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The interfacial characteristic of SiCp/AZ91 magnesium matrix composites fabricated by stir casting

X. J. Wang · X. S. Hu · K. Wu · M. Y. Zheng · L. Zheng · Q. J. Zhai

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Abstract The particle/matrix interfaces in SiCp/AZ91 composite fabricated by stir casting were investigated using transmission electron microscope (TEM) equipped with ultra-thin window energy dispersive X-ray analysis (EDAX) system. Chemical reactions indeed occurred at the interfaces. According to EDAX results, the interfacial reaction products are considered to contain Al_4C_3, MgO, and Mg_2Si phases. The interfaces can be classified into three types (interfaces I, II, and III) according to morphological features of the interfaces: (1) for interface I, interfacial reaction products were in direct contact with the surface of SiCp; (2) for interface II, interfacial reaction products were not in direct contact with the surface of SiCp; (3) for interface III, interfacial reaction products were not observed at the interfaces, i.e., interface III was simply formed by the two surfaces of SiCp and matrix. $Mg_{17}Al_{12}$ and Al_8Mn_5 precipitate phases heterogeneously nucleated at the particle/matrix interfaces.

Introduction

Magnesium matrix composites possess many advantages over monolithic Mg alloys, such as high specific strength and stiffness, high elastic modulus, good creep, and wear resistances [1–14]. Adding SiCp to Mg alloys significantly improves the stiffness and strength of the alloys [1, 2, 4]. In addition, SiCp–Mg composites fabricated by stir casting are very cost effective, promising widespread applications in the aerospace, defense, and automobile industries [1, 2, 4].

In general, the properties of metal matrix composites depend on the interfaces between reinforcement and matrix [5]. An important role of the interfaces is to effectively transfer the load from matrix to reinforcements [5]. The interfacial characteristics of magnesium matrix composites are influenced by many factors [6, 13]; hence, there are many possible interfacial conditions in SiCp–Mg composites fabricated by stir casting [1, 5, 7–10, 14]. The interfacial reaction products (IRPs) have been observed at the particle/matrix interface [1, 6], for example, Mg_2Si [1, 6]. According to Luo et al. [1], there are three possible IRPs in SiCp/AZ91 composite fabricated by stir casting: (1) $Mg_2Si + MgO + Al_4C_3$; (2) $MgO + Al_4C_3$; (3) Al–C–O ternary phase. Intermetallic particles, such as $Mg_{17}Al_{12}$, Cu_5Zn_8, and $MgZn_2$, were observed at the interfaces [6, 8, 9, 12]. On the other hand, some clean and precipitate-free interfaces were also found [6, 7, 10, 14], i.e., the interfaces were simply formed by two surfaces of SiC and matrix. So far, the interfaces in SiCp–Mg composites fabricated by stir casting have not been clearly understood [6].

The particle/matrix interfaces in SiCp/AZ91 composite fabricated by stir casting were investigated in this article with special emphasis on their morphology, IRPs, and precipitate phases at the interfaces.

X. J. Wang (✉) · L. Zheng
Baosteel Structure Steel Technology United Research Center, Baoshan Iron & Steel Co. Ltd, Shanghai, People's Republic of China
e-mail: gyywxj@gmail.com

X. J. Wang · X. S. Hu · K. Wu · M. Y. Zheng
Harbin Institute of Technology, Harbin 150001, People's Republic of China

X. J. Wang · Q. J. Zhai
Shanghai University, Shanghai, People's Republic of China

Experimental procedures

α-SiCp (6H crystal structure) with average diameter of 10 μm were used for this study. After successive rinsing in 5% HF solution for 48 h to remove free silicon and silica impurities, SiCp were dried at 95 °C for 8 h, and then at 250 °C for 8 h. AZ91D alloy, containing Mg-9.3Al-0.7Zn-0.23Mn-0.02Si-0.001Cu-0.001Ni-0.002Fe-0.0015Be wt%, was employed as the matrix alloy. The 10 vol.% SiCp/AZ91 composite was fabricated by stir casting in $CO_2 + SF_6$ protective atmosphere: first, AZ91D alloy was melted at 720 °C and then cooled to 590 °C at which the matrix alloy was in semi-solid condition; SiCp which were preheated to 600 °C were quickly added into the semi-solid alloy. After adequately stirring the melt, the melt was rapidly reheated to 720 °C and held at this temperature for 5 min. Then the melt was poured into a steel mould preheated to 450 °C.

Specimens for TEM were prepared by grinding-polishing the sample to produce a foil of 50 μm thickness followed by punching 3 mm diameter disks. The disks were then thinned by ion beam. The particle/matrix interfaces in the as-cast composite were examined in detail using Philips CM-12 TEM and Philips TECNAI 20 TEM equipped with quantitative EDAX system which is able to detect light elements (including carbon and oxygen). The EDAX system can measure the local content of different elements. More than 30 interfaces were investigated using TEM.

Results and discussion

Morphologies of the interfaces

Figure 1 shows the interfaces morphologies of SiCp/AZ91 composite. According to their features, these interfaces were classified into three types (interfaces I, II, and III). Figure 2 illustrates the schematic diagrams of these three interfaces. For interface I (Fig. 1a), IRPs were directly in

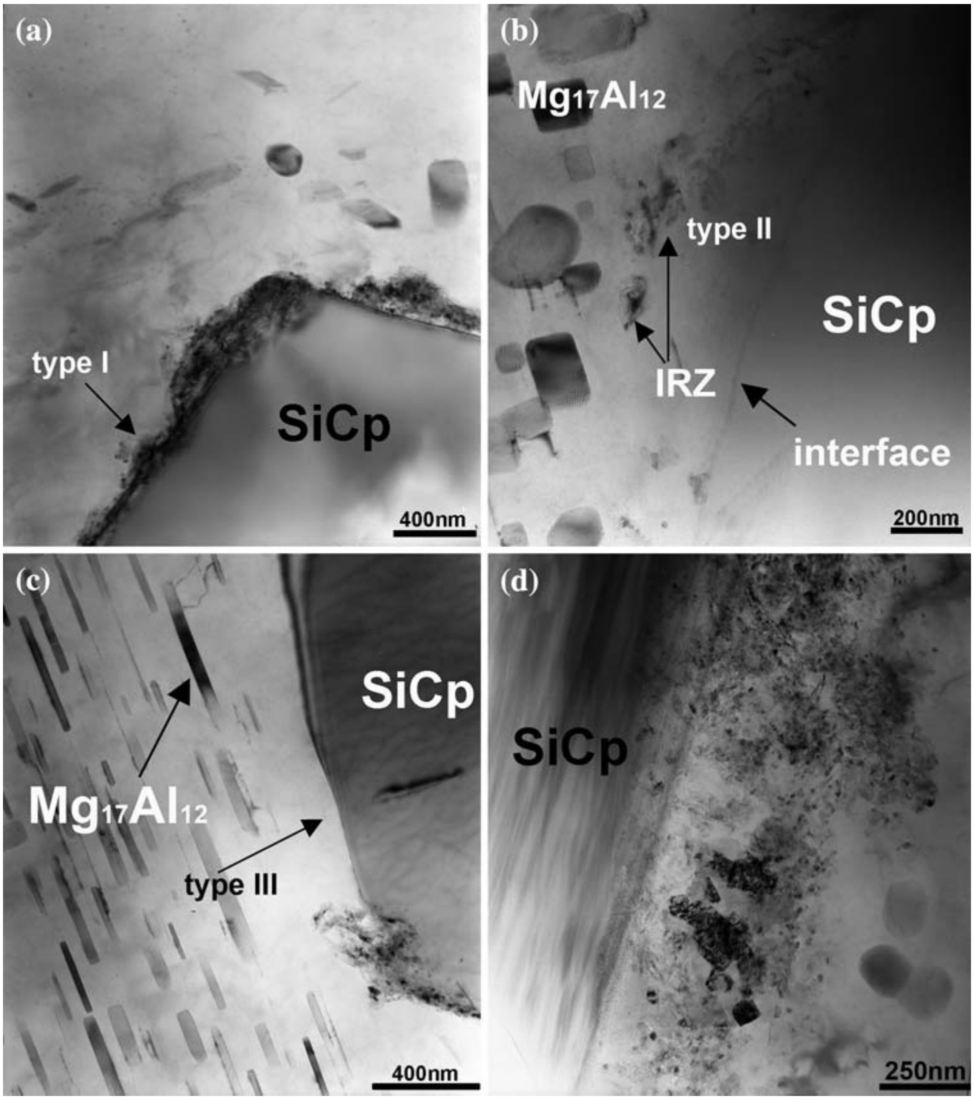


Fig. 1 TEM morphologies of the three distinct interfaces between SiCp and matrix. **a** interface I; **b** interface II; **c** interface III; **d** morphology of IRPs at interface I

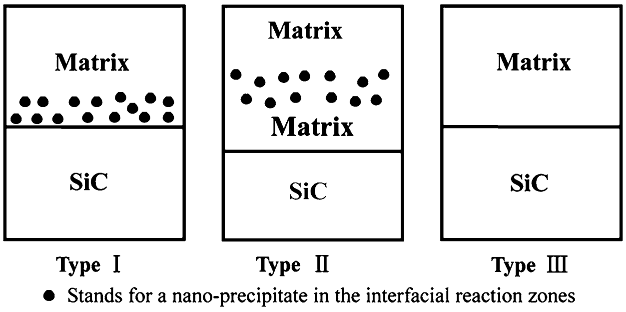
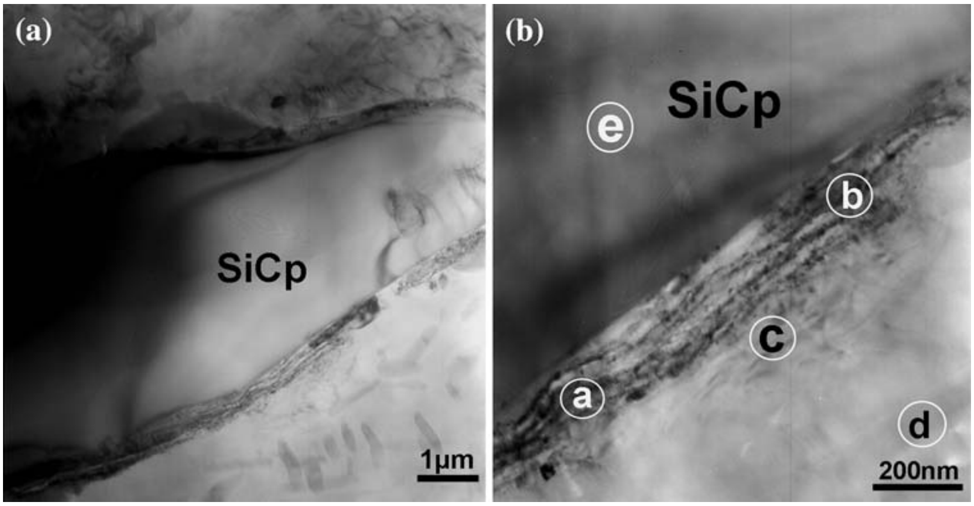


Fig. 2 Schematic representation of the three distinct interfaces

contact with SiCp surface. IRPs were made of dispersed precipitates with mean size of 10–30 nm, as shown in Fig. 1d. For interface II (Fig. 1b), interfacial reaction zone (IRZ) consisted of two distinct layers: the first layer was made of IRPs, and this layer was in direct contact with the matrix; the second layer was in direct contact with SiCp surface, which consisted of matrix that extended along SiCp surface. Thus, for interface II, IRPs were not in direct contact with SiCp surface. This type of interface was also observed in preoxidized-SiCp/pure Mg composite [11]. Interface III is very clean (Fig. 1c), i.e., IRPs are not observed at the interfaces. Interface III was simply formed by two surfaces of SiCp and the matrix alloy. However, most of the observed interfaces were covered by IRPs in the composite (Fig. 3). The reasons for existence of these three kinds of interfaces in the present composite may be the condition for stir casting. The condition for stir casting is very complicated. The friction between the melt and SiCp takes place during stirring, and there is the shearing during pouring. These factors can affect the interfacial morphology of the composite. The IRPs may break away from SiCp because of the effect of friction and shearing during stirring and pouring, resulting in the formation of the interface III. However, IRPs separating from the SiCp and SiCp are often pushed to the last solidified regions by the freezing fronts, leading to the formation of interface II [1]. If IRPs do not break away from SiCp during stirring and pouring, interface I will be formed.

From Figs. 1 and 3, interfacial reactions actually occurred at the particle/matrix interfaces. The formation of thin reaction production layers could strengthen the bonding between the reinforcement and matrix, and therefore improve the mechanical properties of composites, but the formation of thick layers is harmful to the composite performance [15, 16]. For interface I (Fig. 1a), the IRZ was less than 0.4 μm (a thin reaction layer), so that the interfacial reactions could improve the interfacial bond strength and hence enhance the mechanical properties of the composites. For interface II (Fig. 1b), Mg directly contacted with the underlying surface of SiCp [11], i.e., the interfaces between reinforcement and matrix are still mechanically bonded, and the interfacial reactions do not raise its bond strength [16]. In addition, the nonuniform and discontinuous IRPs will cause large stress concentrations at the interface, leading to premature failure of the interface. So, the interface II may be adverse to the mechanical properties. The bonding type for interface III (Fig. 1c) is the mechanical bond produced by differential contractions. The dislocation density is high due to CTE mismatches between SiCp and matrix. So, interface III can improve the mechanical properties of the composites. Although “clean” interfaces (such as interface III) in metal matrix composites are usually expected, Tham et al. have convincingly found that the interfaces with thin reaction layers (such as interface I) could improve the mechanical properties [15, 16]. According to the results of Tham et al. the bond strength of the interface III is derived from the direct electronic bonding between the atoms of the particles and matrix [15, 16]. By contrast, the bond strength of interface I is attributed to the combination of both mechanical and chemical bondings [15, 16]. The reaction

Fig. 3 **a** TEM microstructure of the interface between Mg and SiCp, **b** further magnification of (**a**) [**a**, **b**, **c**, **d** and **e** correspond to the positions analyzed by EDAX in Fig. 4a–d and e, respectively]



layer at the interface I may be “keyed-in” to not only the SiCp but also to the matrix, and the layer tends to form semicoherent interfaces and orientation relationship with the matrix and SiCp [15, 16]. The formation of a thin reaction layer along the interface changes the fracture pattern from the one involving interfacial decohesion to the one where particle breakage was dominant [15, 16]. Therefore, the bond strength of the interface I is larger than that of the interface III [16]. Hence, in terms of mechanical properties of the composites, interface I is the optimal condition.

Interfacial reactions

The IRPs were too small to be identified using selected-area diffraction pattern and micro-diffraction (Fig. 1), but EDAX was used to identify the elements which IRPs contain. Table 1 shows the element contents measured using the EDAX system in the corresponding positions in Fig. 3. Carbon was present in the matrix near to IRZ, but absent in the matrix far away from IRZ. SiCp is the only source of Carbon in SiCp/AZ91 composite, and carbon content is very high in IRZ (Table 1). So the carbon present in the matrix which is near to IRZ came from the chemical reactions between SiCp and matrix. Magnesium does not have stable carbide [17, 18], but alloying element Al in AZ91D magnesium alloy can form Al_4C_3 with Carbon [18]. SiCp is thermodynamically unstable above the melting point in aluminum alloys free of silicon, and react with Al to form Al_4C_3 [17–20]. So, Al_4C_3 phase is considered to form in the interfaces according to the following chemical reactions at 720 °C, and their related free energy changes (ΔG_{993k}) are also given [13, 17–20]:

$$2Mg_{(L)} + SiC_{(S)} \Rightarrow Mg_2Si_{(S)} + C_{(S)} \quad \Delta G_{993K} = 4.8\,\text{kJ} \tag{1}$$

$$4Al_{(L)} + 3C_{(S)} \Rightarrow Al_4C_{3(S)} \quad \Delta G_{993K} = -176.8\,\text{kJ} \tag{2}$$

$$4Al_{(L)} + 3SiC_{(S)} \Rightarrow Al_4C_{3(S)} + 3Si_{(S)} \quad \Delta G_{993K} = 18.6\,\text{kJ} \tag{3}$$

Although ΔG_{993k} values for reactions (1) and (3) are positive, they are small and refer to equilibrium conditions. The actual reaction condition is nonequilibrium. Other factors, such as temperature, activity of elements, can change the realΔG value to the favorable direction. Hence, all the reactions (1)–(3) are possible to take place. Except reactions (1) and (3), there are no other reactions that could form Al_4C_3 in the present system. Therefore, Further researches are required to confirm which reaction takes place in the present system.

Table 1 Element contents obtained by quantitative EDAX system in the corresponding positions for EDAX in Figs. 3 and 4 (Atomic wt%)

Positions	Elements				
	C	O	Mg	Al	Si
a	4.7	5.8	65.0	9.7	14.7
b	3.2	3.8	75.7	6.6	10.7
c	1.8	–	95.1	3.1	–
d	–	–	88.6	11.4	–
e	11.6	–	–	–	88.4

As shown in Table 1, O element was present in IRZ. The source of O in IRPs is considered to be SiO_2 which was formed at the surface of the SiCp [7, 18]. It should be noted that, due to its natural process of oxidizing even at room temperature, SiCp tend to be covered with a SiO_2 film [7]. SiCp used for this study were dried at 250 °C for 8 h and preheated to 600 °C before they were added to the Mg melt**.** So, SiO_2 can be formed at the surfaces of SiCp. Both Mg and Al can react with SiO_2 at high temperature, and their possible reactions are shown in reactions (4)–(7) with ΔG_{993k} [5, 6, 11–13, 18–22]. According to thermodynamic calculation results, Al_2O_3, MgO, and $MgAl_2O_4$ can be formed in Mg–Al alloy, but Mg content significantly affects their kinetics [19, 20, 23]. In SiCp-reinforced aluminum matrix composites, Mg often used to react with SiO_2 at the surface of SiCp to impede the formation of Al_4C_3 because of the high

$$SiO_{2(S)} + 2Mg_{(L)} \Rightarrow 2MgO_{(S)} + Si_{(S)} \quad \Delta G_{993K} = -255.8\,\text{kJ} \tag{4}$$

$$4Al_{(L)} + 3SiO_{2(S)} \Rightarrow 2Al_2O_{3(S)} + 3Si_{(S)} \quad \Delta G_{993K} = -528.1\,\text{kJ} \tag{5}$$

$$Mg_{(L)} + 2Al_{(L)} + 2SiO_{2(S)} \Rightarrow MgAl_2O_{4(S)} + 2Si_{(S)} \quad \Delta G_{993K} = -429\,\text{kJ} \tag{6}$$

$$4Al_{(L)} + 2MgO_{(S)} + 3SiO_{2(S)} \Rightarrow 2MgAl_2O_{4(S)} + 3Si_{(S)} \quad \Delta G_{993K} = -608.8\,\text{kJ} \tag{7}$$

$$2Mg_{(L)} + Si_{(S)} \Rightarrow Mg_2Si_{(S)} \quad \Delta G_{993K} = -60.9\,\text{kJ} \tag{8}$$

chemical affinity of Mg toward O [23]. In preoxidized, SiCp-reinforced Al–Mg composites, MgO is initially formed by the interfacial reactions between the oxidized SiCp and Mg element [19, 20]. Whether MgO transforms to the $MgAl_2O_4$ or not depends on Mg content in the matrix [19]: MgO converts to $MgAl_2O_4$ if Mg content is less than 2 wt%, because Mg content is not sufficiently great to ensure constant its availability for reaction (4); MgO formation persists if Mg content is more than 4 wt%. Moreover, chemical reaction between SiO_2 and Mg is dominant in high Mg content systems [18]. So the reactions (5)–(7) cannot occur in SiCp/AZ91 composite because Mg content is large enough to be available for reaction (4) constantly, i.e., only reaction (4) can occur in the composite, and MgO is formed at the interface. MgO is often found to be formed at the interface through reaction (4) in SiC–Mg composites [6, 11, 22]. Another source of O element is the air absorbed at the surface of SiCp, which also aids in the formation of MgO at the interfaces.

Both the reactions (3) and (4) produce Si, leading to the high content of Si in IRZ (Table 1). Since the solubility of Si in Mg is very low (1.16% at 637.6 °C), Mg_2Si is formed according to the reaction (8) in IRZ. When Si content was less than its solubility in Mg melt, reactions (3) and (4) took place at the interface; then when Si content exceeded its solubility, reaction (8) occurred simultaneously [22]. Mg_2Si has been observed at the interface in SiCp–Mg composites fabricated by stir casting [10, 18]. TEM observations have also confirmed the existence of Mg_2Si phase at the interface in a squeeze-cast SiCp/AZ91 composite [6, 13, 22]. In light of the above discussion, it can be deduced that IRPs contain Mg_2Si, MgO, and Al_4C_3. This result is consistent with Luo's speculation [1].

Precipitate phases at the interface

As shown in Fig. 4, precipitate phases nucleated at the interfaces. Electron diffraction pattern identified the precipitate in Fig. 4a as $Mg_{17}Al_{12}$ at the zone axis of $[\bar{1}11]$, as shown in Fig. 4c [8, 9]. EDAX spectrum (Fig. 4e) indicated that the phase in Fig. 4b mainly contains Al and Mn. Electron diffraction patterns further identified the phase as Al_8Mn_5 at the zone axis of [223], as shown in Fig. 4d [25, 26]. From Fig. 4a and b, it can be seen that the wetting angles between SiCp and both $Mg_{17}Al_{12}$ and Al_8Mn_5 are less than 90°, indicating that $Mg_{17}Al_{12}$ and Al_8Mn_5 wet SiCp and then heterogeneously nucleated at the SiCp surface [9]. As shown in Fig. 4b, there are many micro-defects at the surface of SiCp, such as stacking faults, dislocations, and micro-grooves, which are favorable sites for heterogeneous nucleation [9].

Inem et al. found that the $Mg(CuZn)_2$ phase heterogeneously nucleated at SiCp surface in SiCp/ZCM630 magnesium matrix composite [27, 28]. $Mg_{17}Al_{12}$ and Cu_5Zn_8 were observed to heterogeneously nucleate at the SiCp surfaces in SiCp/Mg–9Al–Zn composite fabricated by compocasting [8, 9]. There were crystallographic orientation relationships between SiCp and $Mg_{17}Al_{12}$ as well as SiCp and Cu_5Zn_8, which strongly supports the theory that $Mg_{17}Al_{12}$ and Cu_5Zn_8 can heterogeneously nucleate at SiCp surfaces [8, 9]. Al_8Mn_5 phase has been identified by TEM in the Mg–Al alloys [25, 26]. Al_8Mn_5 was not observed at the interface in SiCp/Mg–9Al–Zn composite

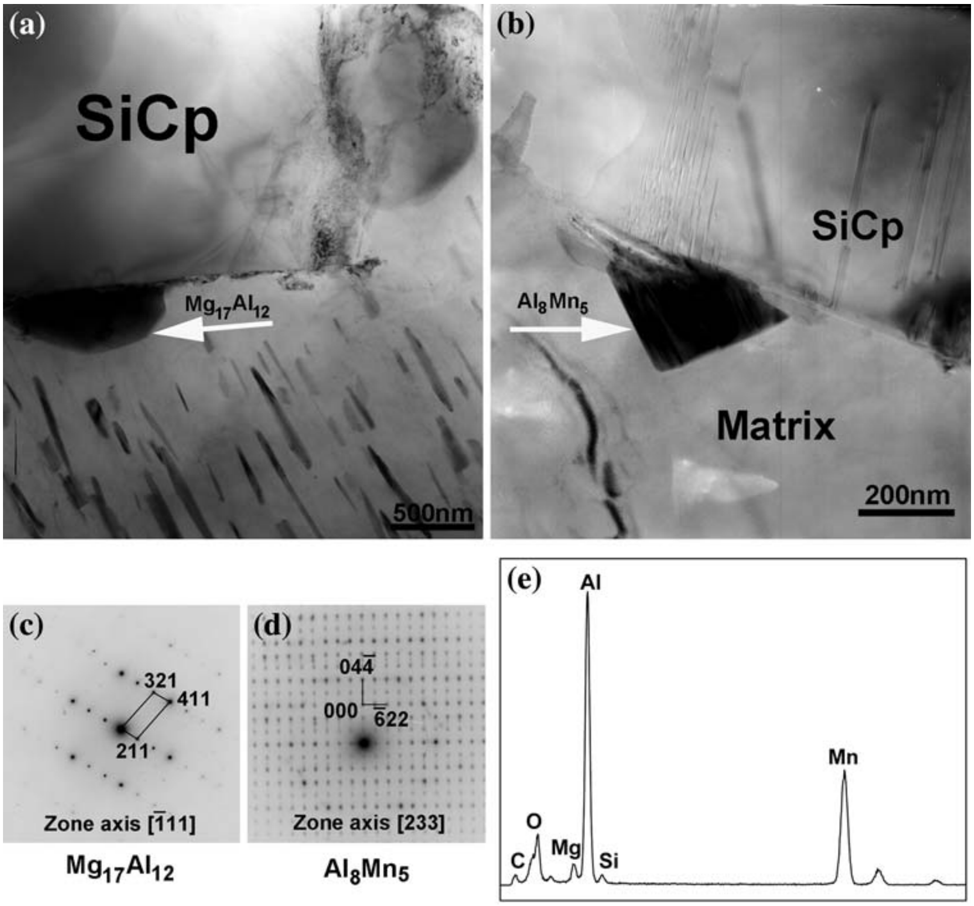


Fig. 4 Illustrating the presence of $Mg_{17}Al_{12}$ and Al_8Mn_5 at the interface. **a** $Mg_{17}Al_{12}$; **b** Al_8Mn_5; **c** and **d** are the corresponding electron diffraction patterns for $Mg_{17}Al_{12}$ and Al_8Mn_5 in (**a**) and (**b**), respectively; **e** corresponding EDAX spectrum for Al_8Mn_5 in (**b**)

by Cai et al. [8, 9], and Cu_5Zn_8 phase was not found at the interfaces of the composite in this study although the composition of Mg–9Al–Zn alloy is very similar to that of the matrix alloy under study. The low fraction of Al_8Mn_5 and Cu_5Zn_8 in Mg–Al alloys significantly reduces the possibility of their formation at the interface. In addition, the content of Cu was very low in the matrix alloy in this study, so that there may be no Cu_5Zn_8 in AZ91D. Hence, it is very normal that Cu_5Zn_8 phase is not observed at the interfaces of the composite under this study.

Conclusions

(1) The particle/matrix interfaces can be classified into three types according to their morphological features in the SiCp/AZ91 composites fabricated by stir casting;
(2) Chemical reactions indeed occurred at the interfaces in the composite, and the reaction products dispersion were about 10–30 nm;
(3) The IRPs are considered to contain Al_4C_3, MgO and Mg_2Si phases according to the EDAX results;
(4) $Mg_{17}Al_{12}$ and Al_8Mn_5 precipitate phases can heterogeneously nucleate at the particle/matrix interfaces.

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