JOURNAL MATERIALS SCIENCE 30 (1995) 5763-5769

Crystallography of the second phase/SiC particles interface, nucleation of the second phase at β-SiC and its effect on interfacial bonding, elastic properties and ductility of magnesium matrix composites

B. INEM
Gazi University, Technical Education Faculty, Metallurgy Department, Beseveler, Ankara, Turkey

The nucleation and crystallographic orientation of both the magnesium matrix and the eutectic $\{Mg(ZnCu)_2\}$ at the β-SiC particle surface were investigated. The eutectic nucleates at the particle surfaces with an identical crystallographic orientation and covers the particle surfaces in ZC63 and ZC71 magnesium matrix composites, but no distinct crystallographic orientation of the magnesium matrix/SiC particle interface has been resolved. At the interface no extensive chemical reaction takes place and no reaction product forms as a layer at the particle surfaces, but in some cases, during composite processing Mg_2Si particles, and during heat treatment Mg_2Si precipitates, nucleated at the particles and in the matrix close to the interface. In addition, other phases having the composition of CuFeCrSi and CuMoMgSi, the formation of which was not known in ZC63, and manganese- and iron-rich phases in ZC71 alloy, were also detected at the particle surfaces. There is some indication that the coarse and brittle manganese- and iron-containing particles may be involved in the fracture, but no direct effect of the other phases on tensile properties and/or fracture toughness was observed. Nucleation of the eutectic resulting in a good interfacial bonding, however, increases both the Young's modulus and the ductility of the composites, modifying the brittle nature of the matrix/particle interface. As well as β-SiC, α-SiC particles are intended for use in the fabrication of magnesium matrix composites. Therefore, the possibility for similar nucleation and orientation relationships between the eutectic and α-SiC particles has been examined.

1. Introduction

Metal/ceramic interfaces are currently receiving a great deal of interest because in metal matrix composites (MMCs) without interfacial bonding, regardless of how strong or stiff the matrix and the reinforcement, the strength of the composite materials is doubtful, and the reinforcement, instead of increasing the matrix properties, creates voids and reduces the efficiency of the matrix. Therefore, the conventional view has been that a sufficient bonding between the matrix and the reinforcement is necessary to distribute the load on the matrix. Thus high strength and stiffness result from the combination of a metal matrix possessing relatively low mechanical properties with a high-strength ceramic reinforcement in the composites. A sufficiently strong isotropic bonding could take place through chemical reaction between the matrix and reinforcement forming an oxide layer along the interface, diffusion of atoms, or an atomic interaction at the interface causing a bond without the formation of distinct reaction products.

These types of bonding are also produced by wetting the reinforcement with the molten metal. This is an important consideration, because it is one of the determining factors for good interfacial bonding. If, however, wetting occurs because of a strong chemical interaction, this causes degradation of the reinforcement and/or some element loss from the matrix or reinforcement increasing the possibility of undesirable phases such as Al_4C_3 in Al/SiC composites [1–2] or Mg_2Si in Mg/SiC composites [3–4]. This may further degrade properties such as the fracture toughness, ductility and impact resistance of the composites. Wetting and bonding takes place even if there is no strong chemical interaction between the reinforcement and the other phases. In this case the properties of the composites would improve without additional sacrifice from fracture toughness due to the absence of massive brittle intermetallic phase formation. Therefore this is beneficial to mechanical properties.

The interface phenomenon in MMCs is not fully understood because of its complexity and dependence on many variables. It is known that at the interface some reaction products or a layer associated with reinforcement appears to be modifying the strength of the composites while maintaining the bonding

0022–2461 © *1995 Chapman & Hall*

between the matrix and the reinforcement. In some cases, it has been found that the reaction products have grown in a specific crystallographic orientation, for example in Mg/Al_2O_3 composite [5]. The possible crystallographic relationship and adhesion between α-SiC, β-SiC and the aluminium matrix interface has also been theoretically examined [6]. A preferred orientation relationship was observed in the 6061/α-SiC composite between the aluminium matrix and α-SiC [7].

In addition to the reaction products, the second phase or the eutectic phase has been observed to associate with the particles. It has been claimed that these phases nucleate at reinforcements [8] but no crystallographic evidence has been published. It is not, therefore, clear whether the second phase nucleated from the particles or had to associate with particles, because the particles were often clustered by the solidification front in the interdendritic region where the eutectic phase forms in aluminium and magnesium matrix composites. If there is any crystallographic orientation, it is likely that regular atomic arrangement, and thus bonding, exists at the interface.

In this study, the crystallographic orientation relationship between the eutectic $\{Mg(ZnCu)_2\}$ and β-SiC particles was examined. The possibility of a similar type of crystallographic orientation and nucleation of the eutectic at α-SiC was investigated. The effect of the nucleation of the eutectic phase on the Young's modulus and ductility of the composites has been discussed.

2. Experimental procedure

2.1. Materials, interface microscopy and analysis

The composite materials used in this study were commercial pure magnesium (CPMg) reinforced with 15% SiC, ZC63 cast alloy (Mg-6% Zn-3% Cu-0.5% Mn) and ZC71 wrought alloy reinforced by up to 15% SiC particles with a diameter between 8 and 15 μm. The cast composites were in the form of plates 250 mm × 250 mm × 25 mm. The wrought composite was initially cast into a water-cooled copper die, 90 mm diameter, and was then extruded into 20 mm diameter bars. The samples were examined using a Joel 200 CX, 2010 TEM and Philips 430 HVTEM at 200 kV. Sample and foil preparation were described in a previous publication [9]. The interface and microstructure were characterized by lattice imaging, selected-area diffraction (SAD) technique and nanoprobe energy spectroscopy (EDX) for microanalysis and secondary ion mass spectroscopy (SIMS) for the fracture surface analysis.

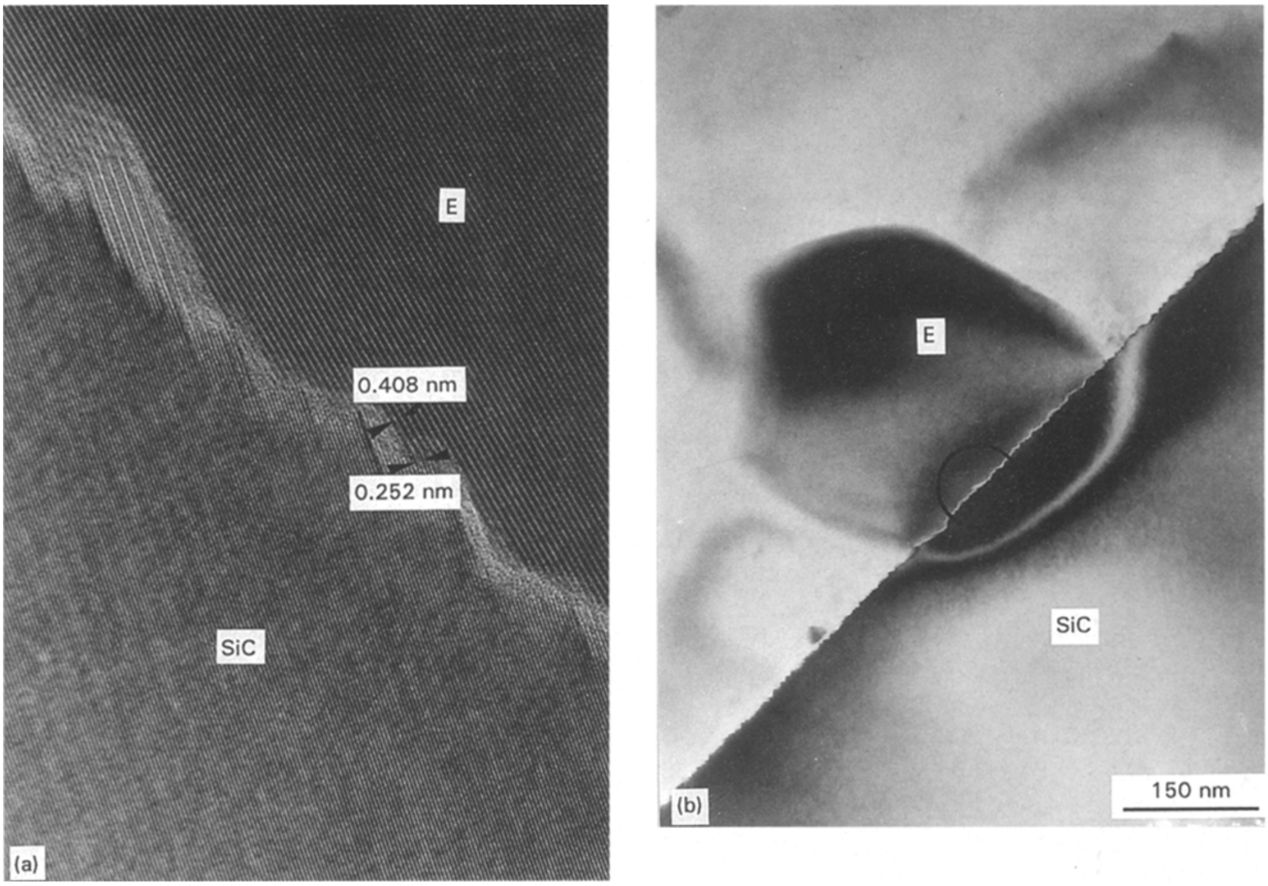
2.2. Determination of Young's modulus of the composites

The elastic modulus (dynamic modulus) of all of the composites was determined by the ultrasonic method (resonant frequency methods), but the static modulus of the extruded composites was also calculated by determining the slope of the straight line portion of the stress–strain curve. However, this second method can be problematic, because the straight portion may not be long or distinct for the composite, and stress relaxation occurs during testing. It is important for design purposes that the correct value of Young's modulus be determined. The accuracy of the ultrasonic method is better than the static method, although in this technique the strain amplitude is low so that the value obtained is, in general, slightly higher than the static modulus values. Therefore, care should be taken, when the stiffness properties are considered.

3. Nucleation of the eutectic phase at the Interface between the eutectic and β-SiC particles

The lattice image of the eutectic/SiC particle interface is shown in Fig. 1. As with the matrix/SiC interface, the eutectic/SiC particle interface was generally smooth. However, there is evidence of some elements (magnesium, copper or zinc) diffusing into the SiC lattice leading to an ordered structure (as indicated in Fig. 1). This conclusion is based on the observation of a four fringe repeat distance in the contrast of the $\{1\,1\,1\}$SiC and the serrated nature of the interface. However, this ordered phase has not yet been resolved. EDX surface analysis of the SiC particles in the composite showed that the surfaces were enriched with copper; a few atomic layers of copper or magnesium at the interface region could produce such an ordered structure leading to a good bonding in the region. Previously, an attempt to produce Mg/SiC fibre-reinforced composites by the liquid processing method, has indicated that the presence of certain elements improved the properties of the composites (manganese, copper, zinc, calcium, silicon, aluminium, yttrium and other rare-earths) [10]. In another study, the benefit of these elements in powder-processed Mg/SiC composites was also indicated [11]. The affinity of magnesium and copper for free silicon in SiC and with a small amount (0.5–1 wt%) manganese in these magnesium alloys, good interfacial bonding should be expected. However, interface cracking was sometimes observed. The possible reason for such cracking could be the concentrated stress in the region, as seen at the matrix/particle interface [12]; and this was quantified. A comparison of the dislocation density of the eutectic in the unreinforced matrix and the composites could reveal the existence of stresses, but the eutectic was too dark to see any structure because of the high absorption of the electron beam. The dislocation density could not therefore be resolved to make such a comparison. However, image contrast on the particle side has been observed, indicating the existence of strain in the particles close to the eutectic/particle interface.

The association of the eutectic with the SiC particles in alloy composites indicated the nucleation of the eutectic at the SiC particle surface. It is generally believed that in metals and alloys, solid particles in the solidifying melt would be favourable sites for heterogeneous nucleation if the conditions are right, because low-energy solid–liquid interfaces are likely sites for



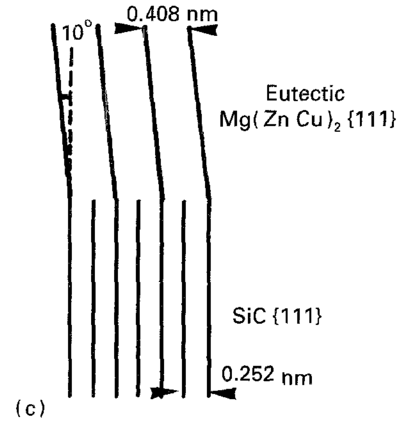


Figure 1 (a) The lattice imaging of the eutectic $\{Mg(ZnCu)_2\}/\beta$-SiC particle interface, (b) corresponding region, and (c) schematic representation. As seen, two lattice spacings of the β-SiC particle corresponds with one lattice spacing of the eutectic with 10° angle to the actual lattice fitting and lowering the interfacial energy.

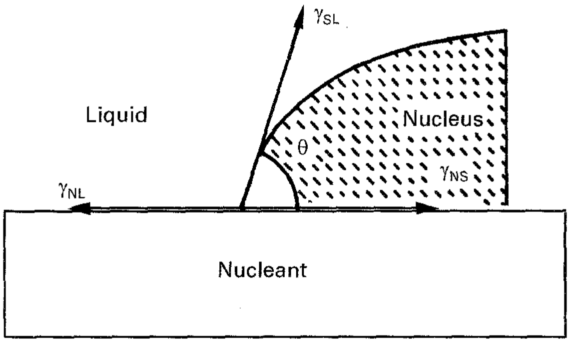


Figure 2 Energy balance in heterogeneous nucleation.

nucleation. It has been indicated [13] that in hypereutectic Al–Si alloys, primary silicon is partially refined by the SiC particles. It has also been indicated that silicon is refined by carbon, Al_2O_3 and SiO_2 particles [8]. In the present work with these magnesium composites, it was observed that the duplex eutectic $Mg(ZnCu)_2$ nucleated on the SiC particle surfaces [3, 9, 14].

The nucleation phenomenon of a liquid phase in the presence of solid particles is complicated and has not been fully established. However, on the basis of the published work, a possible explanation for the nucleation was reviewed by Mondolfo [15] on non-ferrous alloys. It was explained that the best location is where disregistry of nucleant planes is at a minimum.

Another characteristic of heterogeneous nucleation is the variability of fit in atomic distribution. Thus the nucleation takes place by an atom-to-atom replacement in the lattice, such as nucleation of magnesium by zirconium, these two lattices are very similar, with only small differences in lattice parameters. In other cases, the fit is limited to a few atoms, such as the nucleation of aluminium by $NiAl_3$.

In most cases the type of matching is between these two extremes. Also when an intermetallic compound is the nucleant, the plane in which nucleation takes place may be constituted wholly or in part by atoms that are the same as those of the nucleus.

The other strong criterion for nucleation is the energy balance. Fig. 2 illustrates the energy balance which must occur before wetting can take place. If $\gamma_{NL} > \gamma_{NS} + \gamma_{SL} \cos \theta$, the nucleus S can spread on the nucleant N and grow. If γ_{NL} is smaller than the sum of $\gamma_{NS} + \gamma_{SL}$, the nucleus must shrink and disappear.

When a crystallographic orientation between two phases exists, γ_{NS} is generally small because the orientation relationship of the nucleus on the nucleant is facilitated by a crystallographic fit which results in a low interface energy between two phases.

On the nucleation of the eutectic at the β-SiC particles, there is evidence that the wetting angle, θ, is less than 90°. Fig. 1b illustrates the wetting angle of the eutectic on the particle surface. This clearly suggests that the eutectic wets the particles. In addition to this there is a crystallographic orientation relationship between the eutectic and the particles. In order to determine the orientation relationship, several diffraction patterns from the eutectic, particles and the interface were taken. The orientation relationship, as shown in Fig. 3, was found to be as follows

$$\{2\,2\,0\}\ \mathrm{Mg(CuZn)_2} \parallel \{1\,1\,1\}\ \mathrm{SiC}\ (1^\circ\text{–}2^\circ)$$

$$\{3\,1\,1\}\ \mathrm{Mg(CuZn)_2} \parallel \{3\,1\,1\}\ \mathrm{SiC}\ (1^\circ\text{–}2^\circ)$$

$$\{2\,2\,1\}\ \mathrm{Mg(CuZn)_2} \parallel \{2\,2\,0\}\ \mathrm{SiC}\ (1^\circ)$$

$$< \bar{1}\,\bar{1}\,4 >\ \mathrm{Mg(CuZn)_2} \parallel < 1\,1\,\bar{2} >\ \mathrm{SiC}$$

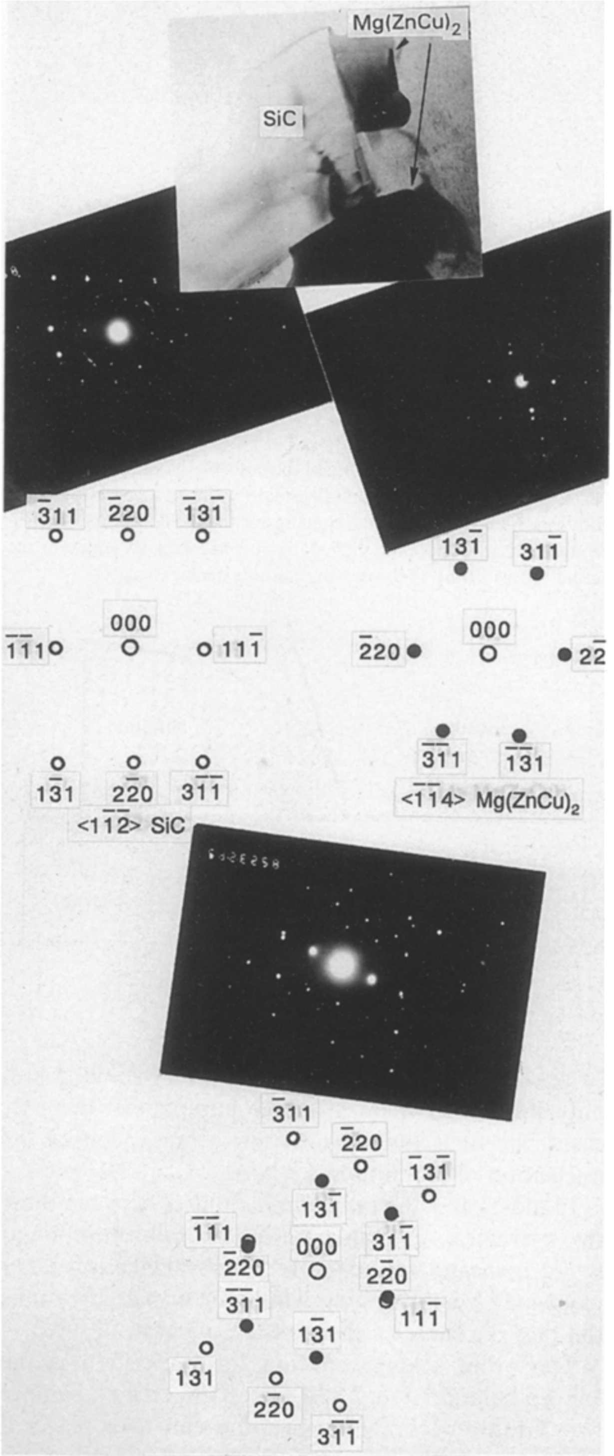


Figure 3 The orientation relationship between the eutectic and β-SiC particles for nucleation.

{2 2 0} planes of the eutectic and {1 1 1} planes of the SiC were found to be the habit planes. During SiC powder manufacture, large SiC granules from the electric furnaces are coarsely crushed followed by a final crushing and milling. In such a process there might be a preferential fracture plane, although no information on the crystallography of β-SiC fracture was found. However, in many fcc single crystals, including diamond cubic materials, fracture occurs on {1 1 1} planes. The {1 1 1} planes of the β-SiC are also the closest packed planes, so that these planes having low energy could well be an easy nucleation site for the eutectic. Moreover, the lattice matching difference between $d_{(2\,2\,0)}$ (0.2553 nm) of the eutectic and $d_{(1\,1\,1)}$ (0.2522 nm) of the SiC is 1%. This can be clearly seen in Fig. 4, in which it is evident that the $d_{(2\,2\,0)}$ lattice of the eutectic almost matches the $d_{(1\,1\,1)}$ lattice of the β-SiC. In this case, the nucleation on {1 1 1} planes of the SiC is the more favourable for {2 2 0} planes of the eutectic. Therefore, the eutectic nucleates and grows at the particle surfaces. This causes most of the eutectic phase to be associated with particles and hence leads to modification of the eutectic phase, resulting in a fine lamellar eutectic morphology in the composites.

It is also possible that as the last liquid reaches the eutectic composition during solidification, this solid-enriched liquid finally nucleates at the SiC particles which had already been clustered in the region. The presence of the copper on the particle surfaces which was mentioned previously could be the driving force for the nucleation of copper-containing eutectic. This seems more likely to occur because the low solubility of copper in magnesium could lead to a copper-rich liquid front which is, in the first place, in contact with the particles throughout solidification. In this case, some copper atoms may also stay on the particle surfaces and give rise to easy nucleation of the eutectic.

4. The possibility of eutectic nucleation on α-SiC particles

As well as β-SiC, the other types of SiC particles have also been used in metal matrix composites and are suitable for the production of magnesium matrix composites. However, there are six types of α-SiC and three types of rhombohedral SiC, and before production of a composite one should determine which type of particle could be useful and lead to the best properties. From results given in the previous section, the possibility of nucleation of the eutectic at α-SiC

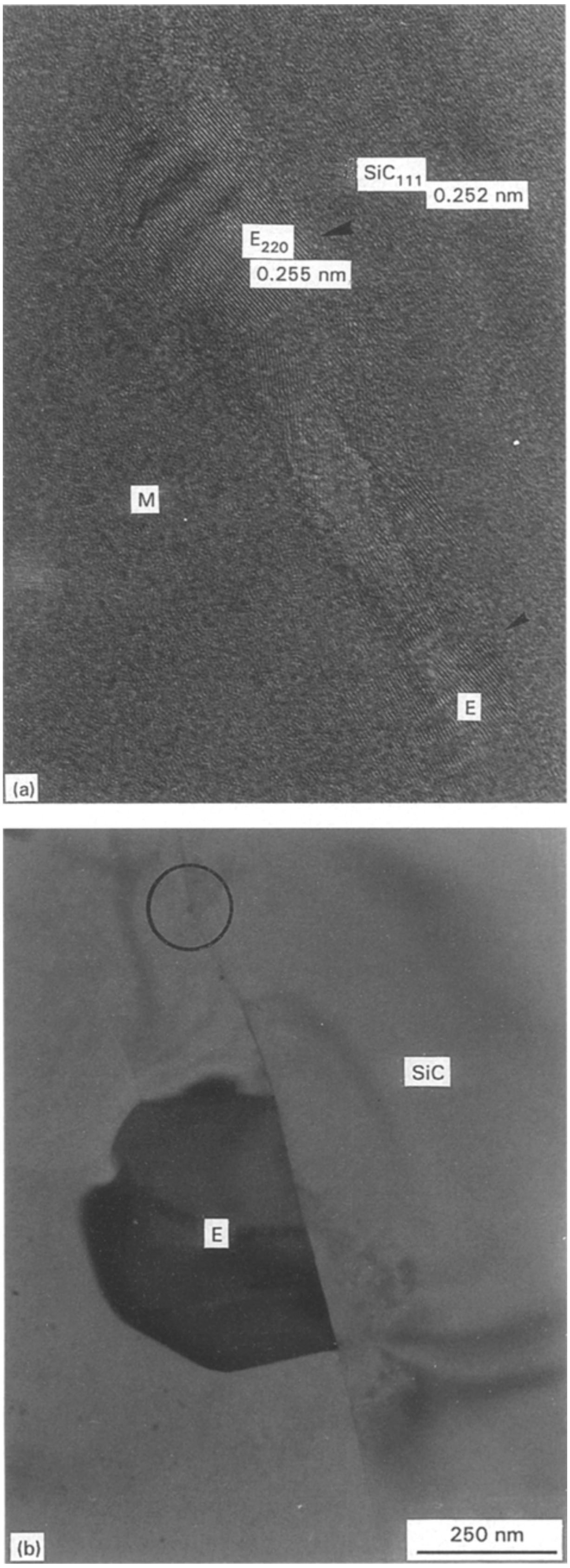


Figure 4 (a) The lattice image of the matrix/particle interface with eutectic droplets in the alloy matrix composite, and (b) the corresponding region at the matrix/particle interface. As seen, the eutectic (2 2 0) lattice spacing almost matches the (1 1 1) lattice spacing of the β-SiC.

particles has been examined. It was found that two 6H polytype α-SiC (29-1126 and 29-1130) are particularly suitable. Their lattice parameters are $a = 0.3081$ nm, $c = 0.503$ and $a = 0.307$, $c = 0.504$ nm respectively, and in particular the (1 $\bar{1}$ 0 0) plane of α-SiC, having almost the same lattice spacing as the (1 1 $\bar{2}$) plane of β-SiC, similar atomic configuration and diffraction pattern (Fig. 5), indicates that this plane could provide nucleation sites for the eutectic {Mg(ZnCu)} in ZC63 and ZC71 alloys. Table I gives some of the *d*-spacings of some planes in β-SiC and α-SiC. As with the β-SiC{1 1 1} when the {0 0 0 2} plane of these α-SiC become the habit plane on the particle surface, the eutectic could nucleate easily, because like the (1 1 1) plane in β-SiC, the (0 0 0 2) plane in α-SiC is the closest packed plane with a low surface energy. The possible orientation relationship may take place as follows

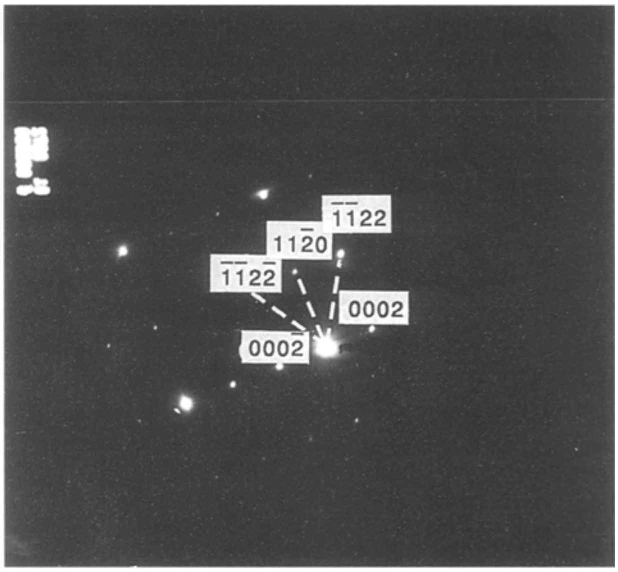


Figure 5 Indexed diffraction pattern of (1 1 0 0) plane of α-SiC.

TABLE I *d*-spacings of some planes in β-SiC and α-SiC

α-SiC	β-SiC (29-1129)	(29-1130)	α-SiC (29-1126)
2.51	2.5166 (1 1 1)	2.52 (0 0 0 2)	2.51 (0 0 0 2)
1.55	1.5411 (2 2 0)	1.53 (1 1 2 0)	1.54 (1 1 2 0)
1.31	1.3142 (3 1 1)	1.31 (1 1 2 2)	1.31 (1 1 2 2)

$$(2\,2\,0)\ \mathrm{Mg(ZnCu)_2} \parallel (0\,0\,0\,2)\ \alpha\text{-SiC}$$

$$(3\,\bar{1}\,1)\ \mathrm{Mg(Zn(Cu)_2} \parallel (1\,1\,\bar{2}\,\bar{2})\ \alpha\text{-SiC}$$

$$[2\,\bar{2}\,1]\ \mathrm{Mg(ZnCu)_2} \parallel [1\,1\,\bar{2}\,0]\ \alpha\text{-SiC}$$

$$[1\,\bar{1}\,2]\ \mathrm{Mg(ZnCu)_2} \parallel [1\,\bar{1}\,0\,0]\ \alpha\text{-SiC}$$

5. The effect of SiC particle/eutectic interfacial bonding on the modulus and ductility of the composites

Interfacial bonding is the main determining factor of the mechanical properties of the composites. In the magnesium matrix composites with good and adequate interfacial bonding, a substantial increase in elastic modulus was evident [3]. However, the increase in elastic modulus of several magnesium matrix

TABLE II Elastic modulus of matrices and composites

Materials	Elastic modulus (GPa)	Condition
CPMg	43	Sand cast
CPMg + 15% SiC	48	Sand cast
ZC63	46	Porosity free
ZC63 + 12% SiC	53	Sand cast
ZC63 + 15% SiC	60	Sand cast
ZC71	46	Porosity free
ZC71 + 12% SiC	55	Die cast
ZC71 + 12% SiC	57	Extruded

composites was different, although all the unreinforced matrices have almost the same elastic modulus. Table II gives the elastic moduli of matrices and composites. The biggest increase in modulus was observed for ZC63 + 15% SiC sand-cast composites, despite the casting defects which essentially cause a low dynamic modulus value. The results and the comparison of the modulus of CPMg composite and the alloy composites, showed that good interface relation and atomic bonding, maintained by the eutectic as well as the matrix in alloy matrix composites, cause a higher modulus for the alloy composites. This is expected, because in CPMg the interfacial bond strength only depends on the atomic interaction or bonding between the magnesium matrix and the SiC particles because no eutectic nor alloying elements other than impurities exist in pure magnesium. It is also important to take into account that the solidification time in pure magnesium is much shorter than the alloys, so that relatively little time exists for a high degree of atomic diffusion or interaction at the interface during solidification. Therefore, this may also cause relatively weak bonding to develop, resulting in a low elastic modulus.

For CPMg composites, it was also evident that with decreasing volume of the eutectic around the particles, the elastic modulus decreased. For example, the highest stiffness improvement was observed from the ZC63 composite because in this composite a high volume of eutectic was associated with the particles. The high volume of eutectic is mainly as a result of 1 wt % more alloy content in this alloy compared with ZC71. In the extruded ZC71 composite, most of the eutectic also dissociated from the particles during the extrusion, and dispersed throughout the structure. Consequently, despite a much fewer voids or structural defects, for the ZC71 composite a slightly lower modulus was measured than for the ZC63 composite. It should be borne in mind that a high 3 vol % SiC particles content in the ZC63 composite can make some difference. However, this composite contains a substantial number of casting defects which is more than enough to compensate for the effect of slightly higher particle content. Also it would not be expected that increasing the amount of particles by only 3 vol % could increase the Young's modulus by 5 GPa, while a 15 vol % particle causes a 14 GPa increase in elastic modulus.

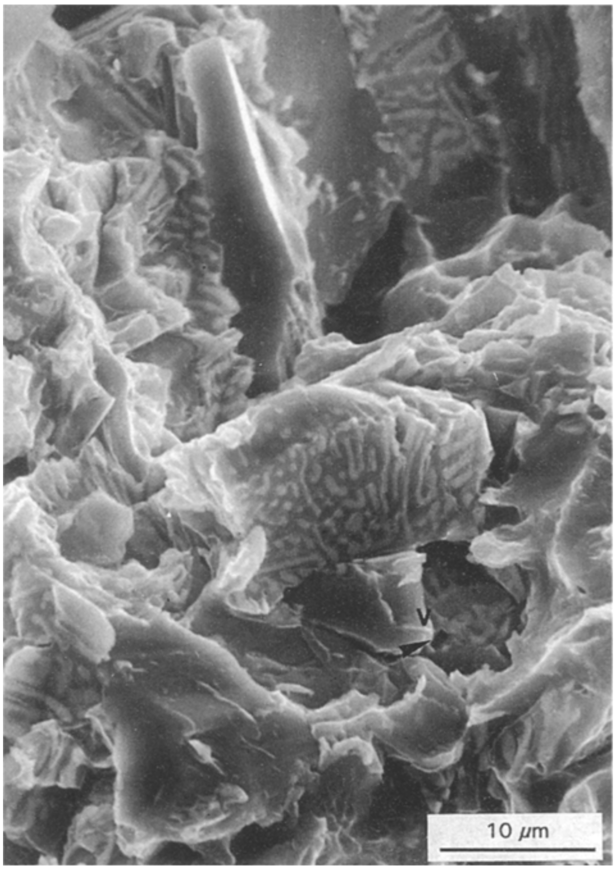


Figure 6 Scanning electron micrograph showing most of the eutectic attached to the particle after fracture of the composite indicating that the interfacial bonding between the particle and the eutectic is stronger than that between the matrix and the eutectic. Notice also in the matrix at the eutectic/matrix interface, a void has nucleated (arrowed).

During examination of the fracture surface, it was observed that after fracture a substantial amount of eutectic remained at the particle surface (Fig. 6). This is further indication of strong bonding between the particle and the eutectic, which is possibly stronger than the bonding between the matrix and the eutectic. A gradually developing plastic deformation and ductile debonding at the matrix/eutectic interface takes place instead of brittle failure, leaving mainly the eutectic at the particle surface with its bond intact. Therefore, the particle/eutectic relation not only increases the elastic modulus but may also modify the brittle nature of the interface of the composites. Consequently, unlike Al/SiC and other Mg/SiC composites, in ZC63 and ZC71 matrix composites, the fracture toughness and elongation may possibly be somewhat higher than the value which was usually observed for the particle-reinforced composites, if the defect-initiated failure can be prevented by reducing macrocasting defects in the composites. In both ZC71 and ZC63 composites, elongation was, however, measured to be 1.7–2% because in almost all the specimens, the macocasting defects initiated failure, whereas this is about 6%–8% for unreinforced alloys.

6. Conclusions

In both ZC63 and ZC71 magnesium matrix composites, the eutectic $Mg(ZnCu)_2$ nucleated at the β-SiC particle having an identical crystallographic orientation, but no distinct similar orientation relationship between magnesium matrix and the β-SiC particle has been resolved.

As a consequence of the eutectic nucleation, a good interfacial bonding is maintained at the eutectic/particle interface. This results in a significant improvement of the Young's modulus and also a modification of the interface fracture where instead of brittle debonding, a ductile breakage takes place.

There is a promising possibility that a similar type of nucleation and eutectic/α-SiC relationship can arise because the 6H type of two α-SiCs have similar planes at which nucleation can take place, as in β-SiC. On $\{1\,1\,0\,0\}$ planes, *d*-spacings are very close to those of the $\{1\,1\,2\}$ planes of β-SiC. Therefore, when these two types of α-SiC particles are chosen for magnesium alloys containing zinc, copper and manganese, it is possible to obtain good interfacial bonding and thus a high composite properties.

Acknowledgement

The author thanks Professor B. Rand for his kind permission to carry out the research at the School of Materials, University of Leeds, Dr T. Wilks, Magnesium Elektron Limited, for supply of the materials and permission to use the facilities at MEL, Manchester, Dr A. Dickens for comments on the text, Dr C. Hammond and the late Dr G. Pollard for discussions and comments.

References

1. T. ISEKI, T. KAMEDA and T. MARUYAMA, *J. Mater. Sci.* **19** (1984) 1692.
2. J. VIALA, F. BOSSELET, P. FORTIER and J. BOUIX, in Proceedings of Sixth International Conference on Composite Materials, Vol. 2, London, 1987, edited by F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson and J. Morton (Elsevier, Amsterdam, 1987) pp. 146–156.
3. B. INEM, PhD, thesis, University of Leeds, U.K. (1993).
4. E. M. KILLER, A. MORTANSEN, J. A. CORNE and M. C. FLEMINGS, *J. Mater. Sci.* **26** (1991) 2519.
5. M. PFEIFER, J. M. RIGSBCE and K. K. CHAWLA, *ibid.* **25** (1990) 1563.
6. S. LI, R. J. ARSENAULT and P. JENA, in "Proceedings cast reinforced metal composite", Chicago, Illinois, 1988 edited by S. G. Fishman and A. K. Dhingra (ASM International, 1988) pp. 33–7.
7. P. M. BRANSVELD, H. LUKKIEN, D. J. VAN DIJK, J. Th. M. De. HOSSON, M. A. SARGEN and C. RENSEN, in Proceedings of Symposium on Composite Materials, International Conference on Advanced Materials, Strasbourg, France, May 1991, edited by A. T. Benedetto, L. Nicolais and R. Watanabe (Elsevier, Amsterdam, 1992) pp. 215–20.
8. P. K. ROHATGI, R. ASTAHANA and F. YARANDI, in Proceedings of Conference on Solidification of Metal Matrix Composites, Indianapolis, 1989, edited by P. K. Rohatgi (TMS, 1990) pp. 51–75.
9. B. INEM and G. POLLARD, *J. Mater. Sci.* **28** (1993) 4427.
10. S. YAJIMA The Research Institute for Iron, Steel and Other Metals of the Tohoko University DE-PS 2 647 862.
11. A. R. BEGG, British Petroleum Company p.l.c, EP-PA 0 240 251 (1990).
12. B. INEM, *Mater. Sci. Eng.*, **A197** (1995) 91.
13. I. JIN and J. D. LLOYD, in Proceedings of the Congress on Fabrication of Particle Reinforced MMCs, Montreal, September 1990, edited by J. Masounave and F. G. Hamel (ASM International, 1990) pp. 47–52.
14. B. INEM, N. HAN, G. POLLARD and R. STEVENS, Proceedings of Symposium on Composite Materials, International Conference an Advanced Materials, Strasbourg, France, May 1991, edited by A. T. Benedetto, L. Nicolais and R. Watanabe (Elsevier, 1992) pp. 173–8.
15. J. F. MONDOLFO, in Proceedings of Symposium on Grain Refinement in Casting and Welds, Missouri, October 1982, edited by G. J. Abbaschian and S. A. David (The Metallurgical Society of AIME, 1982) pp. 1–49.

Received 10 March 1994
and accepted 17 May 1995