(\bar{t}) n0 o0 m0</td>
<td>A3</td>
<td></td>
</tr>
<tr>
<td>225 Fm3m</td>
<td>F4/m32/m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>226 Fm3c</td>
<td>F4/m32/c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>227 Fd3m</td>
<td>F4/3d32/m</td>
<td>00(\bar{t}) t = 4n+2 d</td>
<td>(0k) 00 h = 4n+2 d</td>
<td>A3</td>
</tr>
<tr>
<td>228 Fd3c</td>
<td>F4/3d32/c</td>
<td>00(\bar{t}) t = 4n+2 d</td>
<td>(0k) 00 h = 4n+2 d</td>
<td>A3</td>
</tr>
<tr>
<td>229 Im3m</td>
<td>F4/m32/m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230 I43d</td>
<td>I4/m32/d</td>
<td>00(\bar{k}) t = 4n+2 d (0k) 00 h = 4n+2 d</td>
<td>(h_{bb}) 00</td>
<td>A3</td>
</tr>
</tbody>
</table>

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2.3 Results and Discussion

2.3.1 Statistical Distribution of $\Sigma$

From the geometrical analysis of grain boundaries, a statistical distribution of grain boundary types was obtained in the B-doped ductile polycrystalline Ni$_3$Al. Grain boundary misorientations were measured from 73 boundaries. In order to determine the proportion of special boundaries in randomly oriented polycrystals, a scheme based on the Brandon's criterion for maximum deviation, at which a boundary remains special, was adopted. In the present work, therefore, grain boundaries were classified as random boundaries when the boundary has $\Sigma$ values higher than 29 or when the deviation from the exact CSL orientation is larger than the maximum allowable deviation.

The $\Sigma$ distribution of grain boundaries, expressed as percentages, is shown in Fig. 2.8 from ductile Ni$_3$Al (24% Al with 500ppm B). There are about 15.1% of $\Sigma$=3 boundaries, 19.2% of boundaries between $\Sigma$=5 and $\Sigma$=29, and 65.7% of random grain boundaries. In order to compare $\Sigma$ distributions between ductile and brittle Ni$_3$Al, the $\Sigma$ distribution of brittle Ni$_3$Al (25% Al) by Hanada et al [43] was employed in Fig. 2.8. It shows that ductile Ni$_3$Al has more low $\Sigma$ boundaries than brittle Ni$_3$Al. However, low angle grain boundaries were not found in the present results. The absence of low angle grain boundary in ductile Ni$_3$Al is believed to come from the limited amount of grain boundaries sampled to get a statistical distribution and the way the grain boundaries were selected.

In the previous work by Farkas and Lewus [8] showed a similar result that low $\Sigma$ grain boundaries were appeared more than random boundaries using backscattered electron channeling patterns (BECP) of SEM. On the other hand, Mackenzie et al reported that there is no significant difference in $\Sigma$ distributions between ductile Ni$_3$Al and brittle Ni$_3$Al using BECP. The difference between two results is believed to come from the methods employed
Fig. 2.8 The Σ distribution of grain boundaries, expressed as percentages, for ductile Ni$_3$Al (24% Al with 500 ppm Boron) and brittle Ni$_3$Al [43].
to determine $\Sigma$ values and histories of the samples.

It has been pointed out that the effect of grain boundary structures cannot be ignored in discussing the fracture process in polycrystals. The importance of the effect may increase as intergranular fracture becomes dominant. The ductility of polycrystals is considered to be related to the frequency of special type of grain boundaries such as low-angle boundaries and low coincidence boundaries. A high frequency of random boundaries will bring about poor ductility of polycrystals. Watanabe [44] showed that random grain boundaries were preferential sites for intergranular fracture in most situations. The current result of the grain boundary character distribution in Ni$_3$Al polycrystals is consistent with the Watanabe’s experimental evidence. This is further supported by the work of Brokman and Balluffi [45]. They calculated the grain boundary energy according to $\Sigma$ values and showed the tendency of low grain boundary energies at low $\Sigma$ boundaries. Therefore, the present result of $\Sigma$ distribution of Ni$_3$Al shows the strong relation between $\Sigma$ distributions and fracture modes of the material.

The grain boundary energy of a certain $\Sigma$ grain boundary varies as a function of the boundary plane orientation. Low $\Sigma$ boundaries also can have high grain boundary energies when the plane is oriented randomly. Thus grain boundary plane orientations also should be considered besides the value of $\Sigma$. This has been suggested by the grain boundary energy calculations using the atomistic simulation [46]. The next section reports results on the distribution of grain boundary plane orientations in Ni$_3$Al.

2.3.2 Statistical Distribution of Grain Boundary Planes.

A review of geometric criteria for low interfacial energy proposed that the energetically stable grain boundary structure is related with the high planar density of coincident sites [47]. The planar CSL site density depends on the grain boundary plane orientation. So the statistical distribution of the grain boundary plane is important to investigate the
energetically stable orientation of grain boundary planes.

Using the methods in section 2.5.3, the statistical distribution of grain boundary plane orientations was obtained up to $\Sigma = 29$. The distribution allowed us some insight about the energetically stable grain boundary plane geometries for each $\Sigma$ and a transition point of $\Sigma$ which starts to choose random plane orientations. Figure 2.9 shows the result on grain boundary plane orientations adopted in each $\Sigma$. In the case of $\Sigma=3$ grain boundaries, all the planes showed \{111\} or \{112\} plane orientation. These orientations are the lowest energy, \{111\}, and second lowest energy, \{112\}, configurations in $\Sigma=3$ grain boundaries. The low energy configurations are expected for grain boundary planes having indices (hkl) which follow a rule of $n\Sigma = h^2+k^2+l^2$, where $n$ is 1 or 2, since these are the planes that are high in coincident sites. The trend of having low energy plane orientations was maintained on low $\Sigma$ boundaries up to $\Sigma=9$, and random orientations of grain boundary planes became dominant after $\Sigma=11$. The trend of deviating from the energetically stable geometries after $\Sigma = 11$ is believed to come from the fact that driving forces to choose energetically stable orientations of boundary planes are not strong in high $\Sigma$ boundaries. Similar results are reported by Farkas [46] on the computer simulation of the grain boundary energies in Ni$_3$Al as a function of the plane orientation for $\Sigma=3$. The author showed that \{111\} and \{112\} plane geometries were the most stable planes from energy calculations. This reasoning is supported by experimental results by Watanabe [44]. Watanabe showed experimental evidence that crack paths tended to follow random boundaries or high coincidence boundaries rather than low $\Sigma$ boundaries.

The present results imply a possible relation between grain boundary strength and the geometry of the grain boundaries since the low $\Sigma$ grain boundaries showed the tendency of having geometries of low energy boundary planes. On the other hand, high $\Sigma$ boundaries tends to adopt randomly oriented planes. In terms of the grain boundary energy, a transition point of $\Sigma$ values between coincidence boundaries and random boundaries is around $\Sigma = 11$ and grain boundaries after $\Sigma = 11$ may behave as random boundaries.
Fig. 2.9 Distribution of grain boundary plane orientations up to $\Sigma = 29$. 
2.3.3 Grain Boundary Accommodation of Slip in Ni$_3$Al.

It has been well known that the mechanical behavior of materials closely related to the reactions between grain boundaries and dislocations during deformation. Since the stress concentration occurred at the dislocation pile-up at grain boundaries, dislocation reactions with the grain boundaries are one of the important factor to be considered. If those dislocations at the grain boundary can move across the grain boundary, the stress concentration will be relaxed at the grain boundary. These occasions are expected to be associated with dislocation adjustments at the grain boundary in certain ways with an exception of coherent twin boundaries. In case of ordered intermetallic compounds such as Ni$_3$Al, the Burgers vector of dislocations are quite big compared to disordered materials and the adjustment of dislocations of ordered intermetallic compounds is difficult. However, in case of ductile Ni$_3$Al, it was found that dislocations were reoriented near the grain boundary and accommodated to grain boundaries.

Fig. 2.10 shows the typical dislocation reorientation near a grain boundary in ductile Ni$_3$Al. The reorientation of dislocations near grain boundaries were not found in case of brittle Ni$_3$Al since it was too brittle to observe the reaction of dislocation with grain boundaries. A possible explanation for the reorientation of dislocations in ductile Ni$_3$Al is the co-segregation of Ni and B atoms near the grain boundary.

The co-segregation by Boron and extra Ni atoms expect to change the ordered atomic structure to the compositionally disordered structure and result in the dislocation behavior like fcc materials. Similar results have been reported by Baker et al [48,49]. They also found that the dislocation rearrangement and accommodation near grain boundaries and its transmission across the grain boundary could occur more easily if the region in the vicinity of a grain boundary was disordered.
Fig. 2.10 Reorientations of dislocations as they approach to the grain boundary. The reorientations of the dislocations are expected to appear at the disordered region near grain boundaries.
2.3.4 Symmetry Determination Using CBED Techniques.

The symmetry groups of Ni₃Al were obtained following the same procedure as section 2.6.3. The procedure for point group determination is described in the Fig. 2.11 (a) and (b) with CBED patterns of [111] and [100] using the matrices constructed from two zone axes. The point group of the Ni₃Al was m̅3m. With the knowledge of the point group symmetry, a space group was determined from four different zone axes patterns, such as [100], [110], [0kl], and [hhl]. The Ni₃Al crystal does not show any GM lines in the patterns, Fig. 2.12 (a) and (b). Using the GM line rules for the point group m̅3m in the Table 2.8, the space group of Ni₃Al could be determined as Pm̅3m providing the information of the lattice type as a primitive cell.

The main purpose of the symmetry determination of the Ni₃Al was not just to determine the symmetry groups of single crystal Ni₃Al. The other aim to achieve was to determine the bicrystal symmetry in the grain boundary. With the full information of the symmetry in the grain boundary, the rigid body translation of one grain boundary with respect to the other was believed to be obtained. Symmetry determination of the grain boundary using CBED techniques has been studied on the case of diffuse-bonded, artificially made grain boundary which the grain boundary plane is parallel or perpendicular to the surface of the specimen [41]. In order to simulate the similar condition as the artificially made grain boundary case, the grain boundary which has greatly inclined from surface of the specimen was tried to get a clear CBED pattern. However the CBED pattern was not clear enough to obtain symmetry information from the discs of the CBED patterns. The reason for smearing of the CBED patterns is believed to come from an effect of local atomic distortion and thermal diffuse scattering. In order to avoid the local heating of the specimen, a cooling stage sample holder is needed. Thus the approach to determine the bicrystal symmetry information was not successful and remained in doubt. The investigation of Ni atom segregation and the quantitative measurement of disordering effect near grain boundaries using CBED techniques was not successful. This is because the segregated and disordered layer is too thin to be detected by convergent beam techniques.
[111] CBED pattern of Ni$_3$Al.

<table>
<thead>
<tr>
<th></th>
<th>Bright Field</th>
<th>Whole Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Symmetry</td>
<td>3m</td>
<td>3m</td>
</tr>
<tr>
<td>Projection Symmetry</td>
<td>6mm</td>
<td>6mm</td>
</tr>
</tbody>
</table>

Results from [111] CBED pattern: Diffraction group is $6_{\tilde{m}} m m$. There are two possible point groups, $\bar{3}m$ and $m\bar{3}m$ from Table 2.4. An ambiguity to determine the exact point group can be done by interpreting another zone axis for example [001] in the next page.

Fig. 2.11 (a) Zone axis patterns of [111] beam direction and a table constructed from symmetry of CBED patterns to determine the point group of Ni$_3$Al.
Results from [001] CBED pattern: Four different Diffraction groups can be chosen because of the insufficient symmetry information. These are $4m\bar{m}1\bar{a}$, $4mm$, $4\bar{a}m\bar{m}1\bar{a}$, $4m\bar{m}1\bar{a}$. By consulting the Table 2.4 and 2.5, only $4mm$ is the possible diffraction group. Then the point group of Ni$_3$Al can be determined as m$3m$ by comparing the previous symmetry interpretation from the [111] zone axis.

Fig. 2.11 (b) Zone axis patterns of [001] beam direction and a table constructed from symmetry of the CBED patterns to determine the point group of Ni$_3$Al.
[001] zone axis CBED pattern of Ni$_3$Al.

[011] zone axis CBED pattern of Ni$_3$Al.

Fig. 2.12 (a) Zone axis patterns of [100] and [110] to examine the possible GM lines. No GM line is shown from above zone axes to identify screw axes and glide planes.
[112] zone axis CBED pattern of Ni3Al.

[013] zone axis CBED pattern of Ni3Al.

Fig. 2.12 (b) Zone axis patterns of [112] and [013] to examine the possible GM lines. No GM line is shown from above zone axes to identify screw axes and glide planes.
2.4 Conclusions.

A schematic way of determining the geometry of the grain boundary was designed using TEM. The geometry includes the rotation axis, the rotation angle and the grain boundary plane orientation which is adopted in certain $\Sigma$ boundaries. Using the above method, the statistical distribution of the grain boundary in Ni$_3$Al and that of grain boundary planes were obtained. The present result supported a possible relation between mechanical behavior of the Ni$_3$Al and the distribution of the grain boundary types. However, it was also found that the dislocation reorientation near the grain boundary also plays one of the major role for the ductility of Ni$_3$Al. Therefore, the fracture behavior of Ni$_3$Al is believed to depends not only on the grain boundary distribution but also on the dislocation motion in the vicinity of the grain boundaries. Using CBED techniques, the symmetries of the single crystal Ni$_3$Al was obtained including point group and space group of Ni$_3$Al. However, the attempt to obtain bicrystal symmetries using CBED techniques was not successful and remained for further research.
2.5 References


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[33] Y. Ishida and M. Mclean, Phil. Mag., 27 (1973) 1125.


Chapter 3

Atomistic Grain Boundary Structure Simulations in Ordered Ni$_3$Al.

3.1 Introduction

Segregation and disordering in the vicinity of grain boundaries are important phenomena to understand the grain boundary behavior since they have marked effect on the property of materials. Particularly, in Ni$_3$Al, those phenomena were expected to explain dislocation motions near grain boundaries in section 2.3.3. However, there is no direct evidence of those phenomena except a few reports on segregation effects near the boundary [1,2]. The purpose of this chapter is, therefore, to study the segregation and disordering effect near the boundary using Molecular Statics atomistic computer simulation.
In the present work, three different compositions of a $\Sigma = 5$ grain boundary were simulated to study the segregation and disordering effect near the grain boundary. This multiplicity of structures arises from possible differences in composition and ordering state [3]. In order to study the influences of composition on the segregation and disordering near grain boundary, we have studied the interactions of antisite defects with grain boundaries. We consider the addition of one antisite defect per boundary period in different positions in the grain boundary structure. By considering initial boundary structures of different compositions, further information can be obtained on segregation behavior to the grain boundaries. By addition of two antisite defects of opposite kinds in the binary ordered alloy one can study the energetics of disordering processes in these boundaries. It is interesting to note that although disordering of the grain boundary region is inherently a high temperature process the energetics of antisite defects in the grain boundary region are closely related to ordering driving forces and one can therefore infer general trends of the order-disorder behavior without actually carrying out a high temperature simulation. The methods that can be used to study the energetics are those of molecular statics, with embedded atom interatomic potentials [4,5]. We then compare the results and the implications for segregation and ordering behavior to the results of other techniques, particularly the Cluster Variation Method [6] and Monte Carlo simulation [7].

3.2 Simulation Technique

3.2.1 Structures of $\Sigma = 5$ grain boundaries of Ni$_3$Al

The grain boundary structures we studied are $\Sigma = 5$ grain boundaries of symmetrical tilt type in the (210) plane. In this grain boundaries two different (210) planes are possible in Ni$_3$Al. The planes can have either 100% Ni atoms or 50% Al atoms and 50% Ni atoms.
Therefore three different $\Sigma = 5$ (210) grain boundaries are possible by combinations of two different planes. We identify them as 50/50, 100/100 and 50/100 Ni atomic % grain boundaries following the nomenclature used by Chen et al [3]. The 50/50 boundary would refer to a boundary whose touching planes from either crystal have a composition of 50% Ni and 50% Al. Similarly a 100/50 boundary implies that one of the boundary planes contains all Nickel atoms while the other has equal amount of Ni and Al atoms. Therefore, while the 100/50 grain boundary has the same stoichiometry as the bulk Ni$_3$Al, the 100/100 boundary is Ni rich and 50/50 grain boundary is an Al rich boundary. The unrelaxed initial configurations of the grain boundary structures are shown in Fig. 3.1.

### 3.2.2 Atomic interaction potentials

The grain boundary simulations in this study employ embedded atom type local volume potentials [6,7]. The term local volume indicates that there is a term in the energy expression for each atom that depends on the local atomic density about that atom. The model for potentials consists of two distinct terms; a pairwise term and a local density (volume) term. The energy of an n-atom system is

$$E = \sum_{i}^{n} E_i$$

(3.1)

where the energy of atom i is given by

$$E_i = \frac{1}{2} \sum_{\{r_{ij}\}} \Phi(r_{ij}) + F(\rho_i)$$

(3.2)

Here $r_{ij}$ is the distance between atom i and j, $\Phi$ is a pairwise interatomic potential, and $\rho_i$ is the density at atomic site i due to all its neighbors.
Fig. 3.1 The unrelaxed \( \Sigma = 5 \) (210) symmetric tilt boundary structures of Ni\(_3\)Al 100/50 (a), Ni\(_3\)Al 100/100 (b) and Ni\(_3\)Al 50/50 (c). Square and cross symbols represent two different layers of (001) planes and numbers in atom positions are used to identify sublattices.
\[ \rho_i = \sum_{j(r_{ij})} \rho(r_{ij}) \]  

(3.3)

The embedding energy, \( F(\rho_i) \), can be interpreted as the energy from embedding atom \( i \) in an electron gas of density \( \rho_i \) and contains the quantum mechanical interaction between the embedded atom and the host atom. On the other hand the pairwise term is account for the classical electrostatic interaction. The details of the form and fit of the potential are in references [6].

### 3.2.3 Simulation procedure

The initial configurations of the grain boundaries can be constructed by overlapping two infinite perfect crystals and performing the appropriate rotation (9) about an axis [hkl] to achieve the desired misorientation. In the case of \( \Sigma = 5 \) (210) grain boundaries one crystal was rotated 180° about an axis [120] with respect to the other grain. The grain boundary plane was chosen such that the grain boundary was symmetric. In pure metals, there is only one unique way of performing the initial overlap of two infinite crystals. However, in an ordered binary alloy, one must consider the element type of each lattice site. Since the L1_2 structure consists of four interpenetrating simple cubic lattice (three occupied by Ni and one by Al in Ni_3Al), a choice must be made to which type of atom occupies each sublattice. For an L1_2 structure, one can imagine three different grain boundary configurations by specifying the percentage of Ni (100% or 50%) in the first layer of the each of the two grains as described in section 3.2.1.

After the grain boundary construction, the boundary conditions need to be established before the numerical procedures. Through appropriate boundary conditions, one can simulate the computational cell as if they were part of an infinite system. A natural approach to the problem is to surround the borders of the system with more atoms, which can be treated on a somewhat simpler basis than those inside. For convenience, let's call the atoms within the
computational cell "Region I" atoms and "Region II" for the rest as shown in Fig. 3.2. The assumption to make for region II atoms is that they are fixed on normal lattice sites. They interact with neighbor Region I atoms across the border, but their coordinates do not change. Therefore, the atoms in Region I are free to move under the influence of the potentials while atoms in Region II are treated to satisfy the long range elastic interactions of the defects. On the other hand, the use of periodic boundary conditions offers another method of deluding the border atoms as if they are part of an infinite system. However, introducing the periodicity can cause some spurious effects which is not a characteristic of the unconstrained infinite solid. In case of grain boundaries, the periodic boundary condition and fixed boundary condition was used to build the computational block more realistic. This is because the grain boundary plane has an infinite two dimensional periodicity but the direction normal to the boundary plane does not maintain its periodicity.

For the relaxation of atoms inside computational cell (the Region I), the conjugate gradient method was used. In this relaxation procedure the atoms are moved from their initial positions toward a steepest gradient direction, i.e., the direction in which the rate of energy decrease is a minimum. The atoms are moved in this direction until the energy gradient is zero. Once the lowest energy position is attained the atoms are moved in a direction perpendicular to the initial direction of motion. This iteration procedure is carried out until no further energy lowering occurs by a movement in a perpendicular direction. The procedure involves all atoms inside the computational cell and valuation of total potential energy of the simulation block by considering all the possible pairs within cutoff radius of interatomic forces. Although the left and right grains are free to translate with respect to each other, the translational state of the relaxed structure may not correspond to the lowest energy configuration, because multiple energy minima may exist. To find a global minimum among the many local minima, rigid body translations of one grain with respect to the other was performed.

Creating antisite defects near grain boundaries was done by interchanging atoms of different sublattice types. By numbering sublattices, the atomic type was identified such as 1
Fig. 3.2 Schematic drawings of the simulation blocks of atoms. The cell has periodic boundary conditions in the X and Z directions and has fixed boundary condition in the Y direction which is perpendicular to the grain boundary plane.
for Al and 2,3 and 4 for Ni atoms in the different sublattice sites as shown in the figure below. Three different numbers were used for Ni atoms since each sublattice has different neighbors in the vicinity of the grain boundaries.

The procedure to create antisite defects near grain boundaries were conducted in two ways. First, antisite defects were created one by one as a function of the distance from the grain boundary by switching with different sublattice types to calculate the antisite defect energy. Then, pairs of antisite defects of different atom types were created by switching an Al atom at sublattice type 1 and a Ni atom at sublattice type 3 to calculate the antisite defect energy for the pair.

In order to calculate antisite defect formation energies, the grain boundary energy is considered first. The grain boundary energy is defined as follows;

\[ \gamma_{gb} = \frac{1}{A} \Delta E \]  

(3.4)

where A is the unit area of the grain boundary plane of region 1 in Fig. 3.2 and \( \Delta E \) is the energy change due to the presence of the grain boundary,

\[ \Delta E = E^{gb} - E^{bulk} \]  

(3.5)
$E^{gb}$ is the energy of the simulation cell which contains the grain boundary and $E^{bulk}$ for the energy without the grain boundary. When an antisite defect is created, the grain boundary energy obtained from equation (3.4) and (3.5) involves the antisite defect formation energy as well as the grain boundary energy. Thus, the antisite defect formation energy, $E_{ASD}$, is the energy difference between the grain boundary energy with an antisite defect, $\gamma_{gb+ASD}$, and without an antisite defect, $\gamma_{gb}$.

$$E_{ASD} = \gamma_{gb+ASD} - \gamma_{gb} \quad (3.6)$$

In computing the grain boundary energies with the defect it is important to take into account that when the antisite defect was created, Al was substituted for Ni or vice-versa. The substitution involves the energy of the antisite defect plus a difference in energy related to the fact that the cohesive energy of the material is not the same per Ni atom or Al atom. The later term should be subtracted from the observed total energetic difference. This correction is not necessary when considering a pair of antisite defects that maintain the composition of the block of atoms being relaxed.
3.3 Results

We have studied in detail the antisite defect formation energies in the vicinity of a $\Sigma = 5$ grain boundary of symmetrical tilt type in the (210) plane. There are several possible configurations of this boundary with different stoichiometries. These different configurations are obtained starting from initial configurations that have different values of the rigid body translation of one crystal with respect to the other in the direction perpendicular to the grain boundary plane. As a result, there are structural vacancies in some of these structures that imply different chemical compositions. We have chosen three of these that have different stoichiometries. All three configurations are obtained by relaxing the structure with the initial configuration having no rigid body translation of one crystal with respect to the other in the directions parallel to the grain boundary plane. The relaxation process then yields the equilibrium values for the rigid body translation in the three directions. The three structures represent local minima in the energy functional. In the terminology of Takasugi and Izumi [8] all are fully symmetrical boundaries. In the terminology used by Chen et al [3] they are named as a 100/50 boundary, a 50/50 boundary and a 100/100 boundary. These two latter boundaries have structures that contain structural vacancies and have therefore different stoichiometries. The 50/50 boundary contains two Ni structural vacancies per period, whereas the 100/100 boundary contains one Al and one Ni structural vacancy per period. In previous studies of grain boundary energies in Ni$_3$Al Chen et al found that the energies of these different types of boundaries were different, with differences of up to 20% [3]. Furthermore, in a recent study of the energy of $\Sigma = 3$ boundaries for different grain boundary planes it was found that the behavior of two types of boundaries are different [4]. It is expected that the boundaries that are Ni-rich will behave in a way that is similar to that of pure Ni and other FCC metals, whereas the boundaries that are stoichiometric and Al-rich are expected to present particular features associated with the ordering in the alloy and will also be affected by factors like the
different atomic sizes and bond lengths that occur in the ordered system. In particular, by introducing antisite defects, they will present Al-Al nearest neighbor bonds that are not present in the bulk structure [9].

3.3.1 Relaxed grain boundary structure without defects

Fig. 3.3 shows the structure of the relaxed boundaries without antisite defects. In this figure the boundaries are shown in a (100) projection, including two consecutive planes, which are indicated as squares and pluses. Numbers in the atom positions represent different sub-lattice sites, that is, sublattice 1 for Al atoms and sublattices 2, 3 and 4 for Ni atoms.

Note that the 100/50 boundary structure is symmetric with respect to the grain boundary plane (mirror plane). In the cases of the 50/50 and 100/100 boundary this symmetry is broken due to the presence of the structural vacancies.

3.3.2 Formation energies for antisite defects

The energies of antisite defects in the bulk were computed and are shown in table 3.1. The energies reported in this table have already been corrected for the different cohesive energies attributable to Al or Ni and are therefore only the energies of having an atom in the incorrect sublattice. The table includes vacancy formation energies for comparison. The vacancy formation energies are part of the set of properties used in the development of the interatomic potentials. As expected, the substitution of Al into a Ni site involves a large energy, since it introduces nearest neighbor Al-Al bonds that are not present in the bulk. These nearest neighbor bonds occur with bond lengths that are about 10% shorter than Al-Al bonds in pure Al or other known stable Al compounds. On the other hand substituting a Ni atom into an Al site actually involves a negative energy and is a favored defect. This means that the present interatomic potentials actually predict that the lattice can easily accommodate extra Ni by
Fig. 3.3 Structural units obtained after relaxations in the present simulation for the lowest energy configurations, (a) 100/50, (b) 100/100 and (c) 50/50. Square and cross symbols represent two different layers of (001) planes and numbers in atom positions are used to identify sublattices.
Table 3.1 Energies of point defects in bulk Ni₃Al [in eV].

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy [Al]</th>
<th>Energy [Ni]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td>1.87</td>
<td>1.64</td>
</tr>
<tr>
<td>Antisite defect</td>
<td>-0.14 [Ni in Al site]</td>
<td>0.46 [Al in Ni site]</td>
</tr>
<tr>
<td>Pair of antisite defects</td>
<td>0.32 [switching Al and Ni]</td>
<td></td>
</tr>
</tbody>
</table>
substituting it in Al sites. This is also expected from the phase diagram and it is known that Ni-rich Ni₃Al has better mechanical behavior than the stoichiometric material and can be ductilized in its polycrystalline form by adding Boron. The energy of a pair of antisite defects refers to the interchanging of positions of Ni and Al atoms and is of course positive as expected for an ordered material. This number is simply the sum of the energies of the two single antisite defects, including no interaction among them. This applies to the case of the two defects being far apart. Fig. 3.4 shows the results for the energy of antisite defects as a function of the distance from the boundary plane for the stoichiometric 100/50 boundary. The calculations are shown in the form of grain boundary energy differences for grain boundaries containing one defect per boundary period. These values are plotted for the different sublattices, with sublattice 1 being occupied by Al. Sublattices 2, 3 and 4 are all Ni and are equivalent to each other in the bulk. Due to the presence of the boundary in the (210) plane antisite defect energies from different sublattices near the boundary are not equivalent to each other in the results of Fig 3.4 (a). This can be readily understood if it is noted that the environment of the different sublattices is different in the grain boundary structure shown in Fig. 3.3 (a) for sites in the vicinity of the grain boundary. Far from the grain boundary the three sublattices become equivalent, recovering the bulk behavior. For the 100/50 structure one can again observe the mirror symmetry with respect to the boundary plane.

These results indicate that for Al substitution into Ni sites the grain boundary will act as a strong segregation site, and all extra Al will go to the grain boundary. On the other hand this particular boundary will not be a strongly favored site for the location of extra Ni as shown in Fig. 3.4 (b). At high temperatures this boundary is expected to present Al segregation and not Ni segregation. Fig. 3.5 shows similar calculations for the Ni rich boundary (100/100 boundary). In this case the results are not symmetric with respect to grain boundary plane since the boundary contains two structural vacancies per boundary period. The same general features are observed as in the previous case of the stoichiometric boundary. The expectation of Al segregation to this boundary is now more pronounced, due to the fact that the initial
Figure 3.4 Distributions of the defect energies by creating an antisite defect near a 100/50 boundary. Ni(3)-Al(1) means Al atom in the sublattice site 1 is substituted to the position of Ni atom in the sublattice site 3.
Figure 3.5 Distributions of the defect energies by creating an antisite defect near a 100/100 boundary. Ni(3)-Al(1) means Al atom in the sublattice site 1 is substituted to the position of Ni atom in the sublattice site 3.
configuration of the boundary is now Ni rich. Fig. 3.6 shows the same type of calculation for an Al rich boundary. The results now show a tendency for the extra Ni to go to the boundary. This is expected since this is an originally Al rich structure.

Another feature to be noticed in the results is the oscillatory nature of the defect formation energies plotted as a function of the distance to the grain boundary plane. This behavior is consistent with the oscillatory behavior found in the lattice relaxation displacements, as analyzed in reference [10]. This type of behavior was also found for the vacancy formation energy in the grain boundary region [11].

3.3.3 Implications for grain boundary ordering behavior

In order to study grain boundary ordering behavior the energy of creating a pair of antosite defects per grain boundary period was studied as a function of the distance from the boundary plane. As mentioned for the case of the bulk, the energies are those of creating the pair of defects with no interaction between them so as to simulate a certain amount of disorder per boundary period. The results are shown in Fig. 3.7 for the three different boundaries considered in the present study. It is seen that in all cases the energies decrease in the boundary region and disordering is expected in the vicinity of the grain boundary at temperatures lower than in the bulk. These results can be compared to those obtained by using the cluster variation method for a high temperature simulation in a two-dimensional lattice gas model system as shown in section 4.3.2. The dependence of the order-disorder parameter on the distance to the grain boundary follows a remarkably similar pattern of CVM results in Fig. 4.6. The present results are also consistent with the calculations obtained by Foiles [7] using a Monte Carlo simulation with embedded atom potentials for Ni3Al. The latter author calculated the energy of formation of antosite defects in the vicinity of the grain boundary at high temperature and obtained similar results to the ones reported in the present work.
Figure 3.6 Distributions of the defect energies by creating an antisite defect near a 50/50 boundary. Ni(3)-Al(1) means Al atom in the sublattice site 1 is substituted to the position of Ni atom in the sublattice site 3.
Fig. 3.7 Distribution of the defect energies by creating pairs of antisite defects near three types of $\Sigma = 5$ (210) grain boundaries (interchanging Al(1) and Ni(3)).
3.4 Conclusions and Discussion

The important conclusion from the present results is that segregation behavior will vary with the composition and structure of the particular boundary in question. There is a tendency for Al to segregate to the boundaries easier than Ni. This trend, however, is changed when the composition of the boundary is Al rich. The implications of the present results for order-disorder behavior are more general and indicate that the grain boundary appears to be a favored location for disorder in all cases.

Regarding the segregation of antisite defects to the grain boundary region the present results indicate a tendency of segregation to grain boundaries, in agreement with the result of Monte Carlo calculations [7] and recent experimental results by E. P. George et al [12]. However, these results indicate that this segregation behavior is strongly affected by the grain boundary composition. The implication of disordering near grain boundary in the present results also consistent with recent HREM result by Mackenzie and Sass [13].

Another important point in the present results is that the antisite defect formation energy in the vicinity of a grain boundary follows an oscillatory behavior as a function of the distance to the grain boundary plane. This behavior is similar to that found in the lattice relaxation displacements. These oscillations are connected to the fact that local volume dependent interatomic potentials were used. Ordered alloys such as Ni₃Al are particularly expected to present oscillatory relaxations that can be understood as internal relaxation within the four atom motif that constitutes the crystal when located at the nodes of a simple cubic lattice.
3.5 References

Chapter 4

Grain-boundary ordering, segregation and melting transitions in a two-dimensional lattice-gas model

4.1 Introduction

In this chapter, the grain boundary structure calculation is introduced with temperature effects. This is very important because the direct calculation of high temperature structure of the grain boundary is not possible without considering entropy calculation. In particular, grain boundary transitions such as melting and disordering at high temperatures are important factors to theoretically understand the particular features of the grain boundary structure and its behaviors in ordered alloys. However, most of the theoretical studies of the grain boundary structure are performed using energy minimization techniques at absolute zero. In the few
high temperature studies of pure materials there has been some evidence of the possibility of melting transitions of grain boundary at temperatures below the bulk melting point [1,2,3]. Other calculations show significant disordering and segregation effects near a free surface or an antiphase boundary [4,5]. Monte Carlo calculations have been carried out for grain boundaries [5] showing significant variation of the anti-site defect near the grain boundary region. It may be expected that at high temperatures these effects will be significant in controlling the grain boundary behavior.

The purpose of the present work is to study the possible disordering and segregation effects near a Σ = 5 grain boundary at high temperatures. In particular we are interested in studying the influence of important features of the bulk behavior on the grain boundary structure, for example the effects of a large difference in the melting points of the two components of the binary alloy.

The model used in the present work is similar to that of Kikuchi and Cahn for a pure material [1] and is extended by us for two components. The model is very simple and two dimensional. It can, nevertheless, yield general trends which are expected to be valid in a wide variety of cases. Although two-dimensional results will not be necessary over to the three dimensional case, the simple model is particularly useful in studying the relationship of the obtained results to the energetic assumptions in the model.

Both disordering and segregation behavior will be strongly related to the energetic assumptions in the model. In the following section 4.2.2 we discuss the assumptions chosen in the present work. The cases studied are restricted to those for which the low temperature structure of the boundary is perfectly solid and well ordered. These features, as well as the low temperature segregation behavior are discussed in section 4.2.3. As the temperature increases the boundary disorders increasingly both chemically and spatially. All cases studied are for an ordering alloy with a bulk order-disorder temperature lower than the melting point, meaning that the dominant type of transition in the grain boundary will be the chemical disordering and segregation. One particular feature of the structure of grain boundaries in ordered alloys is the fact that different ordering configurations are possible. These do not
have necessarily the same energy. The present model allows the study of the different ordering configurations in the grain boundary region and their energy. We have restricted the present study to the configurations that are actually coincident site structures. In the nomenclature of Takasugi and Izumi [7] these are called fully symmetrical boundaries, as opposed to what they call pseudo-symmetrical boundaries. Also, no rigid body translations of one crystal with respect to the other were allowed. Transitions among the different structures are observed in the calculations. These different types of transitions are discussed in section 4.2.3.

The study of the full phase diagrams corresponding to each of the energy assumptions is essential to fully understand the grain boundary region and is undertaken first. These results are reported in section 4.3.1 Section 4.3.2 includes the results for the grain boundary ordering transitions and section 4.3.3 describes the observed segregation behavior.

4.2 Theory

4.2.1 The Model and Interaction Energy Assumptions

The present model is based on a two dimensional lattice gas with the same assumptions as in reference [1]. The energy computation is performed on a pair wise basis and only two possible interatomic distances are included. One of these distances corresponds to the bulk nearest neighbor distance and the other is slightly larger. The two distances are indicated in Fig. 4.1 as AB and AC, respectively. The ratio of the interaction energies corresponding to the two distances is a measure of the shape of the interatomic potential and may influence the results. In the present work we have used the same ratio as in reference [1], namely 1.2 meaning that the interaction energy for the larger distance is 20% smaller negative than the interaction at nearest neighbor distances. In the present work this assumption is maintained for both components and the cross interaction energies as well. Kikuchi and Cahn [8] recently reported a study of the influence of varying this assumption differently for the different types
Fig. 4.1 The structure of a two-dimensional $\Sigma = 5$ grain boundary and the nine-point basic cluster in the model.
of interactions. In the present work we studied the effect of an asymmetry in the phase diagram and therefore maintained other parameters constant. Interactions at distances lower than the nearest neighbor distance are not allowed, that is, they are strongly repulsive. Interactions at distances larger than AC in Fig. 4.1 are taken as zero and not included in the calculations.

In addition, we assume an ordering system with an ordering energy,

\[ V = \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \]  

(4.1)

Two different cases were tested in the calculations corresponding to two different phase diagrams. The first one is that of a completely symmetric phase diagram where the melting points of the two components are the same. The second one is that of an asymmetric diagram where one of the components has a higher melting point than the other. These cases correspond to two different values of the energy parameter, defined as:

\[ \Delta = \frac{\varepsilon_{AA} - \varepsilon_{BB}}{V} \]  

(4.2)

The value \( \Delta = 0 \) corresponds to a symmetric phase diagram and the value \( \Delta = 1.33 \) corresponds to a phase diagram that is asymmetric with a lower melting point of component B. The ordering energy is maintained the same for both cases. Table 4.1 summarizes the assumptions used for the energy calculation.

For the calculation of the entropy the cluster variation method was used with a basic cluster of nine points. The cluster variation method is one of the methods which improve the degree of approximation by increasing the size of the basic cluster to be arranged at the lattice sites. The degree of approximation which can be improved in a most efficient way depends on the choice of the shape of the basic cluster. This is equivalent to increasing the variational parameters to obtain a better approximation. In the case of the 9-point cluster, an approximate
Table 4.1 Summary of the assumption used for the energy calculation.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$</th>
<th>$V/\varepsilon_0$</th>
<th>$\mu_A/\varepsilon_0$</th>
<th>$\mu_B/\varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0.00</td>
<td>0.45</td>
<td>-1.5</td>
<td>-1.5</td>
</tr>
<tr>
<td>Case 2</td>
<td>1.33</td>
<td>0.45</td>
<td>-2.22</td>
<td>-0.78</td>
</tr>
</tbody>
</table>

a: Stoichiometric alloy in a symmetric phase diagram
b: Stoichiometric alloy in an asymmetric phase diagram
The combinatorial formula to get a configurational entropy is,

$$
\Omega = \left[ \begin{array}{c} \{V\} \{W\} \\ \{Y\} \{X\} \end{array} \right]
$$

(4.3)

where \{ \} is the CVM notation and represents the cluster combinatorial factor such as,

$$
\{V\} = \sum_p \sum_i L(V_i)
$$

(4.4)

$$
\{W\} = \sum_p \sum_k L(W_k)
$$

(4.5)

$$
\{Y\} = \sum_p \sum_i L(Y_i)
$$

(4.6)

$$
\{X\} = \sum_p \sum_i L(X_i)
$$

(4.7)

where \(L\) is Stirling's approximation. The subscript \(p\) means each plane number in the crystal structure and, subscripts \(i, j, k, l\) represent different configurations of the basic cluster and subclusters. Shapes of clusters considered in the formula (4.3) are listed in Table 4.2.

Since distances lower than the nearest neighbor are not allowed, at most two out of the nine points in the cluster can be occupied. This reduces the number of possible configurations of the cluster that have to be considered in the calculation of the entropy. There are 59 configurations of the basic cluster. Table 4.2 shows all possible configurations for the basic cluster and subclusters used in cluster variation calculations. The geometry of this cluster allows the calculation of the free energies for bulk solid and liquid phases as well as for \(\Sigma = 5\) grain boundary. The minimization of the free energy is then carried out for each of these cases with respect to the equilibrium distribution of each of the possible configurations of the basic cluster. In finding the minimum free energy with respect to these large number of
Table 4.2 All possible configurations of basic clusters (Y) and subclusters (V,W,X) used in the cluster variation calculations.

### Basic cluster (Y)

![Basic cluster (Y) configurations]

### Subcluster (W)

![Subcluster (W) configurations]

### Subcluster (V)

![Subcluster (V) configurations]

### Subcluster (X)

![Subcluster (X) configurations]
variables, a special linear iteration technique, called the natural iteration method (NIM), was used. NIM has a unique feature that the free energy function being minimized always decreases step by step at each iteration until maximum convergence limit reaches to a given value.

The different bulk phases and the grain boundary have different symmetry constraints that have to be considered in the calculation. For all the bulk phases neither cluster distributions nor chemical concentrations are fixed. Rather the chemical potential of both species is fixed and the minimization process yields the equilibrium configurational distribution and concentration. A number of lattice planes have to be considered for all phases. For the solid phases five points per plane are considered, as shown in Fig. 4.1. The number of lattice planes is at least 10 for the bulk solid phases. We used 15 for all bulk phases. As the minimization proceeds, the configurations in planes n and n+10 are maintained equal. For the grain boundary the number of planes needs to be much larger since the periodicity is broken in the direction perpendicular to the boundary. We used at least 37 planes in this case. The configuration of the planes far from the boundary is fixed and set equal to the bulk equilibrium configuration at that temperature and for the same chemical potentials. The numerical method used for the minimization is natural iteration, as described by Kikuchi [9].

4.2.2 Low Temperature Behavior

The low temperature behavior of the system is readily understood based on the energetic assumptions described above. The stable bulk phase at low temperature will be the ordered solid and there are two equivalent variants of this ordered solid which are the ones shown as upper and lower crystals in Fig. 4.1.

The low temperature structure of the boundary will be determined by the fact that distances closer than nearest neighbor are not allowed. This means that one atom per boundary period has to disappear. This will occur in the two planes that are immediately adjacent to the grain boundary plane in both crystals giving rise to the W-shaped density of the boundary found by Kikuchi in the pure material. In the case of the ordered alloy with the energetic
assumptions discussed above the grain boundary region will be ordered at low temperatures. There will be two possible configurations of this low temperature ordered boundary corresponding to the location of the boundary plane at a plane of A or B atoms respectively. For the case of a symmetric phase diagram these two configurations will be equivalent, not so in the case where the two melting points differ. In this later case the boundary located at a plane of (low melting point) B atoms will be lower in energy.

The segregation behavior at low temperatures is determined by the shape of the potential, i.e. the assumption that the interaction energies at distances AC of Fig. 4.1 is 20 percent lower than that of nearest neighbors, and the fact that this assumption is also maintained for the cross interactions in the ordering system. It can be shown easily that for both pure A and pure B the other type of atom present as impurities will be rejected from the boundary. This is seen if the energies associated with a B impurity in pure A are calculated for the different locations of the impurity. These are as follows: 1) the B atom located in the bulk consisting mainly of A atoms, $1.2 \times 4(\epsilon_{AB} - \epsilon_{AA})$; 2) the B atom located at sites 1 or 3 in the grain boundary, $1.2 \times 3(\epsilon_{AB} - \epsilon_{AA})$; 3) the B atom located at grain boundary site 2, $(1.2 \times 3 + 1)(\epsilon_{AB} - \epsilon_{AA})$ where sites 1, 2 and 3 refer to the ones indicated in Fig. 4.1. For the symmetric energy parameter ($\epsilon_{AA} = \epsilon_{BB} > \epsilon_{AB}$) it is clear that the bulk is the energetically most favorable location and the impurity will therefore be rejected from the boundary. A similar reasoning yields the conclusion that A impurities in pure B will also be rejected from the boundary. Since in the stoichiometric alloy of case 1 in Table 4.1, A and B are completely equivalent in this case, there will be no segregation. On the other hand in the stoichiometric alloy of case 2 in Table 4.1 the boundary will be enriched in the lower melting point element since $\epsilon_{AA} > \epsilon_{BB} > \epsilon_{AB}$.

4.2.3 Types of Transitions

The first type of transitions that can be observed in the present model is the order-disorder transitions in the bulk and in the grain boundary region. The order-disorder transition
in the two dimensional model used here is of second order for all compositions, since both ordered and disordered phases will have very few vacancies at temperatures close to the transition. It is expected that the calculated transition behavior for the bulk will be the same as that predicted by a two dimensional square Ising model in the pair approximation. The critical issue is the order-disorder behavior in the grain boundary region. It is possible that this transition will be different from that of the bulk. Previous work studying the order-disorder phenomena near the surface region observed that the surface region is more disordered than the bulk [4]. Two types of transitions have been observed [10]. The first one, called ordinary is one where the actual order-disorder temperature of the surface is the same as in the bulk, even if the surface region is more disordered than the bulk at temperatures below the transition. The second one is called an extraordinary transition, where the temperatures are different.

In addition to the order-disorder temperatures the present model can study melting transitions. These are of first order in the bulk and have been shown to occur in the boundary region at temperatures lower than the melting point of the bulk. This type of transitions are clearly evident in the density profiles of the boundary at high temperatures, as shown by Kikuchi and Cahn [1]. for a pure material. In the present model it is important to note that as we move in composition it is essential to maintain constant pressure in the calculations and since vacancies are included in significant amounts close to the melting point this condition is not necessarily maintained. The Gibbs-Duhem equation has to be satisfied as composition changes, as described below in the calculation of the phase diagrams.

Finally, it is interesting to study the transition that occurs among the different possible grain boundary structures. This is the case in the asymmetric phase diagram, where the two possible locations of the grain boundary plane are not equivalent and a transition among them may occur. For this transition to occur the boundary plane has to shift a total of five planes to the next coincident site plane.
4.3 Results

4.3.1 Phase diagram calculation

The phase diagram for a pure component has already been calculated using the present model by Kikuchi and Cahn [1] and will not be reproduced here. We have calculated the binary diagrams corresponding to the two different energetic assumptions listed in Table 4.1. The diagrams were constructed as it is usually done in cluster variation calculations, that is calculating the grand potential for the different phases. The difficulty in constructing binary diagrams with the present model is that since vacancies are included, it is necessary to insure that the coexistence temperatures for different compositions are calculated at constant pressure. In order to do this we started with the stoichiometric compound and moved away from the equiatomic composition in small enough steps so as to satisfy the Gibbs-Duhem equation at constant pressure:

\[ \sum X_i \mu_i = 0 \]  \hspace{1cm} (4.8)

The size of the steps was found to be of a few percent and decreasing the steps further did not change the results. Fig. 4.2 and Fig. 4.3 show the computed complete diagrams for both cases mentioned in Table 4.1. For the stoichiometric alloy of case 1 we used a chemical potential \( \frac{\mu_a}{\epsilon_o} = -1.5 \) for both components. The melting transitions are all of first order and for the stoichiometric alloy the melting temperature is \( k_B T_m / \epsilon_o = 1.23 \). The order-disorder transitions are all of second order and for the stoichiometric alloy the transition temperature is \( k_B T_c / \epsilon_o = 0.78 \). As expected from the small number of vacancies at these temperatures this transition agrees very well with the reported values from a square lattice Ising model in a pair approximation.
Fig. 4.2 The complete binary phase diagram corresponding to the symmetric energy assumption (case 1).
Fig. 4.3 The complete binary phase diagram corresponding to the asymmetric energy assumption (case 2).
For the asymmetric phase diagram of Fig. 4.3 we started from the stoichiometric alloy with values of the chemical potentials:

\[
\frac{\mu_A}{\varepsilon_{AA}} = -1.708, \quad \frac{\mu_B}{\varepsilon_{BB}} = -1.114
\]  

(4.9)

This insured the stoichiometric composition for the solid disordered phase. The parameters of the calculation shown in Table 4.1 are such that the ordering energy is the same as in the symmetric phase diagram and therefore the order-disorder temperature of the stoichiometric composition is the same as in the diagram of Fig. 4.2. The diagram is of course not symmetric about the equiatomic composition in neither the solidus, liquidus nor the order-disorder boundaries. It is interesting to note how similar these diagrams are to actual phase diagrams, in spite of the simplicity of the model. This similarity illustrates how the general trends of the present results are expected to have quite general validity in a qualitative way. It is clear for example that the present model, when applied to a segregating system instead of an ordering system will yield a simple eutectic diagram.

4.3.2 Grain Boundary Ordering Transitions

The behavior of the grain boundary region was studied by computing the density, composition and long range order parameter across the grain boundary. For case 1 of a symmetric phase diagram two types of phenomena were observed as temperature was increased, namely the disordering of the boundary region and the transformation of the structure to one with increasingly liquid like properties. This liquid-like structure is shown in Fig. 4.4 for a stoichiometric alloy of case 1. Note that this behavior is very similar to that obtained for a pure material [1]. The order-disorder transition does not seem to affect this transition significantly. The thickness of the region affected by the presence of the boundary increases logarithmically with temperature and diverges for the melting temperature as
Fig. 4.4 Density profiles across the grain boundary for several temperatures. The center of the grain boundary is the lattice plane number 19, and the profiles of each temperature are repeated on the right side as a mirror image. The energy assumptions are those of case 1 in the text.
discussed by Kikuchi and Cahn [1] for a pure material. The ordering in the alloy is disturbed in the grain boundary region as shown in Fig. 4.5 where composition profiles are plotted for a boundary of the stoichiometric alloy in case 1. The oscillations of the composition plane by plane decrease in amplitude in the vicinity of the grain boundary, meaning significantly more disorder. Fig. 4.6 shows the long range order parameter calculated plane by plane for the stoichiometric alloy in cases 1 and 2. In this figure it can be seen that the stoichiometric alloy disorders more in the case of the symmetric phase diagram than in the asymmetric one. Also the thickness of the disordered layer diverges logarithmically as the order disorder transition temperature is approached. The present results indicate that although the boundary region is significantly more disordered than the bulk the actual transition temperature for the boundary is the same as that of the bulk. These results are very similar to those obtained by Foiles for Ni3Al [10,11] using Monte Carlo Simulation and results from Molecular Statics simulation as shown in section 3.3.3. In particular the calculated anti-site defect energies for Ni3Al follow the same behavior as the order parameter calculated in the present work in the vicinity of the grain boundary.

In addition to the disordering transition we observed transitions among the different variants of the grain boundary structure. This variants correspond to the two possible location types of the grain boundary plane and are not equivalent in case 2 of the asymmetric diagram. In this case starting with a grain boundary located at a plane rich in A atoms at temperatures below the order-disorder temperature the boundary shifts by five planes to the next coincident plane which is rich in B atoms. This structure has lower energy than the initial location. The same starting configuration subject to the minimization process at temperatures above the order-disorder transition does not present any shift in the boundary plane location. This is shown in the density profiles of Fig. 4.7. These results indicate that at temperatures higher than the order-disorder transition there is only one variant of the grain boundary, which is a disordered one.
Fig. 4.5 The composition profile across the grain boundary for the stoichiometric alloy (case 1) at $T/T_c = 0.765$. 
Fig. 4.6 Long-range order parameter profile across the grain boundary for both stoichiometric alloy case 1 and 2 at $T/T_c = 0.765$. 
Fig. 4.7 Density profiles across the grain boundary. In the case of the asymmetric energy assumption (case 2), the center of the grain boundary shifts five planes from the original boundary plane (from 19 to 24) for temperatures below the order-disorder temperature $k_B T / \varepsilon_o = 0.785$. 
4.3.3 Segregation Behavior

In Fig. 4.5 the composition oscillations are such that their average in the bulk is the equiatomic composition. Even though they decrease in amplitude in the grain boundary region, the average composition is still maintained to be the same as in the bulk. That is in the stoichiometric alloy for the symmetric phase diagram and there is no segregation of either component to the grain boundary. This is not the case for the asymmetric phase diagram, or when the composition is varied away from stoichiometry. Fig. 4.8 shows composition profiles for a stoichiometric alloy of type 2 (asymmetric phase diagram case). The oscillations not only decrease but the average is now enriched in the lower melting point component. Similar effects can be seen if the composition changes, as shown in Fig. 4.9. In this figure we plot the composition of the grain boundary as a function of the bulk composition. It is seen that the asymmetry in the phase diagram of the alloys of type 2 is reflected in these results as well. It is important to discuss how the composition of the grain boundary is defined since there are several possible definitions and they may yield different results. We used the composition defined plane by plane and then the composition of the grain boundary plane itself was averaged with that of the two adjacent planes. Note that when the boundary is located at planes of type A, B atoms are preferentially removed and vice versa.

4.3.4 The effect of planar boundary transitional states on ordering and melting transition

We studied the effects of rigid body translations on a $\Sigma = 1$ pure translational boundary and a $\Sigma = 5$ high angle grain boundary. Fig. 4.10 shows the density profile obtained across the pure translational boundary with a rigid body translation of $(1/5,2/5)$ in terms of the crystal lattice (Fig. 4.11). This profile is shown for a temperature which is well below the melting point. The profile, nevertheless, shows a density similar to that of the liquid (0.796) and
Fig. 4.8 The composition profile across the grain boundary for the stoichiometric alloy (case 2) at $T/T_c = 0.765$. 
Fig. 4.9 The plot of the grain boundary composition as a function of the bulk composition for a $\Sigma = 5$ boundary at $T / T_c = 0.765$. 
Fig. 4.10 Density profile across a pure translational boundary with a rigid body translation of 
(1/5,2/5).
Fig. 4.11 The structure of a two-dimensional ordered alloy with a pure translational boundary created by a rigid body translation of $(1/5, 2/5)$. 
represents a structure which closely resembles that of a super-cooled liquid. This is a result of the rigid body translation which completely destroys the perfect coincident structure of the boundary. The results also show that despite the liquid-like structure of the boundary region, some degree of chemical order is maintained, as indicated by the oscillatory configuration of Fig. 4.12 at $T / T_c = 0.765$. As the temperature is increased, there is an order-disorder transition in the boundary region and by $T / T_c = 0.891$ the boundary region is completely disordered (Fig. 4.13). These results show that there are strong effects of rigid body translation on both spatial and chemical order.

We also studied the effects of a second type of rigid body translation, that would not completely destroy the spatial nature of the coincident boundary, but rather mismatched the atom type (i.e. APB or in general what Takasugi and Izumi (6) called pseudosymmetrical boundaries). This is achieved by a rigid body translation which is an antiphasing vector of the unit cell or the DSC lattice. For this type of translation we found strong effects on the ordering at the boundary region, but not on the boundary density. This is shown in Fig. 4.14 for a $\Sigma = 5$ grain boundary where the density and long range order parameters are shown for a $(1/2, 1/2)$ translation and without translation. The density profile with rigid body translation is the same as that obtained for no translation but the boundary region is significantly more disordered in the case of rigid body translation. Furthermore the order-disorder temperature for the boundary region is lower than that of the bulk for the case with translation, whereas it is the same for the case without translation.
Fig. 4.12 The composition of a two dimensional alloy near a $\Sigma = 1$ pure translational boundary with a ridge body translation of $(1/5,2/5)$ at $T/T_c = 0.76$. 

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Fig. 4.13 The composition of the ordered alloy at $T/T_c = 0.891$, showing a completely disordered region near the center of the grain boundary.
Fig. 4.14 Density and long-range order parameter profiles across the $\Sigma = 5$ grain boundary with and without rigid body translation of $(1/2,1/2)$. 
4.4 Discussion

First we would like to point out that the simple model used can yield complete phase diagrams that are quite similar to actual ones. The model is also adequate to study a variety of grain boundary phenomena, particularly, for the high temperature chemical order, and spatial structure.

We would also like to discuss the general implications of the present results for the high temperature behavior that can be expected in grain boundaries in ordered alloys. It is clear that the results that have been found for surfaces also apply to grain boundaries, that is, there will be a region around the grain boundary more disordered than the bulk. The thickness of this region diverges logarithmically as the temperature approaches to the order-disorder temperature. Also, segregation effects observed in the vicinity of surfaces will appear in grain boundaries. The disordering phenomenon does not seem to depend strongly on the details of the atomic interaction energies used in the simulation. On the other hand, the type of segregation observed will depend on the phase diagram and therefore the energetic assumptions used in the calculation. The present results show that there will be segregation effects and that they can be very significant. It appears that when high temperature properties of grain boundaries in ordered alloys are studied, the segregation and disordering effects are essential features that have to be considered. Similar results were shown in section 3.3.3 using Molecular Statics Simulation and Monte Carlo Simulation results by Foiles in the case of Ni₃Al [10].

The rigid body translation of the crystal with respect to the other can significantly affect grain boundary transitions. If the translation affects the coincident site nature of the boundary the boundary region tends to be more liquid-like. If the translation is such that it only affects the chemical order in the boundary region but presents coincident sites (i.e. a pseudo symmetrical boundary) the boundary region tends to be more disordered but the density profile is not affected.
4.5 References

Chapter 5

Conclusions

Several techniques were employed to study the structure and behavior of grain boundaries in the ordered intermetallic compound Ni$_3$Al. Geometrical analysis of grain boundaries was done using conventional techniques and convergent beam electron diffraction techniques of a transmission electron microscope. As theoretical calculations two different computer simulation techniques were employed to study the structure, transitions and segregation around grain boundaries.

Using transmission electron microscopy, grain boundary geometries and dislocation behavior near grain boundaries were investigated. The conclusions from the TEM work are listed below:

- From the comparison of $\Sigma$ distributions between ductile and brittle Ni$_3$Al, there are more low $\Sigma$ boundaries in ductile Ni$_3$Al than brittle Ni$_3$Al.
• In case of ductile Ni$_3$Al, grain boundary accommodation of dislocations were found many times in the vicinity of grain boundaries. However, those reorientations of dislocations near grain boundaries were not found in brittle Ni$_3$Al.

• From the distribution of grain boundary plane orientations, it was found that the trend of having high density plane of coincident sites was maintained on low $\Sigma$ boundaries up to $\Sigma = 9$, and random orientations of grain boundary planes become dominant after $\Sigma = 11$.

• Using convergent beam electron diffraction techniques, point group and space group of Ni$_3$Al were determined. The point group of Ni$_3$Al was $m3m$ and space group of Ni$_3$Al was $Pm3m$. However, an extension to bicrystal point group and space group determinations was not successful and still required further research.

In order to study the possible disordering and segregation near grain boundaries, Molecular Statistics atomistic computer simulation was performed. This study is related to the grain boundary accommodation of dislocations since the accommodation phenomena can be possible assuming the existence of a disordered layer in the vicinity of grain boundaries. Conclusions from Molecular Statics atomistic simulation are listed below:

• Considering the energetics of antisite defect energies as a function of distance from the grain boundary, it was found that segregation behavior varies with the composition and structure of the particular boundaries. There was a tendency for Al to segregate to the boundaries easier than Ni. This, however, was changed when the composition of the boundary is Al rich.

• The implications of order-disorder behavior were more general and indicated that the grain boundary appeared to be a favored location for disorder in all regardless of grain boundary compositions.

As a first principle calculation, two-dimensional lattice-gas model was employed to investigate the grain boundary ordering, segregation and melting transitions. This model is inherently versatile to study the properties of grain boundaries, particularly, the high tem-
perature chemical order and spatial structure. Using this model, systematic studies were performed covering bulk properties as well as the behavior of grain boundaries. Conclusions from the two-dimensional lattice gas model are listed below:

- There was a disordered region around the grain boundary and the disordered region were diverged logarithmically as the temperature approached to the order-disorder temperature. The disordering phenomena did not seem to depend on the details of the atomic interaction energies used in the simulation.

- The type of segregation observed was dependent on the energetic assumptions used in the calculation.

- The rigid body translation of the crystal with respect to the other significantly affected grain boundary transitions. If the translation affects the coincident site nature of the boundary the boundary region tends to be more liquid-like. If the translation is such that it only affects the chemical order in the boundary region but presents coincident sites (ie. a pseudo symmetrical boundary) the boundary region tends to be more disordered but the density profile is not affected.

Summarizing the conclusions listed above, several distinct features of the grain boundary were found in ordered intermetallic compound Ni$_3$Al. The first important point is the disordering phenomena near the grain boundary. Two different atomistic computer simulation techniques showed a similar trend of disordering in the vicinity of the grain boundary regardless of grain boundary compositions and atomic interaction energy assumptions. The second important point is the grain boundary accommodation of slip near grain boundaries. Contrary to dislocation motion in brittle Ni$_3$Al, dislocations in ductile Ni$_3$Al reoriented and merged into grain boundaries and reduces stress concentration. This reorientation of dislocations near the grain boundary is a general character in ductile fcc materials which do not show intergranular fracture. Thus, the orientation of dislocations near the grain boundary is believed to come from the fact that the atomic configuration in the vicinity of grain boundary disorders and behaves like fcc materials. This assumption is consistent with our computer simulation results that shows disordered structure near the grain boundary. The third
important point is the difference in statistical distributions of grain boundary types between ductile and brittle Ni₃Al. This result showed that the mechanical property of intermetallic compound Ni₃Al is appeared to be related to the distribution of grain boundary types.
Vita

The author was born on August 21, 1957 in Pusan, Korea. He attended Daeshin high school in Seoul and entered the undergraduate engineering program at Korea University, Seoul in 1977. After graduating from Korea University in 1981 with Bachelor degree of Metallurgical Engineering, the author continued his graduate study in the Department of Metallurgical Engineering until he earned his Master of Science degree in 1983. After his military service in Korea Army the author joined the Ph. D. program in Materials Engineering and Science at VPI&SU. During his Ph.D. dissertation works he spent five months in Materials Science Center in Gronigen, the Netherlands and four months in Atomic Energy Commission of Argentina, Buenos Aires, Argentina as a visiting scientist. The author’s career goals are in research and development.

[Signature]