INTRODUCTION

Hot rolled, 7xxx series aluminium alloy thick plate is increasingly in demand for structural aerospace applications. To obtain the optimum balance of high strength and toughness in this material, it is necessary to minimise recrystallization during processing [1]. In an attempt to achieve this, dispersoid forming elements are added to 7xxx series alloys. Zirconium is currently the most widely used dispersoid forming element in high strength aerospace alloys such as 7050. This element precipitates as coherent, metastable L1$_2$ Al$_3$Zr dispersoids during homogenisation, which are capable of suppressing recrystallization via the Zener pinning effect [2].

The Al$_3$Zr dispersoids do not, however, completely eliminate recrystallization. During solution treatment, bands of recrystallized grains form in regions where the dispersoids are depleted. These regions occur towards the edges of the cast dendrites. This can be traced back to the peritectic segregation of zirconium towards the dendrite centres during casting [3, 4]. Although it is possible to encourage dispersoid precipitation through use of controlled heating ramps or multi-step homogenization practices [5], it is not possible to completely eliminate the dispersoid free regions this way.

One potential route to reduce recrystallization is to add another dispersoid forming element that segregates in the opposite sense to zirconium and thus promotes dispersoid formation in zirconium depleted regions. An ideal element for this purpose is scandium. The aluminium–scandium system shows a eutectic reaction during solidification, and scandium is thus expected to segregate towards the dendrite edges. Furthermore, scandium and zirconium precipitate from solid solution as a single L1$_2$Al$_3$(Sc,Zr) phase. This phase is capable of forming fully coherent particles, minimizing the impact of dispersoid precipitation on the quench sensitivity of the alloy.

This potential has led to several experimental investigations of commercial aluminium alloys [6] (including 7050 [7, 8]) with additions of both scandium and zirconium. The combined addition of these elements has been shown to reduce, or completely suppress, recrystallization under normal processing conditions. Scandium is, however, a costly alloying addition. Therefore, it is particularly critical to determine the minimum scandium addition required to give benefits, and the point at which adding further scandium become unprofitable. It is also important to know how to optimize the homogenization practice to make maximum use of any scandium addition.

In previous work, we have shown how modelling can be applied to predict dispersoid precipitation in alloys containing either zirconium [3, 9] or scandium [10], and how these models can be used to develop new homogenization practices to optimize dispersoid formation [5]. Examples of some of these calculations are presented here. The majority of this paper, however, focuses on extending these mod-
els to predict dispersoid precipitation in 7xxx alloys that contain both scandium and zirconium. The new model is used to investigate the effects of scandium concentration and homogenization practice on the dispersoid evolution, and the predicted effect on the recrystallized fraction expected in hot rolled plate.

**THE MODEL**

In previous work, the authors have shown how models based on the Kampmann and Wagner N–model (KWN) framework [11] can be used to reliably predict the precipitation kinetics of Al$_3$Zr and Al$_3$Sc [3, 10]. The KWN method allows a full prediction of the particle evolution, from the early, nucleation dominated, stages to the late, coarsening dominated stages. Furthermore, by coupling the precipitation kinetics model to a Scheil solidification model, which predicts the non–uniform initial distribution of alloying elements, it is possible to predict the variation in dispersoid size and number across a dendrite [3]. This can be used to make an estimate of the recrystallized fraction, by calculating the volume of material in which the pinning pressure due to the dispersoids falls below the critical value required to prevent recrystallization [12].

The N–model method, as applied to dispersoid precipitation, is outlined below. Further details are available elsewhere [3, 10].

- The continuous time evolution of the particle distribution is considered in terms of discrete time steps. The spatial distribution of dispersoids across a dendrite is modelled by considering a series of slices of material between the dendrite edge and centre.
- At each step and for each slice, the number of new dispersoid nuclei is calculated using classical nucleation theory. The driving force for nucleation is calculated from the local instantaneous value of the supersaturation.
- The growth of existing particles is calculated by assuming a spherical particle morphology, with growth controlled by diffusion of solute to the particle/matrix interface. The influence of surface energy (and hence particle size) on the interfacial composition (the Gibbs Thomson effect) [13] is accounted for.
- The particle size distribution and the volume fraction of the dispersoid particles are updated at each time step, and used to recalculate the local matrix composition, using the mean field approximation applied locally to each slice.
- During each time-step solute is allowed to redistribute between slices, governed by composition gradients according to Fick’s second law. The updated solute concentrations are used in the next time-step.

At each spatial point across the dendrite, the full particle size distribution of the dispersoids is tracked. The particle size distribution itself is divided into a large number discrete size classes. Particles are exchanged between size classes as a result of growth or dissolution [9]. Numerical accuracy is ensured by using a third order Runge-Kutta integration scheme, which includes an adaptive timestep routine to ensure that the timesteps are sufficiently small when the particle size distribution is evolving rapidly.

In previous work, the method above has been applied to predict the formation of the binary, stoichiometric Al$_3$Zr and Al$_3$Sc phases. In these cases, the growth of the phase is controlled by diffusion of a single element (Zr or Sc), and the concentrations of solute at the interface are fixed by the phase diagram.

The aim of new model developed here was to predict precipitation of the non-stoichiometric Al$_3$(Sc,Zr) ternary phase. The addition of an extra element adds new degrees of freedom that increase the complexity of the problem, and also introduce some unknown parameters. For example, the energy of the Al$_3$(Sc,Zr)/matrix interface is an important parameter in controlling both nucleation and growth rates. The value of the interfacial energy for the mixed dispersoid phase is not known. Furthermore, in a ternary system, the requirement for local equilibrium at the interface between the precipitate and matrix does not uniquely define the interfacial composition, as in the binary case [13]. The situation is further complicated because atom probe investigations suggest that zirconium within the Al$_3$(Sc,Zr) phase is preferentially partitioned to the interface [14]. Attempting a rigorous model for these complex processes is beyond the scope of the work here.

To avoid some of these difficulties, an approximate
method was adopted to model the precipitation of the ternary phase, which has the benefits of simplicity and transparency. In this method, the mixed Al$_3$(Sc,Zr) phase is modelled by considering the effective evolution of the two end-point components, Al$_3$Sc and Al$_2$Zr. The volume fraction of the mixed phase can then be calculated by summing over both component phases. The composition of the mixed phase can be estimated by considering the proportion of each component phase. This method has been successfully employed previously to model precipitation of the mixed Al$_3$(Sc,Zr) phase in 6xxx alloys [15].

The presence of scandium will influence the solubility of zirconium in the matrix, and vice versa. Therefore, it is necessary to consider the pseudoternary Al-Sc-Zr phase diagram to determine the equilibrium solubilities used in the model. In this work, these solubilities were calculated using thermodynamic data due to Murray [16]. Unfortunately, there is not yet a reliable assessment of the enthalpy of mixing of scandium and zirconium on the L1$_2$ Al$_3$(Sc,Zr) lattice. Therefore, as a first approximation, ideal conditions were assumed (no enthalpy of mixing). The model was also tested using two alternative assumptions; a positive and a negative enthalpy of mixing. Although this does alter the numbers predicted by the model, the same trends were reproduced in all three cases.

Of particular interest in this work is modelling the effect that scandium additions have on the distribution of dispersoid particles across a typical dendrite in AA7050. To evaluate this, it is first necessary to know the distribution of the alloying elements after casting. In this work, a simple Scheil model, fitted to experimental composition measurements, was used to predict the initial distribution of scandium and zirconium. Three 7050 variants, containing 0.13wt% Zr and 0, 0.1, and 0.3wt% scandium were considered. Note that the addition of 0.3wt% scandium is insufficient to cause the formation of primary Al$_3$(Sc,Zr) particles during solidification. Only the scandium remaining in solution (0.18wt%) is available for dispersoid precipitation. Further details of the experimental measurements are given elsewhere [17, 8].

Fig. 2 shows the measured and predicted scandium and zirconium distributions after casting across a typical dendrite (from centre to edge). The predicted concentrations were derived from a 1-dimensional Scheil model, fitted to the experimental data:

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

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.

The solvus concentrations are also required by the model, and were predicted using the multicomponent thermodynamic calculation discussed above. In practice, the level of major alloying elements (Cu, Mg, and Zn) in solution will evolve during homogenization as the soluble constituent particles dissolve; this will have an influence on the solvus concentrations. Since the dissolution of these phases is not yet incorporated in the model, it is necessary to assume either that the constituents remain fully soluble elements in 7050 and 2024 (i.e. Cu, Mg, and Zn) is predicted to lead to a significant shift in solvus position, moving it towards lower scandium and zirconium concentrations. Therefore, for the same level of Zr and Sc addition, the supersaturation of these elements will be greater in the commercial alloys than they are in ternary alloys.
undissolved, or are fully dissolved, as the dispersoids precipitate. In this work, the first of these assumptions was used. The implications of this choice are discussed in detail elsewhere [9].

Fig. 2: Measured (exp) and fitted (fit) matrix solute concentrations after casting, across a typical dendrite (from centre to edge), for three 7050 alloys containing 0.13wt% Zr and 0 wt% Sc, 0.1 wt% Sc and 0.3 wt% Sc. Note that the mean scandium level in solution in the 0.3 wt% Sc alloy is $\approx 0.18$wt%; the rest of the scandium forms primary $\text{Al}_3(\text{Sc},\text{Zr})$ particles.

**PREDICTIONS**

The predictions of the kinetics model, when applied to alloys that contain only zirconium or scandium, will be briefly discussed first. These alloys have been subject to a number of experimental investigations that provide data for testing the model. For example, Fig. 3 shows the calculated precipitation kinetics of $\text{Al}_3\text{Zr}$ dispersoids at the dendrite centres in 7050 (0.13wt% Zr), compared to experimental data [3], after model calibration. The $\text{Al}_3\text{Zr}$ model was calibrated using datasets for a range of temperatures from 350 to 500°C, obtained using TEM and FEGSEM observations [3]. Model calibration involves tuning the interfacial energy and nucleation site density parameters to give the best agreement with experiment across the entire temperature range. Once set, these tuning parameters can then be used to make predictions for other compositions and temperatures.

Fig. 3: Measured and predicted evolution of $\text{Al}_3\text{Zr}$ dispersoids in 7050 (0.13wt% Zr) at 500°C.

Fig. 4 shows the predicted variation in $\text{Al}_3\text{Zr}$ dispersoid volume fraction across a typical dendrite (from centre to edge) for both a binary Al–Zr alloy, and two 7050 alloys (both with 0.13wt% Zr but different amounts of the major alloying elements), after ramp heating and homogenization at 480°C. The non-uniform distribution of dispersoids is correctly predicted. At the edge of the dendrites, the dispersoid volume fraction is predicted to fall to zero. This is consistent with experimental observations and is due to zirconium segregation, as discussed previously.

The model for the precipitation of $\text{Al}_3\text{Sc}$ has also be
compared to experimental data for this phase. For example Fig. 5(a) shows the predicted evolution of mean particle radius in an Al–0.3wt% Sc alloy aged at 350°C after model calibration. The model correctly captures the observed coarsening behaviour of the Al₃Sc particles at long times, and also predicts the early stage precipitation kinetics [10]. The particle size distributions predicted by the model are in good agreement with those measured experimentally, and an example is shown in Fig. 5(b).

One difficulty is that, as discussed previously, the dispersoid size (and number density) can vary significantly as a function of position relative to the original cast dendrites, and thus the measured values will depend strongly on the point at which observations were made.

Because of these difficulties, no attempt has been made to tune the model for the ternary Al₃(Sc,Zr) phase (e.g. by optimizing the interfacial energy) to get the best fit with experimental data. Instead, all the adjustable parameters have been fixed at their values for the binary Al₃Zr and Al₃Sc phases. The similarity of these two phases and the mixed phase suggests that this is a reasonable first approximation.

Experimental data for precipitation of the ternary Al₃(Sc,Zr) phase in 7050 is more scarce. Furthermore, there appears to be considerable discrepancy between different datasets. For example, Riddle and Sanders [7] report a mean dispersoid size of z=4 nm in a 7050 alloy containing 0.1wt% Sc, homogenized for 10 h at 480°C. Costello [17], on the other hand, reports a mean dispersoid radius of 11 nm (almost three times larger) in the same alloy, heated for the same time at a similar temperature (475°C). It is not possible to rationalize both of these apparently contradictory observations using the current model.
in this alloy compared with the 0.1wt% Sc alloy is relatively modest. As expected, an increased scandium concentration leads to an increase in the final volume fraction of dispersoids, and also accelerates the overall transformation kinetics. It is not clear whether the kink in the volume fraction curve at short times and high scandium levels is a numerical artifact or not; in any case, it does not effect the predictions at longer times, typical of industrial homogenization practices.

The predicted increase in number density of the particles with the addition of scandium would be expected to enhance their effectiveness in preventing recrystallization. However, for the purposes of recrystallization control, it is more important to consider the effect that scandium additions have on the distribution of dispersoid particles.

Fig. 7(a) shows the predicted variation of dispersoid volume fraction and composition across a typical dendrite after a 24 h heat treatment at 480°C. Fig. 7(b) shows the corresponding variation in number density and mean radius. The initial variations of scandium and zirconium across the dendrite were assumed to be given by the Scheil fits (Fig. 2). Diffusion controlled redistribution of the solute in the dendrite during homogenization was accounted for. However, the model predicted that dispersoid precipitation was effectively complete before there was time for complete redistribution of either scandium or zirconium. Therefore, the pattern of dispersoid precipitation across the dendrite strongly reflects the original distribution of zirconium and scandium in the as cast structure.

Without scandium, a dispersoid free zone is predicted, as already discussed. Adding scandium increases the concentration of dispersoid forming elements. The segregation of scandium towards the dendrite edges is beneficial, since this concentrates the available scandium where it is most needed, i.e. where the zirconium concentration is least. The model predicts that an addition of 0.1wt% Sc is sufficient to completely eliminate the dispersoid free zone.

The prediction that scandium is highly effective in reducing the dispersoid free zone width in 7050 is supported by experimental evidence [8, 17]. However, experiments also show that even with high scandium addition, a narrow dispersoid free zone (less than 1 μm wide) often occurs adjacent to grain boundaries. This is likely to be due to an effect that is not yet accounted for in the present model, such as the role of grain boundary precipitation.

Since the local scandium to zirconium ratio varies across the dendrite, it might be expected that the dispersoid composition also changes. The model was used to investigate this, again assuming that scandium and zirconium behave ideally. As expected, it is predicted that the mixed phase becomes increasingly scandium rich towards the dendrite edges. For example, for the 0.1wt% Sc containing alloy, the predicted composition of the mixed phase is $\text{Al}_3\text{Zr}_{0.3}\text{Sc}_{0.5}$ at the dendrites centre, and $\text{Al}_3\text{Zr}_{0.2}\text{Sc}_{0.8}$ at the edges. This prediction is in agreement with recent experimental measurements.
of dispersoid composition variations [17].

Fig. 7(b) shows that the addition of scandium is also predicted to lead to a far more uniform dispersoid size across the dendrite. In the scandium free alloy, there is a predicted to be a region, towards the dendrite edges, that contains a small number of large dispersoid particles. This has been confirmed experimentally, and is due to the marginal zirconium supersaturation at this location, making nucleation of dispersoids difficult [3].

In practice, in alloys containing zirconium alone, dispersoid nucleation in these regions occurs only on heterogeneous sites, such as dislocations, or undissolved M–phase precipitates [3]. These coarse dispersoids (which appear in bands around the edge of the dendrites) are semicoherent with the matrix and degrade the quench sensitivity of the alloy by acting as preferential nucleation sites for equilibrium M–phase precipitation [20]. Coarse dispersoid bands are not predicted in the scandium containing alloys because in this case there is sufficient supersaturation for nucleation of fine dispersoids right across the dendrites. This prediction suggests that scandium additions may help to reduce quench sensitivity by eliminating coarse dispersoid bands. Further experimental investigation is required to confirm this.

Scandium is an expensive alloying element. Therefore, it is important to determine the minimum scandium level required to have a beneficial effect on dispersoid distribution, and hence recrystallization. The model was used to investigate this. 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 [12]. It is this ratio that controls the Zener pinning pressure that the dispersoids exert on grain and subgrain boundaries [2]. It is assumed that recrystallization occurs in regions where this ratio falls below the critical value required to prevent the migration of high angle grain boundaries. This critical value will depend on the driving pressure for recrystallization, which is a function of the deformation conditions.

Fig. 8(a) shows the predicted variation in $V_f/r$ across a dendrite, after homogenization for 24 h at 480°C, for varying scandium levels. This was calculated by dividing the total volume fraction at each point by the local average dispersoid radius. As expected, the addition of scandium boosts $V_f/r$, particularly near the dendrite edges. The critical value of $V_f/r$ that corresponds to a recrystallized fraction of $\simeq$30% in 7050 without scandium is marked on the plot.

![Graph showing predicted variation in dispersoid volume fraction to radius ratio ($V_f/r$) across a dendrite after 24 h homogenization at 480°C. The critical value of $V_f/r$ corresponds to 30% recrystallization in 7050 without scandium.](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAmAAAAAbCAYAAADlU8KAAAAGXRFWS3x3vAAAAwFSC1herAAAABHIewDARkAAACmJREFUeJfrf/8qFzAQAAAAASUVORK5CYII=)
to almost completely eliminate recrystallization for a case where the recrystallized fraction is 30% without scandium. In practice, some recrystallization may occur, even with scandium additions in excess of 0.02wt%, due to the presence of a narrow dispersoid free band at the grain boundaries, as discussed previously. Nevertheless, Riddle and Sanders have demonstrated the potent effect of small scandium additions in suppressing recrystallization in 7050 [7], in qualitative agreement with the predictions of the present model.

All the results presented so far have been for isothermal homogenization treatments. In commercial practice, however, it is usual for the ingot to be heated slowly to the homogenization temperature. Previous work has shown that this slow heating can be beneficial, since it encourages dispersoid nucleation [3].

Fig. 9(a) shows a plot of the variation in dispersoid size and number density across a dendrite for two cases; the first corresponding to isothermal homogenization (24 h at 480°C), and the second to the same homogenization treatment, but with a 20 h heat up time. These predictions were performed for 7050 with a very small scandium addition (0.02wt% Sc). Using ramp heating leads to a small increase in dispersoid number density, particularly towards the dendrite edge. This is due to enhanced nucleation during the heat up. The enhanced nucleation due to ramp heating is also predicted to slightly reduce the mean dispersoid size. The change in size and number density predicted for ramp heating also gives a small change the $V_f/r$ ratio (Fig. 9(b)). This would be expected to lead to a small ($\approx 1\%$ absolute) reduction in the recrystallized fraction.

The effect of ramp heating to homogenization in scandium containing 7050 is predicted to be less than in scandium free 7050, where enhanced nucleation of Al$_3$Zr dispersoids during heat up increases the $V_f/r$ ratio towards the dendrite edges [12]. This effect can be seen in Fig. 9(b); in the scandium free alloy, the predicted $V_f/r$ ratio towards the edge of the dendrite becomes several times larger when ramp heating is used. This has been shown to have a significant effect on recrystallization [12]. The effect of ramp heating is less potent when scandium is present because scandium already enhances dispersoid nucleation in the low zirconium regions and the extra boost due to ramp heating is comparatively small.

**CONCLUSIONS**

A model has been developed for non-uniform dispersoid precipitation in commercial aluminium alloys containing both zirconium and scandium. This model has been used to investigate the effects of adding scandium to the dispersoid distribution in 7050.

It has been shown that scandium and zirconium segregate in opposite directions during casting, and this is predicted to promote a more uniform distribution of dispersoids across a dendrite arm than with either element alone. In particular, scandium encourages dispersoid precipitation towards the edges of the dendrites, where the zirconium concentration is...
The presence of the major alloying elements (e.g. Cu, Mg, Zn) further encourages dispersoid precipitation by lowering the solubility of scandium and zirconium in the matrix. The addition of scandium is predicted to significantly increase the recrystallization resistance of 7050 as a result of the improved dispersoid distribution. It is estimated that a scandium level of as low as 0.02 wt%, when added with 0.13wt% Zr, will almost completely eliminate recrystallization in hot rolled plate under typical processing conditions.

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