CHARACTERISATION OF THE SOLIDIFICATION IN $A\ell$-7Si-0.5Mg BASED METAL MATRIX COMPOSITES BY THERMAL ANALYSIS

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Abstract

The solidification characteristics of A356 aluminium alloy based metal matrix composites reinforced with $A\ell_2O_3$, MICRAL™-20[1] and SiC particulate have been investigated. Conventional thermal analysis and differential scanning calorimetry (DSC) techniques were used with cooling rates ranging between $8x10^{-3}$-$8x10^{-1}$ °C/s. Within the range of cooling rates examined, the temperatures for onset of nucleation and eutectic growth were observed to be higher in the composites than the matrix alloy and independent of cooling rates. In all the composites very little undercooling was observed compared to the unreinforced alloy. Secondary dendrite spacings (DAS) were measured for samples solidified between 3 - $8x10^{-1}$ °C/s and were correlated to the cooling rates by a relationship of the form $DAS = A\ (T)^{-n}$ where n was found to be 0.33 and 0.26 for the matrix alloy and the composites respectively. Metallographic evidence was found for the nucleation of primary aluminium on reinforcement particles in the composite reinforced with $A\ell_2O_3$ particles.

Introduction

The interaction of the reinforcement particles with the molten matrix alloy changes the physico-chemical nature of the surface of the reinforcement particles and the matrix in its vicinity. These interactions can have a marked influence on the resulting solidification microstructures and hence the physical and mechanical properties. For example, the presence of reinforcement particles in $A\ell$-Si alloys of near eutectic compositions has been found to promote the nucleation of primary silicon and in some cases primary α-aluminium nucleation on the reinforcement particles (1). Some grain refinement due to the presence of reinforcement particles has been observed in $A\ell$-7Si-0.5Mg alloys reinforced with MICRAL-20 and SiC particulate (2). An increase in the absolute temperature at which primary solidification begins has also been reported in $A\ell$-7Si-0.3Mg based MMCs reinforced with SiC particulate (3). The reported increase in the solidification onset temperature was attributed to the nucleation of primary aluminium on the SiC particles. As well as the nucleation related interactions, the thermal profile ahead of the solidification front could be altered due to the presence of the ceramic particles.

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[1] "MICRAL" is a trade mark of Comalco Aluminium Limited.

The present study was undertaken with the objective of providing an understanding of the steady state aspects of solidification in liquid metallurgy processed A356 based MMCs reinforced with MICRAL-20, SiC and $A\ell_2O_3$ particulate. Conventional thermal analysis and differential scanning calorimetry (DSC) were used to achieve very slow cooling rates.

Experimental

The materials investigated included the unreinforced matrix alloy, A356, and A356 based composites reinforced with 20vol% $A\ell_2O_3$, MICRAL-20 and SiC particulate. The MICRAL-20 particulate had an average particle size ~20μm. The particles consist mainly of corundum (α-$A\ell_2O_3$) and mullite ($3A\ell_2O_3$-SiO_2) phases, which also contained some dissolved Fe and Ti. The $A\ell_2O_3$ and SiC particulate had an average size of ~15μm. The $A\ell_2O_3$ particles contained some TiO_2 and Fe impurities. The same nominal alloy chemistry was used to prepare each composite and no alloy additions were made (for example to compensate for reaction effects).

Thermal analysis and DSC were used to investigate near equilibrium solidification conditions. For conventional thermal analysis, 400g of test material was melted in a graphite crucible (ϕ50x100mm) in an induction furnace. Cooling curves were determined for all the materials investigated. Prior to recording the temperature of the melt as a function of time, the furnace power was switched off and a K-type thermocouple was inserted approximately mid-way into the melt.

DSC work was carried out using a Perkin-Elmer DSC7 instrument. Test samples between 15-25mg were melted in alumina crucibles using high purity aluminium (99.999%) as a reference. Scanning rates ranged between $8x10^{-3}$ and $8x10^{-1}$ °C/s. From the DSC outputs, the nucleation onset and eutectic onset temperatures were determined. The enthalpy associated with a given phase transformation was determined from peak analysis calculations. After testing, the DSC samples were mounted and polished using standard metallographic techniques and examined by optical microscopy.

Results

Thermal Analysis

The results from the conventional thermal analysis are summarised in Table 1. The cooling rate was of the order of 1°C/s. By comparison to the matrix alloy the composites show very little undercooling. In the composites the absolute temperature at which primary solidification occurs and the eutectic transformation temperatures are higher than for the matrix alloy. The effect is greatest for the $A\ell_2O_3$ reinforced composite.

Table 1. Summary of conventional thermal analysis for the composites and the matrix alloy.

Material	Liquidus Temperature (°C)	Liquidus Undercooling (°C)	Eutectic Temperature (°C)
A356	610	2.6	563
A356 + $A\ell_2O_3$	624	0	575
A356 + SiC	616	0.7	573
A356 + MICRAL-20	613	0.7	567

DSC Analysis

The nucleation onset temperatures, T_N, and the eutectic temperature, T_E, from the DSC study are summarised in Table 2. Under the cooling rates examined (8×10^{-3} - 8×10^{-1} °C/s) the onset temperatures for nucleation and the eutectic were found to be fairly independent of cooling rate. Compared with the conventional thermal analysis experiments there is slightly less spread in the temperatures between materials, but the trends are consistent.

Table 2. Nucleation onset and eutectic temperatures and latent heat evolution (J/g) determined from DSC analysis.

Material	T_N (°C)	T_E (°C)	Primary Phase (ΔH_p)	Eutectic (ΔH_e)	Ratio ($\Delta H_p/\Delta H_e$)
A356	613	570	201	175	1.15
A356 + $A\ell_2O_3$	623	577	161	143	1.13
A356 + SiC	617	576	149	171	0.87
A356 + MICRAL-20	615	572	152	146	1.04

The peak analysis calculations for the latent heat evolved are also included in Table 2. Separate calculations were made for the primary alpha-phase (semi-solid region), and the eutectic. Note that the latent heat for the composites is lower than for the matrix alloy due to the lower metal content (per gram of composite). As indicated by the latent heat results, the proportion of primary phase and eutectic is not the same in all the materials, in particular the SiC composite has a larger eutectic transformation (indicative of a higher Si content).

Microstructures

In order to further characterise the composite materials, the secondary dendrite arm spacing (DAS) was measured as a function cooling rate on tested DSC samples. The effect of reinforcement type appeared to be minor for the slow cooling rates examined. The DAS was found to be related to cooling rate by an equation of the form: $DAS = A(T)^{-n}$ where $n = 0.33$ for the matrix, 0.27 for $A\ell_2O_3$, 0.26 for SiC and 0.26 for MICRAL-20.

Representative micrographs of the Si morphology were taken from the DSC samples cooled at a rate of 3×10^{-2}°C/s (Figure 1). The Si has nucleated and grown from the particles in each of the composites. Note that the eutectic Si fibres in the SiC composite appear to have coarsened to sizes comparable to the SiC particles whereas this was not observed in the other two composites nor in the matrix alloy.

In order to examine the possibility of primary α-aluminium nucleation on the reinforcement particles in the composites, samples of the composite reinforced with $A\ell_2O_3$ particles were quenched from above and below the liquidus temperature. The samples were quenched from 655°C and 617°C into water at 20°C. Optical micrographs from the samples are shown in Figure 2(a) and (b). The $A\ell_2O_3$ reinforced composite was selected because it had the highest measured liquidus temperature of the materials examined.

In the sample quenched from 655°C, Figure 2(a), very fine dendrites with DAS ranging between 3-5μm can be observed as well as some evidence of primary α-aluminium nucleation on the reinforcement. The microstructures of the sample quenched from 617°C, Figure 2(b), shows more clearly evidence of nucleation of primary α-aluminium on the particles of $A\ell_2O_3$.

Discussion

Nucleation and Undercooling

The very small undercooling (Table 1) in the composites compared to the unreinforced matrix alloy suggests that a large number of heterogeneous nucleation sites are available in the composites. In a similar study of a near eutectic composition $A\ell$-Si alloy reinforced with MICRAL-20 particulate, an even more pronounced difference between the matrix alloy and composite was observed. In that case, the composite showed virtually no undercooling while an undercooling of 7-8°C was recorded for the unreinforced alloy (4).

The observation that primary α-aluminium appears to nucleate on the $A\ell_2O_3$ particles (Figure 2) is interesting in that it has been widely reported that primary α-aluminium does not nucleate on reinforcement particles (7). The lack of nucleation and persistent growth of primary aluminium on reinforcement particles has been attributed to the high wetting angles ($>90^\circ$) between liquid aluminium and the reinforcement particles (6). Microstructural evidence indicates that it is possible for primary α-aluminium to nucleate and grow on the reinforcement particles. Similar observations have also been made in TiC reinforced $A\ell$-4.5 Cu alloy (8).

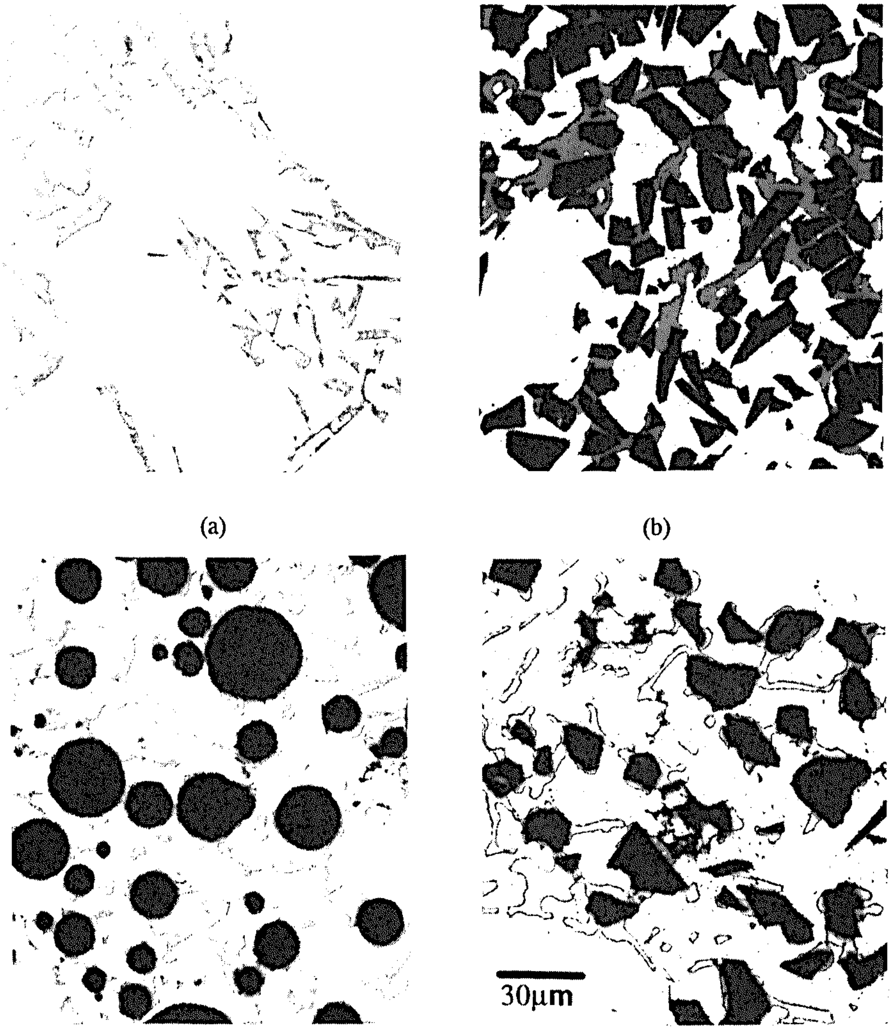
The contradictory observations of primary α-aluminium nucleation on reinforcement particles may be due to the complex nature of the liquid metal/particle interface. The interfacial reaction layer depends on the matrix composition, reinforcement type and processing (9), so it may be that nucleation is only promoted in specific instances. Furthermore, the purity of the particulate may play a role in determining nucleation. For example, both MICRAL-20 and $A\ell_2O_3$ particulate contain Ti as an impurity. If Ti enrichment occurred at the interface by a reaction with the matrix, then nucleation on the interface could be more favourable.

Thermal effects of the reinforcement phase

In the thermal analysis experiments, the initial cooling rates were similar for all the materials. An effect of the lower thermal conductivity of the various particulates or the relatively high thermal heat capacity of the SiC was not apparent.

Cooling rates determined from the semi-solid region, that is, below the formation of the α-phase and above the onset of the eutectic on the cooling curves, were also similar for the composites (1.2°C/s), but the composites had a higher cooling rate than the matrix (1.0°C/s).

The reason is simply that for the same volume of material, under similar conditions, there is more metal in the matrix alloy and therefore more latent heat to be extracted during solidification. This difference is also reflected in the latent heat data (Table 2).



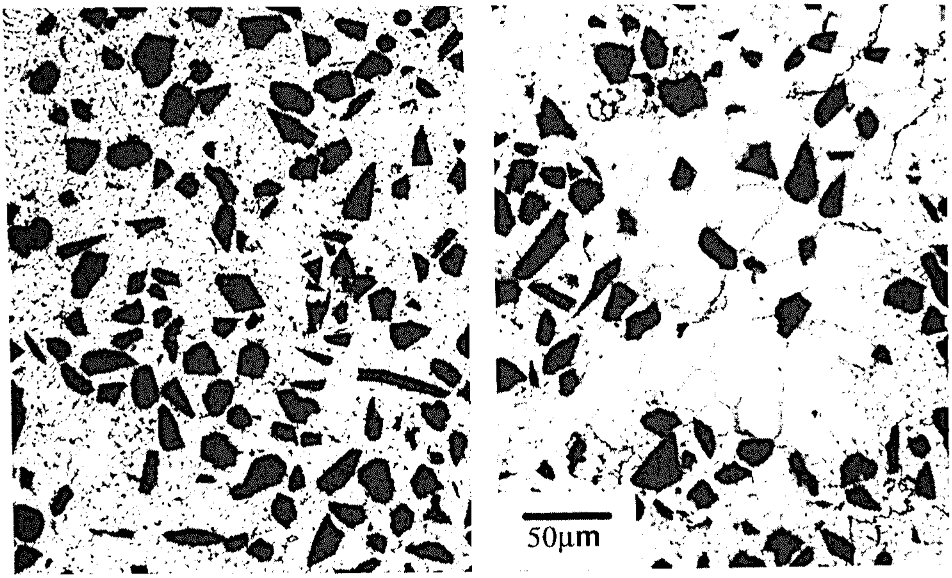
(a) (b)

(c) (d)

Figure 1: Optical micrographs at $3x10^{-2\circ}$C/s cooling rate, (a) matrix, (b) SiC composite, (c) MICRAL-20 composite and (d) $A\ell_2O_3$ composite.

On a microscope scale, there may be an effect of the reinforcement type. The eutectic Si in the SiC composite (Figure 1) is coarser than in the other materials. The SiC does have a high heat capacity compared with the matrix and compared with other reinforcement types

(1118 J/kg/°C c.f. 1080 for the matrix alloy and 780 for $A\ell_2O_3$). This, combined with the low thermal conductivity of SiC (a factor of ten lower than for the matrix alloy), may explain the coarsening of eutectic Si nucleated on the SiC.



(a) (b)

Figure 2. Optical micrograph of the composite reinforced with $A\ell_2O_3$ particles (a) quenched from 655°C (above the liquidus) (b) quenched from 617°C (below the liquidus).

Matrix Chemistry

The different liquidus and eutectic temperatures in the composites compared with the matrix alloy (Tables 1 & 2) can be accounted for, at least in part, by differences in the matrix chemistry.

The Mg in the matrix is known to react with the reinforcement phase to form a Mg containing interfacial layer (9). The extent of reaction depends on the processing conditions and reinforcement type. Based on previous experience, and for a nominal starting Mg content of 0.5wt%, the matrix Mg level in the composites is estimated to be 0.15, 0.2 and 0.3 wt% for $A\ell_2O_3$, SiC and MICRAL-20 particulate respectively. The DSC work supports these estimates : Mg_2Si precipitation reactions were observed for the matrix alloy and the composite with MICRAL-20 particulate but not in the SiC or $A\ell_2O_3$ reinforced composites, suggesting the latter had very low matrix Mg contents.

It is well established in the literature that among alloying additions in A356, Mg has a marked effect on the eutectic temperature. For example for every 0.1wt% Mg about a 1°C decrease in the eutectic temperature can be expected (5). A comparable decrease is also expected for the liquidus temperature. The different matrix Mg contents in the composites can therefore account for a 2-4°C increase of the liquidus and eutectic temperatures.

Another possible composition change is increased Ti, from dissolution of the mechanical stirrer used to prepare the composites or from reaction with the reinforcement (in the case of MICRAL-20 and $A\ell_2O_3$ particulate, which contain some Ti as an impurity). Matrix alloys with various Ti impurity levels were prepared and DSC analysis conducted to assess the possible temperature differences. Increases in the liquidus of ~3°C, with no change in the eutectic temperature, are likely for each of the composites, given the Ti impurity level expected of 0.15-0.20wt%.

A change in the Si content can also alter the liquidus temperature by about 8°C for a change of 1wt% Si (estimated from the equilibrium phase diagram). The latent heat data (Table 2) provides a way of estimating the Si content. For a shift in Si content, the proportion of eutectic will be slightly altered. Since the latent heat of silicon is almost five times that of aluminium, a very small change in the silicon content of the composites or the matrix alloy will have a marked effect on the latent heat evolved. For example, 0.5wt% increase in Si content will increase the eutectic fraction by ~5% which will result in an increase in latent heat of ~30 J/g of metal for the eutectic transformation.

In order to make an exact determination of Si content from the measured latent heats the exact volume fraction and matrix densities would be needed. An estimate can nevertheless be made from the ratio $\Delta H_p/\Delta H_e$ in Table 2. It is clear that the composite containing SiC has a higher proportion of eutectic and hence higher Si content than the other materials. A likely explanation for the increased Si is the well known reaction between SiC and molten aluminium to form aluminium carbide, thereby releasing Si. A similar effect, though less marked, is indicated in Table 2 for the composite reinforced with MICRAL-20 particulate. Presumably the mullite phase can react to release Si in this composite. It is estimated that the increased Si will act to lower the liquidus temperature by ~2°C for MICRAL-20 particulate and ~6°C for SiC reinforcement.

The net result of the chemistry changes outlined above (Mg, Ti and Si) is an expected increase in the liquidus of 0 to 7°C and an increase in the eutectic temperature of 2 to 4°C compared with the matrix alloy (increasing from SiC to MICRAL-20 to $A\ell_2O_3$). These ranges compare with the actual increases (Table 2) of 2 to 10°C and 2 to 7°C respectively. A more rigorous analysis would require the exact composition of the materials and improved knowledge of the phase diagram for the ternary alloy, in particular the effect of all minor element additions.

Conclusion

From this work the following conclusions can be made:

1. Liquidus undercooling is reduced or eliminated in A356 composites. In this particular investigation, primary α-$A\ell$ has been observed to nucleate and grow from the $A\ell_2O_3$ reinforcement particles.

2. Si nucleates on the reinforcement particles in each of the composites. The reinforcement type, in particular, the heat capacity and thermal conductivity of the reinforcement phase, has been found to influence the size and morphology of eutectic Si under the slow cooling rate conditions examined.

3. As a result of chemical reaction during processing of the composites, the matrix Si content was found to increase (for SiC and to lesser extent MICRAL-20 particulate). These changes in Si content were deduced from the proportion of primary and eutectic phases, as determined from the latent heat evolution. The increased liquidus and eutectic temperatures in the composites can be explained (in part) by changes in the levels of Si, Mg and Ti in the matrix of the composites.

4. Under very slow cooling conditions, liquidus onset and eutectic temperatures are independent of cooling rate. The reinforcement particles have a very minor influence on DAS, which is described by $DAS = A(T)^{-n}$ with $n = 0.33$ and 0.26 for the matrix alloy and composites respectively.

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