High Temperature Strength and Whisker/Matrix Interface of β Silicon Nitride Whisker Reinforced 6061 Aluminum Alloy

Katsuaki Suganuma*, Genn Sasaki*, Teruaki Fujita* and Mitsuhiro Tokuse**

*Department of Materials Science and Engineering, National Defense Academy, Kanagawa 239, Japan

**Japan Ultra-High Temperature Materials Research Center, Yamaguchi 755, Japan

The 6061 aluminum alloy matrix composite reinforced with 13 vol% β -phase silicon nitride whisker was fabricated by squeeze casting and its high temperature strength and interface microstructure between whiskers and matrix were examined with TEM. As compared with the 6061 alloy, the strength of the composite increased about 20% and the elongation reached about 4% at room temperature. The strength beyond 300°C was quite excellent.

The whisker has the [001] axis as the growing axis and a hexagonal cross-section surrounded by six {100} planes. The whisker has a few nm thick amorphous layers on the surface. The layer binds whiskers tightly in the preform. No trace of a severe reaction after casting was observed but a few nm thick crystalline layers were found on the (100) face of the whisker, which was determined to be aluminum nitride. The orientation relationship between the whisker and the aluminum nitride layer is expressed as follows:

$$\begin{array}{l} \{100\}_{\beta\text{-silicon nitride}} // \{001\}_{\text{Aluminum nitride}} \\ [100]_{\beta\text{-silicon nitride}} // [100]_{\text{Aluminum nitride}} \end{array}$$

The bottom faces and the (110) side faces, which did not have any clear crystalline layer, showed a severer reaction than the (100) side faces. Those two faces of the whisker seem not to have a suitable crystallographic orientation for growing aluminum nitride as the (100) plane. The α -silicon nitride particles 1 μm in diameter were also observed in the matrix.

(Received February 24, 1992)

Keywords: silicon nitride whisker, composite, reaction, interface, squeeze casting, strength, transmission electron microscopy, aluminum alloy, microstructure

I. Introduction

Ceramic whisker reinforced aluminum alloys have excellent physical properties such as light weight, high strength and high modulus up to elevated temperatures, and good abrasion resistance. They have been expected to be established as the structural components not only for the aeroplane and aerospace industries but also for the general industrial fields such as the automobile one, in which increasing the heat conversion ratio of engine systems has been earnestly desired from an air pollution control viewpoint. Several ceramic whiskers are available for reinforcing aluminum alloys⁽¹⁾⁻⁽⁴⁾. The silicon nitride whisker⁽³⁾ is well-known as one of the whiskers which give good strength and modulus to composites as well as silicon carbide whisker⁽¹⁾ and as aluminum borate whisker⁽²⁾. Two types of the silicon nitride whisker are commercially available today. Both have hexagonal phases and are designated as α and as β . The β -phase silicon nitride whisker is as thick as about 1 μm in diameter and the aspect ratio is as small as about 10–50, while the α -phase silicon nitride whisker has a large aspect ratio reaching 200 (0.1–1.0 μm thick). No data is available today on the possibility of this whisker for aluminum matrix composites. In using whiskers, the toxicity of whiskers to human body has been pointed out. It is desired that whiskers be both chemically non-reactive with human body and thicker than about 1 μm ⁽⁵⁾. From

the latter requirement, the β -silicon nitride whisker seems to be better than the α -silicon nitride whisker. Therefore, it is worthwhile to examine the potential of β -silicon nitride whisker as a reinforcing material of aluminum alloys.

Several methods have been examined and established for producing whisker reinforced aluminum alloys and each has its own benefits. Squeeze casting is one of the most common methods, which enables the production of a high quality composite economically. This process has been widely used in industrial applications. At the first step of squeeze casting, whiskers are sintered into the preform which has a certain shape and a volume fraction to be desired in a composite. Usually, silica is added to whiskers as a binder. Under the squeeze casting condition, an whisker preform must be strong enough to sustain the pressure applied for infiltrating an alloy melt into the whisker network. For this purpose, a certain amount of silica is required and a volume fraction of whiskers must be higher than about 20%. However, silica reacts with aluminum alloys easily at elevated temperatures. Aluminum and its active alloying elements such as magnesium reduce silica into silicon, which dissolves into the melt resulting in the precipitation of large silica particles during solidification. The large silica particles become serious defects in a composite. In addition, the alloying elements such as magnesium, which are important to reinforce the matrix, segregate around whiskers. This segregation also results in softening the matrix.

Thus, it has been desired to establish a new method for binding whiskers which does not have these problems. It is known that without use of the binder, the β -silicon nitride whisker can form a strong preform even with a relatively small amount of whiskers⁽⁶⁾. This whisker is, therefore, expected to overcome the problems mentioned above.

The aims of the present work are to evaluate the mechanical properties of the composite reinforced with the β -silicon nitride whisker and to examine the interfacial reaction between the whisker and the aluminum alloy matrix under squeeze casting.

II. Experimental Procedures

1. Materials and fabrication of composites

β -silicon nitride whisker and its preform were supplied from Ube Industries Co. Ltd. The chemical compositions and the selected properties of the preform are listed in Table 1. The whisker contains a slight amount of yttrium. The strength of the preform is several times higher than those fabricated by the conventional silica binding method. The preform was a 30 mm $\times$ 30 mm $\times$ 15 mm block. The volume fraction of whisker in a composite was 13%. The commercial 6061 aluminum alloy was used as the matrix alloy.

Fabrication of a composite was carried out by squeeze casting in air. The temperatures of the preform, of the alloy melt and of the mold were 500, 800 and 500°C, respectively, and the casting pressure was 50 MPa.

For comparison, the 6061 composite reinforced with 20 vol% β -silicon carbide whisker was fabricated by the same process and its mechanical properties was evaluated. The silica binding method was used in preparing a preform.

2. Tensile test

Strength of composites was evaluated by the tensile test up to 400°C in air. The tensile specimen, 1.5 mm $\times$ 4.0 mm in cross-section and 10 mm in gage length,

was cut from the composites. The specimen was heat-treated under the T6 condition (520°C–30 min solution treatment + water quench and 175°C–8 h aging). Tensile speed was 8.3×10^{-4} /s.

3. Microstructural observation

Microstructures of the whiskers, the preform and the composite were investigated by SEM, analytical TEM (EDX analysis in the STEM mode) and HREM. In the present EDX analysis, elements heavier than magnesium were detected. Because the β -silicon nitride whisker used in the present work has been developed recently, it is worth-while to know the microstructural feature of the whisker itself. TEM specimens of the composite were prepared in two different ways. One sample was a thin foil and the other was extracted whiskers from the composite. The thin foil was first cut from the composite and ground into the 0.2 mm thick plate. Then it was thinned by electrolytic polishing and finished by argon ion thinning. Extraction of the whiskers was carried out by dipping a small piece of composite in a dilute HCl solution. The extracted whiskers and reaction products were dispersed on a carbon grid for TEM. For both samples, thin carbon was coated in order to prevent charging up during the TEM observation. The transmission electron microscope used in the present work was JEOL JEM200CX operating at 200 kV. X-ray diffraction and ESCA were also carried out for the starting whiskers, the whisker preform and the extracted whiskers.

III. Results and Discussion

1. Tensile properties of composites

Table 2 summarizes the 0.2% proof stress, tensile strength and elongation of each composite at room temperature. The composite with silicon carbide whiskers showed a higher strength by more than 100 MPa than the β -silicon nitride reinforced composite which seems to be primarily because of the larger volume fraction of whiskers. However, the elongation of the silicon carbide whisker reinforced composite was as small as about 1% which is the usual case for the composite with a large volume fraction of whisker. The decrease in elongation of the composite at room temperature often becomes a problem not only for silicon carbide whiskers but also for other whiskers and fibers. By lowering the volume fraction of whiskers the degradation in ductility can be mitigated though the desired strength is sometimes not obtained. In addition, when the volume fraction of

Table 1 Characteristics of β -Si₃N₄ whisker and its preform.

Whisker	
Diameter	0.5–1.5 (μ m)
Length	10–30 (μ m)
Crystalline phase	β -phase
Chemical compositions (in mass)	
N	40%
O	< 1%
Fe	< 100 ppm
Ca	< 30 ppm
Al	< 10 ppm
Y	0.5%
Preform	
Whisker volume fraction	13%
Flexural strength	> 10 MPa

Table 2 Tensile properties of 6061 alloy and 6061 matrix composites with β -Si₃N₄ and β -SiC whiskers at room temperature.

Materials	Properties	0.2 proof stress (MPa)	Tensile strength (MPa)	Elongation (%)
6061 alloy		238	273	6.2
6061/Si ₃ N ₄		267	358	3.9
6061/SiC		366	475	1.4

whisker is low, the strength of the preform decreases and the preform cannot sustain the pressure applied during squeeze casting. Therefore, the minimum volume fraction of whiskers required in the squeeze casting process is considered to be about 20%. On the other hand, although the present composite with the β -silicon nitride whisker has a low volume fraction of 13%, no casting defect such as cracking of the preform was observed in the composite because of the high strength of the preform. The elongation of the composite became three times higher than that of the composite with 20 vol% silicon carbide whisker, which seems to be mainly due to the low volume fraction of the whisker.

Figure 1 shows the temperature dependence of the tensile strength of the 6061 matrix composites with 13 vol% β -silicon nitride whisker and 20 vol% silicon carbide whisker and the 6061 alloy. Although in the temperature range under 300°C the strength of the composite with the silicon nitride whisker was lower than that with the silicon carbide whisker, both values became comparable beyond 300°C. There is no available data on the composite strength in the low volume fraction range because such a composite is hardly fabricated by squeeze casting. It was reported that the 6061 matrix composite with 17 vol% β -silicon carbide whisker fabricated by squeeze casting had a strength of 180 MPa at 300°C⁽⁷⁾, and that the same composite with 13 vol% β -silicon carbide whisker aligned uniaxially by hot-pressing followed by hot-extrusion had 130 MPa (this value is the extrapolated one)⁽⁸⁾. At 400°C, even if the composite had a high volume percent of 20%, the strength was about 100 MPa⁽⁹⁾. Compared with those values obtained with the β -silicon carbide whisker, the present composite reinforced with β -silicon nitride whisker possessed high strength in the high temperature range, e.g. 220 MPa at 300°C and 120 MPa at 400°C, in spite of the lower volume fraction of the whisker.

Thus, both facts that the composite reinforced with the β -silicon nitride whisker possesses an excellent ductility even at room temperature and that strength beyond

300°C is compatible with that with larger volume fraction of β -silicon carbide whisker indicate the great potential of the present composite for practical uses because the most desired feature for the aluminum matrix composites is not the high strength at room temperature but the strength at elevated temperatures beyond 200°C, in which monolithic aluminum alloys inevitably become soft, without sacrificing the ductility at room temperature.

2. Observation of raw β -silicon nitride whisker

Figure 2(a) shows the X-ray diffraction pattern from the β -silicon nitride whisker. A slight amount of $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$ was detected in addition to β -phase silicon nitride. Figure 3 shows a TEM micrograph of the whisker. Most of the whisker was thicker than 1 μm in diameter and grows almost linearly, which is much different from the morphologies of the α -silicon nitride whisker and the β -silicon carbide one bending with many knots. Figure 4 shows HREM images of the surface region of the whiskers viewed from the vertical direction to the whisker axis. The β -silicon nitride whisker has a hexagonal cross-section (see Fig. 5 and Fig. 12). The whisker axis is parallel to the $\langle 001 \rangle$ axis of hcp crystal. The side faces of the whisker basically consists of six $\{100\}$ planes. At the corners, $\{110\}$ planes were sometimes observed. Figure 4 is showing the edge-on views of (100) and (110) planes. Although, inside the whisker, no defects such as the stacking fault, which is frequently observed in the β -silicon carbide whisker, was observed, the diffraction pattern showing a streak along

Fig. 1 Temperature dependence of tensile strength of 6061 alloy, β -silicon nitride whisker reinforced 6061 alloy and 20 vol% silicon carbide whisker reinforced 6061 alloy.

Fig. 2 X-ray diffraction profiles. (a) The starting whisker, (b) the preform and (c) the extracted whisker.

Fig. 3 TEM photograph of β -silicon nitride whisker.

(a)

(b)

Fig. 4 HREM of the whisker surfaces. (a) (100) surface and (b) (110) surface.

the $\langle 010 \rangle$ direction seems to indicate the presence of some plane defect. In addition, a thin amorphous-like layer, which is a few nm thick; was observed on the whisker surface. Independent of the observed directions, no lattice image was recognized in the surface layer. EDX analysis revealed only silicon and no yttrium was ob-

Table 3 The peak energy positions of Si2p and Al2p in the ESCA profiles of β -silicon nitride whisker, the whisker preform and the extracted whisker from the composite (in eV).

Materials \ Peaks and etching time	Si2p		Al2p	
	0 min	2 min	0 min	2 min
Whisker	101.7	101.7	—	—
Whisker preform	101.6	102.2	—	—
Extracted whisker	101.7	101.9	74.5	74.5

Reference data: Si2p(Si_3N_4) = 101.6 eV, Al2p(AlN) = 74.2 eV
The etching was carried out by argon ion bombardment.

served as one of the impurities. In order to identify the chemical compositions of the surface layer, the chemical shift of the Si2p peak in the ESCA profile was examined for the β -silicon nitride whisker. Table 3 summarizes the ESCA data. The peak of the Si2p from the raw whisker is located at 101.7 eV, which is well equal to that in silicon nitride. Therefore, this surface amorphous layer was decided to be the amorphous silicon nitride.

In general, the whisker growing in the VLS mechanism always has some traces on one end which indicates the presence of liquid during whisker growth. This whisker did not show any such traces but had flat ends.

3. Observation of whisker preform

Figure 5 shows the SEM photographs of the whisker preform with EDX analysis of the large particles. It is obvious that the whisker has a hexagonal cross-section. Steps were frequently observed on the side faces of the whisker as indicated by the arrow. The steps is formed vertically to the side faces and, therefore, they are on the $\{001\}$ plane of β -silicon nitride. From the SEM photograph no information on the binding among whiskers was obtained. In a preform, large particles were sometimes observed as shown in Fig. 5(b). From the EDX analysis of these particles, a small amount of yttrium was detected in addition to silicon. Combined with the X-ray diffraction analysis shown in Fig. 2(b), it can be concluded that the phase of these particles is $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$.

Figure 6 is the TEM micrograph showing the binding between two whiskers. It is obviously observed that the binding between whiskers is achieved through a thin surface layer on the whisker, which is shown in Fig. 4. From this observation, the high strength of the preform seems to depend on the fact that the uniform formation of a thin layer on every whisker makes whiskers to form a tight connection at every point in contact. In general, when the silica binder is used to form a preform, silica attaches onto whiskers discretely and no uniform binding among whiskers can be obtained⁽¹⁰⁾.

4. Macroscopic observation of composite and extracted whisker

The X-ray diffraction data on the extracted whisker in Fig. 2(c) showed the presence of α -phase silicon nitride in addition to the β -phase. Because no α -phase was detected

Fig. 5 SEM photographs of the preform. (a) The whisker showing the hexagonal cross section and (b) Large particles with EDX analysis.

in the preform, the reaction between the whisker and the aluminum alloy melt seems to produce α -phase silicon nitride. On the other hand, the peak height of the $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$ phase showed little change after casting. Figure 7 shows the TEM photograph of the extracted whisker. There was little evidence for a severe reaction on the whiskers such as erosion or precipitation. Thus, the β -silicon nitride whisker is compatible with the aluminum alloy melt under squeeze casting conditions. However, large particles about 1 μm in diameter were frequently observed as shown by the arrow. The electron

Fig. 6 TEM of whisker/whisker binding. (a) Whiskers connecting at a point and (b) high magnification image of the binding.

Fig. 7 TEM of the extracted whisker. The diffraction pattern was taken from the arrowed particle.

diffraction pattern with EDX analysis of the large particles revealed that these particles are α -phase silicon nitride, in agreement with the X-ray data in Fig. 2(c). Thus, the whisker slightly reacts with the aluminum melt to form α -silicon nitride particles dispersing in the matrix. Inside the particles, small voids were frequently observed as shown in Fig. 8. The void was surrounded by the $\{111\}$ planes of α -silicon nitride, a part of which is shown in the figure. Unfortunately, the identification of the detailed mechanism of the void formation is beyond

Fig. 8 TEM of voids in an α -silicon nitride particle in the matrix.

Fig. 9 HREM of the whisker near the end in the composite.

the scope of the present work. It is plausible that the β -silicon nitride whisker decomposes by the reaction with the aluminum melt releasing silicon and nitrogen into the alloy melt. Nitrogen does not dissolve into the aluminum matrix and exists as bubbles while silicon can dissolve in large amounts. During solidification, if the dissolved silicon reacts with nitrogen bubbles to form stable α -phase silicon nitride at low temperatures below 800°C, the voids will disperse in the α -silicon nitride particles.

Figure 9 shows the TEM photograph of the interface region between the whisker and the matrix. The interface between the side face and the matrix is relatively flat but there was a thin interface layer a few nm thick observed. In general, when an whisker reacts with an aluminum matrix, two cases on the whisker surface morphologies have been reported. In the cases of silicon carbide and aluminum borate whiskers, the surface of the whisker becomes irregular both by reaction erosion and by precipitation of reaction products⁽²⁾. On the contrary, the potassium titanate whisker does not react with aluminum severely⁽¹⁰⁾. It forms the fine alumina particles from the reduction reaction of the silica binder on whiskers though the interface becomes flat without the silica binder. In the present case, there was no large reaction

product nor alumina particles from the silica binder on an whisker because the preform did not contain silica as the binder. Therefore, even if some reaction occurs between the whisker and aluminum matrix, it must be faint. From the photograph, only the end of the whisker became somewhat irregular as compared with that before casting. This seems to indicate that the end of the whisker is more reactive than the side face.

5. HREM observation of the whisker/matrix interface

Figure 10 shows the HREM photograph of the whisker/matrix interface. The whisker lies on the sheet and the (100) side face is just edge-on viewed. The lattice image in the whisker is that of the {100} plane of β -silicon nitride. The aluminum matrix is inclined slightly from the $\langle 110 \rangle$ axis and only one set of the (200) planes is observed. Between the whisker and the matrix a few nm thick layer is observed. This layer showed lattice fringes parallel to the (100) plane of β -silicon nitride, which is different from the fact that the thin layer on the whisker was amorphous before casting as seen in Fig. 4. At the greater part of the interfaces between the (100) face of the whisker and the matrix, the same reaction layer was observed. The high magnification image of the interface is shown in Fig. 11. The whisker is exactly aligned along the $\langle 010 \rangle$ axis and the (100) face was edge-on. In the reaction layer, the lattice fringes vertical to the surface of the whisker is observed in addition to the parallel one. Such a vertical lattice fringes were often recognized. From the photograph, the lattice distance of the parallel to the whisker surface is about 0.25 nm and the vertical one is about 0.27 nm.

Figure 12 shows the HREM photograph of the interfacial region as viewed from the whisker axis. The reaction layer with the lattice fringes was observed only on the (100) side face of the whisker but not on the (110) side face. In addition, some eroded sign by the reaction was observed at the latter interface as indicated by the

Fig. 10 HREM of the whisker/matrix interface. The whisker lies in the sheet and the electron beam is parallel to the (110) surface of the whisker.

Fig. 11 HREM of the surface layer/whisker interface. The electron beam is incident along the [010] axis of the whisker and the (100) surface is just edge-on.

Fig. 13 Enlarged photograph of the edge portion of the whisker in Fig. 12.

arrows. Figure 13 shows the enlarged image of Fig. 12 showing the corner region of the whisker. It is clearly shown that the reaction layer which has the lattice fringes spacing of 0.25 nm is formed only at the (100) face of the whisker/matrix interface and that at the (110) face of the whisker/matrix interface does not show such a crystalline layer but an amorphous-like layer thinner than 1 nm. Thus, the (100) and (110) side faces of the β -silicon nitride whisker have different reactivity against the aluminum alloy melt. Only on the (100) face, the reaction layer grows as the crystalline layer, which seems to

Fig. 12 HREM viewed along the whisker axis. The arrows show the eroded portion on the {110} planes.

Fig. 14 HREM of the whisker end/matrix interface. The incident beam is along the [010] axis of the whisker.

prohibit further reaction with the aluminum melt, and on the (110) face the reaction proceeds even though there is a thin amorphous-like layer formed.

On the other hand, the whisker end became rougher than before casting and showed a few nm thick amorphous-like layer as shown in Fig. 14. This layer, there-

Fig. 15 X-ray diffraction profile taken from the extracted whisker from the composite reacted at 800°C for 60 min.

fore, seems to have no clear orientation relationship with the whisker or to be amorphous.

6. Identification of crystalline reaction layer on the (100) plane

The reaction layer observed at the (100) face of the whisker/matrix was too thin to be identified with EDX

Fig. 16 TEM image of the extracted whisker of the composite reacted at 800°C for 60 min with EDX analysis.

analysis in the STEM mode. To make the reaction product clearer, the composite was heated at 800°C, which was the same temperature of the aluminum melt, for 60 min and was analyzed.

Figure 15 shows the X-ray diffraction pattern of the whisker extracted from the composite reacted for a long time. Two new phases which could not be identified in the composite just after squeeze casting were recognized. They were silicon and aluminum nitride. Figure 16 shows the TEM photograph and the result of EDX analysis. The surface reaction layer grew up to about 20 nm thickness and partly became particles. The EDX profile from the reaction product indicated that this is composed of aluminum and silicon. Figure 17 shows the HREM image of the surface area of the whisker shown in Fig. 16 with diffraction patterns. Combined with the results from the X-ray diffraction, the electron diffraction and the EDX analysis, the reaction product formed on the (100) whisker face is identified as aluminum nitride. It can be deduced that the reaction layer in a squeeze cast composite is also the same aluminum nitride. This conclusion is supported by the ESCA analysis on the extracted whisker from the as cast composite shown in Table 3. The Al2p peak showed the chemical shift of aluminum nitride clearly. The lattice images of the reaction layer also coincides with this result. However, the EDX analysis in Fig. 16 showed the presence of silicon in the reaction products. This indicates that this product might be 15R-type sialon. In the present observation, no long

range ordering inside the layer, which is the typical sign of this compound, was recognized and, therefore, this layer is called as aluminum nitride in the present work. On the other hand, the segregation of magnesium, which is sometimes a serious problem in fabrication of composite with silica binder, was not recognized even in the composite after long reaction. It can be said that this composite is also superior in this feature.

The following crystallographic orientation relationship is derived between the aluminum nitride layer and the β -silicon nitride whisker.

$$\begin{aligned} \{100\}_{\beta\text{-silicon nitride}} // \{001\}_{\text{Aluminum nitride}} \\ [100]_{\beta\text{-silicon nitride}} // [100]_{\text{Aluminum nitride}} \end{aligned}$$

From the fact that there is an exact orientation relationship between two crystals, it is presumed that a good matching between two phases exists at the interface. In fact, the (001) planes of β -silicon nitride and the (100) planes of aluminum nitride connected directly with little strain at the interface as shown in Fig. 11. The mismatch between the two lattice spacings, the (001) spacing of β -silicon nitride (0.2908 nm) and the (100) spacing of aluminum nitride (0.2695 nm), is about 7.3% with the former as a standard.

7. Surface layer of whisker and reaction at whisker/matrix interface

From the observations of the whiskers before and after casting in the foregoing sections, it became clear that the surface layer which the β -silicon nitride whisker already had before casting has a quite important role to make a preform and that the surface aluminum nitride layer formed during casting has a certain role in the composite properties.

The surface layer on the raw whisker was identified as the amorphous silicon nitride by ESCA with HREM. This whisker is fabricated by the thermal decomposition of silicon di-imide ($\text{Si}(\text{NH}_3)_2$). When the reaction system does not contain yttrium as one of the reactants, an whisker becomes α -phase silicon nitride. With yttrium, β -silicon nitride is obtained. The α -silicon nitride whisker fabricated by this process also had a similar amorphous layer on the whisker surface in a few nm thickness⁽¹¹⁾ while the conventional one grown in the VLS process did not have. Therefore, the surface amorphous layer is one of the features of the whisker grown in the silicon di-imide thermal decomposition process. The whisker growth process can be expressed that Si-N amorphous is formed on the surface and through this amorphous layer the whisker grows along the [001] axis. The role of yttrium in forming the β -phase silicon nitride has not been clear at this moment. Two effects, however, can be plausible. The surface layer might contain a little amount of yttrium which cannot be detected by the EDX analysis and promote the growth. The other is that yttrium acts on the formation of nuclei for the whisker, in which case yttrium is not to be included in the surface layer.

If the surface layer is amorphous silicon nitride, it is easy to react with aluminum melt to convert into a

Fig. 17 HREM of the whisker surface in Fig. 16. The incident beam is along the [010] axis of the whisker. The diffraction pattern in the top is from the surface reaction product and that in bottom is from the whisker. The top pattern and that indicated by the arrows in the latter shows that from the (100) plane of AlN.

crystalline aluminum nitride in a very short time. In addition, the whisker itself can react with the aluminum melt. The reaction is expressed as:

As the free energy change of this reaction at 800°C is negative (−440 kJ/mol), the reaction proceed naturally. In fact, both compounds were detected after prolonged reaction as shown in the X-ray analysis (Fig. 15). Aluminum nitride can, however, grow only on the preferred position such as the (100) plane of β -silicon nitride but not on the (110) side face nor on the end face of the whisker. The whisker dissolves into the matrix melt to be silicon and nitrogen from the latter faces because they are not covered with aluminum nitride. During solidification, the dissolved elements forms α -silicon nitride particles more stable than β -silicon nitride at low temperatures.

Occasionally, no lattice image was observed in the surface reaction layer on the (100) face after casting. Such imperfect crystalline structure in the reaction layer seems to be caused by the facts that the reaction during squeeze casting finishes within a quite short time and that the lattice mismatch between the whisker and the aluminum nitride layer induces a certain strain.

IV. Conclusion

In the present work, the 6061 matrix composite reinforced with a high strength β -silicon nitride whisker preform was fabricated by squeeze casting and its mechanical properties was evaluated by tensile test. The microstructure of the whisker, of the whisker preform and of the composite were observed mainly by TEM. The following results were obtained.

(1) While the tensile strength of the 13 vol% whisker reinforced composite increased strength only by about 20% as compared with that of the 6061 alloy at room temperature, the elongation reached about 4% which is a good value for the metal matrix composites. In addition, high temperature strength beyond 300°C was quite excellent.

(2) The whisker has the [001] direction of the β -phase silicon nitride as the growth axis and has a hexagonal cross-section surrounded primarily by six {100} planes. The whisker has a thin layer on the surface. This layer is amorphous silicon nitride.

(3) The whiskers in the preform are bound each other through the amorphous layer. This binding seems to give high strength to the preform.

(4) Although no severe reaction was observed between the whisker and the matrix, a few nm thick reaction layer was recognized at the interface. On the {100} side face of the whisker, an aluminum nitride layer was observed which had the following crystallographic orientation relationship with the whisker:

$$\begin{aligned} \{100\}_{\beta\text{-silicon nitride}} // \{001\}_{\text{Aluminum nitride}} \\ [100]_{\beta\text{-silicon nitride}} // [100]_{\text{Aluminum nitride}} \end{aligned}$$

(5) The ends and the (110) side faces of the whisker became rougher because of the reaction and the few nm thick interlayer at these interfaces did not have clear lattice structure. Apart from whiskers, α -silicon nitride particles about 1 μm in diameter were observed.

REFERENCES

- (1) For instances, D. L. McDanel: *Met. Trans.*, **16A** (1985), 1105.
- (2) K. Sukanuma, G. Sasaki, T. Fujita and N. Suzuki: *J. Japan Inst. Light Metals*, **41** (1991), 297.
- (3) Y. Nishida, T. Imai, M. Yamada, H. Matsubara and K. Shiroyanagi: *J. Japan Inst. Light Metals*, **38** (1988), 515.
- (4) K. Sukanuma, T. Fujita, N. Suzuki and K. Niihara: *J. Mater. Sci. Letters*, **9** (1990), 633.
- (5) J. D. Birchall, D. R. Stanley, M. J. Mochford, G. H. Pigott and P. J. Pinto: *J. Mater. Sci. Letters*, **7** (1988), 350.
- (6) M. Tokuse, H. Uchida, K. Shimizu, M. Suzuki, K. Matsunaga and Y. Waku: *Proc. 75th fall meeting of the Japan Inst. Light Metals*, (1987), p. 40.
- (7) K. Ohori, H. Watanabe and Y. Takeuchi: *Mater. Sci. Technol.*, **3** (1987), 57.
- (8) Y. Morimoto and G. Ouchi: *J. Japan Inst. Light Metals*, **38** (1988), 658.
- (9) M. Fujita: *J. Iron and Steel Inst. Japan*, **75** (1989), 1516.
- (10) K. Sukanuma, T. Fujita and K. Niihara: *J. Japan Inst. Metals*, **54** (1990), 1422.
- (11) K. Sukanuma: unpublished work (1991).