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Microscopic examination of the interface region in AC8A/$Al_{18}B_4O_{33}$w composites reinforced with as-received and artificial nitrided $Al_{18}B_4O_{33}$ whiskers

GANG BI
School of Materials & Engineering, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China; Baosteel Technology Center, Shanghai 201900, People's Republic of China

QUNLI RAO*
Instrumental Analysis Center, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China

HONGWEI SONG
Baosteel Technology Center, Shanghai 201900, People's Republic of China

Aimed to control the interfacial reaction in $Al_{18}B_4O_{33}$/Al composites, the artificial nitridation process is proposed based on thermodynamic calculations, which leads to a 50-nm thick artificial nitrided coating surrounding a $Al_{18}B_4O_{33}$ whisker. Aluminum (AC8A) matrix composites reinforced with different $Al_{18}B_4O_{33}$ whiskers were processed and $Al_{18}B_4O_{33}$ whiskers were used in their as-received form and after artificial nitridation. The interface region between the aluminum matrix and $Al_{18}B_4O_{33}$ was charactered using transmission electron microscopy. Results show that extensive reaction takes place during the incorporation process between the as-received $Al_{18}B_4O_{33}$ whiskers and the aluminum matrix and Mg in the base alloy forms $MgAl_2O_4$ spinel phases. Such interfacial reaction is enhanced after T6 heat treatment. In the case of artificially nitrided $Al_{18}B_4O_{33}$ whiskers, even though the artificial nitrided coating surrounds the $Al_{18}B_4O_{33}$ whisker, it can react with the AC8A alloy to produce $MgAl_2O_4$, but the degree of the interfacial reaction is reduced. The interfacial reaction only consumes the artificial nitrided coating instead of the reinforcement whiskers and the integrity of the whisker is preserved.

1. Introduction

Aluminum composites reinforced with ceramic whiskers ($Al_{18}B_4O_{33}$w) have been developed for their high specific strength, high modulus, excellent wear resistance and thermal stability as compared with conventional materials. The problems are that the ceramic whiskers are expensive and the wide applications of these composites are limited. Recently, aluminum borate whiskers have been developed in Japan, and the superior feature is that its price is far below that of the silicon carbide whisker (almost one twentieth). $Al_{18}B_4O_{33}$ whisker reinforced aluminum composites fabricated by squeeze casting exhibit strength and modulus comparable to those of SiC whiskers reinforced aluminum composites, the thermal expansion is lower and abrasion resistance is better [1–4]. Aluminum borate whiskers, therefore, will give a good possibility for expanding the applications of the aluminum matrix composites in the future.

One of the important features of $Al_{18}B_4O_{33}$ whisker reinforced Mg-containing aluminum alloy composites is the serious interfacial reaction and spinel, $MgAl_2O_4$, forms at the interface [3–6]. Interfaces are considered to be particularly important in the mechanical behaviour of metal matrix composites since they control the load transfer between the matrix and reinforcement [6, 7]. It is has been suggested that the serious reaction between $Al_{18}B_4O_{33}$ whiskers and the aluminum matrix is a direct reason for the degradation of the reinforcement and interfacial strength. To overcome this problem, techniques for sol-gel coating surface treatment [8–11] have been developed. Unfortunately, no effective method has yet been found. In this work, the artificial nitridation process of $Al_{18}B_4O_{33}$ whisker is proposed based on thermodynamic analysis [12]. The aim is to produce an artificial nitrided coating on the surface of the whiskers.

The present work mainly characters the interface regions in AC8A/$Al_{18}B_4O_{33}$w composites by

*Author to whom all correspondence should be addressed.

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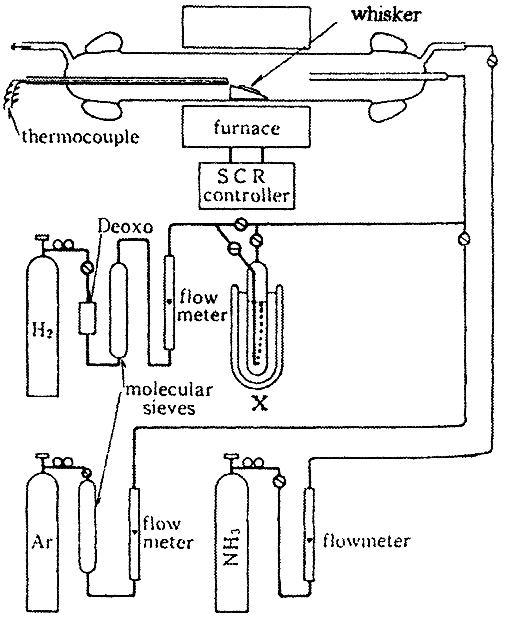

Figure 1 Schematic diagram of the apparatus used for the preparation of artificial nitrided coating.

transmission electron microscopy (TEM) observations, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Special attention is given to the influence of the artificial nitrided coating on the composite interface.

2. Experimental procedures

2.1. Preparation of nitrided $Al_{18}B_4O_{33}$ whiskers

The schematic diagram of the apparatus for the nitridation process of the whisker is shown in Fig. 1. The $Al_{18}B_4O_{33}$ whiskers are placed in an alumina boat, which is then heated to 1300°C and ammonia (99.9%), hydrogen (99.9%), and argon (99.9%) are used to grow an artificial nitrided coating. The $Al_{18}B_4O_{33}$ whiskers are held under these conditions for a period of 9 h, and detailed information about the nitridation process can be found elsewhere [12].

2.2. Liquid processing of $Al_{18}B_4O_{33}$/AC8A composite

The aluminum matrix used in this investigation is an industrial AC8A alloy (11–13 wt%Si, 0.8–1.3 wt%Mg, 0.5–1.5 wt%Cu, 0.8–1.5 wt%Ni, Al balance). This alloy was then reinforced with 25 vol% of $Al_{18}B_4O_{33}$ whiskers by squeeze casting. The temperature of the molten alloys, the preform and the mould were kept at 750°C, 750°C and 350°C, respectively. The casting was carried out in air under a pressure of 100 MPa.

In order to evaluate the sensitivity of interfacial reaction, some of the composites specimen were given a T6 heat treatment under the conditions: 520°C for 3 h for solid solution, followed by quenching 75°C, and heating to 160°C for 24 h age.

2.3. Observations and characterization

Optical microscopy was performed to examine the distribution of the $Al_{18}B_4O_{33}$ whiskers within the composite. Observation of detailed three-dimensional morphologies of the as-received and nitrided whisker was carried out using scanning electron microscopy (Philips XL-30). Surface phase identification of the nitrided $Al_{18}B_4O_{33}$ whisker was analyzed by X-ray photoelectron spectroscopy (VG MICROLAB MKII). The microstructures of the reaction products and artificial nitrided coating were examined by transmission electron microscopy (HITACHI H-700).

3. Results and discussion

Since as-received and nitrided whiskers are used as reinforcements in the AC8A matrix, the results obtained with these two types of whiskers are presented and discussed separately.

3.1. As-received whisker

Fig. 2 shows the microstructure of the composite and that the distribution of the whiskers is generally uniform, except for some areas that are free of $Al_{18}B_4O_{33}$ whiskers.

The microstructure of aluminum borate whisker was studied by TEM observation. Fig. 3a shows TEM micrographs of an as-cast $Al_{18}B_4O_{33}$w/AC8A composite. It can be observed that discontinuous reaction products, $MgAl_2O_4$, with a spinel structure, as observed by other researchers [3–11], were found on the $Al_{18}B_4O_{33}$ whisker surfaces. After the T6-treatment, the morphology and the distribution of interfacial reaction products become different, as shown in Fig. 3b. The degree of reaction grows in quantity and the reaction products become larger. Almost all the whisker surface is covered by the products. As a result, the serious interfacial reaction damages the reinforcement $Al_{18}B_4O_{33}$w and is expected to degrade the whisker/matrix interfacial strength. Meanwhile, the formation of $MgAl_2O_4$ at the Al-$Al_{18}B_4O_{33}$w interface reduces the amount of Mg present in the matrix and thereafter in solution in the Al matrix. This affects the age-strengthening behaviour of the material [7].

To the authors had knowledge, there is no thermodynamic calculation to predict the reaction in Al/$Al_{18}B_4O_{33}$w composites. Possible reactions for the formation of $MgAl_2O_4$ involving $Al_{18}B_4O_{33}$ whiskers

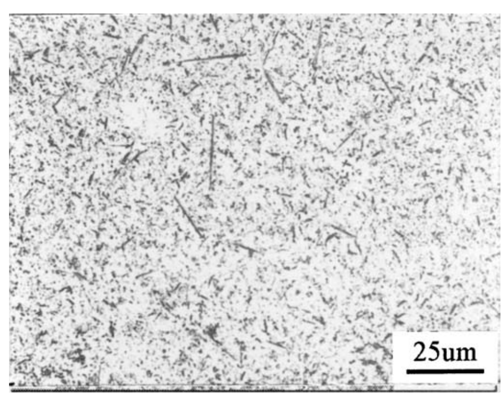

Figure 2 Optical micrograph of the as-cast composite showing a fairly uniform distribution of whiskers.

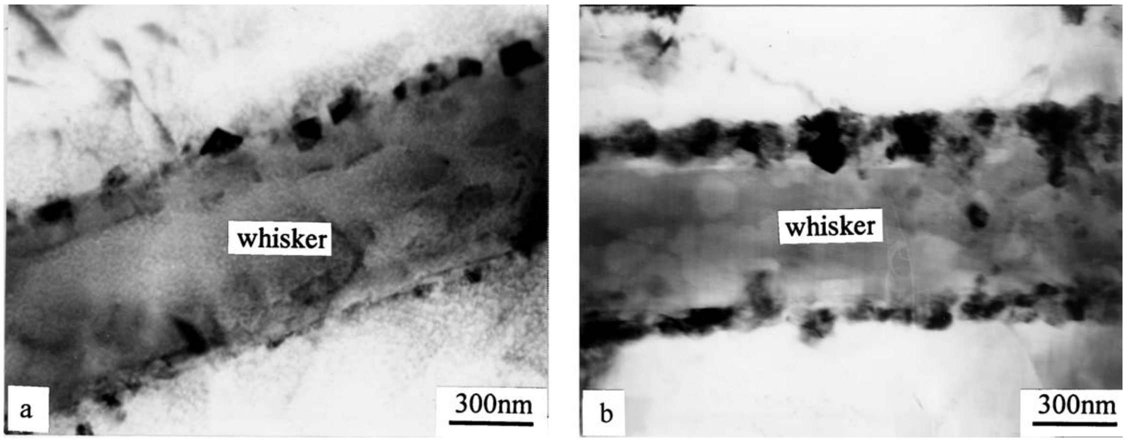

Figure 3 TEM micrographs of the interface in as-received $Al_{18}B_4O_{33}$w/AC8A composites showing the interfacial reaction products in: (a) the as-cast composite and (b) the T6-treated composite.

reacting with molten aluminum containing Mg, include (thermochemical data of pure substances come form reference [26]):

$$9Mg + Al_{18}B_4O_{33} + 3[O] \rightarrow 9MgAl_2O_4 + 4B$$
$$\Delta G(298\,K) = -3514.0\,KJ/mol \quad (1)$$
$$33Mg + 4Al_{18}B_4O_{33} \rightarrow 33MgAl_2O_4 + 6Al + 16B$$
$$\Delta G(298\,K) = -4750.0\,KJ/mol \quad (2)$$

Reactions (1) and (2) would lead directly to the formation of $MgAl_2O_4$, without intermediate steps. If, however, reaction (3) occurs to form γ-Al_2O_3, then the following reaction (4) and (5) would account for the formation the $MgAl_2O_4$ achieved:

$$4Al + Al_{18}B_4O_{33} \rightarrow 11\gamma - Al_2O_3 + 4B$$
$$\Delta G(298\,K) = -446.0\,KJ/mol \quad (3)$$
$$Mg + \gamma - Al_2O_3 + [O] \rightarrow MgAl_2O_4$$
$$\Delta G(298\,K) = -842.9\,KJ/mol \quad (4)$$
$$3Mg + 4\gamma - Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$$
$$\Delta G(298\,K) = -269.6\,KJ/mol \quad (5)$$
$$3Mg + \gamma - Al_2O_3 \rightarrow 3MgO + 2Al$$
$$\Delta G(298\,K) = -143.0\,KJ/mol \quad (6)$$

Reaction (6) may occur based on thermodynamic calculation, but it does not take place in this composite. The reason can be achieved from other researchers [13–15]. Mclend *et al.* [13], who studied composites made by stirring Al_2O_3 particles into melts of Al containing different amounts of Mg, ranging from 0 to 8 wt pct Mg, observed that Mg oxides formed more frequently in samples with 4 and 8 pct Mg and that MgO is observed for relatively high Mg contents (8 pct Mg) and $MgAl_2O_4$ for low as Mg contents (4 pct Mg). In addition, Lloyd *et al.* [14] and Fishkis *et al.* [15] came the same conclusions. Although these results were obtained for Al_2O_3/Al-Mg composites, they do suggest that MgO would not be likely to form from the small amounts of Mg contained in the AC8A alloy studied here.

3.2. Surface-nitrided $Al_{18}B_4O_{33}$ whiskers

Fig. 4 shows SEM images of as-received and surface-nitrided whiskers. It is observed that the surfaces of the whiskers are smooth even after the nitridation.

As shown in the X-ray diffraction pattern, comparing two patterns (a) and (b) in Fig. 5, it is clear that almost all the positions of the peaks for the whiskers before and after nitridation, are the same. The intensity of nitrided whisker peaks is, however, lower and some weak peaks disappear. A new substance, Al_2O_3, was also found after nitridation.

In order to further character the nature of nitridation, the whiskers before and after nitridation have been studied using X-ray photoelectron spectroscopy. XPS results of the B1s, N1s and Al2p binding energies are presented in Fig. 6. As can be seen, the B1s peak is shifted towards lower binding energy. The high energy component (192.3 eV) is attributed to the aluminum borate whisker and suggests that B atoms are bonded with oxygen. However, the low energy one (190.2 eV), after nitridation, is assigned to an atomic arrangement surrounding the boron atom consisting of only nitrogen atom, similar to that occurring in boron nitride [16–21]. Thus, the value of the B1s binding energy agrees with the replacement of an oxygen atom bonded to a boron atom by a less electronegative nitrogen atom, which causes a decrease in the binding energies of the boron core electrons. The N1s spectra indicates that nitrogen present neither as NH_3 nor as AlN. The N1s binding energy of the 397.7 eV agrees with reported values of 397.6 eV for boron nitride [16–21]. Furthermore, see the Fig. 6c, the Al2p peak for the as-received whisker occurs at a binding energy of 74.2 eV, but after nitridation, the Al2p peak position of 74.7 eV agrees very well with reported values for alumina [16–21]. The shift of the Al2p peak from low energy (74.2 eV) to high energy (74.7 eV), therefore, indicates that the Al—O bond becomes more stable.

Based on the above results and analysis, a possible nitridation reaction is:

$$Al_{18}B_4O_{33} + 4NH_3 \rightarrow 9Al_2O_3 + 4BN + 6H_2O \uparrow \quad (7)$$

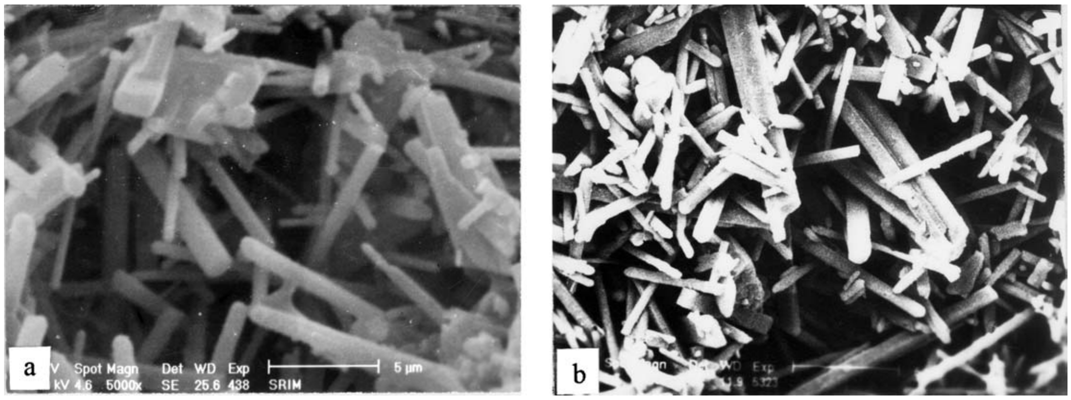

Figure 4 SEM images of: (a) as-received $Al_{18}B_4O_{33}$ whiskers and (b) surface-nitrided whiskers.

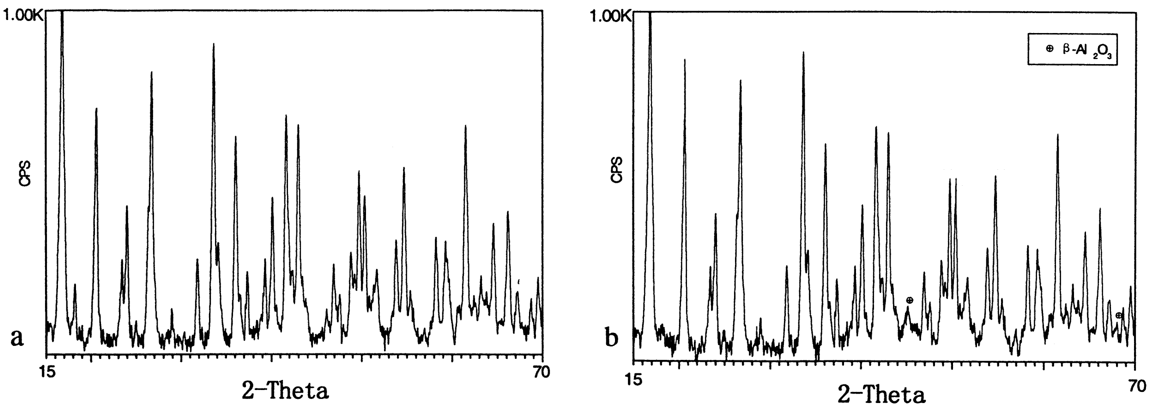

Figure 5 X-ray diffraction patterns showing the aluminum borate whisker: (a) whisker as-received and (b) whisker surface-nitrided.

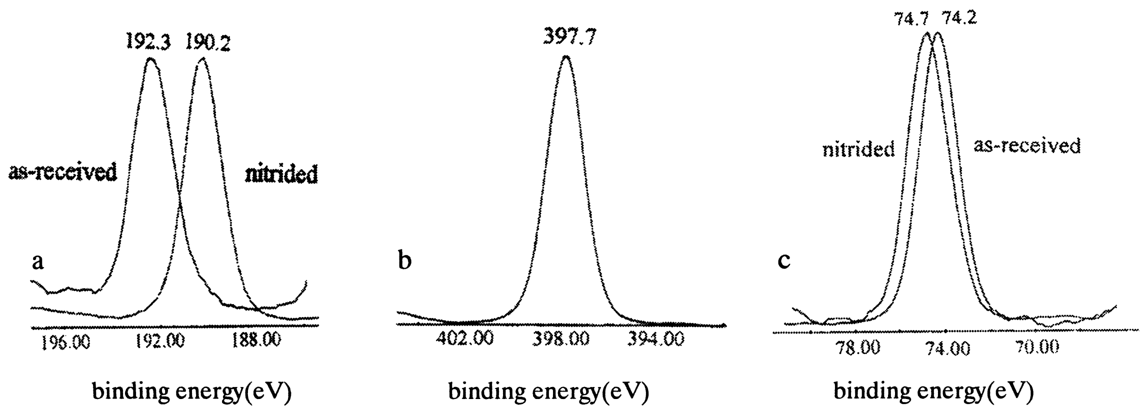

Figure 6 XPS survey scan of the aluminum borate whisker before and after nitridation: (a) the B1s, (b) N1s and (c) Al2p peaks.

The microstructure of composites with $Al_{18}B_4O_{33}$w nitrided prior to incorporation, observed in the optical microscope (shown in Fig. 7), appears very similar to that of as-received whisker. Comparing Figs 7 and 2 reveals that slightly fewer solidification defects and voids are found in the composite containing surface-nitrided whiskers.

Fig. 8 shows a typical TEM micrograph obtained for artificial nitrided whiskers. From the profile, it can be seen that an artificial nitrided coating is homogeneous around the $Al_{18}B_4O_{33}$ whisker. The thickness of the layer is, however, found to vary from point to point, which suggests that this behaviour is attributed to the fact that nitridation depends very much on the surface exposed to the ammonia atmosphere.

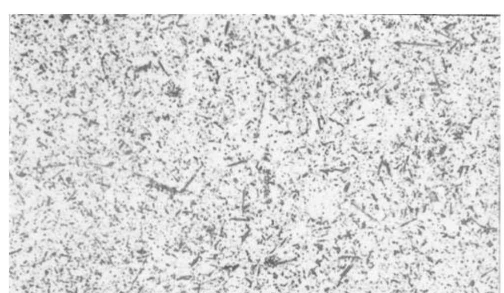

Figure 7 Optical micrograph of as-cast composites showing a fairly uniform distribution of nitrided whiskers.

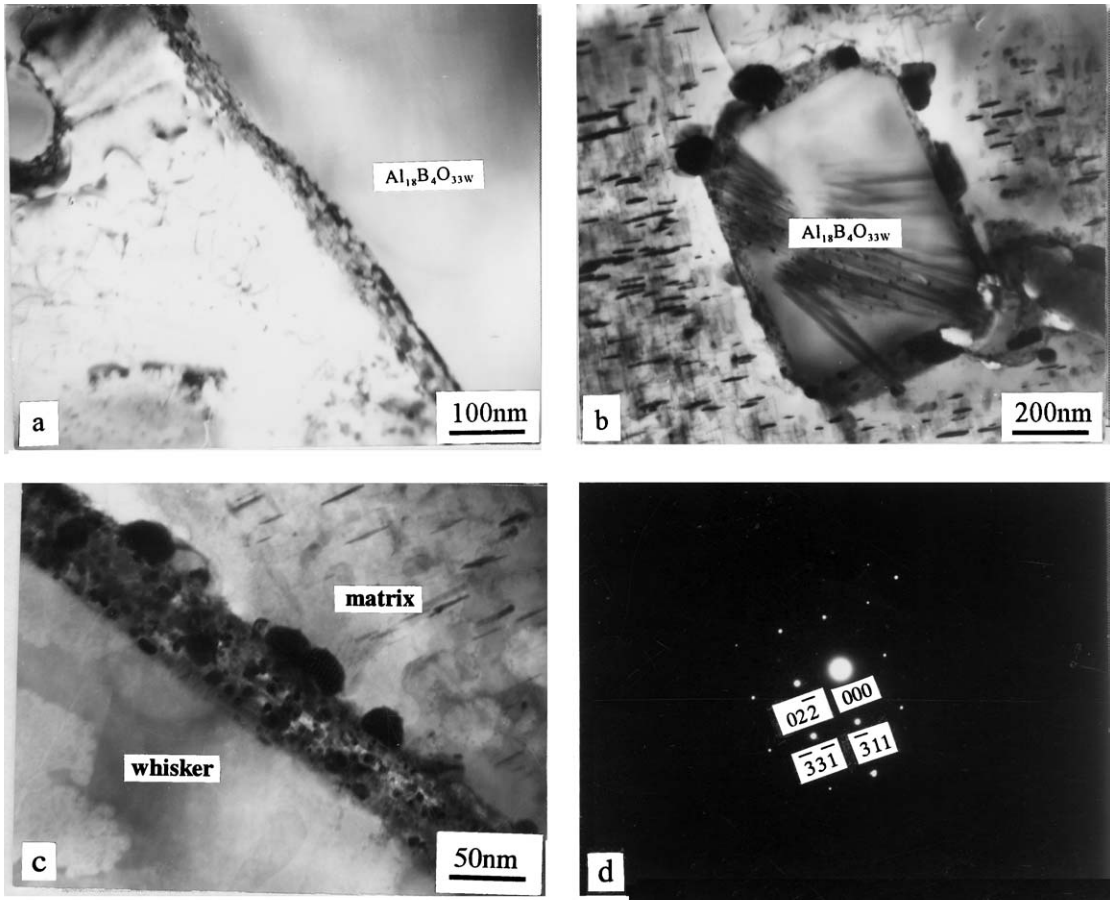

Figure 8 TEM micrographs of the interface in surface-nitrided $Al_{18}B_4O_{33}$w/AC8A composites: (c) longitudinal section of T6 composite, (d) SADP of reaction production corresponding to (c).

Nevertheless, from several measurements performed on various whiskers, an average value of 40–60 nm for the thickness of the nitrided layer can be determined. In these composite, the $Al_{18}B_4O_{33}$ whiskers and the Al matrix are separated by the layer and the Al/coating interface is free of reaction products (see Fig. 8a). The T6-treated composite (see Fig. 8b and c) shows that the interfacial reaction occurred between the nitrided coating and the matrix alloy. By indexing the diffraction pattern (see Fig. 8d), it can be determined that the interfacial reaction product is $MgAl_2O_4$ with spinel structure. In principle, the boron nitride in artificial coating has good chemical inertness to many molten metals, including Al, Mg and their alloys [22, 23], and thought to be impossible to take part in the interfacial reaction. The alumina in artificial nitrided coating is unstable in Mg-containing aluminum alloys, thermodynamically the $MgAl_2O_4$ reaction is favoured at low Mg content (<4% wt) [13, 24, 25], and the interfacial reaction [8] can occur. So, the spinel crystals is formed at the interface according to the reaction:

$$3Mg + 4Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al \qquad (8)$$

Moreover, comparing TEM micrographs with the corresponding as-received whisker reinforced AC8A composites (Fig. 3), demonstrates that the interfacial reaction can be greatly restrained due to the existence of artificial nitrided coating. The degree of interfacial reaction in the T6-treated nitrided whisker reinforced AC8A composite is weaker than that in the as-cast untreated-whisker/AC8A composite. It is worth noting from Fig. 8 that the interfacial reaction only consumes the artificial nitrided coating instead of the reinforcement whisker, and the integrity of the whisker is preserved.

4. Summary and conclusions

A detailed character of the interfaces in AC8A/$Al_{18}B_4O_{33}$ composites fabricated by a squeeze casting technique was carried out. The main conclusions of the investigation are as follows.

4.1. For as-received whiskers

1. Interfacial reaction between $Al_{18}B_4O_{33}$ whiskers and the aluminum matrix is observed and the product is spinel, $MgAl_2O_4$, which mainly results from the whisker and magnesium at the interface. The formation mechanism of magnesium aluminate is discussed.
2. T6 heat treatment has a strong influence on the interfacial reaction, and there is worse reaction in the composites after T6 treating.

4.2. For nitrided whiskers

1. Using the artificial nitridation process, a homogenous artificial nitrided coating is formed and surrounds the $Al_{18}B_4O_{33}$ whisker with a thickness of 40–60 nm.
2. The artificial nitrided coating, which isolates the whisker and Al matrix, is a good protective barrier

from $Al_{18}B_4O_{33}$w/AC8A interfacial reaction. The layer predominant restrains the formation of the spinel $MgAl_2O_4$. The interfacial reaction only consumes the artificial nitrided coating instead of the reinforcement whisker, and the integrity of the whisker is preserved.

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