Interfacial reaction in squeeze cast SiCw/ AZ91 composites with different binders ①

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[Abstract] The whisker/ matrix interfaces in squeeze cast SiCw/ AZ91 composites with different binders (silica binder, acid aluminum phosphate binder and without binder), were studied by transmission electron microscopy (TEM) and high resolution electron microscopy (HREM). The SiCw/ AZ91 interface is very clean in the composites with no binders. For the composites with acid aluminum phosphate binders or silica binders, there exists fine discrete interfacial reaction products MgO at the interface, and a definite orientation relationship between MgO and SiCw. The interfacial reaction products MgO is unevenly distributed at different parts of the composite ingot with silica binder, and mainly distributed to the interface at the side part of the composite cylinder. While in the SiCw/ AZ91 composite with acid aluminum phosphate binder, MgO particles are distributed evenly at the interface in almost all the parts of the composite ingot.

[Key words] SiC whisker; magnesium alloy; composites; binder; interfacial reaction

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1　INTRODUCTION

In recent years, discontinuously reinforced magnesium matrix composites are of great technological and commercial interests for use in aerospace and automotive industries. This is due to their low density, high specific strength, high specific stiffness and low coefficient of thermal expansion[1, 2].

Squeeze casting is one of the most cost-effective methods of fabricating discontinuously reinforced magnesium matrix composites[2]. It is classified into two steps: fabrication of the preform and infiltration of the preform by molten metal under pressure[2]. In order to produce near-net shape composites, the preform should have enough strength to withstand high pressure and resist cracking and deformation during squeeze casting. The use of a binder in the preform is necessary in order to stabilize the shape of the preforms and improve the strength of the preform[3]. On the other hand, the binder in the preform modifies the interface in the composite[4], which may have a significant effect on the properties of composites. Because of the high reactivity of molten Mg, Mg MMCs have a tendency to form reaction products at the interface. In comparison with aluminum matrix composites, there is very little information in the literature on the interface between matrix and reinforcer in discontinuously reinforced Mg composites[5, 6]. In the present study, SiCw/ AZ91 magnesium matrix composites are fabricated by squeeze casting technique using preforms with different binders (silica binder, acid aluminum phosphate binder and without binder). The whisker/ matrix interfaces in the composites with different binders are studied by transmission electron microscopy (TEM) and high resolution electron microscopy (HREM). Special attention is paid on the morphology, structure, distribution and the formation mechanism of the interfacial reaction products.

2　EXPERIMENTAL

The composites used in this investigation were fabricated by squeeze cast under CO_2/ SF_6 atmosphere. The matrix alloy is commercial heat-treatable AZ91 magnesium alloy (8.5%~ 9.5% Al, 0.45%~ 0.90% Zn, 0.15%~ 0.30% Mn, 0.20% Si, 0.01% Ni, balanced Mg), the reinforcer is β-SiC whisker.

The SiC whisker preforms were prepared by wet forming method. In order to eliminate the influence of inclusions at the surface of the whiskers, the whiskers were leached in the 10% HF acid for 24 h, then washed in distilled water. Two kinds of binders were selected: aluminum phosphate (Al(PO_3)$_3$) binder and silica colloid (SiO_2) binder. The mass fraction of binder in the preform was about 3%. The volume fraction of the whisker in the preforms was about 20%. Same preforms without any binder were also prepared. The preforms were dried in the air at

room temperature for 3 d, then kept at 100 ℃ for 24 h. To increase the strength of the preform, the preforms were sintered at 800 ℃ for 3 h. In squeeze casting, the mold and the preform are preheated to 500 ℃. Magnesium melt overheated to 800 ℃ was poured into the preform. The casting pressure exerted was 100 MPa.

TEM specimens were sectioned from as-cast composites. Thin foil specimens were ion milled to performation using a liquid nitrogen cold stage to prevent the heat effect during the ion milling process. The interfacial reaction products of the composite were examined in detail by JEOL200CX, JE-OL2000EX-II and JEOL3010 high resolution transmission microscopes.

3   RESULTS AND DISCUSSION

3. 1   Interfacial reaction products and their distribution

Fig. 1 shows the TEM micrograph of interface between SiC_w and AZ91 in SiC_w/AZ91 magnesium matrix composites without any binder. The interface is very flat and clean.
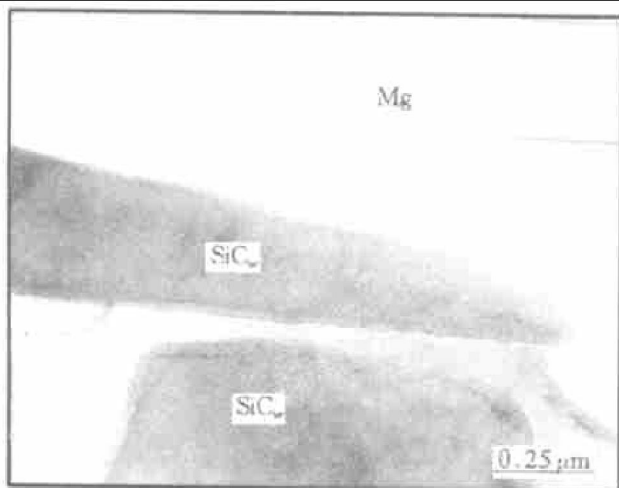

Fig. 1   TEM micrograph of interface between SiC_w and Mg in SiC_w/AZ91 composites without binder

Fig. 2 is the TEM micrographs of the interface in SiC_w/AZ91 composite with silica binder from different parts of the composite ingot. Fig. 2 show the interface in samples from central part and side part of the composite cylinder. It can be seen that there exist fine discrete interfacial phases at the interface from the side part of the composite cylinder, the size of the phase is about 20~ 50 nm. While at the center part of the composite cylinder, very few interfacial phases can be observed at the interface.

Because the interfacial particles were too small to be identified by conventional selected area diffraction or micro-diffraction, HREM was preformed to identify the interfacial phases. Fig. 3 shows an HREM image of the interfacial phase presented at the SiC_w/AZ91 interface in the composites with silica binder. Two sets of basic lattice planes with a measured spacing of 0. 24 nm (labeled (111) and ($\bar{1}11$)) and an angle of 70° were observed. The measured angle between the two lattice planes is 55°. The above-measured crystallographic parameters correspond closely to the cubic MgO (a= 0. 42 nm) phase in ⟨101⟩ direction.

The possible reaction products that can form at the interface of SiC_w/AZ91 composite are $Mg_{17}Al_{12}$, Mg_2Si, Al_4C_3, Al_2O_3, $MgAl_2O_4$ and MgO, etc. Because the Mg-O, Al-O and Si-O bonds are significantly stronger than Al-C, Al-Mg and Mg-Si bonds[7], oxide phases should form in preference to other possible compounds such as Mg_2Si, Al_4C_3 and $Mg_{17}Al_{12}$ until all of the available oxygen is consumed. Among the possible oxides, the formation free energy for MgO is lower than those of $MgAl_2O_4$ and Al_2O_3[8]. The study on thermodynamic stability of Al-Mg oxides in Al-Mg alloys[9] shows that the formation of Al_2O_3, $MgAl_2O_4$ and MgO are competitive processes, with preferential MgO formation for high Mg content. These thermodynamic considerations show that the most stable oxide in Mg MMCs is MgO. On the basis of structure and thermodynamic analysis, the
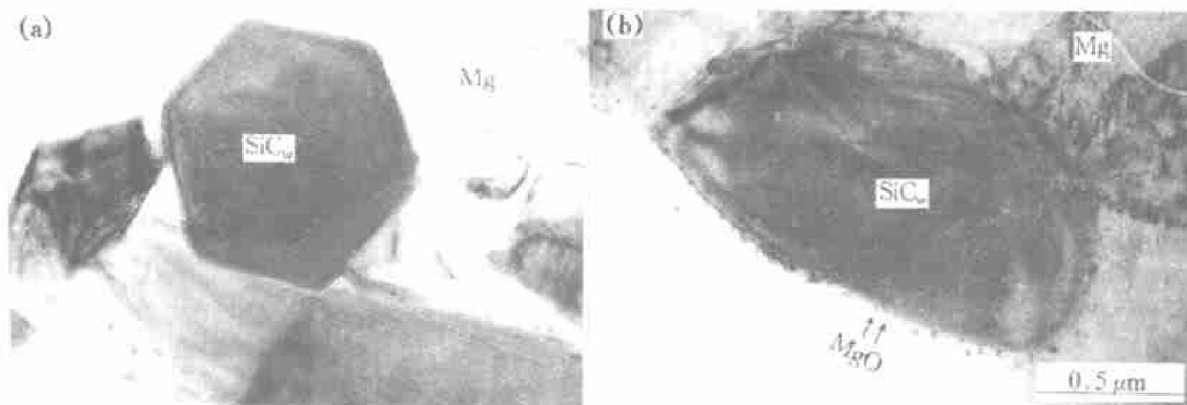

Fig. 2   TEM micrographs of SiC_w/AZ91 interface in different parts of SiC_w/AZ91 composite with silica binder
(a) —Central part of composite cylinder; (b) —Side part of composite cylinder

fine interfacial phases are identified as MgO (a = 0.42 nm).

As shown in Fig. 3, the interfacial phase (MgO) is perfectly bonded to SiC whisker without amorphous transition layer at the surface of SiC whisker. There exists a definite orientation relationship between MgO and SiC whisker, that is: $\{111\}_{MgO} \parallel \{111\}_{SiC}$, $\langle101\rangle_{MgO} \parallel \langle101\rangle_{SiC}$. The lattice matching between the two phases at the interface is good, the mismatch between the two lattice spacing, the $\{111\}$ spacing of β-SiC (0.25 nm) and the $\{111\}$ spacing of MgO (0.24 nm), is about 4.0% with the former as a standard.

From above analyses, it can be seen that MgO mainly distributes at the interface at the side part of the composite cylinder using silica binder, indicating uneven distribution of interfacial reaction products at different parts of the composite ingot.

Massive Mg$_2$Si compound was observed in the matrix near the interface in the composites using silica binder, as shown in Fig. 4. Figs. 5(a) and (b) show the SiC$_w$-AZ91 interface in samples from central part and side part of the composite cylinder with Al(PO$_3$)$_3$ binder, respectively. It can be seen that there exist fine discrete interfacial phases at the interface from different parts of the composite cylinder. The interfacial phases distribute evenly in almost all the parts of the composite.

Fig. 6 shows an HREM image of the interfacial phase in the composite with Al(PO$_3$)$_3$ binder. Two sets of basic lattice planes with a measured spacing of 0.24 nm (labeled (111) and (1$\bar{1}$1)) and an angle of 70° were also observed. From the HREM observation, the interfacial phases were also identified as MgO. Specific orientation relationship between phase MgO and SiC whisker in the composites were observed, $\{111\}_{MgO} \parallel \{111\}_{SiC}$, $\langle101\rangle_{MgO} \parallel \langle101\rangle_{SiC}$, which is the same as those in the composites with silica binder.

3.2   Mechanism of interfacial reaction
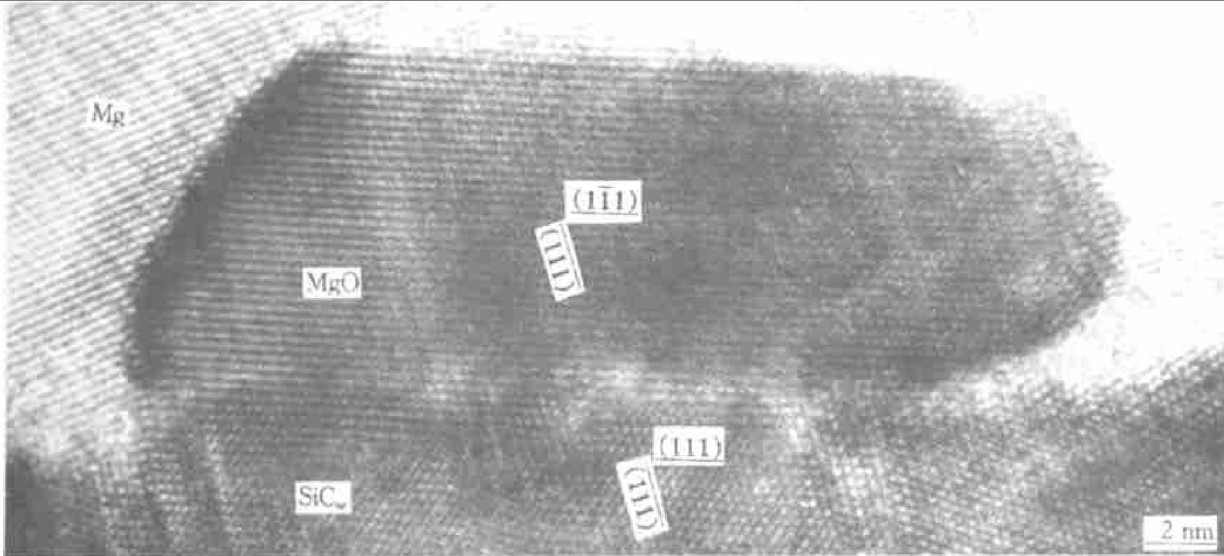
The main difference at the interface among the

Fig. 3   HREM image of interfacial reaction product MgO in SiC$_w$/ AZ91 composite with silica binder
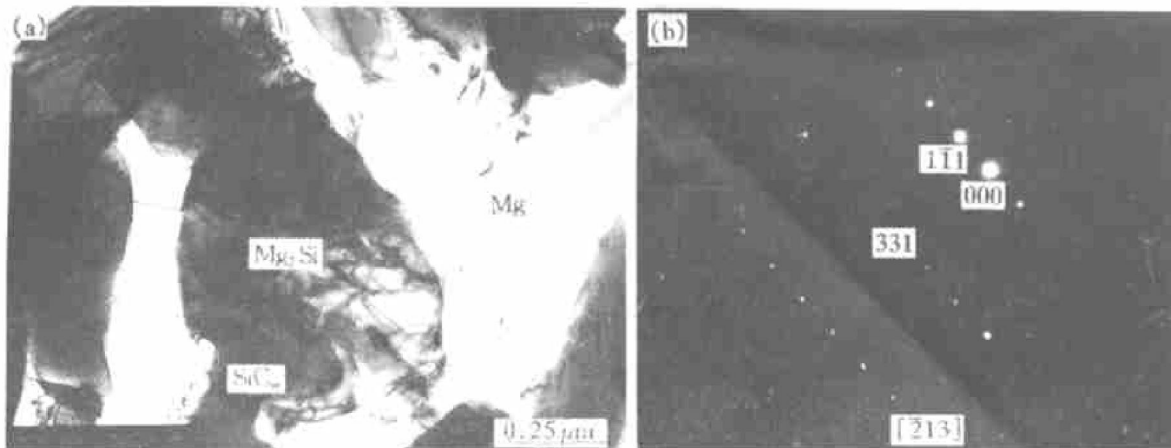(Incident beam is along [10$\bar{1}$] axis of SiC whisker)

Fig. 4   TEM micrographs illustrating massive Mg$_2$Si in matrix near interface of composites with silica binder
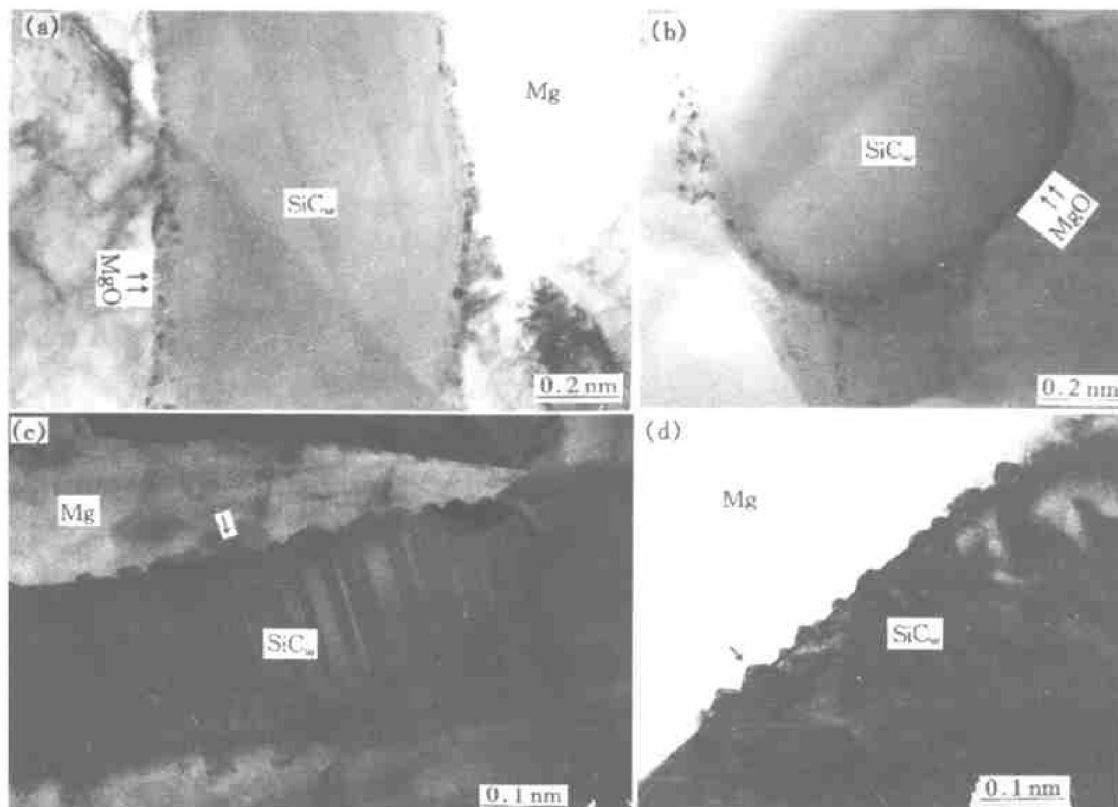(a) —Morphology; (b) —SADP of Mg$_2$Si

Fig. 5　Micrographs of $SiC_w/AZ91$ interface in different parts of $SiC_w/AZ91$ composites with $Al(PO_3)_3$ binder
(a) and (c) —Central part of composite cylinder; (b) and (d) —Side part of composite cylinder
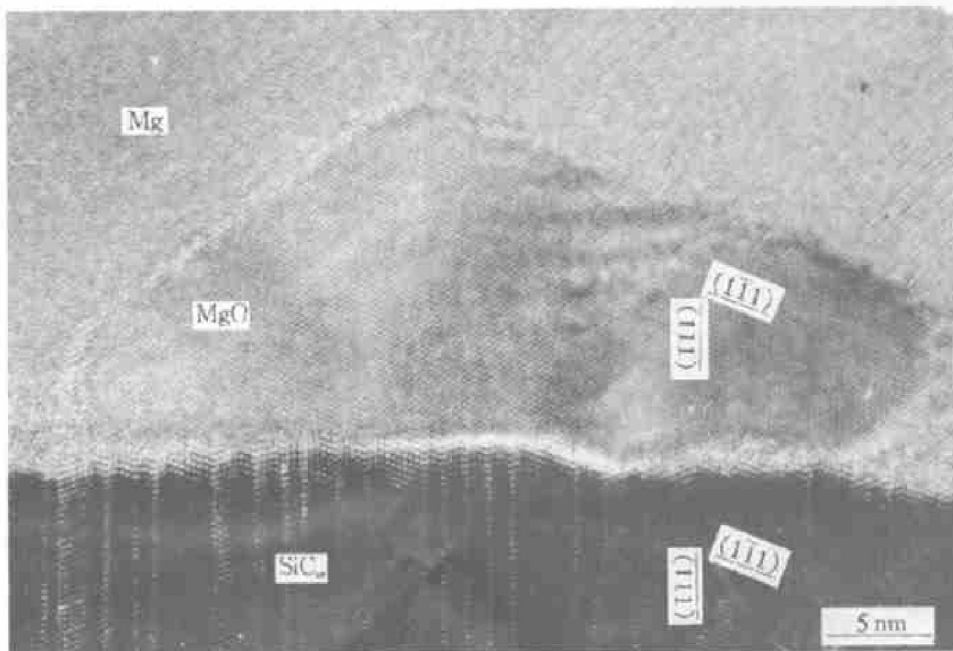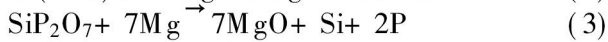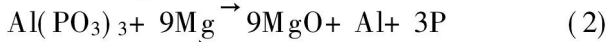

Fig. 6　HREM image of interfacial reaction product MgO in $SiC_w/AZ91$ composite with $Al(PO_3)_3$ binder
(Viewed from $[10\bar{1}]$ axis of SiC whisker)

three kinds of composites is the amount and distribution of the interfacial phase MgO.

　　The MgO probably originated from: 1) the reduction of the binders by the molten Mg, as Eqns. (1) and (2); 2) the reaction between oxide, such as $SiO_2^{[4]}$ (with silica binder) and $SiP_2O_7^{[4]}$ (with acid aluminum phosphate binder) formed as a layer at the

SiC_w surface during the sintering of preform, and molten Mg, as illustrated in Eqns. (1) and (3); 3) the oxide film formed at the melt Mg surface, or the reaction between the molten Mg and oxygen (in the form of atom and molecular) entrapped in the preform prior to the infiltration of preform, as Eqn. (4), these oxides were broken up and dispersed during

processing, then left at the fiber/matrix interface.

$$SiO_2 + 2Mg \rightarrow 2MgO + Si \qquad (1)$$
$$Al(PO_3)_3 + 9Mg \rightarrow 9MgO + Al + 3P \qquad (2)$$
$$SiP_2O_7 + 7Mg \rightarrow 7MgO + Si + 2P \qquad (3)$$
$$Mg + O \ (or \ O_2) \rightarrow MgO \qquad (4)$$

It should be noted that the SiC whisker was HF-treated in our work, the oxide layer and impurities were removed from the surface of SiC whisker.

Because there exists no fine interfacial phases at the composites without any binder, it can be thought that the amount of oxides formed at the surface of SiC$_w$ during sintering of preform and oxygen entrapped in the preform prior to the melt infiltration were much less. In addition, because the melting and pouring of Mg alloy were operated under protective atmosphere, the molten Mg were very clean with less MgO in the molten Mg. Furthermore, the preform can act as a filter to prevent MgO particles in the molten Mg from entering into the composites during infiltration[8].

From the above analyses, it can be thought that the interfacial reaction products MgO originated mainly from the reaction between silica binder and Mg in the SiC$_w$/AZ91 composites using silica binder, as shown in Eqn. (1). This was further confirmed by the presence of the massive Mg$_2$Si near the interface. In the composites with Al(PO$_3$)$_3$ binder, the reaction products MgO are mainly formed by the reaction between Al(PO$_3$)$_3$ binder and Mg, as outlined in Eqn. (2). Because no SiP$_2$O$_7$ was detected in the SiC$_w$ preform by XRD analysis in our work[8], Eqn. (3) can be neglected.

Because the interfacial reaction products were originated from the reactions between the binders and molten Mg, the different distribution of interfacial reaction products MgO in different kinds of composites was resulted from the different distribution of binders in the original preforms[8]. The silica binders dispersed unevenly in the SiC$_w$ preforms with silica binders, most of the binders distributed on the side part of the preform. While the Al(PO$_3$)$_3$ binders distributed evenly in the SiC whisker preform with Al(PO$_3$)$_3$ binder, which lead to the high compressive strength of preform[8]. The uneven distributions of silica binders in the C fiber preform[4], Al$_2$O$_3$ short fiber preform[10,11], and SiC whisker preform[4], have been observed by other researchers. The uniform distributions of Al(PO$_3$)$_3$ binders in the SiC whisker preform[4], C fiber preform[4] and Al$_2$O$_3$ short fiber preform[11] have also been observed. The mechanism of the different distribution of the two kinds of binders in the preforms is not fully understood, which may be related to the different bonding power of the two kinds of binders.

4 CONCLUSIONS

1) There exists fine discrete interfacial reaction products MgO at the interface of the composites with acid phosphate binders or silica binders. Interfacial reaction products MgO are resulted from the reaction between the binders and the molten Mg.

2) There exists a definite orientation relationship between MgO and SiC$_w$.

3) The distribution of interfacial reaction products MgO is uneven at different parts of the composite ingot with silica binder. While in the SiC$_w$/AZ91 composite with acid aluminum phosphate binder, interfacial reaction products MgO are distributed evenly in almost all the parts of the composite ingot.

4) The different distribution of the interfacial reaction products MgO is resulted from the different distribution of the binders in the preforms using different binders.

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