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Low-temperature interface reaction in aluminium–silicon carbide particulate composites produced by mechanical alloying

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An experimental investigation has been carried out on the reaction that takes place between 3 and 20 μm SiC particles and the aluminium alloy 1050 matrix of composite materials prepared by a mechanical alloying process. The work is different from that undertaken by other researchers in that the SiC–Al interface reaction has been studied in the temperature range 853–933 K, i.e., with the matrix initially in the solid state. Differential thermal analysis, X-ray diffraction and scanning electron microscopy all show that the SiC–Al reaction initiates in the solid state at temperatures as low as 883 K. The reaction produces Al_4C_3 and Si, the latter entering into solid solution in the aluminium matrix. At temperatures exceeding 903 K, the reaction produces a liquid phase and at this stage the speed of the interface reaction increases significantly. The results are discussed in terms of Al–Si–C metastable equilibrium and the kinetics of the reaction.

1. Introduction

Metal matrix composite systems based on aluminium alloy matrices containing SiC particles have been extensively studied on account of their high strength and stiffness. This type of composite can be fabricated by various techniques including liquid or semisolid casting, powder metallurgy and mechanical alloying. Where there is extended high-temperature contact between the matrix alloy and the SiC particles, chemical reaction can take place at the SiC–Al interface which, if excessive, can impair ductility and lower the strength of the composite.

The nature of the interface reaction between SiC and liquid aluminium has been widely studied [1–7] and at temperatures of 923–1272 K it is generally agreed that the reaction can be represented by

$$3\text{SiC} + 4\text{Al} \rightarrow \text{Al}_4\text{C}_3 + 3\text{Si} \qquad (1)$$

For the free-energy change of the reaction to be negative, the silicon produced by the reaction must dissolve in the liquid aluminium in order to reduce its activity [2]. The Al_4C_3 is largely insoluble in the liquid aluminium and it is present as second-phase crystals at or near SiC–Al interfaces. The products of the reaction are therefore Al_4C_3 and an Al–Si liquid phase which also contains a very small concentration of carbon. Viala *et al.* [4] have proposed a metastable Al–Si–C phase diagram to describe the reaction and a liquidus projection of the aluminium-rich region of the diagram is given in Fig. 1. Two invariant transformations are represented on the diagram. At 849 K there is a eutectic reaction

$$\alpha_{\text{Al}}(\text{solid}) + \text{Si}(\text{solid}) + \text{SiC}(\text{solid}) \rightleftharpoons \text{liquid} \qquad (2)$$

The carbon content of the liquid is very small, the silicon concentration is similar to that of the binary α_{Al}-Si eutectic (about 12 at %) and the transformation temperature is almost the same as that of the binary α_{Al}-Si eutectic (850 K). For the calorimetry data to be discussed in the present paper it is therefore justifiable to treat the ternary eutectic as being indistinguishable from the binary α_{Al}-Si eutectic.

The other invariant reaction on the phase diagram is a quasiperitectic transformation taking place at 923 K as follows:

$$\alpha_{\text{Al}}(\text{solid}) + \text{SiC}(\text{solid}) \rightleftharpoons \text{Al}_4\text{C}_3(\text{solid}) + \text{liquid} \qquad (3)$$

The liquid phase contains 1.5 ± 0.4 at % Si and a small amount of carbon.

Heating a mixture of SiC and pure aluminium at temperatures below 923 K is claimed not to produce any reaction, i.e., the two phases are in thermodynamic equilibrium. At temperatures above 923 K, a reaction occurs, producing a three-phase monovariant equilibrium between SiC, Al_4C_3 and an Al–Si–C liquid phase [4].

The SiC–Al interface reaction has been widely studied with the aluminium in the liquid form since this simulates processing routes involving liquid or semiliquid aluminium alloys. Little or no work has been reported about the reaction when the aluminium

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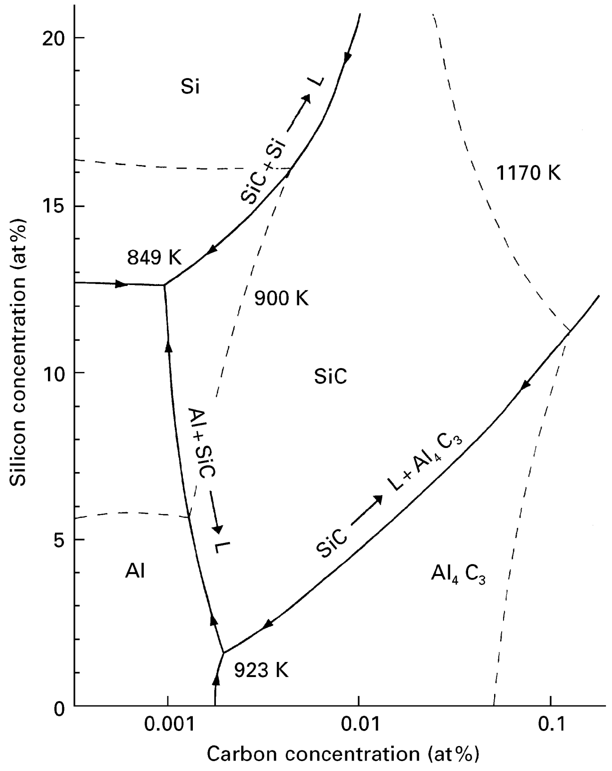

Figure 1 Metastable phase diagram of the Al–Si–C system [4].

is in the solid state, other than to say that it does not occur below 923 K. This lack of attention is probably because processing in the solid state does not usually involve long-term contact between aluminium and SiC in the temperature range 873–923 K. However, to further the understanding of the general nature of the SiC–Al interface reaction, it is relevant to examine whether this reaction can take place when the aluminium is in the solid form. To this end, the present work has investigated the SiC–Al reaction at temperatures around 900 K where, at least initially, the aluminium matrix is in the solid state. The composites that have been employed to study the reaction have been prepared both by mechanical mixing and by mechanical alloying processes. The emphasis of the work has been on the latter type of material where the SiC and the aluminium matrix will be in intimate contact.

2. Experimental procedure

The main body of results have been obtained on powder-formed aluminium alloy 1050 containing 0 or 17 vol% of 3 and 20 μm SiC particles. The SiC was manufactured by Elektroschmelzwerk Kempten GmbH with an α hexagonal structure and density of 3200 kg m^{-3}. The composites, together with the composition of the alloy 1050 material used in the investigation, are given in Tables I and II, respectively. Note that all chemical compositions in this paper are expressed in at%. Two production routes were used; mechanical mixing–pressing of the aluminium powder–SiC particles, and high-shear mechanical alloying followed by scanning, vacuum degassing and hot isostatic pressing. The mechanical alloyed material was finished by hot rolling to sheet 2.6 mm thick at 748 K to produce grain sizes in the range 5–100 μm. Microexamination of all materials showed that an even distribution of SiC particles had been achieved.

X-ray diffraction (XRD) determinations were carried out on a Siemens D500 diffractometer using Cu Kα radiation and employing a step size of 0.005° and a dwell time of 5 s. Integrated intensity measurements were taken from the following reflections: SiC (1 0 1), SiC (1 0 2), SiC (1 0 4), Si (1 1 1), Si (2 2 0), Al$_4$C$_3$ (1 0 1), Al$_4$C$_3$ (0 1 2) and Al$_4$C$_3$ (1 0 7). The extent of the interface reaction was measured by comparison with appropriate mixes of Al–Si and Al–Si–SiC powders.

Calorimetric evaluation using differential thermal analysis (DTA) was undertaken on a DuPont 901 instrument over the range 300–973 K at a heating rate of 20 K min^{-1}. Samples were of mass 6–8 mg and contained in graphite pans. Prior investigation had shown that no detectable reaction took place between the aluminium sample and the graphite pan with the time and temperature conditions used for the investigation. Dried high-purity argon gas was continuously passed through the analyser cell to minimize oxidation of the samples.

3. Results and discussion

3.1 Cast Al–Si alloys

When aluminium and SiC react in the composites, one of the products of reaction is silicon which has to dissolve in the aluminium matrix in order for the reaction to proceed. Carbon will also pass into the aluminium matrix but the amount of dissolved carbon is extremely small, just a few parts per million [4]. Consequently, an effective way of monitoring the reaction is to determine the extent to which silicon has entered the aluminium matrix by measuring the DTA characteristics of the reacted composite. The first step of the investigation was therefore to prepare a series of cast Al–Si alloys containing 1.0, 1.9, 6.2 and 12.0 at%

TABLE I Alloy types and particle reinforcement parameters

Alloy code	Particle fraction (vol%)	Particle size (μm)	Production route
MM 1050	0	—	Mechanically mixed (without the addition of SiC particles)
MM 17–3	17.1	3	Mechanically mixed
MA 1050	0	—	Mechanically alloyed (without the addition of SiC particles)
MA 2.5–3	2.5	3	Mechanically alloyed
MA 17–3	17.2	3	Mechanically alloyed
MA 17–20	17.5	20	Mechanically alloyed

TABLE II Composition of the aluminium alloy 1050 powder

Element	Al	Si	Fe	Cu	Mn	Mg	Ti	Zn
Amount (at%)	> 99.8	0.05	0.06	0.001	0.002	0.001	0.002	<0.001

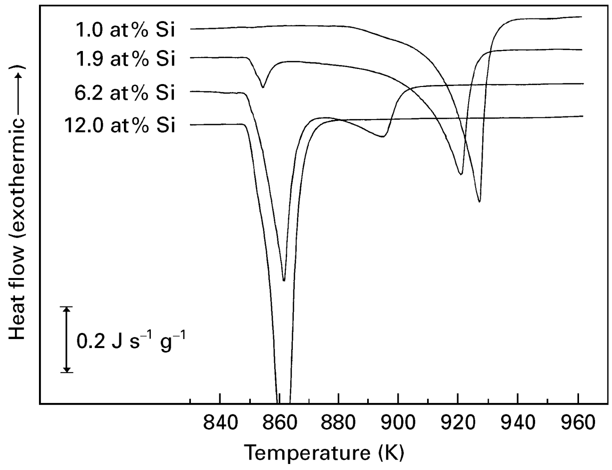

Figure 2 DTA thermograms of cast Al–Si alloys containing 1–12 at% Si.

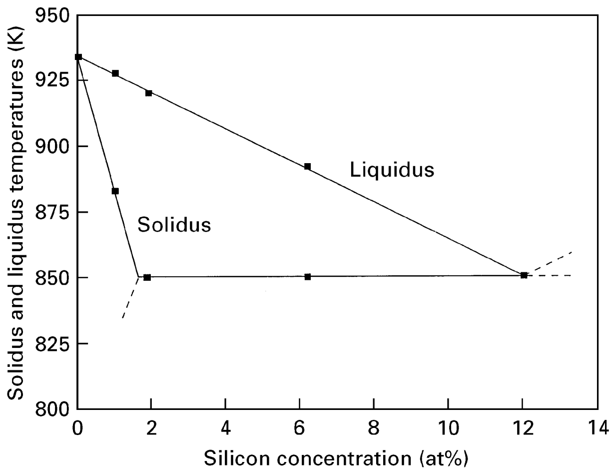

Figure 3 Liquidus and solidus temperatures of the cast Al–Si alloys as determined from the DTA data.

Si and to determine their solidus, liquidus and melting enthalpy characteristics. These data were then used to interpret the thermograms from the composite materials. Fig. 2 shows typical DTA plots for cast and annealed Al–Si alloys. The endotherm commencing at 850 K is the result of α_{Al}-Si eutectic melting and the higher-temperature endotherm is caused by melting of primary α_{Al}.

Fig. 3 presents the solidus and liquidus temperatures for the Al–Si alloys and the data are in excellent agreement with those predicted from the equilibrium Al–Si phase diagram.

3.2. Mechanically mixed 17–3 material

To provide a basis for comparison with the mechanically alloyed materials, mechanically mixed Al–SiC composites have been examined. The data for these mechanically mixed materials are presented first because they have been prepared in a manner similar to the composites used by other researchers to investigate the Al–SiC interface reaction at temperatures of 933 K or above, i.e., when the aluminium is liquid.

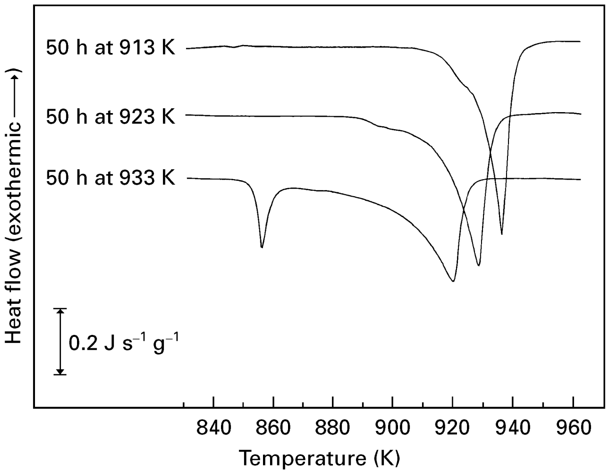

Figure 4 DTA thermograms of MM 17–3 composite after holding at various temperatures in the range 913–933 K.

Fig. 4 shows typical DTA thermograms on mechanically mixed 17–3 material after holding for 50 h at 913, 923 and 933 K. After holding for 50 h at 933 K, i.e., with the aluminium just molten, the subsequent DTA analysis shows a sharp endotherm commencing at 850 K followed by a second endotherm peaking at 918 K. This is entirely in agreement with previously published work [3, 4, 7, 8] where similar composites have been held for shorter times at higher temperatures. The molten aluminium reacts with the SiC particles, producing Al_4C_3 and Si, with the latter entering into liquid solution to produce an Al–Si liquid phase (reaction 1). On cooling from the holding temperature (933 K) the liquid matrix transforms to primary α_{Al} and solid α_{Al}-Si eutectic. Subsequent heating in the DTA run then produces melting of the eutectic at 850 K (invariant reaction) and melting of the α_{Al} at a higher temperature (monovariant reaction).

This reaction of SiC with liquid aluminium is well documented in the literature. The present work differs in that it has investigated the effect of holding the Al–SiC composite at temperatures below 933 K, i.e., with the aluminium matrix initially in the solid state. Fig. 4 shows that holding the mechanically mixed Al–SiC composite for 50 h in the range 913–923 K caused significant changes in the DTA thermogram. The changes in the thermogram took the form of an early onset of DTA melting and a progressive displacement of the liquidus peak to lower temperatures. Such changes can be used to calculate the silicon concentration that results from reaction between SiC particles and the aluminium matrix. The calculation can be undertaken using the solidus temperature, the liquidus temperature, or the temperature difference between the liquidus and solidus, and comparing the values with those of the cast Al–Si alloys shown in Fig. 3. The solidus temperature would not normally be used for this purpose because it is less well defined than that of the liquidus, since during heating the initial melting event causes only a small deviation from the DTA baseline. Nevertheless, in the present work, where eutectic melting was absent, it was felt preferable to use the solidus temperature as a measure of the silicon concentration in the matrix. This was because, once the matrix had become molten during DTA heating, there was the possibility of further reaction between SiC particles and molten aluminium, and this would then affect the liquidus temperature. Where eutectic melting was present during DTA heating, the method of calculation of the silicon concentration had to be either from the temperature difference between liquidus and solidus, or from the melting enthalpy of the eutectic reaction.

Holding at 923 K for 50 h resulted in an onset of DTA melting at 888 K. This demonstrates that, although the aluminium matrix was solid at the start of the hold period, it must have become partially liquid before 50 h had elapsed. This is consistent with the results of Viala *et al.* [4] which predict the quasiperitectic reaction (3) to be taking place at 923 K, thus producing the liquid phase. Calculation of the silicon concentration in the matrix using the data in Fig. 3 gives a value of 0.9 at % (Table III) which is just outside the range quoted for the quasiperitectic reaction, i.e., 1.5 ± 0.4 at % Si.

Holding at 913 K for 50 h produced a thermogram that showed DTA melting to commence at 913 K, indicating that the matrix remained solid during the hold period. The silicon concentration in the matrix after this period calculates to be 0.4 at % (Table III) which corresponds to the maximum amount that the solid solution can attain at 913 K. Once this value is reached, the interface reaction will stop (in the solid state) because no more silicon can be accommodated.

XRD determinations confirmed these results. Elemental Si phase was present only after holding at 933 K; at lower temperatures the Si phase was absent but small amounts of Al_4C_3 could still be detected. The XRD results will be dealt with in greater depth when the mechanically alloyed materials are considered in Section 3.3.

The silicon concentrations in the matrix have been converted to the fraction of SiC consumed by the interface reaction. This has been done by calculating the number of silicon atoms that had dissolved in the aluminium and dividing this by the total number of silicon atoms contained in the SiC particles. The resulting fractions are shown in Table III where it can be seen that for holding at low temperatures the fraction of SiC consumed by the reaction is very small, approximately 0.03 after a hold time of 50 h at 913 K.

TABLE III Transformation temperatures and matrix silicon concentration of mechanically mixed 17–3 material

Holding conditions	Solidus temperature (°C)	Si concentration (at %)	Fraction of SiC reacted
Held for 50 h at 913 K	913	0.40	0.034
Held for 50 h at 923 K	888	0.86	0.075
Held for 50 h at 933 K	70[a]	1.92	0.166

[a] Difference between liquidus and solidus temperatures.

A final point to note from the DTA thermograms is the presence of an additional thermal event that occurred as a small inflection on the low temperature side of the major melting peak, for holding temperatures of 913 and 923 K. This thermal event will be considered in a later section.

3.3. Mechanically alloyed 17–20 Al–SiC composite

XRD analysis has been carried out for material in the as-manufactured condition and after holding for 50 h at temperatures of 883, 898, 903 and 913 K. All these hold temperatures were below the solidus temperature of the as-manufactured material, which was measured as 930 K. Any reaction detected between the SiC and the aluminium in these mechanically alloyed materials will therefore have commenced in the solid state. Fig. 5 shows typical XRD traces obtained after use of various holding temperatures and these traces show that, after 50 h at 903 K, Al_4C_3 is produced but there is no separate silicon phase. After 50 h at 913 K, both elemental Si and Al_4C_3 phases are present in the XRD trace. The concentration of silicon in the matrix after holding at 913 K was calculated using XRD calibration data from the Al–Si–SiC mixes and found to be 1.9 at % Si.

To test whether silicon was present in solid solution in the aluminium after hold temperatures lower than 913 K the lattice parameter of the matrix was carefully measured from the positions of the aluminium diffraction peaks. In the as-manufactured composite, the lattice parameter was measured as 0.404 98 nm and this decreased to 0.404 85 nm after holding at 903 K. The lattice parameter of aluminium is known to decrease by 0.000 18 nm per at% silicon in solid solution [9]. Since the Al_4C_3 phase is insoluble in aluminium, this relationship can be used to calculate the concentration of silicon in solid solution in the matrix of the composite. Holding the MA 17–20 material for 50 h at 903 K produced a silicon concentration of 0.72 at % in the matrix aluminium, i.e., within the limit of solid solubility of silicon in aluminium (1.6 at % Si).

DTA measurements on the MA 17–20 mechanically alloyed material produced thermograms similar to those from mechanically mixed materials but with the changes in the thermograms occurring after lower holding temperatures (Fig. 6). This, of course, meant that the interface reaction had occurred at lower temperatures in the MA 17–20 material.

Again, the information given in Fig. 3 can be used to calculate the concentration of silicon in the matrix that had resulted from the interface reaction (Table IV). Holding temperatures of 883–903 K produced silicon concentrations that did not exceed the Al–Si solidus concentration at a given holding temperature, which meant that at these temperatures the composite had remained in the solid state throughout the 50 h holding period. The results are also consistent with those from XRD where no separate Si phase was detected.

At a holding temperature of 913 K the DTA thermogram showed the presence of a sharp endotherm at

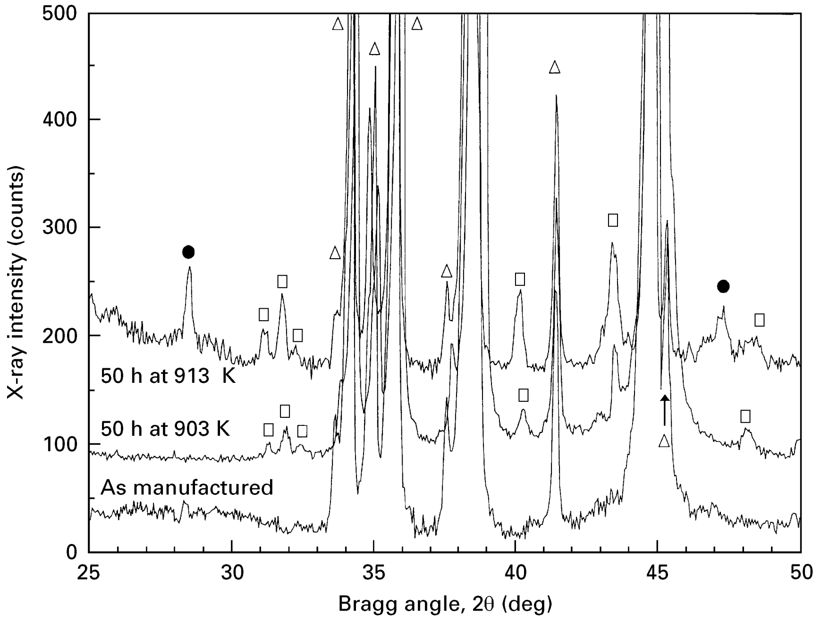

Figure 5 XRD spectra of MA 17–20 composite after holding at temperatures of 903 and 913 K. (●) Si; (□) Al_4C_3; (△) SiC.

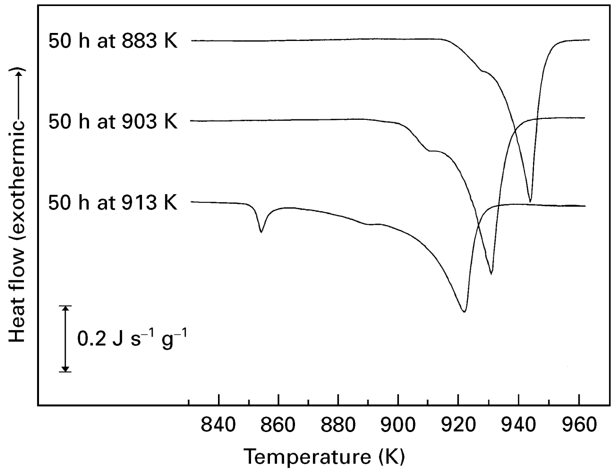

Figure 6 DTA thermograms of MA 17–20 composite after holding at various temperatures in the range 883–913 K.

850 K caused by melting of α_{Al}-Si eutectic which must have been present in the composite after holding for 50 h at 913 K. Small regions of this eutectic were just visible in the composite by scanning electron microscopy (SEM) together with crystals of Al_4C_3 (Fig. 7). This means that the matrix became molten during the hold at 913 K and is probably the result of the quasiperitectic reaction 3 referred to earlier, which in the MA 17–20 material was able to occur at a temperature lower than 923 K. This would mean that the true thermodynamic temperature of this invariant reaction lies somewhere in the range 903–913 K, the previously reported [4] higher value of 923 K being the result of very slow reaction kinetics in mechanically mixed materials.

TABLE IV Transformation temperatures and matrix silicon concentration of mechanically alloyed 17–20 material

Holding conditions	Solidus temperature (°C)	Si concentration (at %)	Fraction of SiC reacted
Held for 50 h at 883 K	916	0.31	0.026
Held for 50 h at 898 K	907	0.48	0.041
Held for 50 h at 903 K	901	0.60	0.050
Held for 50 h at 913 K	71[a]	1.82	0.154

[a] Difference between liquidus and solidus temperatures.

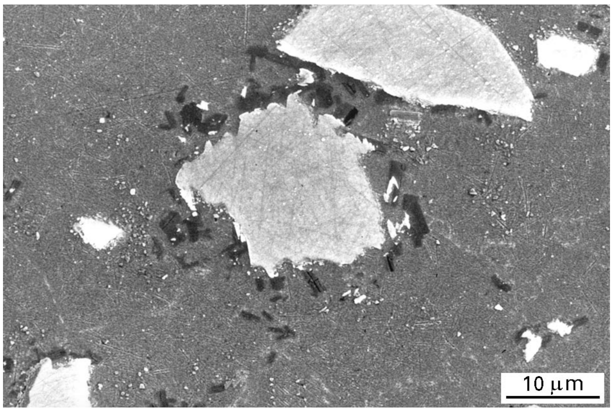

Figure 7 Scanning electron micrograph of MA 17–20 composite after 50 h at 913 K.

The average silicon concentration in the matrix after holding at 913 K was calculated from the data in Fig. 3 and found to be 1.8 at % (Table IV). The silicon content was also calculated by comparing the enthalpy, ΔH, of the eutectic reaction with that from binary Al–Si alloys; this produced a value of 1.7 at % Si. The XRD determination gave a value of 1.9 at % Si.

3.4. Mechanically alloyed 17–3 Al–SiC composite

XRD analysis again showed that the reaction between SiC and aluminium had taken place in the composite and, compared with both MA 17–20 and MM 17–3 materials, the extent of reaction was greater at any given temperature (Fig. 8 and Table V). Calorimetric

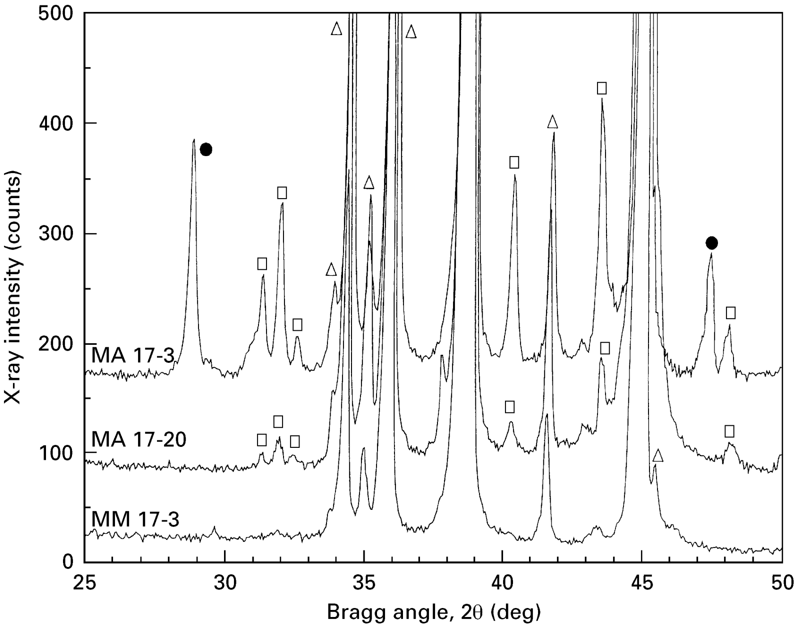

Figure 8 XRD spectra of the three different composites after holding for 50 h at 903 K. (●) Si; (□) Al_4C_3; (△) SiC.

TABLE V Silicon concentrations in various composite materials held for 50 h at 903 K as measured by XRD

Composite material	MM 17–3	MA 17–20	MA 17–3
Si (at %)	< 0.50[a]	0.72[a]	5.8[b]

[a] Lattice parameter measurements.
[b] Al–Si–SiC calibration.

analysis on the MA 17–3 material supported the XRD results. Fig. 9 shows typical DTA thermograms after holding for 50 h at 883 and 903 K. Calculation of the average silicon concentration in the matrix as a result of the interface reaction can again be obtained from the DTA data; the values are given in Table VI. These silicon concentrations indicate that the composite had remained in the solid state for holding temperatures of 853–893 K. However, at a hold temperature of 903 K the silicon concentration indicates that the matrix had been molten during the holding treatment and this had allowed the interface reaction to progress to the stage where 44% of the SiC particles were consumed. This produced a silicon concentration in the matrix of 5.1 at % which should be compared with a value of 5.4 at % Si if the calculation is based on the enthalpy of eutectic melting. These results are supported by XRD and SEM observations; silicon particles were detected only after holding at temperatures of 903 K or above. The micrograph in Fig. 10 of MA 17–3 held for 50 h at 903 K clearly shows the eutectic structure, the extent of which is much higher than that in MA 17–20 held for 50 h at 913 K (Fig. 7).

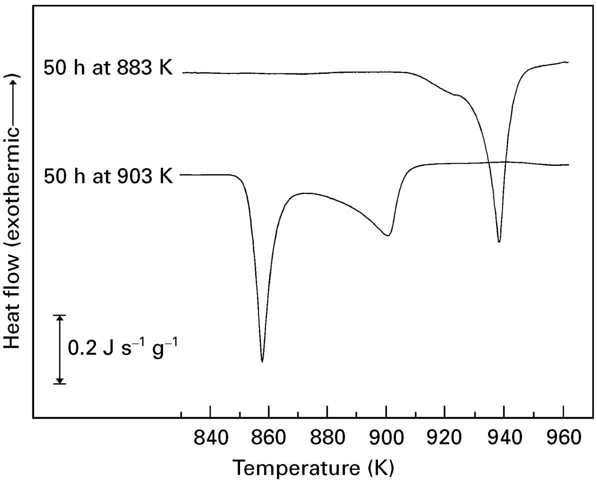

Figure 9 DTA thermograms of MA 17–3 composite after holding at various temperatures in the range 883–903 K.

TABLE VI Transformation temperatures and matrix silicon concentration of mechanically alloyed 17–3 material

Holding conditions	Solidus temperature (°C)	Si concentration (at %)	Fraction of SiC reacted
Held for 50 h at 853 K	923	0.20	0.017
Held for 50 h at 883 K	910	0.43	0.037
Held for 50 h at 893 K	898	0.60	0.052
Held for 50 h at 903 K	47[a]	5.12	0.441

[a] Difference between liquidus and solidus temperatures.

3.5. Kinetics of the SiC–Al interface reaction

Previous sections have dealt with the SiC–Al interface reaction in composite materials held for 50 h at a range of temperatures. An intermediate temperature of 903 K was selected from this range which was high enough to produce appreciable interface reaction but still 30 K below the melting point of the aluminium matrix. The MA 17–3 material was then held for 1–50 h at this temperature. XRD analysis showed that a holding time as little as 10 h was sufficient to produce some interface reaction, i.e., diffraction peaks from both Si and Al_4C_3 phases were present in the XRD spectrum. Extending the holding time produced

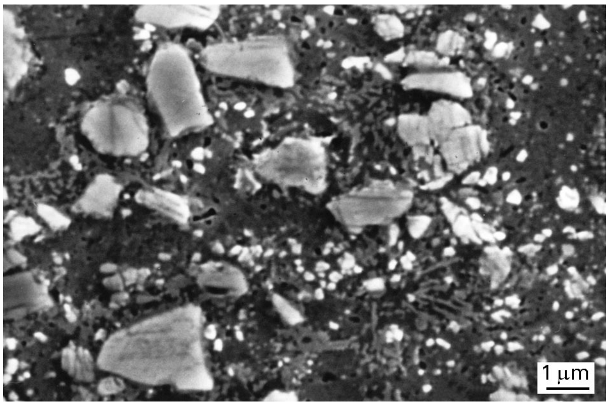

Figure 10 Scanning electron micrograph of MA 17–3 composite after 50 h at 903 K.

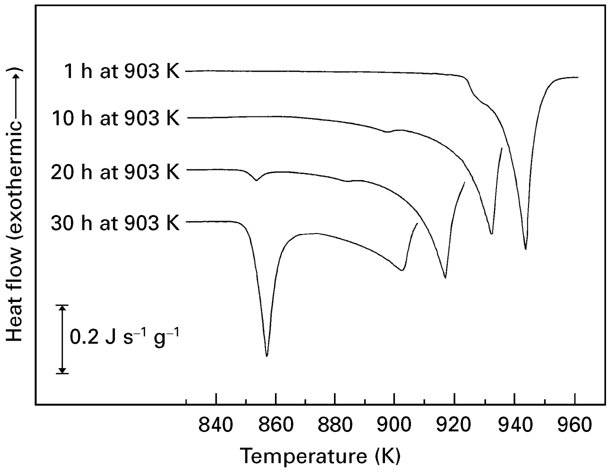

Figure 11 DTA thermograms of MA 17–3 composite after holding at different times at 903 K.

an increasing amount of reaction. A more detailed analysis using DTA confirmed these results (Fig. 11). Silicon concentrations have been calculated from the DTA data and converted to the fraction of SiC consumed by the interface reaction; the latter are plotted as a function of time in Fig. 12. The plot shows approximately linear reaction kinetics for a holding time of up to 30 h which corresponds to 4.2 at % Si in the matrix.

Beyond 30 h the rate of interface reaction decreased and this is likely to be the result of the high silicon concentration that would have accumulated in the liquid matrix (5.1 at % Si after holding for 50 h) which, according to reaction 1 should reduce the SiC–Al reaction as the activity of the silicon increases. The interface reaction will stop completely once the Al–Si liquid phase reaches equilibrium with SiC and Al_4C_3. The silicon concentration of the liquid phase at which this occurs has been calculated or measured by several researchers [3, 4, 10] as a function of the reaction temperature. Their data are summarized in Fig. 13 where a considerable spread of results are apparent, probably owing to experimental difficulties in measuring the silicon concentration and/or allowing for the carbon content of the liquid phase when making thermodynamic calculations. Also in Fig. 13 are plotted the results of the present work but it must be emphasized that these results apply to silicon concentrations in the matrix after holding for 50 h; it is not known whether equilibrium has been attained, although Fig. 12 suggests that it is rapidly being approached.

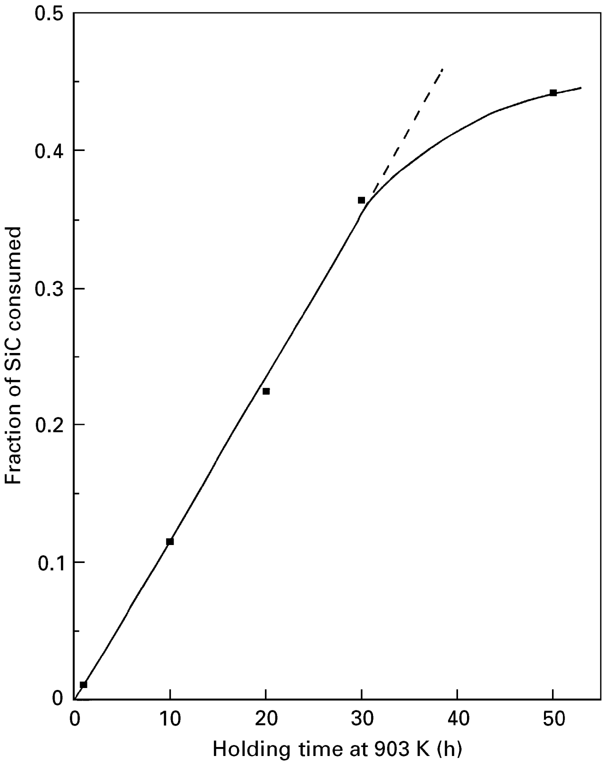

Figure 12 Fraction of SiC consumed by the interface reaction as a function of time at 903 K.

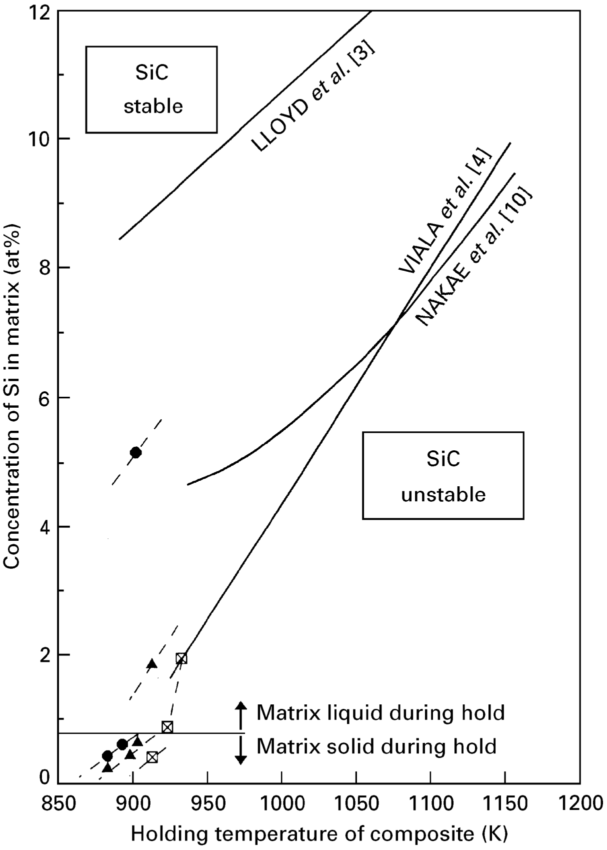

Figure 13 Concentration of silicon in the aluminium matrix that will prevent the interface reaction from taking place at the indicated temperatures ■ MM 17–3; ▲ MA 17–20; ● MA 17–3.

For mechanically mixed materials the data fall approximately on the extrapolated results of Viala *et al.* [4]. For mechanically alloyed material, higher silicon concentrations are measured for a given holding temperature. For the case of MA 17–3, the data at 903 K are approaching those calculated by Lloyd *et al.* [3].

The reaction kinetics for hold times, t, of less than 30 h can be represented by the relation

$$x = kt^n$$

where x is the thickness of the interface reaction zone, k is a rate constant and n is the time exponent. A value of $n = 1$ would be expected where the reaction is being controlled by activation processes at the interface, and $n = \frac{1}{2}$ for diffusion control of the reaction [11]. If the SiC particles are regarded as simple cubes, then for small values of x the fraction of SiC consumed by the reaction is linearly related to x. The results shown in Fig. 12 for MA 17–3 give a value very close to $n = 1$, suggesting that nucleation events at the interface dominate the reaction kinetics at 903 K. Linear reaction kinetics have also been observed in the Al–SiC system at 941 K [4] and 1073 K [7] where the aluminium matrix was molten for the whole of the reaction period.

3.6. Effect of temperature on the interface reaction

In all the materials investigated in the present work the SiC–Al interface reaction has been observed to initiate at temperatures where the aluminium matrix was in the solid state. Using the silicon concentration in the matrix as a measure of the interface reaction, Fig. 14 shows how the extent of the reaction changes with holding temperature for MM 17–3, MA 17–3 and MA 17–20 materials. A rapid interface reaction starts to occur at temperatures where the matrix becomes liquid during the holding period, which in MA 17–3 is around 903 K, in MA 17–20 is 913 K and in MM 17–3 is 923 K. Where the matrix remained solid throughout the holding period, there are sufficient data to enable the rate, k, at which the SiC interface has been consumed by the reaction, to be plotted as a function of temperature according to the relation

$$k = k_0 \exp\left(-\frac{Q}{RT}\right)$$

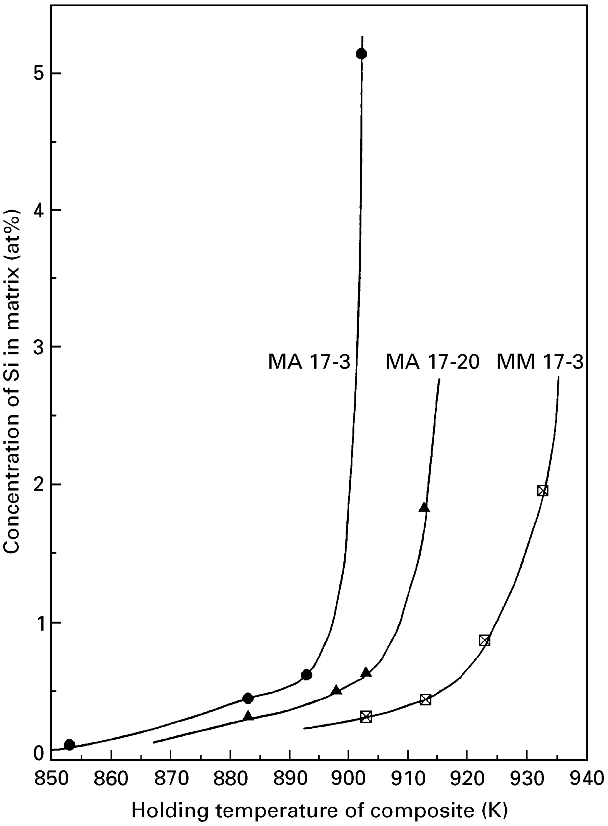

Figure 14 Concentration of silicon in the aluminium matrix after holding the various composite materials for 50 h at different temperatures.

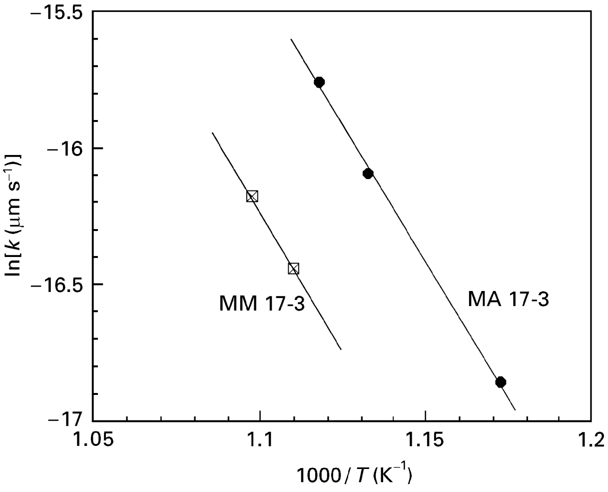

Figure 15 Rate of the interface reaction plotted as a function of $1/T$.

Fig. 15 shows such a diagram for the two directly comparable materials, MA 17–3 and MM 17–3, and it can be seen that the limited data plots are parallel lines. An activation energy, Q, can be estimated from the slope of these lines and the value obtained is 186 kJ mol^{-1}. Bearing in mind all the different processes taking place in the matrix during the holding period and the effect that these have on the DTA thermograms, too much weight should not be placed on the numerical value of the activation energy except to say that it is well above that for the diffusion of silicon in solid aluminium, which is approximately 130 kJ mol^{-1}. This, like the kinetic results of the previous section, suggests that the rate-controlling event may be nucleation at the SiC–Al interface.

It remains to explain why, at a given temperature, the rates of SiC consumption are significantly different in MA 17–20, MA 17–3 and MM 17–3 materials (Fig. 14). The differences occurring in MA 17–20 and MA 17–3 will be the result of different SiC–Al interfacial areas in the two materials. This is clearly demonstrated in Fig. 16 which shows DTA thermograms for three mechanically alloyed materials containing 17 vol% of 3 μm SiC particles, 2.5 vol% of 3 μm particles and 17 vol% of 20 μm particles. The surface area per unit volume of the SiC particles are in the

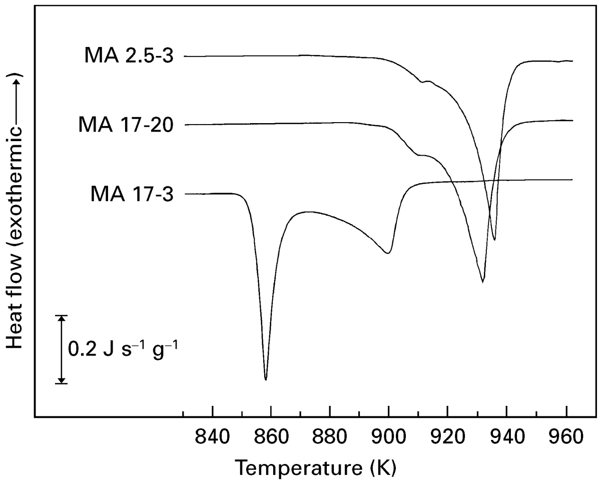

Figure 16 DTA thermograms of MA 2.5–3, MA 17–3 and MA 17–20 after holding for 50 h at 903 K.

approximate ratio 7:1:1, respectively. It will be seen that the DTA thermograms for MA 17–20 and MA 2.5–3 are very similar even though the volume fractions and sizes of SiC particles are widely different; it is the surface area of the SiC that is controlling the extent of the reaction.

A surface area explanation cannot account for the different interface reaction behaviours in MA 17–3 and MM 17–3 since the two materials contain the same fraction and size of SiC particles. However, the materials differ in two important respects. First, MM 17–3 had been prepared with "as-manufactured" SiC particles whilst MA 17–3 contained SiC particles whose surfaces had been modified by the mechanical alloying process. The SiC particles in MM 17–3 will have a thin surface film of SiO_2 several nanometres thick which may act as a barrier to the SiC–Al interface reaction [12, 13]. This barrier will become more difficult to surmount, the lower the reaction temperature. Consequently, at 923 K, the barrier may be relatively easily overcome and the interface reaction can proceed in the MM 17–3 material. However, at 903 K, the reaction becomes much more difficult to initiate in MM 17–3, but it is still able to occur in MA 17–3 because of the absence of a SiO_2 surface film.

The second difference between MM 17–3 and MA 17–3 is the nature of the solid aluminium matrix. In the former case there will be a relatively low concentration of lattice defects in the aluminium, but in the mechanically alloyed material there will be a high concentration of dislocations and a very small grain size. Where the aluminium is in the molten state, these factors, of course, will not be relevant. However, the present work has been concerned with the SiC–Al interface reaction initiating whilst the aluminium matrix was in the solid state. The high defect concentration in the mechanically alloyed material may therefore assist the transfer of silicon and carbon into the aluminium, i.e., encourage initiation of the SiC dissolution reaction

$$\mathrm{SiC(solid)} \rightarrow [\mathrm{Si}]_{\mathrm{solid\ solution}} + [\mathrm{C}]_{\mathrm{solid\ solution}} \quad (4)$$

3.7. The thermal event at 893–923 K

DTA thermograms from all composites studied, especially the mechanically alloyed materials, showed a definite thermal event on the low-temperature shoulder of the main matrix endotherm (Figs 4, 6 and 9). There are two possible explanations for this event, based on the presence of iron intermetallics and the development of a non-uniform concentration of silicon in solid solution. Each of these will be considered.

A small amount of iron (0.06 at%) was present in the aluminium alloy 1050 powder used for the investigation. During holding at a high temperature, this may react with aluminium and silicon (the latter from the interface reaction) to produce the intermetallic $FeSiAl_5$ [14]. This intermetallic can form eutectic systems with α_{Al} or α_{Al} + Si which melt at the following temperatures:

$$\alpha_{\mathrm{Al}} + \mathrm{FeSiAl_5} \rightleftharpoons \text{liquid } 885\,\mathrm{K} \quad (5)$$

$$\alpha_{\mathrm{Al}} + \mathrm{FeSiAl_5} + \mathrm{Si} \rightleftharpoons \text{liquid } 848\,\mathrm{K} \quad (6)$$

However, these melting temperatures are lower than the thermal event observed in the DTA thermograms of the materials used in the present work. Additionally, the temperature of the thermal event varied with holding time and reinforcement particle size, whereas the intermetallic melting processes are invariant reactions.

An alternative cause of the thermal event could be a high concentration of silicon near the SiC–Al interface caused by the difficulty of silicon diffusing away into the matrix, particularly at low reaction temperatures. On subsequent DTA heating, these local regions of high silicon concentration would melt before the bulk of the matrix with its lower level of silicon, thus producing a thermal event on the low-temperature side of the main melting endotherm. To test the likelihood of such a process a simple calculation can be made of the distance, *l*, that silicon atoms are able to diffuse during a holding time *t*, at 903 K, using the expression

$$l = (Dt)^{1/2}$$

D is the diffusion coefficient of silicon in aluminium and is equal to $2.72 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$ at 903 K. The diffusion distance after a 50 h hold time at 903 K is calculated to be 700 μm. The distance between SiC particles in MA 17–20 is 63 μm (10 μm in MA 17–3 material). Therefore, there should not be a large build-up of silicon at the SiC–Al interface. However, it is possible that the Al_4C_3 crystals forming at the SiC–Al interface trap, or at least retard the diffusion of, silicon atoms.

4. Conclusions

1. The reaction between aluminium and SiC particles has been studied in powder-based materials held at a temperature of 933 K or below and found to follow

$$3\mathrm{SiC} + 4\mathrm{Al} \rightarrow \mathrm{Al_4C_3} + 3\mathrm{Si}$$

2. With mechanically mixed powders, appreciable reaction takes place only at temperatures approaching

923 K. A quasiperitectic transformation occurs, producing a liquid phase during the holding period.

3. With mechanically alloyed composites the reaction will proceed at temperatures 883–893 K. The reaction is very slow because the aluminium matrix remains in the solid state. The low temperature at which this reaction can take place may be due to a combination of a high defect concentration in the aluminium matrix, the absence of a SiO_2 film on the SiC particles, and intimate contact between the aluminium and the SiC particles.

4. With mechanically alloyed composites containing 17 vol% of 20 μm SiC particles held at 913 K, or 17 vol% of 3 μm SiC particles held at 903 K, a slow solid-state reaction takes place initially. This is followed by a quasiperitectic transformation that produces a liquid phase, resulting in a much more extensive reaction.

5. The kinetics of the interface reaction of the mechanically alloyed material containing 17 vol% of 3 μm SiC particles held at 903 K follow a linear relationship suggesting that the reaction is nucleation controlled at the SiC–Al interface; it is not diffusion controlled.

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