

A Study of Grain Boundary Structure in B Doped Ni_3Al

by

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(ABSTRACT)

A theoretical and experimental study of Grain boundary structure in B doped Ni₃Al was carried out. Geometrical modelling was done to obtain the grain boundary structure in L1₂ compounds for different misorientations between two grains. The size of interstitial sites in these boundaries was calculated to understand the segregation of B to the boundaries. Ratios of the B-B equilibrium interatomic distance to the nearest neighbour distances in various (A₃B) L1₂ compounds were calculated, in an attempt to predict the grain boundary fracture behaviour in these compounds. Selected area channeling patterns were obtained from a number of grains to solve for the orientation relationship between grains, in order to predict the structure of the boundaries between them. A distribution of grain boundary structure that is different from the distribution for a undoped Ni₃Al is obtained in this work and is compared with results from other investigators.

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1.0 INTRODUCTION

The intermetallic compound Ni_3Al , having the L1_2 structure (Cu_3Au structure - page 85) below the peritectic temperature, 1395°C , has the unique property of increasing yield strength with increasing test temperature (1). However, a polycrystalline sample of Ni_3Al shows low ductility and brittle fracture, due to weak boundaries. The weakness is probably an intrinsic property of the boundary; Cu_3Au does not show weak boundaries. Microalloying with Boron, Hafnium and certain other elements seems to alleviate this problem. The doped Ni_3Al shows a good amount of ductility and segregation of B to the grain boundaries. B strengthens the boundaries; but the mechanism of strengthening is not known and is being investigated. A study of grain boundary structure in Ni_3Al is essential for understanding the mechanism of strengthening in these boundaries. This work attempts to do this using the concept of the C.S.L model for grain boundaries which is based on orientation relationships between the grains and the experimental procedure of electron channeling patterns, that help in determining these relative orientations.

If we imagine two interpenetrating crystal lattices, at certain relative orientations, called coincidence orientations (2), a three dimensional lattice of coincident crystal lattice points exist, which is known as a coincident-site-lattice. The reciprocal density of coincident sites, with respect to the crystal lattice, is denoted by Σ . It is in terms of this reciprocal of coincident site density Σ , that the various favourable boundary structures are classified, theoretically (fig 1). It is to be noted

that irrespective of whether the boundary between the two grains is a pure tilt, twist or a mixture of both (which depends on the location of the grain boundary), the value of Σ remains the same and depends only on the relative orientation between the grains.

Geometrical Variable Sphere Modelling was used to construct the grain boundary structures for different values of Σ in two $L1_2$ compounds - Cu_3Au and Ni_3Al . This model modifies the hard sphere model (3) used by earlier investigators, on the basis of size considerations. The criteria used to determine the grain boundary structure is the same as in the hard sphere modelling, which is maximization of density or reduction of excess volume.

Calculations of size ratios, which is the ratio between the B-B equilibrium interatomic distance and the nearest neighbour distance in a (A_3B) $L1_2$ compound, were done for some compounds in an attempt to predict the fracture behaviour of grain boundaries. The predictions are compared with experimental results, when available.

Electron Channeling Patterns are being used increasingly to obtain information on orientation of crystal grains. It is a fast and fairly accurate method for the orientation analysis of crystalline grains. By obtaining orientation information on two adjacent grains, the relative orientation between the two grains can be determined. This information is used to characterize the boundary between the two grains, based on the concept of the coincident site lattice model for the structure of grain boundaries.

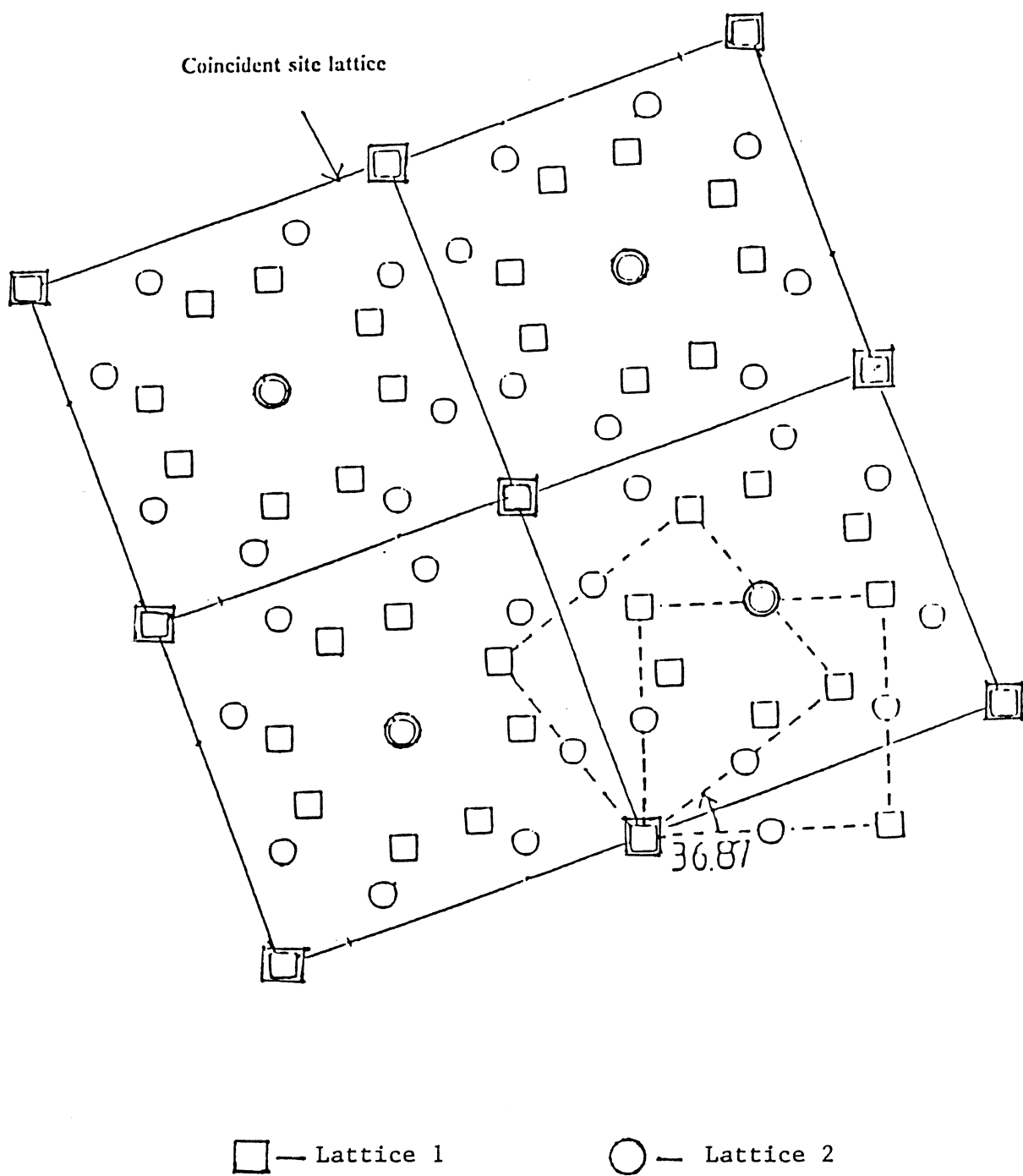


Figure 1. Coincident site lattice: Two interpenetrating lattices forming a $\Sigma = 5$ boundary (Ref. 6)

2.0 Theory

2.1 *Geometrical Theory of Grain Boundaries*

2.1.1 Hard Sphere Model

Hard sphere modelling for symmetric tilt and twist boundaries was done by Frost and Spaepen (3). They showed, on comparison with computer-relaxation studies, that this method can be used as a first approximation for description of grain boundaries in metals. They also stated that, this type of modelling will work best for systems which can be modelled by hard spheres in the perfect crystalline state, such as f.c.c metals with a central force interatomic interaction. Hard sphere modelling can be done graphically or with actual spheres. The configuration that gives the maximum density of atoms at the boundary, which implies minimum excess volume is the stable

grain boundary structure for the given orientation of the grains. This model is therefore based on the assumption that maximizing density, minimizes the energy of the grain boundary. Frost and Spaepen found that the excess volume correlated directly with the grain boundary energy found by static relaxation methods. This implies an inverse relationship between the density and the energy of the grain boundary energy, which justifies the assumption in the model.

Relaxation studies also attempt to arrive at a minimum energy configuration for the grain boundary (4). To calculate the energy of the grain boundary structure, the atoms are assigned positions and considered to interact with other atoms by a central force pair potential, in the presence of an explicit volume dependent potential. The energy of a given configuration is obtained by summation of the interactions between all the atoms in the block being considered. This energy is minimized by relaxation of the positions of the atoms in the configuration to obtain a different configuration. This is done till a minimum energy structure is obtained. The positions of the atoms initially, correspond to the two lattices misoriented by the required angle. There are two methods of relaxation - static and dynamic. The difference between the two methods is the absence of kinetic energy for the atoms in the static method of relaxation. In the static relaxation method, the results of which support the results of hard sphere modelling, the energy of the block is minimized by simultaneous relative translations between sub-blocks of atoms as well as individual relaxation of the atoms.

Hard sphere modelling is a simple method for analyzing many configurations. Also, for certain potentials, such as Al, the configurations obtained by Frost and Spaepen, were close to computer relaxed configurations. Determination of interstitial sites and sizes can be done easily, in this type of modelling. However, in the case of Copper, which has a soft potential, (i.e) where the repulsive force at short distances rises relatively slowly, hard sphere modelling did not predict the correct grain boundary structure.

Hard sphere modelling is the basis for Variable sphere modelling described later in the chapter. Here the atomic radii of atoms vary depending on what atoms they are paired with. For example the distance between an A-B pair may not be equal to the distance obtained by adding the atomic radii of A and B, calculated from the A-A and B-B equilibrium interatomic distances, re-

spectively. The concept of variable spheres is based on studies of interatomic potentials and analysis of these distances in other intermetallic phases, in the binary system close in composition to the $L1_2$ compound being studied. The model is described in detail later on in this chapter.

2.1.2 Coincident Site Lattice Model

The concept of Coincident Site lattice Model (5) came into existence, after it was known that certain special boundaries have properties like lower grain boundary energy or higher migration rate. It was found that these boundaries have a low value of Σ or a high density of coincident sites. The misorientation angles corresponding to these high coincident site density configurations, are the special orientations and generally favoured orientations for two adjacent crystals meeting at an interphase. Some special boundaries corresponding to low values of Σ are however not favoured boundaries in metals (6). Σ is a discontinuous function of the misorientation angle θ and has a low value at certain angles and at these values of θ , we generally have energy cusps. It was also found that, the special boundary planes were, low-index planes of the C.S.L corresponding to the particular value of Σ , and therefore possessed two-dimensional symmetry. The assumption therefore, in C.S.L model is that when two crystal lattices are at a misorientation corresponding to a dense C.S.L, the energy of the grain boundary is minimum. The model however has some problems. If we consider two lattice points (one from each of the interpenetrating lattices) separated by an extremely small distance, physically it may not be different from a situation where the two points coincide exactly, and hence we have a coincident site in both cases. However, mathematically they are two different cases. Based on the same idea, if two lattices deviate slightly from a misorientation angle corresponding to a dense C.S.L, the coincident site lattice disappears, although physically the change is negligible. When this happens, (i.e) when crystal misorientation deviates from a misori-

entation corresponding to the dense C.S.L, it has been proposed that a network of grain boundary dislocations (GBDs), is formed to accomodate the deviation and an equilibrium structure consisting of the GBD network embedded in the low energy interface structure associated with the high density C.S.L is formed (7). The burgers vector of the GBDs are generally, vectors of the corresponding Displacement Shift Complete (D.S.C) lattice (5). If we have two interpenetrating lattices at some coincidence orientation, and translate one lattice with respect to the other by a vector, t , which joins lattice points from either of the crystal lattices in this coincidence orientation, the pattern will be again produced, but the origin of the C.S.L will be shifted (2). All such translations can be the burgers vectors of these GBD's. These GBD's try to localize the deviation from a coincidence orientation. This can probably be compared to the dislocations at a low angle boundary. Fig. 2 shows the C.S.L unit cell and the D.S.C unit cell for a $\Sigma = 13$ boundary. The C.S.L unit cell contains the D.S.C cell 13^2 times. All the vectors joining any two points on the figure can theoretically be the burgers vector of the GBD's. The new C.S.L unit cell resulting from such displacements, can also be rotated with respect to the original unit cell. The totality of these displacements constitutes the D.S.C lattice corresponding to the C.S.L..

The concept of C.S.L and D.S.C lattices and the relation between them can be explained in terms of group theoretical considerations based on the set of symmetry operations for an ordered and disordered crystal (7).

The Frank-Bilby equation relating the net Burgers vector B of interfacial dislocations crossing any given vector p in the interface, to the lattice deformations S_1 and S_2 producing lattices 1 and 2, from a reference lattice S , is given by

$$B = (S_2^{-1} - S_1^{-1})p.$$

Here, S_1 and S_2 can be replaced by $U_1 S_1$ and $U_2 S_2$, where U_1 and U_2 are lattice invariant deformations that shear lattices 1 and 2 into themselves, resulting in no change to the lattices or the interface(symmetry operations). However, B depends on the choice of S_1 and S_2 and therefore we have a multiplicity of descriptions for a given interface and reference lattice (6). If we have perfect

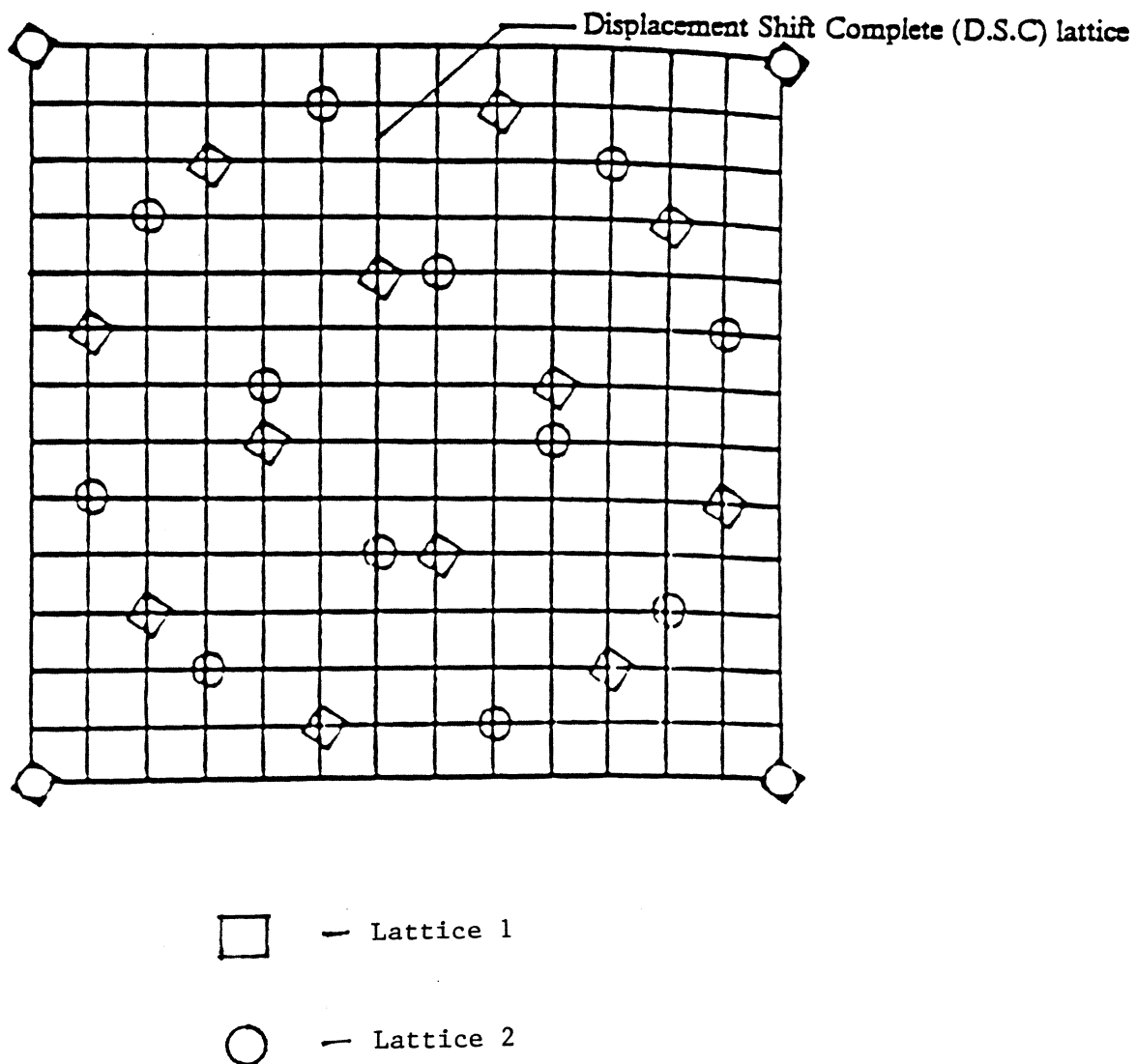
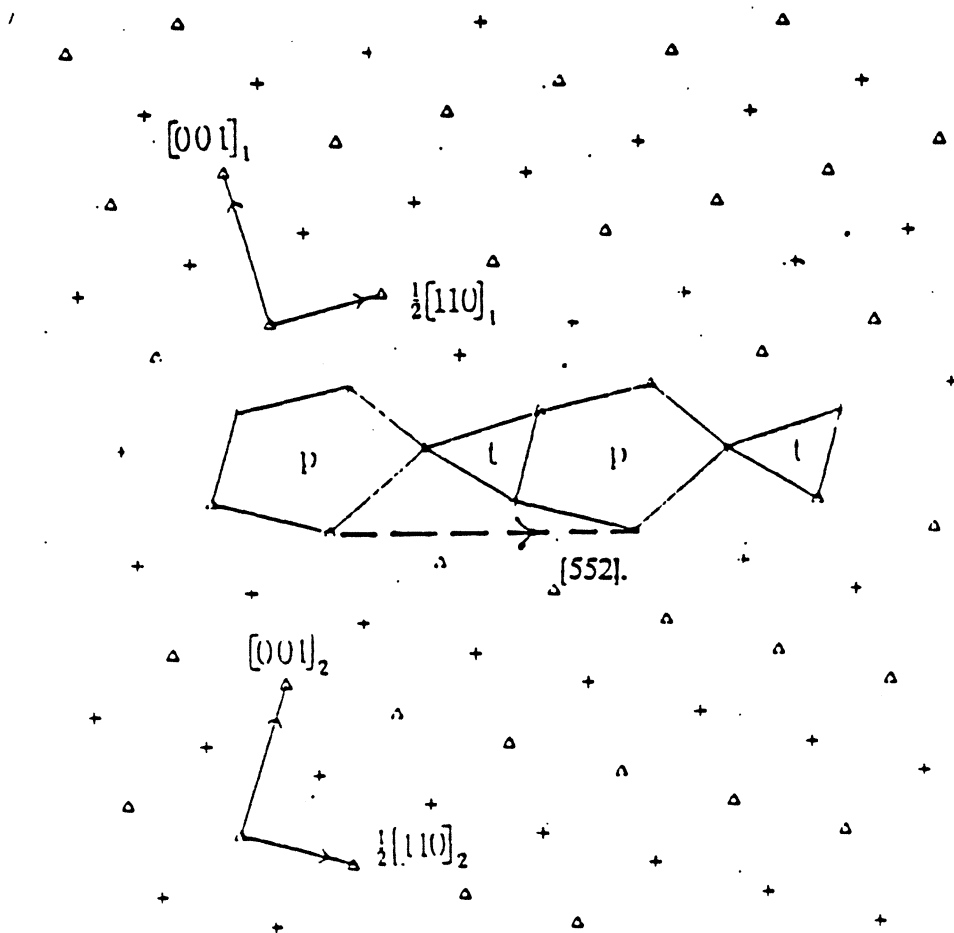


Figure 2. The CSL and DSC lattices: A $\Sigma = 13$ configuration with the CSL and DSC unit cells (Ref. 6)

lattice matching at the interface then we have a boundary plane that is an invariant plane of simple shear. The dislocation content of such a boundary will be zero. The boundary in a deformation twin can be considered to be a plane of simple shear. The reference structure is either an ideal lattice or a special boundary unit. The burgers vectors of GBDs based on the ideal lattice are those of the lattice dislocations and the burgers vector of the GBDs based on special boundary unit are the vectors of the DSC lattice, associated with the CSL of the special boundary. Hence the total dislocation content of a high-angle boundary comprises of primary dislocations associated with the "special boundary" reference structure and secondary GBDs compensating for deviations from this structure.

Sutton and Vitek (6) have come up with the term "favoured boundaries" to denote certain special boundaries which form the fundamental units of other non-favoured long-period tilt boundaries. A favoured boundary is a continuous sequence of a particular type of unit which is said to be in it's undeformed state. A non-favoured boundary in the misorientation range between two adjacent favoured boundaries is then viewed as a mixture of structural units of the adjacent boundaries. This is called the "structural unit model". There will be misorientation difference between two different units adjacent to each other in a non-favoured boundary, as each unit tries to relax into it's ideal misorientation. Thus we need some secondary GBDs to accomodate these differences and make these units compatible. These GBD's can be thought of as analogous in function to the lattice dislocations reducing misfit strain in an incoherent interface. A favoured boundary is therefore free of secondary GBDs and can also be free of all dislocations if the boundary plane can be described as an invariant plane of simple shear.

Considering fig.3 (from ref. 6) we have the repeat unit of $\Sigma = 27$ favoured boundary. Each half period of the unit is same as the other half, except that the atoms are different (i.e) they are relatively displaced by $\frac{1}{4}[110]$ parallel to axis of tilt. The repeat cell can be characterized by a period vector parallel to the tilt axis (i.e) $\frac{1}{2}[110]$ and a period vector perpendicular to the tilt axis (i.e), $\frac{1}{2}[552]$. In general if we have a non-favoured boundary composed of units A and B of two adjacent favoured boundaries, and if these boundaries are characterized by vectors l_a and l_b perpendicular to the tilt axis, then the vector l characterizing this boundary, is



*Labels mark structured units.

Figure 3. Structure of $\Sigma = 27$ boundary: The period vectors that form a unit cell of a $\Sigma = 27$ coincident site lattice (Ref. 6)

$$l = x.(l_a) + y.(l_b)$$

where, the ratio of units of A to the units of B is as x:y; l, ofcourse is perpendicular to the tilt axis. If we allow x and y to take on any positive integer values we have a lattice defined, whose basis vectors are l_a and l_b , and where every lattice point represents a non-favoured boundary which has been decomposed into a specific combination of A and B units. This is called the Decomposition lattice (6).

The above discussion introduced some of the basic concepts used in the analysis of grain boundary structure. The results will differ in the case of an ordered compound like Ni_3Al compared to a pure metal or a dis-ordered compound since some of the symmetry operations like certain lattice translations of the disordered compounds are not symmetry operations in an ordered crystal (8). For example, the translation by $\langle 0 \frac{1}{2} \frac{1}{2} \rangle$ is a symmetry operation in pure f.c.c metals, while it is an antiphasing vector in an L1_2 compound like Ni_3Al .

2.1.3 Variable Sphere Model

In this work a modified hard sphere model was used to obtain configurations of fully symmetrical tilt boundaries in two ordered compounds with the L1_2 structure, Cu_3Au and Ni_3Al . The model includes the consideration of the different atomic sizes as well as the possible translational states of the boundary. The structural unit model was then used to analyze the intermediate high index boundaries, as well as the possible ordering states present in these boundaries.

It is now well established that the type of interatomic potential assumed for the calculation of grain boundary structures strongly influences the results. This influence has been shown for pure metals, and is likely to be even more critical in alloys, since the accuracy of potentials between

unlike atoms is lower. Wolf (9) showed that the unrelaxed and relaxed grain boundary energies in twist boundaries in Al depend on the choice of potential. Furthermore, the directions of relaxation were also potential dependent. Even the basic structure of the boundary may change, as pointed out by Frost (3). An example of this is the $\Sigma = 5$ boundary in Al and Cu. Due to the relative softness of the copper potential, a structure presenting nearest neighbor distances shorter than those in the bulk arises that cannot be expected for hard spheres. This is true for the Cu splines potential of Crocker and Faridi (10) used by Sutton and Vitek (6) in the simulation of tilt boundaries. Al, on the other hand presents relaxed structures that are similar to those obtained by hard sphere models. However, with the Lennard-Jones potentials used by Wetzal and Machlin (11) the structure for Cu is similar to that of Al. It seems that the hard sphere models can give reliable starting configurations for relaxation studies in most cases. However, results can be improved by analyzing the interatomic potentials and determining a minimum allowed distance between atoms to be used in the geometrical models. This consideration applies especially to distances between unlike atoms. The minimum of the potential in this case need not be at an intermediate position between those of the components of the bond. Shao and Machlin (12) point out that this is the case for bonds that have a polar component, as in heteroelectronic compounds. It should also be pointed out that the analysis of the distances of closest approach found in the different intermetallic phases that may be present in the binary system will also help in estimating the minimum interatomic distance that can be expected in the grain boundary. In the present study, two different cases were considered as representative of "soft" and "hard" potentials. In the soft potential case the distances of closest approach allowed are similar for all bonds. In this case the model reduces to the hard sphere model as used by previous investigators (3). The grain boundary configurations in this case are expected to be similar to those obtained by maximizing order in the structures that have been reported for pure fcc metals. Cu_3Au is an example of a system where the basic structural units of fcc metals are expected to be stable. Note that in this system both Cu_3Au and Au_3Cu are stable with L1_2 structures that have lattice parameters differing by only 5 %.

The case of hard interatomic potentials was studied using geometrical models where the allowed distances of closest approach were estimated from an analysis of the interatomic potentials

and the available crystallographic data for the system. The example chosen is Ni_3Al . Several potentials for Al were considered (9) together with the Morse potential of Ni given by Milstein (13). Studies of grain boundaries in Al (14) using pseudopotentials show that Al behaves as a hard sphere and the configurations obtained by geometrical methods agree with those obtained by computer simulation. In Ni_3Al the nearest neighbor distance (0.252nm) is 12% shorter than the equilibrium distance in pure Al (0.286nm). This indicates that for this material Al-Al bonds at the nearest neighbor distance of Ni_3Al may not be present in the grain boundary structure. This is supported by analysis of the other (non-coherent) phases present in the Ni-Al system. These are Ni_2Al_3 , Al_3Ni and NiAl (15). In all these structures the Al-Al distance does not deviate by more than 1% from the equilibrium distance in pure Al. In constructing grain boundary structures it is necessary to estimate the position and depth of the minimum in the Ni-Al pair potential. The position of this minimum is not intermediate between that of Al and Ni but is similar to that of Ni (0.25nm), as reported in experimental studies of Ni-Al liquids by Enderby and Howells (16). This is due to the heteroelectronic nature of the Ni-Al bond as reported in pairwise studies of intermetallic phases using Lennard-Jones potentials (12). From this qualitative discussion of the pairwise interactions it is clear that the structures of grain boundaries in Ni_3Al may not be similar to those found in pure metals, and that they may be formed by the removal of atoms, maintaining bond-distances. Based on the preceding analysis the minimum Al-Al interatomic distances allowed in the construction of the Ni_3Al boundaries were 13.53% longer than the nearest neighbor interatomic distance in the bulk. This means that in our model Al atoms are considered variable spheres, with different radii, depending on whether it is bonded to another Al or a Ni atom.

2.2 *Procedure for Determining Grain Boundary*

Configuration

The procedure for generating and analyzing grain boundary configurations is as follows: The first step is to identify the "favored", low index boundaries in a series and the structural units that conform them in pure fcc metals. If different types of structural units are possible (17) they are considered separately. Secondly, the densest configurations are determined, using the minimum allowed distances discussed above. Translations perpendicular to the tilt axis both perpendicular and parallel to the boundary plane were allowed. For the favored coincident site boundaries the coincident sites are assumed compatible with order in both crystals (i.e. fully symmetrical boundaries). This choice can in some cases be taken in two different ways (corresponding to the first coincident site considered as an A or B atom). For most boundaries this will result in two different configurations or variants. The analysis of the obtained structures involves the identification of the different ordering configurations that occur in the structural units. Finally, the constitution of intermediate boundaries is determined in terms of the ordered structural units. It should be noted that density considerations are not the only factor that determines the actual choice of grain boundary structure and structural units (17). This means that the present results are only a first approximation and our results should be confirmed by relaxation studies.

3.0 Experimental Procedure

3.1 Electron Channeling Patterns

3.1.1 Mechanism of Channeling contrast

Electron channeling patterns is widely used in the analysis of orientation, structure, distortion and perfection of a single crystal or an individual grain in a polycrystalline sample. These patterns consist of pairs of parallel lines and bands criss-crossing the field of view, and are explained in terms of electron channeling effects. These effects take place when we have a beam of electrons incident on the surface of a specimen at angles close to the Bragg angles for some of the crystallographic planes in the material. These patterns are therefore dependent on the relative orientation between the beam and the crystal grain. There is a contrast difference between the regions

where electrons channel through by satisfying the Bragg angle for the set of planes and regions where they do not. This results in the formation of bands having a width of approximately 2θ , where θ , is the Bragg angle for a particular set of planes. The angles between the pairs of lines and the ratio of their widths are important details in a electron channeling pattern. Thus the electron channeling patterns are pseudo-Kikuchi diffraction lines, obtained in the scanning mode due to the difference in back-scattered electron yield, caused by the diffraction of the primary beam into the crystal at certain regions. Kikuchi lines are the corresponding actual diffraction lines, produced in the transmission mode from a relatively thick transmitting specimen.

Figure 4 explains the channeling concept in a simple illustration. In the case of 4a, due to strong interaction at the surface(absence of channeling), we will have a higher backscattered or secondary electron yield. Electron channeling is a result of differing atomic density along different crystallographic directions; which implies that the incident beam of electrons will penetrate to differing degrees when incident at different directions relative to the crystal.

The mechanism of electron channeling can be described in terms of the Bloch waves, which is used to describe the properties of high energy primary electrons in a crystal (18).

3.1.2 Practical Considerations

There are several ways in which channeling or diffraction can be satisfied (19). One way is to rock the crystal (Fig. 5) about two orthogonal axes, in synchronization with the raster on the videoscreen (cathode ray tube - CRT), keeping the beam stationary. Another way would be to scan as well as rock the crystal. A third way will be to move the specimen in the plane perpendicular to the beam direction and also simultaneously scan the beam, such that the same selected area on the specimen surface is illuminated all the time. The movement of the specimen must be synchronized with the raster movement on the CRT. Almost all these methods require the rocking of the crystal

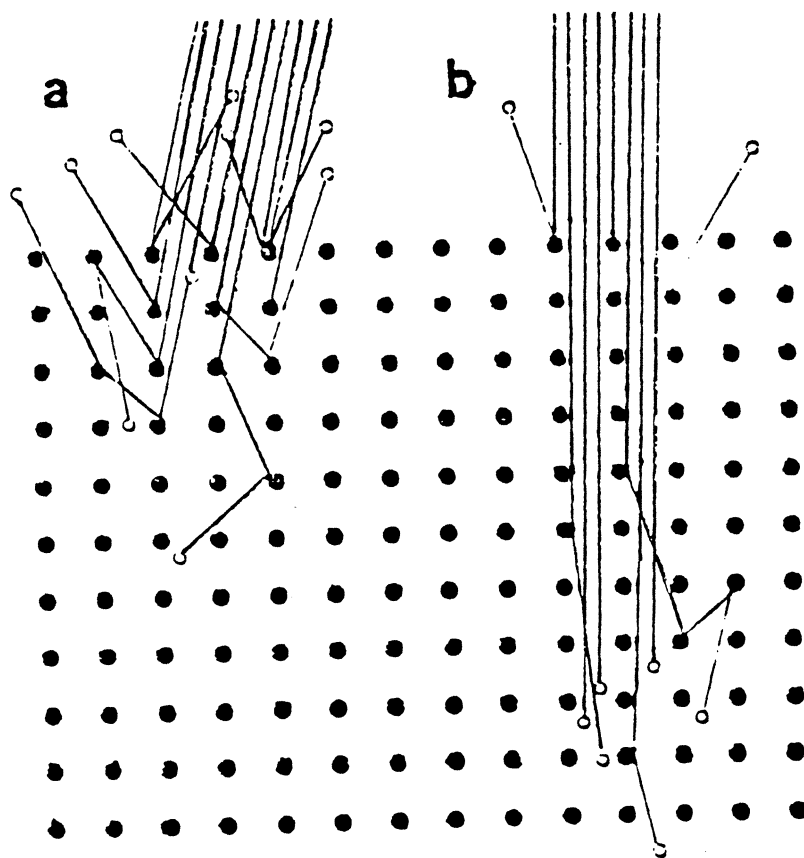
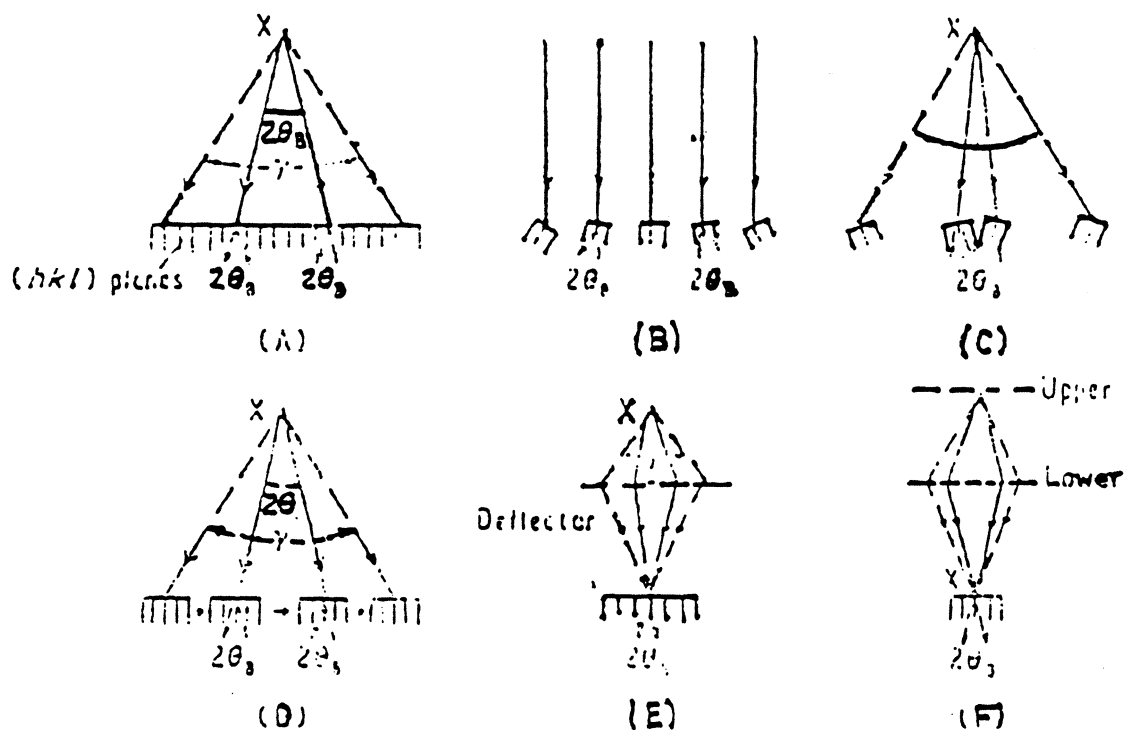


Figure 4. Mechanism of channeling (from Ref. 18)



- A) Normal scanning
- B) Stationary beam, rocking crystal
- C) Beam scanning + crystal rocking
- D) Beam scanning + 2-D movement of crystal
- E) Rocking beam: Deflection focussing
- F) Rocking beam: Double deflection

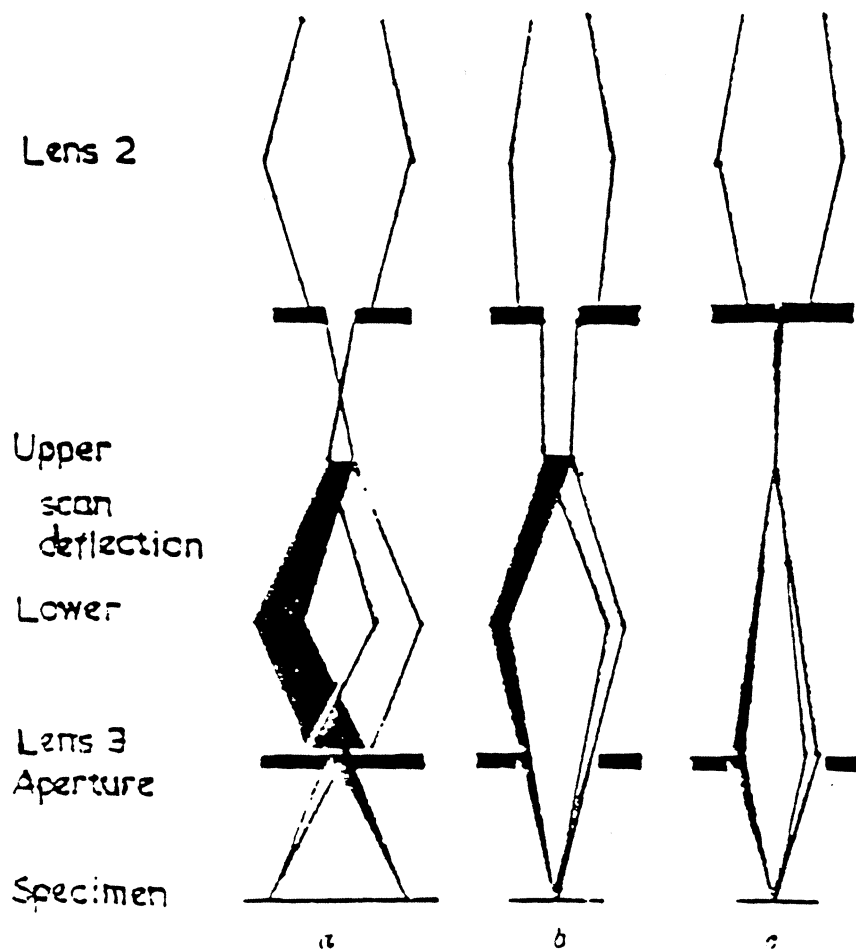
Figure 5. Channeling techniques (from Ref. 19)

to be in synchronizaton with the rapid line scan on the videoscreen and therefore present some difficulties. A better method for channeling, which avoids all these complications is the so called 'Rocking Beam' method, where the cross-over point of the incident beam is transferred onto the surface of the specimen (Fig. 6). No ancillary equipment is necessary in this method. Here the beam is incident on the region of interest, varying it's direction of incidence in synchroniztion with the raster on the CRT. An undisturbed electron channeling pattern is obtained, if the directions of the beam when back-projected on a plane perpendicular to the optic axis(also the normal to the surface of the specimen), forms an array of points that corresponds to the points on the screen (20). The rocking beam can be accomplished by either the double deflection scan system by attenuating the current in the lower scanning coil (Fig. 6) or by having a final focussing lens which focusses the scan back onto a point on the optic axis, in conjunction with single deflection (21). The rocking beam method provides us with channeling patterns from a selected area, which is the area covered by the cross-over point on the specimen surface. Hence, the patterns obtained are also called selected area channeling patterns.

The size of the selected area depends on factors like astigmatism and spherical aberration of the incident beam. Patterns can be obtained from grains 10μ wide. Spherical aberration and astigmatism cause the cross-over point to become a circle of confusion of definite diameter. Spherical aberration is the most important limiting factor. It has been suggested that (21), spherical aberration can be reduced by superimposing a small correction signal on the main scan currents activating the coils, in the case of a double deflection system and by applying correction waveforms to an auxillary set of deflection coils in a final lens focussing system. The selected area is estimated to improve to $2-3\mu$ with these corrections for spherical aberrations. The minimum obtainable area is given by

$$d_{\min} = \frac{1}{2}C_s\phi^3$$

where C_s is the coefficient of spherical aberration and ϕ is the semiangle of rocking. We would ideally like to minimize the selected area and maximize the angle of rocking, so that as many bragg



- a) Normal scanning
- b) Rocking beam - Double deflection method
- c) Rocking beam - Deflection focussing method

Figure 6. Two methods of Beam rocking (from Ref. 21)

angles as possible, may be satisfied and we get a large number of lines representing different sets of planes. The cross-over point should coincide with the specimen surface for minimum area and as said earlier aberration could cause the beam to focus over a small finite length along the optic axis giving rise to a larger scanned or selected area on the surface. It is advantageous to have a small value for C_s . This can be achieved by increasing the excitation of the final lens. In such a case, our working distance will have to be reduced. This may be beneficial from the rocking angle aspect, since the angle is more for a shorter working distance.

Both back-scattered and secondary electrons can be used for obtaining electron channeling patterns. However, the back-scattered electrons are more suited because of their relatively strong signal intensity. The contrast however is weak and needs some signal processing. The beam current must be considerably higher than a certain estimated threshold value to get even this weak contrast. Some of the signal processing techniques include black level suppression, which increases the percentage of contrast and time differentiation of the signal which enhances the sharp transitions at the edges. The beam divergence must be minimum if electron channeling effects are to be observed. Also the channeling process results in significant changes in the back-scattered or the secondary electron yield only at the surface. Scattering causes divergence of the beam very quickly that, at depths more than a small distance from the surface, we do not have a parallel beam of electrons and hence no electron channeling effects. Beam divergence can be reduced by collimation; however, collimation reduces the beam current at the surface. Therefore if we want a reasonable beam current, we will have to allow some divergence. It was found that with the conventional tungsten hairpin filament as the electron source, at small beam diameter of 1 or 2μ , low current and high divergence is obtained (22). Hence to get good resolution in patterns from small areas, a Lanthanum Hexaboride cathode or a field emission gun which have a much higher brightness value will be preferable, as they produce sufficient current in a small beam. Also, the LaB_6 filaments are operated at lower temperatures compared to W, and this gives rise to a smaller energy spread, which in turn can improve the resolution (28). Also a relatively higher accelerating voltage improves the resolution of the patterns.

These are some of the factors that have to be considered while attempting to obtain channeling patterns from a single crystal or an individual grain in a polycrystalline sample. In the present day microscopes, all the instrumental parameters are adjusted within the microscope when the SACP(selected area channeling pattern) mode is selected.

3.2 *Specimen Preparation*

In order to obtain a good channeling pattern, we need a very well polished surface. The surface should be free of scratches, cracks, pits and other defects. Also, it helps to have as strain free surface as possible. Mechanical polishing will leave a layer of worked material on the surface. If this layer is thin, we can still obtain channeling patterns. However, chemical or electrochemical polishing of the surface as a final treatment after the mechanical polishing, is preferable for getting good patterns. If the specimen surface has some roughness or distortion or an oxide layer of thickness ≥ 50 nm, it is difficult to obtain the channeling patterns. The information in such patterns are from the surface and hence the requirement for a good surface. Defects on the surface scatter the primary beam and prevent proper channeling of the primary electrons. We therefore lose the channeling contrast from such surfaces. The surface can be polished by mechanical and chemical or electrochemical polishing. Recent studies (27) show that electropolishing gives best results, while chemical polishing gave good results.

In the present work, samples of Ni_3Al were cut into small pieces of approximately 10mm length, 4mm breadth and 1.5mm height, so as to fit into the specimen holder of Philips 420 STEM. The samples were then annealed at 1050° in argon atmosphere, for about 5.5 hrs.. The purpose of annealing was to reduce the defect density and strain in the sample, besides increasing the grain size. The samples were mechanically polished prior to the annealing treatment so as to minimize the post anneal polishing requirements. After annealing the samples were subjected to micro polishing with 1.0, 0.3 and 0.05 μ alumina powder successively. Electropolishing was tried subsequently. The

electrolyte is a solution of 70% ethanol, 10% butyl cellosolve, 12% water and 7.5% perchloric acid, by volume. The electrolyte was kept in a beaker immersed in ice to which NaCl was added for depression of freezing point. Whether the samples were electropolished could not be determined from examining the surface under an optical microscope; however, they could have been chemically polished while they were dipped in the electrolyte. Since the samples were subjected only to micropolishing after the annealing treatment, the thickness of the deformed material on the surface is expected to be very small. The samples gave good channeling patterns after the micropolishing and therefore no work was done on establishing the optimum conditions for electropolishing of the samples. The surface after the polishing was very smooth with very few faint scratches. New polishing cloth was used for each sample. The samples were etched with the solution containing 20% nitric acid, 20% phosphoric acid, 20% water, 10% hydrofluoric acid, 10% acetic acid and 10% hydrochloric acid by parts, for about 2-3 mins. On etching the grains became clearly visible. This is necessary to go from one grain to another, to take channeling patterns from individual grains.

3.3 Pattern Solution

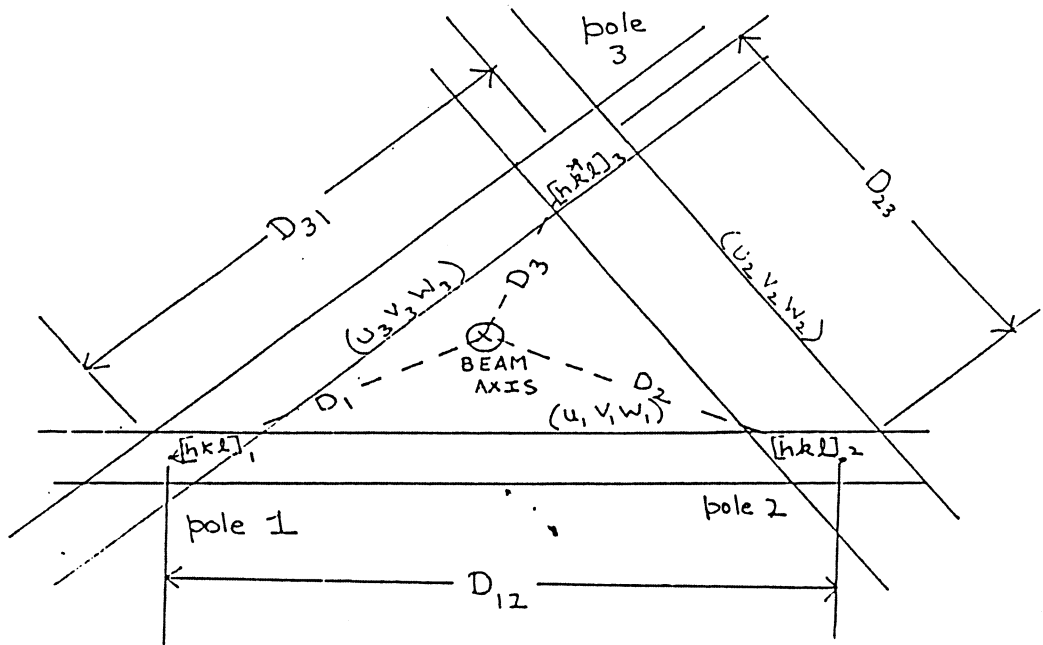
The channeling patterns obtained from the individual grains need to be solved for their orientation. A collection of channeling patterns for all possible orientations relative to the beam can be assembled into a channeling map. For cubic crystals a complete map can be obtained within the triangle defined by [001], [011] and [111] poles. All other orientation can be obtained from this region by mirror and/or rotation operations (18). The determination of orientation is now a problem of pattern recognition by comparison with the channeling map. Confirmation of the pattern comes from comparison of angles between the bands which must be equal to the angles between the corresponding planes that give rise to these bands and the ratio of bandwidths which must be equal to the ratio of the interplanar spacings of these planes. The ratio of bandwidths are independent

of the camera length used and also independent of the lattice parameter in cubic systems. In cubic crystals the angles between bands and poles are independent of the lattice parameter.

The program KPLOT (23) was used extensively in the solution of the channeling patterns. It is a very useful and versatile program that can produce a computer plot of a number of patterns like the Kikuchi patterns, Kossel patterns, diffraction spot patterns etc. Kikuchi patterns for an f.c.c crystal were plotted, with bands and poles indexed by the program, for a given beam direction. The plots were then used to make a unit triangle consisting of the [001], [011] and [111] poles, besides the others within the triangle. This map was then used for comparison of the channeling patterns obtained from individual grains. Channeling patterns are essentially pseudo or reciprocal Kikuchi patterns and therefore can be analyzed with the help of the plots of Kikuchi patterns obtained from the program.

Once three poles in the picture were identified, the distances between them on the picture were measured and used to calibrate the picture in terms of degrees/per unit distance. This helps in finding the angle between each of the three poles and the beam axis (assumed to be at the centre of the picture) by measuring the distance between the beam axis and the respective poles, on the phototgraph. Once these angles are determined the beam axis can be determined uniquely, with good accuracy (see fig 7 for the procedure). Once the beam axis, which is assumed to be normal to the surface of the specimen, is determined in the first grain and again in the second adjacent grain, the angle between these two directions is equal to the misorientation angle between the two grains. When this angle is known, the value of Σ for the boundary can be found from the tables given by Sutton and Vitek (6).

In comparing with these tables, a tolerance of $\pm 1^\circ$ was easily given since the error in determination of the exact positions of the poles, especially the poles that are out of picture, could lead to some error in beam axis determination. Table 1 shows the values of angles obtained and the actual angle for the various Σ s. The measurements of distances were made with an accuracy of 0.5mm. For some grains the three pole solution was not used but an approximate estimate of the beam axis was made if it was close to a pole. Also, in determining the position of the poles, a line had to be drawn bisecting the bands as shown in the Fig. 7. If the edges of the bands are not well



Index the bands. Then,

$$\text{pole 1} = (u_3 v_3 w_3) \times (u_1 v_1 w_1) = [hkl]_1$$

$$\text{pole 2} = (u_2 v_2 w_2) \times (u_1 v_1 w_1) = [hkl]_2$$

$$\text{pole 3} = (u_3 v_3 w_3) \times (u_2 v_2 w_2) = [hkl]_3$$

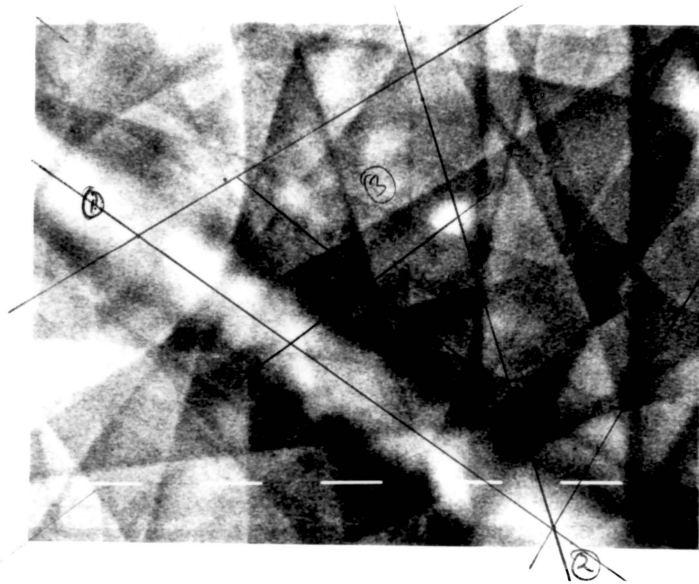
D_{12} = distance between pole 1 and pole 2

D_1 = distance between beam axis and pole 1

θ_{12} = angle between $[hkl]_1$ and $[hkl]_2$ directions

Now, procedure given next page is followed to arrive at the direction of beam axis in the grain.

Figure 7. Method of pattern solution



- i) Index poles 1, 2 and 3
- ii) Measure distances between poles D_{12} , D_{23} and D_{31}
- iii) Calculate calibration factors C_{12} etc., where $C_{12} = \frac{(\text{angle between pole 1 and pole 2})}{D_{12}}$
- iv) Calculate average calibration factor $C_{av} = \frac{C_{12} + C_{23} + C_{31}}{3}$
- v) Measure distances between beam axis and poles and convert to angles
- vi) Cosine of angle between pole 1 $[hkl]$ and beam axis $[xyz]$ is

$$\cos \theta = \frac{h(\frac{x}{\sqrt{s_2}}) + k(\frac{y}{\sqrt{s_2}}) + l(\frac{z}{\sqrt{s_2}})}{\sqrt{s_1}}$$
- vii) Repeat step (vi) for other two poles and solve for the beam axis $[xyz]$ from the resulting simultaneous equations

Figure 7. Method of pattern solution

Table 1. Misorientation angles obtained between grains

<u>Σ</u>	<u>Angles Obtained</u>	<u>Actual Angle</u>
5	36.58 35.67	36.87
9	40.37 37.39 38.79	38.94
13	27.63	27.80
17	28.17 28.56	28.07
19	25.03 26.97	26.53
21	21.56	21.79
25	16.93 16.92	16.26
27	31.35 31.62 32.18 32.29 31.64 31.55	31.59
31	17.51	17.90
37	19.87 18.70 19.77 18.65 18.46	18.92
41	12.35	12.68
43	15.11	15.18
51	22.68 23.51 22.73 23.61 22.18	22.84
57	44.89	44.00
89	34.40	34.89
137	29.97 29.67	29.70

defined , there is a possibility of an error occurring in the location of the pole position upto a couple of mm or about 0.3-0.5°.

There exists some ambiguity about estimation of the value of Σ for a given misorientation angle between two crystals. In this work the orientation angles were compared with the given misorientation angles and grouped into the various Σ s. Hanada et al,(24) developed a rotation matrix to express the relation between the coordinate axes in the first crystal and the coordinate axes in the second crystal. The eigen vector of this matrix gave the rotation axis. The matrix representing the deviation from exact coincidence relation was also obtained from which the angle of deviation was calculated. If this angle of deviation $\Delta\theta$ was less than $15^\circ / \sqrt{\Sigma}$ (25), then the boundary belonged to this value of Σ .

The random boundary in Hanada et al's work corresponds to a boundary between two crystals oriented relative to each other by an angle that deviates by more than the allowable limits, from any C.S.L orientation corresponding to values of $\Sigma \leq 29$. A random boundary can be described by a dislocation sub-boundary superimposed on a coincident site lattice, to accomodate the deviation from exact coincidence relation. Brandon developed the relation for allowable deviation for coincidence boundaries (25). Brandon et al (26), suggested that any deviation from an exact C.S.L orientation is compensated by a network of dislocations forming a sub-boundary in the coincidence lattice. However a coincidence boundary persists if the spacing between the dislocations is considerably greater than the spacing between the coincident sites. Therefore the density of the coincident sites places a restriction on the spacing between the dislocations or the density of the dislocations, if a coincidence boundary is to exist, which implies a limit on the allowable deviation from an exact coincidence orientation. This is reflected in the equation for allowable deviation which is $\text{Const.}/\sqrt{\Sigma}$. As Σ increases, the density of coincident sites decreases, and therefore the density of dislocations also decreases and hence only a small deviation is allowed. The description for a random boundary still holds for such a coincidence boundary (i.e) this boundary is still described by a sub-boundary of dislocations superimposed on the C.S.L.

It is necessary to determine whether a direct comparison of the misorientation angles with the tabulated angles for the various Σ values, will give any error in the analysis. A reason for error

could be that the axis of rotation determined, for a particular case with a misorientation angle close to the angle for exact coincidence, may not be a vector in the corresponding C.S.L. In such a case even though the angles match very well, since the axis of rotation is not a vector of the C.S.L the boundary cannot be classified as belonging to this value of Σ . Hanada et al., have used a three-dimensional matrix to represent the transformation from one crystal to the other (here a rotation matrix). The eigen vector of this matrix remains the same in both crystals and is therefore the rotation axis. A simpler method was used in this work.

If the direction of the beam axis in the first crystal is $[uvw]$ and in the second crystal is $[xyz]$ then the coordinate axes in the second crystal is rotated with respect to the axes in the first crystal, in such a way that the direction $[uvw]$ in the first crystal becomes $[xyz]$ in the second. This rotation is equivalent to rotation of a unit vector along $[uvw]$ into a unit vector along $[xyz]$ in the same crystal (let us assume in the first crystal), since both crystals have the same cubic structure. Hence the cross-product of these two vectors gives the axis of rotation of this transformation. Since this direction remains unaltered during the transformation this is a common axis for both the crystals. Therefore this has to be a vector of the corresponding C.S.L, which is common to both the interpenetrating lattices. If the cross product of the two beam axes yields a common axis which is a vector in the C.S.L, then the boundary can be classified as a coincidence boundary with the corresponding Σ value, provided the misorientation angles match.

The case analyzed was a $\Sigma = 27$ boundary. Six boundaries were classified as coincidence boundaries corresponding to this value of Σ among 55 boundaries analyzed in this work. The cross-product of the beam axes, in the two crystals which were considered as having the misorientation required to produce this value of Σ , was obtained in all six cases. As mentioned earlier in the section on coincident site lattice, the period vectors in the unit cell of a coincident site lattice corresponding to a Σ of 27, are from the families $\langle 110 \rangle$ and $\langle 552 \rangle$. The unit cell of this coincidence lattice is a centered orthorhombic cell with the third vector belonging to the family $\langle 115 \rangle$, such that all three vectors are mutually perpendicular and form an orthogonal coordinate system. It was found that the common axis obtained in all these cases were (within $2-3^\circ$) perpendicular to a member of one of the three families of direction. This implies that they lie in a plane perpendicular

to this direction and therefore can be described by a combination of the other two vectors forming the three mutually perpendicular vectors of the unit cell. Thus the common axis is a vector of the C.S.L. Hence a direct comparison of the misorientation angles with the tabulated values for the various Σ s within a deviation of $\pm 1^\circ$ in most cases, does seem to give correct results.

It must be noted that in cubic crystals which possess a high degree of symmetry even for high coincidence boundaries a large number of solutions exist for the axis-angle pair to describe the misorientation. Only in triclinic we have unique values for the axis and angle of misorientation (26).

3.4 Instrument Conditions

Philips 420 STEM was used for obtaining the patterns. A selected area channeling pattern mode(SACP) is available on the microscope which is selected for getting the channeling patterns. As such there are very few instrumental parameters to be concerned with. When the SACP mode is chosen, the microscope automatically switches to the nanoprobe mode. Here the strength of the first condenser lens controls the probe size and this is achieved by using the spot size knob. There are 6 positions for this spot size knob - pos. 1 to 6. Position 6 gives the smallest spot size. However with very small spot size the amount of signal generated may not be sufficient and hence a spot size of 4 was selected for this work. Condenser lens 2 is used to focus the image. The condenser 2 lens aperture determines the spherical aberration of the beam. Spherical aberration is least with an aperture of smaller size. A 30μ C2 aperture was chosen for the experiment. This is the smallest C2 aperture available on the microscope. For these selections of spot size and C2 aperture the effective spot size is expected to be approximately 8nm. The magnification selected determines the rocking angle. Higher the magnification smaller the rocking angle. A magnification of 200X was chosen. Any higher magnification than this would result in a very small rocking angle. The only lower magnification available, less than 200x, was 100x, but at this magnification the picture on the screen

was not clear. Back-scattered electron detector was used for reasons of stronger signal and improved contrast.

To obtain channeling patterns from individual grains, a backscattered electron image of the specimen surface is obtained in low mag./SEM mode, with the above mentioned instrumental conditions. The grain from which the channeling pattern is desired, preferably a large grain, is centered on the screen. SACP mode is selected and the magnification is reduced to 200X. The scan speed is reduced to about 10 secs per frame. The objective lens current is increased to very large value till the channeling pattern is obtained. The gain of the backscattered electron detector signal amplifier is increased to increase the contrast in the picture.

Fig. 8 shows the ray diagram for the STEM mode in a Philips 400 STEM, (28). Fig. 5 shows the two methods for the production of a rocking beam and fig. 9 shows a possible mechanism by which a rocking beam could be produced in a Philips STEM. Not much information is available about the SACP mode in the Philips 420 STEM. Here the objective lens could be used as a final focussing lens to focus the scan back onto a point on the optic axis. The lower deflection scan coil must be off. In these experiments care must be taken not to tilt the specimen relative to the beam.

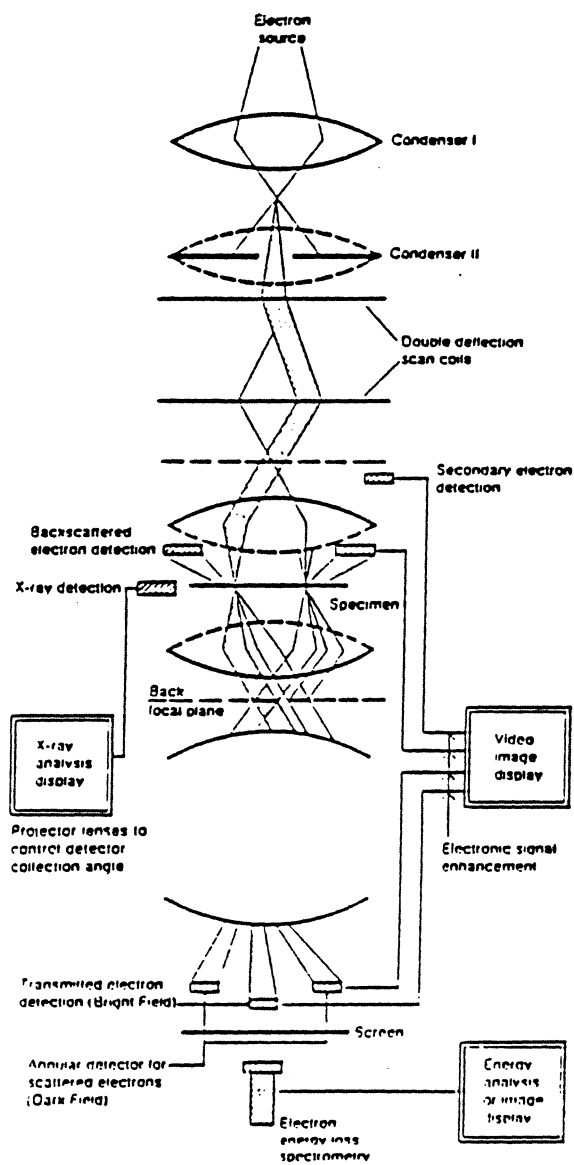


Figure 3. STEM mode in PHILIPS 400 (from Ref. 28)

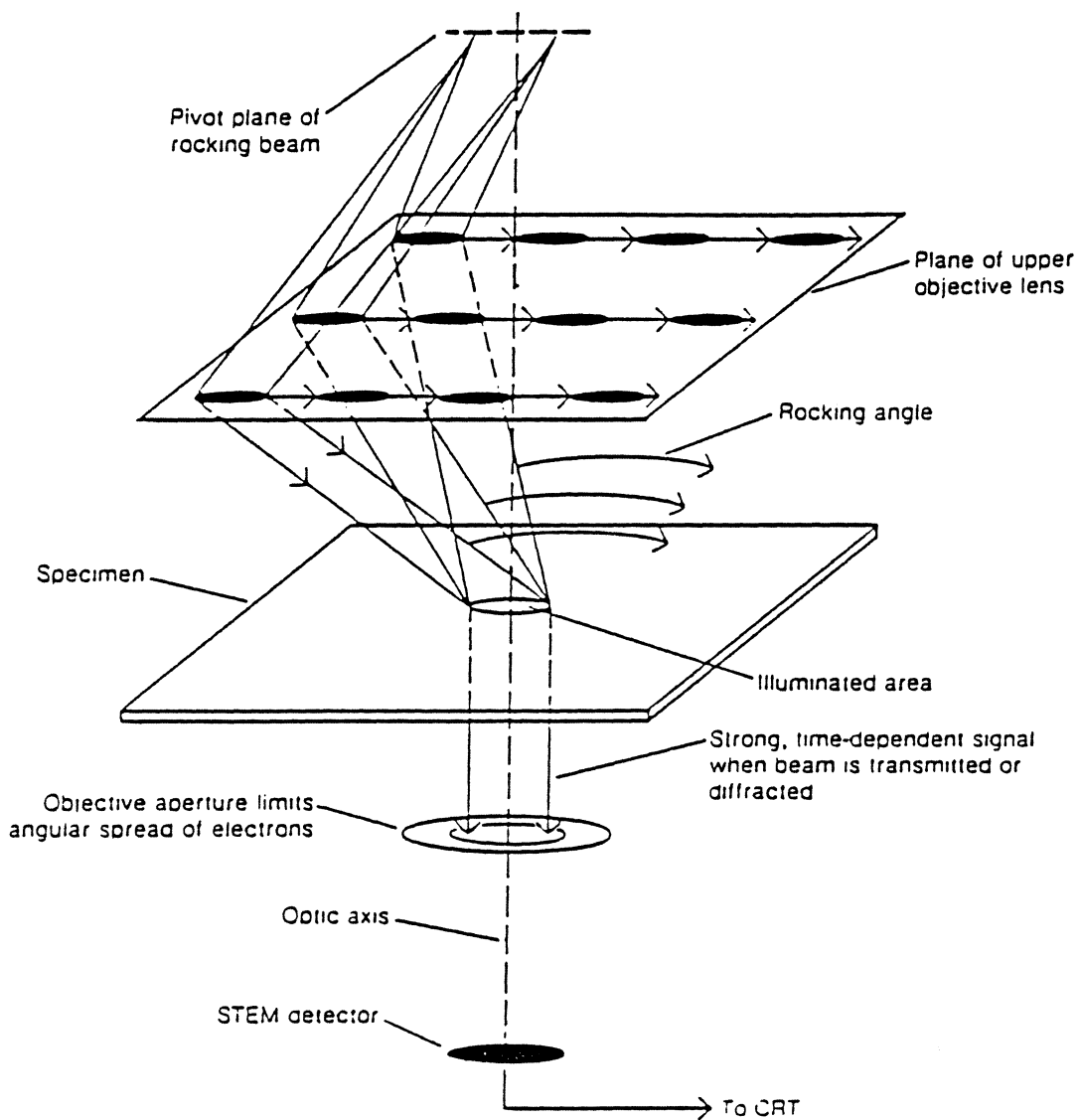


Figure 9. Possible beam rocking method in PHILIPS 400/420 STEM (from Ref. 28)

4.0 Results

4.1 *Results from Geometrical Modelling*

The structure of tilt boundaries in the [001] and [011] series, for both favoured and intermediate misorientations were obtained by geometrical modelling. The unit cell in a $L1_2$ structure and the [100] and [110] projections of the atoms in the unit cell are shown on page 85.

4.1.1 Structure of [100] tilt boundaries

The favored boundaries in this family are the $\Sigma = 5$, $\theta = 53.1^\circ$ (120) (Figs. 10c and 10d) and $\theta = 36.9^\circ$ (130) (Figs. 10a and 10b) respectively (θ measured from $[100]_1$ to $[100]_2$). The $\Sigma =$

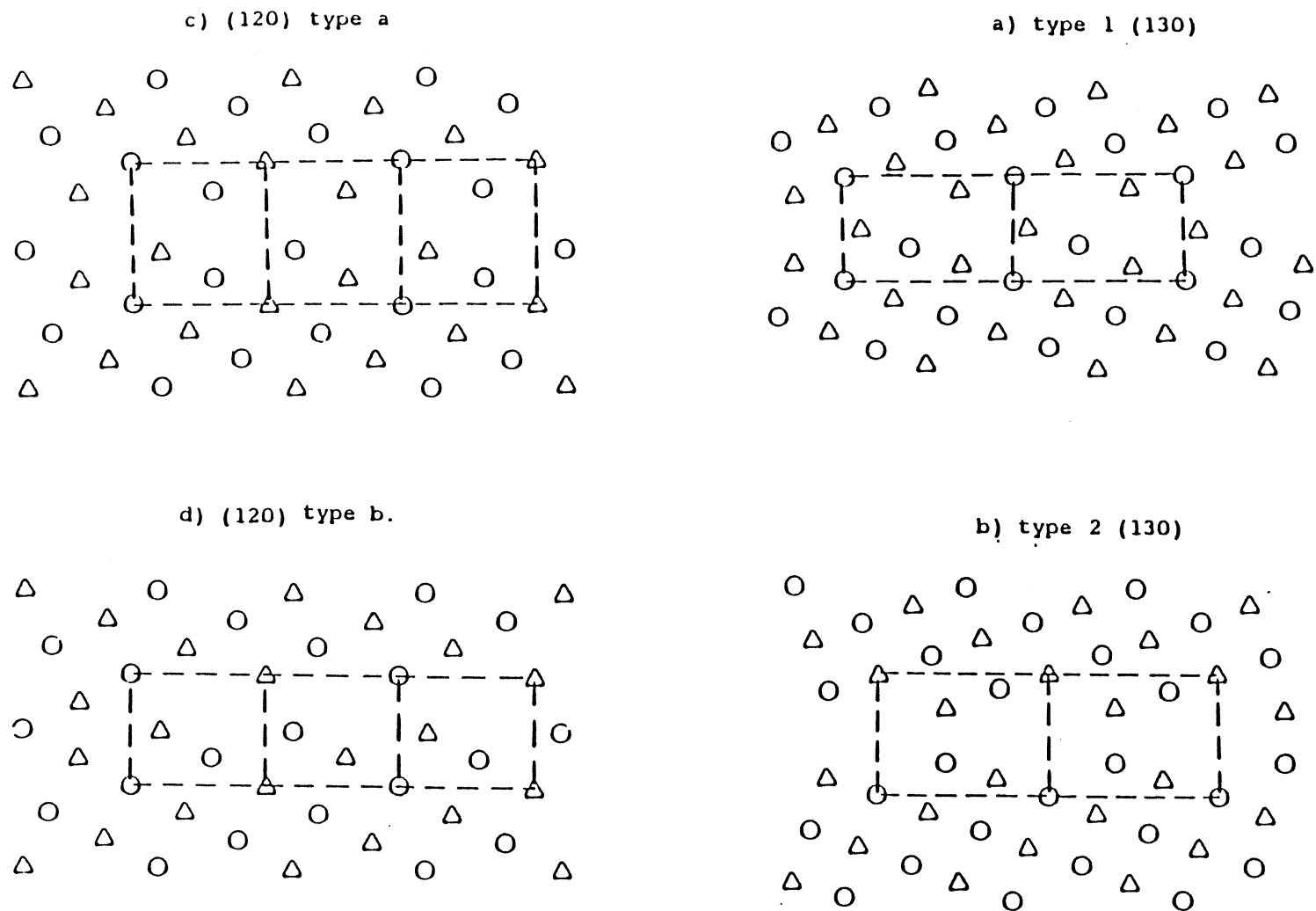


Figure 10. $\Sigma = 5$ [100] boundaries: a) type 1 (130) b) type 2 (130) c) type a (120) d) type b (120)

5, (130) boundary has been studied extensively in aluminium. Two types of structures have been reported for pure metals. Type one (Fig. 10a) is characterized by no translation parallel to the grain boundary plane. On the other hand, type two (Fig. 10b) is characterized by a translation parallel to the grain boundary plane. Hashimoto et al. (29,30) calculated the energies of both types in Al and found that type one is stable. In the present work type one boundaries were found to be most dense in ordered compounds with the $L1_2$ structure having equal atomic sizes for the components (i.e. Cu_3Au). This is shown in Fig. 11. In analyzing type one boundaries it can be noticed that there are 4 different configurations of the structural unit, labeled $DD'D''D'''$ in Fig. 11. The units D and D' originate in taking the coincidence sites in this boundary as A atoms. The boundary is formed by the sequence DD' (here called α (130)). If the coincidence sites are B atoms the structural units D'' , D''' result and form β (130). It is also evident from the structures that α and β (130) are boundaries of different compositions. Table 2a gives the composition of the 4 layer units. If no grain boundary segregation is present the boundary should be constituted by equal fractions of α and β structures. Since the α and β portions have different compositions this two phase boundary can also be thought of as a clustering effect.

Tables 2a and 2b shows the average number q of A-B bonds per atom in each unit. The β phase of the (130) boundary is Au rich and therefore presents a larger value of q compared to the perfect lattice. On the other hand α (130) has a much lower value. The average q of both β and α is lower than that of the perfect lattice (clustering effect).

The disordering contribution to the energy of the GB will be:

$$T_{\text{disord}} = (q - q_0)\epsilon N / \text{area}$$

where q is the number of AB nearest neighbor bonds in the first coordination shell atom, N is the number of atoms in the repeat unit, and Area refers to the area of the repeat unit in the grain boundary plane.

$$\epsilon = V_{AB} - (V_{AA} + V_{BB})/2$$

For values typical of Cu_3Au this gives:

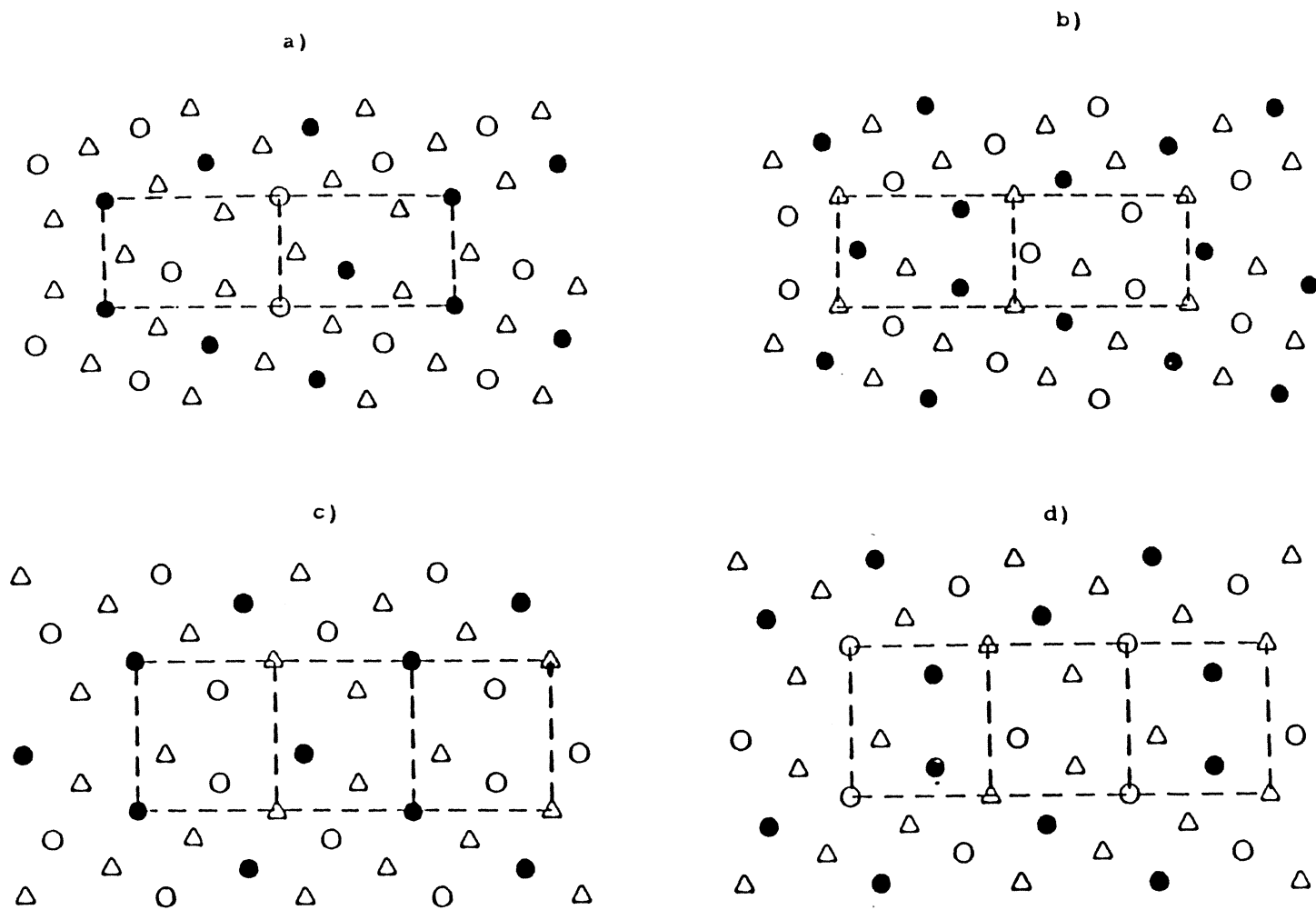


Figure 11. Type I $\Sigma = 5$ $[100]$ boundary in Cu_3Au : a) $\alpha(130)$ (DD') b) $\beta(130)$ ($\text{D}'''\text{D}''$) c) $\beta(120)$ ($\text{E}'\text{E}$) d) $\alpha(120)$ ($\text{E}'''\text{E}''$)

Table 2. Structure and Composition of [100] boundaries in

Boundaries in Cu₃Au Type Compounds

Structural Unit	Boundary	Composition		q		q _{av}
A A'	perfect lattice	0.25 0.25	0.25	4 8	6	6
A'' A'''	perfect lattice	0 0.5	0.25	4 8	6	
B B'	β' (120)	0.5 0.167	0.333	7.5 5.5	6.5	5.8
B'' B'''	α' (120)	0 0.333	0.167	3.5 6.7	5.1	
E E'	β (120) 4 layers	0.375 0.125	0.25	7.8 4.4	6.1	5.575
E''' E''	α (120) 4 layers	0.5 0	0.25	7.4 2.9	5.05	
D D'	α (130) 4 layers	0.10 0.30	0.20	3.9 5.5	4.7	5.55
D'' D'''	β (130) 4 layers	0 0.60	0.30	5 7.8	6.4	

Table 2 cont'd

Boundaries in Ni_3Al Type Compounds

Structural Unit	Boundary	Composition		q		q _{av}
Z	Pure translational boundary	0.125	0.25	3.625	5.625	5.625
Z'		0.125		5.75		
Z''		0.625		8.625		
Z'''		0.125		4.5		
H	γ (130)	0.25	0.25	6.07	6.0	5.605
H'	4 layers	0.25		5.93		
H''	δ (130)	0.45	0.25	7.28	5.21	
H'''	4 layers	0.05		3.14		
L	γ (120)	0.05	0.25	3.6	5.60	5.65
L'	4 layers	0.45		7.6		
L''	δ (120)	0.30	0.25	6.1	5.7	
L'''	4 layers	0.20		5.3		

$$T_{\text{disord}} = 0.15 \text{ J/m.}$$

Hashimoto et al. (30) calculated the difference in energy between type one and type two boundaries to be 0.3 J/m. This suggests that type one will also be stable in Cu_3Au , as in pure metals.

In the absence of segregation the α and β structures have to occur in a mixture. Furthermore, several defects present in the bulk will result in a transition from α to β boundary. Since the boundary contains Al-Al bonds of nearest neighbor length, type one structures for Ni_3Al require a larger translation perpendicular to the grain boundary plane. In this case structures of type two, shown in Fig. 12, were found to be most dense. These boundaries are characterized by structural units H, H', H'', H''', as shown in Table 2b with composition equal to that of the bulk. These boundaries do not destroy the ordering of the perfect lattice and will be stabilized for ordered compounds of high ordering energy. Note that these structures do not contain Al-Al nearest neighbor bonds. The density of these structures are lower than that found for Cu_3Au , which is of type one. The other $\Sigma = 5$ boundary, $\Sigma = 5 (210) [100]$, $\theta = 53.1^\circ$ boundary has also been investigated in detail. Shown in Fig. 10c and 10d are two different structures, called type a and type b, that have been reported for pure metals. Structure a has been obtained by Smith et al. (31) for aluminium and Wetzal et al. (11) for several fcc metals. Sutton and Vitek (6) report structure b for Cu. The difference in these two structures is due to the fact that different interatomic potentials were used. Lennard-Jones type potentials yield structure a for Al, Cu, Ni and Au (11). The splines potential of Crocker and Faridi (10) yields type b for Cu. Hard sphere models (3) yield configuration a for all fcc metals. The results of this work are also similar to structure a for Cu_3Au (Fig.10). Both of these structures can be classified as type one structures. For ordered Cu_3Au type compounds they result in two variants, containing Au-Au nearest neighbor bonds. Tables 2a and 2b also include data for the (120) boundary. Note that for type one boundaries the effect of ordering on grain boundary energy is somewhat smaller in the (210) case than in the (310) boundary. Structures of type two have not been reported previously for the (210) boundary. In this work type two configurations, shown in Fig. 12, are obtained using hard sphere models for Ni_3Al , where the atomic sizes are different. As in the (130) case these boundaries do not destroy order and are less

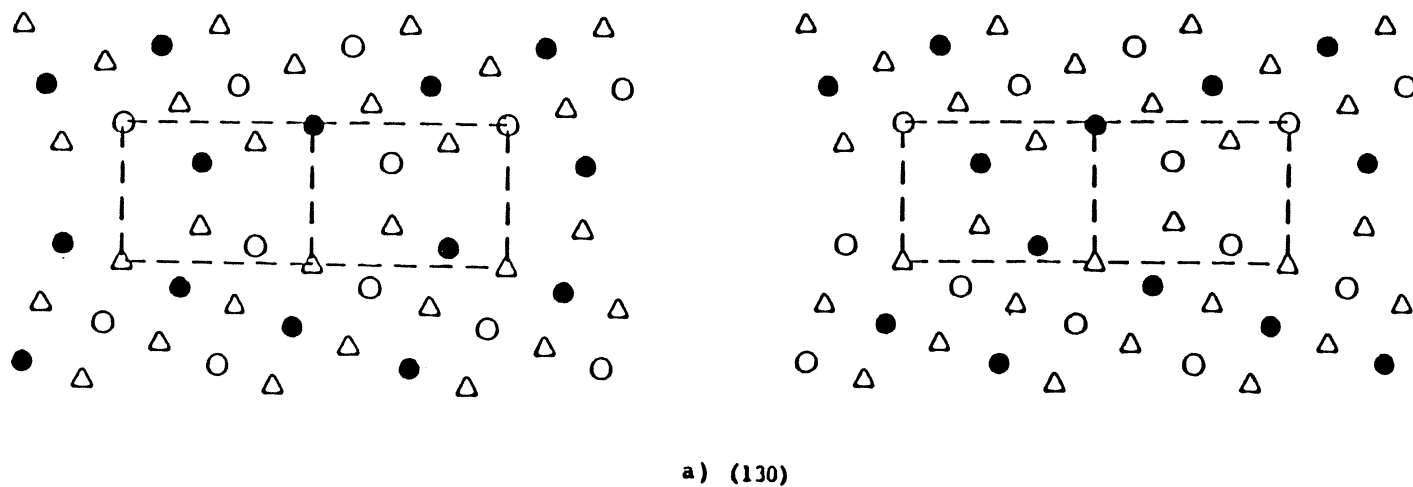


Figure 12. Type 2 $\Sigma = 5$ [100] boundary in Ni_3Al : a) (130) boundaries (III' & II''II''') b) (120) boundaries (I'I' & I'''I''')

b) (120)

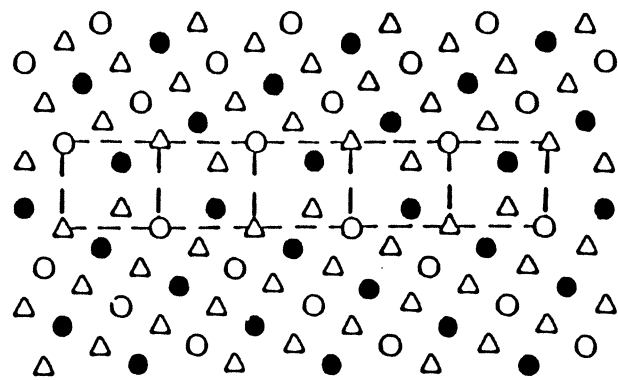
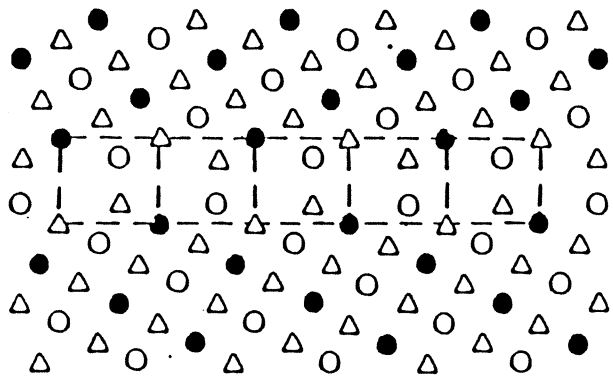
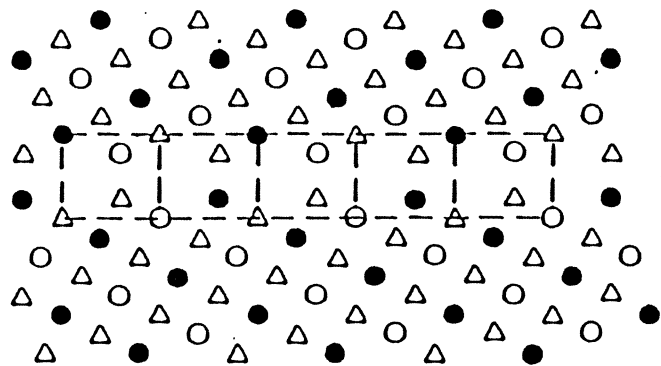


Figure 12 cont'd

dense than type one boundaries. The method of hard spheres is not adequate to describe the differences among the different type two structures, since they are equally dense. The intermediate boundaries in the [100] family are listed in Table 3A for boundaries in Cu_3Au type compounds. The constitution of these intermediate boundaries in terms of structural units is indicated in the last column. The unit A appears in some of these boundaries and is characteristic of the perfect lattice (32). The ordering states of this type of unit are shown in Fig. 13, and some of the intermediate boundaries are shown in Fig. 14. Table 3b shows the constitution of intermediate boundaries in Ni_3Al . Note that these results are very similar to those of Cu_3Au if the units corresponding to type one boundaries are replaced by the corresponding units of type two boundaries. The unit A of the perfect lattice is replaced by the unit Z of the perfect lattice with a translational boundary, as shown in Fig. 15. Shown in Fig. 16 are the structures of some of these intermediate boundaries in Ni_3Al . In summary, type one boundaries are most dense for Cu_3Au , whereas type two boundaries are densest for Ni_3Al . Also, the disordering contribution to grain boundary energy is smaller in type two boundaries.

4.1.2 Structure of [110] boundaries.

The results for this series of boundaries differ from the previous series in that the $\Sigma = 3$ [(111) and (112)], $\Sigma = 9$ (221) boundaries were found to have the same structure for both types of L1_2 compounds analyzed.

The only variant of $\Sigma = 3$ (111) boundary is shown in Figure 17. This is a type one structure (no translation parallel to the boundary). Note that the AB stacking of (110) planes shown in Figure 17 should be interpreted as ABA'B stacking where the type of atoms have been interchanged in going from A to A'; that is, in the plane of circles immediately above and below the plane of paper, the white and the black circles (representing different atoms respectively) actually

Table 3. Structural unit composition of Intermediate [100] boundaries

Structure of [100] Boundaries in Cu_3Au Type Compounds

Boundary	Σ	θ	Pure Metals Structure	Ll_2 Structures	
Perfect lattice	1	90	AA	AA'	A''A'''
(310)	5	36.87°	DD	DD'	D''D'''
(210)	5	53.08°	BB EE	BB' EE'	B''B''' E''E'''
(320)	13	67.38°	AB AE	AB''A'''B' A'E'A''E''A'	A'BA''B''' AE'''A'''E
(530)	17	61.93°	ABB AEE	AB''B''''A'BB'AB''B''' A''B''E'''A''	A'B'EA
(540)	41	77.32°	AAAB AAAE	A''''A''A''''BA'AA'B''' A'AA'E'A''A'''	A''A''''A''B''AA'AB' AA'AE'''A'''A''
(520)	29	43.60	DB DE	D'B''''D''BD' DE'''D''E	DB'D''''B'' D'E'D''''E''

Table 3 cont'd

Structure of $\{100\}$ Boundaries in Ni_3Al Type Compounds

Boundary	Σ	θ	Ll_2 Structure	
Pure Translational	1	90°	ZZ'	$\text{Z}''\text{Z}'''$
(310)	5	36.87°	HH'	$\text{H}''\text{H}'''$
(210)	5	53.08°	FF'	$\text{F}''\text{F}'''$
(320)	13	67.38°	$\text{Z}'\text{FZF}$	$\text{ZF}'\text{Z}'\text{F}'$
(530)	17	61.93°	$\text{ZF}''\text{F}''\text{Z}'\text{F}'''$	$\text{Z}'\text{F}''''\text{F}''''\text{ZF}''$
(540)	41	77.32°	$\text{Z}'\text{ZZ}'\text{FZZ}'$	$\text{ZZ}'\text{ZF}'\text{Z}'\text{Z}$
(520)	29	43.60°	$\text{F}''\text{H}'\text{F}''''\text{H}$	$\text{F}''''\text{HF}''\text{H}'$

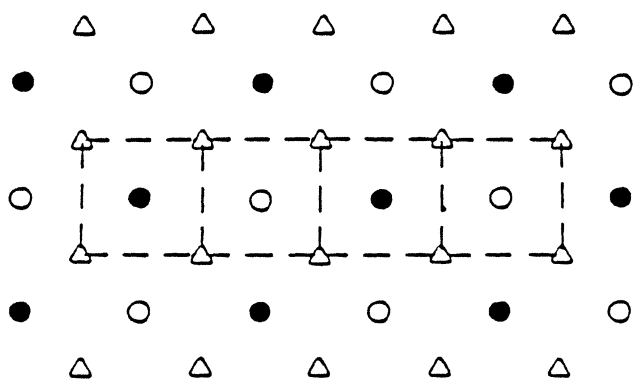
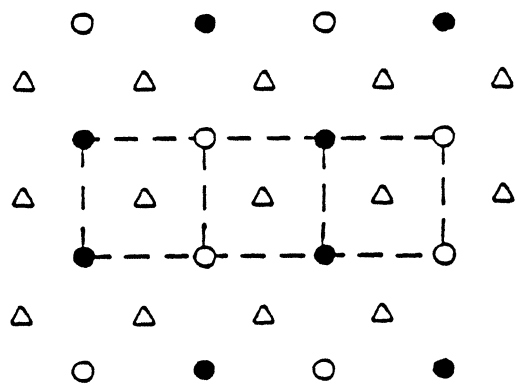


Figure 13. Structural units of perfect lattice: "A"

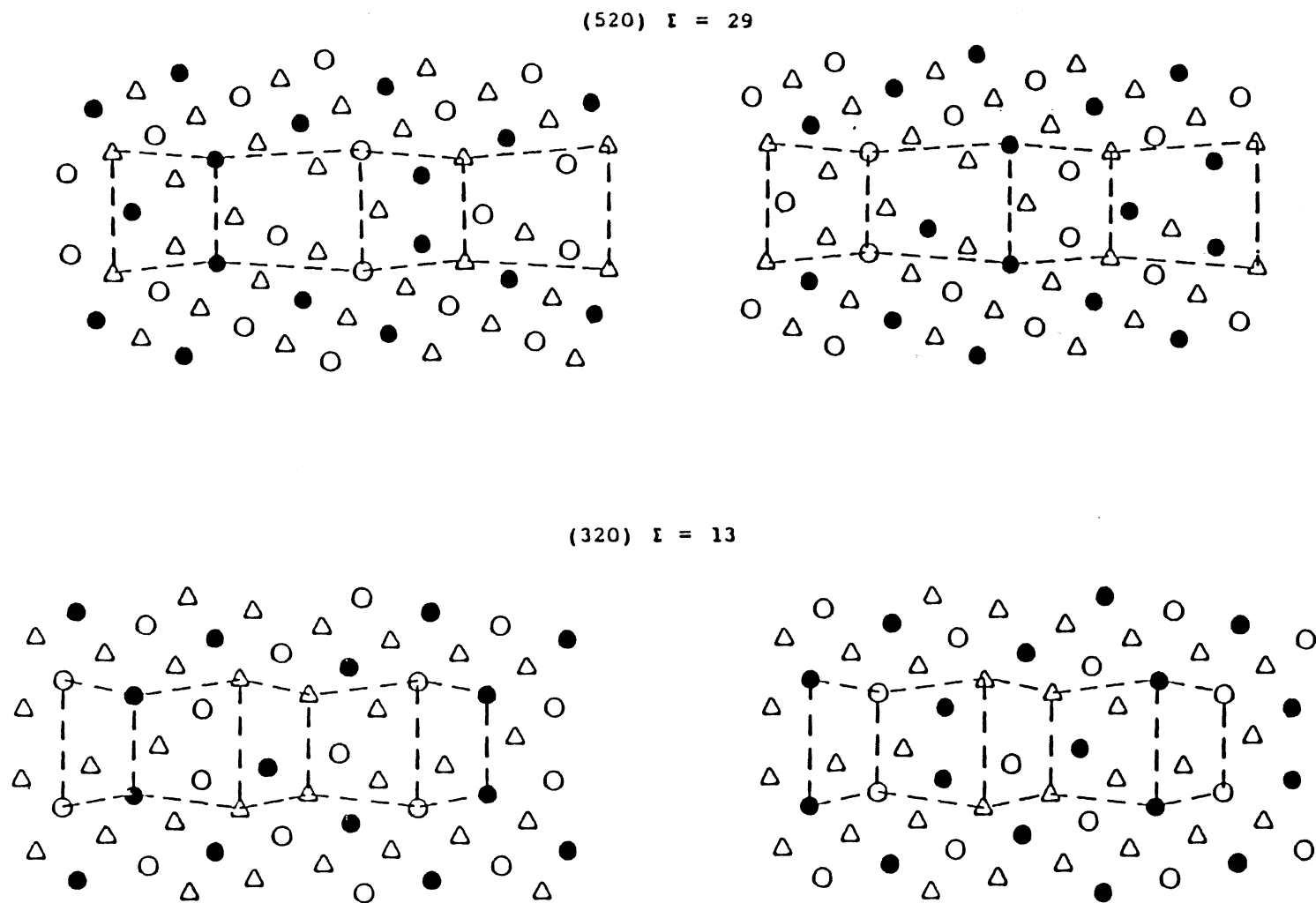


Figure 14. Intermediate $[100]$ boundaries in Cu_3Au : a) $\Sigma = 29$ (520) b) $\Sigma = 13$ (320) c) $\Sigma = 17$ (530) d) $\Sigma = 41$ (540)

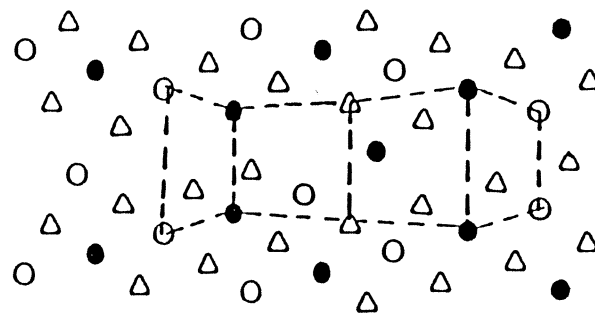
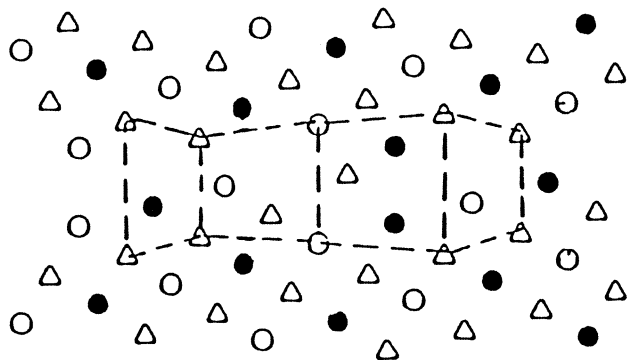
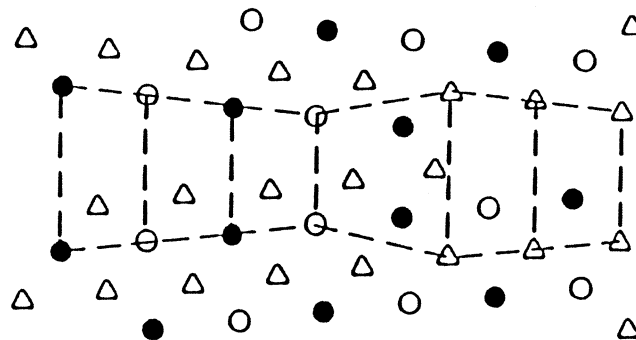
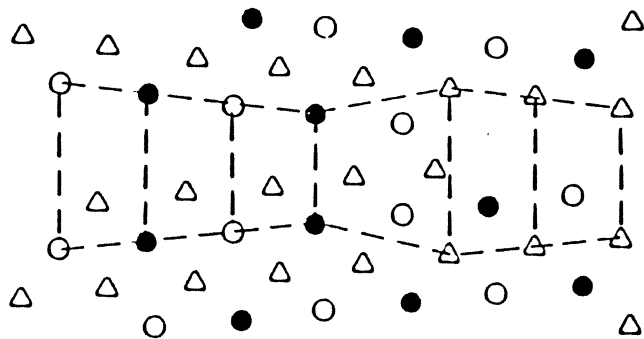
(530) $I = 17$ (540) $I = 41$ 

Figure 14 cont'd

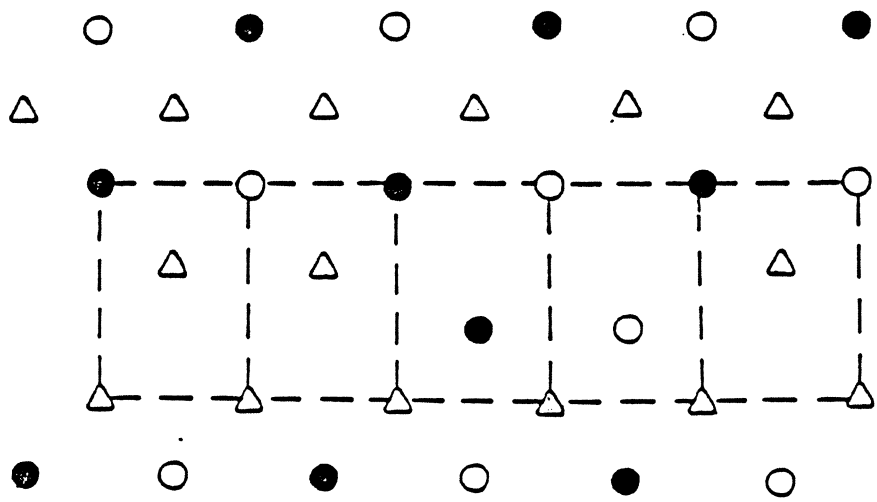


Figure 15. Structural units of a translational boundary: "Z"

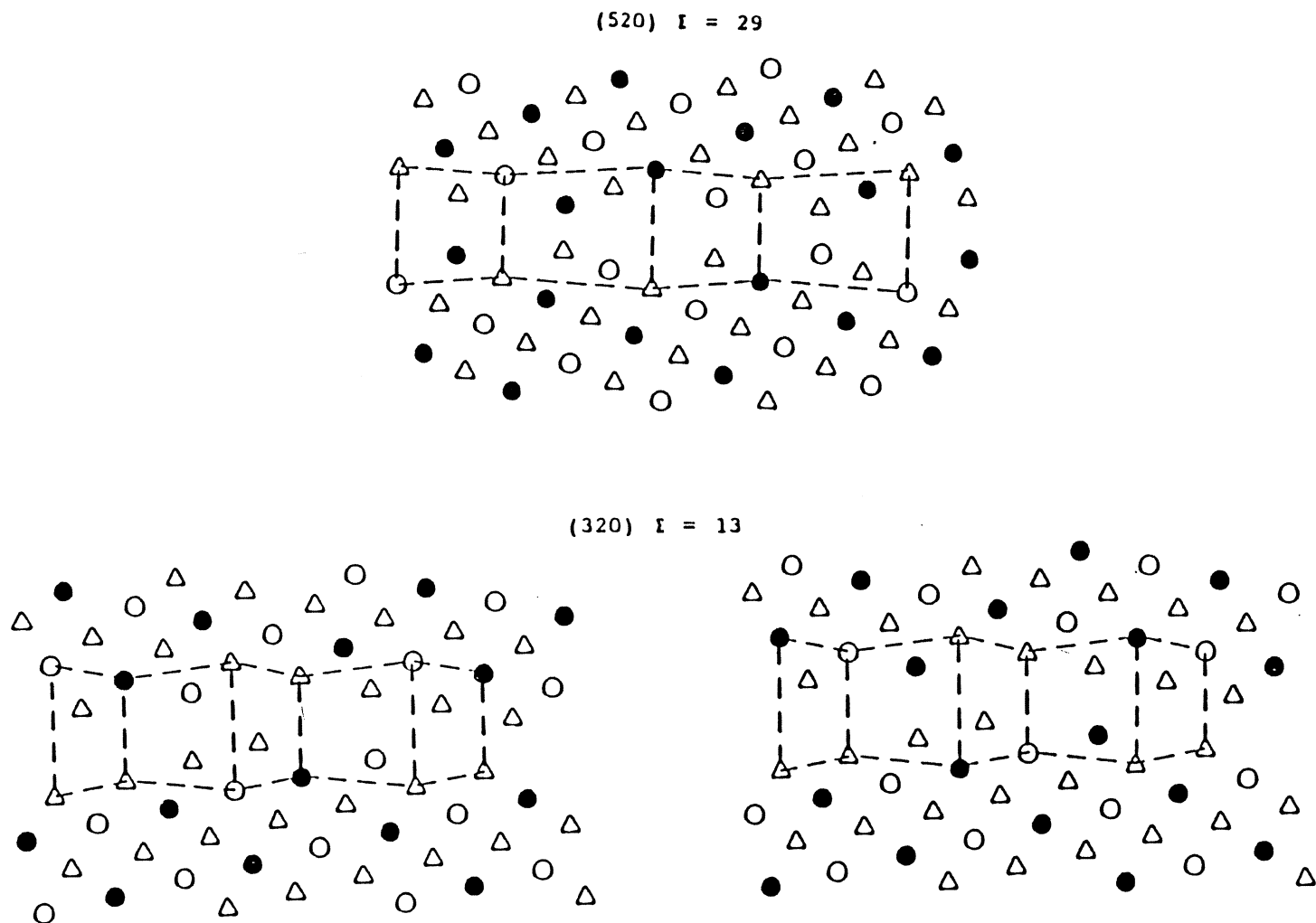


Figure 16. Intermediate $[100]$ boundaries in Ni_3Al : a) $\Sigma = 29$ (520) b) $\Sigma = 13$ (320) c) $\Sigma = 17$
d) $\Sigma = 41$ (540)

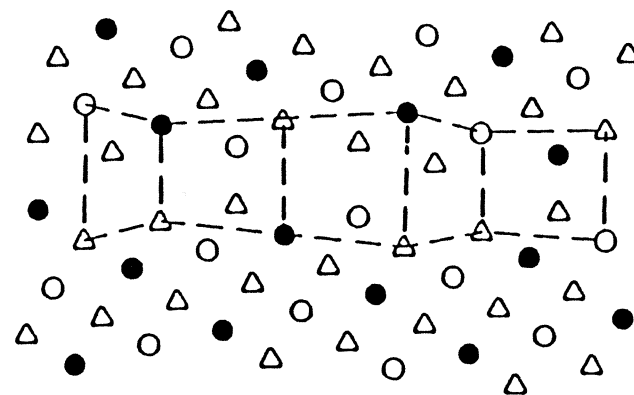
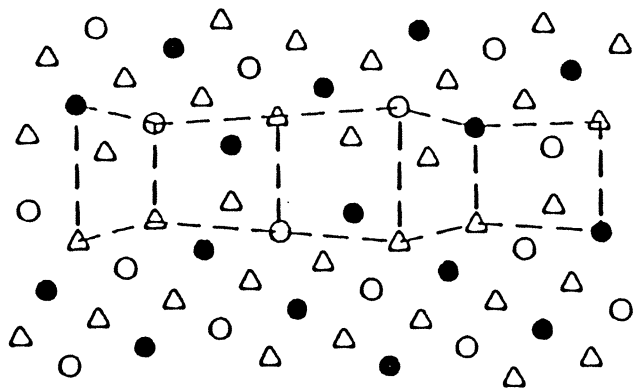
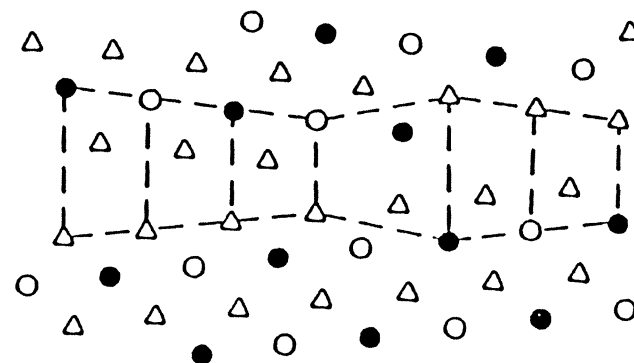
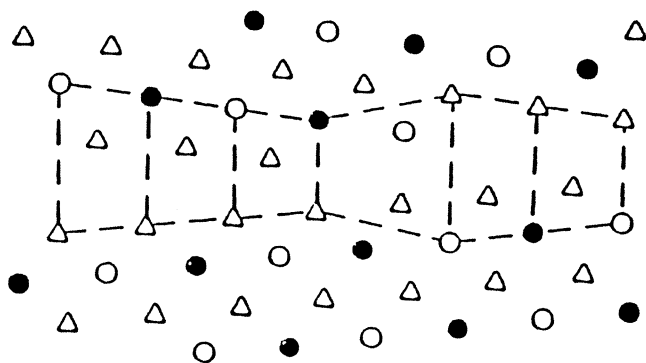
(530) $I = 17$ (540) $I = 41$ 

Figure 16 cont'd

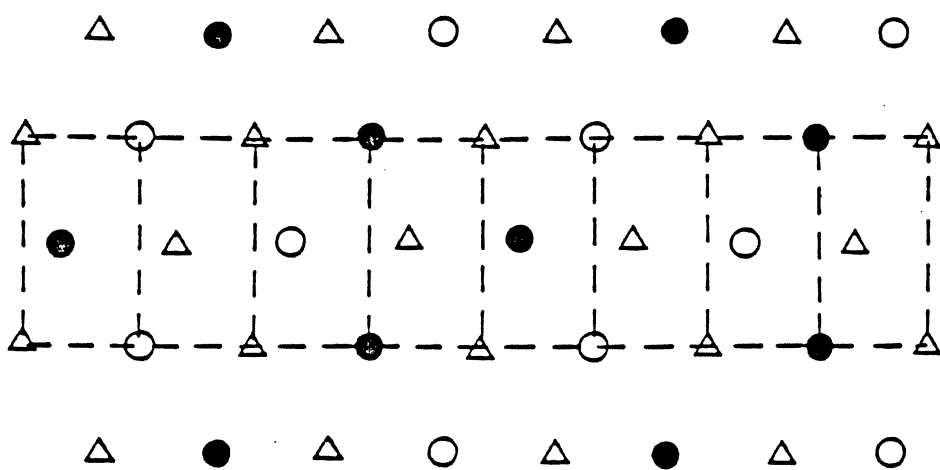


Figure 17. Type I $\Sigma = 3$ (111)[110] boundary in $L1_2$ structures

interchange positions. This becomes clear when we look at two successive (110) planes of atoms in this structure. The structure of Figure 17 will be stable also for Ni_3Al since it does not present nearest neighbor Al-Al bonds.

The other $\Sigma = 3$ boundary, (112) [Fig. 18] was found to be of type two for both cases. This structure is allowed for Ni_3Al since the Al-Al bonds have interatomic distances of 0.289 nm. In the case of Ni_3Al this is expected to stabilize the boundary since this is close to the equilibrium interatomic distance of pure Al.

For the $\Sigma = 9$ (221) boundary, type one structures are less dense for pure metals, in agreement with the work of Sutton and Vitek (6). A configuration of type two, shown in Fig.19, was found to be the most dense configuration for both types of L1_2 compounds.

Another favored boundary in the series is the $\Sigma = 11$ (113). The structure found for this boundary for Cu_3Au type compounds is shown in Figure 20. In Ni_3Al a configuration of type two was found, as shown in Figure 21.

The $\Sigma = 27$ (115) boundary in Cu_3Au takes a configuration of type two which is in agreement with the results of Sutton and Vitek for Al (6). The type 2 structure for this boundary, found in Ni_3Al and Cu_3Au , is shown in Figure 22.

The $\Sigma = 9$ (114) boundary is not a favored boundary, it is intermediate between the $\Sigma = 11$ (113) and $\Sigma = 27$ (115) boundaries. The structure of this boundary for Cu_3Au is shown in Fig. 23, and is in agreement with the results of Sutton and Vitek for Al. In Cu_3Au this is a two phase, type one boundary. For Ni_3Al the structure is of type two.

4.1.3 Sites for interstitial segregation

In this section we will consider the sizes of available sites for interstitial occupation in the two types of boundaries discussed above. We choose as an example the (100) $\Sigma = 5$ (310) bound-

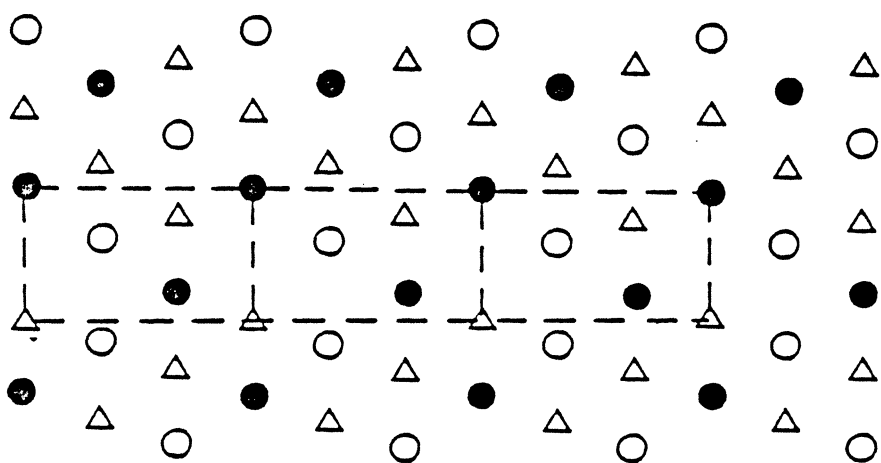


Figure 18. Type 2 $\Sigma = 3$ (112) [110] boundary in $L1_2$ structures.

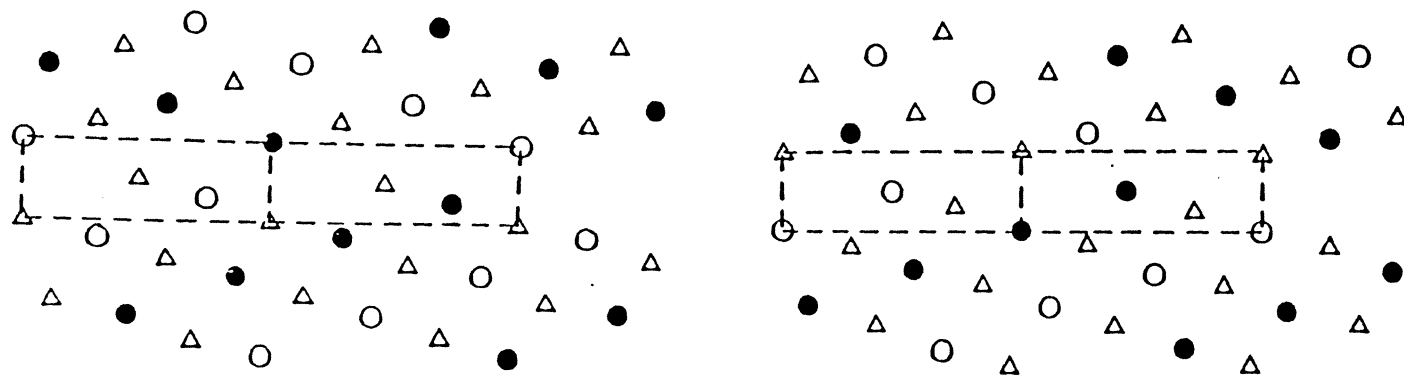


Figure 19. Type 2 $\Sigma = 9$ (221) [110] boundary in $L1_2$ structures

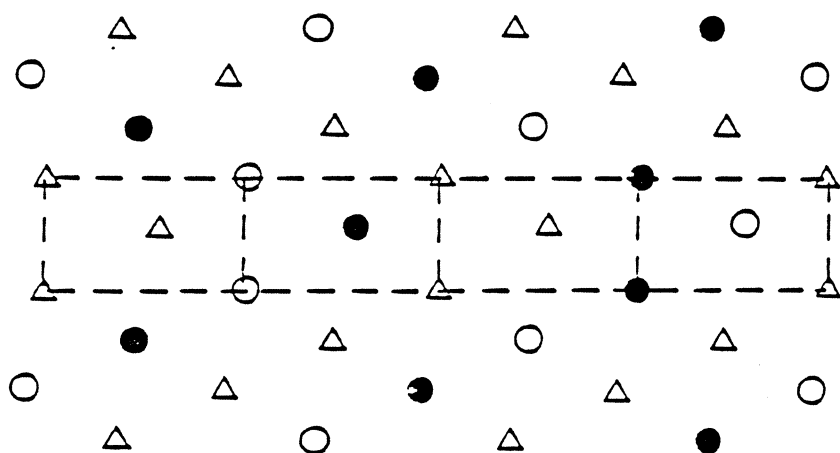


Figure 20. Type I $\Sigma = 11$ (113)[110] boundary in Cu_3Au

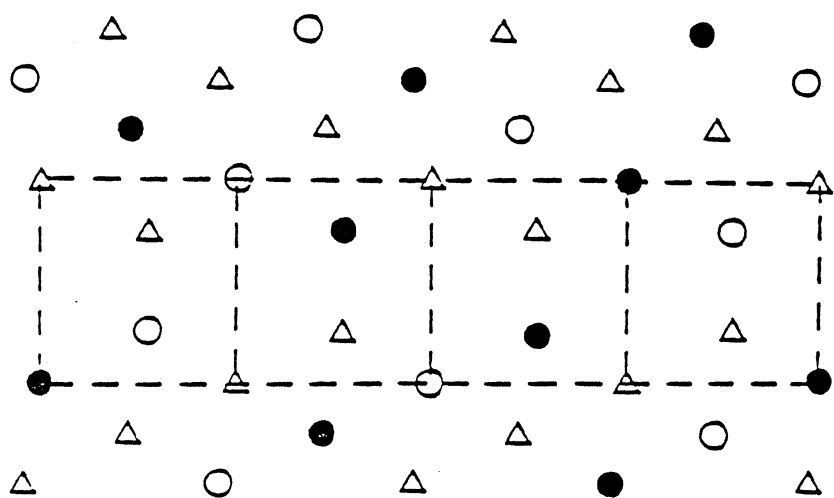


Figure 21. Type 2 $\Sigma = 11$ (113) [110] boundary in Ni_3Al :

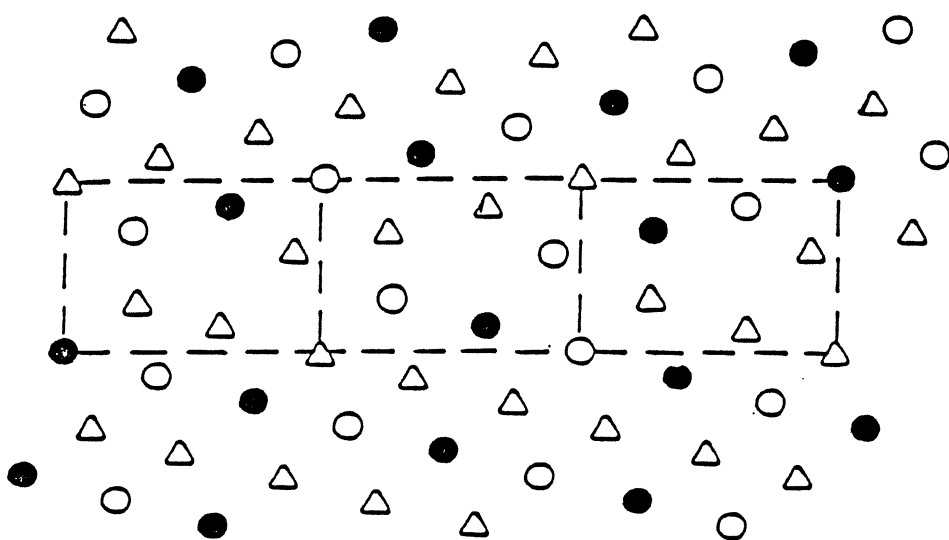


Figure 22. Type 2 $\Sigma = 27$ (115) [110] boundary in $L1_2$ compounds

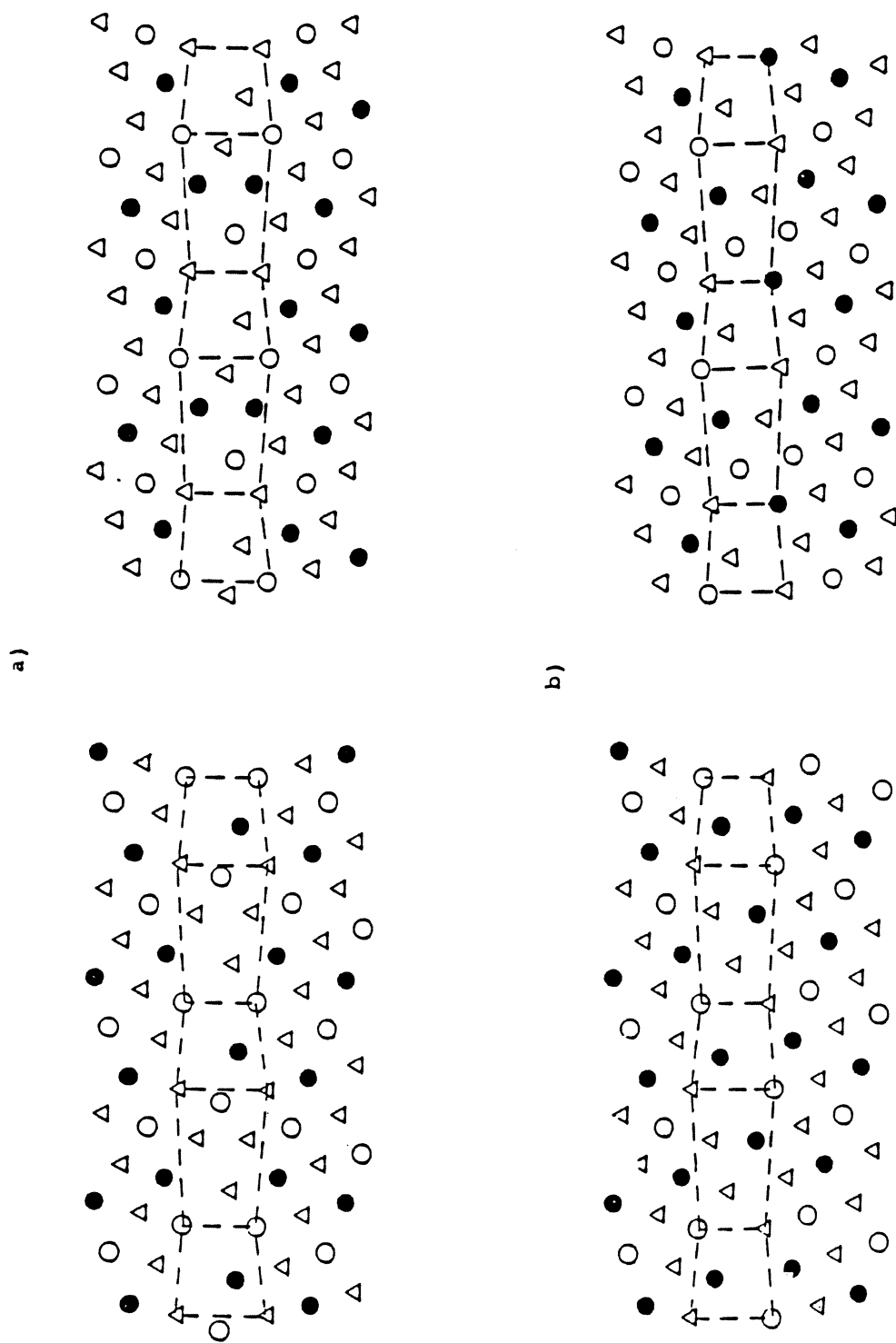
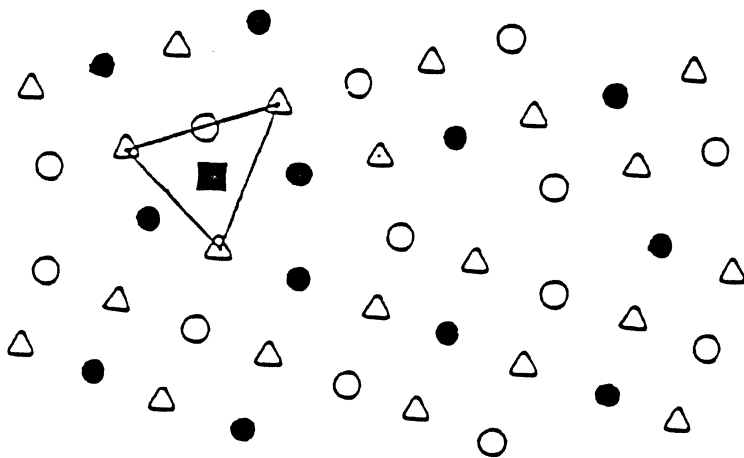


Figure 23. The $\Sigma = 9$ boundary: in a) Cu_3Au b) Ni_3Al

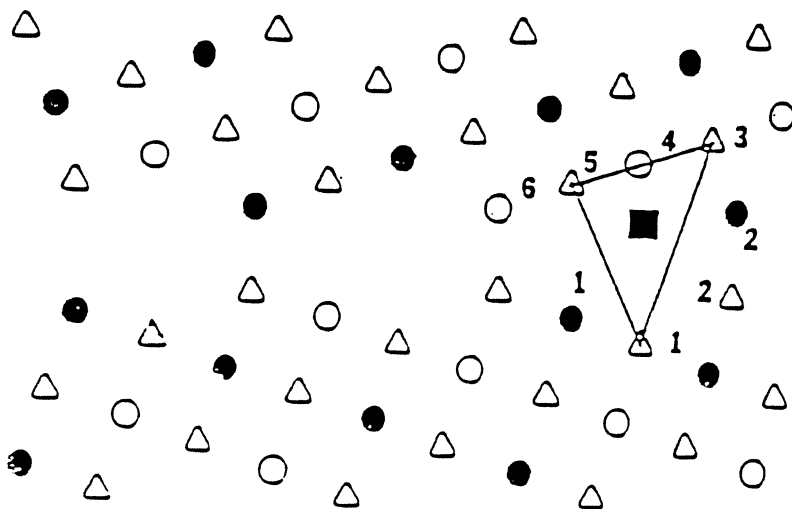
ary, and apply our results to the possible segregation of B to both types of boundaries. Frost et al (33) have calculated interstitial site diameters for grain boundaries in pure metals. For the (100) $\Sigma = 5$ (310) boundary the largest interstitial site is 0.66 a, where a is the bulk nearest neighbor distance. The present calculation for boundaries of type 1 (Cu₃Au) agrees very well with his results, and the location of the largest site is shown in Figure 24a. Figure 24b shows the largest interstitial site available in boundary of type 2 (Ni₃Al), where a much larger size of 0.88a was obtained.

It is of particular interest to consider the implications of this difference for B segregation. For this purpose we considered the B-Ni and B-Al distances present in known binary compounds of the B-Ni and B-Al systems. Rundqvist (34) studied the Ni-B system. Tables 4 and 5 show the interatomic distances he reports for Ni₄B₃ in its two crystal structures. The Ni-Ni distances agree very well with the value found in pure Ni (0.25 nm), and NiAl (0.25 nm). The B-B distances average 0.183 nm; whereas the B-Ni ones are around 0.21 nm. Note that this distance is very close to the average of the Ni-Ni and B-B. This is contrary to what was found in the Ni-Al case, where the Ni-Al nearest neighbor distance is similar to the Ni-Ni. The B sizes in Ni borides also agree very well with those reported for B-B bonds in AlB₁₀ (35), which are 0.177 to 0.191 nm. They also agree with those for elementary Boron. We will therefore assume a hard sphere diameter for B of 0.183 nm which is 0.75 of the nearest neighbor distance in Ni₃Al.

Geometrical considerations suggest that limited segregation values are expected in a boundary of type 1, since the interstitial sizes are not large enough for B (0.66 a, compared to 0.75 a). This means that a large distortion of the boundary structure will probably occur around the interstitial B atom, thus decreasing the segregation energy. For boundaries of type 2 (Ni₃Al) the interstitial sizes available are indeed large enough for B (0.22 nm). The distances of B to nearest neighbors in these positions are given in Table 6, for the boundary of Figure 24b. Note that they are even larger than those shown in Tables 4 and 5. The actual interstitial site sizes will be different after relaxation is allowed, but we expect the qualitative trend of the sizes being larger in type 2 to hold. This trend was also confirmed for other boundaries of higher Σ value.



B segregation in (130) boundary of type 1



B segregation in (130) boundary of type 2

Figure 24. Sites for segregation of B in $\Sigma = 5$ (130) boundaries.: a) in Cu_3Au b) in Ni_3Al

Table 4. Interatomic distances in orthorhombic Ni-Boride Ni_3B_4

	Ni _I	Ni _{II}	Ni _{III}	Ni _{IV}	B _I	B _{II}	B _{III}
Ni _I	.30	.26 .29	.25 .26	.28 .30	.21 .21		.21 .25
Ni _{II}		.30	.25	.26 .29	.21 .21	.20 .21	.22
Ni _{III}			.30	.25 .26		.20	.20 .20
Ni _{IV}				.30	.20	.21 .21	.22
B _I					.18		
B _{II}						.17	
B _{III}							

Table 5. Interatomic distances in monoclinic Ni-Boride Ni_3B_4

	Ni _I	Ni _{II}	B _I	B _{II}
Ni _I	.25,.26	.25,.25,.26,.26 .28,.38,.31	.20,.21 .21,.21	.23 .24
Ni _{II}		.26,.25	.20,.20 .20	.21
B _I			.18	.18
B _{II}				

	Ni ₁	Ni ₂	Ni ₃	Ni ₄	Ni ₅	Ni ₆	Ni ₇	Al ₁	Al ₂
distance (nm)	.25	.27	.35	.23	.28	.23	.35	.24	.24

Table 6. Interatomic distances in $\Sigma = 5$ (130) boundaries

4.2 *Size Ratios and Interstitial segregation to Boundaries*

Calculations of size ratios were made in an attempt to predict the fracture behaviour of grain boundaries in intermetallic compounds, A_3B , having the $L1_2$ structure. The size ratio is the ratio between the B-B equilibrium interatomic distance and the nearest neighbour distance in the $L1_2$ compound. The B-B equilibrium interatomic distance was calculated from other phases in the binary system with a composition close to that of the $L1_2$ compound, for eg. A_2B or AB . The idea is to estimate the amount of B-B interatomic distance in excess of the nearest neighbour distance, that the $L1_2$ compound can tolerate and still remain ductile (i.e), have type 1 boundaries and B atoms in the nearest neighbour locations at the boundaries. Once the B-B equilibrium interatomic distance exceeds this limit, the boundaries should take on the type 2 structure and exhibit brittle intergranular fracture, since they can not have B-B atoms in nearest neighbour locations. Table 7 shows the results of these calculations. Unfortunately, there is no experimental information for a significant number of $L1_2$ compounds, to confirm the theoretical predictions. Here the excess interatomic distance that an $L1_2$ can take seems to be about 4% of it's nearest neighbour distance. These ratios however do not reflect the extent of brittleness in these compounds.

In the previous section it was shown that the interstitial sizes in type 2 boundaries are larger and favour B segregation in Ni_3Al . Ni_3Al has a size ratio of 1.13 which is > 1.04 and therefore has a type two boundary for reasons explained above. Type two boundaries have a larger interstitial site which favours the segregation of impurities. Segregation of impurities like B seems to strengthen the boundary. Also, since the density of atoms at the boundary increases with segregation, this could probably result in a reduction of the grain boundary energy. Thus $L1_2$ compounds with a size ratio > 1.04 , in general may have a type two boundary which will probably result in increased segregation of interstitial impurities to these boundaries; and this could result in the strengthening of these boundaries.

Table 7. Size ratios

Compound (A ₃ B)	Nearest neighbor distance in L1 ₂ compound A ₀ (nm)	Minimum B-B distance found in bulk phases (nm)	From phases	Size Ratio
Ni ₃ Al	0.252	0.286	Al, Al ₃ Ni ₂ , AlNi	1.135
Ni ₃ Cu	0.253	0.264	NiGa, Ni ₂ Ga, Ni ₂ Ga ₃	1.04347
Ni ₃ Si	0.248	0.2588	γ-NiSi, NiSi ₂ , Ni ₂ Si-LT	1.0435
Ni ₃ Ga	0.252	0.265	GeNi, GeNi _{1.7}	1.0516
Ni ₃ Fe	0.251	0.248	α-Fe	0.988
Ni ₃ Mn	0.254	0.257	β-MnNi δ-MnNi	1.012
Zr ₃ Al	0.309	0.270	Zr ₂ Al ZrAl Al ₂ Zr ₃	0.874
CaSn ₃	0.335	0.376	CaSn CaSn ₂	1.122
FePd ₃	0.272	0.273	FePd	1.003

Table 7 cont'd

Comparison With Experimental Results.

<u>L1₂ Compound</u>	<u>Prediction</u>	<u>Experimental Results*</u>
Ni ₃ Al	B	B
Ni ₃ Ga	B	B
Ni ₃ Si	B	B
Ni ₃ Ge	B	B
Xli ₃ Fe	D	D
Ni ₃ Mn	D	D
Zr ₃ Al	D	-
CaSn ₃	B	-
FePd ₃	D	-

*From Ref. 36.

4.3 *Experimental results*

About 55 misorientation angles were found between different grains, from a set of approximately 50 grains that were solved for their orientations. From these misorientation angles the value of Σ for the corresponding boundaries can be found out by comparison with tables given by Sutton and Vitek (6). A good number of the boundaries were low angle boundaries, with no listed value for Σ . Among the rest an almost random distribution of Σ was found. There were 6 boundaries of $\Sigma = 27$, which was the maximum for any one Σ value. No $\Sigma 3$ boundaries were found. The distribution of the Σ values is listed in table 8. These results are discussed in the next section.

Table 8. Distribution of the Grain boundary Σ values

Σ	<u>Number</u>
3	0
5	2
9	3
13	1
17	2
19	2
21	1
25	2
27	6
31	1
37	5
41	1
43	1
51	5
57	1
89	1
137	2

Total number of boundaries analyzed = 55

% of low angle boundaries = 25.45%

% of Σ 5-29 boundaries = 34.54%

% of random boundaries = 40%

5.0 DISCUSSION

5.1 *Geometrical Modelling*

The present analysis shows that simple geometrical models can be extended in a straight forward manner to include atoms of different sizes. Although this still implies all the limitations generally recognized in hard sphere models it is possible to obtain physical insight regarding grain boundary behavior using these models. Obviously the present structures are to be taken only as initial configurations for relaxation studies if a certain degree of confidence in the actual grain boundary structure is desired. Also, the presence of stresses may result in different grain boundary structures. The problem of carrying on relaxation studies is that it is very difficult to construct reliable pair potentials for intermetallic compounds. The present approach appears valuable as a first approximation. The results clearly show that the grain boundary structure in the compounds is not necessarily similar to that of the corresponding boundary in pure fcc metals. This basic conclusion will most probably be confirmed by relaxation studies. Furthermore, the differences are very im-

portant in the case of Ni_3Al . The disordering contribution to the grain boundary energy is apparently smaller for boundaries of type two than for the corresponding type one. This can be seen from a comparison of Tables 1a and 1b, and it means that in compounds with very high energy of ordering, boundaries of type two will be further stabilized, independently of size considerations. Note that Ni_3Al has indeed a high ordering energy; thereby suggesting that, boundaries of type two will be found in this compound. These boundaries are less dense than those of type one, found in pure metals and Cu_3Au . This is a result of the heterogeneous bonding and different atomic sizes present in this compound. It implies that the grain boundary weakness observed in Ni_3Al is an intrinsic characteristic and is not due to segregated elements.

The relatively low density of these boundaries also may explain why the segregation of elements of smaller atomic size and strong chemical affinity for Ni or Al will strengthen the boundary. Boron is an example of this. Geometrical models, suggest that the sizes of interstitial sites are much bigger in boundaries of type 2. In particular B can be segregated interstitially without any distortion to boundaries in Ni_3Al . The configuration of B sites in these boundaries is somewhat similar to those observed in Ni borides.

The method of hard spheres using different atomic sizes is adequate to analyze grain boundary structures in ordered compounds in a first approximation. The structural unit model can also be applied to ordered compounds if the different ordering configurations of a given structural unit are considered. The structures obtained for ordered compounds with similar atomic sizes (i.e. Cu_3Au .) are similar to those found for pure metals. For compounds with significantly different atomic sizes (i.e. Ni_3Al) the structures are in general different. The new structures are less dense than the corresponding ones for pure metals but they preserve order.

5.2 *Size Ratios*

Size ratios seem to give theoretical predictions on grain boundary behaviour in $L1_2$ compounds, that are consistent with other theoretical predictions based on valency difference (36). However they do not seem to predict the exact order of the compounds with regards to the level of brittleness of the boundary. These theoretical predictions need to be refined further, with the help of more experimental information on grain boundary behaviour in $L1_2$ compounds. Also, since the size ratios predict the grain boundary structure, qualitative assessments can be made regarding interstitial segregation of impurities like B and their effects, on the boundaries in these compounds.

Takasugi and Izumi (36) postulated a correlation between the valency difference between the two types of atoms in an $L1_2$ compound and the tendency for intergranular fracture. Compounds with a larger valency difference are more prone to intergranular fracture. Thus, based on this valency difference, it is possible to rank the $L1_2$ compounds for their grain boundary cohesive strength. Taub et al (37) tried to further differentiate these compounds for the cohesive strength of the boundaries, by considering size effects. They compared the lattice parameter of the (Ni_3X) $L1_2$ compound (where $X = Fe, Mn, Al, Ga, Si, Ge$) to the lattice parameter of Ni, and correlated the difference between the two lattice parameters to the fracture behaviour of the compound.

In this work the X-X equilibrium interatomic distances were compared with the nearest neighbour distances in the corresponding $L1_2$ compounds. Though the size ratios obtained here seem to predict the fracture behaviour of the compounds, consistent with the valency difference approach and size effects as considered by Taub et al, they do not indicate the correct relative rankings of these compounds based on cohesive strength of the boundaries.

5.3 *Experimental Results*

The experimental results seem to suggest a distribution of Σ that is close to a random distribution. However there seems to be a shift in the distribution of the Σ towards low angle boundaries and low Σ values compared to that of pure Ni_3Al . No definite conclusion can be made, unless statistics is obtained from a large number of boundaries. Hanada et al (24), arrived at the conclusion that the distribution of Σ is random in pure Ni_3Al after characterizing 200-300 boundaries in each of their four samples: a cast sample and three recrystallized samples with three different grain sizes. The results they published is shown in table 9.

An important aspect of the result from this work is the absence of the $\Sigma 3$ boundaries. $\Sigma 3$ boundary has the same structure in the case of a soft potential compound like Cu_3Au and a hard potential compound like Ni_3Al . The results of Hanada et al. also show a significantly low percentage of $\Sigma 3$ boundary in all their samples. Their samples showed intergranular fracture and the path of crack propagation appeared to avoid the $\Sigma 3$ and low angle boundaries. It was therefore considered that the low angle boundaries and $\Sigma 3$ boundaries have strong resistivity against intergranular fracture. Hence in a specimen of Ni_3Al with 23.5% Al, 0.2% B and 0.5% Hf, which is ductile, one would expect larger percentages of these boundaries. Though the number of low angle boundaries were considerable, about 19 out of 55 had angles $\leq 10^\circ$, there were no $\Sigma 3$ boundaries. With statistics over a larger number of boundaries, the result would have probably showed a very small percentage of $\Sigma 3$ boundaries, atmost.

The $\Sigma 3$ [111] boundaries are of type 1 for both Cu_3Au and Ni_3Al , which do not have interstitial sites of required sizes for B to segregate. Hence we would expect to find no B segregation at these boundaries. Segregation could reduce the energy of the grain boundaries due to increased density at the boundary as explained in the description of hard sphere models. Hence the energy of the $\Sigma 3$ boundaries should remain the same in both a pure Ni_3Al and a B doped Ni_3Al due to absence of segregation to the boundaries. However, B segregation to a random boundary could

Table 9. Results from other Investigators (S. Hanada et al- Ref. 24)

	Total No. of g.b.	Low angle	CSL g.b.		Random	Elongation	Fracture mode
			$\Sigma 3$	$\Sigma 5 \sim 29$			
Cast Ni ₃ Al	242	8.7%	0%	5.8%	85.5%	0%	Intergranular
Recrystallized Ni ₃ Al (grain size: 0.3 mm)	249	8.0	12.4	4.4	75.1	5	Intergranular + transgranular
Recrystallized Ni ₃ Al (grain size: 1 mm)	234	3.0	14.5	3.0	79.5	7	Intergranular + transgranular
Recrystallized Ni ₃ (Al, Ti) (grain size: 0.5 mm)	313	12.5	7.0	7.3	73.2	0	Intergranular
Recrystallized Al ^a	44 181	10 49	19 ~ 31		28 ~ 64		
Recrystallized Ni ^b	220	—	59		41		

reduce the energy of the boundary and hence an equilibrium state would consist of very few Σ 3 boundaries. These Σ 3 boundaries could very well be the [112] boundaries, which are of type 2.

Hafnium is known to increase the high temperature strength of Ni_3Al . It has very little effect on the ductility of Ni_3Al . It is not known whether Hf segregates to the grain boundaries. It is believed to induce some solid solution strengthening in this alloy. Hf may substitute for Al atoms in Ni_3Al (38). Not much information is available on Hf doped Ni_3Al except that B still is responsible for the increased ductility and is present for this reason in Hf doped alloys. Hence the distribution of grain boundaries for a ductile material, could probably be explained on the effects of B on the boundaries, although nothing is known on the effects of Hf on grain boundaries.

Table 8 shows the percentages of the low angle boundaries and the low Σ boundaries. These results suggest a distribution that is close to a random one, with a higher probability for a boundary to take on a low angle boundary configuration or a low Σ value between 5-29. Ofcourse, it has a very small probability to have $\Sigma = 3$ value. Hanada et al's results suggest a truly random distribution, with equal probability for all Σ values, except $\Sigma = 3$ and low angle boundary. If all Σ 's have equal probability of occurring, the group "random" should have a higher percentage since it covers a wider range of Σ . This could explain why their results show a higher percentage of random boundaries.

In comparing with Hanada et al's work the different annealing times and temperatures that were employed must be considered. They annealed a sample for about 2 hrs at 1300° . They also annealed another sample for a long period of time at the same temperature. However, there was no significant difference in the distribution of Σ values between the two samples except for some reduction in the percentage of low angle boundaries in the sample annealed for a longer period of time. Both samples did not show any texture. Hence a sample annealed for 2 hrs at 1300° after cold rolling, can be considered as a representative sample of recrystallized undoped Ni_3Al for studying the Σ distribution.

In comparing with this sample from Hanada et al's work, we observe an increased percentage of low angle boundaries in the doped Ni_3Al sample analyzed in this work. This difference could probably be because of the differences in annealing conditions, besides that of B effect on

the energies of the various boundaries. The sample used here does seem to have some texture since the patterns from many grains show [013] as a prominent pole on the picture and therefore the beam axes in these grains are close to this direction. Equilibrium conditions were probably not achieved completely in this annealing treatment. The effect of texture on the distribution of Σ is not known. In Hanada et al's work a as-cast sample showed columnar grains with preferred growth along directions around the $\langle 001 \rangle$. The Σ distribution in this sample differed from the recrystallized sample only in the % of $\Sigma 3$ boundaries which probably is because these boundaries do not result from rotations about $\langle 001 \rangle$. There is no other significant difference in the Σ distribution between this as-cast sample with texture and the recrystallized samples, analyzed by them. The percentage of low angle boundaries could probably be influenced by texture.

To study the effect of B on grain boundaries, in particular the distribution of Σ s, more conclusively, an undoped sample will have to be annealed in conditions similar to what was used in this work and then analyzed using the channeling patterns. An alternate approach would be to anneal a doped Ni_3Al in conditions employed by Hanada et al. This would eliminate all the other factors except for the microalloying additions, while comparing a doped and an undoped Ni_3Al for their Σ distribution.

6.0 Conclusions and Recommendations for future work

Our results indicate a random distribution of Σ value, for the grain boundaries in a doped Ni_3Al , with higher probability for Σ s to be ≤ 29 . Only a small percentage of $\Sigma 3$ boundaries is expected. The significant difference in the distribution of Σ , while comparing with the distribution for an undoped Ni_3Al , is an increase in the percentage of low angle boundaries and low Σ boundaries. This could probably be explained on the basis that B segregation may reduce the energy of a random boundary. $\Sigma 3$ [111] boundary would probably have the same energy, as we expect no segregation to these boundaries. The cause for the increase in the percentage of low angle boundaries is not known. The lower probability of high Σ boundaries is probably because of energy considerations. The possible explanations for a different distribution of Σ in a doped Ni_3Al sample, is summarized on page 77.

Future work should concentrate on indexing more boundaries to confirm the present results. Though the present results do not provide a direct explanation for the mechanism of strengthening at the grain boundaries, they seem to indicate a shift in the distribution of grain boundary structure towards low angle boundaries and boundaries of lower Σ values, in a B doped Ni_3Al sample compared to pure Ni_3Al . This aspect needs to be investigated further. For a more

Possible explanations

- Segregation of B increases density and therefore possibly reduces energy of grain boundary
- grain boundary energies could be altered - therefore an equilibrium distribution of grain boundaries may show different distribution compared to pure Ni₃Al
- $\Sigma = 3$ (111) is not expected to favour segregation and therefore remains unaltered in energy. Hence a lower percentage of these boundaries is expected
- Higher Σ correspond to higher energy and a lower % of these boundaries is expected

conclusive analysis an undoped Ni_3Al sample needs to be annealed in conditions employed here, or a doped Ni_3Al sample needs to be annealed in conditions employed by Hanada et al (24), and then analyzed for misorientation relationships between grains.

Convergent beam diffraction patterns from grain boundary regions can provide information on the translational states of the lattices at the boundary. Convergent beam diffraction patterns, have been used to determine the grain boundary structure in bicrystals. Determination of the bicrystal symmetry based on the concept of dichromatic patterns, can be done with the convergent beam diffraction patterns. By determining the bicrystal symmetry the translational state at the boundary can be determined (39). Convergent beam diffraction could provide more insight into the actual structure of the boundaries occurring in Ni_3Al . Relaxation studies have shown that a relative translation between the grains frequently exists at the $[001]$ and $[011]$ tilt boundaries (6).

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Appendix A. Illustrations of Channeling Pattern and $L1_2$ Structure

Picture next page shows a pattern obtained from an individual grain in the polycrystalline sample analyzed. The prominent pole is the $[111]$ pole. The plot obtained from the program KPLOT shows the Kikuchi pattern for a beam axis along the $[111]$ direction. All the lines are indexed and the poles marked with the corresponding indices. The plot is for an f.c.c crystal with a lattice parameter of $3.567 \text{ \AA}$. The illustration on page 85 shows a unit cell of Ni_3Al having the $L1_2$ structure, and the projection of the atoms in the cell onto a $[100]$ and a $[110]$ plane respectively.

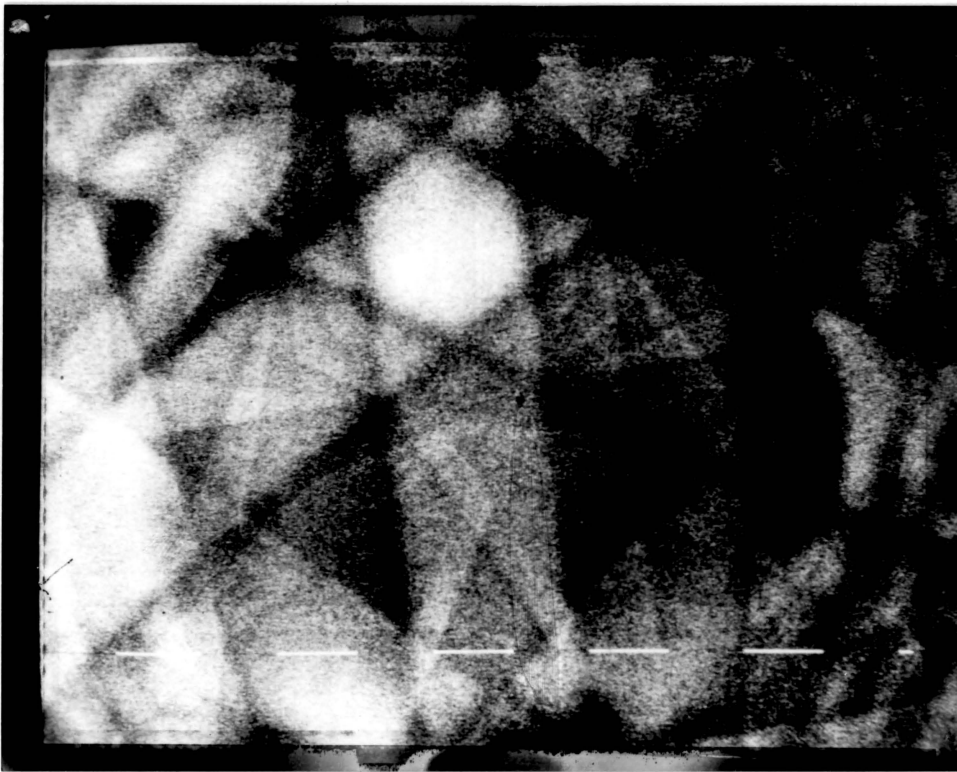


Figure 25. Channeling patterns showing [111] pole

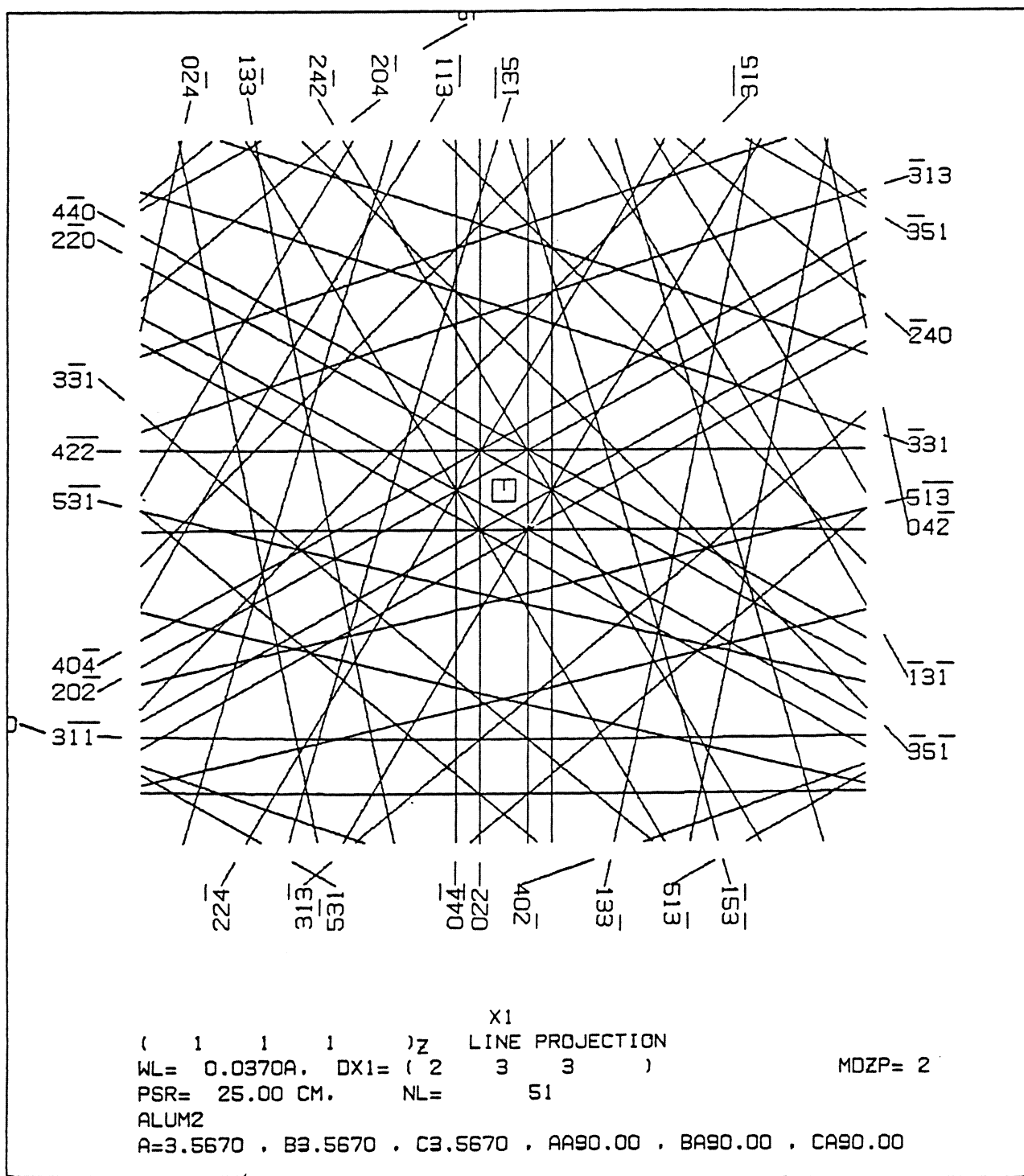


Figure 26. [111] Kikuchi pattern plot from program KPLOTT: beam axis is [111]

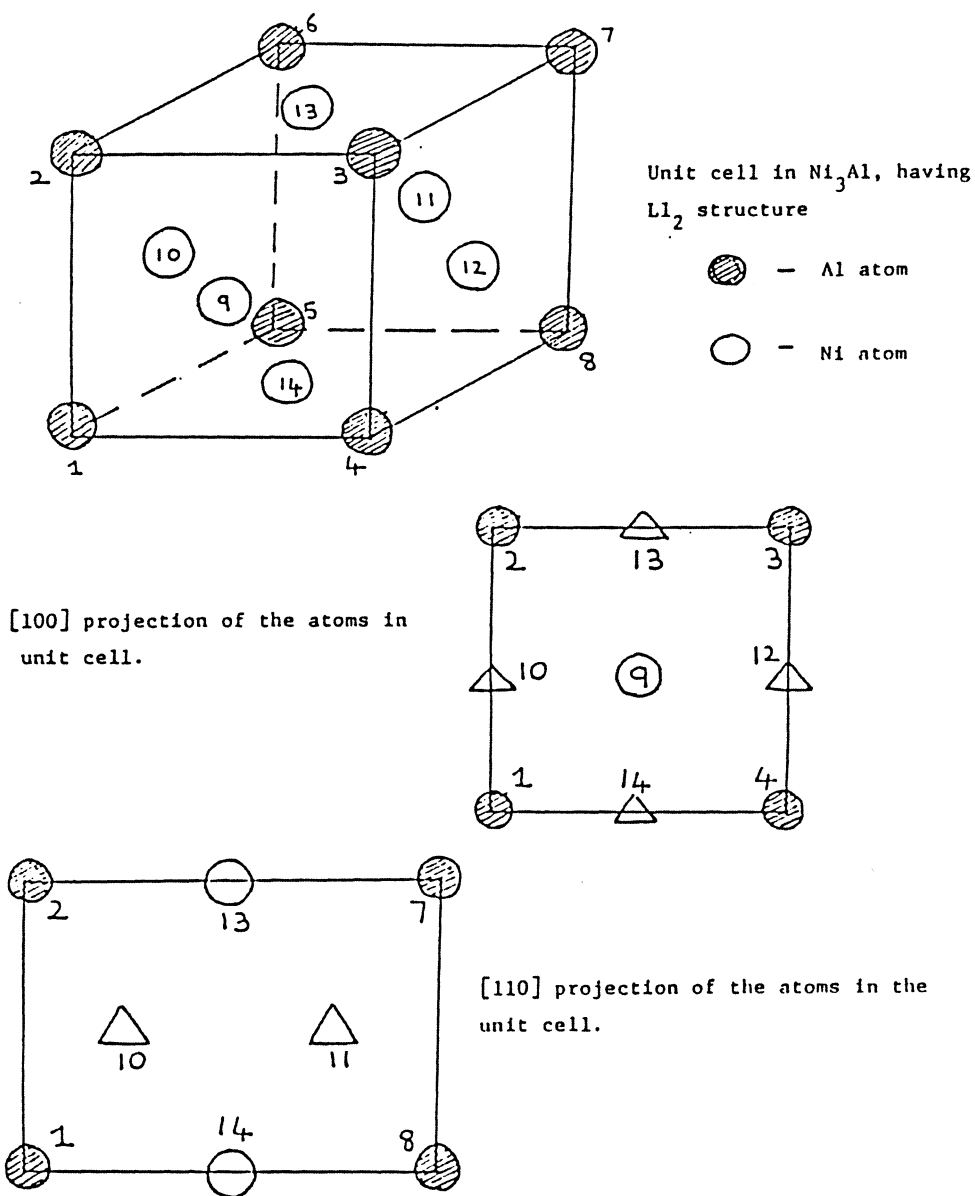


Figure 27. Unit cell in L1_2 structure: also shown are projection of atoms onto a [100] and [110] plane respectively.

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