PRECIPITATION PHENOMENON IN PM SiC WHISKER AND PARTICULATE REINFORCED 2XXX Al COMPOSITES

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Abstract

The precipitation behavior of 2000 series Aluminum alloys reinforced with various volume fractions of whisker and particulate silicon carbide was investigated by means of differential scanning calorimetry (DSC). DSC thermograms showed that the precipitation sequence normally exhibited by 2XXX Al alloys is affected neither by SiC whiskers (SiC_w) nor SiC particulates (SiC_p) at different volume fractions and sizes. However, DSC kinetics analysis revealed that both GPB volume fraction and activation energy depend upon the SiC whisker volume fraction and SiC particulate size. It was found that the GPB volume fraction is reduced either by increasing SiC_w volume fraction or by increasing SiC_p size, while the GPB activation energy increased with increasing SiC_w volume fraction and with decreasing SiC_p size. These results suggest that SiC_p size and SiC_w volume fraction all influence the vacancy supersaturation in as-quenched 2XXX Al-SiC_p composites. This decrease in vacancy supersaturation is proposed to be related to (i) the increase in SiC/matrix interfacial surface area with decreasing SiC_p size and (ii) the increase in SiC/matrix interfacial surface area with increasing SiC_w volume fraction, these interfaces serving as vacancy sinks during quenching.

Introduction

The precipitation sequence in 2xxx Al alloys has been recognized to involve **supersaturated** **α (fcc) $\rightarrow$ GPB I zones $\rightarrow$ GPB II $\rightarrow$ S' $\rightarrow$ S** [1-6]. GPB I zones, which are fully coherent with the α Al_{ss}, form by vacancy aided solute diffusion and as such the rate of solute clustering is extremely sensitive to quenching conditions, notably solution treatment temperature T_s, cooling rate, dT/dt, and the temperature difference between the solution treatment and quench temperature, ΔT. Increasing T_s, dT/dt and ΔT all promote retention of a higher vacancy supersaturation and therefore increase the rate of GPB I formation [2-4]. With continued aging ordered zones, designated GPB II, develop. These remain coherent with the matrix growing in the *[100]* matrix direction. Further aging leads to formation of an orthorombic transition phase, S'. Using atomic resolution electron microscopy, Radmolvic *et al.* [6] reported that S' heterogeneously nucleates at either clusters of Mg and Cu atoms previously formed by GPB formation or at subgrain/grain boundaries, growth being observed to occur by ledge migration. Eventually S' grows until it loses coherency with the matrix and S replaces it.

Extensive investigation has shown that the mechanical performance of 2xxx alloys may be enhanced through the incorporation of hard ceramic whiskers or particulates [7,8]; moreover, influences of reinforcement on the microstructure and age hardening response of the former may be expected. Investigations of 2xxx Al-SiC have reported that the presence of ceramic whiskers in aluminum does not significantly modify the aluminum alloy aging sequence, however, the precipitation kinetics and precipitate volume fraction have been shown to be altered [9-11]. Whisker reinforcements have been shown as well to influence the aging behavior of other MMC's matrices, *e.g.*, 6xxx (Al-Mg-Si) and 7xxx (Al-Zn-Mg-Cu) [12-16]. This influence is believed to be the consequence of a heavily dislocated DRA matrix, this substructure developing during cooling from the solution heat treatment temperature, the large, approximately 10/1, difference in the coefficient of thermal expansion (CTE) between Al matrix and SiC reinforcement causing differential straining at the reinforcement and matrix interface during quenching, subsequent plastic relaxation leading to dislocation generation.

Papazian [9], using differential scanning calorimetry to investigate the age-hardening precipitation reaction in 2124 and 2219 aluminum alloy reinforced SiC whiskers (0, 8 and 20 v/o pct) composites, supports the proposal that the presence of a SiC whisker reinforcement can lead to decreased formation of **GPB** zones; however, no distinction between **GPB I** and **GPB II** was reported. The reduction of GPB zone formation was thought to be due to a reduction in the retained supersaturated vacancy concentration in the composites *vis a vis* that of the unreinforced matrix, the SiC whisker reinforcements providing addition sites for vacancy annihilation [9]. In addition, it was suggested that a finer grain size and the incorporation of oxide particles due to powder metallurgy processing also contributed to the observed changes in precipitation kinetics.

Christman and Suresh [10], investigating the aging response of a powder metallurgy 2124 Al-SiC 15 wt pct whisker composite further observed that the presence of the increase dislocation density facilitates the nucleation of intermediate strengthening precipitates S′. This in turn, reduces the time for achieving peak hardness. Transmission electron microscopy revealed that, at any aging time, S′ precipitate size was larger in the composite when compared with the unreinforced alloy. It was proposed that an increased dislocation density in the composite system accelerates **S** and **S′** precipitation, both known to nucleate heterogeneously, by increasing the number of available sites for nucleation, shortening the mean path of solute atoms and increasing the apparent solute diffusivity in the matrix [*e.g.*, 3,4].

Although the effect of reinforcement presence [9-11], volume content [9], oxide presence due to PM process [11], and matrix composition [16] on the precipitation behavior of discontinuously reinforced 2xxx aluminum alloys have been investigated, details on the influence of reinforcement volume fraction and size on the *precipitate volume fraction* and *activation energy* have not yet been reported. The objective of the present paper was therefore to identify and compare the influence of whisker volume fraction, at constant size, and particulate size, at constant volume fraction, on the precipitation behavior of 2000 series aluminum alloy reinforced with SiC.

Experimental Procedure

2124 Al ingot and 2124 Al powder metallurgy reinforced F9 SiC_w 0, 5, 10 and 20 v/o pct and

2009 Al powder metallurgy SiC_p 20 v/o pct, 4 and 29 μm, composites were investigated [13,17]. The powder metallurgy materials were fabricated by initially wet blending of pre-alloyed helium gas atomized powder. Following blending and drying, the composites where cold compacted to approximately 50 pct theoretical density and vacuum hot pressed in the mushy zone to (15.25) cm diameter billets. These billets were then homogenized in inert atmosphere for (96 hours at 668 K) and extruded to (12.7 cm wide by 1.27 cm) thick plate bars, the extrusion ratio being 11.3:1. The 2124 alloy matrix composition determined following extrusion is given in Table I.

Table I. 2124 Al-SiC_w and 2009 Al-SiC_p Matrix Chemical Composition (wt. pct)

Material	Cu	Mg	Fe	Mn	Si
2124 Ingot	4.7	1.8	0.3	0.9	-
2124 Al-SiC_w (0v/o)	4.65	1.69	0.01	0.92	-
2124 Al-SiC_w (5v/o)	3.55	1.29	0.01	-	-
2124 Al-SiC_w (10v/o)	4.56	1.55	0.27	0.9	-
2124 Al-SiC_w (20v/o)	4.7	1.34	0.07	0.9	-
2009 Al-SiC_p (4 μm, 20v/o)	3.7	1.30	0.05	-	0.18
2009 Al-SiC_p (29 μm, 20v/o)	3.4	1.37	0.05	-	0.05

The investigation of the precipitation phenomenon of the 2xxx Al-SiC composites was performed using differential scanning calorimetry. The latter were performed on DRA 3×3×0.5 mm plate samples immediately after solution heat treatment at 493°C for 1 h and water quenching. DSC results were obtained between 35°C (after an equilibrium stage) and 400°C, the DSC heating rate being 20°C/min, with a pure aluminum disc of equal mass used as the reference (one of the pans serving as reference and the other containing the composite sample). Correction of the DSC thermogram to isolate the heat effect due to reactions occurring within the composite consisted of subtracting the heat flow, in W/g, of the DSC reference, performed with high purity aluminum in both pans, from the original DSC thermograms [5]. Assuming non overlapping precipitation phenomena, the volume of precipitate may be depicted by integrating the corrected DSC curves between the initial T_i and final T_f transformation temperature, (*i.e.*, $A(T_f)$, in K×W/g), divided by the heating rate, ϕ, in K/s, which gives the *heat effect*, H, in J/g, the volume of precipitate being proportional to the heat effect per gram of sample, *i.e.*, the thermal energy per gram of sample, in J/g, taken from the surrounding to form a precipitate [18].

Kinetic analysis of low temperature aging were performed according to the method presented by Jena *et al* [5] assuming that dY/dT can be expressed as:

$$\frac{dY}{dT}=(1-Y)k_0\exp(-\frac{Q}{RT}) \quad (1)$$

where Y(T) is the fraction of precipitate, Q is the activation energy and $k'_0 = k_0/\phi$, k_0 being the frequency factor of the rate of formation dY/dt and ϕ the heating rate, with the fraction of precipitate Y(T) as a function of temperature being defined as

$$Y(T) = \frac{A(T)}{A(T_f)} \qquad (2)$$

where A(T) represents the area under the peak between T_i and T, with $T_i \leq T \leq T_f$.

dY/dT was readily obtained from Equation (2), the logarithm of $dY/dT \times \phi/(1-Y)$ being plotted as a function of $1/1000 \times T$, in K^{-1}. The analysis of this data by least square linear regression analysis gave the slope **s** and the constant **c** of the linearized curve.
Finally, the activation energy, Q, in kJ/mol and the frequency factor, k_0 in s^{-1}, were obtained as

$$Q = s \times R \qquad (3)$$

where R is the Joule constant (8.31 J/mol.K), and

$$k_0 = \phi \times \exp(c). \qquad (4)$$

Experimental Result

Corrected DSC thermograms of 2124 Al ingot and 2114 P/M reinforced with 0, 5, 10 and 20 v/o pct SiC_w, and 2009 Al reinforced with 20 v/o pct SiC_p are shown in Figures 1 and 2, respectively. Activation energies, Q, heat effects H, and frequency factors, k_o, of GPB precipitation being reported in Table II. DSC analysis provide several significant conclusions. First, the volume fraction of the GPB zones, as represented by the area underneath curve A, was significantly lower for the smaller 4 μm SiC particulate size 2009 Al composite when compared to the larger, 29 μm, reinforced composite, Figure 2. Similarly increasing SiC_w reinforcement content in 2124 Al decreased the volume fraction of GPB zones while the transition from 2124 ingot to 2124 P/M did not induce any significant change in the GPB precipitation kinetics, Figure 1 and Table II.

Second 2124 ingot, 2124 P/M unreinforced materials and 2009 Al-SiC_p, 20 v/o, 4 μm, displayed a separation of the S′ and S peaks, B1 and B2, while only a single peak, B, denoting combined precipitation of S′ and S, was detected in the 2124 Al-SiC_w, 5, 10 and 20 v/o and 2009 Al-SiC_p, 20 v/o, 29 μm composites. Moreover, the DSC thermogram showed that the volume fraction of combined S′/S precipitation in the composite reinforced with 29 μm SiC_p, as depicted by the area under curves B, was greater than that observed in 4 μm particulate reinforced composite and increasing reinforcement content in 2124 Al-SiC_w decreases the volume fraction of combined S′/S precipitation.

Finally DSC kinetic analysis, Table II, indicated that the activation energy for GPB zone formation decreased with decreasing SiC whisker volume content and increasing SiC particulate size. Similarly, the total volume of the GPB zones per gram of sample, as depicted by the heat effect [5], Table II, decreased with decreasing particulate size and increasing whisker volume content.

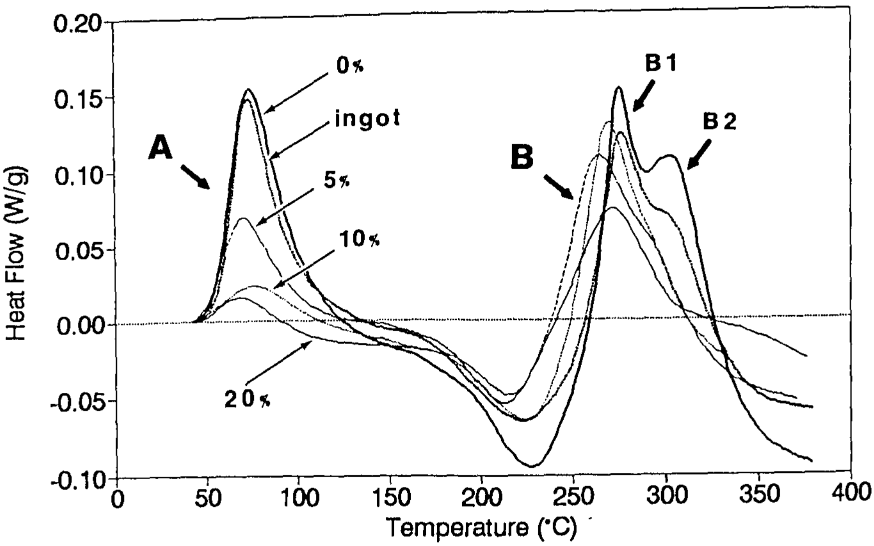

Figure 1. DSC Thermograms of 2124 Ingot and 2124 P/M Aluminum Reinforced with 0, 5, 10 and 20 v/o SiC_p, Solution Treated at 495°C for 1 Hour, Water Quenched. DSC Heating Rate: 20°C/min

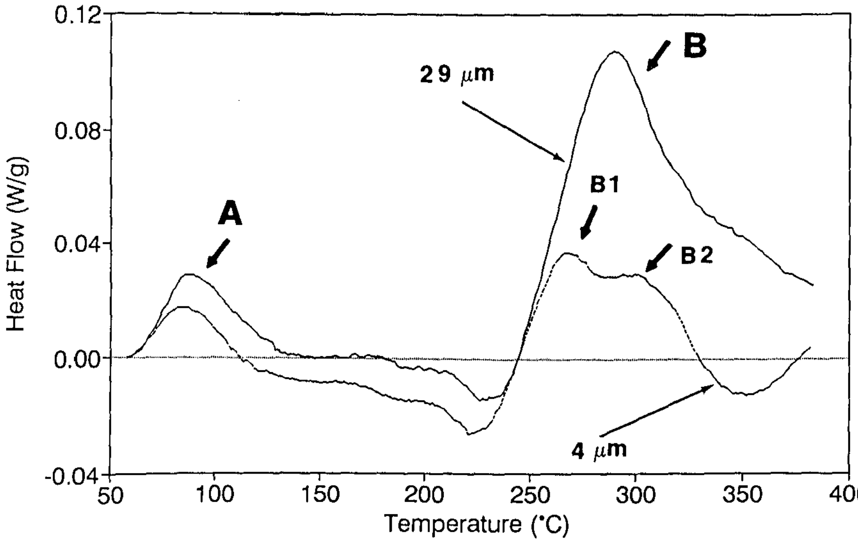

Figure 2. DSC Thermograms of 2009 Aluminum Reinforced with 20 v/o SiC_p, Particulate Sizes of 4 and 29 μm, Solution Treated at 495°C for 1 Hour, Water Quenched. DSC Heating Rate: 20°C/min

Table II. GPB Formation Kinetics Analysis of 2xxx Al-SiC Solution Treated at 495°C for 1 Hour in Inert Atmosphere and Water Quenched. DSC Heating Rate: 20°C/min

	2124 Ingot	2124 P/M	2124 5% SiC_w	2124 10% SiC_w	2124 20% SiC_w	2009 SiC_p 4μm	2009 SiC_p 29μm
Activation Energy Q (kJ/mol)	76.6	83.1	89.6	92.9	109.2	115.2	90.3
Frequency Factor k_0 (sec^{-1})	1.9×10^{12}	9.5×10^{12}	2.3×10^{14}	1.6×10^{15}	1.1×10^{18}	9.4×10^{17}	2.4×10^{14}
Heat Effect H (J/g of sample)	12.15	13.29	9.04	3.59	2.96	2.14	3.32

Discussion

The results of this investigation indicate that, in agreement with prior studies [9-16], the precipitation sequence normally exhibited by 2xxx Al alloys, *i.e.*, **Supersaturated α (fcc) → GPB I zones → GPB II → S′ → S**, is unaffected by SiC whisker volume content and particulate size. However, the latter do affect the details of the precipitation behavior.

The decrease in vacancy supersaturation associated with GPB zone reduction in 5, 10 and 20 v/o pct whisker reinforced 2124 Al-SiC and 4 μm reinforced 2009 Al-SiC_p cannot be due to powder oxide/matrix interface vacancy trapping, as suggested by Papazian [9] or Lee *et al.* [11]. Indeed GPB precipitations in unreinforced 2124 Ingot and P/M, exhibit similar activation energies and heat effects, Figure 1 and Table II. Furthermore 2009 P/M composites, all having been processed in a similar fashion while exhibiting different precipitation kinetics, support this proposition.

Similarly, Kim *et al.* [19 investigating the precipitation behavior of a Al-4 wt% Cu/ SiC whisker 5 to 15 wt pct composite, observed lowering of the θ'' (or GP II) formation, and suggested that this effect was related to the high dislocation density with the composite material. The reduction of GPB zone formation during aging in the 4 μm SiC_p reinforced 2009 Al composite cannot however be associated with this increase in dislocation density. This proposal would require that the dislocation density be a function of particulate size; however, Dutta and Bourell, using continuum mechanics and finite element analysis, have shown that for 20 v/o DRA composites reinforced with SiC particulates larger than 1 μm, the plastic zones overlap [20] and that, at a fixed reinforcement volume fraction, the amount of plastic strain, and therefore the matrix dislocation density, is <u>not</u> dependent on the reinforcement size.

The decrease in vacancy supersaturation in 5, 10 and 20 v/o pct 2124 Al-SiC_w may, however, be related to the increase in SiC/matrix interfacial surface area with increasing SiC_w volume content, these interfaces serving as vacancy sinks during quenching. At equivalent reinforcement size, the total reinforcement/matrix surface area will increase with increasing whisker v/o content. Therefore, the larger interfacial area in the higher whisker v/o content reinforced composite system should provide an increased number of vacancy sinks. The latter would decrease the vacancy supersaturation, thereby decreasing the extent of GPB nucleation. Similarly, decreasing the SiC particulate size, at constant v/o content, in the 2009 Aluminum alloys increases the total reinforcement matrix interface surface area and it is reasonable to attribute the reduction of GPB formation, commonly observed in the 2124 composites when the whisker v/o content increases, to an increased number of vacancy sink provided by the reinforcement/matrix interface.

Finally the last stage of the precipitation behavior consists, for all investigated materials, of heterogeneous nucleation of S′ and S and GPB II→S′/S transformation [5,21]. Indeed, the DSC results for the 2124 Ingot, 2124 P/M unreinforced aluminum and 4 μm SiC reinforced 2009 composite, where S′ and S peaks are separated, suggest that S′ and S are distinct phases. However the influence of reinforcement volume content and size on the precipitation of these phases needs further investigation in order to clarify, when only one peak is observed, whether S′ and S precipitate *simultaneously* or *only one phase* precipitates to the detriment of the other.

Conclusion

Differential scanning calorimetric analysis showed that both whisker volume content and particulate size and has an influence on the precipitation behavior of 2xxx aluminum alloys.

1- Decreasing of GPB zone formation during aging in the SiC_w reinforced 2124 Al suggests that SiC_w volume content influences the vacancy supersaturation in as-quenched 2124 Al-SiC_w composites. Similarly decreasing GPB zone formation during aging in the smaller (4 μm) particulate reinforced 2009 Al suggests that SiC_p size influences the vacancy supersaturation in as-quenched 2009 Al-20 v/o SiC_p composites. This decrease in vacancy supersaturation is proposed to be related to the increase in SiC/matrix interfacial surface area with increasing SiC_w v/o pct and decreasing SiC_p size, these interfaces serving as vacancy sinks during quenching.

2- The last stage of the precipitation sequence consists of heterogeneous nucleation of S′/S and GPB II→S′/S transformation, S′ and S precipitations becoming distinct when increasing SiC_w volume content or increasing SiC_p size.

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