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Microstructure of alpha-silicon nitride whiskers

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Alpha-Si_3N_4 whiskers grown by the vapour–liquid–solid process have been investigated in a transmission electron microscope. The growth directions of the whiskers are determined to be $\{10\bar{1}1\}^*$, $\{10\bar{1}0\}^*$ and $\{0001\}^*$. Defects in the three kinds of whisker have been characterized and branched phenomena are explained on the basis of the TEM observations.

1. Introduction

Silicon nitride is one of the contenders for high-temperature applications. Whiskers of Si_3N_4 have been considered as promising reinforcing materials for light metals, glass and ceramics due to their high-temperature stability, high strength and stiffness. Previous work by Rühle *et al.* [1] demonstrated that the toughness of the whisker normal to the whisker axis would appear to be the most germane whisker property. Consequently, relatively high-toughness whiskers like Si_3N_4 should provide improved composite properties. Whiskers of Si_3N_4 have been prepared by various methods [2–5]. Sasaki *et al.* [6] studied the microstructure of α-Si_3N_4 whiskers by transmission electron microscopy; growth directions of the whiskers were accurately determined and defects were observed.

In the present work, the microstructures of α-Si_3N_4 whiskers are investigated in order to understand the growth mechanism and defect characteristics of the whiskers.

2. Experimental procedure

The whiskers used in the present work were α-Si_3N_4 whiskers prepared at 1300 °C by the vapour–liquid–solid (VLS) process. The raw materials were SiO_2 and carbon. The as-received whiskers were light grey in colour, wool-like, with dimensions of 0.01–1.0 μm diameter and 5–100 μm length. Samples for TEM examination were prepared by the following procedure: dispersing the whiskers in a liquid medium with the aid of ultrasonic stirring and then placing a drop of the suspension on a holey carbon film and allowing it to dry. The samples were examined in a Philips EM-420 transmission electron microscope operated at 120 kV. Defects in the whiskers were identified utilizing diffraction and phase-contrast image techniques.

3. Results and discussion

X-ray and electron diffraction analysis revealed that the whiskers used in the present work were α-Si_3N_4 single crystals. The space group of α-Si_3N_4 is $P3_{1}c$. Because of the characteristic planar spacings of $d_{0001} = 0.56$ nm and $d_{10\bar{1}1} = 0.43$ nm in α-Si_3N_4, it is easy to distinguish it from β-Si_3N_4.

Fig. 1 is a bright-field image of α-Si_3N_4 whiskers at low magnification. Most of the whiskers are straight with a high aspect ratio. Some branched whiskers can also be observed in Fig. 1. Three growth directions have been determined by analysis of electron diffraction patterns in stereograms. The growth directions are $\{10\bar{1}1\}^*$, $\{10\bar{1}0\}^*$ and $\{0001\}^*$, with the latter unreported previously.

A $\{10\bar{1}1\}^*$ whisker is shown in Fig. 2. On one side of the whisker a large amount of triangular planar defects can be observed; faint streaks can be seen in the [0 1 0] electron diffraction pattern (Fig. 2b) because of the existence of these planar defects. By careful analysis of the electron diffraction patterns with the aid of stereographic projections, these defects are determined to be planar defects parallel to the (0 0 0 1) and $(10\bar{1}2)$ planes. The surface of the $\{10\bar{1}1\}^*$ whisker on the defect-free side is smooth, while the other side with plenty of defects is toothed. These defects might be formed during the rapid growth process and may influence the whisker strength.

Fig. 3 is a bright-field image of a $\{10\bar{1}0\}^*$ whisker. Similar to the $\{10\bar{1}1\}^*$ whisker, only one side of the $\{10\bar{1}0\}^*$ whisker is heavily faulted. Sasaki *et al.* [6] reported that the faulted side consisted of a number of

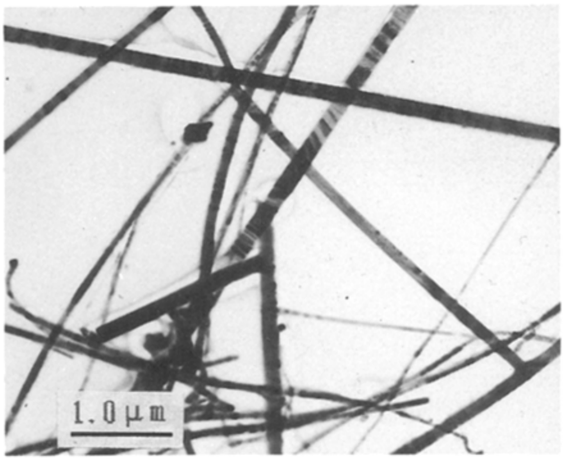


Figure 1 Bright-field image of α-Si_3N_4 whiskers.

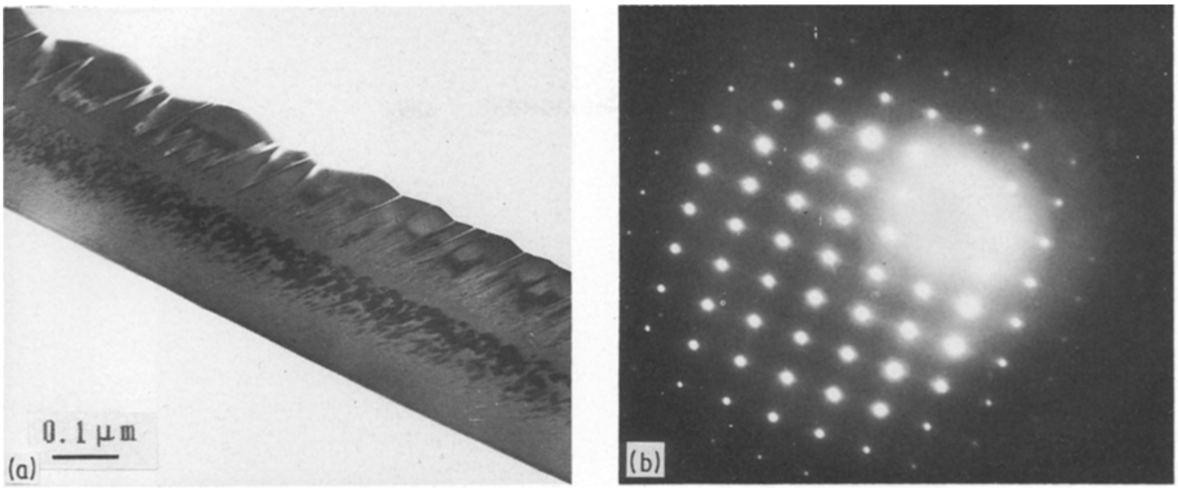


Figure 2 (a) Bright-field image of a $\{10\bar{1}1\}^*$ whisker and (b) [0 1 0] diffraction pattern.

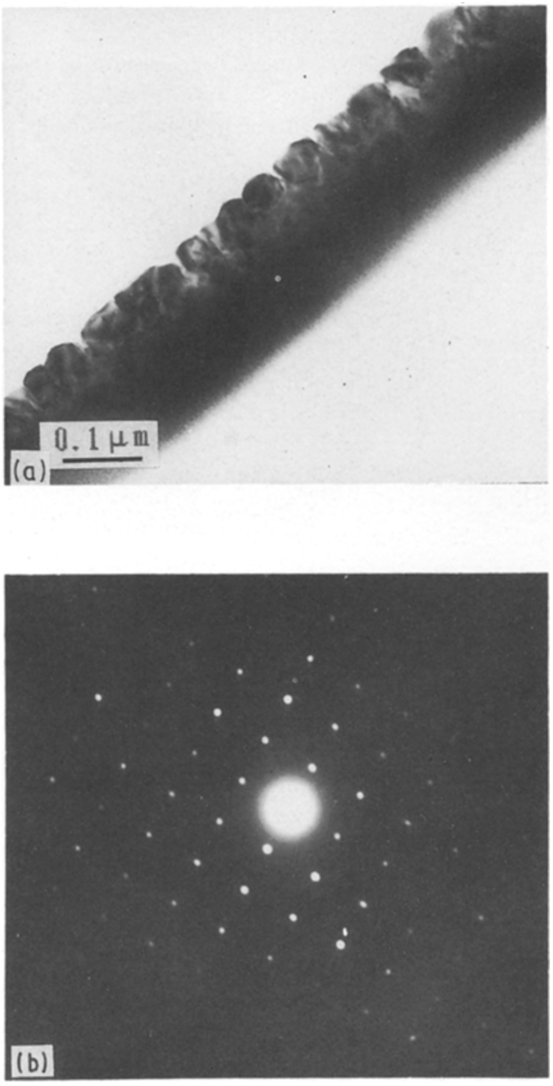


Figure 3 TEM micrograph of $\{1010\}^*$ whisker and the corresponding [0 1 0] diffraction pattern.

"micrograins". In the present work we find that the "micrograins" are about 30 nm in size. As in the $\{10\bar{1}1\}^*$ whisker, the faulted side is unsmooth on the surface. The above results are agreement with those of Sasaki *et al.* [6].

Some whiskers with defects only parallel to the plane normal to the whisker axis were observed in the present work. The appearance of this kind of whiskers is similar to that of β-SiC whiskers. The growth direction of this kind of whisker is $\{0001\}^*$, which was unreported by Sasaki *et al.* [6]. A central core region can be observed in the $\{0001\}^*$ whiskers. This might be explained by the VLS process in which the thin central core grows rapidly, followed by lateral thickening. Interfaces can be identified between the inner and outer parts of the whisker and may be considered as planar defects parallel to the $(10\bar{1}0)$ plane from the appearance of faint streaks in the [0 1 0] diffraction pattern. The interface might be formed due to the lattice mismatch of the inner and outer parts of the whisker grown at different stages. The planar defects in the outer part of the whisker are parallel to the (0 0 0 1) plane. The surfaces of this kind of whisker are smooth (Fig. 4).

Branched whiskers of SiC were observed and explained in previous work [7]. In α-Si_3N_4 whiskers, branched phenomena have also been observed. Fig. 5 gives a profile of a branching whisker occurring in α-Si_3N_4. The branched part A (Fig. 5a) is formed due to two differently oriented whiskers growing together, forming a bicrystalline whisker; this phenomenon has been found previously in β-SiC whiskers [7, 8]. When the whisker grows in crystallographically equivalent directions, e.g. $\{10\bar{1}1\}^*$ and $\{10\bar{1}\bar{1}\}^*$, as in the branched part B of Fig. 5a, the whisker can also branch out. The angle between the two branched axes is about 79°. Because α-Si_3N_4 whiskers can grow in three growth directions, formation of branched whiskers due to growing in different directions is quite common. The branched part C in Fig. 5a is formed when the whisker grows in $\{10\bar{1}\bar{1}\}^*$ and $\{10\bar{1}0\}^*$ directions at the same time. The two axes in part D in Fig. 5a are parallel to $\{10\bar{1}1\}^*$ and $\{01\bar{1}1\}^*$, respectively. Fig. 5b and c show branched whiskers analogous to the B and D parts in Fig. 5a at a large magnification.

4. Conclusions

Three kinds of α-Si_3N_4 whisker with the growth directions of $\{10\bar{1}1\}^*$, $\{10\bar{1}0\}^*$ and $\{0001\}^*$ have been observed in the present work. Both the $\{10\bar{1}1\}^*$ and $\{10\bar{1}0\}^*$ whiskers are faulted only on one side of

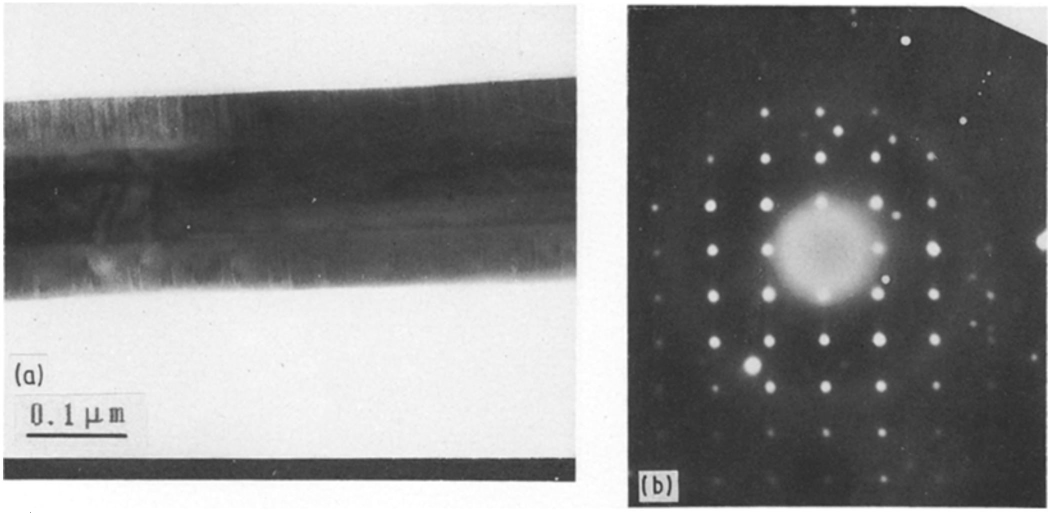
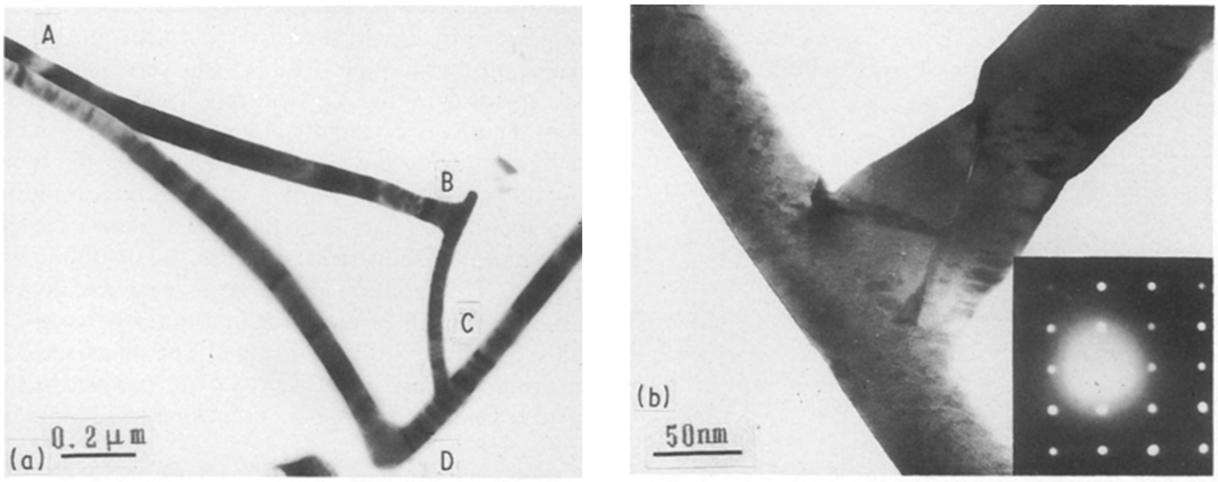


Figure 4 TEM micrograph of $\{0001\}^*$ whisker and the $[010]$ diffraction pattern.



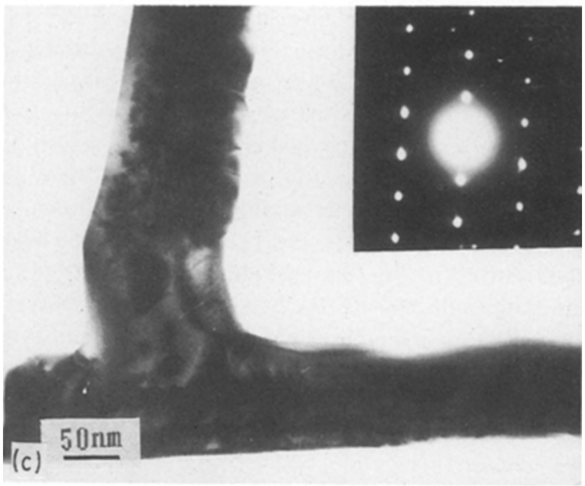


Figure 5 (a) Profile of a branched whisker; (b) branched whisker in $\{10\bar{1}1\}^*$ and $\{10\bar{1}\bar{1}\}^*$ directions; (c) branched whisker in $\{01\bar{1}1\}^*$ and $\{10\bar{1}0\}^*$ directions.

the whisker. The faulted side in $\{10\bar{1}1\}^*$ whiskers is found to consist of $(0001)^*$ and $(10\bar{1}2)$ planar defects, and the faulted side of the $\{10\bar{1}0\}^*$ whisker contains micrograins of about 30 nm in size.

In $\{0001\}^*$ whiskers, central core regions were identified and a small amount of $\{0001\}^*$ planar defects was observed in the outer part of the whiskers.

Branched whiskers in α-Si_3N_4 are formed due to the fact that whiskers grow in different growth directions at the same time, or to the formation of bicrystalline whiskers.

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