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Fine structure of coated whiskers in $Al_{18}B_4O_{33}w/\gamma$-Al_2O_3/6061Al composite

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Sol-gel γ-Al_2O_3 coating was deposited onto surfaces of aluminum borate whiskers to control the spinel reactions between whiskers and matrix alloys. High-resolution electron microscopy (HREM) observations of the whisker defects and coating structure in the squeeze-cast $Al_{18}B_4O_{33}w/\gamma$-Al_2O_3/6061Al composite were carried out. Stacking faults and edge dislocations in the whiskers were directly observed, and zigzag anti-phase boundaries were also found. A deformation of whiskers along sectional direction was observed, which was determined to be a source of *in situ* fracture of whiskers. The sol-gel γ-Al_2O_3 coating was a nanocrystalline material with an average grain size of 5 nm.

1. Introduction

Aluminum borate whisker ($Al_{18}B_4O_{33}$w or AlBOw) reinforced Al matrix composite has become of great interest, because of the whisker's relatively low price and the composite's comparable properties with those of SiCw/Al composites [1–5]. For AlBOw reinforced Al alloy composites, there often occur interfacial reactions between whiskers and magnesium-containing matrix alloys during the squeeze-casting process or the application of the composite at elevated temperature. Many research works [6–8] have reported that the interfacial reaction in the squeeze-cast AlBOw reinforced 6061Al composite is so serious that a deterioration of the mechanical properties of the composite will be found.

To control the interfacial reactions of the composite, sol-gel γ-Al_2O_3 and α-Al_2O_3 coatings were deposited onto whisker surfaces in our previous works [9, 10]. It has been found that both coatings can hinder the reactions by completely preventing the diffusion of magnesium element from coating/matrix interface to the whisker surface. Other works also indicated that the introduction of sol-gel alumina coatings to the whisker/matrix interface helped to improve some mechanical properties of the composite.

But no works on the fine structure of the above sol-gel coatings have been reported. Besides, although the microstructure of AlBOw reinforced composites have been investigated by many researchers, most of these works have been concentrated on the interfacial structure, and many special defects in AlBO whiskers have not been observed by high-resolution electron microscopy to date.

In the present work, the fine microstructure of aluminum borate whiskers and sol-gel γ-Al_2O_3 coating in the squeeze-cast $Al_{18}B_4O_{33}w/\gamma$-Al_2O_3/6061Al composite was investigated with a high-resolution electron microscopy (HREM).

2. Experimental

The as-received aluminum borate whiskers were provided by Shikoku Chemical Company. It has a diameter of 0.5–1 μm and a length of 10–30 μm. The crystal lattice of the AlBOw is orthogonal (space group $Cmc2_1$) with the cell constants $a = 0.7692$ nm and $b = 1.4973$ nm as well as $c = 0.5682$ nm. The whisker's growth axis is parallel to its crystal direction of [001].

A sol-gel γ-Al_2O_3 coating with a thickness of about 40 nm was prepared on the whisker surface by a hydrolysis of aluminum nitrate at 80°C and further a calcination of the gel at elevated temperature like 800°C. After a ball-milling treatment the alumina-coated whiskers were made into a preform and a AlBOw/γ-Al_2O_3/6061Al composite was fabricated by conventional squeeze-casting process [11, 12].

Ion-thinned foils of as-cast composite were prepared with a 5 kV argon ion beam under an angle of 5–15°. HREM observation was conducted in a JEM2000EX-II high-resolution electron microscope operated at 200 kV.

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3. Results and discussion

3.1. Whisker structure

Fig. 1 shows HREM morphology of the squeeze-cast AlBOw/γ-Al_2O_3/6061Al composite by showing transverse section of the whisker. It can be seen that the whisker has a nearly regular shape with small islands adhering to it. Some V-shaped partial dislocations extending from the core region of the whisker also can be found. Most of the whisker surfaces have been protected from an interfacial reaction due to the presence of alumina coating between whisker and matrix alloys.

Fig. 2 presents typical selected-area electron diffraction patterns (EDPs) of the whisker. The zone axis of the EDP in Fig. 2b is [001], which is parallel to the whisker growth axis.

In general, the as-received whisker can be considered as not so perfect a monocrystal with some defects such as stacking faults and dislocations as well as twins. The above defects are mainly caused by compositional and temperature variations during the whisker synthesis process.

For the AlBO whiskers in AlBOw/γ-Al_2O_3/6061Al composites prepared through the ball-milling treatment and squeeze-casting process, extra defects will appear because the whiskers have been subjected to a certain complex forces and a deformation even fracture of whiskers can be observed.

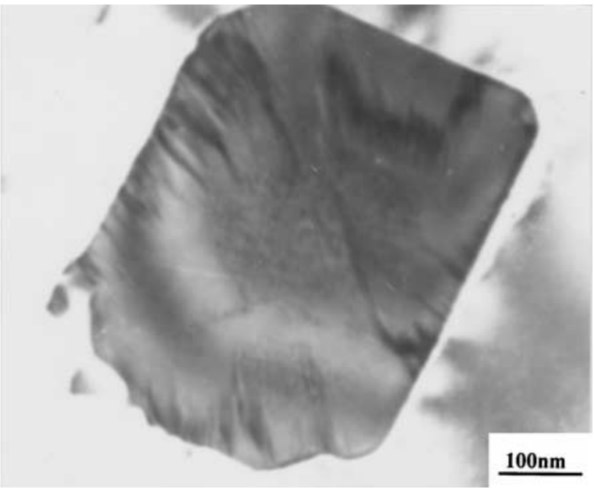

Figure 1 HREM morphology of the AlBOw/γ-Al_2O_3/6061Al composite showing transverse section of the whisker.

Fig. 3a and b show the HREM images of stacking faults and dislocations in the AlBO whisker. It can be sure that the dislocation in Fig. 3b is an edge dislocation. Both of the defects may be caused either in the whisker synthesis process or in the ball-milling and squeeze-casting process.

During the HREM observations, a defect of anti-phase boundary was found in some of the AlBO whiskers. Fig. 4 presents some anti-phase boundaries in the whisker, which is observed along the crystal direction of $[1\,\bar{1}\,0]$. As shown in Fig. 4, the anti-phase boundary has a zigzag shape and tends to be close. As anti-phase boundaries with the above features have never been found in squeeze-cast AlBO whisker- or other whisker-reinforced composites, it is most probable that these anti-phase boundaries have been caused by the ball-milling treatment. During this process ununiform impact forces are applied to the alumina-coated whiskers, this will cause local misfit or relative displacement of the monocrystal structure and finally form the anti-phase boundary.

As indicated above, deformation and fracture of whiskers can occur during the fabrication of composites by squeeze-casting process. Figs 5 and 6 show some deformation of whiskers along longitudinal direction of the AlBO whisker, and Fig. 7 shows fracture of whiskers along the longitudinal and transactional directions.

It can be noticed that the deformation degrees of whiskers in Figs 5 and 6 are different, and the one in Fig. 6 is a little bigger than that in Fig. 5. Fig. 5b indicates that, in addition to the deformation or misfit occurring in the inner part of the whisker, an atomic misfit from region A to B on the whisker surface has also occurred.

After a careful survey of the above HREM observations of the deformation and fracture of whiskers, it can be certain that an *in situ* formation of microcracks and cracks across the whisker is related to the deformation of whiskers along either longitudinal or transactional direction due to applied forces.

A sectional fracture of whiskers may occur as follows. Firstly, a small atomic misfit or deformation across the whisker is formed due to a certain applied force on the coated whisker (Fig. 5). Secondly, the degree of atomic misfit increases with increase of the

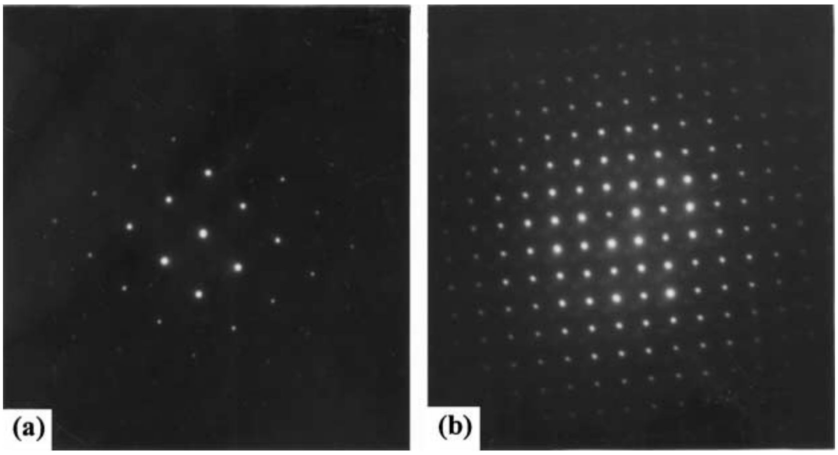

Figure 2 Electron diffraction patterns of the whisker along (a) $[1\bar{1}0]$ and (b) [001] directions.

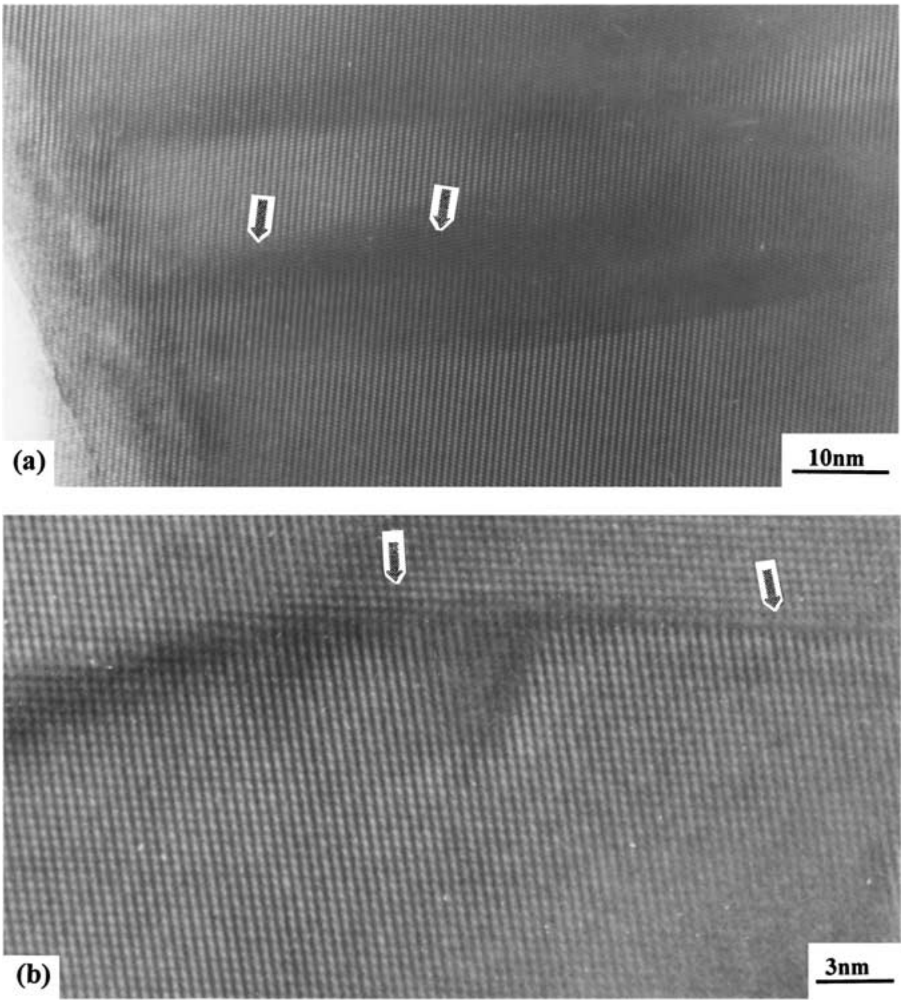

Figure 3 Defects of (a) stacking fault and (b) dislocation in the whisker.

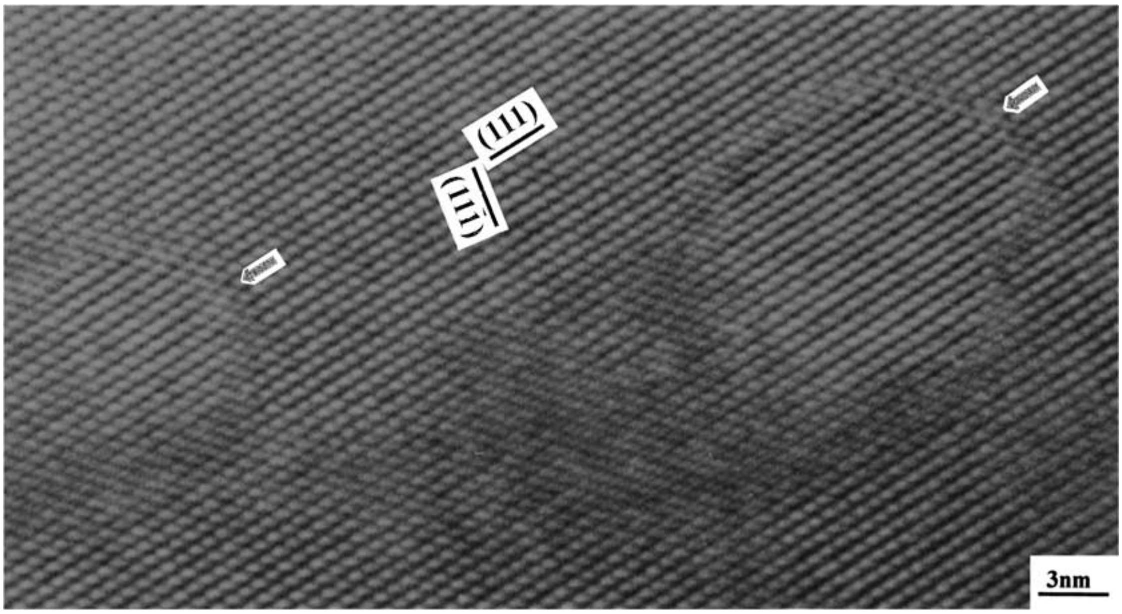

Figure 4 Anti-phase boundaries in the whisker.

applied force (Fig. 6). Thirdly, *in situ* microcrack forms at the above deformation area. Finally, the microcrack propagates and a lose of atomic misfit along the sectional direction occur, which results in a fracture of whisker along either longitudinal (Fig. 7a) or transactional direction.

3.2. Coating structure

Sol-gel method is an advanced technique for synthesizing thin-film ceramic materials like the alumina coating [13–15]. The sol-gel γ-Al_2O_3 coating prepared in this work adheres closely to the whisker surfaces, and it can still exist outside the whisker surfaces even if the

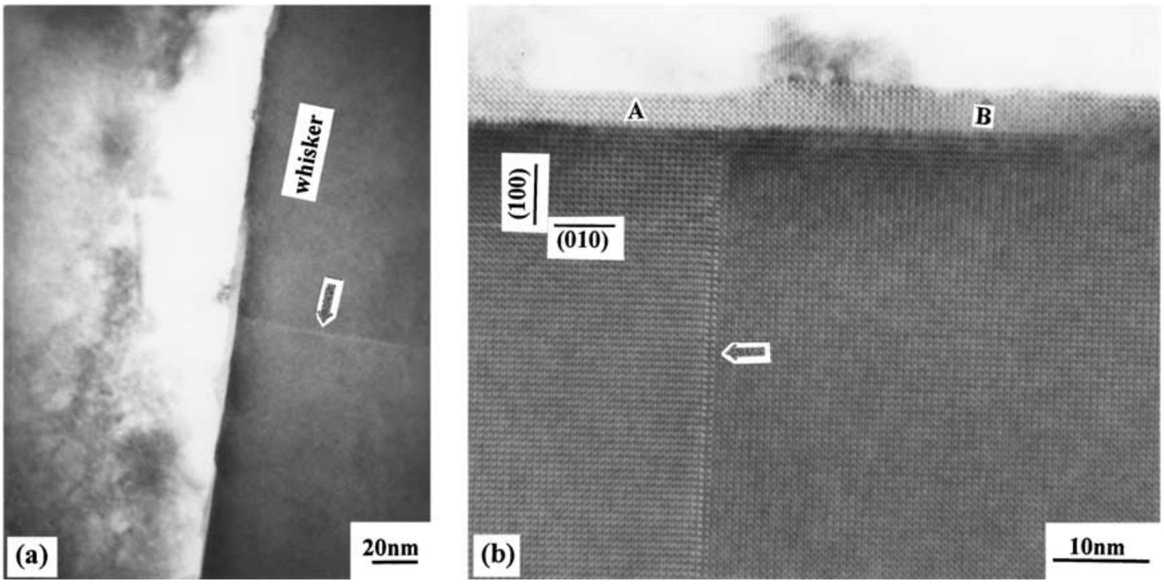

Figure 5 Longitudinal deformation of the whisker (a) HREM morphology (b) HREM image.

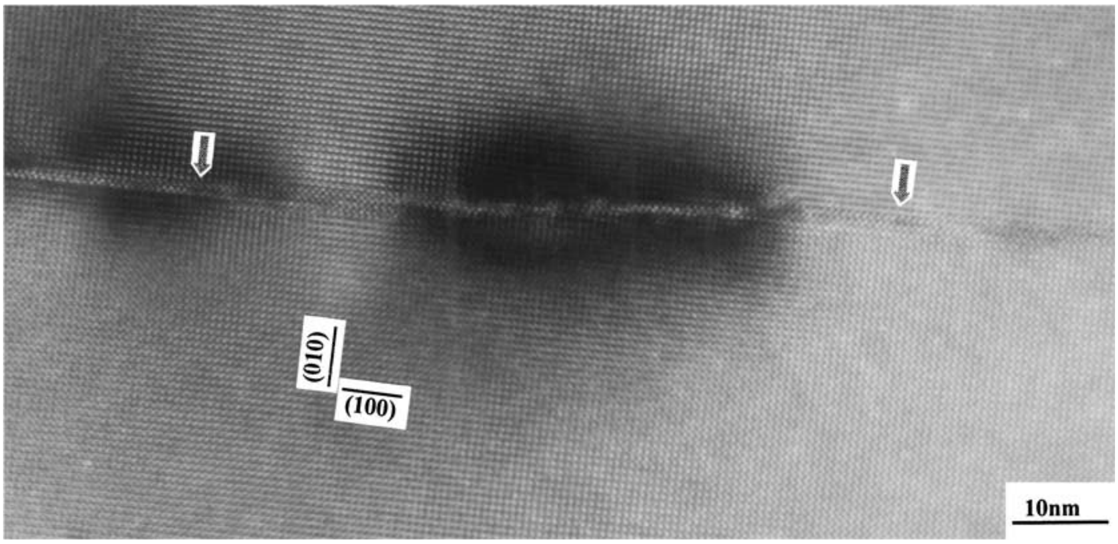

Figure 6 HREM image of the longitudinal deformation of the whisker.

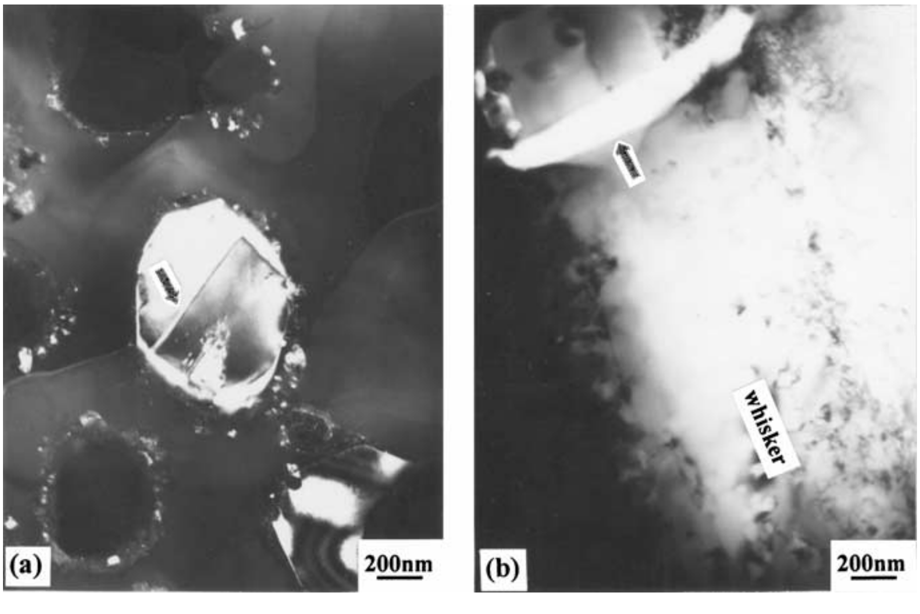

Figure 7 Fracture of whiskers along (a) longitudinal and (b) transactional directions.

whisker has fractured due to a ball-milling treatment. In the AlBOw/γ-Al_2O_3/6061Al composites, the alumina forms a tight bonding with both the whisker and the matrix alloy.

By comparison with other sol-gel materials prepared on large straight substrates or without substrates, the γ-Al_2O_3 coating is found to be with a rather ultrafine structure. Fig. 8 presents an EDP of the γ-Al_2O_3 coated whisker. It can be seen that the alumina coating has a ring-like diffraction pattern, which suggests that it has a multicrystalline structure. The HREM morphology of the coating in Fig. 9 shows bended grain boundaries and the average grain size of the γ-Al_2O_3 coating is only about 5 nm. It thus can be determined that the sol-gel γ-Al_2O_3 coating here is a nanocrystalline material. As the fabrication temperature for squeeze-casting AlBOw/γ-Al_2O_3/6061Al composites is less than either the phase-transformation temperature or the grain-growth temperature of the γ-Al_2O_3 coating, the γ-Al_2O_3 coating is stable throughout the fabrication process. Therefore, the microstructure of the γ-Al_2O_3 coating in Fig. 9 also reflects the original microstructure of the coating state.

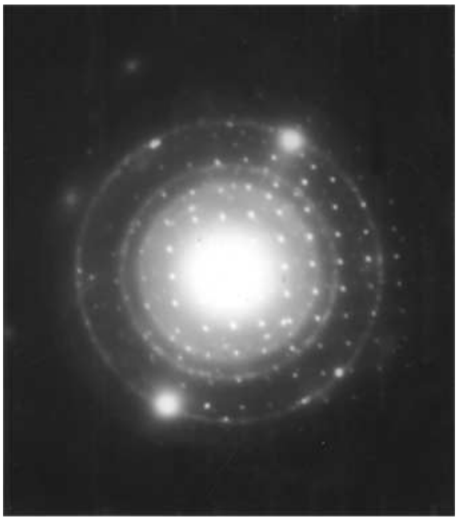

Figure 8 Electron diffraction pattern of the alumina-coated whisker.

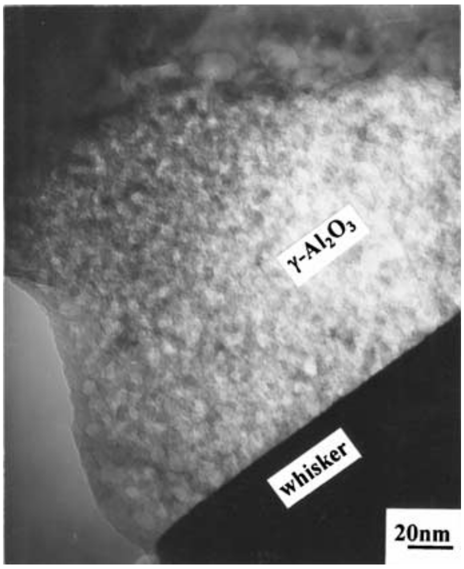

Figure 9 Alumina coating in the AlBOw/γ-Al_2O_3/6061Al composite.

Fig. 9 also shows that the sol-gel alumina coating is tight without showing any pores in it, which is quite different from those conventionally reported results that micropores (pore diameter, $d < 2$ nm) and mesopores ($2 \text{ nm} < d < 50$ nm) always present in sol-gel materials [16, 17]. The above difference may be explained by considering the special deposition process. It can be certain that, due to the rather large curvature of whisker surfaces, aluminum sol particles adsorbed on the whisker surface for preparation of the alumina coating have been rather small. This has resulted in a tight deposition of small gel or alumina particles on the whisker surface. Therefore, under a grain size of about 5 nm, the pores between alumina particles has been correspondingly minimized to so small a size that mesopores cannot exist in the coating. The micropores may be too small to be found by the HREM observations.

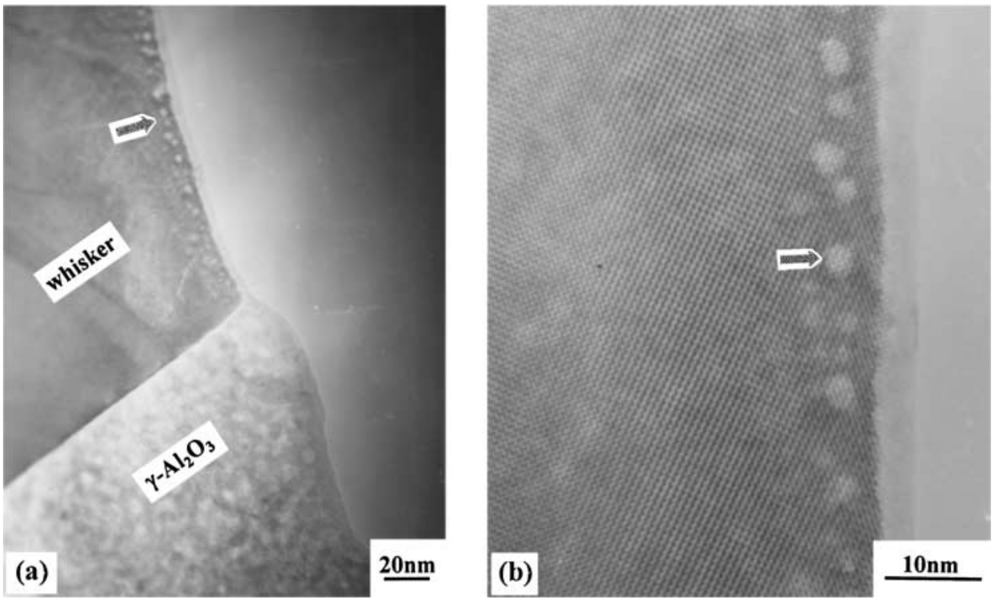

Figure 10 Damage of the alumina-coated whisker after electron radiation (a) HREM morphology (b) HREM image.

To evaluate the stability of the γ-Al_2O_3 coating, an electron ridiation for 20 min was conducted on the ion-thinned area including the alumina coating and the AlBO whisker. Fig. 10a presents the HREM morphology of this area after radiation. It shows that the electron radiation has done little damage to the nanocrystalline coating, but the whisker has suffered a serious damage. As indicated by the arrows in Fig. 10a and b, atoms in the area near the whisker surface tends to move away under the radiation, which has destroyed the structure integrity of the whisker. The above difference in structural stability partly suggests that the sol-gel alumina coating is more stable than the AlBO whisker, and thus the use of alumina coating as a barrier coating is feasible.

4. Conclusions

(1) In addition to the existence of stacking faults and edge dislocations, there also exists anti-phase boundary in the aluminum borate whiskers of the AlBOw/γ-Al_2O_3/6061Al composite.

(2) During the squeeze-casting process a sectional deformation can occur, which will lead to an *in-situ* sectional fracture of whiskers.

(3) The sol-gel γ-Al_2O_3 coating is a dense nanocrystalline material with a grain size of about 5 nm.

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