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Precipitation hardening of cast SiC_p reinforced Mg–6Zn

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Age hardening behaviour of 20 vol % SiC particulate reinforced Mg–6Zn has been studied using hardness, eddy current and transmission electron microscopy techniques. The results show that the precipitation processes in this composite, although accelerated, are similar to those in the unreinforced Mg–Zn alloys; i.e.,

$$\text{supersaturated solid solution} \rightarrow \text{GP zones} \rightarrow \beta' \rightarrow \beta$$

Kinetic analyses of the former indicate that above 423 K, bulk diffusion of Zn controls precipitation, whereas, below 423 K precipitate formation is associated with vacancy migration.

1. Introduction

While age hardening is often utilized to increase the yield and ultimate strength of light alloys, modern technology places increasing demands on achieving higher modulus-to-weight ratio. This requirement has resulted in an extensive effort to develop discontinuously reinforced composite materials that combine high stiffness ceramic reinforcements with light metal matrices [1–14].

A majority of these endeavours [1–9] have considered powder processed aluminium composites and report, in addition to higher specific modulus, an enhancement of the ageing response. This enhancement does not affect the ageing sequence, rather it appears to be associated with the enhanced precipitation of intermediate phases, e.g., S′ in Al–Cu–Mg [6]. Accelerated ageing has in turn been attributed to the presence of a high dislocation density within the matrix, this increased density having resulted from relief of the thermal mismatch strains arising during cooling of the composite from the solution treatment temperature. These thermally induced strains are a consequence of the differences in the thermal expansion coefficient between the ceramic reinforcement and the metal matrix.

Recent studies of cast discontinuously reinforced metal matrix composites indicate that the age hardening response of these composites can be substantially different from powder processed materials and that these differences can, in large measure, be understood by considering the reactions which may occur between the discontinuous reinforcement and the matrix during casting. For example, it has been shown [11] that in cast SiC reinforced aluminium composites, a reaction between the SiC and molten aluminium takes place, i.e., $SiC + Al \rightarrow Al_4C_3 + Si$. Fortunately the rate of this reaction decreases as the matrix Si content is increased. Indeed, high Si containing aluminium alloy matrix composites with SiC reinforcement have been shown to have little or no reaction zone, while the same matrix with a B_4C reinforcement was observed to have a significant reaction zone at the matrix–reinforcement interface [12]. When this reaction does occur it leads to the degradation of the composite by impairing reinforcement and interfacial strength. Further, this interfacial reaction can alter the composition of the matrix material, thereby affecting the ageing behaviour of the composite. For example, the age hardening response of cast 6061 aluminium reinforced with δ Al_2O_3 short fibres has been shown to be inferior to that of the unreinforced alloy [13, 14]. This detrimental effect on ageing has been attributed [14] to both chemical and physical effects during processing of the composite. Chemically, it has been proposed that SiO_2 present at the Al_2O_3 fibre surface dissolves in the matrix [15]. Physically, GP zone formation, a necessary precursor to the development of a fine intermediate phase precipitate substructure [16], may be suppressed; this reduction is caused by a decrease in the quenched-in vacancy supersaturation, the latter due to the ready availability of fibre/matrix interfaces to act as vacancy sinks.

Through these investigations, a clearer understanding of ageing response in discontinuously reinforced aluminium alloys has begun to be achieved. However, little information has been reported for other age hardenable light metal matrix, e.g., Mg, composites, although there is a growing demand for such materials. Magnesium, with suitable alloying and reinforcement, has shown potential in many applications [17, 18], and successful production and characterization of Mg alloy matrix composites [19, 20] have recently been achieved. The present study has therefore undertaken to address hardening response of Mg matrix composites. Specifically, the objective of this investigation was to study the age hardening response of Mg–6Zn reinforced with SiC particulates. The ageing response has been examined utilizing hardness

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and electrical conductivity measurements, with the microstructural development at different stages of precipitation having been characterized by transmission electron microscopy.

2. Experimental Procedure

The material selected for this investigation, an ingot processed Mg–6Zn–0.3Ca alloy reinforced with 20 vol % SiC particulate, was supplied by the Dow Chemical Corporation, Lake Jackson, Texas. This composite was received in the form of 6.35 cm diameter bar extruded from 63.5 cm long and 17.8 cm diameter casting, a 1000 grit, nominally 8–10 μm diameter, SiC particulate reinforcement having been introduced during casting [19, 20].

Age hardening studies utilized 6.5 mm thick discs removed from the extruded bar. All samples were solution treated at 603 K for 1 h in an atmosphere of flowing argon gas and directly quenched in water. Immediately after quenching, the samples were aged at temperatures between 298 K and 473 K, for times up to 2500 h and air-cooled. Each of the heat treated samples was then metallographically polished prior to hardness and eddy current measurements. Hardness was measured using the Rockwell B scale, while electrical conductivity measurements utilized a Verimet eddy current device. Thin foils from selected aged samples were prepared for examination using transmission electron microscopy. Foil preparation included low speed diamond saw sectioning, hand grinding to approximately 75 μm thickness and finally argon ion milling at 5 kV, 0.4 mA and 15° impingement angle.

3. Results

The results of hardness and eddy current measurements are presented in Fig. 1 where Rockwell B hardness and conductivity (in % IACS) values have been plotted as a function of ageing time for different ageing temperatures. Ageing of SiC_p reinforced Mg–6Zn, as shown by variations in hardness and conductivity with ageing time, appears to be typical of many age hardenable alloys. As ageing progresses isothermally, hardness increases, reaches a peak and then decreases showing under-, peak- and over-ageing, respectively. The time required to reach peak hardness and the maximum hardness attained, both decreased with increasing ageing temperature. However, unlike the hardness response, the electrical conductivity did not increase during the early stages of ageing and remained constant after a maximum was reached.

A close inspection of hardness variations at shorter times and/or low ageing temperatures indicate that a number of small but discernible peaks are present. These small hardness peaks, for example, occurring at approximately 1, 8, 128 h at 348 K, are reproducible and have been observed [21, 22] in unreinforced Mg–Zn alloys of similar composition. These hardness peaks are not accompanied by a noticeable change in electrical conductivity.

Characterization using transmission electron microscopy of the aged Mg–Zn composite showed precipitate free zones at grain boundaries and at the interface between the matrix and the SiC_p (Fig. 2). Additionally, little evidence of extensive dislocation loop or network formation associated with SiC_p was observed, in contrast to what has previously been reported for P/M SiC whisker reinforced aluminium composites [6, 7, 23]. However, a careful examination reveals that dislocations can generate at SiC_p/matrix interfaces, this effect being readily evident at sharp corners of the particulates (Fig. 2b).

Samples aged for very short times and/or at low temperatures, where little increase in hardness and no change in electrical conductivity were observed, showed no distinct precipitation in the matrix. Although a mottled appearance suggested the presence of GP zones, the zones could not be resolved, possibly, due to interference of ion milling damage in the foils. However, evidence of GP zone formation in reinforced Mg–6Zn has been observed [24] through the refinement of intermediate phases resulting from pre-ageing below GP zone solvus.

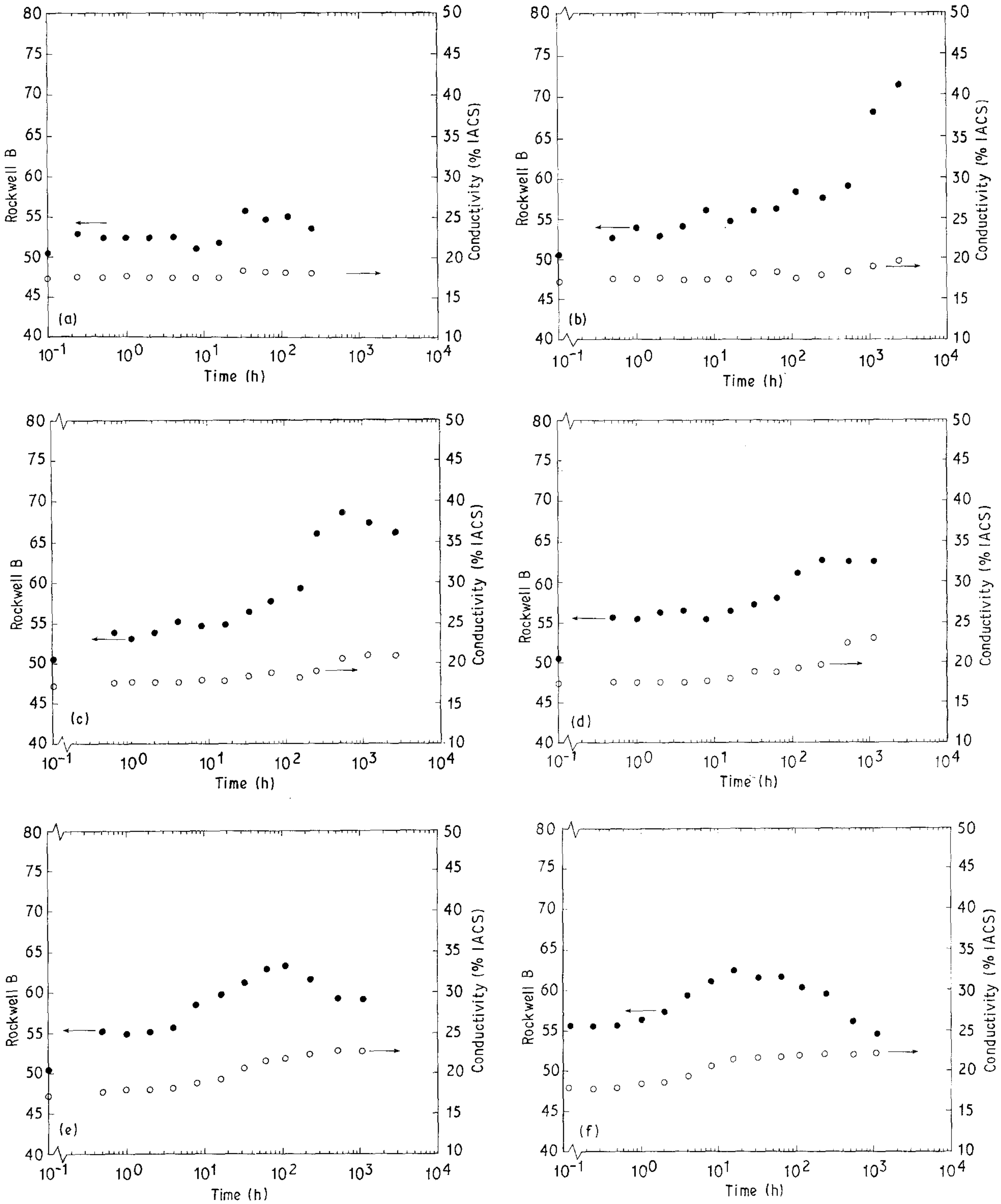
As the ageing progressed distinct precipitation became apparent. Transmission electron microscopic examination of under- and peak-aged samples indicate that the hardening of SiC_p reinforced Mg–6Zn is associated with precipitation of a rod-shaped metastable β′ phase, similar to that observed in unreinforced Mg–(4–8%) Zn alloys [21, 22, 25–28]. Furthermore, the details of precipitation behaviour were observed to differ at low (<423 K), and high (⩾423 K) temperatures. In Fig. 3, typical microstructures showing precipitation behaviour of samples aged below 423 K are shown for (a) under-aged and (b) peak-aged conditions. Initially when both hardness and conductivity increase, Fig. 3a, fine, very closely spaced short rods (β′ precipitates) formed; with subsequent ageing these rod-like precipitates grew in length, Fig. 3b. At higher temperatures (⩾423 K) the metastable β′ precipitates were coarse and relatively widely spaced, and were observed in two orthogonally oriented morphological variants, Fig. 4a and b. The latter observation is consistent with previous observations on unreinforced Mg–6Zn by Bernole *et al.* [27] and Hall [28] who designated these transition phases to be β'_1 and β'_2, with the latter occurring above 418 K.

Finally, in the over-aged condition equilibrium β phase was observed to precipitate regardless of temperature regime, Fig. 5a and b. While intragranular precipitation of β phase predominated, some β occasionally precipitated heterogeneously at grain boundaries.

4. Discussion

A comparison of current results with previous investigations [21, 22, 25–28] on the age hardening behaviour of binary Mg–Zn alloys suggests that the ageing sequence in the reinforced Mg–6Zn is similar to that observed in unreinforced alloys, i.e.,

$$\text{supersaturated solid solution} \rightarrow \text{GP zones} \rightarrow \beta' \rightarrow \beta\,(\text{MgZn})$$



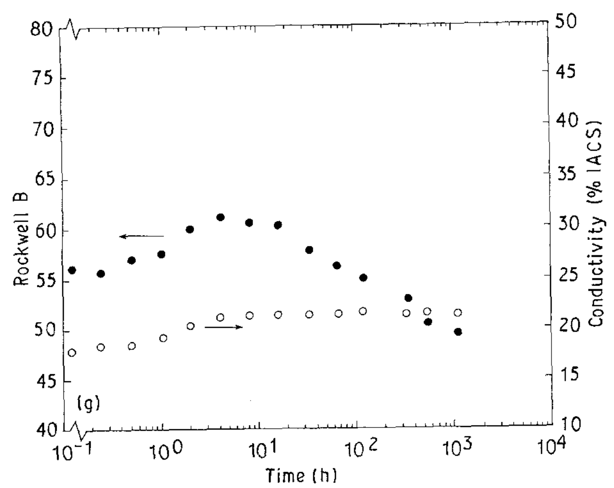


Figure 1 Hardness and conductivity as a function of ageing time for the cast 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, water quenched and aged at (a) 298, (b) 348, (c) 373, (d) 398, (e) 423, (f) 448 and (g) 473 K.

During artificial ageing, hardening results from the precipitation of rod shaped metastable β′ phase. In unreinforced Mg–Zn, precipitation of the β′ phase was observed to occur only at longer times, greater than 500 h, and at ageing temperatures above 383 K [21, 26]. In contrast, the present investigation on SiC_p reinforced Mg–6Zn indicates that appreciable hardening takes place at shorter times and lower temperatures, 348 and 373 K. Peak hardness is associated with rod shaped β′ precipitation and is evident when

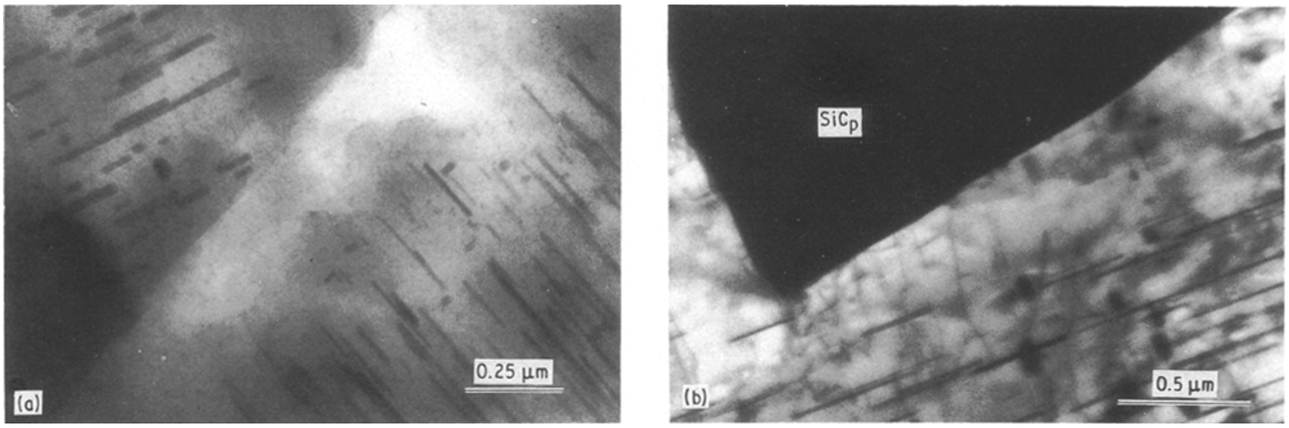


Figure 2 Transmission electron micrograph of 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, water quenched and aged at 423 K for 128 h, showing precipitate-free regions at (a) matrix grain boundary and (b) SiC_p/matrix interface.

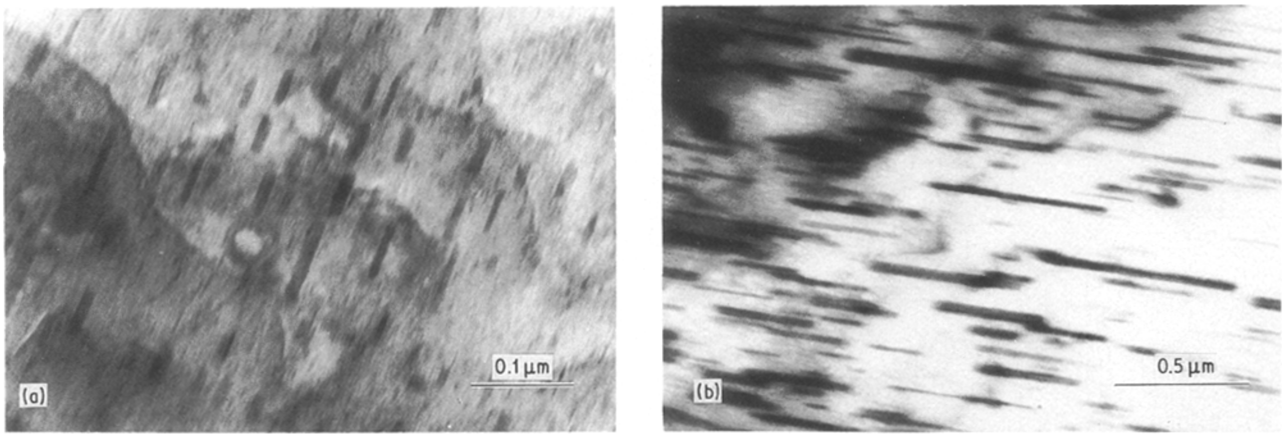


Figure 3 Transmission electron micrograph showing precipitation in 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, water quenched and aged at 398 K for (a) 64 (under-aged) and (b) 256 h (peak-aged).

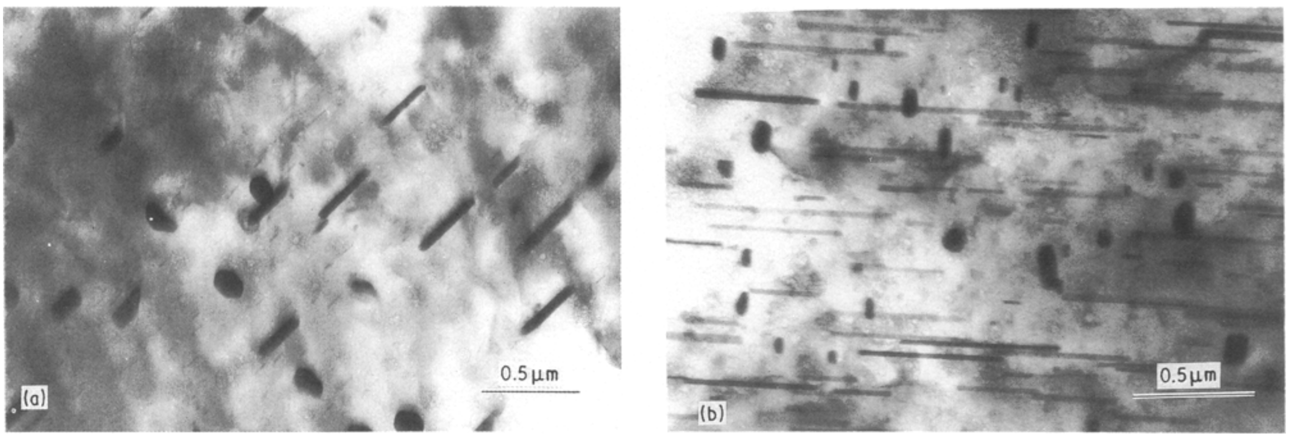


Figure 4 Transmission electron micrograph showing precipitation in 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, water quenched and aged at 448 K for (a) 4 (under-aged) and (b) 16 h (peak-aged).

the SiC_p reinforced Mg–6Zn was aged for 512 h at 373 K. These observations indicate that the presence of SiC_p has enhanced the precipitation kinetics.

In order to examine the precipitation kinetics, the precipitation process may be assumed to be a thermally activated process, then,

$$\delta \ln t / \delta(1/T) = Q/\mathrm{R} \quad (1)$$

where t is the ageing time for a fixed amount of precipitation, T is the ageing temperature in K, Q is the activation energy and R is the gas constant. Following Equation 1, the ageing time, t, both for the initial increase in electrical conductivity and that required to achieve maximum hardness, has been plotted against $1/T$ on a semi-logarithmic scale in Fig. 6. In agreement with those previously reported [21, 22] for binary Mg–Zn alloys, precipitation, over the range of temperature examined, cannot be described by a singly activated process, with the activation energy, as determined from the slope of the best

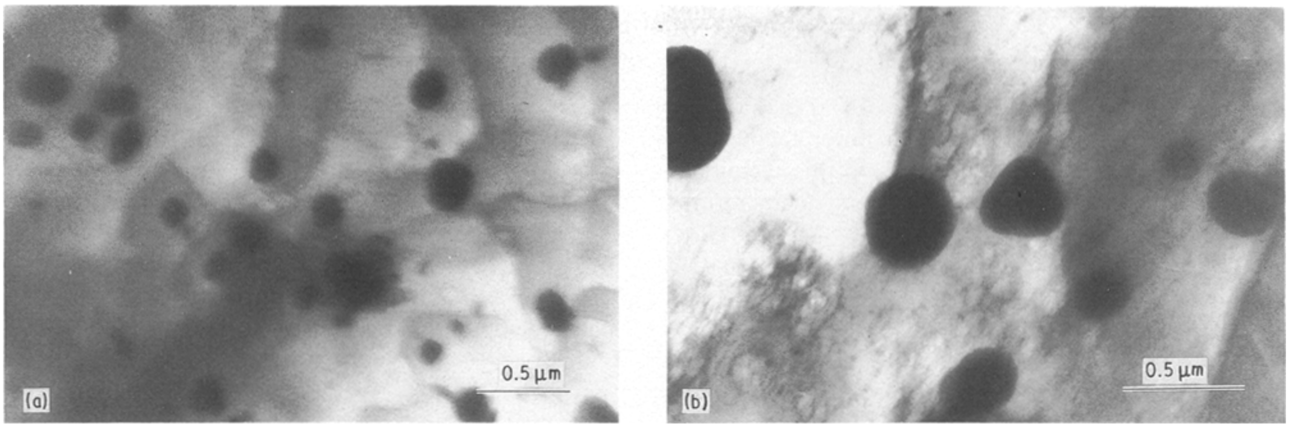


Figure 5 Transmission electron micrograph showing precipitation of equilibrium β phase in over-aged 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, water quenched and aged at (a) 398 K, 1028 h and (b) 448 K, 128 h.

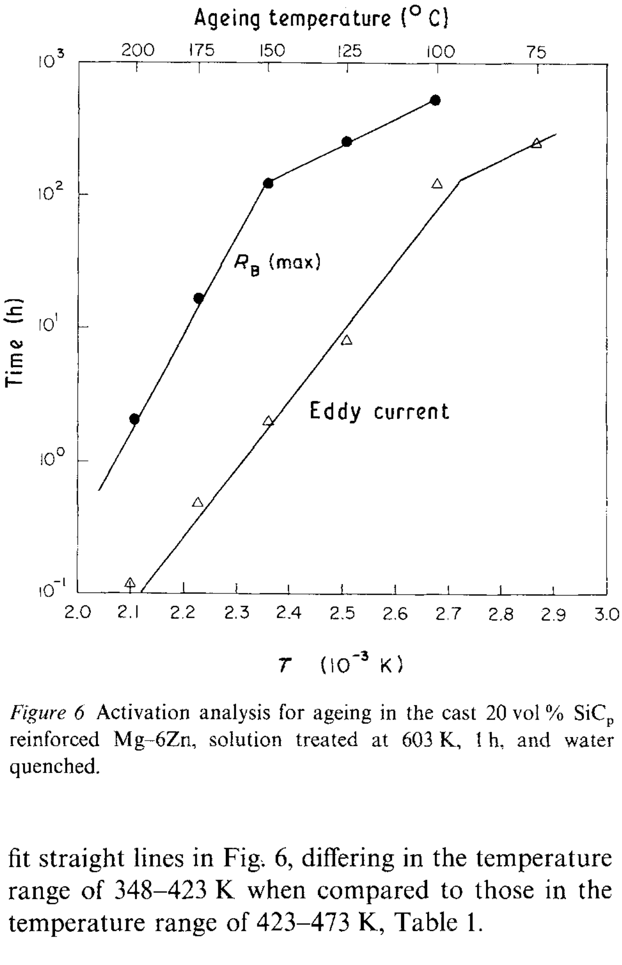


Figure 6 Activation analysis for ageing in the cast 20 vol % SiC_p reinforced Mg–6Zn, solution treated at 603 K, 1 h, and water quenched.

fit straight lines in Fig. 6, differing in the temperature range of 348–423 K when compared to those in the temperature range of 423–473 K, Table 1.

4.1. Precipitation at 348–423 K

The lower activation energy determined in this temperature range suggests that strengthening is related to vacancy migration. Precipitation, therefore, starts at short times and/or low temperatures with vacancy assisted migration and formation of GP zones. On subsequent ageing, the GP zones, together with any excess vacancies, the latter typically in the form of small clusters [29], serve as nucleation sites for fine metastable β′ precipitates, Fig. 3, with growth of the β′ precipitates occurring parallel to the *c*-axis of the matrix [26]. In the reinforced composite, this process may be accelerated by either the presence of a matrix residual stress or structural inhomogeneities, both

TABLE 1 Activation energies for precipitation in SiC_p reinforced Mg–6Zn

Ageing temperature (K)	Method	Q (kJ mol^{-1})
348–423	Hardness	36.85
423–473		138.59
348–373	Eddy Current	36
373–473		101.32

arising as a consequence of the difference in coefficient of thermal expansion between the matrix and SiC particles. The present results, i.e., the rather low dislocation densities observed at the reinforcement/matrix interface, suggest that matrix residual stresses, rather than simply dislocation assisted nucleation and growth are important in accelerating precipitation in Mg composites. Further support for this is given by Dutta and Bourell [30]. These investigators showed the increasing importance of matrix residual stress in accelerating precipitation when the reinforcement/matrix interface dislocation densities are low, i.e., below 10^{13} m^{-2}.

Only after very long ageing times do stable β precipitates appear; in the present investigation β phase was observed in the over-aged condition at 398 K.

4.2. Precipitation at 423–473 K

The activation energy determined at this temperature range is higher and agrees very well with the activation energy for volume diffusion of Zn in Mg [31]. This agreement suggests that at ageing times when maximum hardness is observed, the controlling mechanism is volume diffusion of Zn in the alloy. At these temperatures vacancy migration is rapid, therefore most of the excess vacancies migrate within a short time to form clusters and do not participate in GP zone formation. Indeed, GP zones within this temperature range have not been observed. The nucleation of the β phase appears to occur at vacancy clusters and other structural inhomogeneities. Since small vacancy clusters in Mg are energetically stable [29], these can act as nucleation sites for precipitation of β′ phase and result in what appears to be a homogeneous distribution of β′ precipitates.

Due to the suppression of GP zones within this temperature range, the metastable β′ phase appears less closely spaced than those at lower temperature ageing. In addition, two variations of β′ precipitates, β'_1 and β'_2, were observed at high ageing temperatures. Similar precipitation, in unreinforced Mg–Zn alloys was previously reported [28], with both β'_1 and β'_2 being identified [27, 28] as Laves $MgZn_2$ type structures with different matrix–precipitate habit orientation. The reported [28] lattice parameters and orientation relationships of both these precipitates indicate that the delayed precipitation of β'_2 is due to the difference in interfacial strain energy associated with the anisotropic hcp matrix [32].

At longer ageing times, precipitation of stable β phase is observed resulting in over-ageing. The nature of the β precipitates, i.e., larger size and more widely spaced compared to β′ precipitates, suggests that precipitation of β phase is preceded by dissolution of β′ rods.

The age hardening response due to the presence of reinforcement in Mg–6Zn matrix has been observed to be similar to that observed in Al matrix composites, i.e., accelerated ageing occurs without affecting the ageing sequence. However, there are two major differences between these two composite systems; first, in contrast with aluminium composites, SiC_p reinforced Mg–6Zn does not exhibit extensive dislocation generation close to the reinforcement–matrix interface and second, a precipitate free zone is observed at the interface.

The presence of a high dislocation density in the composite matrix depends on two factors. First, dislocations generate at the reinforcement/matrix interface. These dislocations arise as a result of the differential stresses induced at the reinforcement/matrix interface during cooling from the solutionizing temperature. Second, dislocation multiplication occurs within the matrix. Since both aluminium and magnesium have comparable thermal expansion coefficient (24 and 26×10^{-6} per K, respectively) the extent of induced stress depends only on the temperature difference, ΔT, between the solutionizing and quenching temperature. ΔT for aluminium matrix composite is typically 525 K, while that for the present magnesium composite is 305 K. The stresses induced during quenching will therefore be significantly lower in the magnesium matrix. In addition, h c p metals, unlike f c c metals, exhibit a limited number of slip systems. Thus, it is expected that the dislocation density in magnesium matrix composites will not be as high as that in aluminium matrix composites. However, a limited number of dislocations are still generated at the reinforcement/matrix interface, Fig. 2b, and these can locally accelerate β′ precipitation.

The observation of the precipitate-free zones near the reinforcement/matrix interfaces may be explained in terms of vacancy depletion in those areas. During initial ageing, vacancies migrate to reinforcement/matrix interfaces which act as sinks. This results in both GP zone suppression and the absence of vacancy clusters, either of which can serve to nucleate the β′ precipitates. This phenomenon is not observed in Al/SiC composites because precipitation at the interface is facilitated by the presence of very high dislocation density ($\geqslant 10^{13}\ m^{-2}$).

5. Conclusions

1. Significant hardening can be achieved by artificial ageing of SiC particulate reinforced Mg–6Zn.
2. The age hardening sequence of the composite material is identical to that observed in the unreinforced alloy.
3. In the temperature range of 348–423 K, peak ageing is associated with a low activation energy and precipitation of fine β′.
4. In the temperature range of 423–473 K, peak hardening is associated with nucleation and growth of β′ precipitates, being controlled by bulk diffusion of Zn.
5. While the precipitation characteristics in the Mg–6Zn/SiC_p composite are similar to those observed in Al/SiC composites, the reinforcement/matrix interface region, in this study, is associated with a relatively low dislocation density and may exhibit a precipitate-free zone.

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