1986

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Theodore Douglas. Lowes

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
Precipitation and Nucleation Entropy in the
Al-Ti-Be Alloy System

by

Theodore Douglas Lowes

A Thesis
Submitted to the
Faculty of Graduate Studies and Research
Through the Department of
Engineering Materials in Partial Fulfillment
of the Requirements for the Degree
of Master of Applied Science at
the University of Windsor

Windsor, Ontario, Canada
1986

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ABSTRACT

The effect of Be on precipitation in Al-Ti alloys is studied. The work involves comparing the behaviour of Al-0.2wt%Ti, Al-0.2wt%Ti-0.2wt%Be and Al-0.2wt%Be alloys during aging following a solution treatment at 630°C for 1 hour. Microhardness results show that the Al-Ti alloy does not age harden at room temperature, 150°C or 350°C. Al-Ti alloys containing Be show significant hardening which is characteristic of clustering and GP zone formation prior to stable phase formation at room temperature and 150°C. However, at 350°C, the hardness reaches a maximum and then decreases very rapidly indicating precipitation of the stable phase. Al-Be alloys exhibited a slight hardness increase for room temperature and 150°C aging due to Be clustering; however, aging at 350°C produced an immediate significant hardness decrease.

Electrical resistivity increases in Al-Ti alloys predict no precipitation at aging temperatures of 350°C - 410°C. Al-Ti-Be alloys showed significant resistivity decreases characteristic of precipitation in alloy systems. It is proposed that Ti and Be atoms interact with vacancies to give an increased nucleation rate by forming clusters and GP zones which are very slow to form in Al-Ti alloys without Be.

Optical microscopy and X-ray diffraction data are in agreement with the nucleation entropy theory. That is, incorporation of Be into the precipitating phase produces
an increased nucleation rate evidenced by more precipitates in Al-Ti alloys containing Be.
This thesis is dedicated to my loving wife Heather
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CHAPTER I

INTRODUCTION

Refinement of structure is the sole or principal means for improving the mechanical properties of many alloys, and is the basis of the microalloying processes currently gaining wide usage. In alloy castings, where thermomechanical processing is excluded, the nucleation mechanism in the solidification stage (and any subsequent precipitation stages) must be utilized to obtain the structure refinement.

In industry, small amounts of Ti are added to Al resulting in fine-grained structures with markedly improved mechanical properties. These improvements are the direct result of increased nucleation rates during solidification. In earlier work in the Engineering Materials Department at Windsor, it was shown that small additions of third elements to Al-Ti alloys (e.g., Si, Be) further enhances grain refinement on solidification. A thermodynamic theory based on the entropy of nucleation was developed to account for the enhanced grain refinement results. It was shown that the addition of a third element to the alloy in dilute concentrations will increase the nucleation entropy if it is concentrated in the nucleating or precipitating phase. Small increases in nucleation entropy result in a marked increase in the classical nucleation rate (N) due to the exponential dependence of N on the square of nucleation entropy. It was shown that for Al-Ti-Be alloys, Be concentrated in the primary TiAl₃ phase to give Ti(Al,Be)₃, and the significant enhancement in grain refine-
ment was in agreement with the increased nucleation entropy. Precipitation reactions in Al-Cu-Be alloys were also studied to test the nucleation entropy model for solid-solid reactions. It was found that Be concentrated in the CuAl₂ precipitate to give the approximate stoichiometric compound CuAl₁.₉Be₀.₁, giving a corresponding increase in the calculated nucleation entropy and nucleation rate for the CuAl₁.₉Be₀.₁ precipitate. The experimental results showed a significant increase in the precipitate count and transformation rate as required by an increase in nucleation rate.

The purpose of this study is to examine the effect of Be on precipitation of TiAl₃ in Al-Ti alloys; more specifically to determine if concentration of Be would also occur in the secondary TiAl₃ phase in the precipitation reaction, and if the precipitation rate would correspondingly be accelerated. The experimental procedures used in earlier studies on the Al-Cu-Be alloys were applied in this investigation, viz., optical and electron microscopy for determination of precipitate particle densities, and monitoring microhardness and resistivity changes during aging for determination of the kinetic parameters for the transformation process.
CHAPTER 2
LITERATURE REVIEW

2.1 Liquid-Solid Transformations

Grain refinement of Al castings by small additions of other elements is well known and has been practised for many years. Since it was first extensively reported by Reimann [1] in 1922, researchers have studied effects on Al castings by small additions of a host of elements, including Mg, Zr, V, Ta, Nb, Mo, W, B, Cr and Ti. Of all these elements, Ti is the best grain refiner of Al castings [2-4]. Further, enhancement of grain refinement in Al-Ti alloy castings was observed with small additions of ternary elements. These include B [5], C [5,6] and several other elements studied by Youdelis and co-workers [7-9], who reported significant enhancement by Ti when small amounts of Si and Be were added.

A fine-grained structure is very important for castings where mechanical working is not possible and intricate castings are required. In general as the grain size decreases, ultimate tensile strength increases [10], internal stresses are reduced in alloys with brittle constituents [11], and uniform solidification patterns result, promoting homogeneity and a uniform microporosity distribution [12]. Other benefits are a reduced tendency to hot tearing [10], dramatic increases in casting speeds [4] and reproducible conditions for subsequent metal working [11].

Although it is generally agreed that small additions of specific elements to Al greatly refines the structure, the
refinement mechanism is not agreed upon. Four theories have been proposed to explain the grain refinement mechanism, viz., concentration gradients and undercooling \cite{13}, boride/carbide heterogeneous nucleation \cite{5}, the peritectic reaction mechanism \cite{6}, and the nucleation entropy model \cite{14}. Requirements for effective nucleation are that Al should wet the surface of the nucleant which should be widely dispersed, the onset of nucleation should not be followed by rapid crystal growth so more nuclei may effectively operate, and the $\alpha$-Al and nucleant should have a good crystallographic fit. However, it has been suggested \cite{11} that the potency of a given catalyst is increased for small lattice disregistry in the order of 5-6%.

2.1.1 Concentration Gradients and Undercooling

In pure metals the solid and liquid compositions are the same throughout the solidification process. The resulting microstructure is comprised of columnar crystals grown from the solidification surface inwards \cite{13}. In the case of an alloy system (such as the Al(rich)-Ti system) which solidifies over a temperature range, concentration gradients are set up.

Youdelis and Yang \cite{8,9} reported moderate grain refinement improvement of Al containing Ti by increasing additions of several ternary elements having little or essentially no solubility in Al (extremely small distribution coefficients). These moderate improvements were attributed to concentration gradients in the surrounding liquid and the attendant constitutional supercooling that develops. As the ternary element
composition \( C'_0 \) was increased for a given alloy, grain counts increased. This is in agreement with the increased constitutional supercooling that will result ahead of the advancing solid-liquid interface with an increase in \( C'_0 \). The concentration gradient

\[
\frac{\partial c}{\partial x} = gR C'_0 \frac{1-k}{kD}
\]  

where \( R \) is the interface velocity, \( k(=C_s/C_L) \) the distribution coefficient, \( D \) the liquid solute diffusivity, and \( C_s, C_L \) are the solute concentration in the solid and liquid respectively. The increase in concentration gradient with \( C'_0 \) results in a corresponding increase in the equilibrium temperature gradient, \( \partial T/\partial x' \), which for a simple eutectic system with a linear liquidus line (slope \( m \)) is given by:

\[
\frac{\partial T}{\partial x'} = m \frac{\partial c}{\partial x'}
\]  

The increasing equilibrium temperature gradient exceeds the actual temperature gradient in the liquid, resulting in constitutional supercooling, which initiates the nucleation process.

Many researchers, including Jones and Pearson [4], believe that concentration gradients and constitutional supercooling are merely secondary modes of grain refinement. They maintain that the resulting grain size is a direct consequence of the number of heterogeneous nuclei which effectively nucleate \( \alpha \)-Al crystallites.
2.1.2 Carbide/Boride Heterogeneous Nucleation Theory

Cibula [5] was first to report carbide/boride heterogeneous nuclei as the reason for enhanced grain refinement in hypoperitectic Al-Ti alloys (for which no peritectic reaction can occur). Cibula first based his theory on the facts that no nuclei associated with the Al-Ti system were observed (i.e., TiAl₃), small "black spots" were observed throughout the castings, and carbides are common impurities in commercial Al. Centrifuging molten castings led to the X-ray identification of TiC particles, which segregated to the ingot bottom. Similar results and evidence was given for boron containing Al-Ti hypoperitectic alloys. It is important to note that deliberate additions of C to Al-Ti melts did not reduce grain size and in some cases increased grain size. It was hypothesized that poor wetting of the graphite powder was the cause. Crossley and Mondolfo [6] also studied the effect of C on the grain refinement of Al-Ti alloys and reported results that were contrary to Cibula, i.e., carbon additions decreased the grain refinement potential of Ti. Their explanation was that C tied up Ti preventing it from participating in grain refinement through the peritectic reaction.

In reviewing the literature supporting Cibula's carbide/boride theory, two prominent conditions apply to nucleation by carbides and/or borides. First, some degree of undercooling (1-5°C at least) must take place. Secondly, these particles will nucleate Al only in the absence of a more effective nucleating agent. One such agent is TiAl₃ or
Ti(Al,M)$_3$, where M may be any other element present in the alloy system which substitutionally replaces Al in the tetragonal intermetallic. The TiAl$_3$ intermetallic is the pre-peritectic primary solid which occurs in dilute Al-Ti alloys with an effective concentration above 0.15% or 0.085a/o* [15].

2.1.3 The Peritectic Theory

According to Crossly and Mondolfo [6], the peritectic reaction was first presented as a theory for grain refinement by Asato et al based on work with Cu, Ag and Sb alloys [16]. For the Al-Ti system, the intermetallic compound (TiAl$_3$) particles undergo the peritectic reaction with the remaining liquid to form α-Al crystals. Thus each intermetallic particle that initially precipitates represents a potential Al grain, and grain refinement is increased to the extent nucleation of TiAl$_3$ is increased. From the Al-Ti phase diagram (Figure 1), it is evident that a minimum of 0.15% Ti is required for the equilibrium peritectic reaction to occur.

The nucleating power of TiAl$_3$ has been well studied. It has been shown by various methods such as undercooling [17,18, 19], etch pit orientation [20], optical and electron microscopy [19,21,22,23], selected area diffraction [19] and theoretical considerations [19], that TiAl$_3$ is an extremely powerful nucleant for Al. Given all nucleants present in the melt (i.e., carbides, borides, or detached dendrite arms), TiAl$_3$ will be the first and predominant nucleus for Al [19]. The reason why TiAl$_3$ is such a powerful nucleant stems from

* "All concentrations in weight % - %; atomic % - a/o."
Figure 1 Al-Ti Phase Diagram [15].
its peritectic relationship with Al. First of all, nucleation of α-Al requires no undercooling. The peritectic reaction which produces α-Al on TiAl₃ occurs at 665°C [15], some 5°C above the solidification point of pure Al. TiAl₃ has a very good orientation relationship with Al to give partial epitaxy, i.e., one TiAl₃ particle can nucleate more than one Al crystal with different orientation relationships [20]. According to Klang [19], the most effective nucleating orientation relationship is between the {011}TiAl₃ and the {012}Al planes because it represents a total match between atoms of the same kind in three dimensions.

In hypoperitectic Al-Ti alloys, significant grain refinement occurs especially in the presence of a third element like B [5], C [5], Si [7], or Be [9]. Since these alloys have less than 0.15wt%Ti, they cannot undergo the equilibrium peritectic reaction. However, researchers have proposed three theories which allows the peritectic reaction to take place. Some [17, 24-26] suggest that the insoluble intermetallics nucleate TiAl₃ which then nucleates α-Al by the peritectic reaction. Another theory is that slight ternary additions, which may be present as impurities or deliberately added, shift the limiting peritectic composition to lower values and steepen the liquidus at the l/TiAl₃ boundary [4,7,9,23]. This type of constitutional effect was reported by Youdelis [9] who, using the Kaufman method [27] for calculating phase diagrams, calculated the Al corner of the Al-Ti-Si system. It was shown that the addition of Si will
shift the liquidus line to lower Ti concentrations so that the invariant isothermal peritectic reaction is transformed to a monovariant one. This allowed α-Al to form over a temperature range, and also increased the volume fraction of TiAl₃. Similar grain refinement results in the Al-Ti-Be system [9] suggest the same constitutional effects, although the Al-corner of the system was not calculated. However, thermodynamic studies on the Al corner of the Al-Ti-B system [4, 28] showed no lowering of the peritectic limit or steepening of the 1/ TiAl₃ phase boundary. One final postulation is that Ti, which is introduced to the Al melt in concentrated Al-Ti forms, already contain large TiAl₃ particles, which on long holding at the melt temperature do not dissolve. The result is that TiAl₃ is present in hypoperitectic alloys. However, Kång [19] reports that as a crude approximation, neglecting liquid motions and fluxes, 100μm particles should be dissolved in under one hour at 800°C and 25μm particles should take 5-10 minutes to dissolve. It is therefore unlikely that, in normal alloy making procedures, sufficient TiAl₃ particles would survive to produce the marked grain refinement observed in hypoperitectic Al-Ti alloys.

2.1.4 Nucleation Entropy Theory

The nucleation entropy theory was first presented by Youdelis [14] to account for supercooling and grain refinement in alloys. The theory, as applied to grain refinement, depends on increasing the magnitude of nucleation entropy by incorporating one or more additional elements into the nucleating phase.

According to classical nucleation theory the nucleation
rate ($\dot{N}$) for condensed systems is given by the general rate expression in equation (3):

$$\dot{N} = \exp\left(-\frac{\Delta G^*}{kT}\right)$$  \hspace{1cm} (3)

where $k$ is Boltzmann's constant, $T$ the absolute temperature, and $\Delta G^*$ the free energy of nucleation for a critical sized nucleus. $\Delta G^*$ is given by:

$$\Delta G^* = K\frac{\sigma^3}{\Delta G_v^3}$$  \hspace{1cm} (4)

where $K$ is a system parameter whose value is determined by nucleus geometry including contact angle for heterogeneous nucleation, $\sigma$ the solid/liquid interfacial energy and $\Delta G_v$ the Gibb's free energy of transformation-per unit volume.

For small supercooling ($\Delta T$),

$$\Delta G_v = -\Delta S_v \Delta T$$  \hspace{1cm} (5)

$\Delta S_v$ is the entropy change per unit volume of solid phase nucleated and is referred to as the "nucleation entropy". Substituting (4) and (5) into (3) gives:

$$\dot{N} \propto \exp\left(-K\sigma^3/(\Delta S_v)^3(\Delta T)^2kT\right)$$  \hspace{1cm} (6)

The sensitivity of nucleation rate to small changes in nucleation entropy is evident in equation (6), increasing exponentially with the square of $\Delta S_v$ for the nucleating phase.

For pure metals the nucleation entropy can be readily calculated as $\Delta S_v = \Delta H_v/T$. However, for alloy systems $\Delta S_v$ is much more difficult to obtain due to redistribution of
solute and the general non-ideality of the system. However, \( \Delta S_v \) values can be obtained by suitably combining reactions for which the nucleation entropy is known or can be calculated. First, regular solution behaviour is assumed for the liquid and solid phases, then this constraint is removed through the arrangement of additional reactions. The equation for calculating the nucleation entropy for an n-component system that has regular solution behaviour is given by,

\[
\Delta S = \sum_{r=1}^{n} N_r^S(S_r^S - S_r^L) + R \sum_{r=1}^{n} N_r^S \ln \left( \frac{N_r^L}{N_r^S} \right) \quad (7)
\]

where \( N \) is the mole fraction, \( R \) the gas constant, \( S \) the molar entropy, and \( s \) and \( l \) refer to the solid and liquid phases respectively. The first term in equation (7) represents the freezing entropy for the pure components, and the second term represents the configurational or mixing entropy change for the solid/liquid system. The configurational entropy term shows that the nucleation entropy \( (|\Delta S|) \) increases with difference in composition between the solid and liquid phases and with the number of components present in the liquid which concentrate in the nucleant. Nucleation entropy is particularly significant in precipitation of intermediate compounds because compound formation usually involves a high concentration of one or more components present in dilute concentrations in the alloy. One such example is TiAl\(_3\) in Al-Ti alloys.

The nucleation entropy theory has been successfully applied in accounting for grain and structure refinement of
alloys Al-Ti-Si [7,8,29-32], Al-Ti-Be [9], and carbides in
Co-based superalloys with Ta and Nb additions [33]. Increased
structure refinement in Al-Ti alloys by Si and Be additions
was attributed to the increased nucleation entropy associated
with the concentration of Si and Be into the nucleant as
TiAl$_{2.4}$Si$_{0.6}$ and TiAl$_{2.3}$Be$_{0.85}$. The $\Delta S_v$ values were increased
by approximately 15% however, the nucleation rate ratios are
dramatically increased, e.g., $\frac{N_{\text{TiAl}_{2.3}\text{Be}_{0.85}}}{N_{\text{TiAl}_{3}}} = 10$ and
$10^8$ for $\sigma = 20$ and 40 ergs cm$^{-2}$ respectively. The nucleation
rates were calculated assuming all other factors such as under-
cooling and interfacial energy equal, and because these values
are not known for the respective systems, the rate ratio cal-
culations must be used only as a comparative illustration.

Small additions of Ta and Nb to a Co-based superalloy
resulted in a change in the primary carbide phase from an
M$_{23}$C$_6$ ($M = Cr_{0.77}Co_{0.15}Mo_{0.08}$) type to an MC ($M = Nb$ or Ta)
type for the Ta and Nb containing alloys. Average carbide
particle sizes decreased and average particle counts increased
for the TaC and NbC phases [33]. It was shown that the calcu-
lated nucleation entropy values increased (~111%) for the
MC type carbides, to give a nucleation rate ratio ($\frac{N_{MC}}{N_{M_{23}C_6}}$)
in the order of 10$^{-10^2}$.

For a Ni-based superalloy [34], Ta and Nb additions did
not change the primary MC carbide phase and metallographic
observations showed no particle size reductions or increased
particle counts. The resulting nucleation entropy values
for the MC-type phases increased by less than 0.5% in the Ta
case to a decrease of less than 1.0% in the Nb case [34]. These nucleation entropy calculations are in agreement with the experimental observations.

2.2 Solid-Solid Transformations

2.2.1 Precipitation

Solid state reactions in dilute aluminum alloys have received much attention. Some common methods employed in precipitation studies are microhardness, small angle X-ray scattering (SAXS), electron microscopy, positron annihilation, and resistivity.

The solid solution decomposition process for Al alloys (e.g., Al-Cu) is generally expressed as a series of sequential stages, i.e.,

\[
\text{clusters} + \text{GP} 1 \rightarrow \theta'' \rightarrow \theta' \rightarrow \theta
\]  

For the case of Al-Cu alloys, GP zones are layers of Cu on (200) matrix planes, \(\theta''\) is two parallel Cu-rich layers separated by matrix planes, \(\theta'\) has a bct structure with \(a = 0.404\) nm and \(c = 0.58\) nm, the final equilibrium \(\theta\) phase also has a bct structure with \(a = 0.6076\) nm and \(c = 0.4874\) nm [35]. Although the reaction sequence implies that the previous phase nucleates or transforms to the next phase, this is not necessarily the case.

The concept of a progression through a series of metastable states to a final stable precipitate is a long established concept [36]. Misra and Oswalt [37] and Lutts [38] studied Al-Si-Mg alloys and reported that the previous phase nucleates each successive phase according to the reaction:
Noble [39] reports that the $\Theta'$ phase in Al-Cu alloys is a direct result of clusters which have grown to a critical size. Lorimer and Nicholson [40], Lorimer [41], and Marth et al [42] also support the belief of sequential nucleation of more stable precipitates on less stable ones. On the other hand, Laird and Aaronson [43] reported that for Al-Cu alloys few $\Theta'$ particles acted as nuclei for $\Theta$ phase. Concurrent dissolution of $\Theta'$ particles supplied solute to the growing $\Theta$ phase by volume diffusion and diffusion along dislocation paths. Hirano and Sakai [44] report a similar mechanism for low temperature aging of Al-Au alloys. They state that GP zones grow to a critical size, at which time $\gamma'$ phase (AuAl$_2$) precipitates from the matrix supplied by the resolution of GP zones. They also report that $\gamma'$ phase may change to the stable $\gamma$ phase for high temperature aging. Katz and Ryum [45] believe that the sequential precipitation mechanism may or may not occur depending on the particular alloy system and aging temperature. Aging above the GP zone solvus line will lead to resolutioning of all GP zones and $\gamma'$ or $\gamma$ precipitation; however, prolonged aging within the GP zone region will lead to nucleation by, or transformation of, the GP zone to the $\gamma'$ phase.

The rate and extent to which these phases form is strongly dependent on the solid solution treatment temperature [46-49], quenching temperature [46,49-55], quenching rate [46,50,51],
prior thermomechanical history [49,50,53,57], composition [36,39,58,59], alloy purity [46,50,52,57], and aging temperature [44,60-65]. Interest generated in precipitation hardening reactions stemmed from precipitation-rate calculations, which showed that rates proceeded $10^7$ to $10^8$ times faster than that predicted by volume diffusion [57]. Two theories put forward to explain this phenomenon are a greater than equilibrium amount of point defects (vacancies) [66,67], and enhanced diffusion along short circuits such as dislocations [68]. The majority of the research points to the theory of trapped in vacancies. The equilibrium concentration of vacancies at high temperatures (such as homogenization treatments) is much greater than that at low temperatures. If an alloy is quenched from a high homogenization temperature, a high concentration of vacancies are quenched in. Since vacancies have a very high mobility they enable solute atoms to diffuse and precipitate much faster than in volume diffusion. Various vacancy mechanisms have been reported; however, most reports discuss interactions between vacancies and solute atoms during precipitation reactions [45]. Vacancies and solute atoms bond together and move throughout the alloy, join with other mobile vacancy-solute configurations and form vacancy-solute clusters. In this way the precipitation reaction begins and continues to grow by acquiring more solute via the same mechanism.

The dislocation mechanism provides rapid solute diffusion by short-circuiting the slower volume diffusion process [68].
Solute atoms move along dislocations and precipitate. Often precipitates are found at dislocations or dislocation loops [40]. The "pipe" diffusion model describes solute diffusion as atoms flowing freely down a dislocation pipe forming clusters and ultimately precipitates.

One widely used method in studying precipitation reactions is the resistivity technique because of its simplicity and extreme sensitivity [63]. In an alloy system, precipitation results in a decrease in resistivity [59]. However, pre-precipitation (clustering and GP zone formation) often causes an increase in resistivity, which is sometimes referred to as "anomalous resistivity" [69]. The rate, amount, and location of the resistivity maximum depends on many factors including aging temperature and alloy composition. For complete review of resistivity increases in Al alloys the reader is referred to the text edited by Cotterill et al [55].

Many theories have been put forward to account for resistivity increases including interface dislocations, stress field formation [64], and most noteworthy, Mott's critical size theory [70]. Mott suggested that resistivity increases were due to resonant scattering of conduction electrons by particles of a critical size in the order of the wavelength of electrons ~10 Å. Rossiter and Wells [48] using resistivity and Radomsky and Loffler [71] using small angle X-ray scattering reported maximum resistivity increases corresponded to particle sizes approximating the mean free path of electrons, in agreement with Mott. However, Osamura et al [61] reported
that the scattering power of GP zones in Al-Zn alloys increases monotonically with increasing zone size. Also, Harrison [72] and Hillel [73] calculated the zone size for maximum resistivity increase due to resonant electron scattering to be ~1 atomic diameter. Complex theoretical quantitative modelling of resistivity increases are presented by Schubert and Richter [62], Radomsky and Loffler [71], Hillel [73], Tabusch [74] and Wilkes [75]. The above models are based on advanced electronic functions except those of Hillel and Wilkes. Wilkes based his electron scattering model on Bragg diffraction. He suggests that electrons are scattered by very small regions of local order much like X-rays in solids. Hillel successfully combined Wilkes' theory and Labusch's theory to predict resistivity increases for many Al alloys.

Clearly, the solid state precipitation reactions and factors governing their rates are very complex. The literature provides several models and theories which predict precipitation behaviour for specific conditions; however, a generalized precipitation theory to account for all observed phenomena is still to be developed.

2.2.2 The Effect of Strain on Nucleation

Equation (5) is only applicable to phase changes with negligible strain energies, such as nucleation of a solid phase from the liquid. Transformations in the solid state, however, are usually associated with volume changes that result in elastic strain in either both precipitate and matrix. This
strain must be included in the calculation of the free energy of nucleation of a critical-sized nucleus, \( \Delta G^* \). Two general cases must be considered: (1) incoherent nucleation where there is no lattice continuity between the matrix and precipitate, and the strain is hydrostatic and is either positive or negative; and (2) coherent nucleation in which the lattice of the precipitate and matrix are constrained to match, and the strain is determined by the degree of lattice mismatch. Thus, the free energy of formation of an embryo, including strain energy per unit volume of precipitate (\( W \)), is given by:

\[
\Delta G = (\Delta G_v + W) \dot{V} + \sigma A
\]

(10)

\( W \) is always positive, thus strain energy increases the critical size for the nucleus, which correspondingly decreases the nucleation rate. In general, interfacial energy for a coherent interface is an order of magnitude smaller than that for an incoherent interface, thus, substantial reductions in the free energy of formation of nuclei result when coherent interfaces are present [76].

For the incoherent case, strain energy per unit volume for an ellipsoidal nucleus (oblate or prolate spheroid) is given by [77]:

\[
W = \frac{2}{3} \mu_m (\Delta V/V)^2 f(c/r)
\]

(11)

where \( \Delta V/V \) is the fractional volume change in the matrix for the transformation, \( \mu_m \) is the shear modulus of the matrix, and \( f(c/r) \) is a shape factor characterizing the ellipsoidal particle (\( r \) and \( c \) are the major and minor semi-axes respect-
ively). For an oblate spheroid \((c/r<1)\) the free energy of formation of a critical-sized nucleus is given by [78]:

\[
\Delta G^* = \frac{8\pi^3 \mu_m (\Delta V/V)^c \sigma^3}{3(\Delta G_v)^3}
\]  

(12)

and the nucleation rate is:

\[
\dot{N} \propto \exp \left( \frac{8\pi^3 \mu_m (\Delta V/V)^c \sigma^3}{3(\Delta G_v)^3 kT} \right)
\]

(13)

where \(\Delta G_v\) may be replaced by \((-\Delta S_v \Delta T)\).

For coherent particles, Lee et al [79] show that, for the anisotropic case, strain energy varies markedly with the orientation relationship between the precipitate and the matrix. For the case where the precipitate is "softer" elastically than the matrix, a disc (i.e., classic GP zone of Cu in Al) gives the minimum and the sphere the maximum strain energy. When the precipitate is "harder" elastically than the matrix the reverse is the case. Lee et al [79] give for the free energy of formation of a critical-sized, strained coherent precipitate,

\[
\Delta G^* = \frac{\pi \sigma^3 [2+g(c/r)]^3}{12(c/r)^2 [\Delta G_v + W]^2}
\]

(14)

and the normalized quantity:

\[
\frac{\Delta G^*_h}{\Delta G_v^*} = \frac{[2+g(c/r)]^3}{[8(c/r)(1+W/\Delta G_v)]^2}
\]

(15)

where \(\Delta G_h^* (=16\pi \sigma^3/3\Delta G_v^2)\) is the free energy of formation of a critical-sized spherical, strain free nucleus (c.f., eqn.
(4)). The function $g(c/r)$ characterizes the particle shape, which for $c/r = 1$ defines the sphere (i.e., $g = 16\pi a^3/3$), and oblate and prolate spheroids respectively for $c/r<1$ and $c/r>1$.

It is evident from equation (15), that for a given strain energy level ($W$), an increase in $\Delta G_v$ will allow spherical particles (GP zones or clusters) to form. Graphically, Figure 2 shows that for an elastically isotropic coherent nucleus in an isotropic matrix, the nucleus shape with minimum energy remains spherical ($c/r=1$) with $-W/\Delta G_v$ less than or equal to 0.82. Larger $-W/\Delta G_v$ values correspond to oblate spheroids with $c/r = 0.3$ as the optimum nucleus shape for energy minimization [79].

2.2.3 Precipitation in Al-Cu Alloys

The nucleation entropy model was applied by Youdelis and Karov [80] to nucleation of CuAl$_2$ from solid solution Al-3%Cu and Al-3%Cu-0.1%Be alloys. It was shown that in alloys containing Be, the nucleating phase absorbed Be resulting in the stoichiometric composition CuAl$_1.9$Be$_{0.1}$. The calculated nucleation entropy and strain energy values due to incorporation of Be into CuAl$_2$ increased by ~34% and ~12% respectively for a spherical precipitate ($c/r=1$). However, there was a decrease of ~47% in the free energy of formation of a critical-sized nucleus (c.f., eqn. (14)). The net effect of a decreased $\Delta G^*$ is an increased nucleation rate. Calculations using equation (14) show that the nucleation rate increased by a factor of ~$10^{2.1}$ for $\sigma = 30$ mJ/m$^2$. 
Experimental evidence confirming the calculated nucleation rate increase includes microhardness and resistivity data coupled with scanning and transmission electron microscopy [81-83]. Scanning electron microscopy studies showed that for aging at 380°C, θ phase particles were significantly smaller and their density significantly higher in Al-Cu alloys containing Be, indicating that Be addition increases the nucleation rate of θ phase. Resistivity data also showed that the transformation to θ was completed much faster and the nuclei density was much higher for the Al-Cu-Be alloy [82].

Low temperature aging (room temperature and 100°C) resulted in a significant hardening rate increase for Be-containing alloys. The hardening rate increase was attributed to Cu-Be-vacancy clusters in place of the slower forming GP zones, as evidenced by TEM techniques [81]. Approximate calculations using the appropriate values [76] in equation (15) gave $-W/\Delta G_v$ values of 0.90 and 0.73 for CuAl$_2$ and CuAl$_{1.9}$Be$_{0.1}$ respectively. Thus referring to Figure 2, spherical-like clusters are preferred in the Al-Cu-Be alloy versus the ellipsoidal-like GP zones in the Al-Cu alloy.
Figure 2 Normalized free energy versus nucleus shape for constant \(-W_s/\Delta G_v\) [79].
CHAPTER 3

EXPERIMENTAL METHODS

The experimental methods employed in this study include X-ray diffraction, optical microscopy, scanning electron microscopy, transmission electron microscopy, microhardness and electrical resistivity.

3.1 Alloy Preparation

The alloys in this study had the following nominal compositions: Al-0.2%Ti, Al-0.8%Ti, Al-0.2%Be, Al-0.2%Ti-0.2%Be, and Al-0.8%Ti-0.2%Be. The alloys were made by combining proper amounts of superpurity Al(99.99%), Al-5.6%Ti master alloy and Al-5.23%Be master alloy (supplied by Kawecki Berylco Industries Inc.). Master alloys were used as they have been proven to give superior composition yields compared to complex salt additions [4]. The alloys were induction-melted in a graphite crucible in air. They were heated to \(1000^\circ\text{C}\) and held at that temperature for 5 minutes, stirred and then held for 10 more minutes with periodic crucible rocking to promote further mixing. The molten alloy was then air cast into graphite molds (approximately 2.5 cm dia x 9.0 cm). Sections from the central portion of the ingot were used for all tests performed. The alloy analyses were performed by Met Chem Testing Labs Inc. of Dearborn, Michigan; the results are shown in Table 1. The good agreement between nominal and actual compositions indicate little or no loss of alloying constituents in the melting and casting procedure through oxidation, and good reproducibility of the alloy preparation
### Table 1

#### Alloy Compositions

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal</th>
<th>Actual</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>%Ti</td>
<td>%Be</td>
</tr>
<tr>
<td>1</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.80</td>
<td>0.20</td>
</tr>
</tbody>
</table>
3.2 Precipitate Extraction and X-ray Diffraction

X-ray analysis on the bulk alloy samples showed no signs of second and/or third phases because the particles were too small and too few. Thus, for diffraction analysis, separation of the precipitate particles was required. Several methods for selectively dissolving away the aluminum matrix and leaving the second phase particles unaffected are available [84-87]. However, the only one that proved fruitful was that outlined by Ryvola and Morris [87]. This involved using pure Al for the cathode, a 2.0wt% solution of KI in methanol, for the electrolyte, and a potential of ~5.0 volts. The resulting residue was treated with a saturated aqueous solution of disodium ethylenediamine-tetraacetate, followed by 40 ml of 50%HCl solution to dissolve all non-metallic precipitate. The metallic precipitate was collected using a centrifuge, washed with distilled water and methanol, and dried. A Debye-Scherrer powder diffraction camera, using CuKα monochromatic radiation was used for the X-ray diffraction analyses.

3.3 Optical Microscopy

Specimens for optical microscopy were prepared in the conventional way; however, following the 0.05μm alumina polish, the specimens were polished for an additional 45 minutes using colloidal silica as the polishing media. This procedure is recommended [88] for Al-Ti alloys and other soft metals. The best etchant for these alloys is the Graff-Sargent reagent [89] (15.5 ml HNO₃, 0.5 ml HF (conc.), 3.0g CrO₃, 84.0 ml dist.)
H₂O). The specimen surface was covered with fresh etch for 20-30 seconds and swabbed with a soft cotton ball. A second 10 second etch was sometimes required depending on the individual specimen. Other reagents were used (i.e. Keller's etch); however, less favourable results were produced.

3.4 Electron Microscopy

Specimens for the scanning electron microscope (SEM) were prepared in the same manner as optical microscope specimens. However, due to the different contrast forming mechanisms of the SEM (mainly topographic effects), a longer etching treatment was required for adequate image formation.

Transmission electron microscope (TEM) specimens were prepared by cutting a thin (0.5 mm) slice of material on a low-speed diamond saw. The specimen was further thinned mechanically to 0.1-0.2 mm. Discs 3.0 mm in diameter were then punched out of the material, deburred, and subsequently thinned in a Fishione twin-jet electropolisher with the electrolyte (30% HNO₃, 70% ethanol) maintained at -25°C. The operating potential was 10 volts and the jet speed setting was varied from 4-5.

3.5 Heat Treatment and Microhardness Tests

Microhardness determinations to monitor age hardening progress were carried out on a Leitz Miniload hardness tester with a diamond pyramid indentor, a 50 gram load, and a total test time of 25-30 seconds. Tests were performed on cast and heat treated specimens by interrupting the heat treating schedule. An average of five hardness indentations were used
to obtain one hardness point on a polished (1.0μm alumina) surface. All solution and aging treatments were done in air, in electrical resistance furnaces at temperatures of 630±2°C, 350±2°C, 150±2°C, and room temperature (~21°C). Evacuated capsules were not used for heat treating because thin oxide layers which quickly develop on Al, protect the metal from internal oxidation at elevated temperatures. Also, much faster quenching rates are obtained by direct quenching. After solution treatments, samples were quenched into iced-brine (~-15°C); after aging, samples were quenched into cold water.

3.6 Electrical Resistivity

For electrical resistivity measurements samples were made by cold rolling thin slices (-1.0-2.0 mm) cut from the ingot using a low-speed diamond saw. The final specimen dimensions were approximately 72.0 mm x 4.0 mm x 0.1 mm. Separate voltage and current leads were provided at the specimen ends (c.f., Figure 3) to eliminate contact resistance.

The electrical resistance of the specimen was determined by comparing the voltage drop across the specimen to that of an Al standard. The resistance of the Al standard was determined using a Kelvin bridge with an accuracy of ±0.001 mΩ. The current was supplied by a current regulated power supply (Spectromagnetic Industries Model 6021) with an average current drift of ~0.03%. The potential drop was measured with a Leeds-Northrup potentiometer facility capable of resolving 10⁻⁷ volts. The testing temperature was held at 29±0.01°C using distilled deionized water circulated by a Haake heat
pump. The electrical circuit schematic is shown in Figure 4. The same current flows through both specimens, and since the resistance of the Al standard and the dimensions of the test sample are known, the resistivity is simply calculated as follows:

\[ V_{\text{Al}} = i_{\text{Al}} R_{\text{Al}} \quad \text{and} \quad V_{\text{S}} = i_{\text{S}} R_{\text{S}} \quad (16) \]

where Al is for pure Al, S is for the test sample, and \( V, i, \) and \( R \) have their usual meanings. Since \( i_{\text{Al}} = i_{\text{S}}, \) \( V_{\text{Al}}/V_{\text{S}} = R_{\text{Al}}/R_{\text{S}}, \) or:

\[ R_{\text{S}} = R_{\text{Al}} V_{\text{S}}/V_{\text{Al}} \quad (17) \]

and,

\[ \rho_{\text{S}} = R_{\text{S}} A/\ell \quad (18) \]

with \( A \) the specimen cross-sectional area, \( \ell \) the specimen length, and \( \rho_{\text{S}} \) the test sample resistivity.

Isothermal resistivity curves were obtained by interrupting the heat treatment and taking a reading. The total time for one reading was about 1-2 minutes. The resistivity readings were accurate to within ±0.03%. The experimental setup is shown in Figure 5.
Figure 3 Resistivity specimen dimensions.
i = constant current power supply
R = standard resistor
P = potentiometer

Figure 4 Electrical circuit schematic.
Figure 5  Experimental set-up for resistivity measurements.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Age Hardening of Solution Treated Alloys

Previous work in the Engineering Materials Department at the University of Windsor [90] has shown that Al-Ti-Be alloys, solution treated at 630°C, have a slight tendency for age hardening. The optimum solution treatment time was determined using microhardness results as shown in Figure 6 (see Appendix 1). The results clearly show that the Al-0.2%Ti alloys are insensitive to the solution treatment. Al-0.2%Ti-0.2%Be alloys and Al-0.2%Be alloys reach a hardness plateau in ~30 minutes solution time, and maintain that level. These alloys are also very sensitive to quenching rate with the air cooled specimens showing a significant hardness decrease compared to rapidly quenched specimens. This is a result of rejection of solute atoms from the matrix on slow cooling, which on fast cooling, are trapped in solution. The increase in hardness with solution treatment time for the Al-Be alloy, reaching a plateau hardness of approximately
44HV, indicates that equilibration of the system, and maximum solution of Be in the Al matrix, is reached after approximately 30 minutes. The lower hardness for the Al-Ti-Be alloy is due to the very rapid precipitation process, which cannot be suppressed with the quenching rates used in the present study. The decrease in hardness with increase in solution treatment time for the Al-Ti-Be alloy, reaching the plateau hardness of approximately 24VH after approximately 30 minutes, corresponds to the increase in hardness for the Al-Be alloy and indicates and can be accounted for by the increase in precipitation rate with increase in Be content.

The solution treatment adopted in this work therefore consisted of one hour at 630°C, followed by an iced brine quench. Artificial aging treatments were carried out at room temperature, 150°C and 350°C, and the precipitation reaction monitored by microhardness measurements. The results are presented in Figures 7, 8 and 9 for room temperature, 150°C and 350°C aging respectively. The Vickers hardness scale is used and zero time (t=0) corresponds to the solution treated and quenched condition.

For the binary Al-0.2%Ti alloy, the solution treated hardness value of 21HV, is essentially independent of aging
Figure 6  Hardness versus time for 630°C solution treatment.
temperature and time with the exception of a slight hardness increase of 2 Vickers points at 2-3 hours for the 150\(^\circ\)C aging treatment. The Al-0.2\%Ti-0.2\%Be alloy, on the other hand, shows significant hardening for all temperatures investigated. Room temperature aging produced a hardness increase of ~41\% (from 31 to ~43 HV) in 10 hours; aging at 150\(^\circ\)C produced an increase of ~35\% (from 31 to 42 HV) in 3 hours, followed by a slight decrease (to 40 HV); aging at 350\(^\circ\)C produced a hardness increase of ~26\% (from 30 to 38 HV) at 12 minutes, followed by a rapid decrease to below the solution-treated hardness level after 30 minutes. In comparison, the Al-0.2\%Be alloy had the highest solution-treated hardness values (~44.5 HV). However, aging at room temperature and 150\(^\circ\)C produced only 7\% and 4\% increases in hardness respectively. Hardness values for the Al-0.2\%Be alloy rapidly decreased with aging at 350\(^\circ\)C, to values below those of Al-0.2\%Ti-0.2\%Be and slightly above those of Al-0.2\%Ti (Figure 9).

For the Al-0.2\%Ti-0.2\%Be alloys, the magnitude and time to maximum hardness levels decrease as the aging temperature increases. The general shape of the hardness curves at room temperature and 150\(^\circ\)C is characteristic of age hardenable Al alloys which undergo sequential precipitation, viz., clustering, GP zones, metastable phase formation, and stable phase formation. The first small hardness increase is due to clustering, followed by a larger hardness increase due to GP zones and metastable phase formation, while hardness decreases correspond to formation and growth of equilibrium precipitates [36]. Comparing Al-0.2\%Ti-0.2\%Be and Al-0.2\%Be, the hardness
Figure 7: Hardness versus time for room temperature aging.

VICKERS HARDNESS, kg/mm²
Figure 8  Hardness versus time for 150°C aging.
Figure 9  Hardness versus time for 350°C aging.
increase for all aging temperatures is much greater in the former than the latter. The small Al-0.2%Be hardness increases is due to clustering of Be atoms [91]. The large increases in hardness for the Al-0.2%Ti-0.2%Be alloys cannot be attributed to Be clustering. Be increases the hardening rate of Al-Ti alloys by interacting with Ti to speed up the sequential precipitation process. This phenomenon was also observed in Al-Cu-Be alloys which exhibited similar age hardening behaviour [81]. It was postulated that interactions of Cu-Be-vacancy clusters caused the increased hardening rates and increased precipitation in the Al-Cu system.

4.2 Resistivity and Precipitation Kinetics

In order to determine the reaction kinetics for the age hardening outlined in section 4.1, the aging process was studied using electrical resistivity techniques (c.f., section 3.6).

It is generally accepted that the Avrami equation can be applied to diffusion-controlled transformation processes with some modifications. For recrystallization, the volume fraction transformed at time t has the form,

\[ Y = 1 - \exp(-kt^n) \]  

(19)

where the parameter n is related to the growth mode (linear, planar, or spherical), and k is related to the density of nucleation sites. For diffusion controlled reactions where the nucleation rate is fast and not rate controlling, Wert and Zener [93] give:
\[ k = a(N_0 r_f D)^{3/2} \]  

where \( a \) is a constant, \( D \) the solute diffusivity, \( r_f \) the final mean radius of the particle, and \( N_0 \) is the initial nuclei density. The fraction transformed \((Y)\) can be related to the resistivity changes as follows \([94]\):

\[ Y = (\rho_o - \rho_t) / (\rho_o - \rho_\infty) \]

where \( \rho_o \), \( \rho_t \) and \( \rho_\infty \) are respectively the resistivity values at time \( t = 0 \), \( t = t \), and \( t = \infty \) when the reaction is completed. Plotting the fraction transformed for the precipitation reaction as \( \log[\ln(1/1-Y)] \) vs. \( \log t \) gives a straight line, the slope of which is \( n \), and the abscissa intercept, \( k \).

The resistivity for aging temperatures of 350°C, 380°C and 410°C was monitored. Typical resistivity curves for Al-0.2%Ti and Al-0.2%Ti-0.2%Be alloys are presented in Figures 10 and 11 respectively. Resistivity decreases are characteristic of precipitation, whereas increases in resistivity are attributed to clustering \([55]\). It is evident from Figure 10, that the resistivity increase in Al-0.2%Ti is due to clustering of vacancies and solute atoms, suggesting that no precipitation of TiAl\(_3\) is occurring at this stage of the aging cycle. The absence of resistivity decrease with aging time for the Al-0.2%Ti alloy precludes any comparison of the effect of Be on the precipitation kinetics in Al-Ti alloys using the resistivity method.

The resistivity results for Al-0.2%Ti-0.2%Be show a two-staged curve and not a smooth monotonically decaying function,
Figure 10 Resistivity versus time for Al-0.2%Ti aged at 350°C.
Figure 11  Resistivity versus time for Al-0.2%Ti-0.2%Be aged at 380°C.
Broken curve is corrected for rise in superpurity Al.
suggesting the interference or superposition of an additional process onto the precipitation mechanism. Also, the initial resistivity values differed for each sample, and it was not possible to reproduce the resistivity curves in repeating the experiments. The inability to reproduce the experimental data can be attributed to the high solution temperature (630°C) used in the study. This high solution temperature was used to maximize the Be solid solution composition (c.f., Figure 12); however, the vacancy and impurity (solute atom) concentrations are extremely sensitive to quenching rate.

To obtain a better understanding of the two-stage aging process, samples of superpurity Al were subjected to an identical solution and aging treatment. The results show that (c.f., Figure 13) on aging the resistivity increases rapidly, then slowly decreases to a value below the solution-treated value. It can be assumed that the resistivity increase is due to clustering of vacancies during the aging treatment [55]. It is evident that the above resistivity rise in the Al (due to vacancy clustering) is the cause of the anomalous levelling off in the resistivity curve for the Al-0.2%Ti-0.2%Be alloy. The resistivity curve for Al-0.2%Ti-0.2%Be corrected for the resistivity for superpurity Al, is shown in Figure 10. This treatment has partially smoothed out the anomalous plateau in the Al-0.2%Ti-0.2%Be resistivity curve. The reproducibility problem noted earlier precludes accurate separation and determination of the resistivity associated with the precipitation process. The resistivity results do
Figure 12 Al-Be phase diagram [95].
Figure 13 Resistivity versus time for superpurity Al aged at 410°C.
however, show that precipitation in Al-0.2\%Ti-0.2\%Be alloys occurs much faster and to a much larger extent than in Al-0.2\%Ti.

4.3 Electron Microscopy

Image formation in the scanning electron microscope required heavy etching of metallographic specimens to provide contrast from surface relief and backscattered electrons. The heavy etching resulted in many surface anomalies, such as etch pits, which could not be discerned from precipitates in the alloys. For this reason, no SEM micrographs are included in this work.

Thin foils prepared from the heat treated bulk alloys were examined in the JEOL 100 CX transmission electron microscope. Specimens examined were solution treated 1 hour at 630\°C and aged at 350\°C for varying lengths of time. There were no diffraction patterns identifying precipitates in any of the specimens, and only the diffraction pattern for the Al matrix was observed. However, this does not mean that precipitates are not present in the alloys (c.f., section 4.5).

The techniques employed in sample preparation were not sufficiently refined to produce acceptable thin foils with adequate thin areas for electron transmission.

Extraction of precipitates for TEM observation was also tried by evaporating carbon onto a heavily etched specimen surface forming a thin continuous layer. Removal of the thin carbon film and examination in the TEM resulted in electron diffraction patterns corresponding to h.c.p. \text{SiO}_2. The source
of the SiO₂ is believed to be from the final polishing solution which, when allowed to dry, forms a very tenacious crystalline crust. When this contamination was avoided, the carbon films showed no electron diffraction patterns.

4.4 X-ray Diffraction

X-ray diffraction data on the intermetallic precipitates was obtained by electrolytic dissolution techniques. Data obtained from Al-0.2%Ti samples showed only one very weak reflection for the TiAl₃ structure; thus, in order to increase the amount of TiAl₃ precipitate, Al-0.8%Ti and Al-0.8%Ti-0.2%Be alloys were prepared as outlined previously (c.f., section 3.2). The data in Table 2 compare the Bragg reflection angles (2θ values) for Al-0.8%Ti and Al-0.8%Ti-0.2%Be alloys solution treated for 160 hours at 630°C, quenched, then aged for 24 hours at 350°C. The data show that 2θ has shifted to slightly higher values, indicating that the interplanar spacing and lattice parameter values are smaller. This is in agreement with the work of Youdelis and Yang [9] for x-ray studies in Al-32.3a/oTi-4a/oBe alloys. It was shown that the principal X-ray reflections for primary TiAl₃ shifted to higher 2θ values to give reduced lattice parameters (a and c). The
statistical significance of the lattice parameter changes requires a Nelson-Riley treatment of the data. However, only two of the reflections were sufficiently sharp for the purpose of this calculation, the higher angle reflections being too diffuse, so that the accuracy of the observed shifts in 26 and corresponding changes in the lattice parameters cannot be given. These results, along with microhardness and electron probe data, shows that tetragonal TiAl₃ has a solubility for Be and that the Be preferentially replaces Al. A range of TiAl₂₈Be₀₂ to TiAl₂₃Be₀₈₅ was proposed as the stoichiometric composition. The changes in lattice parameter in this work are about 75% that obtained by Youdelis and Yang, indicating less Be absorption in secondary TiAl₃ which may be related
<table>
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<th>Lattice Plane (hkl)</th>
<th>Al-0.14Ti</th>
<th>TiAl3 (Ict)</th>
<th>Al-0.38Ti-0.2Be</th>
<th>TiAl3 (Ict)</th>
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<td>(004)</td>
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<td>41.20</td>
<td>42.40</td>
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<td>(020)</td>
<td>47.00</td>
<td>65.20</td>
<td>47.40</td>
<td>65.00</td>
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<td>(315)</td>
<td>82.36</td>
<td>84.22</td>
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</tr>
<tr>
<td>(226)</td>
<td></td>
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</tbody>
</table>

Table 2: X-ray Reflections and Calculated Lattice Parameters for TiAl3 and Ti(Al,Be)3 Phases
to a decrease in Be activity (corresponding to the decreased solubility of Be in Al). Accordingly, for the nucleation entropy calculation, the lower Be composition compound will be used (i.e., TiAl$_{2.8}$Be$_{0.2}$).

4.5 Optical Microscopy

Optical microscopy was also used to monitor the aging process in the Al-Ti and Al-Ti-Be alloys. Optical microscopy methods are obviously not sensitive to early precipitation processes (i.e., GP zone and metastable phase formation); however, microstructural changes due to precipitation are readily observed.

4.5.1 Al-0.2%Ti Alloys

The cast structure for Al-0.2%Ti in Figure 14 shows no surviving primary TiAl$_3$ suggesting that Ti atoms are in solution. The micrograph shows a petal-like structure within the grains and many black spots which are artifacts of the specimen preparation procedure. The solution treated structure of Figure 15 is identical to the cast structure except that the grain size is larger due to the 630°C treatment. No precipitation on aging at 350°C was visible until prolonged aging of ~72 hours as seen in Figure 16. The precipitates are congregated into small groups located in the central regions of the petal-like structures. Precipitation is expected in these regions as they are highest in %Ti because they solidified first.

4.5.2 Al-0.2%Be Alloys

Figure 17 shows the cast structure of the Al-0.2%Be alloy. The primary α-Al grains are surrounded by the eutectic solid
Figure 14  Al-0.2%Ti. As cast.
Figure 15  Al-0.2%Ti. 1 hr. at 630°C.
Figure 16  Al-0.24Ti. 1 hr. at 630°C, 72 hr. at 350°C.
which is composed of α-Al (0.3α/αBe) and Be. There is also some fine Be within the Al which presumably came out of solution during solidification. After 1 hr. at 630°C a great deal of the eutectic structure dissolved as well as all Be within the Al grains (c.f., Figure 18). Aging at 350°C for 18 hours produces a fine precipitate throughout the Al grains and an increased amount of Be surrounding the grains as shown in Figure 19.

4.5.3 Al-0.2%Ti-0.2%Be Alloys

The cast structure of the ternary alloy in Figure 20 is similar to the Al-0.2%Be structure in that the α-Al is surrounded by the Al-Be eutectic structure which is last to solidify. The α-Al also has some heavy precipitation in it; however, this precipitation is not located in the petal-like structure which is the primary solid. The solution treated structure of Figure 21 once again shows a significant reduction in the Al-Be eutectic as well as disappearance of the precipitate within the α-Al. The dominating feature of the solution treated sample is the appearance of a new phase which forms throughout the petal-like structure. This phase is believed to be composed of very fine Ti(Al,Be)₃ which precipitates during quenching. Location of the precipitate is in agreement with the observed TiAl₃ precipitation in the petal-like structure in aged Al-0.2%Ti. Since no precipitation of Be occurred on quenching in Al-0.2%Be, the precipitate in Al-0.2%Ti-0.2%Be must contain very little if any Be precipitate. The fact that precipitation of Ti(Al,Be)₃ cannot be suppressed on quenching suggests a lower free energy
Figure 17  Al-0.2%Be. As cast.
Figure 18  Al-0.2%Be. 1 hr. at 630°C.
Figure 19  Al-0.2%Be. 1 hr. at 630°C, 18 hr. at 350°C.
of formation for a critically-sized nucleus, and ultimately, a much faster nucleation rate compared to TiAl$_3$ without Be. Aging at 350°C once again produced precipitation throughout α-Al, and also a significant increase in Ti(Al,Be)$_3$ precipitation as evidenced by particle coarsening in Figure 22. The high density of fine particles precludes particle counting for quantitative comparison; however, the amount of precipitation in Al-Ti-Be alloys is clearly much greater than that in both Al-Be and Al-Ti alloys combined.
Figure 20  Al-0.2%Ti-0.2%Be.
As cast.
Figure 21  Al-0.2%Ti-0.2%Be.  1 hr. at 630°C.
Figure 22 Al-0.2\%Ti-0.2\%Be. 1 hr. at 630\(^\circ\)C, 18 hr. at 630\(^\circ\)C.
CHAPTER 5
NUCLEATION ENTROPY

5.1 Calculations for TiAl₃

Table 3 gives the reaction sequence used for calculating the mole nucleation entropy of TiAl₃. The initial condition is an Al-0.1a/oTi alloy in the solution treated condition, with the reaction temperature 623 K (350°C). The (reverse) formation of 1 mole (4 g atoms) of a regular solid solution Al-25a/oTi alloy is given by reaction 1a, for which the mixing entropy is given by:

\[ \Delta S^\text{reg}_M = -R \left[ N_1 \ln N_1 + N_2 \ln N_2 \right] \] (22)

The formation of 1 mole of TiAl₃ at 623 K is given in reaction 2a. The formation entropy is calculated using the thermodynamic data for TiAl₃ at 623K reported by Stuve and Ferrante [96]. Adding 1a to 2a gives 3a, the reaction and corresponding entropy change, for the formation of 1 mole of TiAl₃ from 1 mole of regular solid solution Al-25a/oTi alloy. Reaction 4a denotes the nucleation reaction by which 1 mole of regular solid solution is formed or precipitated in an infinite (∞) amount of regular solid solution of Al-0.1a/oTi. The entropy change for this reaction is calculated using equation 7, and to differentiate from the solidification process is rewritten as:

\[ \Delta S = \Delta S_m + \Delta S_{tr} \] (23)

where,

\[ \Delta S_m = R \left[ N_{Al}^\beta \ln \left( N_{Al}^\alpha / N_{Al}^\beta \right) + N_{Ti}^\beta \ln \left( N_{Ti}^\alpha / N_{Ti}^\beta \right) \right] \] (24)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Details</th>
<th>ΔS (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>4(Al-25a/oTi)_{reg(s)} → Ti(s) + 3Al(s)</td>
<td>-18.8</td>
</tr>
<tr>
<td>+</td>
<td>623K</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>Ti(s) + 3Al(s)</td>
<td>-28.5*</td>
</tr>
<tr>
<td>3a</td>
<td>4(Al-25a/oTi)_{reg(s)} → TiAl₃ (s)</td>
<td>-47.3</td>
</tr>
<tr>
<td>+</td>
<td>623K</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>γ(Al-0.1a/oTi)<em>{reg(s)} → 4(Al-25a/oTi)</em>{reg(s)} + γ(Al-0.1a/oTi)_{reg(s)}</td>
<td>-38.6</td>
</tr>
<tr>
<td>5a</td>
<td>γ(Al-0.1a/oTi)<em>{reg(s)} → TiAl₃(s) + γ(Al-0.1a/oTi)</em>{reg(s)}</td>
<td>-85.9</td>
</tr>
</tbody>
</table>

*From Stuve and Ferrante [96].
\[ \Delta S_{tr} = N_{Al}^B (S_{Al}^B - S_{Al}^a) + N_{Ti}^B (S_{Ti}^B - S_{Ti}^a) \] (25)

where \(a\) and \(B\) refer to the f.c.c. structure of the solid solution, and the b.c.t. structure of the TiAl₃ compound respectively. Normally, the entropy change in forming the regular solid solution of reaction 4a is given by equation (25). However, the regular solid solution of reaction 3a is in the (fcc-cph) structure, i.e., formed using fcc Al and cph Ti. Thus, in its elimination (by adding 4a) the same standard state must be used, i.e., the regular solution of 4a must also be in the (fcc-cph) structure; consequently, equation (25) need not be applied in the entropy calculation of reaction 4a. Adding 3a to 4a to obtain 5a removes the regular solution constraint for the compound, and reaction 5a gives the nucleation reaction and corresponding nucleation entropy for the formation of 1 mole of TiAl₃ from a regular behaving solid solution of Al containing 0.1a/oTi at the tempering temperature of 623K. The determination of the nucleation entropy of TiAl₃ from the real solid alloy requires the appropriate thermodynamic information which is not available. However, since the difference in molar entropies of mixing for regular and real solutions is small for dilute alloys (both converge and become zero at infinite dilution), the difference in the molar entropy for nucleation of TiAl₃ in the real vs. regular solution will likewise be small, and for the Ti concentrations of the present alloy (\(N_{Ti} = 0.001\)), negligible.
5.2 Calculations for TiAl$_{2.8}$Be$_{0.2}$

Analytical evidence in earlier work [9] shows that TiAl$_3$ can absorb Be corresponding to the stoichiometric range TiAl$_{2.8}$Be$_{0.2}$ to TiAl$_{2.3}$Be$_{0.85}$. The appropriate reactions and sequence for calculating the molar nucleation entropy for the lower limit of the stoichiometric range, TiAl$_{2.8}$Be$_{0.2}$, is presented in Table 4. The initial or starting condition is Al-0.1a/oTi-0.19a/oBe solid alloy, solution treated at 903K to give a solid solution containing 0.1a/oTi and 0.19a/oBe (cf., Figures 1 and 12). It is assumed in reaction 3b, that the formation entropy for the ternary TiAl$_{2.8}$Be$_{0.2}$ is approximately equal to the formation entropy for the TiAl$_3$ phase given in reaction 2a. The basis for this assumption is the common bct structure, with the Be atoms displacing ~6.7% of the Al atoms, to give similar bonding characteristics in the solids. It is noted that the approximately 4J/mol K increase in the absolute molar nucleation entropy derives mostly from the Be contribution to the mixing entropy (cf., reactions 4a and 4b), which is not altered by errors introduced in the above approximations.

5.3 Nucleation Rate Comparisons

A comparison of nucleation rates for the two intermetallic compounds can be obtained using equation 14 for $\Delta G^*$. This equation incorporates strain energy associated with the phase change. For purposes of a comparative calculation, the strain energy for the isotropic, homogeneous case given by Lee et al [79] will be used.
Table 4
Reaction Sequence for Calculating Molar Entropy for Nucleating \( \text{TiAl}_{2.8} \text{Be}_{0.2} \) From Al-0.1a/oTi-0.19a/oBe Alloy at 623K (350°C)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta S , (\text{J/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>( 4(\text{Al-25a/oTi-5.0a/oBe})_{\text{reg}}^{(s)} \rightarrow \text{Ti(s)}+2.8\text{Al(s)}+0.2\text{Be(s)} )</td>
</tr>
<tr>
<td>+</td>
<td>( 2.8\text{Al(s)}+0.2\text{Be(s)} \rightarrow (\text{93.3a/oAl-6.7a/oBe})_{\text{reg}}^{(s)} )</td>
</tr>
<tr>
<td>2b</td>
<td>( (\text{93.3a/oAl-6.7a/oBe})<em>{\text{reg}}^{(s)}+\text{Ti(s)} \rightarrow \text{TiAl}</em>{2.8} \text{Be}_{0.2}^{(s)} )</td>
</tr>
<tr>
<td>4b</td>
<td>( 4(\text{Al-25.0a/oTi-5.0a/oBe})<em>{\text{reg}}^{(s)} \rightarrow \text{TiAl}</em>{2.8} \text{Be}_{0.2}^{(s)} )</td>
</tr>
<tr>
<td>+</td>
<td>( (\text{Al-0.1a/oTi-0.19a/oBe})<em>{\text{reg}}^{(s)} \rightarrow 4(\text{Al-25.0a/oTi-5.0a/oBe})</em>{\text{reg}}^{(s)} )</td>
</tr>
<tr>
<td>5b</td>
<td>( + (\text{Al-0.1a/oTi-0.19a/oBe})<em>{\text{reg}}^{(s)} \rightarrow \text{TiAl}</em>{2.8} \text{Be}<em>{0.2}^{(s)}+\text{TiAl}</em>{2.8} \text{Be}_{0.2}^{(s)} )</td>
</tr>
</tbody>
</table>
\[ W = 2\mu (1+\nu/1-\nu)\varepsilon^2 \quad (26) \]

where \( \mu \) is the shear modulus, \( \nu \) is Poisson's ratio, and \( \varepsilon \) the transformation strain. The strain energy \( \varepsilon \) is calculated from the difference in gram atomic volume \( (\varepsilon = \Delta V/3V) \), assuming that the strain is entirely hydrostatic in character.

The nucleation rate for the TiAl\(_{2.8}\)Be\(_{0.2}\) compound is \( \sim 10^{3.0} \) times faster than for the TiAl\(_3\) compound (c.f., Table 5). The calculation is based on crystal structure data given by Pearson [97], a spherical precipitate, the calculated \( \Delta S_i \) values, \( \sigma = 400 \text{ mJ/m}^2, \Delta T = 150K, \nu_{\text{Al}} = 2.85 \times 10^3 \text{ J/cm}^3 \) [76, 79], \( \nu_{\text{Al}} = 0.30 \), and a volume decrease in TiAl\(_3\) of \( \sim 1\% \) due to Be absorption based on the X-ray data in section 4.4. This calculation shows that the nucleation entropy more than compensates for the increased strain energy. However, it must be stressed that the values used in the calculations are only estimates due to the absence of specific data, and therefore the nucleation rate calculations are only useful as a comparison illustrating the effect of increased nucleation entropy.
Table 5
Comparison of Nucleation Rates for Precipitation in 
Al-Ti and Al-Ti-Be Alloys at 623K

<table>
<thead>
<tr>
<th>Phase</th>
<th>(\frac{\Delta V}{V})</th>
<th>(\epsilon)</th>
<th>(\varphi_S V) (Jcm^{-3}k^{-1})</th>
<th>(W) (Jcm^{-3})</th>
<th>(\Delta G^*) (Jmol^{-1})</th>
<th>({\tilde{N}}<em>{TiAl</em>{2.8}Be_{0.2}})</th>
<th>({\tilde{N}}_{TiAl_3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAl_3</td>
<td>0.044</td>
<td>0.015</td>
<td>8.83</td>
<td>2.27</td>
<td>3.7 \times 10^5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiAl_{2.8}Be_{0.2}</td>
<td>0.054</td>
<td>0.018</td>
<td>9.31</td>
<td>3.36</td>
<td>3.3 \times 10^5</td>
<td>103.0</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The microhardness, resistivity and optical microscopy results all confirm increased precipitation in Al-Ti-Be alloys as compared to Al-Ti alloys. Hardness increases of ~30-40% for Al-0.2%Ti-0.2%Be are attributed to accelerated GP zone and metastable phase formation which precede Ti(Al,Be)₃ precipitation. This accelerated precipitation is believed to be due to interaction of Be and Ti atoms with quenched in vacancies. Resistivity decreases during aging also reflect Ti(Al,Be)₃ precipitation at the temperatures of 350°C, 380°C and 410°C in Al-Ti-Be alloys, whereas Al-Ti alloys show no resistivity decrease associated with precipitation. Optical micrographs of the Al-Ti-Be alloy clearly show many more precipitates than the Al-Ti and Al-Be alloys combined, and that these precipitates are the Ti(Al,Be)₃ compound. Powder diffraction data on aged Al-Ti-Be alloys clearly shows a slight reduction in the lattice parameters of the precipitating compound suggesting Be incorporation into TiAl₃ in agreement with Youdelis and Yang [9].

All of these results are in agreement with the increased nucleation rates in the solid state as predicted by the nucleation entropy theory. Calculations based on the TiAl₂.₈ Be₁₀.₂ compound show that the nucleation entropy (|ΔSⁿ|) increases and even though the strain energy also increases, the free energy of formation of a critical-sized nucleus decreased.
This ultimately results in a nucleation rate approximately $10^3$ times faster for TiAl$_{2.8}$Be$_{0.2}$ than TiAl$_3$.

6.2 Recommendations for Future Work

It is recommended that transmission electron microscopy techniques be refined to monitor the precipitation behaviour of the alloys. Low temperature aging is suggested for this work so that GP zones and metastable phase formation may be directly observed as predicted by the microhardness data. Also, an attempt to modify the resistivity techniques in order to eliminate any anomalous behaviour is recommended. This might involve a lower solution treating temperature and/or slight equipment modifications. The problem of accurate determination of the ternary compound composition is not easily overcome due to the low atomic number of Be. This problem may only be overcome with technological advances and extremely sensitive equipment which are presently unavailable.
REFERENCES


APPENDIX 1

The raw data presented in Tables 6, 7 and 8 is characteristic of the data used in the construction of the micro-hardness and resistivity curves presented in Chapter 4. The standard deviation values quoted in the tables (STD) correspond to the error bars in the figures. The standard error of measurement within the test data of a particular sample is given by,

$$\text{STD} = \sqrt{\sum_{i=1}^{n} \frac{(S_i - \bar{S})^2}{n-1}}$$

where $S$ is a particular data point and $n$ the number of data points.
Table 6
Raw Data for Al-0.2\%Ti 1 hr at 630°C, Quenched

<table>
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<tr>
<th></th>
<th>20.1</th>
<th>20.7</th>
<th>19.2</th>
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Table 7

Raw Data for Al-0.2%Ti-0.2%Be 1 hr at 630°C, Quenched

<p>| | | | | | | |</p>
<table>
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</table>

| 29.6 | 31.2 | 29.6 | 30.7 | 30.7 | 30.95 | 32.6 | 30.1 | 32  |
| 29.6 | 29.35| 31.2 | 30.95| 31.5 | 30.1  | 32.1 | 29.0 | 30.7|
| 30.1 | 31.8 | 29.6 | 32.0 | 31.6 | 29.25 | 31.5 | 31.2 | 30.95|
| 29.0 | 32.4 | 29.35| 31.2 | 31.8 | 31.2  | 29.85| 32.1 | 33.0|
| 29.85| 31.5 | 30.7 | 29.8 | 32.0 | 30.6  | 32.7 | 30.35| 32.1|

AVG. 29.63 31.25 30.09 30.93 31.52 30.42 31.75 30.55 31.75
STD 0.40 0.79 0.81 0.79 0.50 0.77 1.16 1.17 0.93
Table 8

Raw Data for Al-0.2%Be 1 hr at 630°C, Quenched

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<td>0.96</td>
</tr>
</tbody>
</table>
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