Advanced Composite Materials
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tacm20

Mechanical properties of Si3N4 matrix composites reinforced with SiC whiskers with oxide coatings

Masahiro Kato [a] & Yasuhiro Goto [b]

[a] Materials and Devices Research Laboratories, Toshiba Corporation, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

[b] Materials and Devices Research Laboratories, Toshiba Corporation, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

Version of record first published: 02 Apr 2012.

To cite this article: Masahiro Kato & Yasuhiro Goto (1997): Mechanical properties of Si3N4 matrix composites reinforced with SiC whiskers with oxide coatings, Advanced Composite Materials, 6:3, 227-237

To link to this article: http://dx.doi.org/10.1163/156855197X00094

Adv. Composite Mater., Vol. 6, No. 3, pp. 227–237 (1997)

Mechanical properties of Si_3N_4 matrix composites reinforced with SiC whiskers with oxide coatings

MASAHIRO KATO and YASUHIRO GOTO

Materials and Devices Research Laboratories, Toshiba Corporation, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

Received 16 April 1996; accepted 3 September 1996

Abstract—SiC whiskers were coated with MgO or TiO_2 by a sol-gel method in order to vary the interfacial strength between whisker and matrix. These whiskers with oxide coatings were used to fabricate Si_3N_4 matrix composites for the purpose of investigating the effects of the coating on mechanical properties such as fracture strength, fracture toughness, and fracture energy. The composite reinforced with whiskers with MgO coating showed higher fracture energy than that with TiO_2 coating, while the sample reinforced with whiskers with TiO_2 coating exhibited better fracture toughness and strength. These results suggest that MgO coating reduced the interfacial strength, while TiO_2 coating increased it.

Keywords: composite; coating; Si_3N_4; SiC; whisker.

1. INTRODUCTION

Ceramics are promising materials for high-temperature structural applications. However, their use is limited to only a few fields because of their low fracture toughness. Thus, much work has focused on ceramic matrix composites reinforced with fibers or whiskers to increase fracture toughness [1–4]. Whisker composite is a promising material, and it has been found to be effective for increasing the fracture toughness of Al_2O_3. Furthermore, Si_3N_4 matrix composites reinforced with SiC whiskers have also been investigated extensively [5–8], and the effects of whiskers on high temperature properties [9, 10] and fracture energy [11, 12] have been recognized.

Whisker alignment [13–17], and interfacial properties between whisker and matrix [13, 18–20], have been considered the most important factors in improving the fracture toughness of composites. In our previous work [21, 22], Ti and Al coatings on the whisker surface were found to be effective in increasing the fracture toughness of SiC whisker/Si_3N_4 composites because silicide was formed at the interface between whisker and matrix, whereas Mg or Y coatings, which formed nitride at the interface, were effective for increasing fracture energy. Metal coating was, however, a very time-consuming process, since it was done by RF-sputtering.

Therefore, in this study, a sol-gel method was used to coat MgO and TiO_2 on SiC whiskers because the coatings were expected to be formed in a shorter time. In order to clarify the effects of the coating, MgO and TiO_2, which were not used as sintering additives in this experiment, were selected from among the Mg, Y, Al, and Ti oxides. Then, Si_3N_4 matrix composites reinforced with SiC whisker coated with oxide were fabricated to investigate the effects of the coating on mechanical properties.

2. EXPERIMENTAL PROCEDURES

2.1. Sample preparation

2.1.1. Surface coating. Commercially available SiC whiskers (TWS-400 Tokai Carbon Co., Ltd, Japan) were used in the following investigations. In the case of MgO coating, $Mg(CH_3OCH_2CH_2O)_2$ (Soekawa Chemical Co., Ltd, Japan) as a metal alkoxide and $CH_3OCH_2CH_2OH$ (Wako Chemical Co., Inc., Japan) as a solvent were used. In the case of the TiO_2 coating, $Ti(OC_2H_5)_4$ (Soekawa Chemical Co., Ltd, Japan) as a metal alkoxide, C_2H_5OH (Kanto Chemical Co., Inc., Tokyo, Japan) as a solvent, and HNO_3 (Koso Chemical Co., Ltd, Tokyo, Japan) as a catalyst were used. Each solvent was selected according to the alkoxide substituent. The SiC whiskers were put into the solvent and mixed by means of a magnetic stirrer to obtain a well-dispersed whisker suspension. The metal alkoxide was dissolved in the solvent in another vessel. Then, the SiC whisker suspension was added to the metal alkoxide solution and thoroughly mixed. After that, H_2O and the catalyst were added to the metal alkoxide solution with SiC. After the hydrolyzation of metal alkoxide, the whiskers with coatings were filtered and washed with the solvent. Up to the hydrolyzation step, all operations were carried out in dry N_2 to avoid the adsorption of water in the air. Subsequently, the filtered cake was redispersed, dried at 120°C for 3 h in air, and finally heat treated at 500°C for 5 h in air.

In the case of the MgO coating, the molar ratio of H_2O to $Mg(CH_3OCH_2CH_2O)_2$ was varied in the range of 0.1–0.4, and reaction temperature, reaction time, and alkoxide content were kept constant. In the case of the TiO_2 coating, four important parameters, namely, molar ratio of H_2O to $Ti(OC_2H_5)_4$, reaction temperature, reaction time, and alkoxide content, were varied because a uniform TiO_2 coating was more difficult to form than with MgO.

2.1.2. Whisker-reinforced composite. Commercial-grade Si_3N_4 powder (SN-E10, Ube Industries Ltd, Japan) with 5 wt% Y_2O_3 (99.9%, Shin-Etsu Chemical Co., Ltd, Japan) and 2 wt% Al_2O_3 (99.9%, Plax Air Surfaces Technology Inc., USA), as sintering additives, and 20 wt% SiC whiskers with oxide coatings were mixed by ball-milling for 16 h using *n*-butanol as the liquid medium. These powder mixtures were hot-pressed in a carbon die at a temperature of 1800°C under 30 MPa for 1 h in a 0.1 MPa N_2 gas.

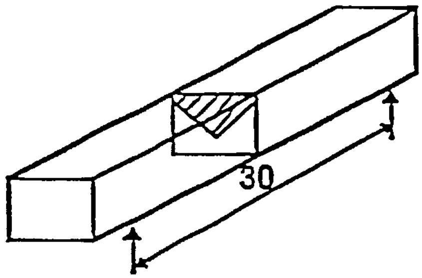

Figure 1. Schematic drawing of CN test piece.

2.2. Evaluation

Rectangular bars, 3 × 4 × 40 mm, were machined from the hot-pressed billets for measuring mechanical properties. Fracture strength of the whisker composites was evaluated by a 3-point bending test with a 30-mm span in accordance with JIS-R1601. Fracture toughness was measured by a 4-point bending test, with a 30-mm outer span and a 10-mm inner span, using single edge-notched beam (SENB) specimens. The notch width and depth were 0.1 and 0.75 mm, respectively. The fracture toughness measured by the SENB method is overestimated when the notch width is greater than the critical value. However, it has been reported that the fracture toughness of Si_3N_4 matrix composites reinforced with SiC whiskers obtained using a 0.1-mm notch width is set due value on [11]. These tests were performed at a displacement rate of 0.5 mm/min. Fracture energy was obtained from the accurate measurement of the load point displacements by a linear variable differential transducer (LVDT) [11] for chevron-notched (CN) specimens in a 3-point bending test. The size of the CN specimen is shown in Fig. 1. This test was conducted at a displacement rate of 0.05 mm/min. Under these conditions, Si_3N_4 matrix composites reinforced with SiC whiskers are fractured stably [11, 12]. Five bars were used to measure each mechanical property.

The whisker surfaces were examined with a scanning electron microscope (SEM; T300A, JEOL Ltd, Tokyo, Japan) and a transmission electron microscope (TEM; CX200, JEOL Ltd, Tokyo, Japan). Compositions of the coating layer were analyzed by energy dispersive spectroscope (EDS; Noran Instrument, Tokyo, Japan). The thickness of the coating layer was measured from the TEM observations. The fractured surfaces of the CN specimens were investigated by SEM.

3. RESULTS AND DISCUSSION

3.1. Whisker coating

An MgO coating layer was easily obtained at an $H_2O/Mg(CH_3OCH_2CH_2O)_2$ molar ratio of 0.4. Figure 2 shows a transmission electron micrograph of the whisker surface for the case of an $H_2O/Mg(CH_3OCH_2CH_2O)_2$ ratio of 0.4. The EDS spectrum

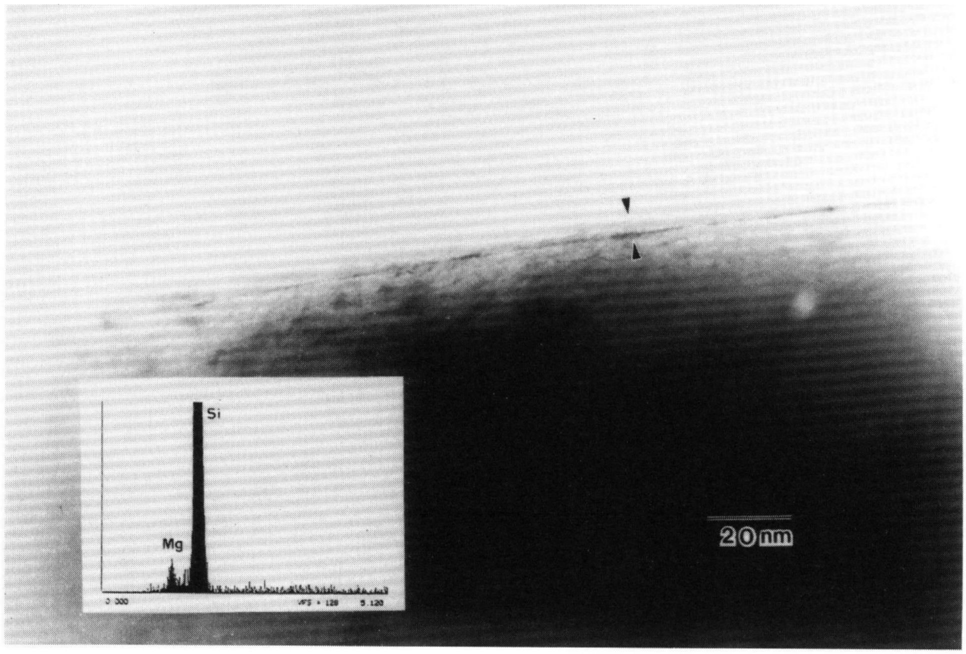

Figure 2. TEM micrograph of whisker surface with MgO coating and EDS spectrum acquired from the coating.

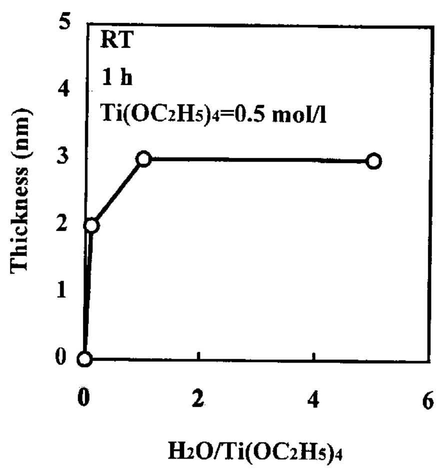

Figure 3. Relation between coating thickness and molar ratio of $H_2O/Ti(OC_2H_5)_4$.

obtained from the coating is inset in Fig. 2. It was confirmed that the coating layer included Mg element and that the thickness was 10–12 nm.

Figure 3 shows the relationship between the thickness and the concentration ratio of $H_2O/Ti(OC_2H_5)_4$. The coating experiment was conducted with a $Ti(OC_2H_5)_4$ content

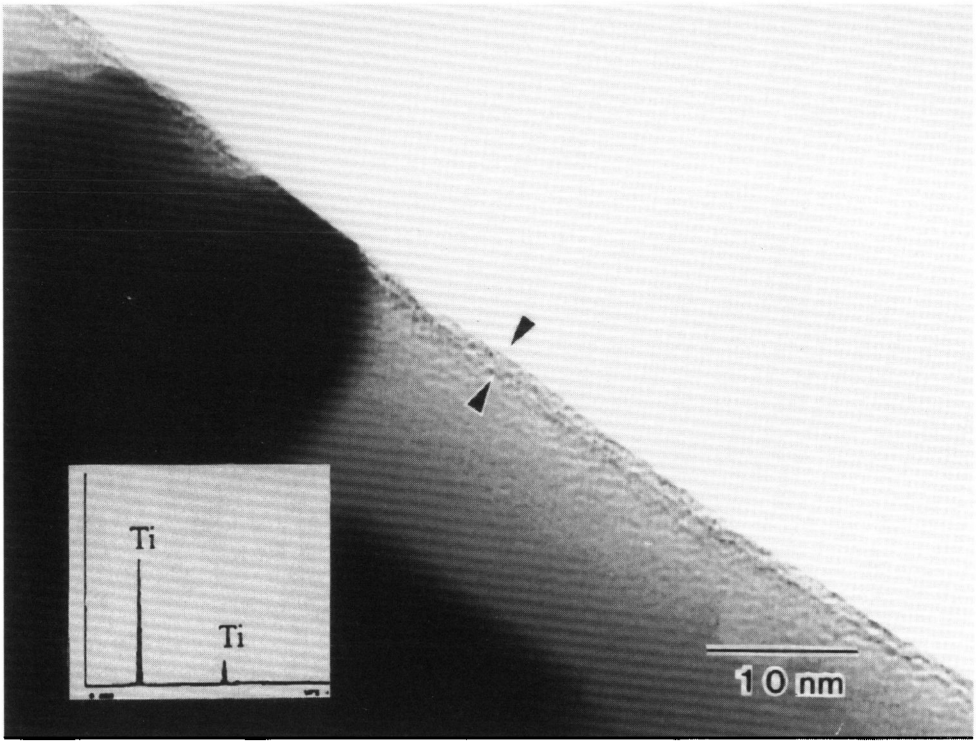

Figure 4. TEM micrograph of whisker surface with TiO_2 coating and EDS spectrum acquired from the coating.

of 0.5 mol/l at room temperature for 1 h. 3-μm-thick coatings were formed at the $H_2O/Ti(OC_2H_5)_4$ ratios above 0.1, while no coating was obtained at an $H_2O/Ti(OC_2H_5)_4$ ratio of 0.01. Figure 4 shows a transmission electron micrograph of a whisker surface for the case of an $H_2O/Ti(OC_2H_5)_4$ ratio of 0.1. The EDS spectrum obtained from the coating is inset in Fig. 4. It was confirmed that the coating layer included Ti element and was 2–3 nm thick. Figure 5 shows scanning electron micrographs of whiskers after drying at $H_2O/Ti(OC_2H_5)_4$ ratios of 0.1 (Fig. 5a) and 5.0 (Fig. 5b). When the $H_2O/Ti(OC_2H_5)_4$ ratio was 5.0, many large particles were observed between whiskers, as shown by the arrows in Fig. 5b. If the molar ratio of alkoxide to water was less than 4, linear polymers were apt to form. When the ratio was above 4, three-dimensional polymers or spherical colloids were prone to form. Linear polymers dehydrated with -OH of the whisker surface to form a coating layer. On the other hand, three-dimensional polymers or spherical colloids tended to peel off even if they dehydrated with -OH of the whisker surface since they were much larger in size than linear polymers. As a result, they seemed to polymerize with each other to achieve larger sizes and remained between whiskers because of the high concentration of water even after washing [23–25].

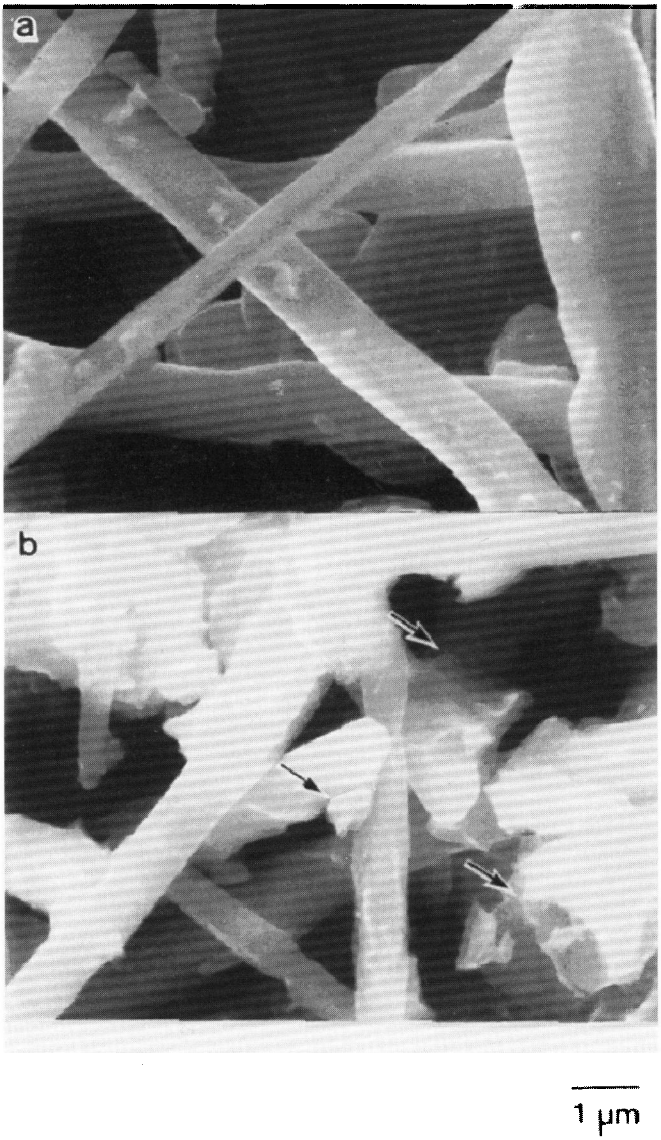

Figure 5. SEM micrographs of whisker surface with TiO_2 coating: (a) molar ratio of $H_2O/Ti(OC_2H_5)_4$ = 0.1, (b) molar ratio of $H_2O/Ti(OC_2H_5)_4 = 5.0$.

Figures 6 and 7 show the relationships between thickness and reaction temperature and between thickness and reaction time, respectively. These experiments were performed at an $H_2O/Ti(OC_2H_5)_4$ ratio of 1.0 and a $Ti(OC_2H_5)_4$ content of 0.5 mol/l. It was found that the reaction temperature and time have no effect on the coating thickness under these conditions. We hypothesize that $Ti(OC_2H_5)_4$ was so reactive that it could hydrolyze sufficiently at room temperature in a shorter time.

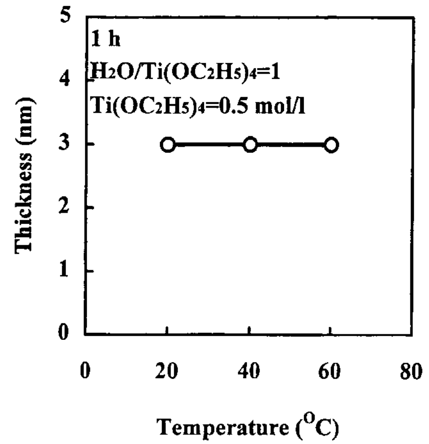

Figure 6. Relationship between coating thickness and reaction temperature.

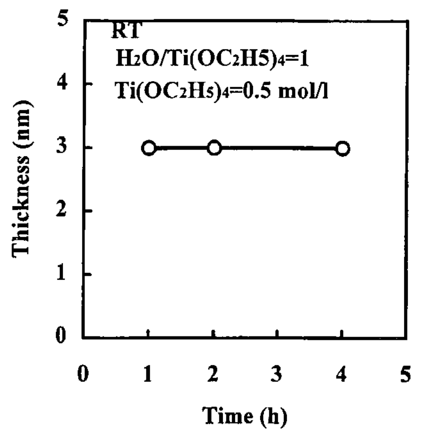

Figure 7. Relationship between coating thickness and reaction time.

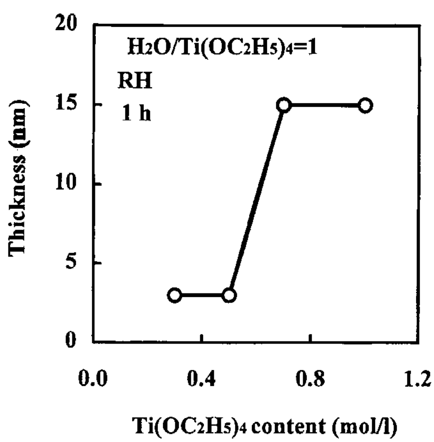

Figure 8. Relationship between coating thickness and $Ti(OC_2H_5)_4$ content.

Figure 8 shows the relationship between the thickness and $Ti(OC_2H_5)_4$ content. The thickness increased steeply to 15 nm in the $Ti(OC_2H_5)_4$ content range of 0.5 to 0.7 mol/l, while it remained constant at about 3 nm in the range of 0.3 to 0.5 mol/l. When the $Ti(OC_2H_5)_4$ content was 1.0 mol/l, many large particles existed around the whiskers, which is similar to the case shown in Fig. 5b. We hypothesize that Ti alkoxides reacted with each other to achieve large sizes and peeled off even if they dehydrated with -OH of the whisker surface.

3.2. *Mechanical properties*

The mechanical properties of the composites are shown in Table 1. Although there were differences in the data, they were significant because the standard deviation was very small. It was found that in the case of the MgO coating, the bending strength and fracture toughness were somewhat low, and fracture energy was high, while in the case of the TiO_2 coating, the bending strength and fracture toughness were relatively high, and fracture energy was low.

Figure 9 shows the SEM micrographs of the fractured surfaces of CN test pieces reinforced with: (a) as-received whiskers, (b) MgO-coated whiskers, and (c) TiO_2-coated whiskers. Careful examination of Fig. 9 revealed whisker pull-out, as indicated by the arrows, and the number of whiskers pulled-out was counted. The results are also shown in Table 1. The number of pulled-out whiskers changed according to the coating oxide. In the sample with MgO-coated whiskers, more whiskers were pulled-out than in the samples with TiO_2-coated whiskers. The number of the pulled-out whiskers with TiO_2 coating was less than that with no coating. The increase in fracture energy seemed to be related to the whisker pull-out since it showed the same trend as the number of the pulled-out whiskers. Because whiskers are pulled out after a crack passes by, the increase in fracture energy is thought to correspond to the increase of fracture resistance to the crack propagation. The results concerning the effects of whisker coatings on the mechanical properties and the trend in the number of pulled-out whiskers are similar to the results obtained for metal coatings [21, 22]. Therefore, we propose that MgO coating, which seemed to form nitride at the interface between whisker and matrix, reduces the interfacial strength and TiO_2 coating, which seemed to form silicide at the interface, enhances it.

Table 1.
Mechanical properties of composites

Coating	Bending strength (MPa)	Fracture toughness ($MPa\,m^{1/2}$)	Fracture energy ($J\,m^{-2}$)	Number of whiskers (mm^{-2})
none	1080 ± 20	8.7 ± 0.1	161 ± 5	3600
MgO	990 ± 40	8.2 ± 0.1	175 ± 6	6000
TiO_2	1130 ± 20	9.0 ± 0.1	150 ± 3	3000

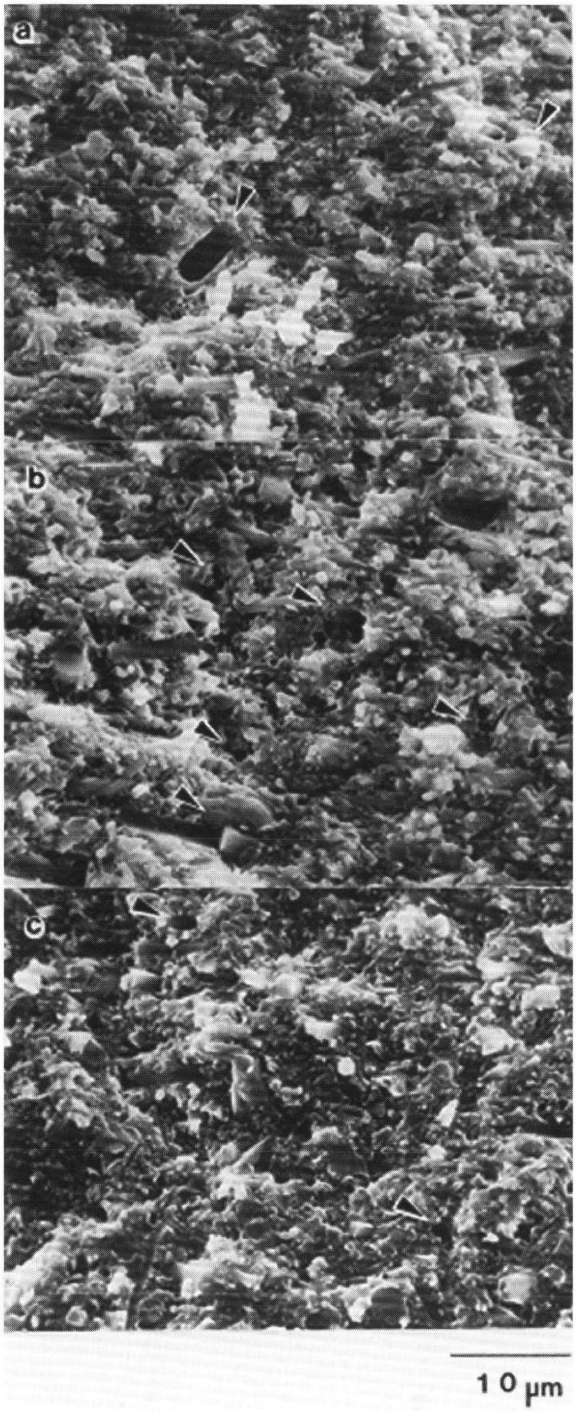

Figure 9. SEM micrographs of fracture surfaces for CN specimens reinforced with: (a) as-received whiskers, (b) MgO-coated whisker, and (c) TiO_2-coated whisker.

4. CONCLUSIONS

The following conclusions were reached based on the results of this investigation.

1) In the case of the MgO coating, bending strength and fracture toughness were somewhat low, and fracture energy was high. On the other hand, in the case of the TiO_2 coating, bending strength and fracture toughness were relatively high, and fracture energy was low.

2) MgO coating on the whisker surface has an effect on the mechanical properties of composites that is similar to that of Mg, and TiO_2 coating has an effect that is similar to that of Ti.

3) TiO_2 coating on the whisker increased the interfacial strength between whisker and matrix, while MgO coating reduced it.

Acknowledgments

This work was performed under the management of the Engineering Research Association for High Performance Ceramics as a part of the Research and Development on Fine Ceramics supported by the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES

1. Goto, Y. Various fibers and the applications for ceramic composites. In: *Proc. of International Forum on Fine Ceramics '90*. Nagoya (1990), pp. 90–95.
2. Becher, P. F. and Wei, G. C. Toughening behavior in SiC-whisker-reinforced alumina. *J. Am. Ceram. Soc.* **67**, C267–269 (1984).
3. Wei, G. C. and Becher, P. F. Development of SiC-whisker-reinforced ceramics. *Am. Ceram. Soc. Bull.* **64**, 298–304 (1985).
4. Becher, P. F., Hsueh, G. H., Angelini, P. and Tiegs, T. N. Toughening behavior in whisker-reinforced ceramic matrix composites. *J. Am. Ceram. Soc.* **71**, 1050–1061 (1988).
5. Ueno, K. and Sodeoka, S. Fracture toughness of SiC whisker reinforced Si_3N_4 ceramics. *Yogyo-Kyokai-Shi* **94**, 981–985 (1986).
6. Goto, Y. and Tsuge, A. Development of fiber-reinforced silicon nitride matrix composites. In: *Proc. of 9th Symp. on Basic Technologies for Future Industries*. Tokyo (1991), pp. 147–154.
7. Goto, Y., Yonezawa, T. and Tsuge, A. Mechanical properties of SiC whisker-reinforced Si_3N_4. In: *Proc. of Ceram. Soc. Jpn of 8th Meeting on High-Temperature Materials*. Asuka, Japan (1988), pp. 95–99.
8. Tsuge, A., Yonezawa, T. and Goto, Y. Properties of SiC-whisker-reinforced Si_3N_4 composites. In: *Proc. of 7th Symp. on Basic Technologies for Future Industries*. Tokyo (1989), pp. 25–29.
9. Ohji, T., Goto, Y. and Tsuge, A. High-temperature toughness and tensile strength of whisker-reinforced silicon nitride. *J. Am. Ceram. Soc.* **74**, 739–45 (1991).
10. Fukasawa, T., Yonezawa, T., Goto, Y. and Tsuge, A. The mechanical properties of SiC whisker/Si_3N_4 matrix composites. In: *Proc. of the 1st Symp. on the Science of Engineering Ceramics*, Kimura, S. and Niihara, K. (Eds). Ceram. Soc. Jpn (1991), pp. 339–344.
11. Fukasawa, T., Goto, Y. and Tsuge, A. The fracture behavior and properties of SiC whisker/Si_3N_4 composites. *J. Ceram. Soc. Jpn* **101**, 621–625 (1993).
12. Fukasawa, T., Goto, Y. and Tsuge, A. The fracture behavior and properties of SiC whisker/Si_3N_4 composites. In: *Ceramic Data Book*. Technoplaza Inc. (1994), pp. 123–127.
13. Matsui, T., Komura, O. and Miyake, M. The effects of surface coating and orientation of whisker on mechanical properties of SiC(w)/Si_3N_4. *J. Ceram. Soc. Jpn* **99**, 1103–1109 (1991).

14. Kobayashi, S., Kandori, T. and Wada, S. Microstructure of Si_3N_4 composites reinforced with SiC whiskers. *J. Ceram. Soc. Jpn* **94**, 903–905 (1986).
15. Willkens, C. A., Corbin, N. D., Pujari, V. K., Yeckley, R. L. and Mangaudis, M. J. The influence of microstructure orientation on the fracture toughness of Si_3N_4 based materials. *Ceram. Engng Sci. Proc.* **9**, 1367–1370 (1988).
16. Goto, Y. and Tsuge, A. Mechanical properties of unidirectionally oriented SiC-whisker-reinforced Si_3N_4 fabricated by extrusion and hot-pressing. *J. Am. Ceram. Soc.* **76**, 1420–1424 (1993).
17. Goto, Y., Yonezawa, T. and Tsuge, A. High-toughness SiC fiber/Si_3N_4 ceramic composite. *Toshiba Review* **44**, 619–621 (1989).
18. Akatsu, T., Tanabe, Y., Matsuda, S., Ishii, H., Munakata, M., Yamada, M. and Yasuda, E. Mechanical properties of SiC whisker/Al_2O_3 composites using whiskers with different surface roughness. *J. Ceram. Soc. Jpn* **99**, 431–433 (1991).
19. Ri, J. X., Matsuo, Y. and Kimura, S. Composition and microstructure of CVD-C, SiC coating on SiC fiber. *J. Ceram. Soc. Jpn* **99**, 1129–1134 (1991).
20. Corbin, N. D., Willkens, C. A., Hammarstrom, J. L., Pujari, V. K., Rossi, G. A., Sievein, K. N., Chang, C. L. and Hansen, J. S. Material development in the silicon nitride-silicon carbide whisker system. In: *Proc. 26th Automot. Technol. Develop. Contract. Coord. Meet. 1988*. Dereborn (1988), pp. 225–241.
21. Kato, M., Fukasawa, T., Goto, Y., Tanaka, S. and Tsuge, A. Effect of surface treatment on mechanical properties of ceramics matrix composites. In: *Proc. Fall Meet. Ceram. Soc. Jpn, 1994*. Sapporo (1994), p. 304.
22. Kato, M., Fukasawa, T. and Goto, Y. Mechanical properties of Si_3N_4 matrix composites reinforced with SiC whiskers with various coatings. *J. Ceram. Soc. Jpn* **103**, 882–885 (1995).
23. Yoko, T., Kamiya, K. and Sakka, S. Photoelectrochemical properties of TiO_2 films prepared by the sol-gel method. *J. Ceram. Soc. Jpn* **95**, 12–16 (1987).
24. Kamiya, K. and Yoko, T. Application of the sol-gel method to surface. *Hyoumen* **24**, 131–142 (1986).
25. Kamiya, K., Tanimoto, K. and Yoko, T. Preparation of TiO_2 fibers by hydrolysis and polycondensation of $Ti(O\text{-}I\text{-}C_3H_7)_4$. *J. Mater. Sci. Lett.* **5**, 402–404 (1986).