Interfacial reaction between the oxidized SiC particles and Al-Mg alloys

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Abstract **The interfacial reactions of oxidized SiC particles reinforced Al-Mg matrix composites were investigated by the field emission-scanning electron microscopy (FE-SEM), TEM and X-ray diffraction. It was found that the nanoscale MgO forms initially due to the interfacial reaction, then whether it reacts with molten Al continuously or not depends on the content of Mg in the matrix and its covering densification at the surface of particles. When there is not enough Mg in the matrix for the formation of dense MgO layer, MgO will transform into $MgAl_2O_4$ crystal owing to the continuous reaction with SiO_2 and molten Al. When dense MgO layer forms at the surface of the particles due to the affluence of Mg for the initial reaction, it will protect the inner SiC from the attack of molten Al. However, the reaction products of both MgO and $MgAl_2O_4$ are thermo-stable phases at the surface of the particles under high temperature. The results clarify the interfacial reaction route and they are of great value to the control of the interfacial reactions and their interfacial design of the composites.**

Keywords: oxidized SiC particle, Al-Mg matrix composite, interfacial reaction, FE-SEM, nanoscale MgO, $MgAl_2O_4$.

SiC reinforced Al-matrix composite is one of the materials that have been frequently studied. It has wide potential applications. However, it is a little bit difficult to control the interfacial reaction between SiC and Al at elevated temperature during its fabrication, no matter what kind of SiC such as fiber, whisker and particle is used as a reinforcement substance in the Al-matrix composite. The reaction product Al_4C_3 is an unstable phase in some environments such as water and methanol. Meanwhile the formation of Al_4C_3 will degrade the surface of the SiC and results in composites with poor mechanical properties. Thus, three primary techniques have been adopted for controlling the deleterious interfacial reactions as follows: i) Utility of some aluminum alloys containing proper silicon, such as A356, A357 and A359. On the basis of the reaction equation $4Al + 3SiC \rightarrow Al_4C_3 + 3Si$, an addition of Si into the aluminum alloy matrix can suppress the interfacial reaction[1−4]. ii) Control of processing parameters; for example, the control of fabrication temperature and holding time can limit the extent of the interfacial reaction and affect the reaction dynamics[5]. iii) Reinforcement surface modification; for instance, coating, electroplating or passive oxidation have been successful to some extent in preventing the deleterious interfacial reaction and enhancing the materials wettabilities[6,7]. The passive oxidation of SiC particles is known as one of the most simple and easy approaches. However, the matrix of aluminum-based composites consists of not only aluminum itself but also the reactive element Mg, such as 2xxx and 6xxx Al alloys series. Mg is prone to react with oxidized layer SiO_2 at surface of SiC particles. Zhong et al.[8] characterized the interfacial reaction products of oxidized-SiCp/Al-Mg (5083Al) composite by X-ray diffraction and TEM, from which the crystal boundaries of the MgO (or $MgAl_2O_4$) reaction products were believed to be the diffusion channels during the interfacial reaction. Gu et al.[12] found a concentration of aluminum within the interface of oxidized SiC by parallel electron energy loss spectrometer (PEELS), the result indicated that the reaction between the oxidized layer of SiC particles and pure aluminum could take place. There are a few of reports on the interfacial characteristics and their corresponding reaction products in oxidized SiCp/Al-Mg matrix composites[8−15]. However, from the available reports it is not clear how the interfacial reaction takes place in the oxidized-SiCp/Al-Mg composite systematically, as their reaction routes are important to the composite engineering application. The purposes of the present work are to characterize the microstructure evolution between Mg contained aluminum matrix and oxidized SiC particles as reinforcement for the composites and to illustrate the interfacial reaction in order to get the significant data for the control of the interfacial reactions by means of FE-SEM, X-ray diffraction and TEM.

1 Experimental

(i) Preparation of the composites. SiC particles used in the study were the hexagonal α-SiC (6H) with an average size of 5 μm. The oxidation of SiC particles was carried out at 1100°C for two or six hours using alumina crucibles in an electric-resistance furnace in dry air at an atmospheric pressure. After oxidation, these oxidized powders were pestled, ground artificially, and sifted using 70 μm grid sifting screen at room temperature in order to make them distribute well during the composites fabrication. In order to facilitate an easier penetration of the molten Al-alloys (2014Al (Al-3.9%Cu-0.54%Si-0.32%-Mg-0.56%Mn, weight percent), Al-2.0%Mg, Al-4.0%Mg and Al-8.0%Mg) through the particles, the tool steel die with an inner diameter of 25 mm, wall thickness of 30 mm, and length of 100 mm loaded with the particles were preheated to a temperature of 600℃. The Al alloys melted in the graphite crucibles using an electric-resistance furnace was poured into the SiC particles kept within the die at 750℃ and pressurized up to arounnd 100 MPa using a hydraulic press. The specimens were cut from the composites with Struers diamond cutting machine and then measurements and analysis were carried out. The volume percent of particles was about 48%—50% via image analysis

(ii) Specimen preparation for the surface and interface analysis. In order to identify the reaction products easily, the composite samples were heat-treated at elevated temperatures such as 550℃, 600℃ and 620℃ for 2 to 5 h in an electric-resistance furnace and 610℃ for 5—20 min in a salt-bath furnace. The ceramic reinforcements with the interfacial reaction products were then extracted from the composites using the electrochemical dissolution method. The principle of this method is to remove all conductive materials from the composite, thus non-conductive materials can remain. The electrolyte used was 33 Vol% HNO_3 + 67 Vol% H_2O. The voltage and current used for the extraction were 10—15 DC Volts and 5—10 Amp, respectively. The detailed 3-dimensional morphologies and interfacial reaction products were examined by FE-SEM (Hitachi S-4200). The interfacial reaction products covering the surface of the extracted particles were identified by X-ray diffraction, which scanned at a rate of 0.01° per 4 s in a step scan mode using monochromated Cu Kα radiation. The detailed interfacial microstructures of the composites were further observed by TEM (JEOL 2010).

2 Results and analysis

Fig. 1 shows the X-ray diffraction profiles of the particles electrochemically extracted from 2014Al, Al-2Mg and Al-8Mg matrix composites reinforced with oxidized SiC particles (SiCp) at 1100℃ for 6 h, which were heat-treated at 600℃ or 610℃ for 2 h. The peaks showed the interfacial reaction product silicon clearly at 2θ = 28.48—28.52°, especially the second composite (Al-2Mg matrix composite); there was also the other peak (2θ = 31.36°) showing the existence of $MgAl_2O_4$. The phenomena show that the interfacial reaction can take place at the above elevated temperatures.

Figs. 2(a)—(c) show the FE-SEM micrographs of the particles extracted from 2014Al composite reinforced with SiC particles oxidized at 1100℃ for 2 h. The nanoscale MgO forms and distributes well at the surface of the particles extracted from the composite heat-treated at 560℃ for 2 h, as shown in fig. 2(a). When the composite was heat-treated at 600℃ for 2 h, the initial reaction product, nanoscale MgO transforms into an octahedral $MgAl_2O_4$ crystal at the surface of the extracted particles, as shown in figs. 2(b) and (c).

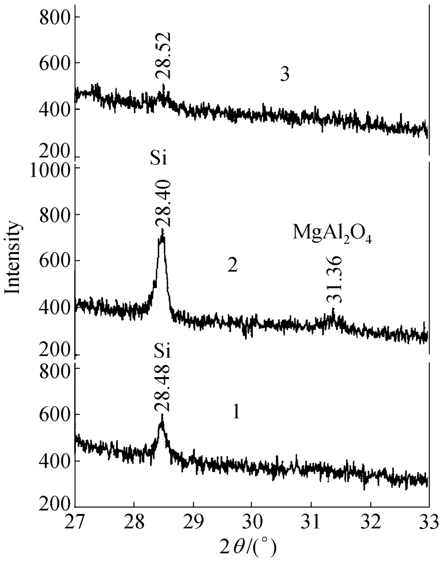

Fig. 1. X-ray diffraction profiles for extracted particles from oxidized-SiCp/Al-Mg matrix composites after being heat-treated at elevated temperatures. 1. Prticles extracted from the oxidized-SiCp/2014Al composite, heat-treated at 610℃ for 2 h. 2. Particles extracted from the oxidized-SiCp/Al-2Mg composite, heat-treated at 600℃ for 2 h. 3. Particles extracted from the oxidized-SiCp/Al-8Mg composite, heat-treated at 610℃ for 2 h.

Figs. 3(a)—(d) show the FE-SEM micrographs of the particles extracted from the oxidized SiC particles reinforced Al-2.0%Mg composite heat-treated at 610℃ for 5, 10 and 20 min in the salt-bath furnace, respectively. It can be found that the nanoscale MgO forms in an average size of 20—30 nm. Anyhow, it will transform into the $MgAl_2O_4$ crystal which is in an average size of 150—200 nm and well-distributed at the surface of the particles extracted from Al-2%Mg composite, as shown in fig. 3(c) and (d).

Figs. 4(a) and (b) show the FE-SEM micrographs of the particles extracted from the oxidized SiC particle reinforced Al-matrix composites with Al-4.0%Mg and Al-8.0%Mg (weight percent) as matrix, heat-treated at 550℃ for 5 h (4(a)) and 610℃ for 2 h (4(b)). It can be found that the dense nanoscale MgO in an average size of about 20—30 nm forms at surface of the extracted particles.

Fig. 5 shows the fine microstructure of the interface between the oxidized SiC particles and Al-2%Mg alloy in the composite heat-treated at 610℃ for 2 h, observed by high resolution TEM (HRTEM). The $MgAl_2O_4$ crystal forms at the surface of vitreous SiO_2 and grows toward the surface of inner SiC.

3 Discussion

As shown in fig. 1, the silicon peak appearance (2θ= 28.48—28.52°) at the X-ray diffraction profiles for the particles extracted from the composites with 2014Al,

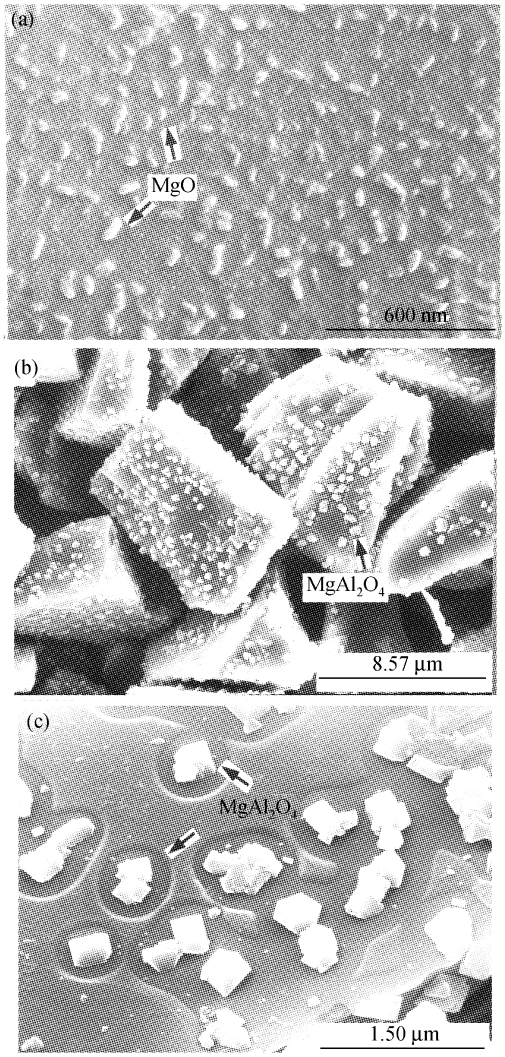

Fig. 2. FE-SEM micrographs showing the surface of particles extracted from the 2014Al matrix composites reinforced with SiC particles oxidized at 1100℃ for 2 h. (a) Heat-treated at 560℃ for 2 h; (b) and (c) heat-treated at 600℃ for 2 h.

Al-2Mg and Al-8Mg as matrix can result from the reaction equations as follows:

$$2Mg + SiO_2 = MgO + Si \tag{1}$$

$$4Al + SiO_2 = Al_2O_3 + Si \tag{2}$$

$$Mg + 2Al + 2SiO_2 = MgAl_2O_4 + Si \tag{3}$$

$$2MgO + 4Al + 3SiO_2 = 2MgAl_2O_4 + 3Si \tag{4}$$

$$MgO + Al_2O_3 = MgAl_2O_4 \tag{5}$$

$$3Mg + 4Al_2O_3 = 3MgAl_2O_4 + 2Al \tag{6}$$

By comparing the morphologies of the particles extracted from these composites with the above aluminum matrix containing different amounts of Mg, it can be found that MgO forms initially in a nanoscale size, as shown in figs. 2(a), 3(a) and (b) and 4(a) and (b), no matter how much Mg is contained in the matrix. This is explained from the fact that Mg is an active element, usually segregating at the interface of the composites. Why and how can the nanoscale MgO transform into the octahedral $MgAl_2O_4$ crystal as shown in figs. 2(b) and (c) and 3(c) and (d)? The nanoscale MgO may transform into an $MgAl_2O_4$ crystal according to the above eqs. (4)—(6). If its transformation takes place as reactions of eqs. (5) and (6), Al_2O_3 must be the initial reaction product at the surface of particles; that is to say, only eq. (2) can supply Al_2O_3 for the following reaction. According to our observation, Al_2O_3 was not found at the surface of extracted particles. Therefore, the surbsequent transformation of $MgAl_2O_4$ from MgO takes palce as eq. (4). When there is not enough Mg in the matrix, the nanoscale MgO cannot cover the surface of particles well, thus it can not protect the inner oxidized-layer from the attack of molten Al and it can also react with the oxidized layer SiO_2 and the molten Al and turn into the $MgAl_2O_4$ crystal. When the content of Mg in the aluminum matrix is more than 4.0%, the nanoscale MgO covers densely the surface of the oxidized SiC particles. The results exhibit that the addition of Mg to the matrix can control the interfacial reaction product and protect the particles from the attack of molten Al at elevated temperature.

Meanwhile, compared with the $MgAl_2O_4$ formed in the composites with 2014Al and Al-2%Mg as matrix, the number of $MgAl_2O_4$ crystals formed at the surface of particles in 2014Al matrix composite is less than that in Al-2%Mg composite, but the size in the former composite is larger than that of the latter under the same conditions. According to the micrographs of figs. 2(b) and (c) and 3(c) and (d), the average size of $MgAl_2O_4$ in the 2014Al composite is about 400—500 nm, while it is about 150—200 nm at the surface of particles extracted from the latter one. This phenomenon shows that the amount of reaction product, either MgO or $MgAl_2O_4$, depends on the number of nuclei present at the initial reaction stage. The more and better the nuclei cover at the surface of the oxidized SiC particles, the less the size is. Thus, according to these results, an addition of Mg to the matrix can be used to control the reaction products and their sizes.

4 Conclusions

The observation of the interfacial reaction products between the oxidized SiC particles and aluminum alloy containing different amounts of Mg shows that nanoscale MgO can form initially. The formation of $MgAl_2O_4$ from MgO depends on the content of Mg in the matrix. When there is not enough Mg in the matrix for the formation of dense MgO layer, the nanoscale MgO will transform into $MgAl_2O_4$ crystal due to the subsequent reaction with SiO_2 and molten Al as the following equations:

$$2Mg + SiO_2 = 2MgO + Si$$

$$4Al + 2MgO + 3SiO_2 = 2MgAl_2O_4 + 3Si$$

When the dense MgO layer forms at the surface of the particles due to the affluent of Mg for the initial reaction, the MgO layer will protect the inner SiC from the

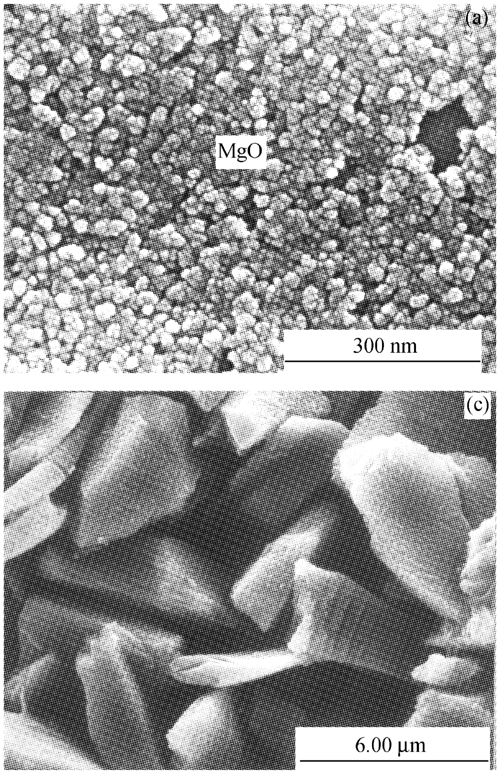

Fig. 3. FE-SEM micrographs showing the interfacial reaction products at the surface of the particles extracted from Al-2Mg composite, heat-treated at 610℃ for 5 ((a)), 10 ((b)) and 20 min ((c) and (d)) in a salt bath furnace.

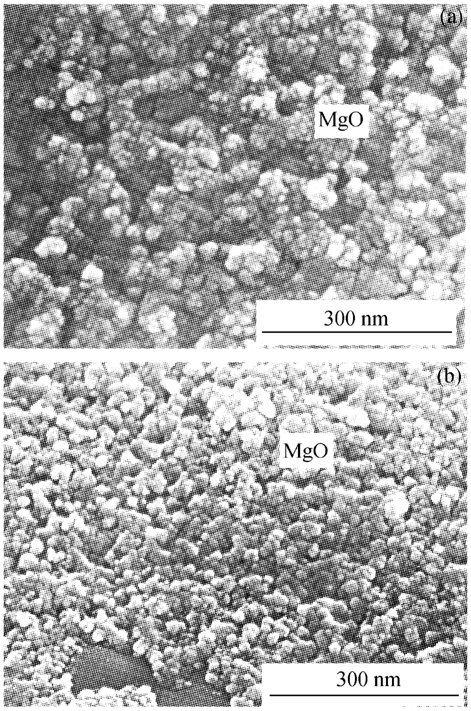

Fig. 4. FE-SEM micrographs showing the surface of the particles extracted from the composites reinforced with SiC oxidized at 1100℃ for 6 h. (a) Al-4%Mg matrix composite heat-treated at 550℃ for 5 h. (b) Al-8%Mg matrix composite heat-treated at 610℃ for 2 h.

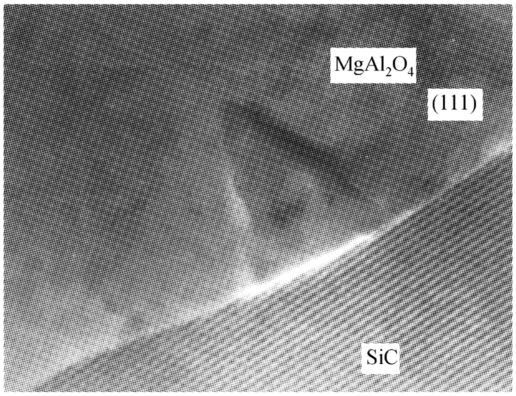

Fig. 5. HRTEM images showing the fine microstructure of the interfacial reaction in Al-2Mg matrix composite reinforced with SiC particles oxidized at 1100℃ for 6 h.

attack of the molten Al. The results clarify the routes of their interfacial reactions.

The amounts and sizes of the reaction products such as nanoscale MgO and $MgAl_2O_4$ depend on the content of Mg in the matrix and their densification at the surface of particles. When Mg content is more than 4% by weight, the nanoscale MgO with an average size of 20—30 nm forms at the surface of oxidzied SiC particles; with less than 2% by weight Mg content, the nanoscale MgO will transform into $MgAl_2O_4$ continuously. The reaction products MgO and $MgAl_2O_4$ are both thermo-stable phases at the surface of particles at high temperature. The results are of great value to the control of these interfacial reactions and their interfacial design of the composites.

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