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Novel Synthesis and Properties of Si_3N_4-Based Nano/Nano-Type Composites

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Abstract Si_3N_4/TiN nano/nano-type composites were successfully fabricated by the combination of a mechano-chemical grinding (MCG) method and a short time sintering process, and their wear resistance was evaluated. Powder mixtures of α-Si_3N_4 and Ti were prepared using mechano-chemical grinding process and the resulting nanocomposite powder mixtures were consolidated using pulsed electric current sintering (PECS). TEM observation showed that the nano/nano-type composites consisted of homogeneous and very fine matrix grains with the size less than 100 nm. The obtained Si_3N_4-based nano/nano-type showed high wear resistance and electric discharge machinability.

Keywords : Nano/nano composite, Si_3N_4/TiN, Mechano-chemical grinding, Machinability

1. Introduction

Silicon nitride is expected to be used for industrial applications requiring excellent mechanical properties such as high strength and toughness.[1] Extensive research has been done on improving the properties. However, a material having new functions and properties is required.

Nano-grained or nanophase materials which are polycrystals mainly consisting of structural elements with nanometer crystallites have recently been a topic of research, motivated by their unusual physical and chemical properties. For example, it is reported that the ZrO_2/Al_2O_3 nano/nano-type composites fabricated from amorphous powder precursors showed superplastic deformation at about 1200°C.[2] In regard to non-oxide ceramics, few studies have been reported. One reason is that it is very difficult to fabricate non-oxide ceramics due to its oxidation.

The purpose of this study is to develop silicon nitride-based nano/nano-type composites and to investigate the relation between fabrication process and microstructure. Also, wear and electric discharge machining properties of obtained materials were investigated.

2. Experimental Procedure

Figure 1 shows the fabrication process of nano/nano-type composites called as mechano-chemical grinding (MCG) process. High purity α-Si_3N_4, titanium, Y_2O_3 and Al_2O_3 powders were used as the starting materials. They were mixed using a high-energy ball mill. To fabricate Si_3N_4/TiN nano/nano-type composites, the obtained powder mixtures were sintered at 1300°C~1500°C for 10 min in nitrogen atmosphere, using a

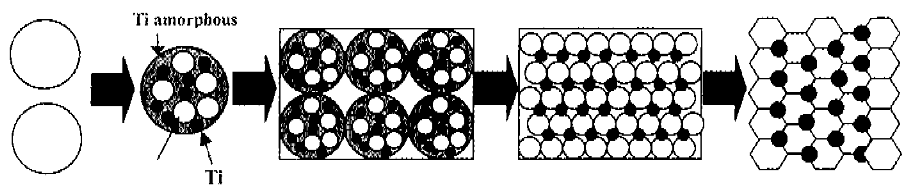

Fig. 1. Schematic diagram of MCG process.

pulsed electric current sintering system. Conventional Si_3N_4/TiN microcomposite was fabricated using commercial Si_3N_4 and TiN powder by hot pressing.

The milled powders and sintered bodies were characterized using a transmission electron microscope (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD) with the CuKα radiation. Wear properties of materials were tested in a ball-on-disk arrangement in humid air at 25-28°C, in which polished Si_3N_4 balls (AS6.0-01, 6.00 mm diameter) were used as counterbodies. Electric discharge machinability (EDM) was tested using wire-EDM and small hole drilling.

3. Results and Discussion

The XRD diagram of milled powder for various times is shown in Fig. 2. It can be seen that the XRD peaks of the α-Si_3N_4 (●) and titanium (△) become weaker and broader with increasing milling time. This behavior indicates that the grain size of Si_3N_4 decreases with increasing milling time, according to the Scherrer equation. Another interesting point is that TiN peaks (□) increase with decreasing α-Si_3N_4 and titanium peaks. This suggests that TiN is synthesized by the mechano-chemical reaction among silicon nitride powder, nitrogen atmosphere and metallic Ti. Fig. 3 shows the typical TEM photograph of milled powder. The powder consists of Si_3N_4 matrix, ultra fine TiN particles and amorphous Ti. The grain sizes of Si_3N_4 matrix and ultra fine TiN particles are 5-20 nm and a few nm, respectively. In this nanocomposite powder, ultra-fine grains were firmly bonded and their apparent grain size was a few micron-meter. This process enables to resolve problems such as oxidation of ultra-fine non-oxide particles.

The obtained nanocomposite powders were consolidated by PECS method. In all composites, α-Si_3N_4 and TiN were identified. The relative density above 99% was obtained at 1500°C for Si_3N_4/10 vol% TiN composites. However, the densification temperature decreased with increasing TiN content. In case of Si_3N_4/30 vol% TiN composites, the densified specimen was obtained at the sintering temperature of 1300°C. The reason for this different densification behavior is considered to be due to three factors: a) the composite powders which contain nano-sized grains have good sinterability, b) the occurrence of plastic deformation due to softening of the added Ti at high temperature, and c) the composite powders which contain electrical conduction powder (Ti and TiN) may be possibly effective for PECS method.

Figure 4 shows TEM photographs of Si_3N_4/30 vol% TiN composites sintered by PECS using the powder mixture with milling time of 16 h and of micro-composites by hot-pressing. As clearly shown in Fig. 4(a), the Si_3N_4-based composite can come under the

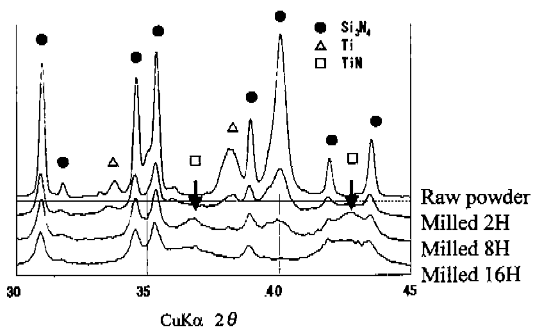

Fig. 2. XRD pattern of the milled powder with various milling times.

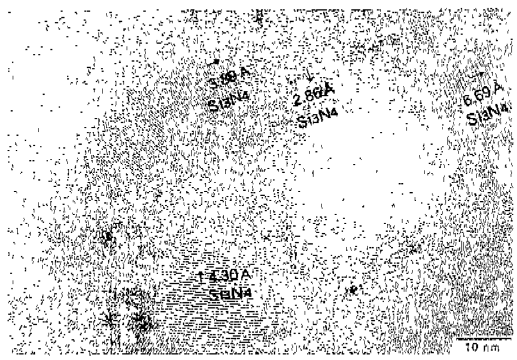

Fig. 3. TEM photograph of nanocomposite powder.

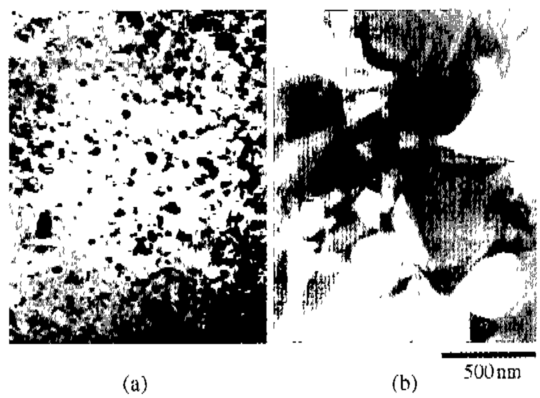

Fig. 4. TEM photographs of (a) nano/nano-type composite and (b) microcomposite.

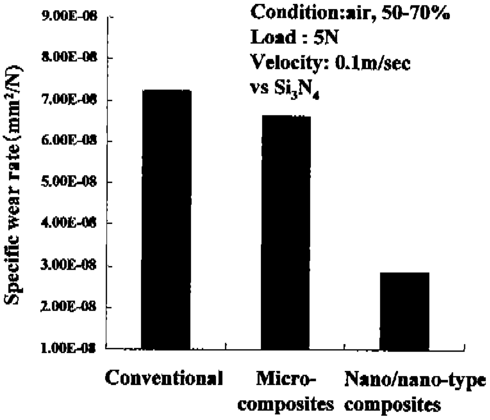

Fig. 5. Comparison of wear rate for Si_3N_4/TiN nano/nano-type composites, microcomposites and conventional Si_3N_4.

categories of nano/nano-type composites. TiN grains were uniformly dispersed in the Si_3N_4 matrix grains. The grain sizes of the matrix and second phase were within 50 nm. Thus, it suggests that optimal processing conditions are the milling time of 16 h and sintering temperature of 1300°C, to obtain nano/nano-type composite with homogenous microstructure.

Figure 5 shows the comparison of the wear rate for the nano/nano-type Si_3N_4/TiN composites, Si_3N_4/TiN microcomposites and conventional Si_3N_4. The important point is that the wear rate of nano/nano-type composites is lower than that of the other specimens. This result indicated that desired wear properties can be obtained by controlling microstructure. Kato et al[3] proposed a wear map that contains the grain size factor. According to the wear map, the wear rate decreases with decreasing grain size. Herrman et al[4] investigated the wear properties of Si_3N_4 ceramics having difference grain sizes. They reported that a wear rate of finer grained Si_3N_4 was lower than that of other Si_3N_4. Our result was in good agreement with the wear map and the results by Herrman et al, despite the wear mechanism not being clarified yet.

Figure 6 shows SEM photographs of the wire-EDM treated surface for nano/nano-type composite and microcomposite. Surface roughness tests show Ra = 0.17 μm for the nano/nano-type composites and Ra = 0.59 μm for the microcomposites, respectively. Fig. 7 shows a hole using small-hole EDM for nano/nano-type composites drilling. The size of hole was only about 15 μm. This result suggested that electric discharge machinability can be controlled by the microstructure, and thus nano/nano-type composite can be used as precision tools.

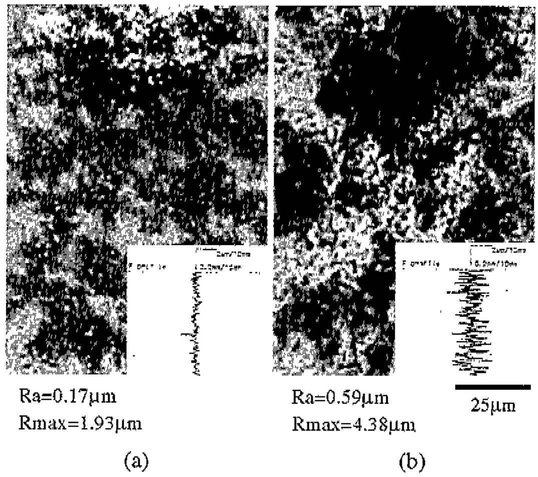

Fig. 6. SEM photographs of wire-EDM treated surface for Si_3N_4/TiN with (a) nano/nano-type composites and (b) microcomposite.

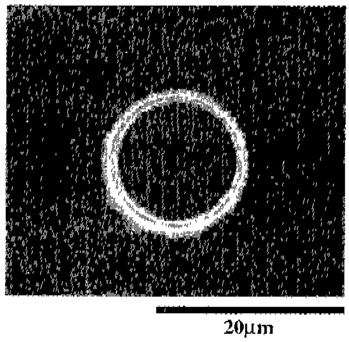

Fig. 7. SEM photograph of small hole EDM drilling for Si_3N_4/TiN nano/nano-type composites.

4. Conclusion

Si_3N_4/TiN nano/nano-type composites consisting of very fine matrix grains and homogeneous TiN dispersions with grain size less than 50 nm were developed by powder metallurgical process. The obtained materials show higher wear resistance and smoother EDM-treated surface compared to conventional micro-composites. These results indicated that the wear resistance and machinability could be controlled by the microstructure.

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