

A QUANTITATIVE INTERPRETATION OF DSC EXPERIMENTS ON QUENCHED AND AGED SiC_p REINFORCED 8090 ALLOYS

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1 Introduction

Differential Scanning Calorimetry (DSC) is a useful technique for the study of phase transformations and has been widely applied to study precipitation in aluminium alloys, but the results are generally interpreted qualitatively. Quantitative interpretation of DSC experiments on binary and ternary aluminium-based alloys has been attempted (see Ref. 1,2,3), and can improve understanding of their thermodynamics and kinetics of precipitation.

In the present paper a quantitative interpretation of DSC heat effects occurring in 8090 alloys with and without SiC particle reinforcement is presented. Hardening of 8090 alloys (nominal composition Al-1.3wt%Cu-1wt%Mg-2.5wt%Li) is generally interpreted in terms of two precipitation sequences (4,5,6):

where δ' is a L1₂ ordered phase (Al₃Li), fully coherent with the Al matrix, and δ is the equilibrium Al-Li phase (AlLi), which forms mainly at grain boundaries (7)

ii) Cu,Mg in Al-rich phase \rightarrow GPB zones \rightarrow S' \rightarrow S

where GPB zones are Cu and Mg containing Guinier-Preston zones (8), and S' is a slightly strained semicoherent version of the incoherent S (Al₂CuMg) (see Ref. 9). Since the formation enthalpies of the two variants are the same (10), S' and S will be considered to be the same phase in this paper.

Furthermore, the icosahedral I phase (proposed composition Al₆Cu(Li,Mg)₃, see Ref. 11), forms on grain boundaries (12). Because of the multiple precipitates involved, interpretation of precipitation reactions in 8090 alloys is complex, and an understanding of the amounts of the different phases formed during ageing is important. This paper sets out to present a quantitative description of the precipitate microstructure in monolithic and reinforced 8090, with particular reference to GPB zones and δ' phase precipitates.

2 Experimental Procedures

2.1. Sheet production The alloys were produced at Structural Materials Centre, DRA Farnborough via a powder metallurgical route and rolled at 510°C to a sheet thickness of about 2.3 mm. Details of the production route are given elsewhere (10). The compositions of the matrix of the alloys are given in Table 1. The metal matrix composite (MMC) contains 20 wt% SiC particles with an average size of 3 μ m.

2.2. Heat treatment Disc-shaped DSC samples (thickness \sim 0.8 mm) were machined and punched prior to heat treatments and were solution treated in air for 0.5 hour at 530°C using a standard convection furnace. The solution treatment and all subsequent heat treatments were terminated by a direct quench into water at room temperature. For ageing treatments the samples were transferred to an oven at 170°C \pm 1.5°C within 1.5 minutes of the solution treatment. Ageing times ranged between 0.17 h (10 min) and 168 h (7 days). Reversion treatments consisting of a 5 min hold at 286°C were performed on samples aged for 7 days.

2.3. Differential Scanning Calorimetry DSC experiments were started 5 min after completion of the previous heat treatment. All runs are corrected for the baseline of the DSC and for the difference of the heat capacity of the sample and reference (10). More details of the experimental set-up and procedure are given elsewhere (10).

TABLE 1: Compositions of the matrix alloys (in weight percent).

Alloy	Li	Cu	Mg	Zr	Al
8090 monolithic	2.34	1.25	1.04	0.11	remainder
8090 MMC	2.40	1.16	0.75	0.10	remainder

3 Results

The first runs of freshly solution treated and quenched specimens of the two alloys studied are presented in Figs. 1 and 2. A total of 6 effects, marked A to F, are observed. The identification of these effects has been discussed previously (see Ref. 10) and is in line with most publications on DSC work in Al-Cu-Mg monolithic alloys and MMCs (5,13,14,15), and Al-Cu-Mg-Li monolithic alloys and MMCs (5,6,16). Effect A is most clearly observed in the monolithic 8090 alloy and is ascribed to GPB-zone formation; some evidence for this effect is observed for the MMC. Effect B in the MMC is ascribed to δ' formation. For the monolithic alloy only at heating rate 2°C/min some indications for the presence a δ' formation effect is observed. Effect C is attributed to δ' and GPB-zone dissolution. Effect D is ascribed mainly to S' precipitation, but δ and I phase formation (both form mainly at grain boundaries, see Refs. 7,12) might additionally contribute to some degree. Effect E is ascribed to the dissolution of the phases formed during effect D. The exothermic effect F is attributed to the formation of Li_2CO_3 or $\gamma-LiAlO_2$ on the surface of the samples. One day ageing at room temperature prior to DSC does not affect the DSC curves.

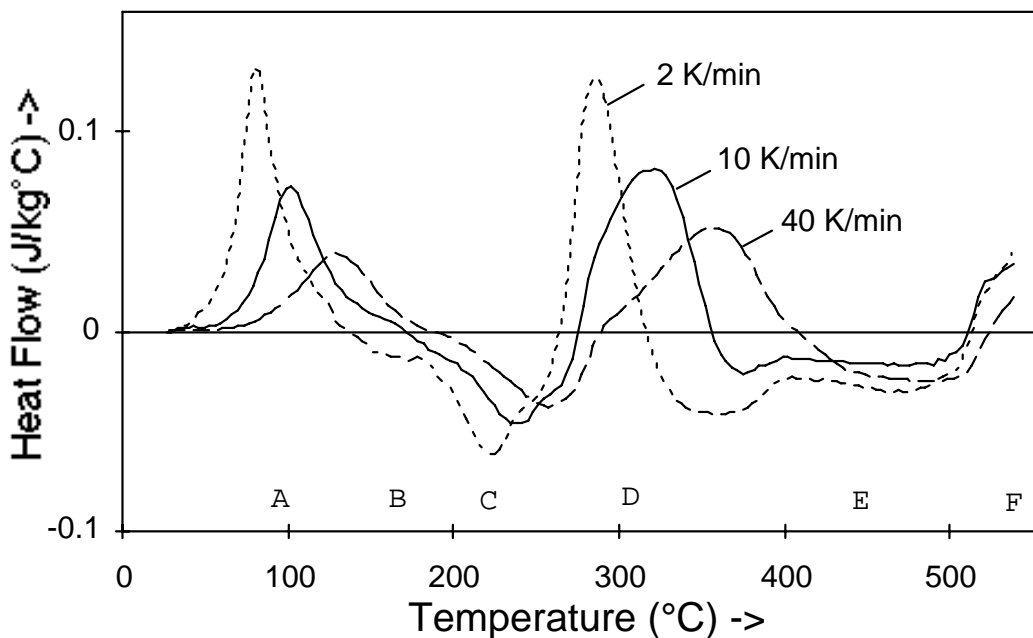


Fig. 1:

DSC curves of the solution treated and quenched monolithic 8090 alloy at varying heating rates.

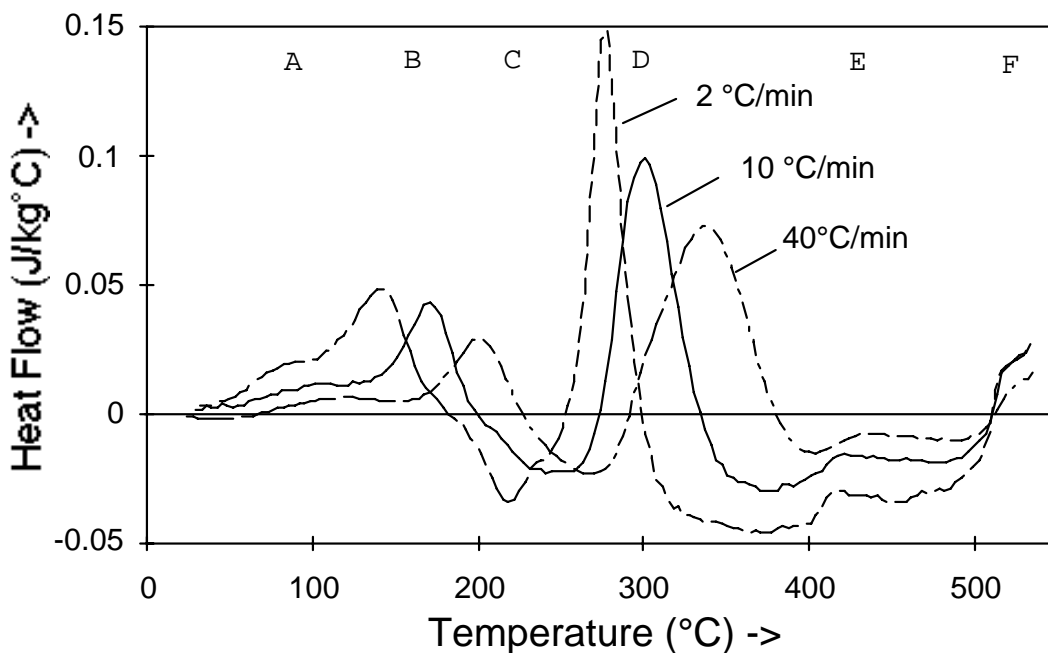


Fig. 2

DSC curves of the solution treated and quenched 8090 MMC at varying heating rates.

As precipitation and dissolution effects are thermally activated processes the heat effects observed in Figs. 1 and 2 shift to higher temperatures with increasing heating rate. From the peak temperatures of the effects the (apparent) activation energies for the precipitation reactions can be obtained using so-called Kissinger plots (17,18,19). This yields: $E_{\delta'} = 74 \pm 4$ kJ/mole, $E_{S'} = 107 \pm 4$ kJ/mole (for the 8090 MMC), and $E_{GPB} = 66 \pm 5$ kJ/mole, $E_{S'} = 122 \pm 6$ kJ/mole (for monolithic 8090). The correlation coefficients of the plots were all better than 0.995. The activation energies for GPB and S' formation in the monolithic 8090 alloy agree well with those obtained by other workers for GPB and S' formation in the monolithic 8090 alloy (6,16) and in Al-Cu-Mg alloys (13).

4 Discussion

It is apparent that some overlap occurs between effect D and the combined δ' and GPB-zone dissolution effect (effect C), but a method for obtaining a correction for this overlap can be developed. From classical reaction kinetics theory it follows that during heating at a constant rate the maximum reaction rate (i.e. the peak of the DSC heat effect) occurs at a fixed stage of the reaction, i.e. at a fixed fraction, f_p , of the total heat evolving during that reaction (17,18,19). Providing that the peak temperature of the S' precipitation effect is not influenced by overlap, it is possible to calculate the amount of overlap using the amount of heat evolved in the part of the heat effect following the peak. It is believed that f_p for the 8090 MMC is identical to that in the solution treated Al-Cu-Mg-1.5Li MMC, and this can be obtained without any interference of overlap from the curve presented in Ref. 10, resulting in $f_p = 0.69 \pm 0.01$. The values for f_p as obtained using the curves by Jena et al. for the monolithic Al-1.53wt%Cu-0.79wt%Mg increase with heating rate from about 0.44 at 5°C/min to about 0.83 at 20°C/min. This is thought to be due to: i) extensive overlap with the GPB-zone dissolution effect at 5°C/min, which would tend to underestimate f_p , and ii) a strongly reduced heat effect at 20°C, rendering the reaction kinetics theory (18,19) invalid. Hence, only the intermediate heating rates (10 and 15°C/min) at which f_p is indeed approximately constant are used, resulting in $f_p = 0.69$ (i.e. the same as for the MMC). Using this value the overlap between effects C and D is obtained.

The combined heat content of effects A, B and C in the solution treated alloys corrected for overlap, $\Delta Q_{\delta'/GPB}$, are presented in Table 2. The table shows that the $\Delta Q_{\delta'/GPB}$ values calculated at heating rates 10 and 40°C/min correspond well, giving a first indication that the overlap correction, when applied for these heating rates, is sound. $\Delta Q_{\delta'/GPB}$ averages -2.2 J/g for the 8090 monolithic alloy and -3.2 J/g for the 8090 MMC. The deviation at heating rate 2°C/min, which is especially large for the monolithic alloy, is thought to be due to extensive overlap with effect C, influencing the peak temperature of effect D. As the overlap correction is very sensitive to the determination of the peak temperature, even a small shift in the peak temperature of about 1.5°C can explain the observed deviation for the monolithic alloy.

TABLE 2 The uncorrected (ΔQ_{ABC}) and overlap-corrected ($\Delta Q_{\delta'/GPB}$) heat effects of GPB-zone and δ' -phase formation.

Heating Rate (°C/min)	f_p measured	8090 monolit		8090 MMC		
		ΔQ_{ABC} (J/g)	$\Delta Q_{\delta'/GPB}$ (J/g)	f_p measured	ΔQ_{ABC} (J/g)	$\Delta Q_{\delta'/GPB}$ (J/g)
2	0.47	3.1 ± 1.2	-6.2 ± 2.3	0.61	6.9	-4.0
10	0.62	1.2 ± 0.9	-2.4 ± 1.4	0.53	5.9	-2.9
40	0.62	0.6 ± 0.8	-2.0 ± 1.1	0.45	2.6	-3.5

From the negative values observed for $\Delta Q_{\delta'/GPB}$ it appears that during the DSC heating a low temperature phase which was present right after quenching, dissolves. This observation is consistent with TEM and high resolution TEM work on reinforced and unreinforced 8090 alloys, which show that directly after quenching a lithium-containing L12 ordered phase is present (5,20).

Using the correction for the overlap $\Delta Q_{\delta'/GPB}$ and the heat effect due to S' formation, $\Delta Q_{S'}$, are calculated from DSC curves of aged reinforced and unreinforced 8090 obtained at heating rate 10°C/min (see Ref. 10). The results are presented in Fig. 3 together with the overlap correction. In one case (marked *) where heat effect D was very much reduced (i.e. S' formation was nearing completion) the overlap correction as described above was judged to be invalid, and the overlap was approximated as the total heat content of effect D. As heat effect E is largely unaffected by ageing at 170°C, and as the freshly quenched alloys do not contain any S' (see Ref. 10), the amount of S' precipitated during ageing is thought to be proportional to the change in $\Delta Q_{S'}$.

To obtain the amounts of GPB zones, δ' phase and S' phase using the ΔQ values as presented in Fig. 3, values for the enthalpies of formation, ΔH , of these zones/phases are needed. Three methods for obtaining ΔH values are assessed in this work.

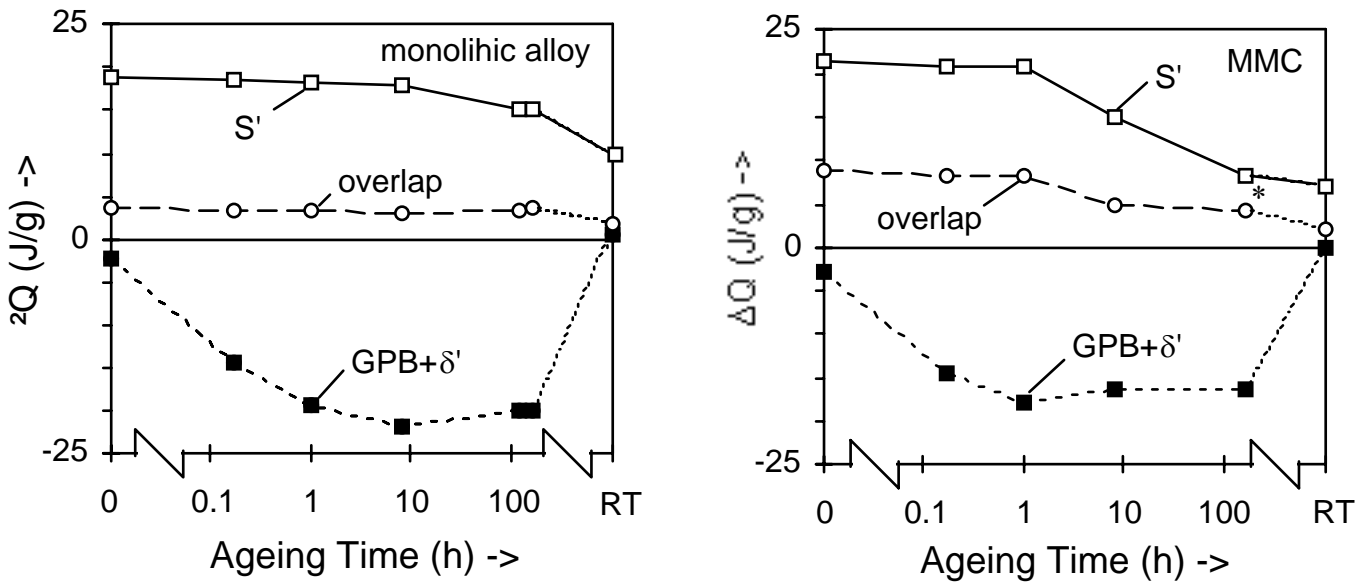


Fig. 3 a,b: Heat contents of the combined GPB-zone/ δ' phase precipitation/ dissolution effect (■) and the S' phase precipitation effect (□) corrected for overlap for the 8090 monolithic alloy and the 8090 MMC. RT = reversion treated.

One method relies on the expression for the solid solubility of element A (in atomic fraction), c_A , as obtained from a regular solution model (see Ref. 2):

$$c_A = c_0 \exp[\Delta H/k_B T] \quad (1)$$

where c_0 is a constant. By fitting solid solubility data for a certain phase with this expression, a value for ΔH can be obtained. A similar equation can be derived for phases containing two elements, A and B which form a compound $M_m A_a B_b$ (M represents the main constituent of the alloy):

$$(c_A)^a (c_B)^b = c_1 \exp[\Delta H/k_B T] \quad (2)$$

In this case ΔH represents the enthalpy of formation of one 'molecule' of $M_m A_a B_b$.

A second method for obtaining ΔH values relies on precipitation effects observed in DSC curves. It can be shown that the end of a precipitation effect should occur when the composition of the matrix around the precipitate reaches (metastable) equilibrium (1,3). If the metastable solvus of a certain precipitate is known, ΔH can be obtained from:

$$\Delta Q = \Delta H (x_{0A} - c_A) \quad (3)$$

where x_{0A} is the initial concentration of element A dissolved in the Al-rich phase.

When no data on the (metastable) solvus is available, a third method can be used to obtain a ΔH value from DSC precipitation effects. In this case data from precipitation effects at different heating rates are necessary and this data is then fitted using Eqs. 2 and 3. For example, for the relatively simple case of a quasi binary alloy (i.e. $x_{0A}=x_{0B}$) and $a=b$ it is obtained:

$$\Delta Q = \Delta H (x_{0A} - c_A) = \Delta H (x_{0A} - c_2 \exp[\Delta H/2k_B T_e]) \quad (4)$$

The latter method was applied to obtain the enthalpy of formation of GPB zones using effect A in the monolithic alloy (Fig. 1) and the enthalpy of formation of S' phase using effect D in the monolithic alloy and the MMC (Figs. 1 and 2). This results in $\Delta H_{S'} = 0.18$ J per g Cu in $S' = 18.0$ J/g (wt% Cu) $^{-1}$ and $\Delta H_{GPB} = 13.5$ J/g (wt% Cu) $^{-1}$. The graphs resulting from the fitting procedure are presented in Fig. 4. (Note that due to their slightly different Cu and Mg contents the fitted curves for the S' precipitation effects are different for the MMC and the monolithic alloy.) Applying Eq. 2 on solid solubility data of the ternary Al-Cu-Mg alloys yields a value of 12 J/g (wt% Cu) $^{-1}$ for $\Delta H_{S'}$. (Using Eq. 3, DSC work on ternary Al-Cu-Mg alloys by Jena et al. (13) and by Zahra et al. (15) yield a similar value for $\Delta H_{S'}$.) The increased $\Delta H_{S'}$ for the quaternary alloy is consistent with the reduction of the Cu and Mg solubility by the addition of Li (see Eq. 2). Two possible reasons for the increase in $\Delta H_{S'}$ with the addition of Li to Al-Cu-Mg can be envisaged. Firstly, Li might be incorporated in S' , thus lowering the free energy of the S' phase. However, no evidence for this is available and more research would be needed to check this possibility. Secondly, the increased $\Delta H_{S'}$ for the quaternary alloy could be due to an interaction of Li atoms in the Al-rich phase with either Cu or Mg atoms in the Al-rich phase, which would increase the free energy of the Al-rich phase. The strong reduction of Mg solubility in the Al-rich phase when Li is added to the Al-Mg alloy (21) suggests that such an interaction between Mg and Li atoms indeed occurs. Using Eq. 3, DSC work on ternary Al-Cu-Mg alloys by Jena et al. (13) indicate a value of about 6 J/g (wt% Cu) $^{-1}$ for ΔH_{GPB} . Again, the increased ΔH_{GPB} in 8090 may be due to incorporation of some Li in GPB zones or to an interaction of Li atoms with Cu or Mg atoms, increasing the free energy of the Al-rich phase, but no direct evidence for either is available.

As the metastable solubility of Li does not correspond with the regular solid solution model, ΔH was estimated using the second method described above. For this effect B in the MMC corrected for overlap with the small effect that occurs up to about 110°C (at 10°C/min) was used. The δ' solvus is not influenced by Cu and Mg additions (8) and obtained from literature data (see for instance Refs. 22,23). Further it was considered that the solution heat treatment will inevitably cause some Li loss at the surface of the samples. The depth at which the maximum amount of δ' precipitation is halved, $d_{0,5}$, is estimated from the diffusion coefficient of Li at the solution treatment temperature ($\sim 3.8 \cdot 10^{-9} \text{ m}^2/\text{s}$, see Ref. 24) and the δ' solvus, yielding $d_{0,5} = 52 \mu\text{m}$ for ageing at 170°C. Hence the effective volume in which δ' precipitates form is reduced by about 13% due to Li depletion. This correction is used throughout the present work. The graphs resulting from the fitting procedure are presented in Fig. 4 and $\Delta H_{\delta'} = 20.5 \text{ J/g (wt\% Li)}^{-1}$ is obtained. From δ' dissolution effects in published DSC curves of quenched Al-Li alloys (25,26) $\Delta H_{\delta'}$ for monolithic Al-Li is estimated at $\sim 18 \text{ J/g (wt\% Li)}^{-1}$.

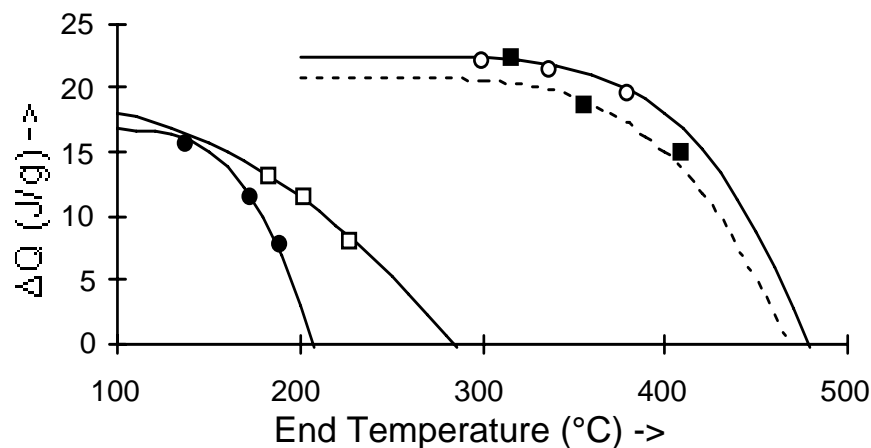


Fig. 4 Total evolved heat (ΔQ) as a function of the end temperature of the DSC heat effect for GPB- zone formation in the monolithic alloy (●), δ' formation in the MMC (□) and S' formation in monolithic alloy (○) and MMC (■). The curves represent fits obtained (see text).

To be able to separate the contributions of GPB-zone dissolution and δ' dissolution to $\Delta Q_{\delta'}/\text{GPB}$, the ageing time, t , (at temperature T_i) required to reach the same state of the reaction as obtained by heating at a constant rate Φ to temperature T_n , is obtained from (see Ref. 10):

$$t \cong \frac{T_n^2}{\Phi} \frac{k_B}{E} \frac{k(T_n)}{k(T_i)} \quad (5)$$

where E is the activation energy of the reaction, k_B is Boltzmann's constant and $k(T) = \exp(-E/k_B T)$. Application of Eq. 5 to the GPB-zone formation effect in monolithic 8090 (Fig. 1) and the δ' formation effect in the 8090 MMC (Fig. 2) indicates that: i) for monolithic 8090 GPB-zone formation is completed within ~ 2.5 min at 170°C, and ii) for the 8090 MMC δ' formation is

completed within ~ 10 min at 170°C. Using these two observations in conjunction with the ΔH values and the correction procedures described above, whilst further assuming that the maximum amount of δ' formed is given by the metastable solvus of δ' (1.6wt% at 170°C, see Refs. 8,22,23), the amounts of zones/phases formed can now be calculated from the data in Fig. 3. The results are shown in Fig. 5.

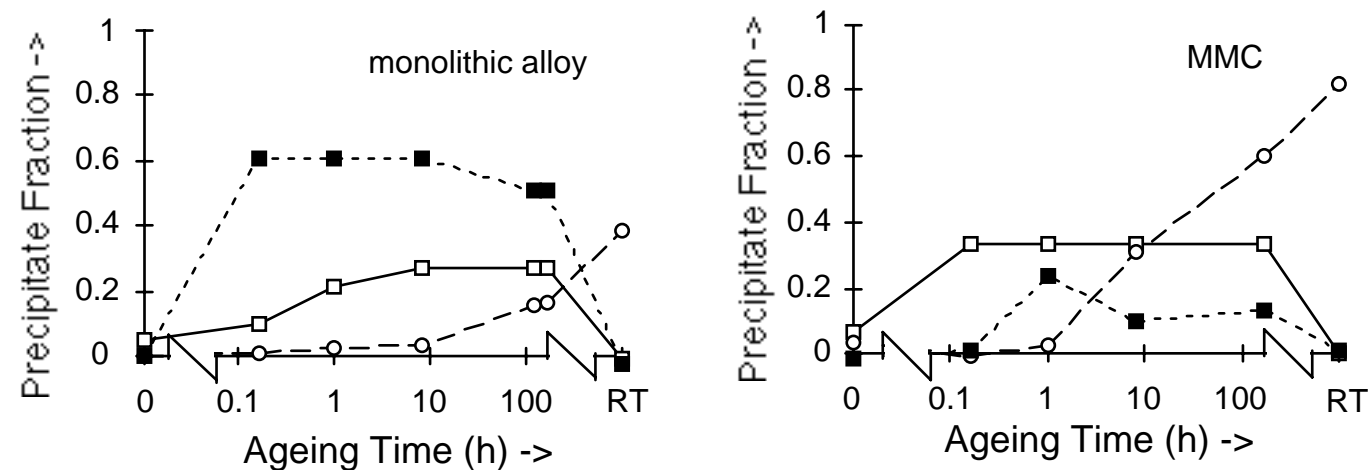


Fig. 5 a,b: Amounts of GPB zones (n), δ' (□) and S' (○) phase in the 8090 monolithic alloy and the 8090 MMC expressed as a fraction of the gross contents of the main constituent (Li or Cu) present in the zones/phases. RT = reversion treated.

Fig. 5 shows that very little S' is formed in the monolithic alloy, whilst SiC addition greatly enhances S' formation. This has been noted in other publications (see e.g. 5,10,14) and hence corroborates the assumptions made in the present work. Further support of these assumptions is obtained from the following observations: i) the sum of the copper fractions incorporated in GPB zone and S' phase is always between 0 and 1, and ii) a reversion treatment at 286°C (above the solvi of GPB zones and δ') reduces the GPB zone and δ' phase content to zero. Further, Eq. 5 indicates that the temperature range of the small δ' formation effect in DSC run at 2°C/min for the monolithic 8090 alloy should correspond to a time range of ~ 10 to 60 min for isothermal ageing at 170°C. This is indeed observed (Fig. 5a).

Apart from observations corroborating other work on monolithic 8090 alloys and 8090 MMCs a number of new observations concerning the thermodynamics and the precipitation kinetics in these alloys can be made. Firstly, Fig. 5 shows that S' phase forms at the expense of GPB-zones and that significant amounts of GPB zones are formed in the monolithic alloy, whilst the addition of SiC particles inhibits their formation. Fig. 4 in conjunction with Eq. 2 defines the metastable solvus of GPB zones and of S'. The maximum amount of GPB zones formed in the monolithic alloy during ageing at 170°C (~60% of the copper is incorporated in GPB, see Fig. 5a) corresponds closely to the metastable solvus in Fig. 4, whilst their stability limit (~205°C) corresponds with a maximum in the endothermic heat flow in the DSC curve at heating rate 2°C/min of the quenched monolithic alloy (Fig. 1). These observations support the metastable solvus of GPB zones as given in Fig. 4. Also the stability limit of S' phase as obtained from Fig. 4 (~475°C) is close to a maximum of the endothermic flow in the DSC curves (~485°C).

5. Conclusions

DSC curves of the quenched monolithic 8090 alloy and the 8090 MMC have been used to obtain values for the heats of formation of GPB zones, δ' and S' phase. Using these ΔH values and a correction for overlap of effects, the DSC curves of the aged alloys have been interpreted in terms of amounts of precipitates present. The presented interpretations are consistent with previous microstructural investigations. The solvus of GPB zones and of S' phase in 8090 alloys has been obtained. Significant amounts of GPB zones are formed in the monolithic alloy, whilst the addition of SiC particles greatly reduces the amount of GPB zones formed.

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