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Sol–gel alumina coatings for whisker reinforced metal matrix composites

D.Y. Ding [a,*], J.C. Rao [a,b], D.Z. Wang [a], Z.Y. Ma [b], L. Geng [a], C.K. Yao [a]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 433, Harbin 150001, PR China
[b] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, PR China

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Abstract

There exist serious interfacial reactions in squeeze-casting aluminum borate whisker reinforced 6061Al composites. To control the spinel reactions a sol–gel coating method was used to deposit γ-Al_2O_3 and α-Al_2O_3 ceramic coatings on aluminum borate whiskers. TEM observations of coating morphology indicate that nanostructured alumina coatings are uniformly deposited on whisker surfaces, with a thickness of about 30–50 nm. Ball-milling has an important effect on final mechanical properties of the composites. γ-Al_2O_3 and α-Al_2O_3 coatings were found to be effective in controlling the interfacial reactions, by completely preventing the diffusion of magnesium from matrix/coating interface to coating/whisker interface.

Keywords: Aluminum matrix composite; Interfacial reaction; Alumina coating

1. Introduction

Interfacial reactions and their control are of great importance in metal matrix composites. For discontinuously reinforced metal matrix composites it often results from remelting or secondary processing at elevated temperature. To inhibit Al_4C_3 interfacial reactions in SiC particle reinforced aluminum matrix composites, Teng and Kindl [1,2] found that a sol–gel γ-Al_2O_3 coating could decrease the rate of Al_4C_3 reactions. Kindl also found that the above γ-Al_2O_3 coating could hinder the Al_4C_3 reaction between SiC whiskers and liquid aluminum alloys [3].

As interfacial reactions in aluminum borate whisker ($Al_{18}B_4O_{33}$ or AlBOw) or potassium titanate whisker ($K_2Ti_6O_{13}$ or KTiOw) reinforced aluminum composites are very serious, various methods have been reported to minimize the amount of reaction. It has been established that a proper selection of fabrication temperature and matrix compositions may help to hinder or avoid the spinel ($MgAl_2O_4$) reactions in AlBOw reinforced composites. A Si_3N_4 coating obtained from reduction in protective atmosphere, can de used to restrain the spinel reactions and therefore enhance the composite flexural strength at elevated temperature [4].

Suganuma [5] reported that, by sintering whiskers at 1400°C, an α-Al_2O_3 coating could be produced on surfaces of aluminum borate whiskers, which will hinder the interfacial reactions in AlBOw/6061Al composites. Wang [6] investigated the effect of a sol–gel alumina coating on the decomposition reactions in KTiOw/Al composites. His results prove that an alumina coating can hinder the decomposition of KTiOw into TiO and KO_2 products, although it cannot totally prevent the diffusion of elements Ti and K from whiskers to aluminum matrices.

The sol–gel coating method has been used to advantage in both metal matrix composites and ceramics, due to its many advantages such as providing optical and oxidation-resistant films on various substrates [7–9]. But its application to AlBOw reinforced composites has not been reported up to now.

In this paper we discuss the application of sol–gel γ-Al_2O_3 and α-Al_2O_3 coatings to squeeze-casting AlBOw/6061Al composites, to control the spinel reaction between magnesium and the whiskers. The coating microstructure, mechanical properties and interface were investigated.

* Corresponding author.

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2. Experimental procedure

Aluminum borate and potassium titanate whiskers provided by Shikoku Chemical Company and Shenyang Jinjian Company, respectively, both had a diameter of 0.5–1 μm and a length of 10–30 μm.

After an ultrasonic dispersion of whiskers in an aqueous sol prepared from $Al(NO_3)_3$ and NH_4HCO_3 the whiskers were extracted and dried at 80–100°C, and then calcinized at about 850–950°C to obtain γ-Al_2O_3 and α-Al_2O_3 coatings. Finally the as-coated whiskers were dispersed by ball-milling treatment or directly used for fabrication of whisker reinforced composites.

Squeeze-cast AlBOw/γ–Al_2O_3/6061Al and AlBOw/α–Al_2O_3/6061Al composites were prepared from silica-bound preforms, with a pouring temperature of 800°C and a pressure of 150 Mpa for 3 min. For comparison KTiOw/α–Al_2O_3/Al composites were also prepared. Whiskers were extracted from the above composites by use of 10% HCl or NaOH solutions.

Specific surface areas of as-received and as-coated whiskers were measured by the BET (Brunauer–Emmet–Teller) method. Scanning electron microscope (SEM) and transmission electron microscope (TEM) observations, as well as X-ray diffraction (XRD) analysis were conducted. A supporting membrane on copper mesh was used to prepare whisker samples for TEM observations with a JEM2000-EX II microscope. Tensile tests on AlBOw/α–Al_2O_3/6061Al composites were also carried out.

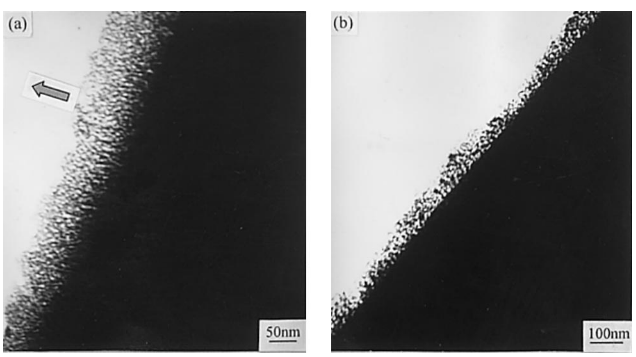

Fig. 1. Alumina coatings on whiskers (a) γ-Al_2O_3 coating (b) α-Al_2O_3 coating.

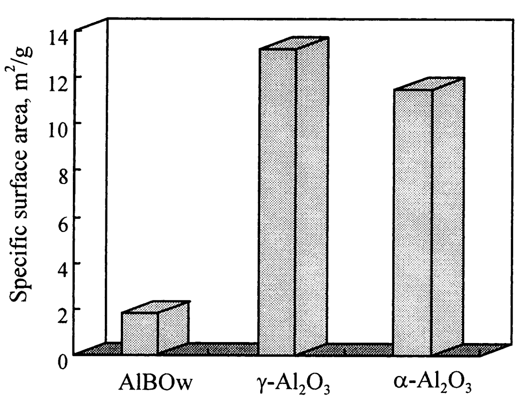

Fig. 2. Specific surface area of alumina coated aluminum borate whiskers.

3. Results and discussion

3.1. Coating process and characterization

During the sol–gel coating process by the aluminum nitrate method, there occurs first absorption of sol particles on whiskers and then a gelation to form macromolecular networks. And when calcinized from a lower temperature to a higher temperature, there occur phase transitions from amorphous coating to γ-Al_2O_3 at 850°C and to α-Al_2O_3 at 950°C, together with an escape of water and other by-products. The phase transitions of the alumina coatings were proven by XRD experiments. The above coating features determine that:

1. Optimizing the sol concentration and the absorption time can control the coating thickness.
2. At least three types of potential coatings on whiskers can be selected to meet different demands, such as the α-Al_2O_3 coating for ceramic matrix composites and γ- or α-Al_2O_3 coatings for metal matrix composites.
3. The uniformity and continuity of alumina coatings on whiskers can be obtained by moderate heat treatment, such as a slower heating velocity and dwelling at proper temperature for the by-products to escape.

Fig. 1 shows TEM morphologies of sol–gel γ-Al_2O_3 and α-Al_2O_3 coatings on whiskers. It can be seen that the alumina coatings are almost uniformly deposited on whisker surfaces, with a thickness of about 30–50 nm, and contain nanometer-sized pores.

TEM observations clearly show that the morphology of the micropores is controlled by the phase transitions. In Fig. 1(a) the arrow shows orientation of micropores in the γ-Al_2O_3 coating, that is, almost all of the micropores are perpendicular to the longitudinal direction of the whiskers. This orientation is consistent with the escaping direction of coating by-products. But after the γ-Al_2O_3 has transformed to the more stable α-Al_2O_3, the micropores no longer show any preferred orientation.

The phase transitions together with the changes of micropore morphology produce a change in the specific surface area (Fig. 2). The specific surface area increases greatly when nanostructured γ-Al_2O_3 and α-Al_2O_3 coatings are applied to the surfaces of aluminum borate whiskers. This suggests that different coating processes could yield different distributions of micropores in the

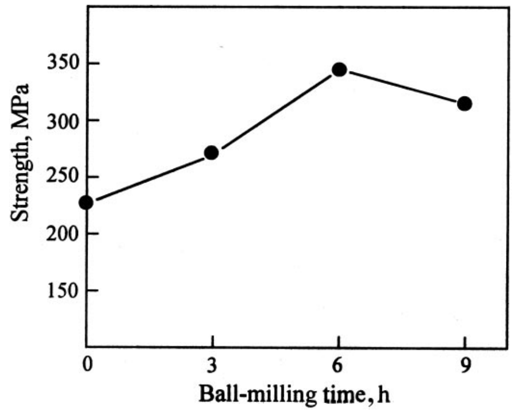

Fig. 3. Influence of ball-milling time on tensile strength of AlBOw/ α–Al_2O_3/6061Al composites.

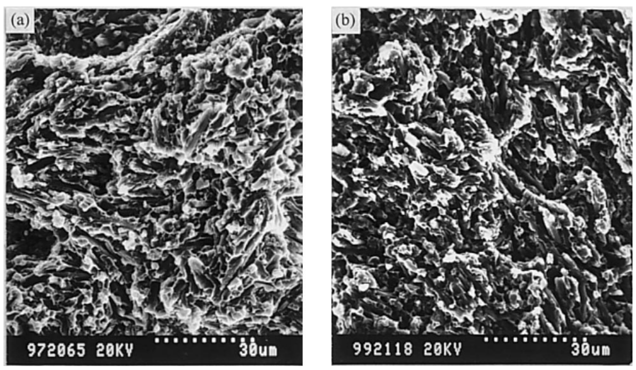

Fig. 4. SEM fractographs of AlBOw/α–Al_2O_3/6061Al composites (a) without ball-milling (b) ball-milling for 6 h.

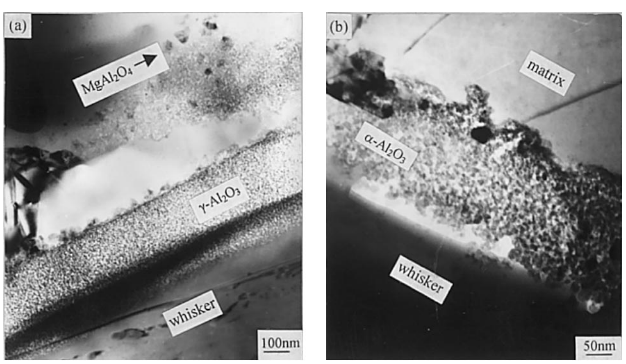

Fig. 5. TEM micrographs of composites (a) AlBOw/γ–Al_2O_3/6061Al (b) AlBOw/α–Al_2O_3/6061Al.

sol–gel alumina coatings. If the size and shape of coating micropores could be controlled to a certain degree, the coating's effectiveness as a diffusion barrier would be enhanced.

3.2. Composite strength and interface

SEM observations of as-coated whiskers indicate that some whiskers are scattered, and other whiskers are bound together due to bridging of whiskers during the sol–gel coating process. For the purpose of fabricating a uniform composite the above binding phenomenon must be eliminated by optimizing coating and ball-milling parameters.

Fig. 3 shows the influence of ball-milling treatment on the tensile strength of 30Vf% AlBOw/α-Al_2O_3/ 6061Al composites. After ball-milling treatment the tensile strength increases greatly, with a maximum strength obtained at ball-milling time of six hours and a decrease of strength again after the ball-milling time exceeds six hours. This suggests that a proper selection of ball-milling time is crucial for fabricating AlBOw/γ-Al_2O_3/6061Al and AlBOw/α-Al_2O_3/6061Al composites.

The great difference in composite strength may be explained as follows. Although there are many factors that determine the tensile strength of squeeze-cast whisker reinforced composites, the aspect ratio and clustering of whiskers may be the two important factors. It can be determined that the strength increases with an increase of aspect ratio and a decrease of clustering degree. For the composite directly reinforced with as-coated whiskers, clustering of whiskers is so extensive that tensile fracture will easily occur at clustered regions. This greatly decreases the composite strength, although the whisker aspect ratio remains high by comparison with that of ball-milled whiskers.

With increase of ball-milling time the clustering degree of coated whiskers decreases, which contributes to the uniformity of composites and the strength. But the aspect ratio of whiskers will decrease at the same time, which is detrimental to the composite strength. Therefore, the above two opposing effects result in a maximum strength, for the best dispersion of whiskers and the least decrease in aspect ratio.

SEM fractographs in Fig. 4 supports the above explanation, by showing nonuniform fracture in the low-strength composite and better uniformity in the high-strength composite.

Fig. 5 presents TEM micrographs of AlBOw/ γ–Al_2O_3/6061Al and AlBOw/α–Al_2O_3/6061Al composites, and Fig. 6 shows a TEM image of extracted whiskers from AlBOw/α–Al_2O_3/6061Al composite. Interfacial reactions in the two composites are found to be greatly restrained, by comparison with those in conventionally prepared AlBOw/6061Al composites [10–12]. Spinel ($MgAl_2O_4$) products are distributed very sparsely on the outer surfaces of the alumina coatings, which are unlike the nearly continuous reaction products in AlBOw/6061Al composites.

As for the alumina coating, it is clean throughout, that is, no spinel can be seen in the inner part of the alumina coatings, especially the part close to the Al_2O_3/ whisker interface. EDX analyses of alumina coatings were performed to investigate the existence of magnesium, as it is an important element for the interfacial reaction. No magnesium was detected inside either the γ- or α-Al_2O_3 coating.

It is evident that, for the spinel reactions in AlBO whisker reinforced composites, nanostructured γ-Al_2O_3 or α-Al_2O_3 coating serves as a tight barrier to hinder the segregation or diffusion of magnesium from the matrix to the matrix/Al_2O_3 interface and the inner part of the Al_2O_3 coating. This completely prevents the direct growth of spinel from the AlBO whisker surface.

The existence of a small amount of spinel at the Al_2O_3/matrix interface may be explained by considering the slight segregation of magnesium from the matrix to the Al_2O_3/matrix interface and the existence of silica binder on outer surfaces of the alumina coatings. The small amount of silica binder absorbed on whisker surfaces has been proven to be a source of reactant for the interfacial reaction.

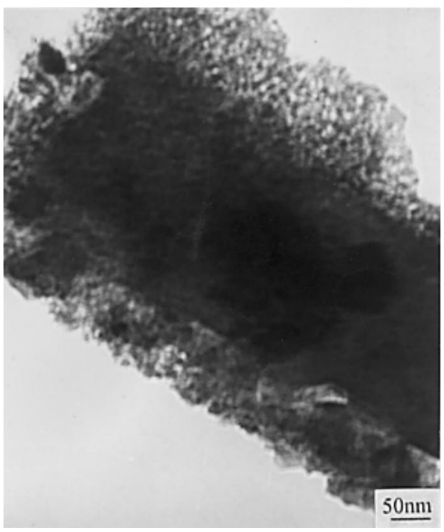

Fig. 6. Extracted whiskers from AlBOw/α–Al_2O_3/6061Al composite.

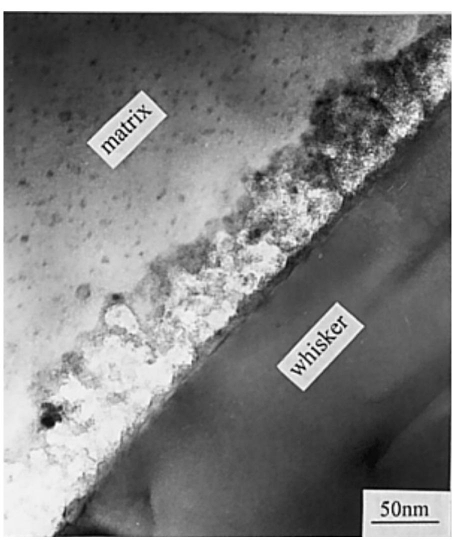

Fig. 7. TEM microgragh of KTiOw/α–Al_2O_3/Al composite.

For the interfacial reactions in KTiO whisker reinforced composites, an α-Al_2O_3 coating is not as effective a barrier as for the spinel reactions. As shown in Fig. 7, decomposition reaction products (TiO and α-KO_2) are present everywhere, that is, reaction products exist throughout the α-Al_2O_3 coating, and no clean alumina coating can be seen. Elements Ti and K were detected throughout the coating by EDX analyses. These results are in accord with those of Wang [6].

In KTiO whisker reinforced composites an α-Al_2O_3 coating can only provide, by introducing a network structure, a longer distance for elements Ti and K to diffuse from the Al_2O_3/whisker interface to the matrix.

4. Conclusions

Alumina coatings were deposited on aluminum borate whiskers by a sol–gel method to hinder the spinel reactions. The sol–gel processed γ-Al_2O_3 and α-Al_2O_3 coatings have nanostructured morphology, with specially oriented micropores in the γ-Al_2O_3 coatings and none-orientation in the α-Al_2O_3 coatings.

To fabricate a sound composite reinforced with coated whiskers, a ball-milling treatment ought to be conducted to disperse the bound whiskers. It is found that composite strength varies with the ball-milling time, as it affects both the uniformity and aspect ratio of the whiskers.

Sol–gel γ-Al_2O_3 and α-Al_2O_3 coatings are effective in controlling the interfacial reactions in aluminum borate whisker reinforced 6061Al composites, by completely preventing the diffusion of magnesium from matrix to whisker. There are different mechanisms for sol–gel alumina coatings to control the interfacial reactions in aluminum borate and potassium titanate whiskers reinforced composites.

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