# Calcia–alumina fibre-reinforced Al 7075 alloy composites produced by melt-infiltration: Interfacial wetting and reaction

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Inviscid melt-spun calcia–alumina (CA) fibre-reinforced aluminium 7075 alloy matrix composites were produced at 700 and 927 °C by using a melt-infiltration method. Interfacial wetting and chemical reaction of the composites were investigated by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The composites processed at 700 °C showed interfacial wetting and magnesium accumulation at the interfacial region. The composites processed at 927 °C showed the formation of a 15 μm thick interphase region as well as excellent interfacial wetting. EDS analysis gave averaged compositions of this interface region at 63.5 at % Al and 31.5 at % Mg, which corresponds to the composition of spinel, $MgAl_2O_4$. The formation of spinel at the interface was confirmed by XRD analysis on the CA fibres separated from the composites.

## 1. Introduction

The purpose of developing metal matrix composites (MMC's) is to improve specific mechanical properties of structural components. The major application of MMC's are as aerospace parts, automobile components, and in sports equipment [1–10].

The high-strength and high-modulus boron fibre has been used for reinforcing aluminium and titanium matrices [4]. However, the drawbacks of the boron fibre namely rapid reaction with molten metals during processing and degradation of mechanical properties after long term exposure to high temperatures, have led to the development of SiC fibres [5]. Due to good bonding between SiC fibres and reactive metals and also only a small loss of strength during high temperature processing, SiC fibre-reinforced metal matrix composites have become viable engineering materials.

Alumina fibre is another ceramic fibre which is widely used for reinforcing metal matrices such as aluminium and magnesium [6]. Alumina fibre-reinforced MMC's are important for weight-sensitive applications operating at elevated temperatures. The chemical and oxidation resistance of alumina can overcome fibre degradation during both composite fabrication and utilization. Owing to the high strength, stiffness, and hardness of alumina, alumina fibre-reinforced MMC's show enhanced creep, fatigue, and wear properties.

In spite of these excellent properties, the use of ceramic fibres as reinforcements for metal matrices, has been limited due to their high cost which is related to their production processes such as chemical vapour deposition, sol-gel processing, pyrolysis, and slurry processing.

The inviscid melt-spinning (IMS) technique has been successfully applied to fibre fabrication [11–24]. By using the IMS technique the spinning of inviscid ceramic melts has become possible. The Rayleigh break-up, which is the critical problem in spinning inviscid melts, can be prevented by introducing a reactive hydrocarbon gas such as propane to the surface of the molten stream. By pyrolysis of the gas a carbon sheath can form on the surface of the molten stream and this carbon sheath can stabilize the molten stream until solidification occurs. The IMS process gives a very rapid production rate for fibres and thus considerably reduces fibre cost. Calcia–alumina (CA) eutectic fibre (46.5 wt % CaO–53.5 wt % $Al_2O_3$) was the first fibre spun by the IMS technique. The CA fibre is in vitreous form as spun and is approximately 30 cm in length and 200–300 μm in diameter. The physical properties of the CA fibre are listed in Table I [22–24]. This fibre would be suitable for reinforcing aluminium alloy matrices since it can retain about 80% of its strength up to approximately 800 °C.

In MMC's, good interfacial bonding is of importance for load transfer from a metal matrix to the reinforcing fibres. It is known that alloying elements such as magnesium, copper, lithium, silicon and nickel, which have a tendency to be absorbed into the interface, can enhance wetting at the interfacial zone [25–32]. The formation of compounds such as

TABLE I Physical properties of IMS CaO–Al$_2$O$_3$ eutectic fibres [22–24]

| Tensile strength (MPa) | Young's modulus (GPa) | Vickers hardness (GPa) | Fracture toughness (MPa·m$^{1/2}$) | Density (g cm$^{-3}$) | Fibre diameter ($\mu$m) | Glass transition temp. (°C) | Crystallization peak temp. (°C) |
|---|---|---|---|---|---|---|---|
| ∼519 | ∼100 | ∼7.1 | ∼0.9 | 2.74 | 200–300 | 850 | 980 |

LiAlO$_2$, MgAl$_2$O$_4$, and CuAl$_2$O$_4$ has been observed at the interface of alumina fibre-reinforced aluminium alloys containing lithium, magnesium, and copper, respectively [28, 29]. This compound formation resulted in greatly enhanced bonding between fibres and the matrix.

Sung *et al.* [32] have examined the wetting and compound formation at the interface of CA fibre-reinforced Al–Si alloy (4032) matrix composites. The composites processed at 700 °C showed good interfacial wetting due to Si accumulation at the interface and those processed at 927 °C showed excellent interfacial wetting due to mullite (3Al$_2$O$_3$ · 2SiO$_2$) formation at the interface. The CA fibre-reinforced Al 7075 alloy (5.6 wt % Zn, 2.5 wt % Mg, 1.6 wt % Cu, and 0.23 wt % Cr) composites were developed by using melt-infiltration. The focus of this study is on the investigation of interfacial wetting and possible interfacial reaction of the composites.

## 2. Experimental procedure

Melt-infiltration was used to fabricate the CA fibre-reinforced Al 7075 alloy composites. A graphite mould was designed for the composite fabrication. High-grade graphite with low ash content (grade ECV, National Carbon, Cleveland, OH, USA) was used in order to reduce the wetting of aluminium alloy melt with the graphite mould. The mould consists of three pieces, a top piston, a main cylinder, and a bottom plate. In order to prevent overflow of the aluminium alloy melt during processing reservoirs were designed. Aluminium 7075 alloy rods manufactured by Alcoa Technical Centre (Alcoa Centre, PA, USA) were used for the present study. This alloy contained 5.6 wt % Zn, 2.5 wt % Mg, 1.6 wt % Cu, and 0.23 wt % Cr. The CA fibres were preloaded parallel to the mould axis and the pieces of Al alloy rods were loaded at the top of the CA fibres. This mould was placed in a hot-press machine (Physical Science Laboratory, University of Wisconsin-Madison, USA) which had a tungsten heating element and a diffusion pump for high vacuum (∼1.316 × 10$^{-7}$ atm$^{-1}$ 1.33 × 10$^{-2}$ Pa). The weight of the top piston of the hot press machine was sufficient to squeeze the aluminium alloy melt to obtain melt-infiltration. Additional hydraulic pressure was not applied. Fig. 1 shows a schematic drawing of the procedure of composite fabrication using the graphite mould. Melt-infiltration was performed at two different temperatures (700 and 927 °C) for 2 h. The 700 °C temperature processing was intended to investigate wetting behavior between fibre and matrix. The temperature of 927 °C, which is slightly lower than the crystallization temperature of the CA fibre (∼980 °C), was used to examine a possible interfacial
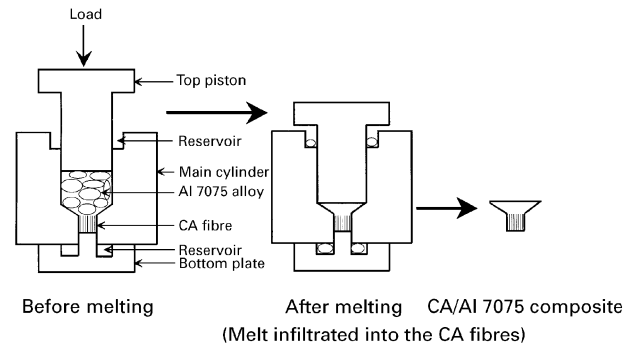


*Figure 1* Schematic drawing of melt-infiltration process used for fabricating CaO–Al$_2$O$_3$ (CA) fibre-reinforced Al 7075 alloy matrix composites. The high-grade graphite mould was designed for this experiment.

chemical reaction without causing a crystallization of the fibre. In a previous study, crystallized IMS CA fibre showed degraded mechanical properties due to rapid grain growth [24]. The nipple-shaped CA/Al 7075 composite was easily released from the graphite mould. For scanning electron microscopy (SEM) studies, a sample surface perpendicular to the fibre direction was polished using SiC papers (grid #600) and alumina powder (1 μm).

Scanning electron microscopy (SEM, Jeol 35-C, Japan) was used for secondary electron imaging (SEI), to investigate wetting behaviour and morphology of the interface/interphase, and backscattered electron imaging (BEI) to obtain compositional contrast at the interface region. Energy dispersive X-ray spectroscopy (EDS, Noran Co. Middleton, WI, USA) was also used with the SEM analysis to provide the composition profiles across the interfacial zones of the composite. X-ray diffraction (XRD, Nicloet Stoe Transmission/Bragg-Brentano, Stoe Co., Germany) with a Cu–K$_\alpha$ source, a 20 s time constant, a 15–90° scan range, and 0.02° step size, was performed for phase identification. This XRD analysis could not be used to detect any new interphase formed in the composite owing to the small volume percentage ( < 5%) of the interphase. Some of the CA fibres could be separated from the composite by dipping the composite into a solution of sodium hydroxide (40 wt %) and distilled water (60 wt %) for about 10 min. To identify a crystalline phase on the surface of these fibres, powdered CA fibres were analysed. The resulting XRD patterns were identified by using the Joint Committee on Powder Diffraction Standards (JCPDS) card.

## 3. Results and discussion
### 3.1. Processing at 700 °C
The CA/Al 7075 composite processed at 700 °C was studied for interfacial wetting. An SEM secondary

electron image (SEI) of the CA/Al 7075 composite is shown in Fig. 2 which reveals wetting between the fibre and matrix. In previous studies, a CA fibre introduced into an Al–Si alloy matrix also showed good interfacial wetting, whereas a CA fibre introduced into a pure aluminium matrix did not [31, 32]. This can be explained as follows.

The work of spreading can be expressed as:

$$W^s = \gamma^s - \gamma^l - \gamma^{sl} \qquad (1)$$

where $\gamma^s$ and $\gamma^l$ are the surface tensions of solid and liquid, and $\gamma^{sl}$ is the interfacial tension between the solid and liquid [25]. In the present study, the surface tension of the CA fibre, $\gamma^s$ is constant. Therefore, decreased values of $\gamma^l$ and/or $\gamma^{sl}$ can increase the work of spreading, resulting in better wettability between the fibre and liquid metal [25].

The surface tension of aluminium alloys in the liquid state can be expressed by the Gibb's adsorption equation as:

$$d\gamma^l = -\sum \Gamma_B \, d\mu_B \qquad (2)$$

where $\Gamma_B$ is the excess solute concentration absorbed on the surface and $\mu_B$ is the chemical potential of the solute in the liquid. Since the chemical potential, $\mu_B$, of the solute in the mixture is given by $\mu_B = \mu_B + RT \ln a_B$ where $\mu_B$ is the chemical potential of pure B and $a_B$ is the activity of solute B in the mixture, then the following equation can be applied:

$$d\mu_B = RT d(\ln a_B) \qquad (3)$$

Combining Equations 2 and 3 gives

$$d\gamma^l = -RT \Gamma_B d(\ln a_B) \qquad (4)$$

It is obvious that when either the excess solute concentration, $\Gamma_B$, at the surface or the activity of the solute, $a_B$, is increased, the surface energy of the aluminium melt, $\gamma^l$ is reduced. This reduced $\gamma^l$ would in turn increase the work of spreading, $W^s$ in Equation 1, resulting in better wettability.

A compound formation at the interface can also decrease the interfacial tension between a solid and liquid $\gamma^{sl}$, leading to an increased $W^s$ in Equation 1 and thus wettability. However, no new interphase
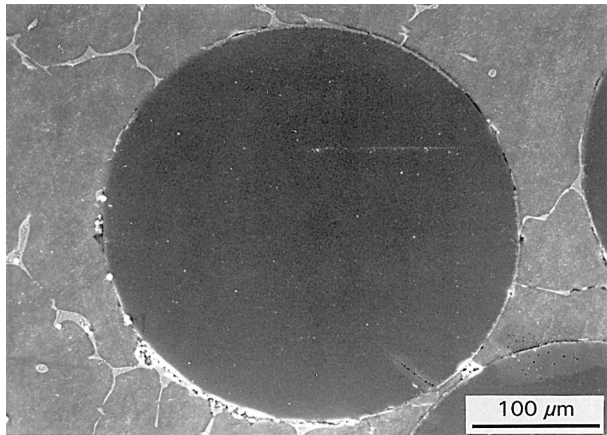
formation at the interface was observed by SEI. EDS analysis on the composite revealed an accumulation of magnesium, ($\sim 26$ wt %) and Cu ($\sim 8$ wt %), Zn ($\sim 6$ wt %), and Cr($\sim 1$ wt %) at the interface regions which evidently lowered $\gamma^l$ and caused interfacial wetting.

## 3.2. Processing at 927 °C

Interfacial wetting and interphase formation were examined in CA/Al 7075 composites processed at 927 °C. Fig. 3 (a and b) shows the secondary electron image (SEI) and backscattered electron image (BEI) of the composite. A new interphase as well as excellent wetting, were observed at the fibre–matrix interfacial zone. Evidently, for 927 °C processing, the work of spreading, $W^s$, is increased due to (a) decreased surface tension of the liquid, $\gamma^l$, caused by alloying elements accumulation at the interface, and (b) decreased interfacial tension between solid and liquid, $\gamma^{sl}$, caused by compound formation at the interface. Therefore, the CA/Al 7075 composite produced at 927 °C should show better wetting than the composite processed at 700 °C. This was confirmed by carefully comparing the scanning electron micrographs of these composites (Figs. 2 and 3). Furthermore, it was also observed that
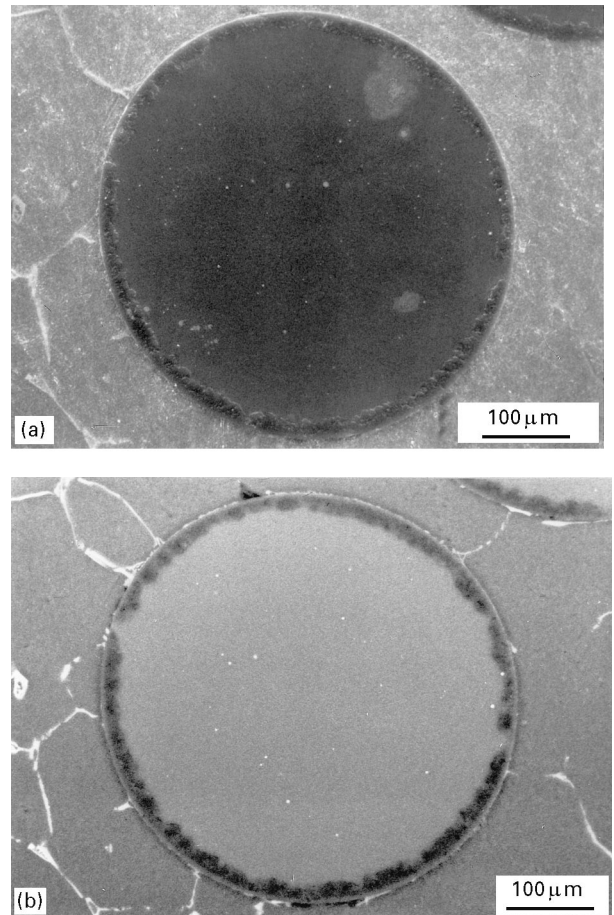
(a)  100 μm

(b)  100 μm

*Figure 3* (a) SEM secondary electron image (SEI) and (b) back scattered electron image (BEI) of the IMS CA fibre-reinforced Al 7075 alloy composite processed at 927 °C for 2 h. A new interphase formation at the fibre-matrix interface as well as excellent interfacial wetting is observed. The interphase region in the BEI of the composite is darker than the IMS CA region, which implies a heavy atomic element (Ca) depletion in the interphase region.

100 μm

*Figure 2* SEM secondary electron image (SEI) of the IMS CA fibre-reinforced Al 7075 alloy composite processed at 700 °C for 2 h. Interfacial wetting is shown.

an interphase was formed inside the CA fibre. This implies that matrix elements diffused into the original boundaries of the CA fibres to form the new interphase. BEI of this composite showed that the interphase was depleted of the high atomic number element (calcium) because the interphase region is darker than the CA fibre area. Fig. 4a shows the blown-up image of the interphase shown in Fig. 3. An interphase, approximately 15 μm thick, was observed. Fig. 4b shows a compositional scan for the corresponding interphase. The interphase is a polycrystalline compound with an approximately 2–5 μm grain size. The EDS for the composite shows a high magnesium content and calcium depletion in the interphase. The amount of calcium in the interphase region was about 0.8 at %. The mechanism of the calcium depletion in the interphase region is unclear at this moment. The averaged amount of aluminium and magnesium in the interphase was 63.5 and 31.5 at %, respectively, possibly indicating the formation of spinel ($MgAl_2O_4$). A large amount of magnesium ac-

cumulation ($\sim 34.0$ at %) was also observed at the interface.

XRD was performed on the powdered CA fibres separated from the composites in order to identify the new interphase. Fig. 5 shows the XRD patterns of the CA fibre. The broad background in the patterns comes from the vitreous CA fibre. The $d$-spacing and diffraction angle of ($2\theta'$) of the XRD peaks were 0.244 (36.83°), 0.202 (44.871°), 0.143 (65.30°), 0.155 (59.42°), 0.286 (31.30°), and 0.466 (19.05°) nm, in decreasing order of intensity. These peaks were identified as belonging to spinel ($MgAl_2O_4$) by comparing the measured $d$-spacings, diffraction angles and peak intensities with the data on JCPDS card no 21–1152. The number at the top of each peak corresponds to the order of peak intensity as listed on the JCPDS card. Both the peak positions and intensities were in good agreement with the data on the JCPDS card. The formation mechanism of spinel at the interface of the composite can be expressed as [33]:

$$2Mg + O_2 \rightarrow 2MgO$$

$$\Delta G° = -987.4 \text{ kJ per mol at } 927\,°C \qquad (5)$$

$$4/3Al + O_2 \rightarrow 2/3Al_2O_3$$

$$\Delta G° = -861.3 \text{ kJ per mol at } 927\,°C \qquad (6)$$

$$4/3Cr + O_2 \rightarrow 2/3Cr_2O_3$$

$$\Delta G° = -538.9 \text{ kJ per mol at } 927\,°C \qquad (7)$$

$$2Zn + O_2 \rightarrow 2ZnO$$

$$\Delta G° = -458.5 \text{ kJ per mol at } 927\,°C \qquad (8)$$

$$4Cu + O_2 \rightarrow 2Cu_2O$$
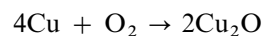
$$\Delta G° = -164.0 \text{ kJ per mol at } 927\,°C \qquad (9)$$

All of the above chemical reactions have a negative free energy value, which means all of the reactions would occur at 927 °C. However, Equation 5 has the lowest $\Delta G°$ value, which implies that MgO will be formed most readily amongst the above oxides. The
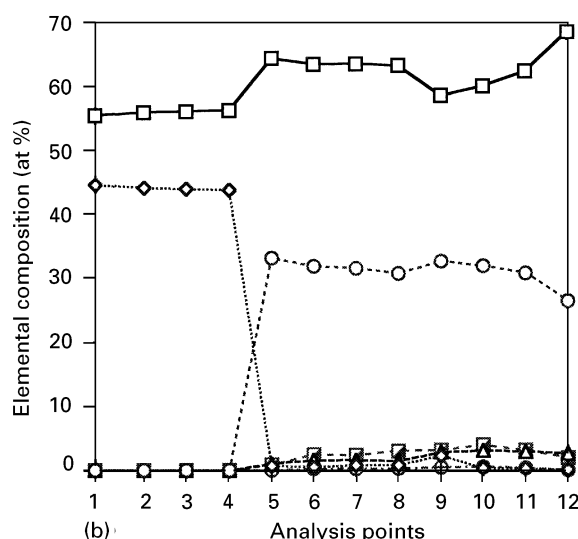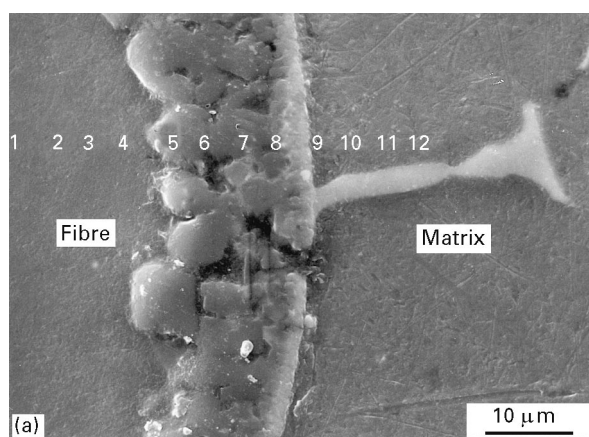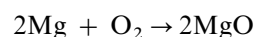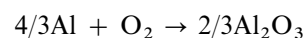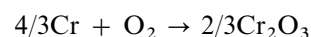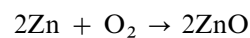
*Figure 4* (a) Blown-up SEM secondary electron image (SEI) of the interface of the IMS CA fibre-reinforced Al 7075 alloy composite processed at 927 C for 2 h and (b) compositional scan for the corresponding interface. Data were taken for; (□) Al, (◇) Ca, (○) Mg, (△) Zn, (■) Cu and (⊕) Cr. The Ca depletion in the interface region is confirmed by this compositional scan. The averaged amount of Al and Mg in the interface region are 63.5 and 31.5 at %, respectively, which implies that the new interphase formed would be spinel ($MgAl_2O_4$).
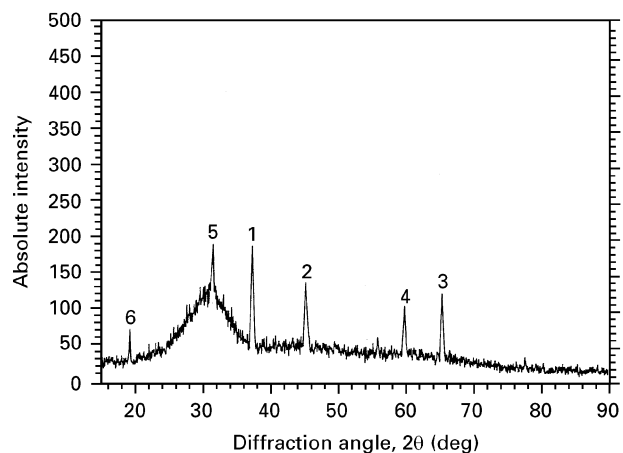
*Figure 5* X-ray diffraction pattern of the powdered CA fibre separated from the IMS CA fibre-reinforced Al 7075 alloy matrix composite processed at 927 °C for 2 h. The numbers at the top of each peak correspond to the order of peak intensity of spinel ($MgAl_2O_4$) listed in JCPDS card no 21-1152. The broad background of the pattern comes from the vitreous IMS CA fibre.

oxygen partial pressure to obtain magnesium oxidation reaction at $927\,^\circ$C is only $1.05 \times 10^{-43}$ atm. ($1.06 \times 10^{-38}$ Pa). Thus, even the high vacuum ($\sim 1.3 \times 10^{-9}$ atm; $1.31 \times 10^{-4}$ Pa) of the hot press machine has a high enough oxygen partial pressure to oxidize magnesium to MgO. The magnesium in the aluminium melt will be oxidized to MgO and continue preventing oxidation of other metals until all the magnesium is consumed in the oxidation to MgO. This MgO would then react with $Al_2O_3$ in the CA fibre to form, $MgAl_2O_4$ at the fibre–matrix interface. The chemical reaction of the spinel formation is given as [34]:

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$

$$\Delta G^\circ = -1804\ \text{kJ per mol at } 927\,^\circ\text{C} \qquad (10)$$
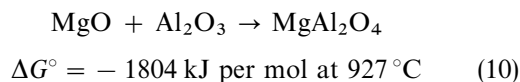
The negative free energy value in Equation 10 means that the spinel is a stable phase at $927\,^\circ$C.

Excellent interfacial wetting behaviour due to the accumulation of the alloying elements and spinel formation at the interface, was observed in the CA/Al 7075 composites processed at $927\,^\circ$C. This well-bonded interface would give greatly enhanced mechanical properties to the composites. The room and high temperature mechanical properties of the composites are presently being studied and will be reported at a future date.

## 4. Conclusions

Interfacial wetting was observed in the CA fibre-reinforced Al 7075 alloy matrix composites processed at $700\,^\circ$C. The alloying element, magnesium, significantly accumulated at the fibre–matrix interface. The wetting was most likely due to the lowering of the surface tension of the molten alloy.

The CA/Al 7075 composites processed at $927\,^\circ$C showed the formation of spinel, which was confirmed by EDS and XRD measurements. The thickness of the spinel phase region was approximately 15 µm. Excellent interfacial wetting was also observed for these composites. This is due to decreased surface tension of the liquid due to magnesium accumulation and decreased interfacial tension between the solid and liquid caused by spinel formation at the interface.

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