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High temperature DSC study on interfacial reaction of aluminum borate whisker reinforced aluminum alloys①

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Abstract: Aluminum borate ($9Al_2O_32B_2O_3$) whisker reinforced ZL109 alloy and pure Al were fabricated by squeeze casting technique. By means of high temperature DSC, the interfacial reaction of these composites was studied in detail, and reaction products were analyzed by using XRD and SEM. It was shown that in the $9Al_2O_32B_2O_{3,w}$/Al composites, the pure Al can react with the $9Al_2O_32B_2O_3$ whisker and the critical temperature is 756 ℃. In the composites, the chemical reaction occurs at the interface and the product is identified to be spinel $MgAl_2O_4$. The magnesium is one of main factors that cause the interfacial reaction, oxygen promotes the interfacial reaction, but Cu, Ni elements in ZL109 alloy don't take part in the interfacial reaction. The temperature is another main factors that cause interfacial reaction. When the temperature is higher than 690 ℃, both Mg and Al elements can react with the whisker. When the temperature ranges from 449 ℃ to 690 ℃, only Mg element reacts with the whisker. T_6 heat treatment causes more serious interfacial reaction.

Key words: composites; aluminum borate whisker; interfacial reaction **Document code**: A

1 INTRODUCTION

Recently, the ceramic whisker reinforced metals have been paid more attention because these composites possess excellent behaviors such as low density, good strength, high specific stiffness and specific modulus, excellent fatigue-resistance and wear-resistance, and then whisker/metal composites become an important branch of metal matrix composites. The early developed whisker reinforced metal are mainly expensive SiC and Si_3N_4 series composites, so that the wide applications of this kind of composites are limited. At present, a state of art whisker—aluminum borate whisker, has been developed on the base of improved production technique. The aluminum borate whisker has excellent physical properties and the outstanding advantage is that its commercial price only ranges from 1/10 to 1/20 of SiC and Si_3N_4 whiskers. The aluminum-based composites with aluminum borate whisker have excellent strength and modulus which are in the same range as that of SiC_w/Al or $Si_3N_{4,w}$/Al composites, but their thermal expansion is lower and abrasion resistance is better[1~5]. It makes this new kind of composites to get wider applications in the future. Interfacial reaction between matrix alloys and reinforcers have considerably strong influence on interfacial microstructure and mechanical properties of the composites[6~8]. In this kind of composites, interfacial reaction is very serious, but the excessive reaction causes whiskers surface degradation and reduction[2,3,9,10]. It is necessary to study the interfacial reaction on aluminum borate whisker reinforced aluminum-based composites for their properties improving, interface design, and application developing.

2 EXPERIMENTAL

2.1 Materials

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Aluminum borate whisker (NICHIAS Co. Ltd., Japan) was employed as reinforcer in this study. The crystal structure of aluminum borate whisker($AlBO_w$) is of orthorhombic, similar to that of Al_2O_3-SiO_2 series substance such as andalusite, sillimanite and mullite. Its space group is $A2_1$ am and physical properties are listed in Table 1[3,11]. The commercial ZL109 alloy and pure Al were used as the matrices, the chemical composition of the alloy is listed in Table 2.

Table 1 Material properties of $AlBO_w$

Property	Value
Average length/μm	10～30
Average diameter/μm	0.5～1.0
Density/(g·cm^{-3})	2.93
Tensile strength/GPa	8
Elastic modulus/GPa	400
Mohs hardness	7
Thermal expansion coefficient/℃$^{-1}$	4.8

Table 2 Chemical compositions of ZL109 alloy (%)

Si	Mg	Cu	Ni	Al
11.0～13.0	0.8～1.3	0.5～1.5	0.8～1.5	Balance

2.2 Preparation of composites

Aluminum borate whisker reinforced aluminum alloys were produced by squeeze casting process. The whisker preform was preheated at 750 ℃, then inseted in a casting die of 300 ℃. The molten aluminum of 750 ℃ was poured into the die and a high squeeze pressure of 100 MPa was applied immediately, then aluminum melt was infiltrated into the whisker preform, solidified and cooled down under the pressure for 30 s. Finally the $AlBO_w$ reinforced aluminum composites were separated from the die.

In order to investigate the effect of heat treatment on interfacial reaction of the composites, the T_6 treatment were done under the conditions as follows: 530 ℃, 3 h for solid solution, and quenching at 75 ℃, then 160 ℃, 24 h for aging treatment.

2.3 Analysis methods

A Netzsch DSC-404 high temperature thermal analyzer was used to measure heat behaviors on interfacial reaction of the composites in detail. The AlBO whisker was etched from the composites by using the chemical dissolution method and the chemical constitution as well as phase identification of reaction products were analyzed by X-ray diffraction analysis (Simens D-500 type X-ray diffractometer, copper target). The morphological changes of the $AlBO_w$ were observed in a Philips XL-30 scanning electron microscope.

3 RESULTS AND DISCUSION

3.1 Interfacial reaction of $AlBO_w$/Al composites

As reported in Ref. [3,9], no any reaction product was found at the interface of $AlBO_w$/Al composites by means of SEM, TEM and HREM. It is generally accepted that pure Al can not react with AlBO whisker in the composites. In the present study, the reactivity between pure Al and $AlBO_w$ was checked based on the thermodynamic calculation (data based on Ref. [12]) and the Gibbs free energy change associated with the reaction (1) is

$$4Al + 9Al_2O_3 2B_2O_3 \rightarrow 11\gamma\text{-}Al_2O_3 + 4B \quad (1)$$

$$\Delta G \approx (0.15T - 500.94)\text{kJ/mol} < 0$$

$$(25\,℃ \leqslant T \leqslant 827\,℃).$$

Besides, the Gibbs function of formation of oxidization reactions are calculated between B, Al, Mg, Cu, Ni and O_2 (O_2 is the per mole) and the curve of ΔG—T was obtained (as shown in Fig. 1). It is known from Fig. 1 that B element can be reduced from its oxide by Al element, which means the chemical reaction maybe exist in the composites according to Eqn. (1).

When reaction occurs at the $AlBO_w$/Al matrix interface, interfacial reaction products formed as a result of the reaction will alter the chemical composition of the matrix alloy, resulting in changes in thermal responses of the matrix alloy. In this study, the thermal behaviors of the as-cast $AlBO_w$/Al composites were measured by high temperature DSC. The specimen was heated from 200 ℃ to 950 ℃ under protection of Ar gas, and the heating rate was 10 ℃/min. The

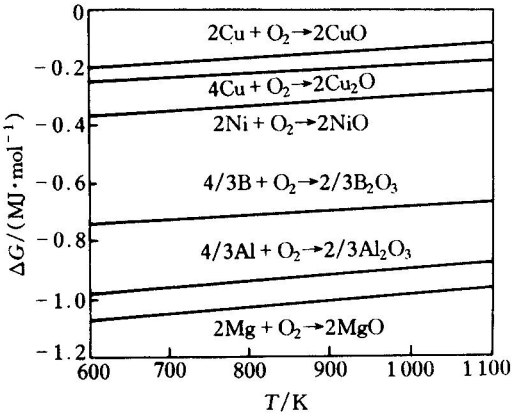

Fig.1 Temperature dependence of Gibbs function of formation of oxidization reaction

curve of the DSC analysis is shown as Fig.2, the endothermal peak during 641 ~ 687 ℃ corresponds to the melt of the Al matrix and the exothermic peak during 756 ~ 908 ℃ should be caused by the chemical reaction in the composites.

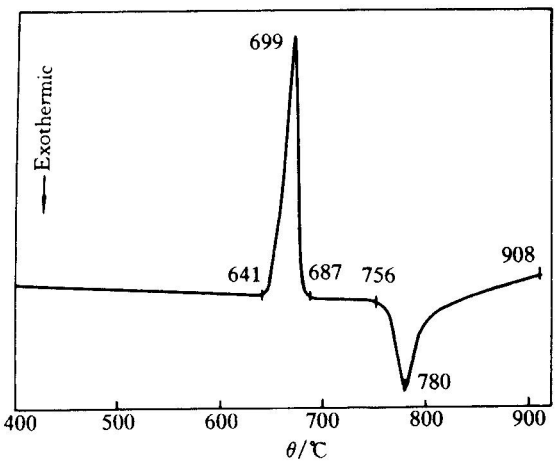

Fig.2 DSC curve of as-cast $AlBO_w$/Al composites

It can be seen from Fig.3(b) by XRD that AlBO whisker is stable after heat treatment at 850 ℃ for 12 h, which indicates the chemical reaction does not related to the discomposition of AlBO whisker. In order to inquire this reaction, the $AlBO_w$/Al composites specimens were treated by T_6 process and at 780 ℃ for 15 min, respectively. When the size and volume fraction of the interfacial reaction products in the composites are relatively small, it is difficult to determine the exact phase identification by means of X-ray diffraction. In order to overcome this problem, $AlBO_w$ as well as the interfacial reaction products were extracted from the composites, so that X-ray diffraction was performed on the extracted whisker. Based on XRD results (Fig.3(c) and (d)), it is known that no new substance was found in T_6-treated composites. But the composites which treated at 780 ℃ for 15 min obviously showed that the pure Al should be reacted with the whisker since γ-Al_2O_3 was formed. In other words, the interfacial reaction Eqn.(1) can take place when the temperature is higher than 756 ℃. In this work, no interfacial reaction is found in the $AlBO_w$/Al composites because the maximum processing temperature is 750 ℃.

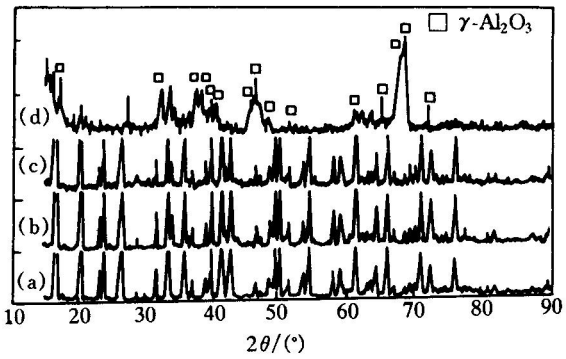

Fig.3 X-ray diffraction patterns of original and extracted AlBO whisker
(a)—Original whisker;
(b)—Whisker at 850 ℃ for 12 h;
(c)—Extracted whisker of T_6-composites;
(d)—Extracted whisker of composites at 780 ℃ for 15 min

3.2 Interfacial reaction of $AlBO_w$/ZL109 composites

The as-cast $AlBO_w$/ZL109 composites was studied by means of the same high temperature DSC analysis, two exothermic responses are observed (Fig.4(a)). This means that chemical

reaction occurs in the $AlBO_w$/ZL109 composites. Fig.4(b) shows the DSC curve of ZL109 alloy under the same conditions as the composites. Compared Fig. 4(a) with Fig. 4(b), it shows that the exothermic responses do not result from the reaction or precipitation among compositions in the matrices but due to the interaction between $AlBO_w$ and matrix alloys. Moreover, it is evident from Fig. 1 that both Mg and Al element can reduce B element from its oxide, but Cu and Ni can't displace B element. As a result, it is reasonable to consider that the chemical reaction is caused by interaction between Mg, Al and AlBO whisker while Cu and Ni elements don't take part in the interfacial reaction.

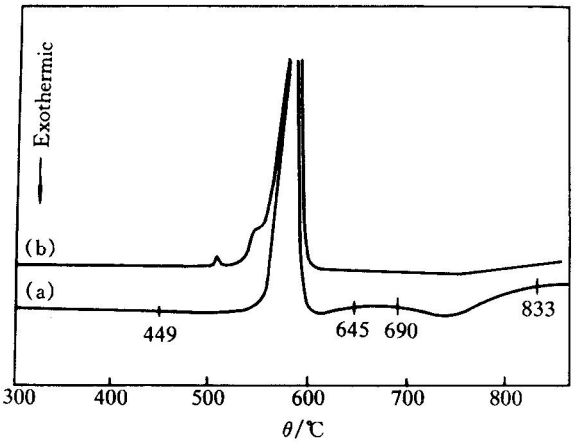

Fig.4 DSC scans of as-cast $AlBO_w$/ZL109 composites and matrix alloy
(a)—$AlBO_w$/ZL109 composites; (b)—ZL109 matrix

In order to determine the exact phase identification by means of X-ray diffraction, AlBO whisker as well as the interfacial reaction products were extracted from the T_6 heat-treated composites by using 10% HCl solution. From the X-ray diffraction pattern (Fig. 5(b)) performed on the extracted whisker, the interfacial reaction products are identified as spinel $MgAl_2O_4$ and Si which is formed by eutectic reaction, and usually nucleate and grow at whisker/Si interface[9], which means the $MgAl_2O_4$ is the interfacial reaction products only. This result indicates that magnesium could react with the whisker during the interfacial reaction of $AlBO_w$/ZL109 composites.

Morphologies of the interfacial reaction products were shown in Fig. 6. It is easy to find that there are more interfacial reaction products in the T_6 heat-treated composites than that in the as-cast one. Because the solid solution temperature of T_6 heat treatment is 530 ℃, it indicates that magnesium reacts easily with the whisker at the temperature of 449～645 ℃, so that T_6 treatment causes more serious interfacial reaction. According to the DSC curve (Fig. 4(a)), it is founded that no thermal responses exist in the composites when the temperature ranges from 645 ℃ to 690 ℃, it means that Mg element at the interface is almost exhausted. Therefore, campared the DSC curves shown in Fig. 4(a) and Fig. 1, it is reasonable to consider that the exothermic peak of 690 ～ 833 ℃ is caused by the reaction between Al and the AlBO whisker.

In general, although it was accepted by most researchers that Mg and O elements in the matrix take part in the interfacial reaction in the $AlBO_w$ reinforced aluminum-based composites, there were different views about interfacial reaction mechanism. For example, Sugumara *et al*[1,2,13] put forward that due to the existence of Mg element, the interfacial reaction is as

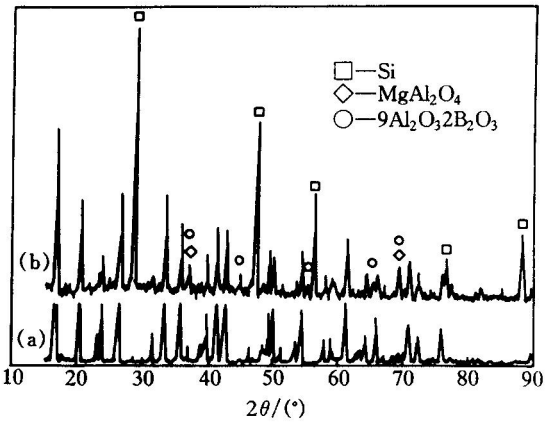

Fig.5 X-ray diffraction patterns of original and extracted AlBO whisker
(a)—Original wisker;
(b)—Extracted wisker of T_6-composites

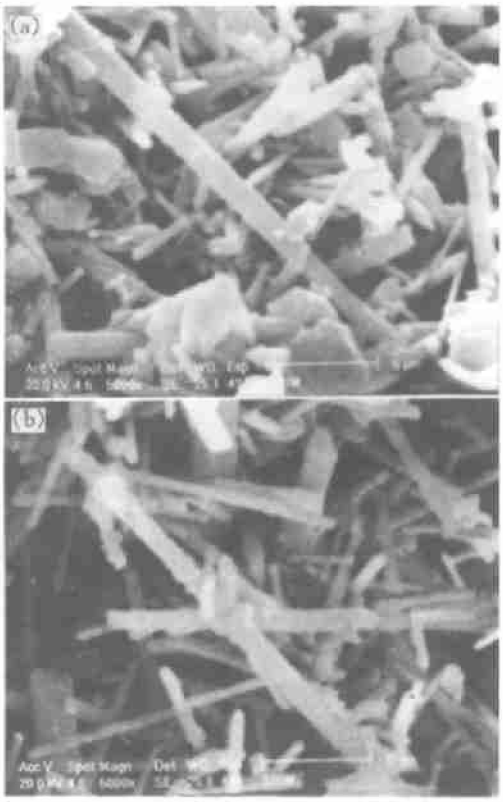

Fig.6 SEM micrographs of whisker extracted from $AlBO_w$/ZL109 composites
(a)—Whisker extracted from as-cast composites;
(b)—Whisker extracted from T_6-treated composites

follows:

$$\begin{cases} 9Al_2O_32B_2O_3 + 4Al \rightarrow 11\gamma\text{-}Al_2O_3 + 4B \\ \gamma\text{-}Al_2O_3 + Mg + [O] \rightarrow MgAl_2O_4 \end{cases}$$

But Pan *et al*[3] proposed the following process:

$$9Mg + 9Al_2O_32B_2O_3 + 3[O] \rightarrow MgAl_2O_4 + 4B$$

However, [O] is not necessary factor that cause the interfacial reaction in spite that it can promote the interfacial reaction greatly(Fig.7). In other words, magnesium can react with the $AlBO_w$ when there is no existence of [O] in the composites. The chemical reaction between Mg and $AlBO_w$ can be given by Eqns.(2),(3):

$$6Mg + 9Al_2O_32B_2O_3 \rightarrow 6MgAl_2O_4 + 3\gamma\text{-}Al_2O_3 + 4B \quad (2)$$

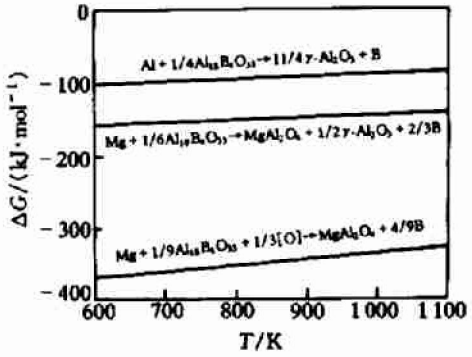

Fig.7 Thermodynamic calculation between Mg, Al and AlBO whisker

$$3Mg + 4\gamma\text{-}Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al \quad (3)$$

The reason for the two interfacial reaction equation can be explained as follows. Firstly, although both Mg and Al elements can displace B element from its oxide, Al element can be also reduced from its oxide by Mg element(Fig.1). This indicates that the reaction between Mg element and $AlBO_w$ is easier than Al element, means Eqn.(2) as well as Eqn.(1) can take place in the composites. Secondly, both Eqns.(3) and (4) may take place. But Lloyd[14] and Fishkis[15] pointed out that

$$3Mg + Al_2O_3 \rightarrow 3MgO + 2Al \quad (4)$$

the interfacial reaction products are not MgO but $MgAl_2O_4$ in the Al_2O_3/Al-4% Mg composites based on the dynamic consideration. In the present study, the ZL109 alloy is selected as matrix and the mass fraction of magnesium in matrix ranges from 0.8% to 1.3%. Therefore, it is reasonable to consider that Eqn.(4) does not occur in the composites. Furthermore, because there exist Mg segregation at the interface between matrix and $AlBO_w$[3,10], the reaction opportunity between Mg and $AlBO_w$ are greater than that between Al and $AlBO_w$.

Based on the experimental results and analyses, the existence of interfacial reaction in the $AlBO_w$/ZL109 composites not only depends on the processing temperature, but also depends on the alloy elements in the matrix. Finally, the process of interfacial reaction in $AlBO_w$/ZL109 composites can be traced:

Both Mg and Al element can react with $AlBO_w$ when the processing temperature is higher than 690 ℃:

$18Mg + 29Al_2O_32B_2O_3 + 3O_2 \rightarrow 18MgAl_2O_4 + 8B$

$6Mg + 9Al_2O_32B_2O_3 \rightarrow 6MgAl_2O_4 + 3\gamma\text{-}Al_2O_3 + 4B$

$2Mg + 2\gamma\text{-}Al_2O_3 + O_2 \rightarrow 2MgAl_2O_4$

$3Mg + 4\gamma\text{-}Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$

$4Al + 9Al_2O_32B_2O_3 \rightarrow 11\gamma\text{-}Al_2O_3 + 4B$

Only Mg element can react with $AlBO_w$ when the processing temperature ranges from 449 ℃ to 690 ℃:

$18Mg + 29Al_2O_32B_2O_3 + 3O_2 \rightarrow 18MgAl_2O_4 + 8B$

$6Mg + 9Al_2O_32B_2O_3 \rightarrow 6MgAl_2O_4 + 3\gamma\text{-}Al_2O_3 + 4B$

$2Mg + 2\gamma\text{-}Al_2O_3 + O_2 \rightarrow 2MgAl_2O_4$

$3Mg + 4\gamma\text{-}Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$

4 CONCLUSIONS

(1) The temperature of reaction between Al and $AlBO_w$ is 756 ℃ in the $AlBO_w$/Al composites. The interfacial reaction product is $\gamma\text{-}Al_2O_3$.

(2) In the $AlBO_w$/ZL109 composites, Mg is one of the main factors that cause the interfacial reaction, Al also can react with $AlBO_w$, O can promote the interfacial reaction, and Cu, Ni don't take part in the interfacial reaction.

(3) For $9Al_2O_32B_2O_3{}_w$/ZL109 composites, the processing temperature is another factor that causes interfacial reaction. When the temperature is higher than 690 ℃, both Mg and Al element react with whisker. When the temperature ranges from 449 ℃ to 690 ℃ only Mg element takes part in the interfacial reaction and the reaction product is $MgAl_2O_4$ with spinel structure.

(4) T_6 treatment causes very serious interfacial reaction between $AlBO_w$ and ZL109 alloys.

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