[Article ID] 1003- 6326(2002)05- 0899- 05

Interfacial microstructure of 20% SO_2/Al matrix composites reinforced with in situ formation ceramic phases ①

SUN Ji-bing(孙继兵)[1], LI Guo-bin(李国彬)[1], CUI Chun-xiang(崔春翔)[1], AN Ya-qin(安雅琴)[2]
LIU Shi-min(刘世敏)[1], LI Jie-min(李杰民)[1], HAN Rui-ping(韩瑞平)[1]
(1. School of Materials Science and Engineering,
Hebei University of Technology, Tianjin 300132, China;
(2. Command Department, Institute of Military Traffic, Tianjin 300161, China)

[Abstract] Al matrix composites reinforced with in situ ceramic phases by adding 20% SiO_2 were fabricated by powder metallurgy process. The interfacial microstructure of the composites was studied by means of SEM and HREM. It was shown that the ceramic phases mainly composed of spinel $MgAl_2O_4$ are formed in situ in the original SiO_2 particle and the size of small $MgAl_2O_4$ crystallites is about dozens of nanometers, which can adjacent to Al and Si. MgO could not found in original SiO_2 particle but a little in matrix and may exist with Si, Mg_2Si and Al. Si is mostly distributed in matrix and forms some segregation zones. The size of Mg_2Si is about 50~ 100 nm and can usually be seen in the matrix.

[Key words] in situ composites; interface; microstructure
[CLC number] TQ 343 **[Document code]** A

1 INTRODUCTION

Owing to behaving outstanding properties such as low density, high specific strength, excellent wear resistance, etc, the particles reinforced aluminum matrix composites attracted many attention[1~ 9]. Different interface structures, which was much more important for the properties of the metal matrix composites, would be formed by the reactions of particle reinforcement and the matrix during fabrication of the composites[10]. So the interface play a significant role for the properties of the composites, and how to describe interfaces precisely and fully was one of the most important foundations for understanding the nature of interface and further controlling and improving the properties of the composites[11]. The authors fore study found that[12], when adding SiO_2 particles into Al-Mg matrix and sintering at 620 ℃ for 30 min, some ceramics mainly including $MgAl_2O_4$ spinel (about 90%, according to the kinetics of SiO_2 and Al-Mg measured by XRD and TEM) were found on SiO_2 particles according to main reaction: $Al+\frac{1}{2}Mg+SiO_2=\frac{1}{2}MgAl_2O_4+Si$, and the rest phases were Si, Mg_2Si, the matrix Al and a little MgO, so Al matrix composites reinforced with in situ formation ceramics mainly including $MgAl_2O_4$ were fabricated, and this type of composites behaved much more excellent wear resistance, in this work the interfacial microstructure of Al matrix composites reinforced with in situ formation ceramics mainly including $MgAl_2O_4$ is examined by means of scanning transmission electron microscope(SEM), transmission electron microscope(TEM) and high-resolution electron microscopy (HREM).

2 EXPERIMENTAL

The composition of the composites is listed in Table 1. Powder metallurgy process was used for fabrication of the composites and the procedure was as follows: charge mixture → mixing → pressing → sintering → analyzing interfacial microstructure. The compressive stress for pressing was 865 MPa, the samples were sintered at 620 ℃ for 30 min under N_2 atmosphere. Scanning transmission electron microscope and energy dispersive X-ray spectroscopy were used to examine the microstructure and the distribution of elements of the composites, then, the composite specimen was spark-eroded to slice of 0.5 mm, reduced mechanically to 40~ 50 μm, and dug into disc of 3 mm in diameter by ultrasonic drilling machine, finally, the TEM foils were prepared by ion thinning machine (model 600CD2F). Transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) were performed on the foils to observe the microstructure of the composites.

3 RESULTS AND DISCUSSION

3.1 SEM micrographs

Table 1 Chemical compositions of composites

Raw material	Content/%	Powder size/μm
Pure magnesium powder	10	< 147
Quartz(99.8% SiO_2)	20	38~ 61
Copper powder	2	43~ 74
Pure aluminum powder	Bal.	43~ 74

The reinforcing particles keep the original shape

① [Received date] 2001- 09- 25; [Accepted date] 2002- 01- 04

(Fig. 1). Fig. 1(a), (b) show the SEM micrographs (BSE), some new phases (showing different color: dark, bright, gray and light gray) could be seen and the EDS spectra of different areas are shown in Figs. 1(c) ~ (h). Figs. 1(c), (d), (e), (f), (g) respectively correspond to A, B, C, D, E areas in Fig. 1 (a), and Fig. 1(h) corresponds to An area in Fig. 1 (b). An area (dark block) in Fig. 1(a) is the original SiO_2 particle which retains the original shape. B and C (bright) areas may be Al and Mg_2Si according to EDS spectra (Fig. 1(d) and (e)), which are similar and both consist Mg, Si, Al and trace O. The EDS spectra of D and E (gray color) areas are uniform, including only one element, which is Al matrix. Compared with Fig. 1(a), An area (light gray rectangle) in Fig. 1(b) is clearly identified as Si by the EDS spectrum (Fig. 1(h)). So SiO_2 must be reacted with the matrix Al-Mg, furthermore, Si is rejected into the matrix and reacted with Mg to form Mg_2Si and the excess Si is singly retained.

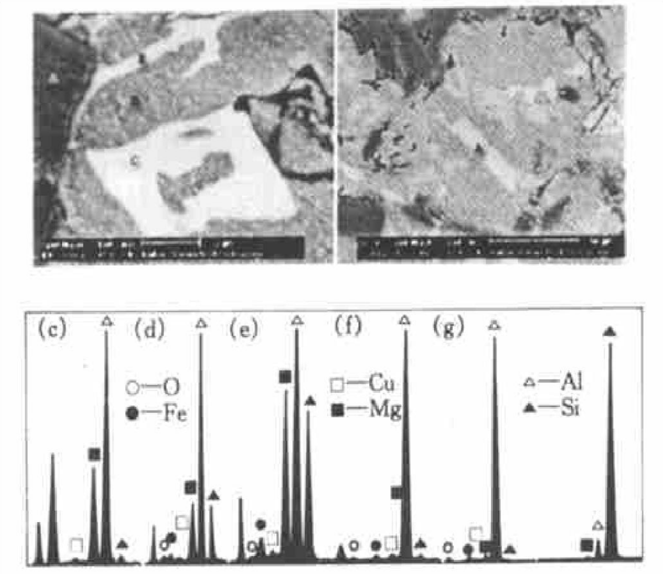

Fig. 1 SEM micrographs (BSE) show distribution and interface of phases of composites
(a), (b) are micrographs; (c), (d), (e), (f) and (g) correspond to EDS spectra of A, B, C, D, E areas in (a) respectively; and (h) corresponds to EDS spectrum of A area in (b)

3.2 TEM and HREM micrographs

3.2.1 Interfaces of $MgO/Mg_2Si/Si$

Fig. 2 shows the TEM micrographs, diffraction patterns and EDS spectra for MgO, Mg_2Si and Si of the composites. Layer structure composed of dark and bright strips near Al matrix and Si, as shown in Fig. 2(a). This verified Fig. 1(b) that Si is in excess compared with Mg, so that both Mg_2Si and Si can be presented in the matrix. At higher magnification (Fig. 2(b)), layer structure is much more clear, but, the diffraction patterns (Fig. 2(c)) of the layer structure is more complex, which are identified as Si, Mg_2Si, MgO and Al matrix, and the zone axes of Si and Mg_2Si diffraction patterns are [237] and [289], respectively. The diffraction pattern between the interface of Si and layer structure is shown in Fig. 2(d) and the zone axis of Si is [147]. The results obtained by EDS spectra on dark strips (Fig. 2(e)) and bright strips (Fig. 2(f)) show that Al peaks are both high, which suggest that these new phases distribute in the aluminum matrix, in addition, bright strips are rich in Mg, O elements, and no Si; however, dark strips are rich in Si and Mg elements, and no O element, furthermore, the content of Si is more than that of Mg. So it can be concluded that bright strips phase may be MgO and dark strips phase may be Si and Mg_2Si, and the first type of interface, $Si+Mg_2Si/MgO/Si+Mg_2Si$, is formed, namely, $Si+Mg_2Si$ eutectoid exists between MgO bright strips, in addition, Si and Mg_2Si may be separated, which results in forming the second type of interface, $Si/Mg_2Si/MgO/Mg_2Si/Si$. Two type models are shown in Fig. 3.

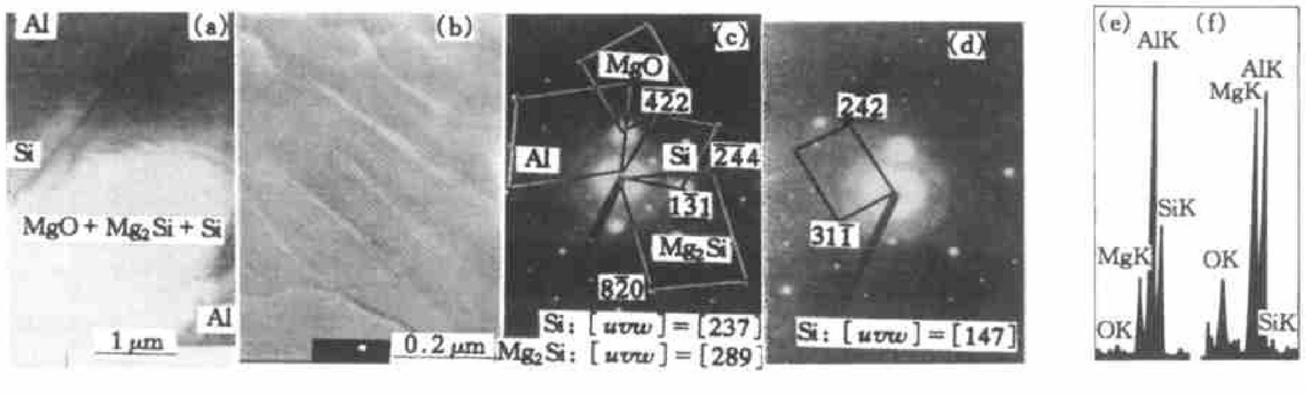

Fig. 2 TEM micrograph (a), magnified image of layer structure (b) correspond to (a), electron diffraction pattern of layer structure (c), electron diffraction pattern of Si (d) correspond to (a), and EDS spectra of dark strip (e) and bright strip (f) of layer structure correspond to (b)

3.2.2 Interface of $MgAl_2O_4$/Al matrix

TEM micrograph, diffraction patterns and HREM image for $MgAl_2O_4$(original SiO_2)/Al of the composites are shown in Fig. 4. The interface outline between the original SiO_2 and Al matrix is clearly seen and the small crystallites of $MgAl_2O_4$ spinel about dozens of nanometer in diameter were formed in-situ in the original SiO_2 particles (Fig. 4(a)) mainly according to reaction

$$Al + \frac{1}{2}Mg + SiO_2 = \frac{1}{2}MgAl_2O_4 + Si \qquad (1)$$

as shown in Fig. 1(a) the dark particles retain the original SiO_2 shape. $MgAl_2O_4$ spinel belongs to a FCC structure and $a = 0.832$ nm, the (111) reflection of $MgAl_2O_4$ has a d spacing of 4.66 Å. As we all know, MgO and $MgAl_2O_4$ have very similar structure and thus, their diffraction patterns are similar (shown in Fig. 4(b) and Fig. 5(c)) except for (111) reflection. For MgO, the latter reflection has the same spacing as the (311) reflection of $MgAl_2O_4$, but (111) reflection of $MgAl_2O_4$ is distinct from any other MgO reflections. According to the diffraction pattern in Fig. 4(b) and the HREM in Fig. 4(c) for (111) reflection of $MgAl_2O_4$, it can be concluded that $MgAl_2O_4$ crystallites have formed in situ on the original particles.

3.2.3 Interface of Mg_2Si/Al

According to reaction (1) and the study on the dynamics of reaction between Al-Mg and SiO_2, it can be concluded: (1) Al and Mg would diffuse into SiO_2 particles and form in situ $MgAl_2O_4$ spinel, simultaneously, (2) Si was rejected into Al-Mg matrix and Mg_2Si was formed in the matrix by reaction

$$Si + 2Mg = Mg_2Si \qquad (2)$$

A smooth and clear interface of Mg_2Si/Al is shown in Fig. 5(a) and no harmful phases are found. At higher magnification in Fig. 5(b), the small Mg_2Si crystallites with 50~100 nanometer diameter are clearly seen and distribute equally in irregular block. The diffraction pattern and results of Mg_2Si are shown in Fig. 5(c).

3.2.4 Interface of $MgAl_2O_4$/Si/$MgAl_2O_4$ and Si/Al

Different types of Si are found as shown in Fig. 6(a) and (d), in which Fig. 6(a) shows the interface of $MgAl_2O_4$/Si/$MgAl_2O_4$. An area in Fig. 6(a) is $MgAl_2O_4$, the original SiO_2 particle, whose diffraction pattern is same to Fig. 4(b). Si distributes in the matrix and in the middle of enforced particles and the zone axis of Si diffraction pattern (Fig. 6(b)) is [112]. The model of $MgAl_2O_4$/Si/$MgAl_2O_4$ is shown in Fig. 6(c). This result is in accordance with the analysis of Fig. 1(b), except forming Mg_2Si, the excess Si distributes singly, in addition, this result is similar to SUI et al[13]. The next type of interface, Si/Al, is shown in Fig. 6(d) and the zone axis of Si in diffraction pattern (Fig. 6(e)) is [123]. In Fig. 6(d), the dispersive Si particles can be seen with a magnifying glass.

3.3 Analysis and discussion

According to the results of interface analyses mentioned above, it can be concluded that small crystallites $MgAl_2O_4$ will form in-situ by reaction (1) and several types of interfaces among $MgAl_2O_4$, MgO, Si, Mg_2Si and Al were seen. These interfaces formed by element diffusion and reactions, but no harmful

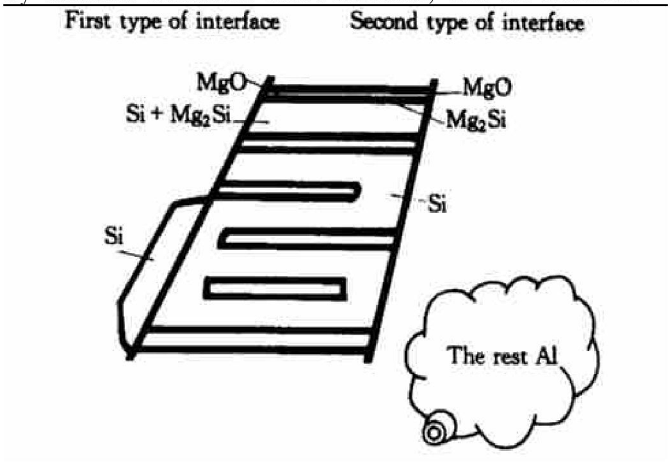

Fig. 3 Interface model of Si-Mg_2Si-MgO/Al

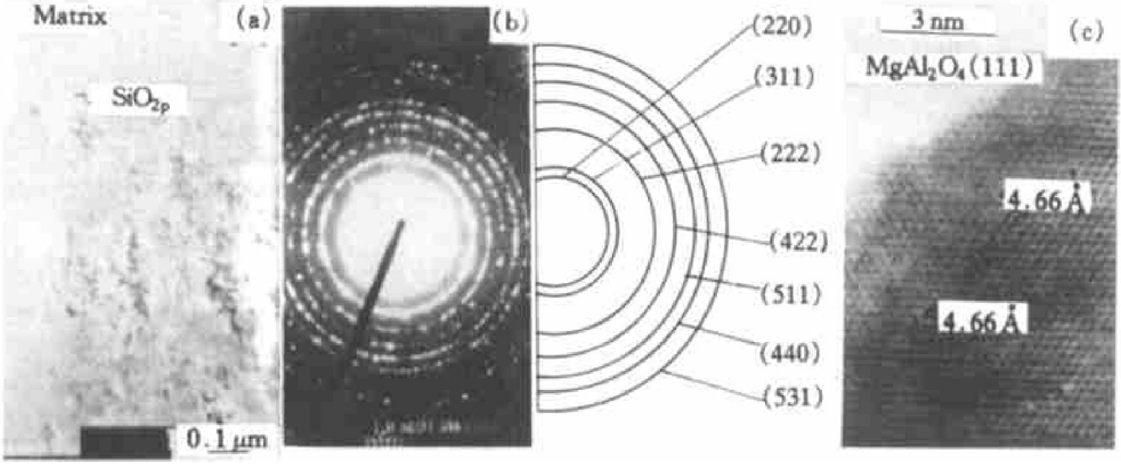

Fig. 4 TEM micrograph (a), electron diffraction pattern (b) and HREM (c) of $MgAl_2O_4$

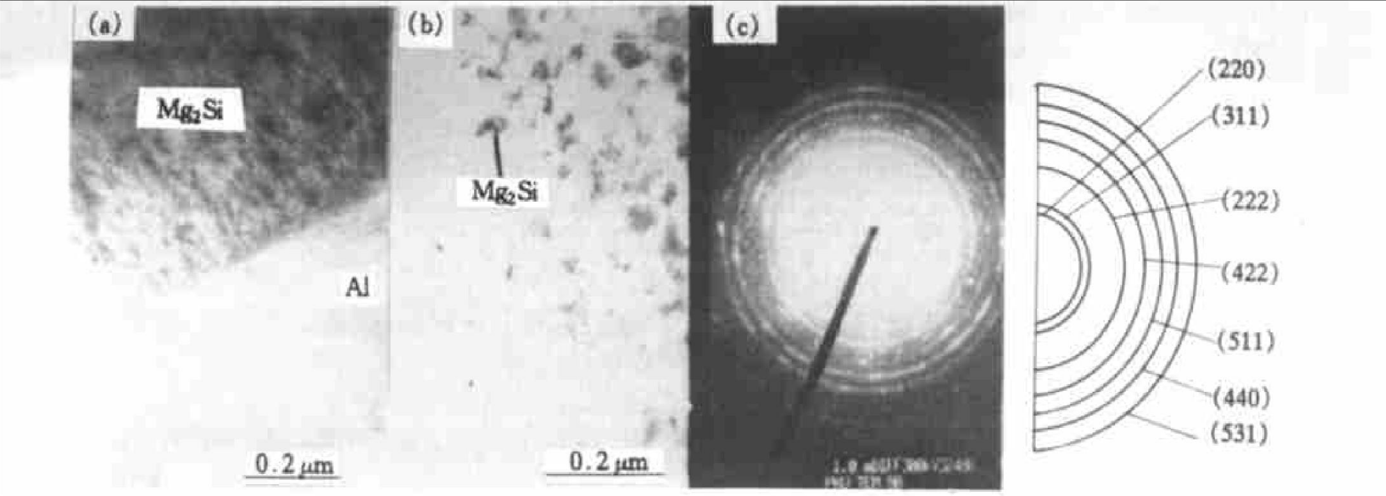

Fig. 5 Interface of Mg_2Si/Al (a), magnified image (b) of Mg_2Si diffraction pattern of Mg_2Si (c)

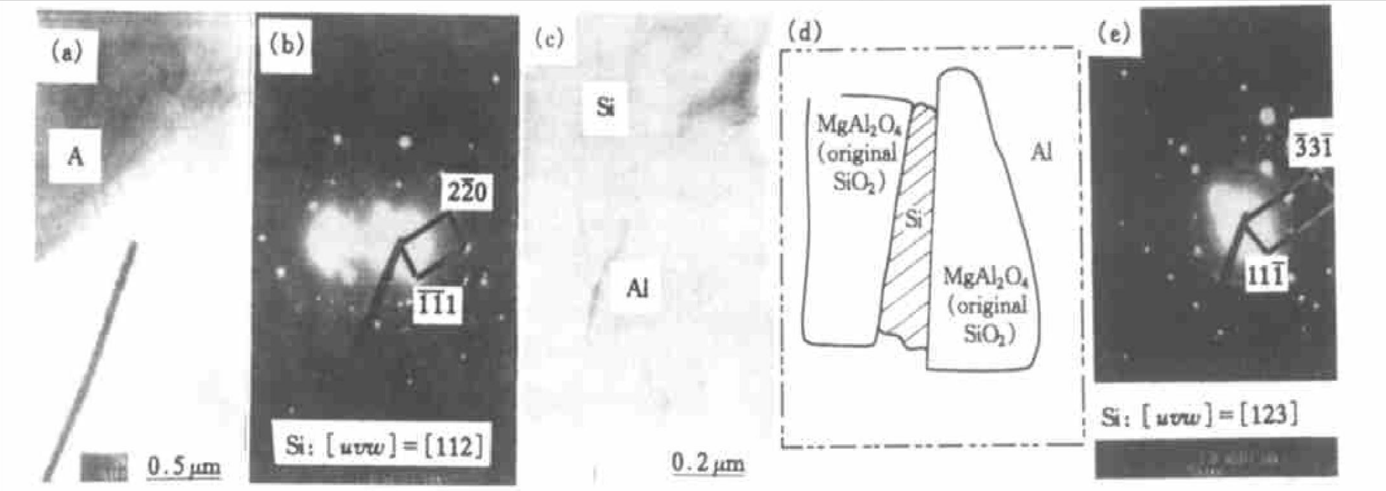

Fig. 6 Interface of $MgAl_2O_4$/Si/$MgAl_2O_4$(a), electron diffraction pattern of Si between two original SiO_2 particles (b), interface model of $MgAl_2O_4$/Si/$MgAl_2O_4$(c), interface of Si/Al (e), diffraction pattern of Si/Al (d)

phases were found. All $MgAl_2O_4$ were observed in original SiO_2 particles, none in matrix, however, MgO was not found in particles, a little in matrix and only existed with Si, Mg_2Si and Al. Mg_2Si can form Mg_2Si/Al by reaction(2) in the matrix and may exist with Si, MgO and Al. Excess Si was seen respectively by SEM and TEM. MEI et al[14] reported that the interface resultant was none but $MgAl_2O_4$ and only Mg_2Si was found in matrix when studying on the 20% SiO_2/Al-4% Mg composites under 800 ℃. No MgO and Si were mentioned in their papers, moreover, none resultant was found below 700 ℃ and SiO_2 did not fully take part in reaction(1) under 800 ℃, which is much more different with our results that all SiO_2 particles (below 0.3 mm in diameter) were reacted when sintered under 620 ℃ for 30 min.

4 CONCLUSIONS

1) The small crystallites $MgAl_2O_4$ can form in-situ by the reaction of Al, Mg and SiO_2; the rest reaction products are MgO, Mg_2Si and Si.

2) MgO is not found in particles and only a little in matrix, moreover, the interfaces of MgO/Mg_2Si/Si or MgO/Mg_2Si+ Si can form.

3) All $MgAl_2O_4$ are observed in original SiO_2 particles, none in matrix. The small crystallites $MgAl_2O_4$ are about dozens of nanometer in diameter and can form the smooth and clean interface with Al or Si.

4) Excessive rejected Si from SiO_2 distributes singly in the matrix and can co-exist with MgO, Mg_2Si and Al.

5) Mg_2Si distributes in the matrix and the small crystallites Mg_2Si are about 50~ 100 nm in size.

[REFERENCES]

[1] LING Xing-zhu, XU Zhen-min. Structure and property of particle reinforced aluminium matrix composites [J]. The Chinese Journal of Nonferrous Metals, (in Chi-

nese), 1998, 8(2): 286– 290.

[2] MA Zong-yi, LU Yu-xiong, BI Jing. Fabrication and properties of in-situ Al_2O_3 and TiB_2 particles reinforced Al-Cu alloys composites [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1999, 9(1): 101–105.

[3] FAN Jian-zhong, YAO Zhong-kai, DU Shan-yi. Interfacial structure of SiCp/Al composites made by powder metallurgy [J]. The Chinese Journal of Nonferrous Metals, 1998, 8(1): 20– 23.

[4] Liu W, Köster U. Microstructures and properties of interpenetrating alumina/aluminium composites made by reaction of SiO_2 glass preforms with molten aluminium [J]. Materials Science and Engineering, 1996, 210A: 1 – 7.

[5] Ribes H, Suéry M, L'espérance G, et al. Microscopic examination of the interface region in 6061-Al/SiC composites reinforced with as-received and oxidized SiC particles [J]. Metall Trans A, 1990, 21(9): 2489– 2496.

[6] Zhong W M, L'espérance G, Suéry M. Interfacial reactions in Al-Mg (5083) Al_2O_3(p) composites during fabrication and remelting [J]. Metallurgical and Materials, 1995, 26A: 2625– 2635.

[7] ZHANG Shou-kui, WANG Dan-hong. In-situ preparation of cast Al-Al_2O_3 particle composite by addition of SiO_2[J]. J Mater Sci Technol, 1997, 13: 179– 80.

[8] ZHANG Jian, WANG Yu-qing, YANG Bing, et al. Effects of Si content on the microstructure and an in situ Al/Mg_2Si composite [J]. J Mater Res, 1999, 14(1): 68 – 74.

[9] Wang Ning, Wang Zhirui, Weatherly G C. Formation of magnesium aluminate (Spinel) in cast SiC particulate-reinforced Al (A356) metal matrix composites [J]. Metall Trans A, 1992, 23A: 1423– 1430.

[10] ZHANG Guo-ding. Interface problem of metal matrix composites [J]. Chinese Journal of Materials Research, 1997, 11(6): 649– 656.

[11] MEI Zhi, GU Ming-yuan, WU Ren-jie. Characterization of metal matrix composite interface and its advances [J]. Materials Science & Engineering, 1999, 14(3): 1 – 5.

[12] SUN Ji-bing, LI Guo-bin, AN Ya-qin, et al. Study on Al matrix composites reinforced by in-situ formation ceramics phases[J]. Journal of Hebei University of Technology, (in Chinese), 2000, 29(6): 93– 96.

[13] MEI Zhi, CUI Kun, GU Ming-yuan, et al. Study on the interfacial reaction of liquid stirred cast SiCp and SiO_2(p) reinforced Al-4% Mg composites [J]. Acta Materiae Compositae Sinica, 1998, 15(4): 43– 47.

[14] SUI Xian-dong, LUO Cheng-ping, OUYANG Liu-zhang, et al. "Interfacial Si" behavior in cast SiCp/Al-Si composites [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1999, 9(Suppl. 1): 20– 24.

(Edited by HUANG Jin-song)