ISOTROPIC AND ANISOTROPIC DEBYE-WALLER FACTORS IN OFF-STOICHIOMETRIC γ-TIAL

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By
Jayanthi Sampathkumar

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Master’s Examination Committee:
Dr. Hamish L. Fraser, Advisor
Dr. Robert L. Snyder
Dr. M.J. Mills

Approved by,

Advisor
Department of Materials Science and Engineering
ABSTRACT

The lack of ductility exhibited by the intermetallic phase $\gamma$-TiAl, has been related to the directional nature of the interatomic bonding, as predicted by several calculations of electron charge density distribution in this compound. It is important to verify these predictions with experimental determination of the charge density distribution in TiAl. The experimental determination of electron charge density requires an accurate measurement of a number of structure factors. The energy-filtered convergent beam electron diffraction (CBED) method has been established as an accurate method for the accurate measurement of structure factors. However, the accuracy of this method is limited by the lack of knowledge of accurate values of the appropriate Debye-Waller factors. In the work presented in this thesis accurate and precise Debye-Waller factors have been measured in off-stoichiometric $\gamma$-TiAl from single crystal x-ray diffraction experiments. These Debye-Waller factors have further been used to determine the 200 structure factor in TiAl with the CBED method.

A procedure for the preparation of un-deformed TiAl single crystals for the four-circle x-ray diffraction experiments has been developed in this work. Weak, diffuse intensities were observed in the x-ray diffraction experiment, which correspond to the kinematically forbidden reflections (hkl) in TiAl with indices $h+k=2n+1$. Calculated static structure factors were fitted with the experimental structure factors which were corrected for polarization, absorption and extinction using a non-linear least square refinement to obtain the Debye-Waller factors. Isotropic and anisotropic, site specific Debye-Waller
factors were extracted from Ti-54Al and Ti-56Al single crystal data. Accurate lattice parameters were also determined from the x-ray diffraction experiments.

The anisotropic Debye-Waller factor calculations result in a better fit between the calculated and experimental structure factors. These calculated structure factors also explain the scatter in the experimental structure factors for higher order reflections, which has previously been attributed to experimental error. The ordering of excess Al atoms on one of the Ti sites, with the anisotropic Debye-Waller factors, explains the diffuse intensities obtained for the forbidden reflections with h+k=2n+1. Compositional uncertainty did not affect the Debye-Waller factors of the Al sites, whereas it affected the Ti site which accommodated the excess Al atoms.

The 200 structure factor in TiAl was determined from the CBED method by using the accurate anisotropic Debye-Waller factors extrapolated to the appropriate composition. The effects of compositional accuracy and changes in sample thickness on the 200 structure factor were also studied. The most accurate measurement of structure factors is obtained for a composition of Ti-52.3 at.% Al. The present results for changes in structure factors with thickness of the sample are contrary in tendency to those previously reported.

Diffuse intensities corresponding to a Ti$_3$Al$_5$ type ordering were observed in the electron diffraction experiments. These intensities exhibited characteristics commonly ascribed to short-range order, in this case, associated with small clusters of Ti$_3$Al$_5$ embedded in the γ-TiAl matrix. However, sufficient intensities corresponding to this ordering were not observed in the x-ray diffraction experiments, which could be attributed to the overall small volume fraction of this secondary phase. Hence, the Ti$_3$Al$_5$ ordering was not used to model the Debye-Waller factors here. However, it is important to understand the effect of such ordering on the determination of structure factors in TiAl in the future.
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VITA

June 6, 1973 ......................... Born - Madras, India

1994 ........................................ B.Tech in Metallurgical Engineering, IT-BHU,
Varanasi, India

1995-present ........................ Graduate Research Associate, The Ohio State
University

FIELDS OF STUDY

Major Field: Materials Science and Engineering
TABLE OF CONTENTS

ABSTRACT .................................................................................................................. ii

ACKNOWLEDGEMENTS ......................................................................................... iv

VITA ........................................................................................................................... v

TABLE OF CONTENTS .......................................................................................... vi

LIST OF TABLES ...................................................................................................... viii

LIST OF FIGURES ................................................................................................... ix

Chapters:

1. INTRODUCTION AND BACKGROUND ............................................................ 1
   1.1: Importance of Electronic Structure ............................................................ 1
   1.2: Off-stoichiometric compositions and sublattice ordering ....................... 5
   1.3: Structure factor determination ................................................................ 7

2. THEORY AND APPROACH .............................................................................. 13
   2.1: Debye-Waller factor ................................................................................. 13
   2.2: Measurement of Debye-Waller factor ....................................................... 18
       2.2.1: Four-circle X-ray diffraction .............................................................. 19
       2.2.2: Absorption correction ...................................................................... 25
2.2.3: Specimen preparation .................................................................28
2.2.4: Extinction correction and Least square refinement ......................34
2.3: Convergent Beam Electron Diffraction ........................................36
  2.3.1: Accurate structure factors from CBED method .......................38
  2.3.2: X-ray and Electron structure factors ......................................41
3. RESULTS AND DISCUSSION ..........................................................42
  3.1: Four-circle x-ray diffraction .....................................................42
    3.1.1: Debye-Waller factors from ‘Wilson plot’ method ..................48
    3.1.2: Ordering schemes for least square refinement ......................53
    3.1.3: Lattice parameters ............................................................56
    3.1.4: Isotropic site specific Debye-Waller factors .......................59
    3.1.5: Anisotropic site specific Debye-Waller factors ....................69
  3.2: Ti$_3$Al$_5$ ordering ............................................................76
  3.3: CBED structure factor refinement ..........................................81
3. SUMMARY AND CONCLUSIONS .....................................................89
REFERENCES ..................................................................................91
LIST OF TABLES

Table 1: Lattice parameters obtained from single crystal x-ray diffraction experiment with other lattice parameters from literature.........................58

Table 2: Comparison of the lattice parameters determined in the current work with other lattice parameters from literature............................................58

Table 3: Isotropic site specific room temperature DWF for Ti-54Al single crystal modeled using Model I and Model II. (DWF - Debye-Waller factor, PP - composition refinement, EXT - isotropic extinction correction and refinement, Compositions are given as atomic percentage of Al)..................62

Table 4: Isotropic site specific room temperature DWF for Ti-56Al single crystal modeled using Model I and Model II. (DWF - Debye-Waller factor, PP - composition refinement, EXT - isotropic extinction correction and refinement, Compositions are given as atomic percentage of Al)...............63

Table 5: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with no composition refinement).............86

Table 6: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with overall composition refinement)......87
LIST OF FIGURES

Figure 1: TiAl L1₀ unit cell with alternating Ti and Al layers along the [001] direction................................................................. 2

Figure 2: Schematic representation of isotropic (left) and anisotropic (right) Debye-Waller parameters with respect to the TiAl L1₀ unit cell. The isotropic temperature factor is represented by a single quantity $\langle u^2 \rangle$. The anisotropic root mean square displacements $\langle u_1^2 \rangle = \langle u_2^2 \rangle$ due to the symmetry in TiAl. $\langle u_1^2 \rangle$ and $\langle u_3^2 \rangle$ are sufficient to express the anisotropic site specific Debye-Waller factor................................................................. 17

Figure 3: Schematic representation of the four circle x-ray diffractometer. The $\phi$ axis is mounted in the $\chi$ circle. The $2\theta$ and $\omega$ axes coincide with the $\phi$ axis when $\chi=0$. ......................................................................................... 21

Figure 4: Schematic representation of the four-circle axis and the cartesian axis $X$, $Y$, $Z$ with respect to which, the crystal reciprocal axes orientation is calculated.......................................................................................... 21

Figure 5: Schematic diagram showing the goniometer head of the four-circle x-ray diffractometer with the mounted sample (not to scale). ................................................. 23

Figure 6: Reflection peak profile from a mosaic crystal ........................................ 30

Figure 7: Reflection peak profile form a crystal which is closer to a perfect crystal... 30

Figure 8: Sample preparation steps involved in preparation of single crystal specimens for x-ray diffraction................................................................. 33
Figure 9: Peak profile corresponding to the (100) reflection (structure factor = 0 as h+k=2n+1) obtained from the Ti-56 Al single crystal.

Figure 10: Plot of Intensity vs. $\sigma(I)$ for kinematically forbidden reflections in Ti-54Al (top) and Ti-56Al (bottom). The line indicates points where $I = \sigma(I)$.

Figure 11: Plot of Integrated intensity vs. error in the integrated intensity collected for the superstructure reflections from the Ti-54Al crystal.

Figure 12: Wilson plot plotted using the diffraction data from the Ti-54Al crystal. The slope of the line gives the Debye-Waller factor which is represented as the B factor.

Figure 13: Wilson plot plotted using the diffraction data from the Ti-56Al crystal. The slope of the line gives the Debye-Waller factor.

Figure 14: TiAl fundamental unit cell. Shaded circles indicate Ti sites which are partially occupied by Al atom in Al-rich off-stoichiometric alloys. Open circles indicate Al sites.

Figure 15: Conventional TiAl L1₀ unit cell. Partly shaded circles indicate Ti sites which are partially occupied by Al atoms (Ti³) in Al-rich off-stoichiometric alloys. Open circles indicate Al sites. Filled circles indicate the pure Ti sites (Ti¹).

Figure 16: Flow chart showing the steps in refining accurate site specific isotropic or anisotropic Debye-Waller factors.

Figure 17: Experimental structure factors and calculated factors fitted using isotropic site specific Debye-Waller factors with random distribution of excess Al atoms in all Ti sites for Ti-54 and Ti-56Al.
Figure 18: A comparison of experimental structure factors and calculated structure factors for forbidden reflection in Ti-54Al and Ti-56Al. The calculated structure factors were fitted using isotropic DWF and Model II. ........................67

Figure 19: Isotropic temperature factors estimated in Ti-54 and 56Al using Model I (fundamental unit cell, top) and Model II (L10 unit cell, bottom). ...............68

Figure 20: Experimental structure factors with fitted calculated structure factors for the fundamental and superlattice reflections, calculated using Model I and anisotropic Debye-Waller factors. ....................................................70

Figure 21: Expanded view of experimental structure factors and calculated structure factors fitting the isotropic (top) and anisotropic (bottom) Debye-Waller factors in Ti-56Al. .................................................................71

Figure 22: Experimental and calculated structure factors for forbidden reflections in Ti-54Al and Ti-56Al computed using Model II and fitted with anisotropic temperature factors.........................................................72

Figure 23: Anisotropic temperature factors obtained by least-square refinement of x-ray data from Ti-54 and 56Al. The temperature factors in Ti-54Al are lower than in Ti-56Al.................................................................75

Figure 24: (001) plane of the Ti3Al5 unit cell. a = 2√2a0 and c = c0 where γ is represented by the conventional L10 unit cell........................................78

Figure 25: Selected area diffraction patterns for the [111]-zone of γ-TiAl alloys with Al-rich compositions of Ti-54Al (a) and Ti-56Al (b) and a simulated selected area diffraction pattern (c) including the weaker reflections arising from Ti3Al5 ordering.........................................................79

Figure 26: Diffraction contrast images of Ti-56 at.% Al alloy, a) many beam bright field and b) dark field using (232) reflection, for the beam direction [111]...80
Figure 27: Anisotropic temperature factors obtained by non-linear least square refinement using Model II to fit structure factor data with *no composition refinement* from single crystal x-ray diffraction. The temperature factors are extrapolated to the composition of 50.3, 51.3 and 52.3 to obtain the anisotropic temperature factors at these composition which are used the CBED method to determine the 200 structure factor in TiAl..................83

Figure 28: Anisotropic temperature factors obtained by non-linear least square refinement using Model II to fit structure factor data *with-composition refinement* from single crystal x-ray diffraction. The temperature factors are extrapolated to the composition of 50.3, 51.3 and 52.3 to obtain the anisotropic temperature factors at these composition which are used the CBED method to determine the 200 structure factor in TiAl..................84

Figure 29: Linear extrapolation of the a and c lattice constants obtained from x-ray diffraction experiments on Ti-54 and 56Al. The extrapolated parameters were used in the CBED method to determine accurate structure factors in Ti-Al.................................................................85

Figure 30: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with *no composition refinement*).............86

Figure 31: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined *with overall composition refinement*)........87

Figure 32: Comparison of 200 structure factor in TiAl obtained from the CBED rocking curve method using anisotropic temperature factors obtained in

xii
the current work with structure factors obtained using isotropic
temperature factors from Swaminathan, et al. (1996). .....................88
CHAPTER 1

INTRODUCTION AND BACKGROUND

γ-Titanium aluminide has received considerable attention in recent years due to its potential application in aircraft turbine engines. This ordered compound has a high strength to weight ratio. Because of its ordered structure it retains very high static strength, stiffness and oxidation resistance at high temperatures. However, it has a low strength at room temperature, and shows limited ductility at temperatures below 600°C. It also shows a positive temperature dependence of yield strength. There have been several studies to understand the mechanical properties of TiAl and its brittle nature at room temperature [Schetchman, Blackburn and Lipsitt (1974); Lipsitt, Schetchman and Schafrik (1975); Court, Vasudevan and Fraser (1990)]. These studies have attributed the low strength of TiAl to the reduced mobility of various dislocations below 600 °C, which control the deformation of TiAl.

1.1: Importance of Electronic Structure

Many researchers have worked on the possible causes for the lack of ductility in TiAl at ambient temperature. The relation between the electronic structure of TiAl and its brittleness are important in the present work. TiAl has a tetragonal structure with alternating layers of Ti and Al atoms long the [001] direction. Figure 1 shows the L1₀ unit cell of TiAl. This section summarizes the various predictions which relate the electronic structure of TiAl to its lack of ductility.
The first suggestions which related the electronic structure of TiAl to its brittleness came from Anisimov, Ganin, Galakhov and Kurnayev (1987) and Greenberg, Anisimov and Gornostirev (1988). They calculated the charge density distribution within a Ti atom in TiAl using the method of linear combinations of muffin-tin orbitals (LMTO). Based on these calculations, they predicted that because of the formation of directional d-d bonds between neighboring Ti atoms, the Ti sublattice forms a rigid network within the TiAl structure. This decreases the mobility of dislocations on certain crystallographic planes due to a higher Peierls stress involved in dislocation movement through planes consisting of unlike atoms (as in covalent crystals). They also suggested that the transformation of glissile super-dislocations to ‘roof’ type barriers is a possible cause for the lack of low temperature ductility.

Morinaga, Saito, Yukawa and Adachi (1990) have studied the electronic effect on ductility using discrete variational cluster calculations. Based on the observed decrease in ductility with increasing Al fraction for off-stoichiometric alloys of Al rich compositions, e.g., Ti-52Al, they suggested that the ductility is related partly to the nature of chemical bonds. Furthermore, they proposed that the p-d interactions are enhanced with increasing Al fraction. The p-d covalent bonds with lower coordination numbers are highly directional.
and hence increase the shear strength with a large barrier to deformation. They also suggested that the enhancement of d-d interaction could enhance ductility.

Fu and Yoo (1990) have calculated the electronic structure in TiAl using total-energy calculations based on local-density-functional theory. They calculated the elastic constants and planar fault energies from first principles. They suggested the existence of directional d-d type bonds in the Ti layer and a strong cohesion between the Ti and Al layers due to directional d-p type bonding. They also showed an increase in shear modulus $C_{44}$ which reflects the difficulty of shear deformation between pure Ti and Al layers. The two above works are consistent, but are contrary to the study by Greenberg, et al. (1988) mentioned earlier who suggested that the d-d directional bonds are the reason for lack of ductility in TiAl.

Woodward, MacLaren and Rao (1992) have calculated the electronic structure of planar faults in TiAl using the Layered Korringa Kohn Rostoker (LKKR) method. The fault region is embedded between two semi-infinite perfect crystals and the scattering matrices for the semi-infinite solid are solved iteratively. The scattering matrices are then used as boundary conditions for the defect plane and the relaxation region and hence, the electronic structure is solved. They have suggested the formation of directional bonds between first nearest neighbor Ti atoms on the Ti planes and p-d type bonds between second nearest neighbor Ti atoms and Al atoms on adjacent Ti-Al planes. They have also suggested that the cohesion of (001) Ti and Al planes through $d^4p^2$ hybrid bonds would produce a narrow dislocation core for dislocations with $\langle 110 \rangle$ line directions and hence, the anisotropy around the core results in poor ductility. Their results are consistent with the formation of deep Peierls valleys for $\langle 110 \rangle$ dislocations as suggested by Greeaberg, et al. (1988) although, the method of calculation is very different.
A study by Eberhart, Clougherty and MacLaren (1993) relates the intrinsic mechanical properties to the electronic charge distribution in intermetallics. Their study, which uses the LKKR method, is based on identifying critical points in the calculated charge density field which are defined as zeros of the gradient of the scalar field. They have shown that in TiAl, the critical points corresponding to the bond between the Ti and Al atoms on the (100) planes does not occur on the inter-nuclear axis and hence, produces a bent bond. They have also suggested that the Al p and Ti s, d electrons are in first neighbor bonding in the regions between the Ti and Al atoms. These first neighbor bonds repel the Al s character and through electron correlation, the unhybridized s character is excluded from this region of first neighbor bonding to the octahedral holes and through Al-Al bonding interactions, the total energy of the alloy is lowered.

In a recent study of the Ti-Ti bonding in γ-TiAl [Song, Tang, Xu, Mryasov and Freeman (1994)] it was shown that the d-d bonding within the Ti (001) planes in TiAl had a much stronger in-plane directionality compared with f.c.c. titanium. Analysis of bonding and energy bands shows that the presence of alternating Al (002) layers in γ-TiAl is the main factor responsible for the d-d in-plane directional bonding in the Ti (001) layers of γ-TiAl. They have proposed that the in-plane directional bonding is linked to the anisotropies in Peierls stress and may influence the ductility of TiAl though the pinning of (110) dislocations along certain line directions. Their results are consistent with earlier studies by Greenberg, et al. (1988). Another first principle study of L10 TiAl by Chubb, Papaconstantopoulos and Klein(1988) using full linearized-augmented plane wave calculations suggested the importance of rigid band-like behavior involving Ti electrons in affecting the ductility of the alloy. This rigid behavior has been previously suggested by other researchers and in particular by Greenberg, et al.(1988).
In the most recent study on directional bonding in intermetallic TiAl, Siegl, Vitke, Inui, Kishida and Yamaguchi (1997) have investigated an ordered twin boundary in L1₀ TiAl by computer-modeling and High Resolution Electron Microscopy (HREM). They have demonstrated the significance of directional covalent-type bonding for the interfacial structure using the full-potential muffin-tin orbital method. In bulk TiAl, they have shown a charge density build up between Ti atoms which can be associated with the formation of covalent directional bond between Ti atoms by d-d electron interactions. Their (\text{\overline{1}1\text{\overline{0}}}) plane structure does not show a localized charge build up between adjacent Ti and Al atoms, while it shows a concentration of charge between adjacent Al atoms corresponding to p electrons, which is more dispersed than the d electrons between Ti atoms. They have suggested that the formation of covalent bonds between Ti and Al atoms at the boundary, when no such bonds exist in the bulk, affects the interfacial structure. Their observations about the bonding in γ-TiAl are similar to those calculated by Fu and Yoo (1990), Woodward, et al. (1991) and Song, et al. (1994).

The results summarized above suggest a relationship between the electronic structure of TiAl and its brittleness. However, these qualitative predictions do not agree on a definite reason for the brittleness in TiAl, and the predictions are based on various theoretical models. Hence, it is important to have definitive quantitative understanding of the effect of electronic structure on lack of ductility in TiAl, which can only be achieved by the experimental determination of the charge density of TiAl.

1.2: Off-stoichiometric compositions and sublattice ordering

TiAl does not exist as a single phase at room temperature for the stoichiometric composition [Ogden, Maykuth, Finlay and Jaffee(1951)] and single phase TiAl alloys cannot be obtained at compositions below 52-at.\% Al. Hence, most of the single phase γ-
TiAl alloys studied are Al rich and therefore, it is important to understand the effect of the excess Al atoms on the ductility of TiAl. Greenberg, et al. (1992) have observed a decrease in ductility with increasing Al fraction. Other studies have shown that the Peierls force relief is sensitive to deviation from the equiatomic composition [Hall and Huang (1989), Greenberg, et al. (1992)]. Elliot and Rostoker(1954) have reported that the presence of excess Al in TiAl forms anti-site defects as opposed to constitutional vacancies. The study by Vujiv, Li and Whang(1988) on rapidly solidified and homogenized alloys also presented similar observations. This complicates the understanding of the Peierls force relief with increasing percentages of Al, as the nature and preference of these anti-site defects to any particular lattice site (Ti site) has to be characterized in detail.

In addition to the complexity outlined above in understanding the effect on the Peierls force relief, in some γ-TiAl alloys with off-stoichiometric compositions, superstructure ordering of the Ti₃Al₅ type has been observed [Miida, Hashimoto and Watanabe (1982), Loiseau and Lasalmonie (1983), Miida and Watanabe (1984), Loiseau and Lasalmonie(1985)]. This superstructure has been observed in the form of small ordered clusters of sizes 50 to 100 nm, embedded in the TiAl matrix (L1₀ structure). The structure of the Ti₃Al₅ phase is based on the L1₀ structure with an additional ordered Ti layer. Overall, this structure has a tetragonal symmetry and can be defined by the space group P4/mmb. The lattice constants of this Ti₃Al₅ superstructure are aₛ =2√2a and cₛ =c, where a and c are the lattice constants of the L1₀ unit cell. This superstructure has been observed in alloys of composition Ti-54 at.% Al or higher Al fractions. In a recent study, Nakano, Matsumoto, Seno, Oma and Umakoshi (1996) have stated that the short-range and long-range orders associated with the Ti₃Al₅ type structure that formed during annealing at 500 °C affected the yield stress, fracture strain and work hardening rate through the change in the deformation mode. The increase in Al concentration suppressed
activation of ordinary dislocations with Burgers vectors $\mathbf{b}=(a/2)[\pm 110]$ as their motion generates antiphase boundaries in the Ti$_3$Al$_x$ clusters.

Hence, it is clear from these observations reported in the literature, that a more quantitative understanding and experimental verification of the charge density distribution in TiAl must be developed. Such efforts must take into account the effect of the superstructural ordering, and determine a definitive scheme for the ordering of the excess Al atoms in off-stoichiometric TiAl compounds.

**1.3: Structure factor determination**

It is necessary to experimentally establish accurate and precise values of low angle structure factors in order to determine the bonding charge density in TiAl. The relationship between structure factor ($F$) and dynamic electron charge density ($\rho_d$) is given by,

$$\rho_d(r) = \sum_g F_g \exp(2\pi ig \cdot r)$$  \hspace{1cm} (1.1)

Here $g$ refers to a reciprocal lattice vector and $r$ is the unit vector corresponding to various atoms positions in the unit cell. In order to determine the electron charge density distribution using the above equation, an infinite number of structure factors have to be determined. However, depending on the experimental technique, only a limited number of structure factors can be measured with sufficient accuracy, which is equivalent to truncating the infinite series in equation (1.1). The fundamental property of a Fourier relation is to transform a diffuse function into a compact form and vice versa. Since $F$ can be expressed as a Fourier transform of $\rho_d(r)$, information related to the compact core electrons in real space are represented by high-angle structure factors in reciprocal space. Similarly, information relevant to the outer shell electrons, which are often associated with the formation of interatomic bonds, is contained mainly in the low angle structure factors. Hence, it is necessary and may be adequate to use the low-angle structure factors in order
to determine at least the nature of the bonding electron density. The errors due to uncertainties related to thermal vibration would be higher for high angle structure factors than for low angle structure factors. This section discusses the experimental methods that have been attempted to determine the low angle structure factors in TiAl.

The low order structure factors in TiAl have been previously determined by a number of researchers [Fox (1993), Swaminathan, Jones, Zalupec, Maher and Fraser (1993), Holmstead, Zou, Spence, Höier and Horita (1995)]. Fox (1993) has determined the low order structure factors using the critical voltage method while Holmstead, et al. (1993) and Swaminathan, et al. (1993) have used energy filtered convergent beam electron diffraction (CBED). It has been identified by Swaminathan, Jones, Maher and Fraser (1996) that it is necessary to include relevant off-systematic and higher order laue zone (HOLZ) reflections for the convergence of Bloch wave calculations. Also, they have shown that it is important to use accurate lattice parameter values and accurate Debye-Waller factors in the energy filtered CBED calculations. Holmstead, et al. (1995) have stated that since the HOLZ reflections have not been used in their refinements, having accurate Debye-Waller factors would not vary the nature of their results. However, they have determined the lattice parameters from the position of HOLZ lines which have not been corrected with accurate Debye-Waller factor measurements. This leads to the importance of determining accurate and precise Debye-Waller factors in establishing accurate and precise values of structure factors.

As part of the current project, a definitive procedure for the determination of accurate structure factors in Ti-Al using the CBED method has been established [Swaminathan, Altynov, Jones, Zalupec, Maher and Fraser (1997b)]. An electron diffraction technique was chosen over the other alternatives in x-ray diffraction like x-ray Pendellösung method and the four-circle x-ray diffraction method, due to the ease of
working with polycrystalline samples rather than having to obtain single crystals necessary for x-ray diffraction. The x-ray Pendellösung method is the most accurate method for measurement of structure factors and can yield structure factors with very small margins of errors (less than $\pm 0.1\%$) [Aldred and Hart (1973); Saka and Kato (1986); Hart and Deutsch (1990)]. This method is based on the principle that in perfect crystals, Bragg reflection results in two different wave vectors which interfere constructively and destructively to produce Pendellösung fringes. The measurement of the fringe spacing is used to determine the structure amplitudes with high accuracy. This method is simple and easy to use. However, it requires a wedge shaped single crystal specimen. Since TiAl cannot be obtained as a single phase at a composition of 50 at.$\%$ Al, a wedge shaped single crystal sample of TiAl is positively difficult to obtain. The other alternative in x-ray diffraction is the four-circle x-ray diffraction method, which yields accuracies of $\pm 0.5\%$ in the structure factor measurements [Larsen and Hansen (1984)] compared to the $\pm 0.1\%$ accuracy given by the electron diffraction methods. This method requires relatively small single crystal samples (cuboidal or spherical with $\sim 100\mu m$ maximum edge or diameter) and has been used in the current work to determined accurate Debye-Waller factors. A detailed description of the theory involved in the measurement of Debye-Waller factors and a description of the preparation of the single crystal TiAl samples is given in chapter 2. Some of the electron diffraction methods which have been used previously in determining structure factors are the critical voltage method, intersecting kikuchi line (IKL) method and the CBED method. In the current work the CBED method has been chosen for determination of accurate structure factors over the critical voltage or the IKL method for the various reasons.

The critical voltage method involves the observation of a minimum of intensity in a second-order reflection at the Bragg condition for a particular accelerating voltage [Spence
(1993)]. This voltage depends sensitively on the ratio of the first to second order structure factors and may be used to measure this ratio with high precision from measurements of the critical accelerating voltage. If the second-order reflection is assumed to depend mainly on the known atomic coordinates, the first-order reflection can be found from it and hence the bonding effects may be extracted. The accuracy is, however, limited by the knowledge of the Debye-Waller factor for the higher order reflections and the contrast of the intensity minimum. The method is generally regarded as the most accurate electron diffraction method for structure factor measurement [Spence (1993)]. The ratio of the magnitude of the first-order structure factor U₁ to that of the second order U₂ is measured and this requires a large range (typically from 100 kV to 1 MeV) of accelerating voltages. Fox (1993) has used this method to determine structure factors in TiAl and has stated that the higher order structure factors could not be measured as the critical voltage exceeded the maximum accelerating voltage of the microscope. The higher order reflections cannot be obtained with high precision due to the excessive radiation damage that occurs at voltages of 1 MeV. Due to these experimental problems and since the critical voltages required would be very high for higher order reflections (critical voltage increases with decreasing d-spacing), the critical voltage method was not chosen here although it would yield very accurate low order structure factors.

The intersecting Kikuchi method involves measuring the width of the gap which appears when Kikuchi lines cross. The result is compared with computer calculations/simulations using the three-beam dynamical theory. Though this method is relatively simple, it is less accurate (±2% at 100 kV) compared to other electron diffraction methods [Terasaki, Watanabe and Gjonnes (1979)] and requires a specific orientation for every reflection.
With the CBED method, one does not have to face the problems of radiation damage and it can be used for accurate structure factor measurements. With the current electron counting devices, such as the CCD (Charge Coupled Devices) camera, with a large dynamic range accurate measurements of weak intensities can be made. The energy filtered CBED method is discussed in greater detail in chapter 2.

At this point, considering all the different types of electron diffraction methods used previously to determine low-order structure factors and the electron charge density in TiAl, it can be noted that knowledge of accurate and precise Debye-Waller factors is crucial to achieving sufficient accuracy in the measured structure factors. The important role played by Debye-Waller factors in dynamical electron diffraction calculations is two-fold. Firstly, the thermal vibration of the crystal lattice smears out the otherwise perfectly periodic crystal potential. The real crystal potential is therefore no longer perfectly periodic. However, in most situations an average potential is defined which is periodic and gives rise to discrete scattered beams, which satisfy the Bragg law as in the case of a perfect crystal. In real space the smearing effect can be described with the harmonic approximation of lattice vibrations and the effect can be described as a convolution of the perfect-crystal potential with a Gaussian function describing the statistical distribution of the lattice displacements. Hence, in reciprocal space the effect is described by the multiplication of the perfect-crystal structure factor with the Debye-Waller factor. A detailed description of the theory behind the Debye-Waller factor is given in chapter 2.

There have been various attempts to determine the Debye-Waller factors in TiAl experimentally. However, it should be noted that most accurate results can only be obtained using x-ray or neutron diffraction and by correcting for absorption and extinction effects. Swaminathan, et al. (1997a) have used the CBED method to determine the 200 structure factor in TiAl. They have established that for accurate determination of structure factors, it
is necessary to know the values of accurate, site specific Debye-Waller factors and accurate sample compositions. However, the Debye-Waller factors they have used and which were previously reported by Swaminathan, et al.(1996), are limited in accuracy by the mosaic spread in the x-ray peaks caused by deformation of the single crystals in the process of sample preparation.

In the current work, accurate x-ray diffraction data have been obtained from nearly perfect single crystals in order to determine the x-ray structure factors and Debye-Waller factors in TiAl. Chapter 2 gives a detailed description of the concepts involved in obtaining diffraction data from a mosaic crystal and the necessary steps to prepare near perfect crystals which yield sharp diffraction peaks. It also discusses the steps involved in correcting integrated intensity data for absorption and extinction. The significance of the present work lies in the fact that accurate and precise anisotropic temperature factors for TiAl have never been reported before and it establishes the anisotropy in off-stoichiometric TiAl alloys. The anisotropic temperature factor results are given in chapter 3. Chapter 3 also discusses the effect of these anisotropic Debye-Waller factors in determining accurate structure factors in TiAl using the CBED method.

*In the work presented in this thesis, accurate and precise anisotropic Debye-Waller factors have been determined using the four-circle single crystal x-ray diffraction method. The effect of these temperature factors on the structure factors determined from the energy filtered CBED method [Swaminathan, et al. (1996)] also has been determined. The results clearly establish that the temperature factors in TiAl are anisotropic and the prediction of the x-ray structure factors using these anisotropic temperature factors are highly accurate and precise. The results also show a possible sublattice ordering of the excess Al atoms.*
CHAPTER 2

THEORY AND APPROACH

This chapter describes the experimental approach used and the theory which forms the basis for such an approach to determine accurate Debye-Waller and structure factors for TiAl. Section 2.1 gives the importance of Debye-Waller factor. Section 2.2 describes the experimental method used to obtain accurate integrated intensity data from four-circle single crystal x-ray diffraction, and the use of this data for accurate Debye-Waller factor determination. Section 2.3 gives a very brief description of the CBED method used in the present work to determine accurate structure factors in TiAl. A more detailed description and the relevant computer program codes can be found in Swaminathan (1994). The conventions and symbols used in expressing temperature factors have been incorporated according to Wills and Pryor (1975).

2.1: Debye-Waller factor

In crystal structure analysis, the importance of thermal vibration parameters stems from its influence on the diffracted intensities of the Bragg reflections. The intensities measured from single crystal four circle x-ray diffraction (used as the experimental method to determine Debye-Waller factors in the present work) can be converted to structure amplitudes, which can then be compared to those calculated from the structure factor formula for reflection H (hkl),
\[ F(\mathbf{H}) = \sum_{k=1}^{n} f_k T_k \exp(2\pi i \mathbf{H} \cdot \mathbf{r}(k)) \] (2.1)

The summation above is over the \( n \) atoms in the unit cell (which would be 4 in the case of TiAl). \( f_k \) is the x-ray scattering factor of the \( k^{th} \) atom, the position of which is given by the vector \( \mathbf{r}(k) \), with respect to the cell origin. The effect of thermal motion is accounted for by the term \( T_k \), which is called the temperature factor. Ignoring thermal vibration is equivalent to setting \( T_k = 1 \) in the above equation; therefore, the temperature factor may be described as a quantity representing the reduction in the effective scattering factor due to lattice vibrations. The corresponding quantity representing the reduction in the intensity of the Bragg reflection is the Debye-Waller factor. The individual temperature factor for each of the atoms in the unit cell can be expressed as,

\[ T_k = \exp(-W_k) \] (2.2)

and can be taken out of the summation sign if the factor \( W_k \) is the same for all the atoms. The Bragg intensity is proportional to \( |F(\mathbf{H})|^2 \); hence, the Debye-Waller factor can be expressed as \( \exp(-2W_k) \) or the square of the temperature factor. In such a case, the Debye-Waller factor can be expressed as a single parameter, which is the same for all the atoms irrespective of the atom type or position, and which reduces the diffracted intensities uniformly. This method of referring to the Debye-Waller factor as a single isotropic parameter is referred to as Method 1 in this thesis. However, in the case of TiAl, the crystal contains chemically distinct atoms (Ti and Al atoms) and the temperature factors would not be expected to be the same for Ti and Al atoms on different sites. Therefore, the Debye-Waller factor becomes a more complicated function of \( \mathbf{H} \). In such a case the individual (for the \( k^{th} \) atom) temperature factor can be expressed as,

\[ T_k(\mathbf{H}) = \langle \exp[2\pi i \mathbf{H} \cdot \mathbf{u}(k)] \rangle \] (2.3)
which can be alternately expressed as

$$T_k(Q) = \exp\left[-\frac{1}{2} \langle(Q \cdot u(k))^2\rangle \right]$$  \hspace{1cm} (2.4)

where \(Q = 2\pi H\) and \(u(k)\) is the total displacement from all modes of vibration for the \(k^{th}\) atom at any instant of time. If the displacements are isotropic (the same in all directions) equation (2.3) can be reduced to

$$T_k(Q) = \exp\left[-\frac{1}{2} Q^2 \langle u(k)^2 \rangle \right]$$  \hspace{1cm} (2.5)

where \(\langle u(k)^2 \rangle\) is the mean square displacement for the \(k^{th}\) atom in any direction. Thus, comparing the expression for \(T_k\) in (2.4) with \(W_k\) defined in (2.2)

$$W_k = \frac{1}{2} Q^2 \langle u(k)^2 \rangle = \frac{8\pi^2 \sin^2 \theta_B}{\lambda^2} \langle u(k)^2 \rangle$$  \hspace{1cm} (2.6)

The quantity \(8\pi^2 \langle u(k)^2 \rangle\) is called the 'B-factor' of the atom and the isotropic temperature factors in further discussions are expressed in terms of \(B\):

$$B_k = 8\pi^2 \langle u(k)^2 \rangle$$  \hspace{1cm} (2.7)

This method of representing the Debye-Waller factor as a specific isotropic displacement parameter, which is different for different atoms in the unit cell is referred to in further discussions as Method 2. This representation assumes that the temperature factor is isotropic.

However, in the case of TiAl, the nearest neighbors are not the same in all directions, so one cannot reasonably expect the displacements to be the same in all directions for such an alloy. For instance, in a stoichiometric composition of \(\gamma\)-TiAl, Al atoms would have Al atoms as nearest neighbors along the x and y directions and would have Ti atoms as its nearest neighbors in the z direction. This is illustrated in Figure 1, which shows the L1₅ unit cell of \(\gamma\)-TiAl. Hence, the displacements in TiAl are expected to
be anisotropic. A schematic diagram of the isotropic and anisotropic mean square displacements in TiAl are shown in Figure 2, as defined with respect to the TiAl L1₀ unit cell. For anisotropic displacements, the temperature factor expression can be written as

\[ T_k(Q) = \exp[-\frac{1}{2}Q^\top B(k)Q] \]  

(2.8)

where \( B(k) = \langle u(k)(\mathbf{u}(k))^\top \rangle \) and this \( B \) matrix can be expanded as (omitting the \( k \) representing a particular atom in the unit cell)

\[
B = \begin{pmatrix}
\langle u_1^2 \rangle & \langle u_1 u_2 \rangle & \langle u_1 u_3 \rangle \\
\langle u_2 u_1 \rangle & \langle u_2^2 \rangle & \langle u_2 u_3 \rangle \\
\langle u_3 u_1 \rangle & \langle u_3 u_2 \rangle & \langle u_3^2 \rangle 
\end{pmatrix}
\]  

(2.9)

For TiAl, the off-diagonal terms become zero as dictated by the symmetry of the space group P4/mmm. Also the root mean square displacements are equal in the x and y directions due to four-fold symmetry along the (001) direction. This implies that the terms \( \langle u_1^2 \rangle = \langle u_2^2 \rangle \). Therefore, the only terms to be determined, with respect to the anisotropic temperature factors are \( \langle u_1^2 \rangle \) and \( \langle u_3^2 \rangle \). This method of expressing the Debye-Waller factor as anisotropic displacement parameters, which are different for different atoms and atom positions, is referred to throughout the further discussions as Method 3.
Figure 2: Schematic representation of isotropic (left) and anisotropic (right) Debye-Waller parameters with respect to the TiAl L1₀ unit cell. The isotropic temperature factor is represented by a single quantity $\langle u^2 \rangle$. The anisotropic root mean square displacements $\langle u_1^2 \rangle = \langle u_2^2 \rangle$ due to the symmetry in TiAl. $\langle u_1^2 \rangle$ and $\langle u_2^2 \rangle$ are sufficient to express the anisotropic site specific Debye-Waller factor.
2.2: Measurement of Debye-Waller factor

Two commonly used methods for temperature factor determination in crystals are x-ray and neutron diffraction. While neutron diffraction records the displacement of the nucleus, x-rays determine the displacement of the electron cloud. If the atom distorts during the periods of a single vibration, these two displacements would not be identical. However, in practice, the difference in the temperature factor influence for x-rays and for neutrons is too small to be observed [Wills and Pryor (1975)]. The difference would be larger in purely covalent compounds, where the valence electrons are shared between atoms, because the analysis of x-ray diffraction measurements, which is used to determine the temperature factor, relies on a theoretical form factor which is a function of the scattering vector \(Q\). In most calculations, the Hartree-Fock atomic wave function is used to obtain the form factor. The Hartree-Fock approximation assumes a spherically symmetric nature of the form factor. Although neutron diffraction measurements are better because they do not assume a spherically symmetric form factor, it has been shown that x-ray measurements do yield sufficiently accurate results for the temperature factor analysis [Larsen and Hansen (1984)]. Moreover, the x-ray diffraction method has a relatively easy procedure and hence has been employed in the current work to determine temperature factors in TiAl.

The temperature factor calculations use the harmonic approximation of the lattice dynamical theory [Wills and Pryor (1975)]. This approximation implies that the forces between pairs of atoms in a crystal are proportional to their relative displacements. This assumption may not be valid as it implies that there would be no thermal expansion or temperature dependence of the elastic constants. Saravanan, Mohanal and Chandrasekaran (1992) have determined the anharmonic temperature factors in Gallium arsenide. They have shown that there is not much difference in the \(R\) factor (residual index for the discrepancy
between measured and calculated structure factors) for the anharmonic and harmonic case (0.01% difference). Also, Sears and Shelly (1991) have determined the Debye-Waller factors in 43 elemental crystals with various structures including Ti and Al. They have shown that, in metals, the anharmonic contribution to the Debye-Waller factor remains at few-percent levels until the temperature exceeds about half the melting point. Therefore, in the present study, since the experiments are conducted at room temperature, the harmonic approximation has been considered as valid.

2.2.1: Four-circle X-ray diffraction

The four-circle x-ray diffraction method has been used extensively for crystal structure analysis, Debye-Waller factor determination and electron density distribution studies in various materials [Larsen and Hansen (1984); Saravanan, Mohanlal and Chandrasekaran (1992)]. In this method the integrated intensity measurements obtained from the diffraction data are corrected for absorption, thermal diffuse scattering and extinction effects and the resulting intensities are compared by non-linear least-square refinement with the calculated diffraction intensities. An artificial factor is used in the least square refinement which gives the Debye-Waller factor. The Debye-Waller factors are normally measured from higher order data with \( \sin(\theta)/\lambda \) in the range 0.8 to 1.3 Å⁻¹ where the effect of thermal vibration is measured more accurately. In the current work, the RIGAKU AFC6 four circle x-ray diffractometer supplied by the Molecular Structure Corporation was used for the measurement of single crystal x-ray data. The TEXSAN® structure analysis software also provided with the diffractometer has been used for analyzing the diffraction data.

The four-circles in the diffractometer are driven by stepping motors controlled by a micro-VAX computer. A schematic diagram of the four-circle x-ray diffractometer is
shown in Figure 3. The four circle stage has two base circles $\omega$ and $2\theta$ which are mounted on a common axis. The $\chi$ circle is mounted perpendicular to the base circles and the diameter of the $\chi$ circle passes through the center of the $\omega$ and $2\theta$ circles. The fourth circle $\phi$ is mounted on the $\chi$ circle and moves on the rim of the $\chi$ circle. When the $\chi$ angle is zero the axis of the $\phi$ circle coincides with that of the $\omega$ and $2\theta$ circles. The sample is mounted on the goniometer, which is mounted on the $\phi$ axis of the diffractometer. The sample is centered in the center of the $\chi$ circle with the help of a telescope attached to the rim of the $\chi$ axis. The rate of movement of the $\omega$ axis is equal to that of the $2\theta$ axis and the detector is moved at the same rate for the $\omega$/2$\theta$ scan. The sample is oriented for the collection of different Bragg reflections using the $\chi$ and $\phi$ axes. The experimental setup consists of a fixed x-ray source and a movable detector, which moves along the $2\theta$ circle. When characterizing a crystal, the setting parameters for crystal orientation and the cartesian coordinates of the reciprocal space with respect to the coordinate system of the goniometer are determined (the orientation matrix). The coordinate system of the goniometer (shown in the schematic diagram in Figure 4 with the four circles) is right handed with the x axis parallel to the direction of the incident x-ray beam, the y axis corresponding to the direction of $2\theta=90^\circ$ and the z axis perpendicular to x and y axes.
Figure 3: Schematic representation of the four-circle x-ray diffractometer. The $\phi$ axis is mounted in the $\chi$ circle. The $2\theta$ and $\omega$ axes coincide with the $\phi$ axis when $\chi=0$.

Figure 4: Schematic representation of the four-circle axis and the cartesian axis $X$, $Y$, $Z$ with respect to which, the crystal reciprocal axes orientation is calculated.
The X-ray beam collimated with the 0.5 mm collimator and is aligned such that it passes through the center of the $\chi$ circle, the diameter of which intersects with the axis of the $\omega$ and $2\theta$ axes. The beam is about 0.5 mm wide and requires a perfect alignment so that the diffracted beam can be seen by the detector. The detector is aligned in the same horizontal plane as the beam such that it sees the beam at all points of rotation of the four circles (as shown in Figure 4). The x-ray source uses a rotating anode cooling system which gives higher x-ray intensities compared to a x-ray tube source. A molybdenum target is used to generate the x-rays. The x-rays pass through a graphite monochromator to yield the Mo $K_{\alpha}$ radiation. As a first step in the experiment, the sample is centered in the center of the $\chi$ circle. The position of the sample on the goniometer can be adjusted using the x-y screws. The set screw which locks the x-y movement is released in order to center the sample. Figure 5 shows a schematic representation of the goniometer head with the sample mounted on it. The mounting procedure is discussed in detail in the sample preparation section. The x and y screws are used to center the sample in the center of the $\chi$ circle and the z screw is used for height adjustments. The goniometer remains in the same place while the sample position is changed finely with this x-y adjustment. While centering the sample, the diffractometer angles are set at $\chi = 13^\circ$, $\omega=10^\circ$ and $\phi = \pm 45^\circ$ or in two other perpendicular directions $\chi$ and the $\phi$ angle. The $\omega$ is adjusted in order to see the sample through the telescope. Centering involves seeing the sample at the center of the telescope cross wire at all points along the axes. This is checked by rotating the $\phi$ axis which runs along the center of the goniometer. The sample should remain at the center of the cross wire during the movement of the $\phi$ or the $\chi$ axes.
Figure 5: Schematic diagram showing the goniometer head of the four-circle x-ray diffractometer with the mounted sample (not to scale).
After centering, the sample is scanned for various peaks (preliminary scan) in a specific range of $2\theta$ in order to determine the orientation of the crystal. In the case of TiAl the samples were scanned for $2\theta$ ranging from 17° to 25°. This would include the \{111\} and \{200\} fundamental reflections. The reflections obtained in this scan are indexed with respect to the TiAl crystal system. Some knowledge of the approximate values of $2\theta_b$ in TiAl based on the L1$_0$ unit cell is required for this preliminary indexing of the reflections. This initial guess is made using the known crystal structure of TiAl [Duwez and Taylor (1952)] with the space group P4/mmm and lattice parameters $a=3.99\AA$ and $c=4.07\AA$.

Then, the crystal orientation matrix which gives the orientation relationship between the crystal axes and cartesian axis system of the diffractometer [Busing and Levy (1967)] is further refined by refining the angular positions ($\chi$, $\phi$ and $\omega$ values) of all the \{111\} and \{200\} reflections. Higher order reflections are then scanned (preliminary fast scan) to ensure that the peaks are sharp and have measurable counts in the desired $\sin(\theta)/\lambda$ range of 0.7 to 1.2 $\AA^{-1}$. If the counts are excessively high, the lower order reflections would have very high counts which would result in increased dead time (time when the detector is saturated and cannot collect the x-ray intensity), as a result, the data would not be accurate. Dead time correction is also complicated in such a case; therefore, an appropriate crystal for data analysis is chosen based on sharp and accurate peaks and sufficient counts. The \{242\} and \{224\} reflections are then refined for the angular positions $\chi$, $\phi$ and $\omega$ so that the centering is on the K$_{\alpha1}$ peak. For the \{111\} or \{200\} reflections, the peak splitting corresponding to K$_{\alpha1}$ and K$_{\alpha2}$ cannot be observed and hence, an average value of wavelength is used, whereas for the \{242\} and \{224\} reflections the accurate wavelength corresponding to the K$_{\alpha1}$ radiation can be used. The lattice parameter is then refined with the orientation matrix from \{242\} and \{224\} reflections and the input $\lambda$ corresponding to K$_{\alpha1}$ radiation, by least square refinement. Using this \{242\}, \{224\} orientation matrix,

24
higher order reflections with \(\sin(\theta)/\lambda\) greater than 0.6 Å\(^{-1}\) are collected. A continuous \(\omega/2\theta\) scan has been used to determine the integrated intensity over a wide range of reflections in the entire accessible Ewald sphere.

The integrated intensity is determined by integration of the diffracted intensity over an angular range for \(\omega\), for which the intensity is collected by continuous rotation of the crystal and summing all the counts received by the counter. The uniform background noise caused by thermal diffuse scattering is subtracted from the measured intensity. The peak position is determined (using the AFC6 software) by calculating the Bragg reflection positions using the orientation matrix. A least-square fit of the peak width is performed assuming that the reflection peaks result from a convolution of instrumental and spectral distribution functions with an anisotropic crystal size and mosaicity distribution function. With this assumption, the estimated standard deviation, \(\sigma(I)\) values are calculated. The Lehmann Larsen criterion [Feil (1977)] is used to determine the optimal values of the end points of the peak (where the peak begins and where it ends). In this criterion, the end points are chosen in such a way that a minimum value of \(\sigma(I)/I\) for the integrated intensity of the reflection is obtained. The integrated intensity is accurately corrected for Lorentz polarization and absorption effects. Lorentz polarization was corrected using the program PROCESS which is a part of the TEXSAN structure analysis software. The following section describes the absorption correction applied to the integrated intensity data in detail.

2.2.2: Absorption correction

Absorption of diffracted x-ray beams is a great source of systematic error in the determination of structure factors by four-circle x-ray diffraction method. In case of a spherical crystal, all the equivalent reflections would be absorbed to the same extent and a simple overall absorption correction can be applied based on the crystal size and the
transmission factor. In case of a non-spherical crystal, equivalent reflections would travel different lengths in the crystal and hence, the absorption correction would vary between two sets of equivalent reflections. In any crystal (spherical or non-spherical) the measured intensity is corrected for absorption by dividing it by a transmission factor, \( A \), given by

\[
A = \frac{1}{V} \int \exp(-\mu L) dV \quad (2.10)
\]

where, \( \mu \) is the linear absorption coefficient for the x-rays in the given crystal, \( V \) the volume of the crystal and \( T \) the sum of the incident beam path length from the point of entry of the x-ray into the crystal up to the volume element \( dV \) and the corresponding diffracted beam path length in \( dV \). The integration is over the volume \( V \) of the crystal. In the equation (2.10) \( \mu \), the mass absorption coefficient for a compound, is calculated from the mass absorption coefficients, \( \mu_i/\rho_i \) of individual elements for the specific x-ray radiation using the formula,

\[
\mu = \rho \sum_{i} g_i \left[ \frac{\mu_i}{\rho_i} \right] \quad (2.11)
\]

where \( \rho \) is the density of the compound and \( g_i \) is the weight fraction of the particular element.

In order to compute the transmission factor analytically, the crystal is assumed to be terminated by flat, planar surfaces and to be constituted of a convex polyhedron. The transmission factor of this multifaceted crystal can be found by subdivision of the crystal into Howells polyhedra and further subdivision of the polyhedra into elemental tetrahedra, and using an analytical method for the evaluation of the absorption over a tetrahedron [Meulenaer and Tompa (1967)]. In each of the smaller polyhedra, \( L \) is a linear function of the coordinates of \( dV \). The transmission factor, \( A \) can be obtained by summing the contributions from all the tetrahedra. The division of the crystal into Howells polyhedra
requires knowledge of the Miller indices of the crystal facets and the shape and size of the crystal. The program ABSORB in TEXSAN structure analysis software (provided by Molecular Structure Corporation with the Rigaku AFC6R diffractometer) accepts the Miller indices of the bounding faces of the crystal and the perpendicular distance of that face to an origin within or on the crystal as inputs. It further uses the method of Meulenaer and Tompa (1967) to apply the analytical absorption correction on structure factors. A polarizing microscope equipped with an image-splitting eye-piece and a spindle stage that accommodates the single crystal x-ray diffractometer goniometer head has been used to characterize the crystal shape and size. A unit vector along the direction of any face pole can be described by the $\chi$ and $\phi$ diffractometer angles. Hence, the crystal face can be aligned into diffracting position ($\omega=0$), the $\chi$ and $\phi$ angles noted, and then the unit vector along the direction for the diffracting vector, which is perpendicular to the crystal face and describes the indices of the faces, can be calculated. In the polarizing microscope, the crystal faces can be seen clearly at a better magnification and can be similarly aligned into diffracting position. The microscope spindle-stage has a similar geometry as the diffractometer and a straightforward relationship between the spindle stage axis and the diffractometer axis can be obtained. Using this relationship and the readings from the spindle axis for each face, the Miller indices of the crystal faces were found. The accuracy to which the angular coordinates of the facets of the crystal could be measured depends on the size of the crystal and the areas of the facets. Usually, one of the corners of the crystal is chosen as the arbitrary origin and hence, the perpendicular distance of the faces intersecting the origin is zero.

Errors in the measured values of perpendicular distances, angular coordinates and the calculated absorption coefficients would introduce systematic errors in the absorption correction. Therefore, in order to keep these errors low, it is necessary to limit the
absorption correction necessary. This could be achieved by minimizing the value of μ or the crystal size in case of a given compound. Decreasing the size of the crystal would decrease the total path length \( L \) in the equation (2.10) and hence, the absorption correction required. The maximum size of the crystal is determined by limiting the value of \( A \) to 0.8 for any reflection, in equation (2.10). Considering the diffracting power of the crystal, intensity of the source, sensitivity of the detector and required reflections (in this case the reflections which have \( \sin(\theta)/\lambda \sim 1 \text{ Å}^{-1} \)), the maximum crystal size can be calculated as a sphere with \( \sim 33\mu\text{m} \) diameter for the full capacity of the diffractometer, 55 kV and 180 mA [Swaminathan (1994)]. However, in order to obtain higher order reflections with measurable intensities, cuboidal crystals with edge size of \( \sim 100 \mu\text{m} \) have been used.

2.2.3: Specimen preparation

The specimen preparation for the four-circle x-ray diffraction experiment involves preparation of a single crystal, cuboidal in shape with a maximum edge of \( \sim 100 \mu\text{m} \), which is not deformed and gives sharp x-ray peaks. Conventional methods of cutting and grinding to the required size cannot be used as this would deform the TiAl crystal and the subsequent x-ray data would reflect a systematic error. In the previous work by Swaminathan (1994) the x-ray specimens were prepared by cleaving a rod about \( \sim 100 \mu\text{m} \) thick and 1mm long using a sharp razor, to obtain the single crystal specimens. This method of preparation introduced a number of dislocations due to deformation of the crystal and hence, a mosaic spread was observed in the peaks obtained from these crystals. Mosaic spread of the x-ray peaks can be explained based on the mosaic model [Zachariasen (1967)]. A real crystal can be described as an aggregate of perfect crystal domains. The boundary between two domains represents a surface of discontinuity with respect to the periodicity and can be described as a small relative rotation between the two domains. If the
real crystal consists of numerous domains, it can be assumed that the misalignment obeys an isotropic Gaussian distribution law described by:

$$W(\Delta) = \sqrt{2}\times \exp(-2\pi \times g^2 \times \Delta^2)$$  \hspace{1cm} (2.12)

where \(\Delta\) measures the angular deviation from the mean orientation. The crystallite boundaries in a deformed real crystal like TiAl can be understood as dislocations. In such a case, the x-ray peaks would not be sharp and would have a spread corresponding to the small variations in orientation and the Gaussian spread of the orientation about the mean.

Figure 6 shows an example of a peak from a mosaic crystal with a mosaic spread in the peak. This data was obtained from Swaminathan (1994). Figure 7 shows a corresponding sharp peak from an undeformed crystal which shows no mosaic spread. This crystal was prepared as part of the current work. The mosaic spread would also result in a dampening of the x-ray intensity of the peaks and would affect the accuracy of the orientation matrix.
Figure 6: Reflection peak profile from a mosaic crystal

Figure 7: Reflection peak profile from a crystal which is closer to a perfect crystal
In the current work, a new method of specimen preparation has been developed with the help of which an undeformed TiAl crystal (cuboidal in shape with a ~100 μm maximum edge) could be prepared and hence, sharp and accurate x-ray diffraction peaks can be obtained. Larsen and Hansen (1984) have used electric arc machining to prepare beryllium single crystals of 100x250x300 μm size. The current work also involves electric discharge machining (EDM) but is different from that used by Swaminathan (1994) in that, the crystals were not deformed at any stage of preparation and the entire cutting used the EDM. TiAl single crystals of nominal compositions Ti-54 at.% Al and Ti-56 at.% Al were obtained from the Wright Patterson Air Force Base. They were prepared by induction melting and further homogenizing. The single crystal samples were heat treated in a vacuum of 10^{-5} Torr for 24 hours at 1000°C. Titanium foil was used to wrap these samples to prevent any oxidation of TiAl single crystals. Discs of ~3 mm in diameter and ~200 μm thick were cut from the heat treated samples using EDM. These discs were further ground to a thickness of ~130 μm using a GATAN disc grinder. The discs were then mounted on a TiAl polycrystal disc of size 3mm x 0.5 mm. Fine grooves were made on the single crystal with EDM using the finest brass wire which was 75 μm thick. These grooves were made in the form of a grid and were ~100 μm deep. Making these grooves required very high precision and an accurate control of the distance moved from one groove to another on the disc during EDM. The TiAl polycrystalline disc which held the brittle single crystal was attached to a much bigger piece in order to be mounted on the electric discharge machine. After the entire crystal was grooved in this manner, it was cleaned and ion milled from the top to remove the oxide layer on the crystal and in the grooves. The oxide layer due to EDM using the 75 μm wire is usually 5-10 μm in thickness. This grooved single crystal was then turned over so that the grooved surface faced down and was stuck on the TiAl polycrystal disc once again. The top surface was now ion milled using an argon ion beam.
until cube shaped specimens were exposed. Figure 8 shows a schematic diagram of the single crystal sample with the grooves on it, the direction of ion milling and the final cube shaped single crystals formed. These cube shaped specimens were then mounted carefully at the tip of a glass fiber which was ~0.2 mm thick using nail polish or equivalent glue. The glass fiber was then mounted on the four-circle goniometer using wax to hold it in the hole of a brass rod which fits exactly into the goniometer head. Figure 5 (shown earlier on page 23) shows a schematic diagram of the goniometer head and the representation of the crystal mounted on it. The four-circle diffractometer, which is a part of the research facility of Dr. Jim Downs in the Geological Sciences Department, was used for the x-ray diffraction experiments. TiAl single crystal specimens were thus prepared. Single crystal specimens were selected for final data collection based on two criteria. The crystal should give good sharp peaks for all reflection and should give sufficient counts in x-ray intensity. Crystals which were large were not selected as absorption correction would increase and also extinction effects would be larger. Also, crystals that were very small were not selected as they would not give sufficient diffracted intensities for higher order reflections.
Figure 8: Sample preparation steps involved in preparation of single crystal specimens for x-ray diffraction.
2.2.4: Extinction correction and Least square refinement

It is necessary to have accurate structure factor measurements in order to determine the Debye-Waller factors to the accuracy of a few percent. Accurate integrated intensities are most easily obtained by careful profile analysis of each reflection throughout the entire accessible Ewald sphere [Downs 1990]. The integrated intensities are then accurately corrected for Lorentz polarization and absorption effects. These integrated intensities are further analyzed to obtain the atomic parameters using least square refinement. It is usually assumed during data reduction that the kinematic approximation is valid. Phenomena which cause deviations from kinematic conditions and cause the absolutely scaled integrated intensity to be less than $F^2$ are collectively called extinction. Intense, low-angle reflections are most affected by extinction. Furthermore, extinction may be anisotropic causing symmetry equivalent reflections to have non-equal intensities even after corrections for absorption. The entire sphere of reflection is sampled normally because it is not uncommon to find some intensities reduced by more than 60% due to extinction. Hence, it is absolutely necessary that extinction be minimized or be adequately corrected for.

Extinction can be described based on two different effects. Assuming a mosaic structure for a real crystal, primary extinction (Type II) is considered as amplitude coupling between the direct and scattered beams within a mosaic block and is strictly a dynamical phenomenon. Secondary extinction (Type I) is ascribed to intensity coupling between mosaic blocks and is usually described by the Darwin transfer equations [Larson (1970)]. Most extinction correction schemes for single crystals realistically deal only with secondary extinction. In the present work, the corrections for secondary extinction have been estimated during the least-squares modeling of crystal structure and electron density using
the formalism of Zachariasen (1967), which is incorporated in the program XTAL\textsuperscript{1} version 3.4. The extinction parameter $r^*$ can be refined along with other structural parameters like the Debye-Waller factor and site occupancy. According to the Zachariasen (1967) formalism, the primary extinction effects are refined simultaneously with secondary extinction, since any secondary extinction affected by particle size will have some primary component and would be dependent on it. The secondary extinction variable $x_s$ is described as

$$x_s = r^* F_c^2 \delta$$

(2.13)

where $r^* = g$ for extinction of Type I and $r^* = \rho$ for extinction of Type II. The values of $g$ and $\rho$ are dimensionless quantities related to the physical properties of the crystal (such as density). The parameter $r^*$ can be explained as representing the size of the mosaic blocks and $F_c$ is the structure factor amplitude.

In the non-linear least square refinement, the function $Q$ (which is defined below) is minimized over all values of (hkl), i.e., summed over all reflections,

$$Q = \Sigma_h \{ w(F_o - F_c)^2 \} = \Sigma_h w \Delta^2$$

(2.14)

Here $F_o$ is the observed absolute structure factor, $F_c$ is the calculated absolute structure factor and $w$ is the least square weight. The function is expanded as a Taylor series and the fitting procedure involves minimizing the resulting $Q$. The value of $F_c$ is calculated assuming no Debye-Waller factor based on the method by Doyle and Turner (1968) and the appropriate Debye-Waller factor is fitted. The conventional R factor, which measures the extent to which the least-square refinement has converged, is defined as the ratio of sum of

\textsuperscript{1} Crystal structure analysis software provided by the University of Western Australia.
square of the difference between calculated F and experimental F to sum of square of experimental F, summed over all the reflections.

\[ R = \frac{\sum (F_o - F_c)^2}{\sum F_o^2} \]  

(2.15)

A scale factor is used to scale the experimental F to be comparable with the calculated F. This is initially adjusted using low order reflections and then kept a constant for further refinements. The structural parameters are refined using a non-linear least square refinement. All the parameters are refined together, since a change in one parameter would affect another and convergence is better when all the parameters are changed simultaneously in refinement. Extinction correction parameter r' is also refined with the structural parameters.

### 2.3: Convergent Beam Electron Diffraction

The energy filtered convergent beam electron diffraction method has been used in the current work to determine accurate structure factors in TiAl. This method involves matching experimental CBED intensities to those calculated based on the dynamical theory of electron diffraction. The Fourier coefficients of the crystal potential \(V_g\) can be refined by matching the intensity variation across a CBED pattern in one or two dimensions. Most attempts to refine \(V_g\) have been restricted to one dimensional pattern matching (matching the variation in intensity along a systematic row) which is alternatively called the 'rocking-curve' method. In this method a CBED pattern is recorded such that the crystal is orientated far from a low order zone axis in order to minimize interactions with non-systematic reflections. The orientation is such that the beam direction is close to or exactly at the Bragg condition of the reflection for which the structure factor is being measured. The CBED disk obtained at this Bragg condition contains parallel fringes perpendicular to \(g\), so called
“rocking curve” fringes. The fringe spacing and the relative intensity of the fringes is used to refine $V_n$. A detailed description of the experimental method used in recording the CBED patterns and the patterns thus obtained can be found in Swaminathan (1994). A brief description of the method developed for accurate structure factor refinements in the current project [Swaminathan (1997b)] is given below.

Fast electrons used in transmission electron microscopy (TEM) undergo elastic and inelastic scattering processes during the interaction with thin foil specimens. The latter ultimately result in the electron energy loss (EEL) spectrum, which can be dispersed using a sector magnet for instance, as in many commercially available EEL spectrometers. A GATAN serial EEL spectrometer was used by Swaminathan (1994) to digitally collect the zero-loss filtered diffracted intensities in appropriately oriented CBED patterns suitable for application of the “rocking curve” method for structure factor refinement. Zero-loss filtering refers to the use of only the elastically scattered part of the EEL spectrum in the CBED pattern collection. Such zero-loss filtered experimental data is much more suitable for comparison with computer simulations since the dynamical theory of electron diffraction offers a very good theoretical treatment of the elastically scattered electron intensities, whereas the effects of absorption which are associated with the inelastically scattered electrons are not satisfactorily treated. Hence, to enable meaningful and high accuracy structure factor measurements, zero-loss filtered experimental data is not only preferred but absolutely necessary.

The Philips EM420 scanning/transmission electron microscope (STEM) with LaB$_6$ electron source and interfaced to a combination of commercial and custom built ancillary equipment for energy filtering, present in the Electron Microscopy Center of Argonne National Laboratory (ANL), has been used by Swaminathan (1994) to record the CBED patterns from TiAl alloy of nominal composition Ti-52 at.% Al. The zero-loss filtered
CBED patterns recorded by Swaminathan (1994) with the facility at ANL were used in the current work for structure factor refinement. The actual composition of the alloy used by Swaminathan (1994) was determined to be Ti-51.3 at.% Al using quantitative energy dispersive x-ray spectroscopy with an Al₃Ti standard. This actual composition was used in CBED pattern matching and also in studying the effect of compositional accuracies on the structure factors in TiAl.

A rocking curve for structure factor refinement is obtained from the CBED pattern for a direction parallel to \( g \) by counting the intensity along an arbitrary line across the CBED pattern close to the center. Structure factor in TiAl is refined by simulating the rocking curve intensity at all points using the Bloch-wave formulation of the dynamical theory of electron diffraction, and matching with the experimental diffracted intensities. Three important parameters which determine the intensity variation in the bright field disc are the foil thickness \( t \), the Fourier coefficient of crystal potential \( V_g \), and the absorption coefficient \( V_g' \). The theoretical rocking curves are fitted to the experimental ones by varying these parameters using a computer program written for this particular application by Swaminathan (1994). The experimental value of \( V_g \) is then measured and converted to \( F_g \).

The following section gives the key points in the Bloch wave theory that are important in understanding the determination of accurate structure factors via the CBED rocking curve method. It also briefly introduces the main features of all the programs used.

2.3.1: Accurate structure factors from CBED method

The calculation of a CBED rocking curve to match with the experimental one is based on the quantum mechanical formulation of the dynamical theory of electron diffraction. This section describes the relevant key points of the theory which are the basis for the programs written to simulate the CBED patterns [Swaminathan (1994)]. A more
A detailed review of the theory can be obtained from Humphreys and Bithell (1992) or Spence and Zuo (1992).

In the Bloch wave formulation, the wave function which represents fast electrons moving in a periodic crystal potential is expressed as a superposition of Bloch waves,

\[ \psi(r) = \sum_i \alpha^{(i)} \psi^{(i)}(r) = \sum_i \alpha^{(i)} \sum_g C_g^{(i)} \exp(2\pi i [\mathbf{k}^{(i)} + \mathbf{g}] \cdot \mathbf{r}) \]  

(2.16)

where \( \alpha^{(i)} \) is the excitation amplitude of the \( \text{i}^{th} \) Bloch wave. These excitation amplitudes are obtained by applying the boundary conditions corresponding to the continuity of the wave function in the entire crystal and is therefore dependent on the crystal shape. It is solved by matching the tangential components of the incident beam and Bloch wave vectors inside the crystal at the entrance surface.

The Schrödinger equation for the wave function of a fast electron moving in a periodic crystal potential \( \mathbf{V}(r) \) can be expressed as

\[ \nabla^2 \psi(r) + \frac{8\pi^2 m |e|}{\hbar^2} [E_0 + \mathbf{V}(r)] \psi(r) = 0 \]  

(2.17)

where \( m \) is the relativistic mass of the fast electron and \( E_0 \) is the accelerating voltage. The periodic crystal potential \( \mathbf{V}(r) \) can be expressed as a Fourier series in reciprocal space with Fourier coefficients \( V_g \). The relation between \( V_g \) and the dynamic structure potential \( U_g \) is given by,

\[ U_g = \frac{2m |e|}{\hbar^2} V_g \]  

(2.18)

and the relation between \( V_g \) and the extinction distance \( \xi_g \) is given by

\[ \xi_g = \frac{1}{\lambda |U_g|} \]  

(2.19)
where $\lambda$ is the relativistic wavelength in Å. From the Schrödinger equation, by expressing the accelerating voltage as a function of the electron wavelength, and substituting (2.18) in (2.17), we get a set of standard dispersion equations for high energy electron diffraction

$$[K^2 - (k^{(i)} + g)^2]C_g^{(i)} + \sum_h U_{g-h} C_h^{(i)} = 0$$

with one such equation for each $g$ or each reflection considered. Equation (2.20) can be expressed as a structure matrix and can be solved as an eigenvalue problem to yield the eigenvalues and eigenvectors. The diffracted amplitude for a certain beam direction is determined by summing the amplitudes of all the Bloch waves in that specific beam. The electron structure factors are complex for a centrosymmetric crystal with absorption and, in such a case, the structure matrix is complex and it is computationally intensive to determine its eigenvalues. Hence, in the present case, the structure matrix is solved as a real symmetric matrix and absorption is treated using the perturbation theory [Swaminathan (1994)]. The aim of this theory is to find the change in a known system (i.e., set of Bloch waves) due to a small perturbation in the structure matrix. In this treatment of absorption, each Bloch wave is exponentially attenuated as it propagates through the crystal.

In the present problem of matching rocking curves from the CBED pattern, the foil thickness $t$, the extinction distance $\xi_g$ and the absorption part of the extinction distance $\xi'_g$ are adjusted to simulate a theoretical rocking that matches the experimental data. Programs for matching the rocking curves by solving the structure matrix have been written by Swaminathan (1994). These programs accept the unit cell parameters, Debye-Waller factors, coefficients of free atom scattering factors, the orientation of the crystal with respect to the electron beam and the diameter of the CBED disk as a fraction of the $g$ as input. A suitable set of beams are selected based on the criterion that $w_h (= \xi_h s_h$ where $\xi_h$ is
the extinction distance of the reflection h calculated from free atom scattering factors and s_h is the deviation parameter for a given beam direction) is less than an input value.

2.3.2: X-ray and Electron structure factors

The intensity of the diffracted beams in an electron diffraction experiment is related to the total crystal electrostatic potential V(r). The Fourier coefficients of the electrostatic crystal potential V_g can be written as,

\[ V_g = \frac{1}{\Omega} \sum f^e(s) \exp(-2\pi i g \cdot r_i) \]  \hspace{1cm} (2.21)

where \( \Omega \) is the volume of the unit cell. The quantity V(r) includes the nuclear potential contribution. A relationship between the Fourier coefficients \( V_g \) and the Fourier coefficients \( F_g^e/\Omega \) of the electron charge density \( \rho(r) \) is important to determine the electron charge density in TiAl from structure factors measured in electron diffraction experiments. The relation can be written as,

\[ V_g = \frac{h^2}{8\pi \varepsilon_0 m_e l e\Omega} F_g^B \]  \hspace{1cm} (2.22)

and \( F_g^B \) is the electron structure factor which includes the contribution due to thermal vibration. In relating the structure factors \( U_g \) with the x-ray structure factors,

\[ F_g^X = \sum Z_i \exp(-B_i s^2) \exp(-2\pi i g \cdot r) - \left( \frac{8\pi^2 \varepsilon_0 h^2 \Omega s^3}{\gamma m_e e^2} \right) U_g \]  \hspace{1cm} (2.23)

where \( \gamma \) is the relativistic constant and \( m_e \) is the relativistic mass of an electron. The parameter most pertinent to the work presented here is \( B_i \), which is the Debye-Waller factors for atom \( i \). A knowledge of the Debye-Waller factor is necessary to convert the structure factor \( U_g \) determined from electron diffraction methods to the corresponding x-ray structure factor \( F_g^X \).
CHAPTER 3

RESULTS AND DISCUSSION

The importance of knowing accurate values of Debye-Waller factors for structure factor calculations using the CBED method has been established in the previous chapters. In the present work, accurate Debye-Waller factors in TiAl have been determined using four circle single crystal x-ray diffraction. Section 3.1 describes the results obtained from four-circle x-ray diffraction (isotropic and anisotropic Debye-Waller factors and lattice parameters) and discusses the significance of these results in accurate structure factor measurements. Section 3.2 discusses the electron diffraction experiments conducted on the TiAl single crystals and the observation of Ti$_3$Al$_5$ type ordering. An attempt was made to refine accurate structure factors using the anisotropic Debye-Waller factors obtained in the present work. Section 3.3 gives these results.

3.1: Four-circle x-ray diffraction

X-ray diffraction data was collected from TiAl single crystals of nominal compositions Ti-54Al and Ti-56Al (all compositions in atomic percent), which were prepared using the method described in section (2.2.3). The lattice parameters were determined by refining angular positions of the {242} and {224} reflections. Integrated intensity data for over 200 families of reflections with $\sin(\theta)/\lambda$ ranging from 0 to 1.2 Å$^{-1}$ for Ti-56Al and 0 to 1.4 Å$^{-1}$ for Ti-54Al were collected using $\omega/2\theta$ continuous scans (as described in the chapter 2). Sharp peaks were obtained corresponding to the fundamental
and super-lattice reflections (with h+k=2n and having non-zero structure factors) in the
collection range from both crystals. Diffuse intensities were also observed for the
kinematically forbidden reflections (with h+k=2n+1 and structure factor=0). Figure 9
shows the peak profile of the kinematically forbidden (100) reflection obtained from the Ti-
56Al crystal. Similar peaks were obtained for forbidden reflections from the Ti-54Al
crystal.

Figure 10 shows plots of integrated intensity I vs. statistical error σ(I) for the
forbidden reflections from Ti-54Al and Ti-56Al crystals. For many of the forbidden
reflections, the statistical error in the integrated intensity σ(I), was lower than the integrated
intensity of the reflection. However, for some reflections, σ(I) was greater than I. When
the integrated intensity value is greater than the error in the intensity, it implies that there is
a diffraction maximum at that point. Therefore, all such forbidden reflections were included
in the determination of Debye-Waller factor.
Figure 9: Peak profile corresponding to the (100) reflection (structure factor = 0 as $h+k=2n+1$) obtained from the Ti-56 Al single crystal
Figure 10: Plot of Intensity vs. $\sigma(I)$ for kinematically forbidden reflections in Ti-54Al (top) and Ti-56Al (bottom). The line indicates points where $I = \sigma(I)$.  

45
Previously, in off-stoichiometric TiAl super-structure ordering of Ti$_3$Al$_5$ type has been observed (discussed in section 1.2). Also, the electron diffraction experiments on the present Ti-54Al and Ti-56Al crystals showed the super-structure ordering (results are presented in section 3.2) of Ti$_3$Al$_5$ type. Hence in the x-ray diffraction experiment, an attempt was made to collect the diffracted intensities corresponding to the super-structure reflections. Sufficient intensities could not be obtained corresponding to these reflections in the x-ray diffraction experiment. Figure 11 shows a plot of intensities of some of the superstructure reflections obtained from the Ti-54Al crystal vs. statistical error. Similar results were obtained for the Ti-56Al crystal. There are very few reflections for which the error in the intensity $\sigma(I)$ is greater than the intensity $I$. Hence the analysis of the Ti$_3$Al$_5$ reflection data using least-square refinement was not considered.

![Figure 11: Plot of Integrated intensity vs. error in the integrated intensity collected for the superstructure reflections from the Ti-54Al crystal.](image-url)
The initial values of integrated intensities from all reflections were corrected for Lorentz polarization using the program PROCESS (described previously). The overall agreement factor $R$, (defined in the TEXSAN$^2$ structure analysis program as the ratio of the root mean square difference between observed and calculated peak profile characteristics over the estimated standard deviation for the peak) was 5.1% for Ti-54Al and 3.9% for Ti-56Al before applying any absorption correction. The Ti-54Al single crystal was cuboidal in shape with $\sim$110 $\mu$m maximum edge length, while the Ti-56Al crystal was cuboidal in shape with $\sim$100 $\mu$m maximum edge length. Hence, following the discussion in section (2.2.2) on absorption correction, the integrated intensity data from crystals of these sizes would have a transmission factor of $\sim$0.8 and an absorption correction is necessary. The faces of the single crystal specimen were characterized using a polarizing image splitting microscope and analytical absorption correction was calculated using the program ABSORB$^3$. The $R$ factor after absorption correction including the forbidden (h+k=2n+1) reflections reduced to 3.2% for Ti-54Al data and 3.0% for Ti-56Al data and was 2.1% and 2.4% respectively without the forbidden reflections. Calculated static structure factors were fitted to these set of integrated intensity data which have been corrected for Lorentz polarization and absorption to estimate the Debye-Waller factor.

Debye-Waller factors in the two TiAl alloys were determined using three methods. In the first method, namely the “Wilson plot” method, no extinction correction was applied to the diffracted intensities. In the second and third methods, which involved calculating the

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$^1$ Structure analysis software provided by Molecular Structure Corporation

$^2$ A program for performing analytical absorption correction provided with the TEXSAN structure analysis software.
isotropic and anisotropic temperature factors by non-linear least square refinement, an
extinction correction was applied to obtain the best fit. The effect of the excess Al atoms on
the sublattice ordering in TiAl was also studied in the non-linear least square refinement
analysis. The three different methods and the Debye-Waller factors thus obtained are
discussed in the following sections.

3.1.1: Debye-Waller factors from ‘Wilson plot’ method

In this method the Debye-Waller factor is expressed as a single overall parameter (B
factor) which dampens the x-ray intensities due to thermal vibration of the atoms. It is a
single parameter and is the same for all the atoms in the unit cell. In such a case the
structure factor for any atom in the unit cell can be expressed as

\[ F(H) = F_c(H) \exp(-Bs^2) \]  \hspace{1cm} (3.1)

where \( F_c(H) \) is the static structure factor for the reflection \( H \) and \( s = \sin(\theta)/\lambda \). The
integrated intensity determined from the diffraction experiment is proportional to the square
of the structure factor and can be expressed as

\[ I(H) = kF(H)^2 \]  \hspace{1cm} (3.2)

where \( k \) is the scale factor relating the two quantities. From equations 3.1 and 3.2,

\[ \ln \left( \frac{I}{F(H)^2} \right) = \ln k - 2Bs^2 \] \hspace{1cm} (3.3)

and hence a plot of \( \ln(I/F^2) \) versus \( s^2 \) should yield a straight line and the slope of the line
would be \(-2B\). An equivalent plot is \( \ln(F_o^2/F_c^2) \) versus \( (\sin^2\theta/\lambda^2) \) where \( F_o \) refers to the
observed scaled structure factor, and \( F_c \) refers to the calculated static structure factor. The
free-atom static structure factors \( F_c \) can be calculated using the Hartree-Fock free-atom
scattering factors after Doyle and Turner (1968). The static structure factor in TiAl for a
reflection g (hkl) is given by the expression (using conventional L1_0 unit cell with 4 atoms - 2 Ti and 2 Al - per unit cell as the basis)

\[ F_g(s) = \begin{cases} f_{Ti}^x(s)[1 + \exp(-\pi i [h + k])] + \\ f_{Al}^x(s)[\exp(-\pi i [h + l]) + \exp(-\pi i [k + l])] \end{cases} \]  

(3.4)

where \( f_{Al}^x \) is the Hatree-Fock x-ray free atom scattering factor for Al, and \( f_{Ti}^x \) is the Hatree-Fock free atom scattering factor for Ti. The plot of \( \ln(F_o^2/F_c^2) \) versus \( \sin^2 \theta_n/\lambda^2 \) is given the name “Wilson plot”.

Figure 12 shows the Wilson plot computed using the data from Ti-54Al and Figure 13 shows the same for Ti-56Al crystal. From these plots, the overall B value has been estimated as 0.532 Å² for Ti-54Al and 0.611 Å² for Ti-56Al. By comparison it can be observed that the B factor increases with increasing aluminum percentage in the alloy.

Using this plot to calculate B relies on the assumption that the Debye-Waller factor is a unique parameter for the given alloy and is the same for all the atoms at various sites in the crystal. Though this assumption may not be valid for TiAl, as will be illustrated by the second and third methods in sections 3.1.4. and 3.1.5, it gives a very good idea of the overall ‘B factor’ in TiAl which can be used as the initial value for the site specific Debye-Waller factor refinement. The Wilson plot method is best applicable for cubic materials with a single atom basis and have yielded sufficiently accurate results for Debye-Waller factors in Aluminum [Wills and Pryor (1975)].

Sears and Shelly (1991) computed the Debye-Waller factors of elemental crystals based on the phonon density of states model with the density of states data obtained from neutron inelastic scattering results. Peng, Ren, Duradev and Wheelan (1996) further reviewed their results and also calculated the absorptive scattering factors of elemental crystals. From the calculations on elemental crystals, the isotropic Debye-Waller factor of
elemental Al is 0.746 Å² and that of elemental Ti is 0.4911 Å². Comparing these Debye-Waller factors of elemental Ti and Al to that of the γ-TiAl alloy from present work, the following observations can be made. The overall Debye-Waller factors obtained using the Wilson plot method (0.532 and 0.611 Å²) are close to an average of the isotropic Debye-Waller factors of elemental Ti and Al (0.618 Å²). However, the isotropic elemental Debye-Waller factors of Ti and Al are quite different and it cannot be assumed that for the TiAl compound, the Ti and Al Debye-Waller factors would be the same. Therefore, the representation of the Debye-Waller factor using a single average B factor is not sufficient and it is important to determine independent site specific temperature factors for Al and Ti.

In literature, the Wilson plot method has been used to determine the Debye-Waller factors and the Debye temperatures in many crystals [Dingle and Medlin (1972)]. The determination of the Debye temperature and hence comparing the experimental Debye-Waller factors has not been attempted in the present work due to two main reasons. Firstly, the Debye approximation is applicable mainly to cubic crystals with a monoatomic basis and cannot be applied in the case of TiAl which has a di-atomic basis with four atoms per unit cell. Secondly, the Debye temperature is a temperature dependent quantity and the values obtained from a single diffraction experiment would not be meaningful.
Figure 12: Wilson plot plotted using the diffraction data from the Ti-54Al crystal. The slope of the line gives the Debye-Waller factor which is represented as the B factor
Figure 13: Wilson plot plotted using the diffraction data from the Ti-56Al crystal. The slope of the line gives the Debye-Waller factor.
3.1.2: Ordering schemes for least square refinement

γ-TiAl exists as a single phase between compositions of 52 to 60 at.% Al [Bumps, Kessler and Hansen (1952), Duwez and Taylor (1951), Ogden, Maykuth, Finlay and Jaffee (1951)] and does not exist as a single phase at the stoichiometric composition of 50-50. Hence, TiAl single crystals of the stoichiometric composition cannot be obtained for diffraction experiments. In the present work, non-stoichiometric TiAl single crystals of compositions 54 and 56 at.% Al have been used due to the unavailability of single phase alloy of the stoichiometric composition. Because of this off-stoichiometric composition, it is important to understand the effect of the excess Al atoms present in the structure on the short-range and long-range order in TiAl. The knowledge of sublattice ordering is crucial for accurate determination of Debye-Waller factors.

Elliot and Rostoker (1954) used the x-ray powder diffraction method on TiAl alloys of varying compositions and showed based on density and lattice parameter measurements that, in off-stoichiometric Al rich alloys, the excess Al atoms form anti-site defects and otherwise preserve long-range order. Vujic, Li and Whang (1988) conducted similar experiments on rapidly solidified and annealed samples of TiAl, and concurred that the anti-site defects are predominant in Al-rich off-stoichiometric TiAl alloys.

The TiAl fundamental unit cell, shown in Figure 14 can be used to model the structure of TiAl with the anti-site defects on the Al sublattice. The structure is tetragonal and is defined by the space group P4/mmm. It contains one Ti and one Al atom per unit cell and can be described by two interpenetrating Ti and Al primitive tetragonal sublattices. In this model (Model I), the excess Al atoms in off-stoichiometric TiAl, are randomly distributed in all the Ti sites. As a result the condition for a diffraction maximum (structure factor > 0) does not change and the only reflections that would be observed with respect to
the corresponding \( L1_0 \) unit cell are those with \( h+k=2n \). Hence, even though this model of random distribution of the excess Al atoms on all the Ti sites considers the anti-site defects, it does not explain the observation of diffuse intensities corresponding to kinematically forbidden reflections with \( h+k=2n+1 \) (Figure 9 and Figure 10 on pages 44 and 45). Hence an alternative scheme which could explain these diffuse intensities has been considered.

This alternate model (Model II) is based on the TiAl \( L1_0 \) unit cell shown in Figure 15. The excess Al atoms are preferentially distributed on one of the Ti sites (\( Ti^{ll} \) in the figure). Hence, the static structure factor equation in (3.4) can be modified as,

\[
F_g(s) = \left\{ f_{Ti}^x(s) + [f_{Ti}^x(s) \cdot (1-4x) + f_{Al}^x(s) \cdot 4x] \exp(-\pi [h+k]) \right\} \\
+ \left\{ f_{Al}^x(s) \cdot \exp(-\pi [h+l]) + \exp(-\pi [k+l]) \right\}
\]

(3.5)

where, \( x \) is the fraction of excess Al (0.04 in case of the Ti-54Al alloy). Hence the percentage of Al atoms on the ordered Ti site (\( Ti^{ll} \)) would be four times the percentage of excess Al atoms in the alloy since the \( L1_0 \) unit cell has a 4 atom basis. For example in Ti-54Al, the 4\% excess Al atoms implies a composition of 0.84 Ti and 0.16 Al on this site. Using this method of modeling for excess Al atoms, weak intensities for the kinematically forbidden reflections with \( h+k=2n+1 \) are obtained.

In the present work involving least square refinement to determine Debye-Waller factors, both the schemes of ordering (involving a random distribution of excess Al or an ordered distribution of excess Al atoms) have been used side by side and the results have been compared (sections 3.1.4 and 3.1.5).

The Wilson plot method described in section 3.1.1 uses the \( L1_0 \) unit cell with preferential distribution of all Al atoms on one of the Ti sites in order to account for the forbidden reflections.
Figure 14: TiAl fundamental unit cell. Shaded circles indicate Ti sites which are partially occupied by Al atom in Al-rich off-stoichiometric alloys. Open circles indicate Al sites.

Figure 15: Conventional TiAl L$_1_0$ unit cell. Partly shaded circles indicate Ti sites which are partially occupied by Al atoms (Ti$^{III}$) in Al-rich off-stoichiometric alloys. Open circles indicate Al sites. Filled circles indicate the pure Ti sites (Ti$^I$).
3.1.3: Lattice parameters

Accurate lattice parameters have been determined by refining the \{242\} and \{224\} reflection intensities obtained by four-circle single crystal x-ray diffraction. This involves refining the angular position of all the equivalent reflections of \{242\} and \{224\} type which span the entire accessible Ewald’s sphere. Hence, an accurate orientation matrix can be obtained which would provide accurate lattice parameters. Table 1 gives the lattice parameters of Ti-54Al and Ti-56Al thus obtained. On an average the standard deviation is of the order 0.0005 Å. The \(c/a\) ratio decreases slightly with increasing Al percentage. This could be because the Al atom is smaller than the Ti atom and considering anti-site defects in Al-rich alloys, the volume of the unit cell should decrease with increasing Al percentage. However it should be noted at this point that the compositions of the alloys used in the model are the nominal compositions and that the actual composition of the alloys could be different by as much as ±1%. Comparison of the lattice parameters obtained in the present work to those previously reported is given in Table 2.

Bumps, et al. (1952) used x-ray powder diffraction to determine the lattice parameters from TiAl alloys of various compositions which were heat treated at 1200°C and then quenched to room temperature. Comparing their results on lattice parameters, while the \(a\) parameters from the present work are slightly higher, the \(c\) parameters are very similar. The \(c/a\) ratio decreases slightly in the present case, contrary to their observations.

Vujic, et al. (1988) have used the x-ray powder diffraction method on rapidly-solidified samples of \(\gamma\)-TiAl to determine the lattice parameters. Comparing their results for the Ti-55Al alloy with an average value obtained from the present work, it can be observed that, their \(a\) parameter is lower while the \(c\) parameter is comparatively higher. The \(c/a\) ratio is smaller in the present case.
Braun, Ellner and Predel (1995) have measured the lattice parameters in Ti-Al alloys of composition ranging from Ti-50Al to Ti-60Al using x-ray powder diffraction for various temperatures. In comparison with the present work, both the \( a \) and \( c \) parameters and the \( c/a \) ratio reported by them are higher than those obtained from the present work.

Menon, Fox and Mahapatra (1996) used x-ray powder diffraction to determine the lattice parameters. By comparison of their results with those obtained from the current work, it can be seen that for a given composition, the lattice parameters are quite different. The \( c \) parameters of the current work are lower in comparison and also increase with composition while the \( c \) parameters from Menon, et al. decrease with composition.

The single crystal x-ray diffraction lattice parameters measured in the present work are expected to be accurate because the set of \{242\} and \{224\} reflections span the entire Ewald sphere and give a self consistent accurate measurement of the orientation and lattice parameters of the single crystal. Also, prior to measuring these parameters the lattice constants of a ruby single crystal (used as a standard) were measured and matched with those from literature in order to align the diffractometer perfectly.

The lattice parameters thus obtained for Ti-54Al and Ti-56Al crystals have been used for the non-linear least square refinement of Debye-Waller factors. These parameters were also linearly extrapolated to the required composition and used in the CBED method to determine structure factors in TiAl (discussed in section 3.3).
<table>
<thead>
<tr>
<th>Composition (at. % Al)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.00</td>
<td>3.9922 ± 0.0004</td>
<td>4.0706 ± 0.0004</td>
<td>1.0196</td>
</tr>
<tr>
<td>56.00</td>
<td>3.9907 ± 0.0004</td>
<td>4.0679 ± 0.0007</td>
<td>1.0193</td>
</tr>
</tbody>
</table>

Table 1: Lattice parameters obtained from single crystal x-ray diffraction experiment with other lattice parameters from literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Composition (at. % Al)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current work</td>
<td>54.00</td>
<td>3.9922</td>
<td>4.0706</td>
<td>1.0196</td>
</tr>
<tr>
<td>Current work</td>
<td>56.00</td>
<td>3.9907</td>
<td>4.0679</td>
<td>1.0193</td>
</tr>
<tr>
<td>Bumps, et al.</td>
<td>52.13</td>
<td>3.984</td>
<td>4.065</td>
<td>1.020</td>
</tr>
<tr>
<td>Bumps, et al.</td>
<td>55.23</td>
<td>3.972</td>
<td>4.067</td>
<td>1.024</td>
</tr>
<tr>
<td>Vujic, et al.</td>
<td>55.0</td>
<td>3.985</td>
<td>4.071</td>
<td>1.022</td>
</tr>
<tr>
<td>Braun, et al.</td>
<td>52.5</td>
<td>3.994</td>
<td>4.080</td>
<td>1.019</td>
</tr>
<tr>
<td>Braun, et al.</td>
<td>55</td>
<td>3.989</td>
<td>4.081</td>
<td>1.022</td>
</tr>
<tr>
<td>Menon, et al.</td>
<td>54</td>
<td>3.9956</td>
<td>4.0838</td>
<td>1.0221</td>
</tr>
<tr>
<td>Menon, et al.</td>
<td>56</td>
<td>3.9912</td>
<td>4.0815</td>
<td>1.0226</td>
</tr>
</tbody>
</table>

Table 2: Comparison of the lattice parameters determined in the current work with other lattice parameters from literature.
3.1.4: Isotropic site specific Debye-Waller factors

Isotropic site specific Debye-Waller factors were determined using non-linear least-square refinement to fit the x-ray diffraction data from Ti-54Al and Ti-56Al crystals. The software XTAL4 3.4 installed on an SGI Indy was used for the calculations. The program CRYLSQ (least square analysis program) in XTAL was used for the least square refinement to fit the calculated structure factors with the experimental ones. This program accepts the crystal structure information (space group, number of atoms), atom positions and occupancy of each site as input and calculates the static structure factors. The experimental structure factors are fitted by the introduction of Debye-Waller factor, according to the isotropic or anisotropic model specified, to account for the reduction in the diffracted intensities due to thermal vibration. The scale factor is refined by matching the experimental and calculated intensities of fundamental low order reflections and with a input overall B factor. Figure 16 gives a flow-chart which shows the steps used in the refinement procedure to obtain accurate Debye-Waller factors.

The agreement factor R (which is defined as the ratio of the sum of the absolute difference in experimental and calculated structure factors over the sum of experimental structure factors - section 2.2.4) was used to estimate the goodness of the fit. Isotropic extinction correction was applied with the least-square refinement of Debye-Waller factors. Unique temperature factors were refined for Ti and Al atoms at different sites. Both the ordering schemes of distributing excess Al atoms randomly on all Ti sites and preferentially on one of the Ti sites (described in section 3.1.3) have been used and the results thus obtained are compared below.

4 Crystal structure analysis software provided by the University of Western Australia
Integrated intensity data from single crystal x-ray diffraction of Ti-54Al and Ti-56Al

Lorentz-Polarization and absorption correction using TEXSAN structure analysis software

Wilson Plot method to determine overall "B factor"

using the B-factor determined from Wilson plot method as the initial value, least square refinement with the program XTAL Parameters refined:
1. isotropic or anisotropic Debye-Waller factors
2. isotropic extinction correction
3. composition or occupancy

Figure 16: Flow chart showing the steps in refining accurate site specific isotropic or anisotropic Debye-Waller factors.
Figure 17 shows the experimental and calculated structure factors for Ti-54 Al and Ti-56Al estimated using a random distribution of excess Al atoms on all Ti sites (Model I) with the TiAl fundamental unit cell as basis. These experimental structure factors have been corrected for extinction. The two sets of reflections seen are the fundamental (with a higher intensity) and superlattice reflections. The forbidden reflection intensities are cannot be fitted in this model. Figure 18 shows the experimental and calculated structure factors for the forbidden reflections in Ti-54Al and Ti-56Al using an ordered distribution of excess Al atoms on one of the Ti sites (Model II). The fit for the fundamental and superlattice reflections from Model II was similar to that obtained from Model I (Figure 17). The calculated structure factors predict a good average value for the structure factors of the forbidden reflections.

The values of isotropic Debye-Waller factors obtained from Model I and II for various cases of refinement with the Ti-54Al and Ti-56Al data are given in Table 3 and Table 4 respectively. The refined isotropic extinction parameter is also shown in the tables. These results show that, while the extinction correction improves the agreement with the experimental data (reduces the R factor), it does not change the Debye-Waller factor. The extinction correction is higher for the Ti-56Al alloy. Occupancy of the Ti sites (percentage of excess Al and hence composition of the alloy) was also refined. The least square refinement of composition yields the compositions of the two alloys to be lower than their nominal composition. The best fit is obtained by refining the extinction correction and site occupancy / composition. The R factor is lower or the fit is better for fundamental and superlattice reflection (Model I).
<table>
<thead>
<tr>
<th>Refined parameters</th>
<th>Model</th>
<th>Fitted Composition</th>
<th>B$_{\text{Al}}$ ($\text{Å}^2$)</th>
<th>B$_{\text{Ti}}$ ($\text{Å}^2$)</th>
<th>B$_{\text{Ti/Al}}$ ($\text{Å}^2$)</th>
<th>Extinction parameter</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWF only</td>
<td>I</td>
<td>-</td>
<td>0.515</td>
<td>0.592</td>
<td>0.592</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>DWF only</td>
<td>II</td>
<td>-</td>
<td>0.657</td>
<td>0.707</td>
<td>0.486</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>DWF, EXT</td>
<td>I</td>
<td>-</td>
<td>0.514</td>
<td>0.592</td>
<td>0.592</td>
<td>17.6</td>
<td>2.8</td>
</tr>
<tr>
<td>DWF, EXT</td>
<td>II</td>
<td>-</td>
<td>0.518</td>
<td>0.707</td>
<td>0.486</td>
<td>55.4</td>
<td>3.5</td>
</tr>
<tr>
<td>DWF, PP</td>
<td>I</td>
<td>52.2</td>
<td>0.511</td>
<td>0.613</td>
<td>0.613</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>DWF, PP</td>
<td>II</td>
<td>52.7</td>
<td>0.516</td>
<td>0.710</td>
<td>0.516</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>DWF, EXT, PP</td>
<td>I</td>
<td>52.05</td>
<td>0.509</td>
<td>0.614</td>
<td>0.614</td>
<td>51.6</td>
<td>2.7</td>
</tr>
<tr>
<td>DWF, EXT, PP</td>
<td>II</td>
<td>52.6</td>
<td>0.515</td>
<td>0.709</td>
<td>0.516</td>
<td>45.4</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 3: Isotropic site specific room temperature DWF for Ti-54Al single crystal modeled using Model I and Model II. (DWF - Debye-Waller factor, PP - composition refinement, EXT - isotropic extinction correction and refinement, Compositions are given as atomic percentage of Al).
<table>
<thead>
<tr>
<th>Refined parameters</th>
<th>Model</th>
<th>Fitted Composition</th>
<th>$B_{\text{Al}}$ (Å$^2$)</th>
<th>$B_{\text{Ti}}$ (Å$^2$)</th>
<th>$B_{\text{Ti/Al}}$ (Å$^2$)</th>
<th>Extinction parameter</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWF only</td>
<td>I</td>
<td>-</td>
<td>0.539</td>
<td>0.651</td>
<td>0.651</td>
<td>-</td>
<td>3.1</td>
</tr>
<tr>
<td>DWF only</td>
<td>II</td>
<td>-</td>
<td>0.548</td>
<td>0.676</td>
<td>0.645</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>DWF, EXT</td>
<td>I</td>
<td>-</td>
<td>0.537</td>
<td>0.650</td>
<td>0.650</td>
<td>77</td>
<td>2.8</td>
</tr>
<tr>
<td>DWF, EXT</td>
<td>II</td>
<td>-</td>
<td>0.546</td>
<td>0.674</td>
<td>0.644</td>
<td>111.7</td>
<td>3.8</td>
</tr>
<tr>
<td>DWF, PP</td>
<td>I</td>
<td>54.5</td>
<td>0.534</td>
<td>0.670</td>
<td>0.670</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>DWF, PP</td>
<td>II</td>
<td>53.3</td>
<td>0.540</td>
<td>0.663</td>
<td>0.736</td>
<td>-</td>
<td>4.4</td>
</tr>
<tr>
<td>DWF, EXT, PP</td>
<td>I</td>
<td>54.0</td>
<td>0.530</td>
<td>0.675</td>
<td>0.675</td>
<td>116.3</td>
<td>2.7</td>
</tr>
<tr>
<td>DWF, EXT, PP</td>
<td>II</td>
<td>53.2</td>
<td>0.536</td>
<td>0.660</td>
<td>0.737</td>
<td>174</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 4: Isotropic site specific room temperature DWF for Ti-56Al single crystal modeled using Model I and Model II. (DWF - Debye-Waller factor, PP - composition refinement, EXT - isotropic extinction correction and refinement, Compositions are given as atomic percentage of Al).
Figure 19 shows plots of the isotropic site specific Debye-Waller factors estimated using both Model I and Model II against the nominal composition of the alloy. The effect of compositional inaccuracies on Debye-Waller factors were also investigated in this work. This was performed by varying the composition of the alloy from the nominal composition by ±0.5% and measuring the variation in the Debye-Waller factor. The results are shown as error bars in Figure 19. The error bars shown in this plot are very small and, in most cases they are smaller than the symbol used to represent a data point.

From the results of the least-square refinement of Ti-54Al and Ti-56Al alloys the following observations can be made on isotropic site specific Debye-Waller factors:

1. The representation of Debye-Waller factors as isotropic mean square displacement amplitude assumes that the amplitude of vibration is same in all directions.

2. Site specific Debye-Waller factor measurements show that the Debye-Waller factor of the Al atom is lower than that of the Ti atom. The mixed site (Ti site which contains the excess Al atoms) in case of Model II has a intermediate Debye-Waller factor in Ti-54Al and has the highest Debye-Waller factor in Ti-56Al.

3. The fit for the fundamental and super-lattice reflections is very good. However, there is a scatter in the experimental data for higher order reflections while the calculated data describes a smooth curve. The scatter in the experimental data is normally construed as experimental errors in measurement of integrated intensity data. However, the anisotropic Debye-Waller factors, discussed in the following section, explains this scatter.

4. The calculated structure factors obtained using the isotropic Debye-Waller factors and Model II, predict a good average value for the experimental structure factors for the kinematically forbidden reflections with $h+k=2n+1$. The prediction is better in the case of Ti-54Al than Ti-56Al.
5. Extinction correction improves the goodness of fit (R factor) and indicates that isotropic extinction correction is required for accurate Debye-Waller factor measurements from experimental data.

6. The Debye-Waller factors obtained for Ti-56Al are overall higher than those for Ti-54Al. This is consistent with the observations from the Wilson plot method.

7. The errors in composition affect the Debye-Waller factor of the site with Ti site with excess Al atoms the most. The Debye-Waller factor of the Al sites do not change with errors in composition. This is consistent with the model used as the Al site composition is modeled to remain the same even if the alloy composition changed by a percent. Overall, the error in Debye-Waller factors with change in composition is very small.

8. The goodness of fit is better for fundamental and superlattice reflections (Model I) then when the forbidden reflections are included (Model II).
Figure 17: Experimental structure factors and calculated factors fitted using isotropic site specific Debye-Waller factors with random distribution of excess Al atoms in all Ti sites for Ti-54 and Ti-56Al.
Figure 18: A comparison of experimental structure factors and calculated structure factors for forbidden reflection in Ti-54Al and Ti-56Al. The calculated structure factors were fitted using isotropic DWF and Model II.
Figure 19: Isotropic temperature factors estimated in Ti-54 and 56Al using Model I (fundamental unit cell, top) and Model II (L1₀ unit cell, bottom).
3.1.5: Anisotropic site specific Debye-Waller factors

Following the determination of isotropic Debye-Waller factors in TiAl, the anisotropic site specific Debye-Waller factors were obtained in a similar manner using Model I and Model II for the ordering of excess Al atoms. Due to the symmetry in TiAl, the only thermal displacement parameters that need to be determined for each specific site are \( \langle u_i^2 \rangle \) and \( \langle u_j^3 \rangle \) (section 2.i). In the program XTAL the values of the thermal displacement parameters \( \langle u_i^5 \rangle \) and \( \langle u_j^3 \rangle \) were refined for each atom in a different site. The isotropic site specific Debye-Waller factors were used as the initial value for the anisotropic site specific factors such that \( \langle u_i^2 \rangle = \langle u_j^5 \rangle = \langle u \rangle \) and the independent values of \( \langle u_i^5 \rangle \) and \( \langle u_j^3 \rangle \) were then refined. Simultaneous isotropic extinction correction was also applied to the experimental structure factor data.

Using these anisotropic temperature factors gave a very good agreement between experiment and theory. Figure 20 shows the experimental and calculated structure factors obtained in Ti-54Al and Ti-56Al using Model I. The structure factors for the fundamental and superlattice reflections using Model II were similar to those from Model I. An expanded view comparing the structure factors fitted using the isotropic Debye-Waller factors and anisotropic Debye-Waller factors for Ti-56Al with L_1_0 unit cell basis is shown in Figure 21. Similar results were obtained for Ti-54Al. From this plot it is evident that the calculated structure factors fit the scatter in the experimental structure factors for higher order reflections accurately. Figure 22 shows the comparison of experimental and calculated structure factors for forbidden reflections computed using Model II and anisotropic temperature factors. The scatter in the forbidden reflections is also predicted well in this model which assumes a preferential ordering of excess Al atoms on one of the Ti sites and calculates anisotropic temperature factors.
Figure 20: Experimental structure factors with fitted calculated structure factors for the fundamental and superlattice reflections, calculated using Model I and anisotropic Debye-Waller factors.
Figure 2i: Expanded view of experimental structure factors and calculated structure factors fitting the isotropic (top) and anisotropic (bottom) Debye-Waller factors in Ti-56Al.
Figure 22: Experimental and calculated structure factors for forbidden reflections in Ti-54Al and Ti-56Al computed using Model II and fitted with anisotropic temperature factors.
The effects of compositional uncertainties were also evaluated by varying the composition of the alloy from the nominal composition by ±0.5% and measuring the variation in the Debye-Waller factor. This uncertainty is shown as error bars on the plot of anisotropic temperature factors vs. composition in Figure 23. The y2 axis on this plot shows the factor corresponding to the refinement. R factors are much lower compared to the isotropic case which indicates a better fit. Compositional inaccuracies do not affect the Debye-Waller factors of the Al sites while they affect the Ti sites with excess the most.

From the results of anisotropic temperature factors determined by least-square refinement to match experimental and calculated structure factors in Ti-54Al and Ti-56Al alloys, the following observations can be made:

1. The representation of Debye-Waller factors as anisotropic mean square displacement amplitude is consistent with the symmetry in the alloy and is important.

2. Site specific anisotropic Debye-Waller factor refinements show that the Debye-Waller factor of the Al site is lower than that of the pure Ti site in case of Model II. The values of the Debye-Waller factors of the Ti and Al sites are about the same as in Model I. The mixed Ti site in case of Model II has the lowest values of \( <u_2^2> \).

3. The fit for the fundamental and super-lattice reflections is very good and it also predicts the scatter in the experimental data for higher order reflections accurately when anisotropic Debye-Waller factors are used. The scatter in the experimental data is normally attributed to experimental errors in measurement of integrated intensity data. However, the anisotropic Debye-Waller factors show that it is associated with the anisotropic thermal behaviour of TiAl.

4. The calculated structure factors obtained using the anisotropic Debye-Waller factors from Model II, fit the experimental structure factors for the kinematically forbidden reflections very well and also show a scatter with respect to the higher order reflections
which is observed in the experimental structure factors. However, the larger scatter in
the experimental structure factors could be due to error in measuring the integrated
intensities for these weak reflections. The prediction is better in the case of Ti-56Al than
for Ti-54Al.

5. Extinction correction improves the goodness of fit (R factor) and indicates that isotropic
extinction correction is required for accurate Debye-Waller factor measurements from
experimental data. The extinction correction was higher for Ti-56Al suggesting that it
could be closer to a perfect crystal.

6. The Debye-Waller factors obtained for Ti-56Al are overall higher than those for Ti-
54Al. This is consistent with the observations from the Wilson plot method (page 48).

7. The errors in composition do not affect the Debye-Waller factors obtained from Model I
significantly. In Model II the root mean square amplitude of vibration of the site with Ti
site with excess Al atoms is the most affected. The Debye-Waller factor of the Al sites
do not change with errors in composition. This is consistent with the model used as the
Al site composition is modeled to remain the same even if the alloy composition
changed by a percent. Overall, the error in Debye-Waller factors with change in
composition is very small.

8. The goodness of fit is better for fundamental and superlattice reflections (Model I) than
when the forbidden reflections are included (Model II). This has been attributed to large
statistical error associated with the low intensity of the forbidden reflections. The
lowest R value of 1.1% was obtained for Ti-56Al reflections fitted with Model I (not
including the forbidden reflections).
Figure 23: Anisotropic temperature factors obtained by least-square refinement of x-ray data from Ti-54 and 56Al. The temperature factors in Ti-54Al are lower than in Ti-56Al.
3.2: Ti<sub>3</sub>Al<sub>5</sub> ordering

Ti<sub>3</sub>Al<sub>5</sub> superstructure type ordering has been reported previously in various studies on Al rich γ-TiAl alloys of compositions 54-63 at.% Al (discussed in section 1.2). The Ti<sub>3</sub>Al<sub>5</sub> ordering involves the substitution of excess Al into selected Ti sites on the Ti plane. The x-y projection of the Ti<sub>3</sub>Al<sub>5</sub> unit cell is shown in Figure 24. The unit cell parameters of the Ti<sub>3</sub>Al<sub>5</sub> superstructure (s) are related to those of L1<sub>0</sub> γ-TiAl unit cell as a<sub>s</sub> = 2√2a and c<sub>s</sub> = c. It can be seen that four Ti sites have been replaced by Al atoms. This structure is tetragonal and is defined by the space group P4/mmbm.

In the present work such Ti<sub>3</sub>Al<sub>5</sub> ordering was observed in electron diffraction studies of single crystal γ-TiAl of compositions Ti-54 at.% Al and Ti-56 at.% Al. Figure 25 shows the experimental and simulated selected area diffraction (SAD) patterns obtained from the [111] zone axis of TiAl. A row of extra reflections which appears between the reflections corresponding to the L1<sub>0</sub> structure can be clearly discerned in the experimental patterns. The simulated SAD pattern presented here has been generated assuming the presence of Ti<sub>3</sub>Al<sub>5</sub> precipitates (ppt) in a γ-TiAl matrix with an orientation relationship that can be expressed as (001)<sub>ppt</sub>∥(001)<sub>r</sub> and {100}<sub>ppt</sub>∥{110}<sub>r</sub>. This pattern matches the experimental patterns obtained from Ti-54 and 56 Al alloys. The distance between the superstructure reflections and their exact positions changes with the varying aluminum percentage. This could be attributed to the change in the lattice parameters of the L1<sub>0</sub> phase (reported in section 3.1.3) due to varying the Al compositions and the correspondingly affected lattice parameters of the Ti<sub>3</sub>Al<sub>5</sub> phase. The ordering is more pronounced in Ti-56Al than in Ti-54Al. These results are also consistent with earlier reports of ordered precipitation of Ti<sub>3</sub>Al<sub>5</sub> type in Al-rich γ-TiAl alloys [Mikla, et al. (1982)].
characteristics of the SAD patterns from Ti-54 and 56Al for other low index zone axes (other than [111]) were also consistent with Ti$_3$Al$_5$ type ordering.

Diffraction contrast images from the Ti-56 at.% Al alloy are shown in Figure 26. The bright field image does not show any distinct features, while the dark field image generated with the (232) superstructure reflection reveals the presence of ordered domains of Ti$_3$Al$_5$. These domains are seen as strongly diffracting bright regions in the image and are about 5.0 nm in size.

From these observations of Ti$_3$Al$_5$ ordering in the Ti-54Al and Ti-56Al crystals the following observation can be made:

1. Ordering was observed in the Al rich off-stoichiometric γ-TiAl alloys for Al compositions of 54 and 56 atomic percent. The ordering is more pronounced in Ti-56Al. However, the ordering could not be detected in the x-ray experiments (section 3.1). This may be attributed to the difference in scattering cross sections for x-ray and electron diffraction.

2. The observation of forbidden reflections (hkl) with h+k=2n+1 (discussed in section in 3.1.1) in the x-ray diffraction experiments indicated a substitution of excess Al onto the Ti sublattice in an ordered fashion. Hence, it may be suggested that this sublattice ordering could be a precursor to the Ti$_3$Al$_5$ type ordering.

3. The presence of this ordered phase in the Ti-54Al and Ti-56Al alloys could reduce the amount of excess atoms in these off-stoichiometric alloys. The lower composition obtained for these alloys from least square refinement analysis (section 3.1.4 and 3.1.5) may therefore be potentially attributed to the presence of precipitates of this Al rich phase.
Figure 24: (001) plane of the Ti₃Al₅ unit cell. \( a = 2\sqrt{2}a \) and \( c = c_\gamma \) where \( \gamma \) is represented by the conventional \( L1_0 \) unit cell.
Figure 25: Selected area diffraction patterns for the [111]-zone of γ-TiAl alloys with Al-rich compositions of Ti-54Al (a) and Ti-56Al (b) and a simulated selected area diffraction pattern (c) including the weaker reflections arising from Ti₃Al₃ ordering.
Figure 26: Diffraction contrast images of Ti-56 at.% Al alloy, (top) many beam bright field and (bottom) dark field using $\langle 23\bar{2} \rangle$ reflection, for the beam direction [111].
3.3: CBED structure factor refinement

The energy-filtered CBED method has been used to determine accurate structure factors in TiAl (Swaminathan, et al. (1996)). It was established in the previous sections that the accurate and precise measurement of structure factors using the CBED rocking curve matching is limited by the uncertainties in the values for the site specific Debye-Waller factors (section 2.3.2). In the present work accurate site specific anisotropic Debye-Waller factors have been determined for Ti-54 and 56 at.% Al (section 3.1.5). Hence, it appears now possible to determine accurate structure factors in TiAl using these anisotropic Debye-Waller factors.

The CBED patterns for Ti-51.3 at.% Al and the programs written for matching of rocking curves by Swaminathan (1994) were used for the determination of the 200 structure factor in TiAl. The programs were modified to calculate structure factors using the anisotropic Debye-Waller factors. The temperature factors obtained for the Ti-54 at.%Al and 56 at.%Al nominal compositions have been linearly extrapolated to compositions of Ti-50.3 at.%Al, 51.3 at.%Al and 52.3 at.%Al to determine the anisotropic temperature factors at these composition (as shown in Figure 27). This linear extrapolation appears to be reasonable since it only bridges a narrow composition range. The lattice parameters obtained from the x-ray diffraction experiments were also extrapolated to the compositions of Ti 50.3 at.%Al, 51.3 at.%Al and 52.3 at.%Al as shown in Figure 29. The 200 structure factors in TiAl have been calculated using these extrapolated anisotropic temperature factors and lattice parameters during the matching of the rocking curve intensities by the CBED method. The 200 structure factors determined by this approach, for two different sample thickness’ are shown in Table 5 and have been plotted against composition in Figure 30. For the composition of Ti-52.3 at.%Al, the error due to variation in thickness is
at a minimum. These structure factors can be compared with the earlier results reported by Swaminathan, et al. (1997a), which involved linear extrapolation of isotropic Debye-Waller factors as shown in Figure 32. The slope which represents the change in structure factors with compositional change is lower for the current work than that of the earlier results. Also the best accuracy with respect to varying foil thickness is obtained at a composition of 52.3% which is more accurate than the earlier results. The structure factors obtained from a foil thickness of ≈185 nm are higher than those obtained for a foil thickness of ≈85 nm in the present work, whereas by Swaminathan, et al. (1996) reported the reverse trend to be true.

The composition refined x-ray temperature factors were also extrapolated to the specific compositions of Ti-50.3 at.%Al, 51.3 at.%Al and 52.3 at.%Al and were used in the CBED method to determine the 200 structure factors (e.g. Figure 28). The composition refined temperature factors of the pure Ti site and the Ti site with excess Al atoms when linearly extrapolated, meet near a composition of 50%. This is an interesting result as this is what would be expected on extrapolation of the sublattice ordering of excess Al atoms. At 50% when there are no off-stoichiometric excess Al atoms the Debye-Waller factors of both the Ti sites are expected to be equal, as is observed here. The 200 structure factors obtained using the compositionally refined temperature factors are shown in Table 6. Figure 31 shows a plot of the structure factors versus composition for the two different thickness’ (85 and 185 nm). From this plot it can be seen that the errors due to changes in foil thickness is maximum values in this case. There is a very large difference between the structure factors obtained from the two thickness’ for the composition of 51.3. Hence, although this model with compositionally refined temperature factors fits the x-ray data well, it does not give precise results of 200 structure factors in TiAl.
Figure 27: Anisotropic temperature factors obtained by non-linear least square refinement using Model II to fit structure factor data with no composition refinement from single crystal x-ray diffraction. The temperature factors are extrapolated to the composition of 50.3, 51.3 and 52.3 to obtain the anisotropic temperature factors at these composition which are used the CBED method to determine the 200 structure factor in TiAl.
Figure 28: Anisotropic temperature factors obtained by non-linear least square refinement using Model II to fit structure factor data with-composition refinement from single crystal x-ray diffraction. The temperature factors are extrapolated to the composition of 50.3, 51.3 and 52.3 to obtain the anisotropic temperature factors at these composition which are used the CBED method to determine the 200 structure factor in TiAl.
Figure 29: Linear extrapolation of the a and c lattice constants obtained from x-ray diffraction experiments on Ti-54 and 56Al. The extrapolated parameters were used in the CBED method to determine accurate structure factors in Ti-Al.
Table 5: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with no composition refinement)

<table>
<thead>
<tr>
<th>Composition</th>
<th>200 structure factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness 85 nm</td>
</tr>
<tr>
<td>50.3 Al</td>
<td>43.7480</td>
</tr>
<tr>
<td>51.3 Al</td>
<td>43.1730</td>
</tr>
<tr>
<td>52.3 Al</td>
<td>42.6756</td>
</tr>
</tbody>
</table>

Figure 30: Compositional dependence of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with no composition refinement)
Table 6: Compositional dependency of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with overall composition refinement)

<table>
<thead>
<tr>
<th>Composition</th>
<th>200 structure factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness 85 nm</td>
</tr>
<tr>
<td>50.3 Al</td>
<td>43.5198</td>
</tr>
<tr>
<td>51.3 Al</td>
<td>42.9539</td>
</tr>
<tr>
<td>52.3 Al</td>
<td>42.6593</td>
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</tbody>
</table>

Figure 31: Compositional dependency of 200 structure factor in TiAl; Structure factors were determined from the CBED method using anisotropic temperature factors (determined with overall composition refinement)
Figure 32: Comparison of 200 structure factor in TiAl obtained from the CBED rocking curve method using anisotropic temperature factors obtained in the current work with structure factors obtained using isotropic temperature factors from Swaminathan, et al. (1996).
CHAPTER 4

SUMMARY AND CONCLUSIONS

The work presented in this thesis has been summarized below.

1. Accurate and precise Debye-Waller factors have been determined for Ti-54Al and Ti-56Al alloys from single crystal x-ray diffraction experiments.

2. The Debye-Waller factors in TiAl are anisotropic with the \( u^2 \) values being higher than the \( u^2 \) values. This implies that the amplitude of vibration is higher perpendicular to the [001] direction (on pure Ti or Al planes) than along the [001] direction.

3. The model which used anisotropic Debye-Waller factors with preferential ordering of excess Al atoms on one of the Ti sites (sublattice ordering) appeared suitable to explain the weak intensities observed for the kinematically forbidden reflections.

4. Composition refinement changed the values of the anisotropic temperature factors while the extinction correction improved the goodness of fit and did not change the temperature factors.

5. Linear extrapolation of the composition-refined Debye-Waller factors showed that near a composition of 50% Al the temperature factor of the pure Ti site and the Ti site with excess the Al atoms is the same. This is consistent with the sub-lattice ordering model used.
6. Compositional inaccuracies did not significantly affect the Debye-Waller factors determined from non-linear least-square refinement.

7. Accurate lattice parameters were determined for Ti-54Al and Ti-56Al from the x-ray diffraction experiment.

8. Ti₃Al₄ type ordering was observed in the electron diffraction experiments from the Ti-54Al and Ti-56Al crystal, but sufficient intensity could not be detected in the x-ray diffraction experiments. Because of this, and weak intensities obtained for the kinematically forbidden reflections, it could be suggested here that the sublattice ordering observed in the x-ray diffraction experiment could be a precursor to the Ti₃Al₄ type ordering.

9. The anisotropic temperature factors and lattice parameters obtained from x-ray diffraction for Ti-54Al and Ti-56Al were extrapolated to composition up to 50% Al. The extrapolated values at these compositions were used in the CBED method to determine the 200 structure factor in TiAl.

10. Structure factors in TiAl were determined using the CBED method. Effect of compositional uncertainties and sample thickness was also studied. The structure factors obtained from a foil thickness of ≈185 nm are higher than those obtained from a foil thickness of ≈85 nm. This result is contrary to the results reported by Swaminathan, et al. (1997).

11. The most precise values of the 200 structure factor in TiAl was obtained using the anisotropic temperature factors which were fitted by correcting for extinction but not for sample composition.
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93