A new model for prediction of dispersoid precipitation in aluminium alloys containing zirconium and scandium

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Received 17 October 2003; received in revised form 24 November 2003; accepted 25 November 2003

Abstract

A model has been developed to predict precipitation of ternary Al(Sc, Zr) dispersoids in aluminium alloys containing zirconium and scandium. The model is based on the classical numerical method of Kampmann and Wagner, extended to predict precipitation of a ternary phase. The model has been applied to the precipitation of dispersoids in scandium containing AA7050. The dispersoid precipitation kinetics and number density are predicted to be sensitive to the scandium concentration, whilst the dispersoid radius is not. The dispersoids are predicted to enrich in zirconium during precipitation. Coarsening has been investigated in detail and it has been predicted that a steady-state size distribution is only reached once coarsening is well advanced. The addition of scandium is predicted to eliminate the dispersoid free zones observed in scandium free 7050, greatly increasing recrystallization resistance.

Keywords: Aluminium alloys; Phase transformation kinetics; Recrystallization; Modelling; Dispersoids

1. Introduction

The development of microstructural models for complex industrial alloys has become a major activity over the last twenty years. An area of particular focus has been the creation of models for precipitate evolution, since precipitate particles play a key role in determining the properties of many industrially important alloys. One approach to this problem has been to extend the classical numerical precipitation model of Kampmann and Wagner (KWN model) [1], which was originally developed for simple binary systems. It has a number of features that make it suitable for industrial process modelling. Firstly, it is based on well established classical kinetic theory [1,2], and does not contain arbitrary fitting parameters. Secondly, the model naturally accounts for the full range of transformation, from the early nucleation dominated stages, to the late coarsening dominated stages. Thirdly, the model tracks the full particle size distribution; this is particularly important for heat treatments involving multiple processing steps, in which the size distribution from one step influences the microstructural evolution in the next step. Finally, the numerical nature of the model makes it very flexible, for example, it is straightforward to investigate multi-step and non-isothermal heat treatments [3,4].

The KWN model has been applied to a number of industrial alloys, including commercial aluminium alloy systems, such as 6xxx [3] and 7xxx [5] alloys. In all cases, progress was made by approximating the true multi-component nature of the precipitating phases to the appropriate pseudo-binary system. Precipitation was therefore assumed to be controlled by a single alloying element, and the precipitate composition was assumed to be given by the pseudo-binary equilibrium phase diagram.

Recently, this model has been extended to predict the precipitation of metastable L12 Al3Zr dispersoids in 7xxx aluminium alloys containing zirconium [6]. The purpose of these dispersoids is to stabilize the grain structure of the alloy and prevent recrystallization after hot working by pinning grain and subgrain boundaries. To model their formation, it was necessary to account for the fact that precipitation occurs directly from a cast structure in which the alloying elements are highly

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segregated. The evolution of dispersoid particles is therefore a function of position, as well as time and temperature. This non-uniformity in the particle distribution is of practical importance because it is found that recrystallization can occur in regions that are locally depleted in dispersoids, and this degrades the properties of the alloy [6].

There is currently strong interest in adding scandium to 7xxx aluminium alloys to improve the dispersoid distribution and hence minimize recrystallization [7–9]. The effect of adding scandium in combination with zirconium is to form a ternary Al3(Sc, Zr) dispersoid phase. It would be very valuable for alloy and process design to be able to model the precipitation and distribution of this phase as a function of alloy composition and processing conditions. The KWN model provides a good framework for developing such a model. However, it requires extending to properly treat the precipitation of a ternary phase and this was one of the goals of the work reported here.

The resultant model accounts for both the non-uniform initial distribution of alloying elements and the multicomponent nature of the precipitation process. This yields a much more powerful precipitation model in which the phase compositions and rate controlling elements are no longer artificially predetermined inputs (as is the case using the pseudo-binary approximation), but instead become outputs. As well as providing useful predictions of the effect of scandium additions to zirconium containing aluminium alloys, the method developed here also has potential application to modelling precipitate evolution in other multicomponent alloy systems.

2. The model

2.1. Thermodynamics

To produce a reliable kinetic model, it is first necessary to have a sufficient understanding of the phase equilibria of the system being modelled. Quantities such as equilibrium solubilities and driving forces must be predicted and used as inputs to the kinetic model.

Phase stability in the Al–Sc–Zr system is complicated by the fact that there are two forms of the Al3Zr phase, metastable L12 Al3Zr (which has the same crystal structure as the equilibrium L12 Al3Sc phase) and equilibrium D023 Al3Zr. However, in commercial alloys such as 7050, experimental studies show that over a wide range of scandium (0–0.3wt%) and zirconium (up to 0.13wt%) concentrations, and even after prolonged heating typical (e.g. 40 h at 475 °C) all the dispersoids have the same L12 crystal structure, and the D023 Al3Zr phase does not form [8,9]. Therefore, in this work, only precipitation of the L12 Al3(Sc, Zr) phase is considered, which significantly simplifies the analysis.

The Alcoa thermodynamic database was used to calculate phase stabilities and compositions, assuming L12 Al3(Sc, Zr) is the only dispersoid phase present [10]. Previous work has shown that elements such as Cu, Mg, and Zn, present in high strength 2xxx/7xxx wrought aluminium alloys, have a significant effect on dispersoid stability [11]. These elements were therefore included in the present calculations. A difficulty arises because the thermodynamics of the ternary L12 Al3(Sc, Zr) (which at the zirconium rich end is metastable) are not fully characterized. For example, the value for the enthalpy of mixing of Sc and Zr on the ordered sub-lattice is not available in the thermodynamic database. Therefore, as a first approximation, it was assumed that mixing is ideal (the enthalpy of mixing is zero). The limited available experimental evidence suggests this is a reasonable approximation. For example, the fraction of zirconium in Al3(Sc, Zr) is found to increase in direct proportion to the fraction of zirconium in the alloy [12]. This would not be the case if mixing were far from ideal.

The effect of the major alloying elements on the solvus of the Al3(Sc, Zr) phase was then investigated by performing calculations for a ternary Al–Sc–Zr alloy and two commercial compositions 2024 and 7050 (with Zr and Sc additions). The predicted solvus lines are shown in Fig. 1. It can be seen that the presence of other solute elements in 7050 and 2024 (i.e. Cu, Mg, and Zn) is predicted to lead to a significant shift in the solvus position, moving it towards lower scandium and zirconium concentrations. The shift is greatest for 7050, which has the highest solute content. This is consistent with previous observations and predictions for alloys containing zirconium alone, where the presence of other alloying elements was found to increase the zirconium supersaturation [13,11]. An important consequence of this prediction is that less scandium or zirconium are required in

![Fig. 1. Calculated solvus boundary for Al3(Sc, Zr) at 480 °C in ternary Al–Sc–Zr, 7050 with Sc and Zr, and 2024 with Sc and Zr.](image-url)
commercial alloys to produce the same volume fraction of Al₃(Sc, Zr) as in a simple ternary alloy.

When considering the precipitation of small particles, the phase compositions deduced from the phase diagram have to be modified to account for the reduction in phase stability due to the curvature of the particle/matrix interface (the Gibbs–Thomson effect [2]). For the binary case, this equation can be written

\[ c_r = c_{\infty r} \exp \left( \frac{2\sigma V_m}{R_g T} r \right), \]  

where \( c_{\infty r} \) is curvature compensated matrix composition at the interface for a particle of radius \( r \), \( c_{\infty} \) the matrix composition for a planar interface, \( \sigma \) is the interfacial energy, \( V_m \) the molar volume of the product phase and \( R_g \) and \( T \) have their usual meanings.

For the ternary case, Eq. (1) can be applied to both solute elements and used to calculate the position of the curvature compensated solvus line [14].

The calculated solvus lines at 480 °C for a range of particle sizes are shown in Fig. 2. This, and subsequent, calculations were performed using a value for \( \sigma \) of 0.1 J m⁻². This value lies close to the fitted value deduced previously for Al₃Zr [6] and Al₃Sc dispersoids [15] and was deduced by tuning the model, so may not be a measure of the true interfacial energy. However, this choice of \( \sigma \) is physically reasonable, and falls within the range (0.06–0.18 J m⁻²) reported experimentally for Al₃Sc, Al₃Zr, and Al₃(Sc, Zr) [16].

An additional complication arises in predicting the precipitation of dispersoids in conventional direct chill (DC) cast aluminium alloys as a result of non-equilibrium segregation of the alloying elements during the casting process. In the case of alloys containing only zirconium, this segregation results in a highly non-uniform distribution of dispersoids after heat treatment. In previous work, electron microprobe analysis was used to measure the distribution of scandium and zirconium in direct chill cast 7050 ingots containing 0.13wt% Zr and either 0, 0.1 or 0.3wt% Sc [8,9]. Note that in the highest scandium alloy (0.3wt% Sc) almost half of the scandium formed primary Al₃(Sc, Zr) particles during solidification, leaving an average concentration of 0.18wt% Sc in solution. Plots of the concentrations of scandium and zirconium in the three alloys, as a function of the distance from the centre of a dendrite arm to the edge, are shown in Fig. 3.

Zirconium tends to segregate to the dendrite centres (the first solid to form), and scandium to the edges (the last solid to form). Also shown in Fig. 3 are fitted concentration profiles, obtained using a simple one-dimensional Scheil model:

\[ c = k\bar{c}(1 - f_s)^{(k-1)}, \]  

where \( c \) is the local concentration of scandium or zirconium, \( \bar{c} \) is the mean concentration, \( k \) is the fitted partitioning coefficient and \( f_s \) is the fraction of solid formed (which is assumed to be equal to the fractional distance from dendrite centre to edge). A value of \( k = 1.4 \) for zirconium and \( k = 0.9 \) for scandium gave the best fit to the experimental data. Concentrations profiles determined by the simple fitted Scheil equation were used to initialize the dispersoid precipitation model when attempting to predict how the dispersoid distribution varies across a typical dendrite.

### 2.2. Effect of segregation

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### 2.3. Kinetics model

The Kampmann and Wagner Numerical model for precipitate evolution has been described in detail elsewhere [1,3,6]. The essential features of this model are:

1. The continuous time evolution of the particle distribution is considered in terms of discreet time steps.
2. The continuous size distribution of the particles is discretized into a large number of size classes.

3. The number of new particles in each time step is calculated using classical nucleation theory. The exchange of particles between size classes is calculated assuming solute diffusion is the rate limiting process and a spherical growth morphology. The Gibbs–Thomson relationship is used to calculate the modified interfacial compositions for each size class and at each time step.

4. The change in matrix solute level due to precipitate formation or dissolution is calculated at each time-step using the mean field approximation. The resultant model is capable of predicting nucleation, growth and coarsening without artificial constraints, whether these processes occur concommitantly or sequentially. The model developed here builds on two previous models, developed for Al3Zr [6] and Al3Sc [15] precipitation. As in these models, numerical efficiency and accuracy were ensured by using an adaptive Runge–Kutta time-step routine with in-built error checking. The following discussion focuses on describing the development of these models to treat the precipitation of the ternary Al3(Sc, Zr) phase.

2.4. Nucleation

The addition of an extra component adds considerably to the complexity in obtaining a rigourous solution for the nucleation rate [18]. Unlike in the binary case, in a multicomponent system there are multiple pathways across the nucleation energy barrier, and which path is followed depends on both kinetic and thermodynamic factors. Although this problem has been solved rigorously for simple systems [19], the solution is mathematically complex and does not account for solute depletion. In addition, it is difficult to justify this level of complexity given the large uncertainty in the predicted nucleation rate that arises from a lack of accurate knowledge of the interfacial energy. Therefore, in this work, an approximate method was used to calculate the nucleation rate. Ignoring any incubation time prior to nucleation, classical theory gives the nucleation rate in terms of the critical radius as:

\[
I = N_v \frac{kT}{h} \exp \left[ \frac{-4 \pi \sigma r^2 + Q^*}{3kT} \right],
\]

where \(N_v\) is the number of nucleation sites per unit volume, \(h\) and \(k\) are the Planck and Boltzmann constants, respectively, \(Q^*\) is the activation energy for transfer of atoms across the nucleus/precipitate interface (assumed to be approximately 2.07 eV atom\(^{-1}\), which is within the range reported for both Sc and Zr [20,21]) and \(r^*\) is the critical radius.

Calculation of the nucleation rate therefore reduces to finding the critical radius for nucleus formation, \(r^*\). Since the KWN method treats nucleation, growth and coarsening as concommitant processes it is essential that the method used to find the critical radius for nucleation is consistent with the method used to find the critical radius for growth. Capillarity theory defines the critical radius for growth as being the size at which the interfacial solute concentration in the matrix is equal to the mean matrix composition. The critical radius was therefore found by determining the particle size for which the capillarity compensated solvus line passed through the mean alloy composition. During precipitation, this size increases as the scandium and zirconium concentrations in the matrix fall. Using this value of the critical radius, the nucleation rate was calculated according to Eq. (3). Following the standard KWN procedure, newly nucleated particles were arbitrarily set 10% larger than the critical radius to allow them to grow.

2.5. Growth and coarsening

Calculating the growth rate of each precipitate requires a knowledge of the interfacial compositions. Local equilibrium is maintained at the interface as growth and dissolution occur. In a binary system the interfacial compositions are uniquely defined by a single tie line on the phase diagram. These compositions can then be corrected for the effect of particle size using the Gibbs–Thomson relationship. In the ternary case, there is an additional degree of freedom, and for any tem-
perature there are a whole series of tie lines that lead to local equilibrium at the interface [17,14]. Therefore, to find the unique tie line for growth or dissolution of any particular particle, an additional kinetic constraint is required. This constraint is that the diffusion flux of every element towards (or away from) the interface must be such that the interfacial velocity is the same regardless of which element is considered [17]. In the present case, where the supersaturations of Sc and Zr are small, the growth rate equation to be satisfied can be adequately approximated as

\[
\frac{dr}{dt} = \frac{D_{\text{Sc}} c_{\text{Sc}} - c^a_{\text{Sc}}(r)}{r} \frac{D_{\text{Zr}} c_{\text{Zr}} - c^a_{\text{Zr}}(r)}{r} = \frac{D_{\text{Sc}} c_{\text{Sc}} - c^b_{\text{Sc}}(r)}{r} \frac{D_{\text{Zr}} c_{\text{Zr}} - c^b_{\text{Zr}}(r)}{r},
\]

(4)

where \( D \) is the diffusion coefficient (of Sc or Zr), \( c \) is the concentration in the far field matrix, \( c^a(r) \) is the interfacial concentration in the matrix (which is a function of the particle radius due to the Gibbs–Thomson effect) and \( c^b \) is the concentration in the precipitate. The interfacial compositions are therefore defined by the tie line which gives values of \( (c^b_{\text{Zr}}, c^b_{\text{Sc}}) \) and \( (c^a_{\text{Zr}}, c^a_{\text{Sc}}) \) which satisfy this equation. The growth rate of particles is thus calculated for each size class by finding the tie line for that class which satisfies (4). A standard Newton–Raphson iterative method [22] was used to deduce the correct tie lines, one for each size class.

As in the standard KWN method, Eq. (4) is also used to calculate the dissolution rate for particles where the mean matrix composition lies below the solvus line for that size class. Coarsening arises naturally as the matrix becomes depleted in solute, leading to concentration gradients away from the smaller particles and towards the larger ones. A flowchart showing how the components of the kinetics model are integrated is presented in Fig. 4.

### 2.6. Segregation effects

As already discussed, in DC cast alloys, scandium and zirconium are segregated prior to precipitation. A method to predict precipitation of Al3Zr dispersoids from such a segregated structure was developed in previous work [6] and is used here. To predict the distribution of dispersoids across a dendrite arm, the composition profile is first divided into a number of segments (typically 50) each corresponding to a slice of material between the dendrite centre and edge. The mean local compositions for each element are then used as inputs to the dispersoid precipitation kinetics model. The kinetics model is run in parallel for each slice to predict the spatial distribution of dispersoids. Solute is also allowed to diffuse between slices, although in practice this was found to have a minor effect on the solute distribution, due to the relatively slow long range diffusion of scandium and zirconium.

### 3. Results

#### 3.1. Overall kinetics

The model was first run for a single concentration point (i.e. without considering the effects of segregation). Four 7050 alloys with different levels of scandium and zirconium additions was chosen for use in the calculations. The concentration of the major alloying elements was 2.2Cu–2.1Mg–6.1wt% Zn in all cases. The variants considered were 0.1Sc–0.13Zr, 0.18Sc–0.13Zr, 0.1Sc–0.07Zr, and 0.02Sc–0.13Zr (all wt%). The first three of these alloys have been investigated as part of a previous study [8,9]. The other alloy (the 0.02Sc–0.13 wt% Zr variant) has not been studied experimentally, but was chosen to investigate the effects of a very small scandium addition.

Fig. 5(a) shows the predicted overall transformation kinetics (evolution of dispersoid volume fraction) for the 0.1Sc–0.13wt% Zr alloy at 480 °C. This shows a sigmoidal form, with the final (near equilibrium) volume fraction being reached after about 1 h. However, even beyond this point there is a very small continuous increase in the volume fraction. This corresponds to a time interval where coarsening has yet to become established, as discussed in detail later.

Fig. 5(b) shows the evolution of the predicted interfacial concentrations of scandium and zirconium in the Al3(Sc, Zr) phase and the concentrations given by the equilibrium tie line (i.e. the tie line passing through the mean alloy composition) for the same conditions. Since these concentrations are a function of the particle size, the values plotted in Fig. 5(b) correspond to those predicted for a particle of the mean size (which is itself
evolving with time). It can be seen that during the early stages of precipitation, the scandium concentration at the interface is predicted to be larger than the concentration given by the equilibrium tie line. The zirconium concentration is correspondingly lower than that expected from equilibrium. This occurs because the diffusion coefficient of scandium is approximately four times greater than that of zirconium. Therefore, to satisfy Eq. (4) a tie line is required that makes the composition dependent term in Eq. (4) approximately four times greater for zirconium than scandium. In practice, this means a tie line is chosen in which the composition gradient of scandium ahead of the interface is reduced, and that of zirconium is increased. For local equilibrium to be maintained, this also requires an increase in the interfacial scandium concentration within the dispersoids. Fig. 6(a) is a plot of the predicted tie lines for growth at various stages during precipitation showing that the interfacial scandium concentration in the dispersoids is initially greater than that defined by the equilibrium tie line (ETL), but as transformation proceeds the growth tie line moves towards the ETL.

The change in the tie line for growth as precipitation proceeds is also reflected in the way the matrix composition changes as the dispersoids evolve. Fig. 6(b) is a plot of the predicted change in matrix composition during precipitation. This shows that, as expected, during the initial stages, precipitation occurs largely through the removal of scandium from the matrix. Only once approximately half the scandium has been removed into the dispersoids does the rate of zirconium depletion start to increase.

The dispersoid size, number density, and size distribution are also all outputs of the model. Fig. 7 shows plots of these variables at 480 °C. As expected, the most rapid kinetics are predicted in the alloy with the highest level of dispersoid forming additions. The 0.02Sc–0.13wt% Zr alloy, which has the smallest supersaturation of dispersoid forming elements, shows the slowest kinetics. The increased precipitation rate when significant quantities of

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**Fig. 5.** (a) Predicted evolution of volume fraction of Al3(Sc, Zr) at 480 °C in 7050 (with 0.1Sc–0.13wt% Zr). (b) Predicted evolution of the dispersoid composition at the interface with the matrix (ETL = composition defined by equilibrium tie line passing through mean alloy composition).

**Fig. 6.** (a) Local equilibrium at tie lines that satisfy the growth equation at various times during dispersoid precipitation at 480 °C in 7050 (with 0.1Sc–0.13wt% Zr). (b) Predicted path followed by the matrix composition.

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**Fig. 7.** Predicted evolution of volume fraction of Al3(Sc, Zr) at 480 °C in 7050 (with 0.1Sc–0.13wt% Zr).
scandium are present is not surprising given the rapid diffusion of scandium compared to that of zirconium. It is interesting to note that the early stage kinetics of the 0.1Sc–0.13wt% Zr alloy and the 0.1Sc–0.07wt% Zr alloy are predicted to be similar, despite the difference in zirconium level. This is because in the early stages, dispersoid precipitation is dominated by scandium, and the scandium level in these two alloys is the same.

The predictions of mean particle radius (Fig. 7(b)) show that despite the significant differences in the scandium level, the three alloys that contain 0.13wt% Zr have similar mean dispersoid radii (≈10 nm) at the point where precipitate volume fraction reaches the upper plateau. This is because, in these alloys, it is predicted that the extra solute has a stronger effect on particle nucleation than growth. Therefore, although the particle number densities are predicted to be much greater in the higher solute alloys, the predicted sizes at the end of nucleation are similar. The dispersoid radius in the 0.07Zr–1wt% Sc alloy is predicted to be slightly larger (≈12 nm) when the volume fraction reaches the upper plateau. This alloy has the highest scandium to zirconium ratio but also a relatively low initial supersaturation (which leads to a low nucleation rate, and therefore fewer particles competing for the available solute). These factors, coupled with the high diffusion rate of scandium compared with zirconium, lead to the larger particle size predicted for this alloy.

The evolution of number density (Fig. 7(c)) follows the expected trend in all four alloys. In the early stages of transformation, the number density increases rapidly since the nucleation rate is high. As solute becomes depleted in the matrix, the nucleation rate falls, and the number density reaches a maximum value. The model predicts that in all alloys there is then an interval in which the number density remains constant; i.e. nucleation is complete, but coarsening has not yet begun to dissolve the smaller particles. Therefore, for the set of conditions investigated, there is predicted to be no overlap of the nucleation and coarsening regimes. Eventually, however, coarsening does take effect and the smaller particles start to dissolve as the larger ones grow, leading to an increase in mean radius and a decrease in number density.

Fig. 7. (a) Predicted evolution of dispersoid volume fraction at 480 °C for four 7050 variants with different scandium and zirconium levels. (b) Predicted radius evolution. (c) Predicted evolution of number density.
The available data on the precipitation of Al₃(Sc, Zr) dispersoids in 7050 are rather sparse. Recently, Costello [8,9] has performed a systematic study of dispersoid evolution in a number of scandium containing 7050 alloys. Table 1 shows a comparison of predicted and measured dispersoid radii for three 7050 variants containing 0.07wt% Zr. These alloys were isothermally heat treated at 475 °C and the mean dispersoid radius was measured by averaging the size of at least 50 dispersoids, measured using bright field imaging in the transmission electron microscope (TEM) [full details elsewhere [9]]. Without any fitting, the model gives mean radii that are in reasonable agreement with those measured experimentally, particularly in the scandium containing alloys.

Both the model and experiments show that the scandium free alloy contains far larger dispersoids after 40 h than the scandium containing alloys. It was shown experimentally that this was not due to transformation of the metastable L1₂ Al₃Zr phase to the equilibrium D₀₂₃ Al₃Zr phase [9]. The model predicts that the comparatively low supersaturation in the scandium free alloy (and the relative effect this has on the critical radius, nucleation, and growth) is responsible for the size difference. As the supersaturation decreases, the critical radius increases, and the nucleation rate decreases more sharply than the growth rate. For example, the critical radius at the start of transformation is predicted to be 1.0 nm in the scandium free alloy, but only 0.15 nm in the 0.07Zr–0.18wt% Sc alloy. Therefore, in the scandium free alloy, far fewer dispersoids nucleate, but those that do form have a larger initial size. In addition, since there are far fewer particles, each dispersoid is able to grow for longer before exhausting the supersaturated solute, further increasing the size difference at later times (e.g. 40 h).

It is important to note that even after 40 h, it is predicted that in the 0.07Zr–0wt% Sc alloy, precipitation is not yet complete (i.e. the volume fraction of dispersoids is still increasing). This reinforces the conclusion that the difference in size is not due to a difference in coarsening rate (since coarsening has yet to play a major role in the determining the size evolution), but rather the difference in nucleation and growth kinetics discussed above.

It is also noteworthy that even though the model correctly predicts a significantly larger particle size in the scandium free alloy, this is still an underestimate of the measured particle size. One explanation for this, which is supported by experimental observations [9], is that due to the low driving force, precipitation in this alloy is predominantly heterogeneous, often occurring at sites associated with enhanced diffusion (e.g. dislocations). This effect is not yet accounted for in the present model, and hence the predicted size is an underestimate of the true size.

### 3.2. Coarsening behaviour

It is common to characterize the evolution of particle size at long times in terms of a coarsening law. In many cases, coarsening is found to obey an equation of the form

$$r^3 - r_0^3 = 2_{LSW}(t - t_0),$$

where $r_0$ and $t_0$ are the mean particle radius and time at the onset of coarsening, respectively, and $2_{LSW}$ is the coarsening constant. The $t^{1/3}$ dependence of the mean particle radius represented by this equation is one result of the classical Lifshitz, Slyozov and Wagner (LSW) theory of coarsening [23,24]. Although originally developed for binary systems, subsequent theoretical treatments have shown that a similar relationship is also expected for higher order systems, with the only difference being in the coarsening constant [25,26]. In common with the LSW theory for binary alloys, these treatments predict that during the coarsening regime, the particle size distribution (PSD) maintains a steady-state shape. The KWN model (as developed here) makes no assumptions about the size distribution, which instead evolves naturally as coarsening becomes more dominant. The present model therefore provides a useful comparison with the predictions of LSW coarsening theory. Previous work has shown that in binary alloys, the KWN method predicts that the size distribution evolves during coarsening to a shape which is close to (but broader than) that expected from LSW theory [1], as commonly observed experimentally. This work investigates the PSD evolution in the ternary case.

Fig. 7(c) shows that for the 0.13Zr–1wt% Sc alloy, the total number of particles is predicted to have started falling after 10 h of heat treatment, as a result of coarsening. Fig. 8 shows the predicted size distributions in this alloy after 50, 200 and 1000 h, all times at which coarsening is well advanced. However, it can be seen that the model predicts that the size distribution is still evolving over this period. For example, the PSD after 1000 h is predicted to be broader and flatter than after 50 or 200 h. The approach to the steady-state distribution (assuming there is one) is therefore predicted to be very slow. Fig. 9(a) shows a log–log plot of the predicted evolution of mean particle radius for the same four alloys as in Fig. 7. It can be seen that the expected $t^{1/3}$

<table>
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<th>Table 1</th>
<th>Predicted and measured mean dispersoid radii in three 7050 alloys with varying levels of scandium after 10 h and 40 h at 475 °C</th>
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<tr>
<td>Alloy</td>
<td>10 h $r_{pred}$ (nm)</td>
</tr>
<tr>
<td>0.07Zr–0wt% Sc</td>
<td>11</td>
</tr>
<tr>
<td>0.07Zr–0.1wt% Sc</td>
<td>8</td>
</tr>
<tr>
<td>0.07Zr–0.18wt% Sc</td>
<td>12</td>
</tr>
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Experimental data due to Costello [9].
kinetics are only approached at long times \((t > \simeq 500 \text{ h})\). This is much longer than the predicted time to reach the equilibrium volume fraction. The model therefore predicts that there is a long transition period between reaching the equilibrium volume fraction, and establishing coarsening behaviour that follows the relationship expected from LSW theory. The slow approach to the steady-state PSD and LSW coarsening kinetics has been widely observed in a range of binary alloy systems \([27]\) and the present predictions suggest the same is true of the more complex case under consideration here.

The size distributions obtained in all four alloys after 1000 h are shown in Fig. 9(b), along with the steady-state LSW distribution. It can be seen that the predicted size distributions all match very closely. However, these size distributions are significantly broader than the steady-state distribution obtained from LSW theory. In particular, the present model predicts that the fall off in number density at particle sizes greater than the critical radius is less sharp than suggested by the LSW distribution.

The predictions of the model were used to calculate an effective coarsening constant \((x_{\text{model}})\), considering only results from times where Eq. (5) was satisfied. A coarsening constant was also calculated using the Kuehmann–Voorhees (KV) model \([26]\), which is an extension of the LSW theory that deals with ternary systems. According to the KV model, the coarsening constant is given by

\[
x_{\text{kv}} = \frac{8\sigma V_m}{9R_e T \left( \left( c_{\text{Sc}}^2 (1 - k_{\text{Sc}})^2 / D_{\text{Sc}} \right) + \left( c_{\text{Zr}}^2 (1 - k_{\text{Zr}})^2 / D_{\text{Zr}} \right) \right)},
\]

where \(k_i\) is the distribution coefficient of the \(i\)th element between the matrix and dispersoid (\(\beta\)) phase (defined as \(c^\beta / c^\alpha\)) and all other variables are as before. The composition terms required in this equation were derived from the predicted phase diagram. Table 2 compares the coarsening constants predicted by the present model with those calculated on the basis of KV coarsening theory using Eq. (6). Also shown in the table is the sole experimental measurement of the coarsening constant in these alloys, derived by Costello \([9]\) from TEM measurements. It can be seen that although the present model and KV theory give coarsening constants that are in broad agreement (to within one order of magnitude), the constant predicted by the model is consistently lower (by up to a factor of five) than that expected from KV theory.

**Table 2**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(k_{\text{model}} \times 10^{-30}) (m(^3) s(^{-1}))</th>
<th>(k_{\text{kv}} \times 10^{-30}) (m(^3) s(^{-1}))</th>
<th>(k_{\text{measured}} \times 10^{-30}) (m(^3) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13Zr–0wt% Sc</td>
<td>1.69</td>
<td>7.02</td>
<td>–</td>
</tr>
<tr>
<td>0.13Zr–0.1wt% Sc</td>
<td>1.88</td>
<td>7.98</td>
<td>–</td>
</tr>
<tr>
<td>0.13Zr–0.18wt% Sc</td>
<td>2.34</td>
<td>8.27</td>
<td>–</td>
</tr>
<tr>
<td>0.07Zr–0.1wt% Sc</td>
<td>2.43</td>
<td>11.38</td>
<td>6.9</td>
</tr>
</tbody>
</table>

The measured coarsening constant is also shown for one alloy.
theory. The one measured value that is reported (and which is expected to be subject to significant error) lies between the value predicted by the current model, and that predicted by KV theory. Both the KV coarsening model and the present model predict that the fastest coarsening occurs in the alloy with the highest scandium:zirconium ratio, and the slowest coarsening occurs in the scandium free alloy. This is not surprising given the faster diffusion rate of scandium. The predictions also show that the coarsening rate is relatively insensitive to the volume fraction of dispersoid phase. For example, the 0.13Zr-0.18wt% Sc alloy, has a lower coarsening rate that the 0.07Zr-0.1wt% Sc alloy despite the fact that the low zirconium alloy has less than half the dispersoid volume fraction.

3.3. Dispersoid distributions

The effect of scandium additions on the recrystallization resistance depends not only on the average particle size and number but also critically on the spatial distribution of dispersoids. This is because, as previously discussed, it is regions that are depleted in dispersoids that are prone to recrystallize during solution treatment. Therefore, the model was used to predict the effect of adding scandium to the dispersoid distribution across a typical dendrite, using the fitted Scheil equation to estimate the initial solute distribution for a range of alloys.

Fig. 10(a) compares the predicted dispersoid size and number density across a dendrite in 7050 (0.13wt% Zr) with either 0 or 0.1wt% scandium after 10 h at 480 °C. Without scandium, it can be seen that a dispersoid free zone is formed at the dendrite edge. This zone corresponds to the region where the initial zirconium concentration is too low for formation of Al₃Zr, and this has been discussed in detail elsewhere [6]. The addition of 0.1wt% Sc is predicted to greatly increase the dispersoid number density at all locations, but particularly towards the dendrite edge. This is because the scandium is initially segregated towards the edge, and therefore compensates for the lack of zirconium in this region.

![Fig. 10. (a) Predicted dispersoid size and number density across a dendrite after 10 h at 480 °C in 7050 with 0.13wt% Zr and 7050 with 0.1Sc-0.13 wt% Zr. (b) Predicted distribution of Sc and Zr in the matrix before and after the same heat treatment in 7050 with 0.1Sc-0.13 wt% Zr. (c) Predicted variation in dispersoid composition for the same alloy and heat treatment.](image)
The model shows that where dispersoids are present, their number is predicted to be far greater in the scandi-um containing alloys, but their size is similar. This is because the increase in the supersaturation due to scandium additions has a much stronger effect on the nucleation rate than the growth rate. Therefore, the additional scandium goes largely to increasing the particle number density, and not the size. Fig. 10(b) shows the predicted distribution of Sc and Zr in the matrix of the 0.1wt% Sc alloy before and after heat treatment for 10 h at 480 °C. The model predicts that the scavenging concentration in the matrix is depleted more than the zirconium concentration; this reflects the rapid drop in the scavenging concentration during in the early stages of dispersoid precipitation, as discussed previously. It can also be seen that both scandium and zirconium are predicted to be more uniformly distributed following heat treatment. This is largely because more of these elements are removed into the dispersoids in regions where the concentration was originally high, rather than as a result of long range diffusion of Sc or Zr.

Fig. 10(c) shows the predicted variation in dispersoid composition for the same conditions. It is predicted that the dispersoid composition will reflect the original distribution of the elements in the matrix; i.e. the dispersoids towards the dendrite edge are predicted to contain more scandium than those towards the dendrite centres. However, at all positions, the dispersoids are predicted to contain more scandium than zirconium, despite the fact that at the dendrite centres the initial scavenging and zirconium levels are almost identical. As already noted, this is because of the enrichment of scandium in the early stages of dispersoid precipitation due to the rapid diffusion of this element compared to zirconium. The prediction of a single dispersoid phase, with a continuously varying composition depending on the local supersaturation is consistent with the microanalysis results of Riddle [7] and Costello [9]. Unfortunately, due to difficulties in the analysis of the small dispersoid particles, these studies did not produce reliable quantitative data to test the composition predictions of the present model. This will be the subject of future investigation.

To assess the effect of scandium on the recrystallized fraction after deformation and solution treatment it is necessary to estimate the potency of the dispersoids in recrystallization inhibition. Previously, it has been shown that the fraction of recrystallization in hot rolled plate can be estimated based on the the variation in the volume fraction to radius ratio (\(V_f/r\)) of the dispersoids [28]. It is this ratio that controls the Zener pinning pressure that the dispersoids exert on grain and subgrain boundaries [29]. A reasonable estimate of the recrystallized fraction can be obtained if it is assumed that recrystallization will only occur in regions where the \(V_f/r\) ratio falls below a critical value [28]. It should be noted that since this recrystallized fraction is calculated using a one-dimensional representation of a dendrite, it is only an approximation to the recrystallized volume fraction, which will also depend on the dendrite geometry. However, for the purposes of comparing the recrystallization resistance of different alloy compositions, this approximation is considered sufficiently accurate [28].

Fig. 11(a) shows the predicted variation in \(V_f/r\) across a dendrite (after homogenization for 24 h at 480 °C) for 7050 (0.13wt% Zr) with various scandium levels. As expected, the addition of scandium boosts \(V_f/r\), particularly near the dendrite edges, where the zirconium concentration is low. It should be noted that in this respect, scandium is complementary to zirconium, and these two elements are therefore most potent when used in combination.

The critical value of \(V_f/r\) that corresponds to a recrystallized fraction of \(\approx 30\%\) in 7050 without scandium is marked on the plot. If it is assumed that the driving force...
pressure for recrystallization is unchanged when scandium is present, it is possible to estimate the expected recrystallized fraction as a function of scandium content by estimating the change in the position at which $V_t / r$ exceeds the same critical value. These estimates are plotted in Fig. 11(b).

Fig. 11(b) shows that the fraction of recrystallization is predicted to decrease linearly as scandium is added, even for very small scandium additions. For example, a scandium addition as small as 0.02wt% is predicted to almost completely eliminate recrystallization (assuming that the recrystallized fraction is 30% in the same alloy without scandium). This calculation relies on the assumption that the driving force for recrystallization remains constant with scandium additions. This is unlikely to be strictly true since the additional dispersoids due to the presence of scandium may also hinder recovery processes during hot deformation, leading to a increase in the driving force for recrystallization. It is therefore expected that the recrystallized fractions predicted by the current model are probably underestimates of the true recrystallized fraction. Nevertheless, the potency of small scandium additions ($<0.1\text{wt}\%$) in reducing recrystallization in AA7050 has been demonstrated by both Riddle and Sanders[7] and Costello [9], in qualitative agreement with the predictions here.

4. Conclusions

A novel model has been developed for the precipitation of ternary $\text{Al}_3(\text{Sc}, \text{Zr})$ dispersoids in commercial aluminium alloys. It is based on an extension of the classical KWN precipitation model that accounts for the multicomponent nature of the precipitating phase. The following conclusions may be drawn from this study

1. Phase diagram calculations suggest that the copper, magnesium, and zinc present in commercial high strength aluminium alloys have a significant effect in shifting solvus of $\text{Al}_3(\text{Sc}, \text{Zr})$ to lower scandium and zirconium concentrations.

2. During the early stages of $\text{Al}_3(\text{Sc}, \text{Zr})$ precipitation, the local equilibrium tie line for growth is such that the dispersoids are enriched in scandium. As growth proceeds, the zirconium level in the dispersoids is predicted to rise.

3. Changes in the levels of scandium and zirconium added to 7050 are predicted to lead to large changes in the dispersoid number density, but small changes in the radius. Predicted radius values are in reasonable agreement with experimental data. Scandium additions of 0.1wt% or more reduce the time taken to reach a given volume fraction by over an order of magnitude.

4. The dispersoid size distribution during the coarsening regime in 7050 with Zr and Sc is broader than the steady-state LSW distribution. Furthermore, the time taken to reach LSW coarsening kinetics (where the mean radius increases with the cube root of time) is predicted to be over two orders of magnitude greater than the time at which coarsening begins.

5. The model gives a predicted coarsening constants that are the same order of magnitude, but smaller than those predicted by the Kuehmann–Voorhees coarsening theory. Both models predict that the coarsening rate increases with an increase in scandium:zirconium ratio in the alloy.

6. Even small (<0.1wt%) additions of scandium are predicted to eliminate the microsegregation induced dispersoid free zone observed in alloys containing zirconium alone. The dispersoids that precipitate towards the edge of the dendrites are predicted to be scandium rich compared to those at the centre, reflecting the original microsegregation.

7. The improved dispersoid distribution obtained by adding scandium is predicted to greatly enhance the recrystallization resistance of hot rolled 7050 plate. The model suggests that scandium additions as low as 0.02wt% could almost completely eliminate recrystallization for typical rolling conditions.

Acknowledgements

The author is grateful to Ralph Shuey and Jaakko Suni of the Alcoa Technical Center, Pittsburgh for useful discussions and to Jaakko Suni for performing the multicomponent thermodynamic calculations.

References