Al(f.c.c.):Al₃Sc(L1₂) INTERPHASE BOUNDARY ENERGY CALCULATIONS

R. W. HYLAND JR¹, M. ASTA², S. M. FOILES² and C. L. ROHRER¹

¹Alcoa Technical Center, Aluminum Company of America, 100 Technical Drive, Alcoa Center, PA 15069, U.S.A. and ²Computational Materials Science Department, Sandia National Laboratories, MS 9161, P.O. Box 969, Livermore, CA 94551, U.S.A.

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Abstract—These calculations assess the applicability of classical nucleation theory to the reaction f.c.c. → L1₂ occurring in dilute Al–Sc alloys. The orientation and temperature dependence of the energies of coherent Al(f.c.c.):Al₃Sc(L1₂) interphase boundaries were studied using atomistic simulation and a low temperature expansion (LTE) of the grand potential. Embedded atom method potentials were developed for both sets of calculations. Atomistic 0 K results for the anisotropy of the interphase boundary enthalpy gave $\gamma_{(100)} < \gamma_{(110)} < \gamma_{(111)}$ with values of 32.5, 51.3 and 66.3 mJ/m², respectively. LTE calculations of the excess grand potential of the (100) interface predicted a nearly temperature independent interfacial energy below 400 K that decreased modestly above 400 K. Monte Carlo (MC) simulations produced a compositional diffuseness of about 4 atomic layers separating the two bulk phases. Because the spatial extent of this region is very similar to the classically determined critical nucleus dimensions extracted from nucleation rate data, it is concluded that critical nuclei of Al₃Sc are most likely of nonclassical design at high undercooling. © 1998 Acta Metallurgica Inc.

1. INTRODUCTION

Although many of the theoretical aspects of homogeneous nucleation in solids are fairly well established [1–4], homogeneous nucleation is a relatively rare phase transformation in the majority of metallic alloy systems of commercial interest. However, the metallurgical benefits obtained from Al alloys containing Sc additions in the range of 0.2 at% [5–10] have been shown by direct microstructural analysis to result from the reaction f.c.c. → L1₂ in which fully coherent, ordered crystals of Al₃Sc form homogeneously from the matrix [11]. In view of the potential commercial importance of this reaction and its relatively simple thermodynamic and crystallographic aspects, it was judged to be desirable to use the f.c.c. → L1₂ transformation in Al rich Al–Sc as a model system for investigating the interfacial structure and chemistry associated with the formation of a strongly ordered intermetallic phase in an aluminum matrix.

The work presented here is a theoretical continuation of previous experimental work by Hyland [11] on the homogeneous nucleation kinetics of Al₃Sc(L1₂) in a dilute Al–Sc alloy. This work was based on TEM observations of the number density of Al₃Sc precipitates vs isothermal reaction time at 561 K and 616 K that permitted the measurement of nucleation rates. Using classical nucleation theory, an average Al(f.c.c.):Al₃Sc(L1₂) interphase boundary energy, γ , was subsequently back-calculated from the measured nucleation rate data. This average γ was compared with separate calculations

based on classical thermodynamic theory for three low index interface orientations, using the Becker model [12] for the chemical component of γ .

A number of assumptions attended the determination of both the average γ extracted from the experimental data and the calculations of γ for individual boundary orientations. First, the nuclei were assumed to be classical in nature and, therefore, to possess physical properties representative of a uniform second phase whose total free energy can be safely partitioned into volume and surface contributions. Second, the f.c.c. solid solution was assumed to follow simple regular solution thermodynamics, and the precipitate phase was assumed to be stoichiometric at 25 at% Sc.

Additional assumptions specific to the Al–Sc system were made in both approaches. The average γ values calculated from experimental nucleation rate data were based on the assumption that the anisotropy of the interfacial energy was negligible in the temperature range where the experiments were conducted. Under conditions where classical theory applies, it is usually the anisotropy of γ that is of overriding importance in determining the shape of the critical nucleus and, therefore, the overall barrier height to nucleation. Hence, the assumption of an isotropic interphase boundary energy requires some justification with increasing undercooling.

The calculations based on the Becker model also involved several additional assumptions. First, the composition gradient normal to the f.c.c.:L1₂ interface was assumed to be a step function, and the

compositions of each bulk phase were, therefore, assumed to be uniform throughout. This approximation neglects contributions to the total free energy from gradient energy terms [1, 13] that are expected to lower the interfacial energy at finite temperatures. Second, each bulk phase is assumed to be disordered in the Becker model; the neglect of long-range order in the Al_3Sc phase is also expected to lead to an overestimate of γ . Third, the atomic interaction energies were derived from continuum level bonding enthalpies for Al and Sc. Finally, the temperature dependence of γ was assumed to be relatively weak based upon the Al–Sc phase diagram [14] which shows very little variation in the phase boundary compositions with temperature. This is an indication that the chemical component of γ should be only weakly temperature dependent and, in view of the highly ordered state of the L1_2 phase [15], entropy contributions are expected to be small.

Classical nucleation theory is based on the assumption that a critical nucleus is large enough that its free energy of formation can be partitioned into a surface and a volume free energy contribution. The work of LeGoues *et al.* [2–4] has shown that classical theory is applicable to critical nuclei of Co rich precipitates in dilute Cu–Co alloys reacted at low to moderate (i.e. less than 200 K) undercooling. A reasonable criterion for the applicability of classical nucleation theory, first suggested in [16] and later modified in [3], is that the dimensions of a critical nucleus must be greater than the thickness of a compositionally diffuse interphase interface at a given reaction temperature. As noted by LeGoues, Lee and Aaronson [3], a classical nucleus is expected to be one that attains a constant composition at some point throughout its volume, though their work suggested that it may not be necessary for the entire nucleus to be compositionally uniform in order for classical nucleation theory to be applicable. If the nucleus composition varies continuously throughout its volume, the use of the classical approximation is inappropriate for establishing the energetics of critical nuclei and for comparing nucleation theory with experiment.

It is known that as the relative undercooling below the solvus is increased, the critical nucleus dimensions decrease, making the application of classical models of critical nuclei problematic. At large enough undercooling, the nuclei become small enough that they are probably not compositionally uniform at any point. In such cases, the critical

nuclei are considered to be nonclassical, and analysis of experimental nucleation rate data requires the use of a theory that can treat nonuniform phases. The continuum nonclassical theory of nucleation due to Cahn and Hilliard [16] is well developed for cases where the free energy of the system can be written as a continuous function of the composition and its spatial derivatives. In the Al–Sc system, such an approach is of limited utility since the Al_3Sc phase is highly stoichiometric, while the f.c.c. solid solution exhibits a vanishing solubility of Sc. These features of the Al–Sc system imply that the interphase boundaries will be fairly sharp compositionally on an atomic scale, thus making difficult a continuum nonclassical formulation of the two-phase microstructure†. For this reason, an alternate means of evaluating the composition profile normal to an f.c.c.: L1_2 interphase boundary is desirable in order to determine whether nuclei are forming classically or nonclassically at a given temperature.

While the spatial extent of a compositionally diffuse interface cannot be probed readily via experiment, it can be estimated by appealing to calculations based on gradient thermodynamics [1–4], or via atomistic simulation of the interfacial region, if the interatomic potentials can be adequately described. In view of the availability of many body, volume dependent interatomic potential models such as the embedded atom method (EAM) [18, 19], atomistic simulations of many metallic systems are desirable. Furthermore, atomistic simulations obviate all of the classical assumptions listed above. In the present work, EAM based atomistic simulations and a low temperature expansion (LTE) approach to be described below were used to determine the applicability of classical vs nonclassical nucleation theory in interpreting the available experimental data in dilute Al–Sc alloys. The LTE method was used to calculate the temperature dependence of the $(100)_{\text{f.c.c.}}|| (100)_{\text{L1}_2}$ interphase boundary energy. Atomistic energy minimization at 0 K and Monte Carlo simulations at 573 K (chosen to coincide roughly with the temperature range used in the experimental work [11]) were used, respectively, to study the orientation dependence of the excess enthalpy and to calculate the width of the probable compositional diffuseness present at the interphase boundaries. A comparison of the predicted width of the compositional gradient to the critical nucleus size calculated from the experimental nucleation rate data should allow for an assessment of the applicability of classical vs nonclassical nucleation theory to the Al_3Sc (L1_2) phase in the Al–Sc binary alloy in the temperature range used.

In the next section, details of the interatomic potentials used in this study are presented along with a discussion of the ability of these potentials to reproduce established thermodynamic behavior. The subsequent two sections discuss the low and

†We note that prior to submission of the present work, Poduri and Chen [17] treated the problem of nonclassical nucleation of δ' in Al–Li alloys within a Cahn–Hilliard formalism. However, the anti site defect energies of this phase are sufficiently low so that a continuous free energy function for the f.c.c.: L1_2 case is a reasonable approximation.

high temperature calculations, respectively. Finally, the likelihood of observing classical nucleation in the temperature range studied in the experimental measurements [11] of the nucleation rate of the $\text{Al}_3\text{Sc}(\text{L}1_2)$ phase in dilute Al–Sc alloys is discussed.

2. DETAILS OF THE INTERATOMIC POTENTIALS

A rough set of EAM interatomic potentials were developed for the Al: Al_3Sc interfacial energy calculations. Within the EAM method [20], the energy of an n atom system is modeled as having two contributions. The first is the energy associated with the binding of a given atom to the local electron density due to all of the other atoms in the system. The second one is a pair interaction that represents the classical electrostatic interactions. Thus, the energy is written as

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{ij, i \neq j} \phi_{ij}(r_{ij}) \quad (1)$$

where $F_i(\rho_i)$ is the energy to embed an atom into the local electron density ρ and $\phi_{ij}(r_{ij})$ is the pair interaction between atoms i and j that are a distance r_{ij} apart.

The electrostatic interaction was chosen to be of the Morse type, and the Al pair potential due to Voter and Chen [21] was used. The potentials were optimized neither for pure Al nor for pure Sc. An approximate form for the Sc potential was obtained by fitting the properties of Sc to an f.c.c. crystal structure having the same molar volume as the standard state h.c.p. structure. This approximation was made because the properties of the f.c.c. solid solution and of the Al_3Sc phase were the main focus of the potential development, both of which incorporate Sc in an f.c.c. environment. The embedding functions $F(\rho)$, pair potentials $\phi(r)$ and electron density functions $\rho(r)$ were derived using the fitting codes due to Foiles and Daw [22] that were originally developed for Ni_3Al . A smooth cutoff radius was used for Al (5.55 Å) and Sc (5.60 Å). This cutoff extends beyond third nearest neighbors in this case. Figure 1(a) displays the effective two body potentials and (b) gives the electron densities for Al and Sc (referenced to an f.c.c. lattice) as a function of radial distance from the nucleus. These functions were obtained from the fitting process using the physical constants that are noted by an asterisk in Table 1.

Calculated properties of Al, Sc and Al_3Sc are compared to experimental information in Table 1. In the table, B , A and $\langle G \rangle_V$ are the bulk modulus, the anisotropy ratio and the Voigt averaged shear modulus, respectively, derived from the elastic constants as follows:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (2)$$

Pair potentials for Al–Al, Sc–Sc, Al–Sc

Electron density for Al and Sc

Fig. 1. The effective two body potentials (a) and electron densities (b) calculated for Al and Sc. The Sc results have been referenced to an f.c.c. lattice.

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (3)$$

$$\langle G \rangle_V = \frac{3C_{44} + C_{11} - C_{12}}{5} \quad (4)$$

A reasonable, if not ideal, fit between calculated and experimental properties was obtained. Note that the calculated value of the pure Sc f.c.c. to h.c.p. transformation energy, $\Delta E_{\text{h.c.p.}-\text{f.c.c.}}$, is negative. This is an interesting result because even though the potentials were fit assuming that Sc atoms occupy ideal f.c.c. sites, the calculated value of $\Delta E_{\text{h.c.p.}-\text{f.c.c.}}$ indicates that the h.c.p. structure should be more stable than the f.c.c. structure for Sc, in agreement with experiment at low temperatures.

A series of Monte Carlo (MC) calculations were carried out to study the stability of the $\text{L}1_2$ phase and to test the ability of the Al–Sc potentials to predict the appropriate equilibrium phases at a specified combination of temperature, pressure and chemical potential difference, $\Delta\mu = (\mu_{\text{Al}} - \mu_{\text{Sc}})$. This test was also applied to potentials for Al, Ni and Ni_3Al by Foiles and Daw [22]. The MC calculations

Table 1. Calculated vs experimental material properties for Al, Sc and Al₃Sc. B , $\langle G \rangle_V$ and the elastic constants are in units of 10^{12} erg/cm³ or 10^{11} Pa. E_{vac} , sublimation energies, E_{sub} , the dilute heat of solution of Sc in Al, H, and the f.c.c. to b.c.c. and f.c.c. to h.c.p. transformation energies, $\Delta E_{\text{b.c.c.} \rightarrow \text{f.c.c.}}$ and $\Delta E_{\text{h.c.p.} \rightarrow \text{f.c.c.}}$, are in units of eV/atom. The Al₃Sc lattice parameter, a_{lat} , is in Å. The Al₃Sc super intrinsic stacking fault energy, sisf , and the (100) and (111) antiphase boundary energies, apb1 and apb2 , are in erg/cm². Properties that were directly fit are asterisked. Unless indicated otherwise, calculations were carried out with all atoms at their ideal crystal sites.

	Al		Sc		Al ₃ Sc	
	calculated	exp	calculated	exp	calculated	exp
B	0.793*	0.793	0.572*	0.572	B	1.011*
A	1.529	1.213	3.760	1.000	E_{sub}	-0.259*
$\langle G \rangle_V$	0.277	0.294	0.284*	0.298	a_{lat}	4.101*
C_{11}	1.073*	1.14 [24]	0.714	0.969 [24]	sisf	256.3*
C_{12}	0.653*	0.619 [24]	0.501	0.373 [24]	apb1	330.2*
C_{44}	0.321*	0.316 [24]	0.401	0.298 [24]	apb2	433.9*
E_{vac}	0.637*	0.67 [26]	1.442*	1.4 ^a		670 [25]
	(atomic relaxation allowed)					
$\Delta E_{\text{b.c.c.} \rightarrow \text{f.c.c.}}$	0.073	0.10 [27, 28]	0.015			
$\Delta E_{\text{h.c.p.} \rightarrow \text{f.c.c.}}$	0.014	0.06 [27, 28]	-0.003			
H			-0.663*	-0.62 ^b		

^aEstimated from $E_{\text{vac}} \sim 9kT_m$.

^bEstimated from regular solution model.

were carried out assuming the system is always in thermodynamic equilibrium. Therefore, in two phase regions, the chemical potentials of the individual atomic species i , in each phase, $\mu_{i,a(b)}$, must be equal by definition; i.e. $\mu_{i,a} = \mu_{i,b} = \mu_i$. Also by definition, the chemical potentials of the individual species must be constant as a function of composition across a two phase region, thus making $\Delta\mu$ constant across this region as well. As shown in the Al–Sc phase diagram in Fig. 2, Al and Sc form a series of line compounds separated by two phase regions. Thus, a plot of $\Delta\mu$ vs Sc content should show a series of horizontal lines separated by sharp vertical transitions at the boundaries between two phase and single phase regions. Our goals were to test whether the fitted potentials could generate such a plot and to identify the appropriate value of $\Delta\mu$ for the two phase Al(f.c.c.):Al₃Sc(L₁₂) region of interest in this study.

The procedure involved setting up a two phase “box” containing a total of 864 atoms, Al in one-

half of the box and Al₃Sc in the other, finding the 0 K minimum energy atomic configuration using a conjugate gradient descent technique [29], and then conducting a series of MC simulations at 573 K, varying $\Delta\mu$. The total number of atoms was held constant, but the relative number of Al atoms to Sc atoms was allowed to change in accordance with the requirements of an open system using the specified values of $\Delta\mu$. A MC step comprised either (i) a random spatial adjustment of a randomly chosen atom plus a replacement of its atomic species (Al $\rightarrow$ Sc or Sc $\rightarrow$ Al) or (ii) a random adjustment of each of the three box lengths. Step type (ii) allows for a change in total volume, which is effectively comparable to the condition of zero applied pressure. Each simulation was equilibrated for 2 500 000 steps, and the composition of the system was averaged over a subsequent 1 000 000 steps. Periodic boundary conditions were enforced on the computational box, the effects of which are discussed in Section 3.

The black dots in Fig. 3 indicate the resulting averaged composition as a function of $\Delta\mu$. Note that the axes have been reversed, making $\Delta\mu$ the ordinate rather than the abscissa, in order to more clearly match the expected $\Delta\mu$ vs at% Sc diagram described above. As shown in the figure, large ranges in $\Delta\mu$ resulted in single-valued Al:Sc compositions. These compositions correspond to the compositions of the line compounds, the boundaries between two phase regions. The potentials did generate both the compositions and crystallographic structures of the Al(f.c.c.), Al₃Sc(L₁₂), AlSc(B2) and Sc(f.c.c.) phases. The Al₂Sc and AlSc₂ phases, however, never materialized. This was not surprising, as the interatomic potentials were not fit for either of these two phases. Furthermore, the constraint on the simulation box volume allowing the lengths of the box axes to change, but not the angles between axes, should have hindered the for-

Fig. 2. The Al–Sc phase diagram after Murray [14].

Fig. 3. Difference in chemical potentials, $\Delta\mu$, vs at% Sc. Abrupt transitions in $\Delta\mu$ indicate thermodynamic phase boundaries. Constant $\Delta\mu$, as represented by horizontal bars, indicates the existence of a two phase region. Dots and crosses designate different simulation initial conditions as discussed in the text.

mation of the h.c.p. AlSc_2 phase. The Al_2Sc phase, on the other hand, is cubic, but possesses a 24 atom unit cell. The formation of such a complex phase is probably beyond the capabilities of the present simulations. Nevertheless, to assure that the two phase initial atomic configuration used in the simulations was not biasing the equilibrated state, additional simulations were run starting with a random f.c.c. solid solution of 61 at% Sc. The results from this set of simulations are designated in Fig. 3 by crosses. All of the final compositions are in good agreement with the original set of simulations except for the composition calculated for $\Delta\mu$ equal to -0.4 . The resulting mole fraction of Sc would lead one to believe that the AlSc_2 phase had been created, but, in fact, the resulting atomic configuration was not single phase. Instead, large blocks of pure f.c.c. Sc were separated by layers of Al. This result illustrates the sensitivity of the equilibrated state obtained from the chosen interatomic potentials to the initial atomic configuration. Nonetheless, the remaining results were consistent, and for the purposes of the present work, the chemical potential difference for the f.c.c.: L_{12} two phase region of interest was established at $\Delta\mu \sim -1.3$ eV.

Little emphasis is placed upon differences among the individual absolute values of the calculated interfacial energies to be discussed in the following section because of the non-ideal fit of the potentials to the limited experimental material properties and thermodynamic data. We expect, however, that the reasonable fit to the available information demonstrated above should result in a valid representation

of the qualitative behavior of the interphase boundary energies thus calculated.

3. LOW TEMPERATURE INTERPHASE BOUNDARY ENERGY CALCULATIONS

The total energy of a system containing a coherent interphase interface separating two phases that possess different molar volumes can be written as a sum of the contributions from (i) the total energies of the two isolated phases, (ii), the chemical work associated with the creation of the composition gradient between phases and (iii), the energy associated with atomic and interplanar displacements at the interface. The difference between the sum of the last two factors and the volume-dependent elastic strain energy is the classically defined interphase boundary energy, γ . An advantage of atomistic simulation is its ability to treat the chemical and atomic relaxation contributions to γ consistently without making the assumptions required in continuum level treatments.

The energies of systems containing (100), (110) and (111) $\text{Al}:\text{Al}_3\text{Sc}$ interfaces were minimized at 0 K. Because the unconstrained lattice parameters of Al and Al_3Sc differ by approximately 1.4%, being 4.05 Å and 4.105 Å for Al and Al_3Sc , respectively, the bulk phase reservoirs are expected to deviate from their far field, undistorted, molar volumes in the vicinity of the interface. Simulations of the chosen interfaces were set up with total number of atoms and total number of bulk atomic layers parallel with and on either side of the interface as listed in Table 2. The initial configuration was established with a uniform lattice parameter of 4.05 Å in both

Table 2. Number of atoms incorporated in the interface simulations

	(100)	(110)	(111)
Total # of atoms:	2560	3584	3024
# Al:	2240	3136	2646
# Sc:	320	448	378
# of layers in each phase parallel with and on either side of the interface:	10	16	9

phases and a perfect match at the interface. Periodic boundary conditions in all directions were employed, making the interface effectively infinite in extent, but producing “image” interfaces parallel to the actual interface. The periodic boundary conditions also caused the outer face of the simulation box parallel to the actual interface to be a second explicit interface. Thus, all calculated excess energies are divided by two and are representative of the average energy of the two explicit interfaces. Figure 4 is a schematic of the simulation conditions.

It is important to emphasize the simulation conditions for the following reason. Based on Fig. 4, it is clear that atomic relaxation in the direction perpendicular to the interface is not artificially constrained by the imposition of periodic boundary conditions. However, the box faces perpendicular to the plane of the interface are constrained to remain flat as a consequence of these boundary conditions. In other words, far from the interface, the lattice constants of the two reference phases parallel to the interface are artificially required to be identical. They are inhibited from fully relaxing to their equilibrated values of 4.05 Å and 4.105 Å. Therefore, neither reservoir attains its undistorted unit cell dimensions far from the interface. This enforced condition is expected to raise the total energy of a system containing an interface by some amount over the value that would be obtained if three-dimensional relaxation was permitted.

Fig. 4. Schematic depiction of interface simulation set-up with periodic boundary conditions. The central bold box with the labeled phases is explicitly simulated. Interactions with the image boxes surrounding the central box occur because of the periodic boundary conditions. Two explicit interfaces are calculated as indicated by arrows.

In order to calculate a barrier height for diffusional nucleation we require the chemical component of the interphase boundary energy. To ascertain this quantity, which is independent of the size of the computational system under study, the following procedure was adopted. The energy of the system containing the interphase boundary was minimized by allowing atomic and volumetric relaxation at zero applied pressure, subject to the boundary conditions discussed above. Similar energy minimizations were carried out on the bulk Al and Al₃Sc phases set up with the same orientations as the interface calculations and using the same total number of atoms. In the simulations of the bulk Al and Al₃Sc, the lattice constants parallel to the interphase boundary were fixed at the value obtained from the system containing the interface. As a consequence of the imposed boundary conditions, the energies of the elastically distorted bulk reservoirs were calculated by permitting relaxation normal to the interface. The interfacial energies, γ , were subsequently calculated as

$$\gamma = \frac{E_{\text{ipb}} - \frac{1}{2}(E_{\text{Al}} + E_{\text{Al}_3\text{Sc}})}{2A} \quad (5)$$

with the values of E_s being the energies of the interface containing systems and of the two elastically distorted bulk reference phases, respectively, and A being the interfacial area. The 0 K excess energies for each of the three crystallographic interfaces at zero applied pressure are listed in Table 3. As shown in the table, $\gamma_{(100)} < \gamma_{(110)} < \gamma_{(111)}$. The ratios of these calculated interfacial energies dictate that both the (111) and (110) orientations are unstable with respect to (100) faceting at 0 K. In particular, since $\gamma_{(110)} > \sqrt{2}\gamma_{(100)}$, and $\gamma_{(111)} > \sqrt{3}\gamma_{(100)}$, both (110) and (111) interfaces are unstable with respect to (100) faceting. The calculated results from [11] are presented in Table 3 for comparison. Note that the trend in energies is opposite to that calculated atomistically. The Becker model predicts that (111) facets should be significantly more stable than (100) or (110) facets. If the Becker model predictions were correct, one would expect $(111)_{\text{L12}} || (111)_{\text{f.c.c.}}$, reflecting the low energy of the (111) interface, since orientation relationships are presumably set at nucleation and survive into

Table 3. Interphase boundary energies (mJ/m²) calculated under the condition of zero applied pressure at 0 K. Hyland's calculated results [11] based on the Becker model [12] are presented for comparison. The (111) interfaces are differentiated as (111) ~ Al:Al₃Sc, (111) a ~ Al(0.25 at% Sc):Al₃Sc and (111) b ~ Al(1 at% Sc):Al₃Sc. Lattice parameters are in Å

	(100)	(110)	(111)
zero applied pressure			
γ (from [11])	32.5 (126)	51.3 (112)	78.2 (28)
$a_{\parallel}$	4.080	4.086, 4.077	4.084
$a_{\perp}$	4.071	4.069	4.066

growth. Experimentally, this orientation relationship is not observed. Repeated TEM investigations [7–11] have shown that Al_3Sc precipitates nucleate with a cube:cube orientation relationship and do not demonstrate an orientation relationship defined by (111) conjugate habit planes. The atomistic calculations described in the present work are more consistent with these experimental observations.

Also listed in Table 3 are the calculated lattice parameters both perpendicular and parallel to the interface. The perpendicular lattice parameters are seen to be close to the average between the pure Al and pure Al_3Sc lattice parameters, as expected, since the bulk phase lattice constants are permitted full relaxation perpendicular to the interface. The values of the lattice parameters parallel to the interface, however, are those that result from the minimization of the total energy subject to the periodic boundary conditions.

4. HIGH TEMPERATURE INTERPHASE BOUNDARY ENERGY CALCULATIONS

To examine the Sc composition profiles near the interphase interface, MC simulations were carried out at 573 K for each of the three orientations, and low temperature expansion (LTE) calculations were performed as a function of temperature for the (100) interface. The MC simulations were carried out with zero applied pressure, constant temperature and constant number of atoms. Unlike in the MC simulations described earlier, atomic MC steps involved randomly choosing *two* atoms, giving each a random spatial adjustment and then *exchanging* their respective element types. This kind of step mimics long range volume interdiffusion, without regard for the path an atom may have taken, but holds constant the relative number of Al atoms with respect to the number of Sc atoms (closed system). The initial atomic configurations used were the 0 K, minimum energy interface and bulk configurations described in the previous section. Each configuration was subsequently equilibrated at 573 K for 5,000,000 MC steps, followed by a 5,000,000 step period over which the total enthalpy, volume, parallel and perpendicular lattice parameters, and atomic positions were averaged.

To determine the temperature dependence of the total interfacial energy, including entropic contributions, LTE calculations of finite temperature grand potentials (Ω) [30] were performed for the bulk Al and Al_3Sc phases, as well as for the (100) Al: Al_3Sc interphase boundary. In the LTE method [31], the grand potential is calculated directly from a Taylor series expansion of the logarithm of the alloy partition function. To second-order, the LTE expression for the grand-potential has the following form:

$$\begin{aligned}\Omega = & E_0 - k_B T \sum_p \exp(\Delta\omega_p/k_B T) \\ & + \frac{1}{2} k_B T \sum_p \exp(-2\Delta\omega_p/k_B T) \\ & - \frac{1}{2} k_B T \sum_{p,p'} [\exp(-\Delta\omega_{p,p'}/k_B T) \\ & - \exp(-(\Delta\omega_p + \Delta\omega_{p'})/k_B T)]\end{aligned}\quad (6)$$

where the sums are over lattice sites p , and where k_B and T represent Boltzmann's constant and the temperature, respectively. In equation (6), E_0 represents the 0 K grand potential, and the variables $\Delta\omega_p$ and $\Delta\omega_{p,p'}$ represent excitation energies. $\Delta\omega_p$ denotes the change in the zero-temperature grand-potential associated with switching the atom type at site p . Similarly, $\Delta\omega_{p,p'}$ is the cost in the zero-temperature grand potential associated with changing atom types at both sites p and p' (note that for close-neighboring sites, p and p' , $\Delta\omega_{p,p'} \neq \Delta\omega_p + \Delta\omega_{p'}$).

Formally, the finite-temperature interfacial energy for an (hkl) interface can be written as follows [30]: $\gamma_{hkl} = (\Omega_{hkl} - \Omega_0)/A$, where Ω_{hkl} is the value of the grand potential for an inhomogeneous alloy system containing an (hkl) -oriented interphase boundary, and Ω_0 corresponds to the elastically distorted homogeneous bulk phase reservoirs. Using the LTE approach, the grand potential difference can be determined once the excitation energies have been computed for all symmetry-inequivalent points in the bulk phases, and for all points inside a region near the boundary where the excitation energies have values which differ from those in either of the corresponding bulk phases.

In the current calculations, we have included terms in the low temperature expansion associated with all single-atom excitations and two-atom substitutions for pairs of atoms separated by a distance less than or equal to the fourth neighbor shell. The inclusion of these terms was found to lead to an expansion for the grand potential difference which was reasonably well converged (the contribution from the second order term is less than one third that of the first order term contribution) for temperatures up to 800 K. Excitation energies were calculated directly from the EAM potentials described earlier using a supercell geometry. The supercell included a total of 12 unit cells normal to the interphase boundary and 6 unit cells in each of the in-boundary plane directions, requiring a total of 1728 atoms. The atomic positions were relaxed to minimize the energy after each atomic rearrangement. Note that in calculating the values of the excitation energies, temperature effects associated with atomic vibrations were neglected. As a consequence, the LTE calculations of the alloy grand potentials include configurational, but not vibrational entropy contributions.

Fig. 5. Excess thermodynamic properties of the {100} interphase boundary orientation in Al(f.c.c.):Al₃Sc(LI₂) based on the LTE method.

In Fig. 5, the total interfacial energy, γ , enthalpy, H , and entropy contribution, $-TS$, are plotted as a function of temperature for the (100) interphase boundary. It is seen that the excess free energy is practically temperature independent up to approximately 400 K, and then decreases by approximately 10% from 400 K to 800 K. The decrease above 400 K can be attributed to the significant configurational entropy contribution at the higher temperatures which accompanies increasing compositional diffuseness at the interface. The experimentally determined average γ is 93 ± 22 mJ/m² at 616 K and 78 ± 20 mJ/m² at 561 K [11], compared to the LTE values of 30.9 mJ/m² at 616 K and 31.5 mJ/m² at 561 K, respectively, for the (100) interface. In spite of the non-ideal fit of the interatomic potentials, the calculated values of $\gamma_{(100)}$ seem reasonable with respect to the experimental results that were secured from the application of classical nucleation theory to the nucleation rate data. It is possible that a somewhat higher LTE derived interphase boundary energies would have resulted from the use of a different Al potential, since very recent research by Liu [32] has demonstrated that the melting temperature of Al based on the Voter and Chen [21] EAM potential is about 30% lower than the experimentally observed value. However, a more accurate Al potential such as that due to Ercolessi and Adams [33] was not available at the time the present research was being conducted.

An important influence on the high temperature interfacial thermodynamic properties is the composition gradient across the interfaces. The average compositions of atomic layers parallel to the interfaces were determined from the MC results and are graphically represented in Fig. 6. For each orientation, distinctly bulk-like regions were found on either side of the interfaces separated by approxi-

mately four atomic layers of compositional diffuseness. The chemical diffuseness was most pronounced for the highest energy (111) interface followed by the (110) and the (100) interfaces.

Two issues are raised pertaining to the Sc distributions in the atomistic calculations and, therefore, to the calculated interphase boundary energies. The first issue is whether or not enough layers parallel to the interfaces were included in the calculations to actually have large enough bulk-like regions so that the explicit interfaces were both fully relaxed and non-interacting. The second is that, even though Sc solubility in Al is negligible, it is not zero. The MC simulations discussed thus far involved pure Al in contact with pure Al₃Sc. Therefore, the slight solubility of Sc on the Al side of the reservoir bounding the interfaces could only come from the bulk Al₃Sc, rather than from equilibrium segregation of Sc in solid solution to the interface. Several calculations were carried out to address these two issues.

To address the first issue, a second set of 0 K energy minimizations and 573 K MC simulations of the Al:Al₃Sc (100) interface were carried out with 18 bulk atomic layers parallel to and on either side of the interface, as opposed to the 10 layers used in the previous (100) interface calculations. 4608 atoms were included in these calculations, as opposed to 2560. The interfacial area was the same as that of the previous system. The 0 K interfacial excess enthalpy was calculated to have the same value, 32.5 mJ/m², as was obtained from the smaller system. The MC calculated composition profile at 573 K for the larger system is shown in Fig. 7. Again, two bulk-like regions are separated by four atomic layers of compositional diffuseness. From these results, it is concluded that the smaller simulation systems are capable of representing non-interacting interfaces separated by bulk phases of infinite extent.

To investigate the temperature dependence of the f.c.c. bulk phase composition and its effect on the spatial extent of the compositionally diffuse region associated with the Al:Al₃Sc interphase boundaries, two 573 K MC simulations of the (111) interface orientation were carried out with 0.25 and 1.0 at% Sc in Al solid solution. Both of these compositions are beyond the solubility limit predicted by the phase diagram. Therefore, the majority of the excess Sc was expected to create additional Al₃Sc, the remainder being necessary to establish the appropriate chemical potential of Sc in the f.c.c. phase in the limit of a non-vanishing solid solubility. For all simulations, the Sc was initially randomly distributed in the solid solution, the systems were energy minimized at 0 K, and then the MC procedure discussed above was carried out. Composition profiles from these two cases showed little difference from that of the pure Al:Al₃Sc interface as shown in Fig. 8. Hence, it is reasonable to

Fig. 6. Interphase (100), (110) and (111) interface composition profiles at 573 K. Dark bars represent mole fraction of Al. Light bars represent mole fraction of Sc.

conclude that the calculated composition profiles are only weakly affected by the exact solubility of Sc in Al because a truly dilute solid solution exists, even at relatively high values of the homologous temperature T/T_{solvus} .

5. APPLICABILITY OF CLASSICAL THEORY TO Al-Sc ALLOYS REACTED AT 573 K

In their treatment of nucleation in a nonuniform regular solution, Cahn and Hilliard [16] suggested that a useful criterion for determining the applica-

Fig. 7. Larger system interphase (100) interface composition profile at 573 K. Dark bars represent mole fraction of Al. Light bars represent mole fraction of Sc.

bility of classical theory can be expressed in terms of γ and the extent of the compositional diffuseness, l , as follows:

$$\frac{\pi\gamma l^2}{45kT} \ll 1 \quad (7)$$

In this expression, k is Boltzmann's constant and T is absolute temperature. As long as the width of the diffuse region is small compared with the nucleus size, classical theory is expected to be a reasonable approximation. Taking the LTE-calculated value of γ at 573 K, ~ 32 mJ/m², and using a compositionally diffuse region of $4 \cdot d_{(100)}$ with a lattice parameter of 4.077 Å, the argument on the left side of equation (7) is approximately 0.75. This value is not small compared to unity. Alternatively, taking the average value of the interfacial energy extracted from experiment [11] and using the definition of the radius of a classical critical nucleus, r^* , in terms of the interfacial energy and the strain energy corrected volume free energy change, the size of the nucleus can be calculated from equation (8) and compared to the width of the diffuse region simulated in the present work.

$$r^* = \frac{-2\gamma}{\Delta F_v + \phi} \quad (8)$$

where ϕ is the elastic volume strain energy. Using values for the interfacial energy of 94 mJ/m² [11], for ΔF_v of -4.855×10^8 J/m³, and for ϕ of 1.92×10^7 J/m³, a value of $r^* = 4.07$ Å is obtained. This value is roughly the unit cell dimension. (The larger of the two experimentally determined values for the interfacial energy was used because it should result in an upper bound for the nucleus radius.) This value of the nucleus radius is smaller than the calculated interfacial thickness, l . With respect to the Cahn–Hilliard criterion discussed above, it is unlikely that

nucleation of Al₃Sc should be described classically in the temperature range examined in [11]. This may be anticipated in view of the large undercooling that was used in [11] to avoid the cellular reaction that occurs at temperatures above about 650 K. Using the phase disappearance method, a solvus temperature of about 840 K was secured for these alloys. This implies an undercooling of greater than 260 K for the experimental measurements of nucleation kinetics. Under such conditions, the classical definition given by equation (8) is not very physical. It is probably sufficient to interpret these findings as a strong indication that a wide range of embryo shapes may become stable nuclei and that analysis of the nucleation barrier heights is best undertaken in terms of nonclassical theory in this case.

6. CONCLUSIONS

The orientation dependence of the Al(f.c.c.):Al₃Sc(L1₂) interphase boundary energy (at 0 K) and the temperature dependence of γ were calculated using EAM based atomistic simulation and low temperature expansion methods, respectively. Atomistic 0 K results indicated that the (100) interface should be the most stable of the three orientations studied and that the (111) interface should be the least stable; thus, Al₃Sc precipitates at 0 K would be expected to be principally cuboidal. LTE calculations of the (100) interface showed that the interfacial energy was roughly temperature independent up to 400 K. Above 400 K, the interfacial energy was observed to decrease with increasing temperature as the entropy contribution became more significant with increasing interfacial compositional diffuseness. At 573 K, MC calculations showed a four atomic layer compositionally diffuse

a) Al(0.25%Sc):Al₃Sc b) Al(1.0%Sc):Al₃Sc

Fig. 8. Interphase (111) interface composition profiles for Al(0.25% Sc):Al₃Sc and Al(1.0% Sc):Al₃Sc at 573 K. Dark bars represent mole fraction of Al. Light bars represent mole fraction of Sc.

region was observed at the interphase interfaces. Independent estimates of the critical nucleus dimensions and the relative barrier heights to nucleation applicable at 573 K in Al–0.1 at% Sc indicate that critical nuclei of Al₃Sc probably are nonclassical and, therefore, are likely to be nonuniform during the early stages of precipitation. A nonclassical treatment such as that due to Poduri and Chen [17], coupled with atomistic simulations of the interphase boundary energy would be useful in examining further the properties of critical nuclei of ordered precipitates at larger undercooling.

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