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## Extension of the N-model to predict competing homogeneous and heterogeneous precipitation in Al-Sc alloys

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## Abstract

A model has been developed to predict the precipitation and coarsening kinetics of the Al<sub>3</sub>Sc phase in Al-Sc alloys. This model is based on the N-model framework of Kampmann and Wagner (KWN), extended to account for competition between heterogeneous nucleation on dislocations and homogeneous nucleation. The predictions of the model have been tested against experimental data in the literature and also new experimental results, which are reported in this paper. Both the predicted particle size distributions and the evolution of particle size with time are in good agreement with the experimental data. The model correctly predicts the transition from homogeneous to heterogeneous domination of nucleation, as the ageing temperature is increased, and has been used to investigate the nucleation behaviour in detail. TTT diagrams for the precipitation of Al<sub>3</sub>Sc have also been predicted for Al-Sc alloys. © 2003 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Aluminium alloys; Nucleation of phase transformations; Phase transformation kinetics; Coarsening; Modelling

## 1. Introduction

The addition of small quantities of scandium to aluminium alloys can lead to a number of benefits, including grain refinement, an increase in strength and enhanced resistance to recrystallization [1]. These effects can largely be attributed to the pres-

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ence of the L1<sub>2</sub> Al<sub>3</sub>Sc trialuminide phase. For hypereutectic alloys (Sc>0.47wt%), this forms as a primary phase from liquid aluminium, and is a powerful grain refiner [2]. For hypoeutectic alloys (with typical Sc concentrations<0.3wt%), the scandium can be taken into solid solution after casting and then precipitated as a dispersion of Al<sub>3</sub>Sc particles by a suitable ageing treatment. The L1<sub>2</sub> Al<sub>3</sub>Sc phase has a lattice parameter of 0.4105nm [3], which is only 1.6% greater than that of the aluminium matrix. As a result of this, and the similar crystal structures of the precipitate and matrix, Al<sub>3</sub>Sc often precipitates homogeneously as fine, fully coherent particles [4,5]. Furthermore,

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these particles are thermodynamically stable and have modest coarsening rates at elevated temperature. These attractive features have led to considerable efforts to characterize and understand  $Al_3Sc$ precipitation in detail (e.g. [4–7]).

In addition to interest in its practical applications, the Al Sc system is also a popular choice for testing the classical theories of precipitate nucleation, growth and coarsening. The small misfit and well matched crystal structures between the matrix and the Al<sub>3</sub>Sc phase means that homogeneous nucleation of spherical precipitate particles is often observed [4] and this is the simplest case to treat with classical nucleation theory. These particles then undergo diffusion controlled growth, largely retaining a spherical morphology. Furthermore, the thermodynamics of the Al-Sc system have recently been well characterized, so that there are reliable data for input into kinetic models [8]. Because scandium is usually only added in very small quantities for the purpose of precipitating Al<sub>3</sub>Sc particles, the equilibrium volume fraction of Al<sub>3</sub>Sc is small and the interparticle spacing (relative to the particle size) is large. Therefore, there is likely to be negligible interaction between the local diffusion and strain fields surrounding each precipitate. Precipitate coarsening is thus expected to be controlled by diffusion and interfacial energy alone, with negligible influence of precipitate volume fraction. This makes coarsening in these alloys an ideal test case for Lifshitz-Slyozov-Wagner (LSW) coarsening theory [9,10].

Several workers have tested the theories of homogeneous nucleation and coarsening by comparing predictions with data from Al-Sc alloys. The early, nucleation stages, of the transformation have been investigated by Hyland [4] under conditions where homogeneous nucleation is dominant. These results were found to be in reasonable agreement with classical, time dependent, nucleation theory [11]. Other studies [5,7,12] have focused on the size evolution of Al<sub>3</sub>Sc particles during the later stages of transformation, where the change in size is dominated by coarsening. In general, the results of these studies are in good agreement with the predictions of LSW theory, with the mean particle radius increasing with the cube root of the ageing time [9,10].

Recent investigations have shown that the precipitation behaviour of  $Al_3Sc$  can be more complex than simple homogeneous formation of spherical particles. For example, under certain conditions of alloy composition and ageing temperature, heterogeneous nucleation on dislocations is observed and can dominate homogeneous nucleation [5,7]. In addition, during coarsening, the  $Al_3Sc$  particles often become semi-coherent, and this partial loss of coherency may be accompanied by a change in particle morphology [5]. To date, these effects have not been considered in attempts to model  $Al_3Sc$  nucleation and coarsening.

Although the classical models of nucleation and coarsening appear successful in predicting the early and late stages of Al<sub>3</sub>Sc formation, under certain conditions, these models are not capable of predicting the full evolution of the Al<sub>3</sub>Sc precipitate size distribution. To produce a model that is valid over the full range of transformation, the competing processes of nucleation, growth and coarsening cannot be considered in isolation, but must instead be treated together [13]. A powerful method for dealing with concomitant nucleation, growth and coarsening has been developed by Kampmann and Wagner, and is now an established tool for predicting the evolution of homogeneously nucleated particles in both simple [14] and complex (commercial) alloys [15,16] with a high level of success.

In the work reported here, the standard Kampmann and Wagner numerical model (KWN) has been extended and modified in a number of ways to predict the evolution of Al<sub>3</sub>Sc particles in Al-Sc alloys. Firstly, the model has been extended to include both heterogeneous and homogeneous nucleation. In addition, the strain energy contribution to the work of nucleus formation, which is usually ignored in the KWN model, is included in the analysis. This is essential to correctly predict the transition from heterogeneous to homogeneous domination of nucleation. Secondly, to obtain a more accurate value for the driving force for nucleation, Calphad methods [17] have been used to calculate the chemical driving force for nucleation, without the need to invoke the dilute solution approximation used in the standard KWN model. Finally, there is evidence that the interfacial

energy associated with the Al<sub>3</sub>Sc nuclei is different from that associated with well established precipitates undergoing coarsening. For example, Hyland has measured a value of 0.094 Jm<sup>-2</sup> for the interfacial energy of Al<sub>3</sub>Sc nuclei, whereas coarsening experiments [5] and first principles calculations [18] suggest that the interfacial energy of Al<sub>3</sub>Sc precipitates is  $\approx 0.2$  Jm<sup>-2</sup>. As discussed later, allowing a transition in interfacial energy is essential to correctly predict both nucleation and coarsening, and a simple method for incorporating this into the KWN framework is presented.

There exist several datasets in the literature with which to test the model [5,7]. However, this data covers only a narrow range of ageing temperatures. To study  $Al_3Sc$  precipitation over a wider temperature range, and provide a more complete dataset for model validation, results from new ageing experiments on an Al-0.25wt% alloy were used. These experiments covered the temperature range 400–600 °C and the results are also reported in this paper.

#### 2. Experimental

The material for the experimental study was supplied by Alcan International Ltd., in the form of a 25 mm DC cast bookmould, with a composition of Al-0.25 wt.% Sc. The billet was prepared with high purity aluminium (99.999%) and a standard Al-2% Sc master alloy.

The alloy was solution heat-treated (ST) at 640 °C for 72 h in air, followed by an immediate quench into water at ambient temperature. Bulk specimens of ST material were then cold rolled to a thickness of 0.5 mm and then re-solution treated, during which time the deformed grains fully recrystallized. Specimens were then aged in a programmable air furnace at temperatures ranging from 400-600 °C for 1 h, followed by an immediate water quench to ambient temperature. Discs, 3 mm in diameter, were then mechanically punched from these samples and ground down to 100 µm thickness. Thin foils for examination in the transmission electron microscope (TEM) were then prepared by electropolishing until perforation with a Struers Tenupol twin-jet electropolisher, containing a solution of 70% methanol and 30% nitric acid at -30 °C and 12 V. These specimens were then examined using a Philips EM400T and a Philips CM200 TEM at 120 and 200 kV respectively. Precipitate sizes were measured directly from TEM photographic plates, with up to 100 precipitates being measured diametrically at various magnifications, for each specimen condition required. These measurements were used to deduce the size distribution of the precipitates after each heat treatment condition.

## 3. Results of experiments

Fig. 1 (a) and (b) show bright field TEM micrographs taken for the 0.25wt% Sc alloy after ageing for 1 h at 450 °C. At lower magnification (Fig. 1(a)), it can be seen that the precipitates are both small in size and appear to be uniformly distributed throughout the matrix. Fig. 1(b), a higher magnification image, shows that the precipitates exhibit a characteristic line of no contrast in the matrix as a result of the misfit strain. This Ashby–Brown [19] strain contrast is typical of fully coherent precipitate particles.

Ageing at 500 and 550 °C results in a significantly different distribution of Al<sub>3</sub>Sc particles. Fig. 2(a) shows a TEM micrograph after ageing at 550 °C. The distribution of the particles is no longer homogeneous throughout the matrix. Instead, most particles appear to have nucleated on dislocations, leading to aligned rows of precipitates. As shown later in this paper, the transition



Fig. 1. Bright field TEM micrographs showing  $Al_3Sc$  particles after ageing at 450 °C for 1 h (a) low magnification (b) high magnification.



Fig. 2. Bright field TEM micrographs after ageing at 550  $^{\circ}$ C for 1 h (a) at low magnification, showing particles lying on dislocations (b) high magnification image of a single particle, showing an interfacial dislocation propagating into the matrix.

from homogeneous to heterogeneous domination of nucleation is a natural consequence of the reduction in driving force for nucleation as the solvus temperature is approached, and the difference in the energy barrier for the two nucleation modes.

The Al<sub>3</sub>Sc particles nucleated at the heterogeneous sites appeared to have retained a spherical morphology, although the precipitate contrast had changed from the Ashby-Brown strain contrast associated with fully coherent precipitates. Fig. 2(b) shows a high magnification image of a particle after ageing at 550 °C. In addition to contrast fringes, a short section of dislocation line can be seen at the interface, propagating into the matrix. This suggests that this particle is semicoherent with the matrix. The change in interfacial coherency, from fully coherent to semicoherent, is expected to occur once the particles radius exceeds a critical value, which for Al<sub>3</sub>Sc precipitates has previously been estimated to be  $\approx 20$  nm [5]. The mean particle sizes measured after ageing at 500 and 550 °C, the temperatures at which the particles were semi-coherent, as well as other data reported in the literature, are consistent with this estimate (see Table 1).

Precipitate sizes and size distributions were measured after each ageing treatment. The maximum, minimum and mean particle sizes are shown in Table 1. These data, along with the full particle size distributions, were used to test the model, as discussed later.

## 4. The model

The model developed here is based on the Kampmann and Wagner N-model framework, extended to include both homogeneous and heterogeneous nucleation. The modelling method is outlined below, with the details of the methods used to calculate nucleation, growth and coarsening rates discussed later.

- The continuous time evolution of the particle distribution is considered in terms of discreet time steps.
- At each step, the number of new Al<sub>3</sub>Sc nuclei is calculated using classical nucleation theory. The driving force for nucleation is calculated from the local instantaneous value of the scandium supersaturation using Calphad methods [17].
- The growth of existing particles is calculated by assuming growth is controlled by diffusion of scandium to the particle/matrix interface. The influence of surface energy (and hence particle size) on the interfacial composition (the Gibbs–Thomson effect) [11] is accounted for.
- The particle size distribution and the volume fraction of the Al<sub>3</sub>Sc particles are updated at each time step and used to recalculate the matrix composition, using the mean field approximation.
- After each time-step, the scandium concentration remaining in the matrix is recalculated and this new value is used in the next time-step.
- Coarsening arises naturally in the model, and becomes dominant when the supersaturation of scandium becomes low enough so that there is a concentration gradient from sub-critical particles towards super-critical particles.

One of the critical factors in implementing such a model is controlling the timestep to ensure both accuracy and efficiency are maintained. In this work, a third order Runge–Kutta scheme [20] with an adaptive timestep was used to update the Al<sub>3</sub>Sc size distribution at each iteration. The timestep was adjusted to ensure that the error in the prediction of number density was less than 0.01 particle/ $\mu$ m<sup>3</sup> and the maximum error in the change in radius was

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Alloy		Temp (°C)	Time (h)	Ē	r <sub>min</sub>	r <sub>max</sub>	Coherency	Ref
0.25wt%	Sc	400	1	3.5	2.5	4.5	С	This work
0.25wt%	Sc	450	1	8.5	4.5	13	С	This work
0.25wt%	Sc	500	1	20	15	24	S	This work
0.25wt%	Sc	550	1	54	38	67	S	This work
0.30wt%	Sc	300	72	2	2.4	1.6	С	[5]
0.30wt%	Sc	350	72	4.8	-	_	С	[7]

Precipitate parameters measured in this study for an Al-0.25wt%o Sc alloy and selected data from the literature. C=precipitates were fully coherent, S=precipitates were semi coherent

less than 0.1 nm between steps. In the early stages of precipitation, when nucleation and growth rates are most rapid, the timestep shrinks to ensure these criteria are met. In the later stages of precipitation and during coarsening, where changes occur more slowly, the timestep expands, allowing more efficient calculation.

Table 1

At each time interval, new particle nuclei were allocated to an appropriate size class. 300 size classes were used to cover the range 0.1 nm–1  $\mu$ m. The width of these size classes was increased logarithmically. This enables the particle sizes during the early stages of transformation to be tracked with a high level of accuracy, without requiring an overwhelming number of classes. The growth rates of all the size classes were calculated at the edges (i.e. upper and lower bounds) of each class. These were used to reallocate the particles from that size class, as shown schematically in Fig. 3. The advantage of this procedure is that even at very small growth rates, some particles are allowed to transfer

into other size classes. This is particularly important to correctly predict coarsening behaviour, since during this regime the growth and dissolution rates for many of the size classes are very small. The implementation of this method was taken directly from the work of Suni et al. [21], where it was originally developed to model the analogous problem of subgrain evolution during recrystallization.

## 4.1. Nucleation

Classical nucleation theory gives the homogeneous nucleation rate as [11,4]:

$$I = N_{\nu} Z \beta * \exp\left[\frac{-4\pi \gamma_n r^{*2}}{3kT}\right] \exp\left(-\frac{\tau}{t}\right)$$
(1)

where r\*, the radius of the critical nucleus (accounting for the misfit elastic strain energy) is given by:



Fig. 3. Method used in the simulation to model particle growth (or dissolution). The redistribution of particles originally in size class 2 is highlighted. The growth rates ( $v_L$  and  $v_U$ ) are calculated at the edges of the size class (points L and U). These growth rates are used to determine which size classes the particles from class 2 will be distributed over after a timestep  $\Delta t$ . In this example, the particles from class 2 will be distributed over classes 3, 4 and 5.

$$r* = \frac{-2\gamma_n}{\Delta G_v + \Delta G_s} \tag{2}$$

 $\gamma_n$  is the interfacial energy of the matrix/nucleus interface,  $\Delta G_{\nu}$  is the chemical volume free energy change driving nucleation and  $\Delta G_s$ , is the elastic strain energy per volume of precipitate. The strain energy term is ignored in the standard KWN approach, but it is essential to correctly predict the transition from homogeneous to heterogeneous domination of nucleation. The pre-exponential terms in Eq. (1) are  $N_{\nu}$ , the number of nucleation sites per unit volume (equal to the number of atoms per volume for homogeneous nucleation), Z, the Zeldovich nonequilibrium factor and  $\beta$ \*, the rate of atomic attachment to a growing embryo.  $\tau$  is the incubation time for nucleation, k is the Boltzmann constant and T the thermodynamic temperature. Using the assumption of a spherical nucleus:

$$Z = \frac{V_a (\Delta G_v + \Delta G_s)^2}{8\pi \sqrt{\gamma_n^{-3} kT}}$$
(3)

$$\beta * = \frac{16\pi \gamma_n^2 cD}{(\Delta G_\nu + \Delta G_s)^2 a^4} \tag{4}$$

$$\tau = \frac{8kT\gamma_n a^4}{V_a^2 (\Delta G_v + \Delta G_s)^2 Dc}$$
(5)

where  $V_a$  is the volume per atom in the matrix, c is the concentration (atomic fraction) of Sc solute in the matrix, a is the lattice constant of the product phase and D is the diffusivity of Sc in Al, which is calculated in the usual way [11]. A value of 174 KJmol<sup>-1</sup> was used for the activation energy for diffusion and  $5.31 \times 10^{-3} \text{m}^2 \text{s}^{-1}$  for the preexponential factor, taken from the tracer diffusion data of Fujikawa [22].

Often, one of the most difficult input parameters to determine from direct experimental measurement is  $\gamma_n$ , the matrix/nucleus interfacial energy. There is no directly measured value for  $\gamma_n$  available for Al<sub>3</sub>Sc nuclei. However, a wide range of values of  $\gamma_n$  have been reported by measurement using indirect methods, or from first principles modelling. Most relevant to modelling nucleation is the interfacial energy reported by Hyland, who deduced a value of 0.094 Jm<sup>-2</sup> by measuring the increase in particle number density for short ageing times and using classical nucleation theory to backcalculate  $\gamma_n$ . This is significantly different from 0.22 Jm<sup>-2</sup>, the value for the interfacial energy as determined by first principle calculations [18]. It is also different from the values of interfacial energy calculated from the coarsening rates of Al<sub>3</sub>Sc during the later stages of transformations. These measurements give values for the interfacial energy around 0.2 Jm<sup>-2</sup> [5,7].

Such a discrepancy between the interfacial energy for nucleation and coarsening is perhaps not surprising and is a common failing of classical nucleation theory. The nucleus size (as calculated from classical theory) is typically less than 1 nm at the start of transformation. This means the nucleus contains only a small number of atoms, which will therefore have considerable freedom to arrange themselves to minimize the interfacial energy. A coarsening particle, on the other hand, will typically contain hundreds of thousands of atoms, organized into well defined crystallographic planes. It seems highly unlikely that these two very different structures will produce the same interfacial energy. Indeed, initial attempts in this work to use a single interfacial energy value to predict both nucleation and growth behaviour were not successful. This is because the interfacial energy measured for coarsening is too large to give a reasonable nucleation rate, and the interfacial energy for nucleation is too small to give the correct coarsening behaviour. Therefore, in this work, the interfacial energy is assumed to be a function of particle size, as discussed below.

The nucleation rate, in particular, is very sensitive to the value of the interfacial energy. The optimum value for the interfacial energy for nucleation was determined by fitting the predictions of the model to the experimental data for one temperature. This fitted value was then tested for all other temperatures. The 'best fit' value was found to be  $0.057 \text{ Jm}^{-2}$ . As the particles grow from small nuclei into distinct precipitates, the interfacial energy will increase to the value measured from coarsening rate experiments [5,7] and calculated using first principles methods [18]. Exactly how the interfacial energy varies as a function of particle size between the nucleation and coarsening stages is unclear. In this work, a very simple

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method was used to deal with this transition in interfacial energy. As a first approximation, it was assumed that there is a gradual, linear, increase in interfacial energy from  $0.057 \text{ Jm}^{-2}$  (the value used for nucleation) to  $0.2 \text{ Jm}^{-2}$  (the value deduced from coarsening data) as particle size increases to 5 nm. Although the change in interfacial energy is probably not linear, and the choice of 5 nm as the size for the completion of the transition is arbitrary, this approximation was adequate to allow good reproduction of the experimental measurements. Furthermore, it was found that the predictions were not very sensitive to the exact value used for the size at the end of the transition, or the form (e.g. linear or logarithmic) of the function used to vary the interfacial energy, so long as it was smaller during the early stages of nucleation.

Following Hyland, who used the method of Barnett et al. [23], the elastic strain energy per unit volume of a fully coherent nucleus is given by:

$$\Delta G_s = 3\varepsilon^2 \delta_p \left[ 1 - \left( \frac{\delta}{\delta_p} \left( \frac{2K+1}{K+M-KM1+\nu} \right) - 1 \right)^{-1} \right]$$
(6)

where M = 1/3 and K = 1 for a spherical nucleus, and  $\epsilon$  is the misfit strain. The variables with a subscript *p* refer to the precipitate phase and those without a subscript apply to the matrix.  $\delta$  and  $\delta_p$ are given by:

$$\delta = \frac{G(1+v)}{(1-2v)} \tag{7}$$

$$\delta_{p} = \frac{G_{p}(1+v_{p})}{(1-2v_{p})}$$
(8)

where G is the shear modulus and v is the Poisson's ratio of the phase in question. The values used for these constants are given in reference [4].

 $\Delta G_{\nu}$ , the chemical driving force for nucleation, was calculated using the parallel tangent method, from the chemical potentials of Al and Sc [11].

$$\Delta G_{\nu} = \frac{\left[(\mu_{Al}^{\beta} X_{Al}^{\beta} + \mu_{Sc}^{\beta} X_{Sc}^{\beta}) - (\mu_{Al}^{\alpha} X_{Al}^{\alpha} + \mu_{Sc}^{\alpha} X_{Sc}^{\alpha})\right]}{V_{m}} \quad (9)$$

where  $\mu_{Al}^{\beta}$  and  $\mu_{Sc}^{\beta}$  are the chemical potentials of aluminium and scandium in the Al<sub>3</sub>Sc phase respectively,  $\mu_{Al}^{\alpha}$  and  $\mu_{Sc}^{\alpha}$  are the (instantaneous)

chemical potentials of aluminium and scandium in the matrix, X is the mole fraction of the stated element in the given phase ( $\beta = Al_3Sc$ ) and  $V_m$  is the molar volume of Al<sub>3</sub>Sc. The chemical potentials were calculated using MT-DATA [24], coupled with a database for the Al-Sc system supplied by the National Physical Laboratory, UK. This method is likely to be considerably more accurate than the dilute solution assumption used in the standard KWN model. As the volume fraction of precipitate increases, the composition of the matrix will change, and the chemical potentials of Al and Sc in the matrix will also change. Therefore, at each step, these values were updated, using the instantaneous value of the matrix composition to calculate the new chemical potentials.

Fig. 4 shows a plot of  $\Delta G_{\nu}$  vs temperature for the alloy used in this work (Al-0.25 wt% Sc). The effect of strain energy on the volume energy change on forming a nucleus is also shown. It can be seen that at low temperatures, the strain energy constitutes only a small proportion of the overall energy change. However, as the temperature increases, the strain energy becomes an increasingly large fraction of the total energy change. It can also be seen that the solvus temperature (which corresponds to the point where the free energy change is zero) is predicted to be lowered by



Fig. 4. Chemical driving force per unit volume for forming a homogeneous Al<sub>3</sub>Sc nucleus ( $\Delta G_{\nu}$ ) and overall driving force for homogeneous nucleus formation, also accounting for the strain energy contribution ( $\Delta G_s$ ).

 $\simeq 10$  °C for a coherent precipitate with strain energy, compared to a strain free precipitate.

As observed in this work, at higher temperatures, where the strain energy term is significant, heterogeneous precipitation of Al<sub>3</sub>Sc on dislocations tends to dominate homogeneous nucleation. Previous models for Al<sub>3</sub>Sc precipitation have not considered this nucleation mode [25]. Heterogeneous nucleation is modelled by modifying Eq. (1) in two key ways. First, the number density of nucleation sites is no longer equal to the number density of atoms, but is replaced by  $N_{\nu}^{D}$ , the number density of atoms per unit volume that lie on dislocation lines. In addition, the effective critical radius for homogeneous and heterogeneous nucleation is different because the energy barrier to forming a nucleus is reduced at dislocations.

Dislocations are favoured nucleation sites largely as a result of the interaction of the strain field of the nucleus with that of the dislocation [11]. Since Al<sub>3</sub>Sc has a positive misfit with the matrix (and therefore compresses the surrounding material when precipitated homogeneously), it will favour nucleation in regions close to dislocations where the matrix is locally in tension in order to reduce the overall strain energy. The reduction in strain energy can be estimated by assuming that the formation of a nucleus results in the destruction of that part of the elastic energy of the dislocation that lies within the volume of the nucleus [26]. The overall energy change on forming a spherical nucleus may then be written:

$$\Delta G_{total} = \frac{4}{3}\pi r^3 (\Delta G_v + (\Delta G_s - \Delta G_{dis}))$$
(10)  
+  $4\pi r^2 \gamma_n$ .

This equation is identical to that for homogeneous nucleation [11], except for the term  $\Delta G_{dis}$ , which is the dislocation strain energy destroyed by nucleus formation (per unit volume) [27]. The critical radius for heterogeneous nucleation is deduced in the usual way by finding the maximum in the  $\Delta G_{total}$  vs r function. The calculation of the nucleation rate then follows the same treatment as for homogeneous nucleation. For heterogeneous nucleation of Al<sub>3</sub>Sc, it was found that, for typical critical radius values, the strain energy liberated by

destroying part of the dislocation was similar to the strain energy associated with formation of the new crystal. Therefore, the resultant strain energy contribution to the energy for heterogeneous nucleus formation was approximately zero.

The site density for heterogeneous nucleation was taken as being  $\simeq (N_v)^{1/3}\rho^D$ , where  $\rho^D$  is the dislocation density (length of dislocation line per unit volume) [11]. Unfortunately, the dislocation density was not measured as part of the experimental study. However, for an annealed alloy (such as that used in this work), it is expected to lie in the range  $10^{10}-10^{12}$  m<sup>-2</sup> [27]. The value of the dislocation density used in this work was  $1.5 \times 10^{11}$ m<sup>-2</sup>, which was found by fitting predictions and measurements at one temperature (550 °C) where heterogeneous nucleation on dislocations was dominant. The fitted dislocation density value lies within the physically reasonable range.

Both homogeneous and heterogeneous nucleation were allowed to occur at all temperatures. No artificial transition between the two types of nucleation behaviour was imposed in the model. Instead, the transition from homogeneous to heterogeneous domination of nucleation was allowed to arise naturally as a result of the competition between the two mechanisms.

## 4.2. Growth

The Al<sub>3</sub>Sc particles appear approximately spherical in shape regardless of whether they are homogeneously or heterogeneously nucleated. The growth rate is limited by the rate at which scandium can diffuse to the particles and is given by

$$\frac{dr}{dt} = \frac{D}{rc^{Al_3Sc} - c_r^{\alpha}} \tag{11}$$

where *r* is the particle radius,  $c_r^{\alpha}$  is the concentration of scandium in the matrix at the interface (which depends on the particle radius due to the effect of capillarity),  $c^{Al_3Sc}$  is the concentration of scandium in Al<sub>3</sub>Sc and *c* is the instantaneous concentration of scandium in the matrix.  $c_r^{\alpha}$  is calculated from  $c_{\infty}^{\alpha}$  (the equilibrium concentration of scandium in the matrix for a planar interface) using the Gibbs–Thomson equation:

$$c_r^{\alpha} = c_{\infty}^{\alpha} \exp\left(\frac{2\gamma_p V_m 1}{R_g T r}\right)$$
(12)

where  $\gamma_p$  is the interfacial energy of the growing (or shrinking) particle. As already discussed, for particles>5 nm in size,  $\gamma_p$  was taken as 0.2 Jm<sup>-2</sup>, which is close to the average value reported from coarsening experiments [7,5]. Growth for heterogeneously nucleated particles is treated in the same way as growth for homogeneously nucleated particles.

#### 4.3. Precipitate coarsening

Coarsening occurs when large precipitates grow at the expense of small ones, without a change the overall volume fraction. This process, driven by a reduction in the overall interfacial energy, arises naturally in the KWN model. As the fraction of solute in the matrix decreases during precipitation, the driving force for nucleation and growth of the Al<sub>3</sub>Sc particles decreases and the critical particle radius increases. Particles in the size distribution which have a radius < r\* will have a negative growth rate according to Eq. (11) and will thus start to shrink. Particles with a radius > r\* will retain a positive growth rate and will continue to increase in size. When the size of a group of shrinking particles reaches zero they are removed from the size distribution. Experimentally it has been shown that coarsening of the precipitates is accompanied by a loss of coherency, which would be expected to be accompanied by an increase in interfacial energy. However, previous studies have shown that coarsening data can be rationalized on the basis of a single interfacial energy value of  $\simeq 0.2 \text{ Jm}^{-2}$ , even when both coherent and semicoherent precipitates are present [5,7]. Therefore, in the absence of data for the interfacial energy of the semi-coherent Al<sub>3</sub>Sc interface, this value was used for all particles above 5 nm in radius.

## 5. Predictions

Fig. 5 shows a plot of the predicted  $Al_3Sc$  particle radii and those measured in this study as a function of ageing temperature (the ageing time is



Fig. 5. Predicted mean radius of  $Al_3Sc$  particles in a Al-0.25wt% Sc alloy after 1 h heat treatment as a function of temperature. Also marked is the measured mean particle radius and upper and lower limits.

1 h in all cases). At 400 °C, the experimental results showed homogeneous nucleation was dominant. Therefore, this was the temperature at which the predicted results were fitted to experiment by adjusting the interfacial energy for nucleation so that the predicted and measured mean particle radii were in good agreement. At 550 °C, heterogeneous nucleation on dislocations is dominant. Therefore, the data from this temperature were used to find the best fit for the dislocation density (as discussed previously), again by obtaining the best agreement between the predicted and measured mean particle radius. The predictions for the other temperatures were made without changes to either of the fitting parameters. The predicted mean particle radii at these temperatures are in reasonable agreement with the measurements from this work, although there is a trend for the model to slightly underestimate the mean radius.

One output of the model is the predicted volume fraction evolution of the Al<sub>3</sub>Sc particles as a function of ageing time. Fig. 6 shows such a plot for three of the ageing temperatures used in this study. It can be seen that after 1 h of ageing (the longest time shown in the plot), the terminal volume fraction has been reached in all three cases. At 500 and 550 °C, precipitation of Al<sub>3</sub>Sc is predicted to be complete considerably before 1 h. Therefore,



Fig. 6. Predicted evolution of volume fraction for Al<sub>3</sub>Sc particles in an Al-0.25wt% Sc alloy at a number of different temperatures.

specimens held at these temperatures are predicted to have spent most of the ageing time in the coarsening dominated regime (i.e. with negligible increase or decrease in volume fraction). In contrast, the specimens heat treated at 450 °C and below are predicted to have undergone little pure coarsening, although coarsening will have occurred in parallel with nucleation and growth during precipitation of  $Al_3Sc$ .

## 5.1. Size distributions

The model also gives the full particle size distribution function for the Al<sub>3</sub>Sc particles. Fig. 7 shows a plot of the predicted and measured Al<sub>3</sub>Sc size distributions for the temperatures studied. These distributions are plotted in terms of f, the frequency distribution function, which was chosen so that the total number of particles (i.e. the area under the curves) was normalized to 1 for both the predicted and measured data. In general, the predicted and measured size distributions are in good agreement. At 400 °C, the experimental data has a considerably higher peak than predicted. However, this may be because some of the smaller particles were not detected in the experimental investigation. Indeed, the shape of the experimental distribution at this temperature suggests truncation of



Fig. 7. Predicted and measured size distributions of  $Al_3Sc$  particles after 1 h in an Al-0.25wt% Sc alloy. *f* is the frequency distribution function.

the distribution has occurred below a particle size of approximately 5 nm. At 550 °C, the measured spread in sizes is somewhat greater than that predicted, and thus the measured peak in the distribution frequency function is lower than the predicted peak. However, considering the wide range of temperatures studied, and the resultant large range of particle sizes (with the mean diameter ranging from 7 to 105 nm), the predictions of the model show an impressive level of accuracy.

In addition to the size distributions measured in this work, the model was tested against measured size distribution data reported in the literature. For example, Marquis and Seidman [5] have measured Al<sub>3</sub>Sc size distributions in an Al-0.3 wt% Sc alloy for ageing times up to 350 h. Fig. 8 shows a plot of the model predictions compared with their experimental data after ageing at 300 °C, a tem-



Fig. 8. Predicted and measured particle size distribution for Al-0.3wt% Sc alloy, aged at 300 °C for (a) 6 h and (b) 350 h. Measurements from Marquis and Seidman [5].

perature where homogeneous nucleation is dominant [5]. For the short (6 h) ageing time, the predicted and measured particle size distributions are in excellent agreement. After long aging, the predicted average size is also in good agreement, but the experimental data shows a slightly greater spread in size than predicted. Note that this level of agreement has been obtained without any recalibration of the model.

Novotyn and Ardell [7] have reported size distributions and size evolution data for Al 0.2wt% Sc and Al-0.3wt% Sc alloys, aged at 350 °C. As they point out, their results for the 0.2wt% Sc alloy are somewhat odd, in that they record no systematic increase in the mean particle radius with time. This is inconsistent with standard theories of nucleation, growth and coarsening and cannot be explained with the current model. However, their results for the Al-0.3wt% Sc do conform to the standard LSW coarsening behaviour observed by other workers. Fig. 9(a) shows a plot of the predicted evolution of particle radius with time for the Al-0.3 wt% Sc, compared with the data of Novotyn and Ardell [7]. It can be seen that excellent agreement is obtained, again without any recalibration of the model. For this set of conditions, the model predicts that the increase in volume fraction of Al<sub>3</sub>Sc is essentially complete after 2000 s. This confirms that the experimental data all lie at long enough ageing



Fig. 9. Predicted particle size evolution for a Al-0.3wt% Sc alloy aged at 350 °C. Measured points, which all fall within the coarsening regime, are from the data of Novotyn and Ardell [7]. A line of slope 1/3, as expected from LSW coarsening theory, is superimposed.

times that coarsening is expected to be the dominant mechanism controlling the particle size evolution. Furthermore, during the coarsening regime, it can be seen that the model predicts that the mean radius varies with the cube root of time, as expected from LSW coarsening theory.

The model has therefore been proven for ageing temperatures ranging from 300 to 550 °C, and for a range of ageing times and scandium levels, giving confidence in its predictive ability. In addition, the fact that the model is capable of reproducing the experimental data reported here, that of Marquis and Seidman [5] and that of Novotyn and Ardell [7], without recalibration suggests that all of these datasets (from different ageing temperatures) are consistent with each other.

It is common to compare the measured size distributions during the coarsening regime with the steady state size distribution predicted by LSW theory. In general, reasonable fit has been found between the LSW size distribution and the normalized, measured distributions [5,7]. It is interesting to compare the size distributions predicted by the present model (which evolve naturally from the basic laws of nucleation, growth and capillarity) and the LSW size distribution. The LSW distribution is derived analytically, using a number of approximations, such as the assumption that the

volume fraction of the precipitate phase is negligible [9,10]. Fig. 10 shows a comparison of the two distributions after 10 h at 450 °C, a time where it is predicted that coarsening is well established. The predicted particle size distribution has been normalized by the predicted mean particle size (which is equal to the critical radius) to enable the comparison to be made. It can be see that the two distributions are indeed very similar. The distribution predicted by the present model is slightly broader, and therefore has a less sharp peak than the LSW distribution. A broadening of the standard LSW distribution is consistent with experimental results and also with modified LSW theories that account for the effect of non-zero precipitate volume fraction [28].

## 5.2. Homogeneous and heterogeneous nucleation

The validated model can now be used to investigate particular aspects of the  $Al_3Sc$  precipitation kinetics in more detail. For example, the predicted evolution of number density in the early stages of transformation can be compared with that expected from experimental measurements. Hyland [4] has used TEM to study the early stage precipitation kinetics in an Al-0.11 atomic% (0.18wt%) Sc alloy. Fig. 11 shows a plot of the predicted evolution of particle number density at 343 °C (616 K), compared with Hyland's experimental



Fig. 10. Predicted particle size distribution at 450°C, compared with size distribution from LSW theory.



Fig. 11. Predicted evolution of particle number density in an Al-0.11 atomic% Sc alloy at 343 °C, compared with measured data from Hyland [4].

measurements. It can be seen that good agreement is obtained between the predictions and measured data. The model correctly predicts the abrupt change in the rate of increase in particle number density at  $\approx 1000$  s. This is a result of a sharp drop in the homogeneous nucleation rate as the scandium supersaturation falls.

Another area of particular interest is the transition from homogeneous to heterogeneous domination of nucleation at low supersaturations. Fig. 12 shows the predicted evolution of the homogeneous and heterogeneous nucleation rates with time at 450 and 550 °C. The curves are characterized by an initial incubation period, where there is no nucleation. The nucleation rate then rises rapidly, reaches a maximum and falls again as scandium is removed from the matrix into the precipitates, reducing the supersaturation. It can be seen that for the combination of composition and temperatures used here, it is predicted that there is no steady state nucleation regime, characterized by a constant nucleation rate. It should be noted, however, that because a mean field approach is used to model solute depletion, these predictions will represent the 'averaged' nucleation behaviour, within and outside the diffusion fields surrounding growing precipitates.

Fig. 12 also shows that at 450 °C, homogeneous nucleation is predicted to dominate, whereas the



Fig. 12. Predicted homogeneous and heterogenous nucleation rates as a function of time for  $Al_3Sc$  particles in an Al-0.25wt% Sc alloy (a) at 450 °C (b) at 550 °C.

opposite is true at 550 °C. Fig. 13 shows the predicted (maximum) homogeneous and heterogeneous nucleation rates as a function of ageing temperature. As expected, at lower temperatures, the homogeneous nucleation rate is predicted to be greater than the heterogeneous rate. At higher temperatures, heterogeneous nucleation is predicted to be dominant. It can be seen that, for this alloy composition and dislocation density, the transition from homogeneous to heterogeneous domination of nucleation is predicted to occur at  $\approx$ 520 °C. The



Fig. 13. Predicted maximum homogeneous and heterogeneous nucleation rates as a function of temperature for  $Al_3Sc$  particles in an Al-0.25wt% Sc alloy for a dislocation density of  $1.5 \times 10^{11}$  m<sup>-2</sup>.

maximum homogeneous nucleation rate is predicted to occur at  $\approx 450$  °C, and the maximum heterogeneous rate is predicted to occur at  $\approx 475$  °C. Although the relative importance of the different nucleation processes is predicted to change as the ageing temperature varies, it is also clear from Fig. 13 that both nucleation processes are expected to make some (albeit possibly small) contribution to the overall particle distribution, across the whole temperature range plotted, i.e. for these conditions there is no regime of pure homogeneous or pure heterogeneous nucleation.

The transition from homogeneous to heterogeneous domination of nucleation is a natural consequence of the reduced driving force for nucleus formation as the temperature increases. At low temperatures, there is sufficient driving force for a large number of clusters to overcome the critical energy barrier for nucleus formation at both homogeneous and heterogeneous sites. Therefore, at these temperatures, homogeneous nucleation dominates, since every atom is potentially a homogeneous nucleation site. As the temperature increases, and the driving force for nucleus formation reduces, it becomes increasingly difficult to overcome the large energy barrier to homogeneous nucleation and above a certain temperature the homogeneous nucleation rate starts to fall rapidly. Since the energy barrier to formation of a heterogeneous nucleus is less, the temperature at which the heterogeneous nucleation rate falls sharply is greater than that for homogeneous nucleation. This means that, as the temperature is increased the heterogeneous nucleation rate overtakes the homogeneous rate, despite the fact that only a small fraction of the total number of atoms are available for heterogeneous nucleation.

Alloy composition, ageing temperature and dislocation density are the variables that will determine whether homogeneous or heterogeneous nucleation will be dominant. To investigate the effect of these variables, a predicted 'nucleation map' was plotted, as shown in Fig. 14. For a given combination of alloy composition and ageing temperature, this map shows which process has the highest nucleation rate. The lines plotted on the map correspond to the predicted transition between the dominant process for different dislocation densities. Each line corresponds to a single dislocation density, expressed as a multiple of the dislocation density used in all previous predictions  $(1.5 \times 10^{11} \text{ m}^{-2})$ . As expected, points falling towards the top left of the map (high temperature, low scandium concentration) lie within the region where heterogeneous nucleation is predicted to dominate as a result of the low scandium supersaturation. Homogeneous nucleation is predicted to



Fig. 14. A nucleation 'map' showing the regions of scandium concentration and temperature where homogeneous and heterogeneous nucleation of Al<sub>3</sub>Sc are predicted to be dominant. Lines corresponding to the transition between dominant nucleation modes are marked for different dislocation densities, expressed as multiples of the original, fitted dislocation density  $(1.5 \times 10^{11} \text{ m}^{-2})$ .

dominate for high supersaturation conditions, corresponding to the bottom right of the map. It can be seen that the transition from the domination of one process to the other is predicted to be sensitive to the dislocation density. For example, a ten fold increase in the dislocation density is predicted to reduce the transition temperature by 15 °C. Note that, had the material been in the heavily cold worked condition prior to ageing, the dislocation density would be expected to be over five orders of magnitude greater than that after annealing. Such a dislocation density, if maintained during ageing, is predicted to lead to the domination of heterogeneous nucleation over the whole range of conditions plotted in Fig. 14.

# 5.3. Predicted time-temperature-transformation kinetics

One advantage of a model, such as that developed here, is that it is possible to obtain output in a number of different forms to suit particular requirements. For example, by running the model at a range of temperatures, and calculating the time to obtain a given volume fraction of Al<sub>3</sub>Sc, predicted time temperature-transformation (TTT) diagrams may be produced. Fig. 15 shows an example of such a diagram for two alloys, the Al-0.25wt% Sc alloy studied here and a more dilute Al-



Fig. 15. Predicted TTT curves for the precipitation of  $Al_3Sc$  in an Al-0.25wt% Sc alloy and an Al-0.15wt% Sc alloy, showing the times to reach 90% of the equilibrium volume fraction.

0.15wt% Sc alloy. The lines plotted on this diagram correspond to the time taken to reach 90% of the equilibrium Al<sub>3</sub>Sc volume fraction and include the contribution from both homogeneous and heterogeneous nucleation. It can be seen that the fastest precipitation kinetics for the Al-0.25wt% Sc alloy are predicted to occur at  $\simeq$ 500 °C. At this temperature, it is estimated to take only 25 s to reach 90% of the equilibrium Al<sub>3</sub>Sc volume fraction. As expected, the peak precipitation rate occurs at a lower temperature in the more dilute 0.15wt% Sc alloy. Even at the peak temperature, it is predicted to take almost 100 times longer to form 90% of the equilibrium fraction of Al<sub>3</sub>Sc in this alloy than it is at the peak temperature in the Al-0.25wt% Sc alloy.

## 6. Conclusions

A model has been developed to predict the full precipitation process for the Al<sub>3</sub>Sc phase, from the initial nucleation stage to the final coarsening dominated stage. The approach used is based on the N-model of Kampmann and Wagner, extended to account for both homogeneous nucleation and heterogeneous nucleation on dislocations. The size distributions and particle size evolutions, predicted by the model, agree well with the experimental data reported in this study and also in the literature across a wide range of ageing temperatures. The model predicts correctly the transition from homogeneous to heterogeneous domination of nucleation as the ageing temperature increases. It has been shown that modest changes in the dislocation density are expected to lead to a change in dominant nucleation mechanism for certain alloy compositions and ageing temperatures. If the dislocation density is high enough, heterogeneous nucleation is expected to be dominant across the whole range of practical ageing temperatures and alloy compositions. The model is also capable of predicting TTT diagrams for Al<sub>3</sub>Sc formation, and examples of calculated diagrams have been shown.

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