JOURNAL OF Materials CHEMISTRY

Highly electroconductive TiN/Si_3N_4 composite ceramics fabricated by spark plasma sintering of Si_3N_4 particles with a nano-sized TiN coating

Shuichi Kawano, Junichi Takahashi and Shiro Shimada*

Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan.
Tel: +81 11 706 6576; Fax: +81 11 706 6576; E-mail: shimashi@eng.hokudai.ac.jp

Received 3rd August 2001, Accepted 25th October 2001
First published as an Advance Article on the web 3rd January 2002

Si_3N_4 particles coated with 20 nm TiN have been sintered by spark plasma sintering (SPS) at 1600 °C. The 25 vol.% TiN ceramic achieved a relative density of 91% without sintering additives. TEM and HREM observations indicate that a glassy phase derived from the Si_3N_4 particles plays a role in densification. Ceramics derived from TiN/Si_3N_4 composite particles containing 25 and 32.5 vol.% TiN possess continuous TiN networks in a Si_3N_4 matrix and their electrical resistivity is of the order of 1×10^{-4} Ω cm, much lower than that of a mechanical mixture of nano-sized TiN particles and Si_3N_4 particles (1 Ω cm).

Introduction

Si_3N_4 ceramics are promising high temperature structural materials[1,2] but are difficult to form by mechanical methods into complex shapes because of their toughness and hardness. Composite ceramics composed of Si_3N_4 with highly electrical conductive TiN have been prepared, and can be easily shaped by electrical discharge machining (EDM). Martin *et al.*[3] reported that for composite TiN/Si_3N_4 ceramics to be machinable by EDM, their electrical resistivity should be less than 5×10^{-3} Ω cm, with a TiN content of about 33 vol.%. When this criterion of electrical resistivity is adjusted to the Si_3N_4 and TiN composites obtained by Kamijo *et al.*[4] and Bellosi *et al.*,[5] the amount of TiN needed for EDM is approximately the same as that reported by Martin *et al.* It is preferable to decrease the TiN content of the Si_3N_4 composites, since TiN is readily oxidized at about 600 °C,[6] causing the degradation of the mechanical and electrical properties.

TiN/Si_3N_4 composite materials are usually made by sintering mechanically mixed powders.[3–5,7,8] However, mechanical mixing of powders introduces inhomogeneity in the mixture and necessitates additional TiN to achieve high electrical conductivity. On the other hand, uniformly coating the matrix particles with the second material is an effective means of obtaining a homogeneous mixture. Si_3N_4 matrix particles coated with sintering additives such as Al_2O_3, Y_2O_3, and MgO[9–11] have been found to require less of the additive for densification. The preparation of TiN-coated Si_3N_4 particles has been reported by Narula *et al.*,[12] who obtained the composite particles by pyrolysis of $(CH_3)_3SiNHTiCl_3$ with Si_3N_4 at 600 °C. Since this method introduces Si, Cl, and C impurities from the reagent $(CH_3)_3SiNHTiCl_3$, a simpler method for preparing composite particles of a high purity is desirable. In our previous paper,[13] we reported a preparation method for nano-sized TiN-coated Si_3N_4 particles by nitridation of TiO_2 in NH_3 gas following thermal hydrolysis of $TiCl_4$ with urea.

Hot pressing (HP) and hot isostatic pressing (HIP) are well known methods for sintering Si_3N_4 particles. Recently, spark plasma sintering (SPS) has attracted much attention for densifying poorly-sinterable materials such as Al_2O_3[14–16] and ZrO_2.[17] In SPS densification, a compacted sample is placed in a graphite die and heated under uniaxial pressure using pulses of current. The processes involved in SPS are initiated by the electrical discharge between the powder particles, which cleans the particles surfaces, promotes mass transfer, and so on.[18] Under these conditions, ceramics are densified in a very short time (several minutes) at low temperatures with suppression of grain growth. It therefore seemed possible that by using SPS to sinter the previously reported[13] TiN-coated Si_3N_4 particles, high-conductivity Si_3N_4 could be made with reduced overall amounts of TiN which were still connected throughout the solid.

The purpose of this study is to fabricate densified TiN/Si_3N_4 composite ceramics by SPS of nano-sized TiN-coated Si_3N_4 particles. The amount of TiN which must be added to produce composite ceramics with low electrical resistivity ($<5 \times 10^{-3}$ Ω cm) to facilitate EDM is determined. The effect on the electrical resistivity of coating nano-sized TiN particles is compared with SPS ceramics prepared from mechanical mixtures. The microstructure of continuously-TiN-coated Si_3N_4 composite ceramics is revealed by transmission electron microscopy and high resolution electron microscopy.

Experimental procedure

Preparation of TiN-coated Si_3N_4 particles

The preparation procedure of TiN-coated Si_3N_4 particles has been reported in a previous paper.[13] The starting materials were Si_3N_4 with a mean particle size of 0.5 μm (α-type >95%,UBE Industries, Tokyo, Japan), $TiCl_4$ (KANTO Chemical, Co., Inc., Tokyo, Japan), and urea (KANTO Chemical, Co., Inc., Tokyo, Japan). Si_3N_4 powder was added to a mixture of HCl, $TiCl_4$, and urea and ultrasonically dispersed for 15 min. The amount of $TiCl_4$ with respect to Si_3N_4 was adjusted to 10, 17.5, 25, 32.5, and 100 vol.% of the reduced volume of TiN in Si_3N_4. The suspension was heated at 105 °C for 190 min in flowing N_2 gas. The resulting TiO_2-coated Si_3N_4 particles were washed several times with distilled water and dried at 60 °C. The TiO_2-coated Si_3N_4 composite particles were nitrided at 1000 °C for 180 min in flowing NH_3 gas (150 ml min^{-1}). The success of the coating procedure was confirmed by transmission electron microscopy (TEM), electron diffraction, and energy dispersive X-ray analysis (EDX).

DOI: 10.1039/b107058b

Fabrication of TiN/Si_3N_4 composite ceramics by SPS

The SPS apparatus (SPS-501L, Sumitomo Coal Mining Co.) used in this experiment is shown in Fig. 1. A 0.25 g compact (6 mm diameter) of the TiN-coated Si_3N_4 composite was embedded in BN powder containing 5 vol.% commercial TiN. The BN powder was used to prevent reaction between the compact and the graphite die.[19] Sintering was carried out at 1600 or 1700 °C in N_2 under a uniaxial pressure of 39 MPa using a controlled electric current. The temperature on the graphite die surface was measured by optical pyrometer. When the sintering temperature was reached, the current was switched off without holding. A typical heating schedule to 1600 °C is shown in Fig. 2, using a current value of 740 A, a heating rate of 20 °C min^{-1}, and a total sintering time of 14.5 min at 1600 °C. For comparison, mechanically mixed powders containing Si_3N_4 and 25 vol.% TiN were sintered at 1600 °C by SPS. The mixtures used in the latter sintering experiment were prepared by two methods. One method involved ball milling commercial TiN (1.43 μm, Soekawa Co., Inc., Tokyo, Japan) and Si_3N_4 and drying at 60 °C for a day (labeled L-mixture). The other method was to ball mill nano-sized TiO_2 (prepared by thermal hydrolysis of $TiCl_4$ and urea) together with Si_3N_4, followed by drying at 60 °C for a day and nitridation at 1000 °C (labeled N-mixture). In both cases the ball milling was carried out for 24 h in ethanol with ZrO_2 balls.

The densities of the sintered TiN/Si_3N_4 composites were measured with distilled water at room temperature by the Archimedes method. Phase identification of the ground powder was made by X-ray diffraction (XRD), and the lattice constant (a_0) of the TiN was determined using silicon powder as an internal standard. The polished surface microstructures of the sintered Si_3N_4/TiN composites were observed by scanning electron microscopy (SEM). The TiN/Si_3N_4 composite containing 32.5 vol.% TiN sintered at 1600 °C was cut into several pieces and a thin foil of one piece was prepared by mechanical dimple-thinning and repeated ion milling. The interfacial area between Si_3N_4 and Si_3N_4 and between Si_3N_4 and TiN was examined with a TEM operating at 200 kV. The interfacial area between TiN and TiN was also observed using a multi beam high voltage electron microscope (HREM) at 1250 kV. The electrical resistivities of the ceramics containing 10–100 vol.% TiN were measured by a two-probe and/or four-probe method at room temperature. The Vickers hardness of the TiN/Si_3N_4 ceramics containing 25, 32.5, and 100 vol.% TiN was measured using a load of 200 g for 15 s. The volume ratio of Si_3N_4 to TiN in the ceramic was determined by computer analysis of the SEM images utilizing the difference in brightness of TiN and Si_3N_4.

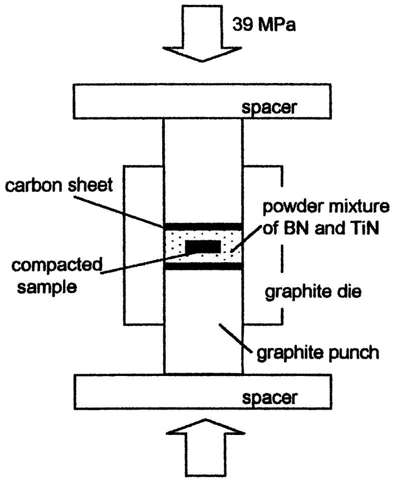

Fig. 1 Schematic diagram of the SPS apparatus.

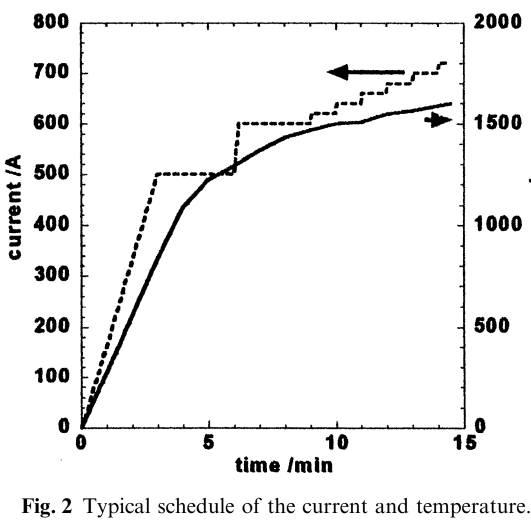

Fig. 2 Typical schedule of the current and temperature.

Results and discussion

Preparation of TiN-coated Si_3N_4 particles

According to a previous report,[13] TiN-coated Si_3N_4 composite particles can be prepared by nitridation of the TiO_2 formed by thermal hydrolysis of $TiCl_4$. TEM observation of composites containing 25 vol.% TiN shows that Si_3N_4 particles are coated with 20 nm TiN particles (Fig. 3). The existence of the TiN particles was confirmed by electron diffraction around the arrow point, which shows TiN diffraction spots, confirming that nano-sized TiN coated Si_3N_4 composite particles had been successfully produced. TiN-coated Si_3N_4 composites containing 10, 17.5, 32.5 vol.% TiN were similarly prepared. The lattice constant of the TiN (a_0) was found to be 0.422 nm for all the composites; this decrease from the value for pure TiN ($a_0 = 0.424$ nm)[20] suggests that the TiN particles contain a small amount of oxygen.

Fabrication of TiN/Si_3N_4 ceramics by SPS

The TiN-coated Si_3N_4 samples were sintered by SPS at 1600 and 1700 °C. The composites sintered at 1700 °C contained within millimetre-sized holes on the surfaces and were metallic silver in color due to the presence of Si as evidenced by XRD, suggesting that Si_3N_4 was decomposed to Si and nitrogen gas during SPS; when nitrogen gas went out through the Si melt, millimetre-sized holes were formed. Since this result shows that 1700 °C is too high a temperature for sintering TiN/Si_3N_4 composite particles, the process was carried out at 1600 °C. The XRD patterns of the sintered ceramics indicate the presence of only Si_3N_4 and TiN, the lattice constant of the latter increasing from $a_0 = 0.422$ to 0.424 nm, probably because heat treatment

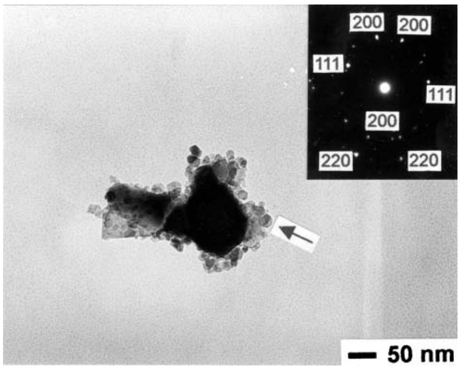

Fig. 3 TEM image of TiN-coated Si_3N_4 particles in the sample containing 25 vol.% TiN.

at 1600 °C in N_2 replaces the oxygen impurity, resulting in TiN with a lattice constant approaching that of pure TiN.

Fig. 4 shows backscattered electron images in SEM of the polished surfaces of composites containing 25 vol.% TiN prepared from TiN-coated Si_3N_4 particles, the L-mixture, and the N-mixture, all sintered at 1600 °C. The difference in the backscattering properties of the lighter and heavier atoms shows up as the gray and white regions corresponding to Si_3N_4 and TiN, respectively. The composites prepared from TiN-coated Si_3N_4 [Fig. 4(a)] show aggregated gray Si_3N_4 regions surrounded by successive white TiN layers, even though some aggregated TiN particles are formed. Computer image analysis of the gray and white regions in this figure indicates a TiN content of 25 ± 1 vol.%, in very good agreement with the nominal 25 vol.% composition. The ceramics derived from the L-mixture are porous and have *ca.* 1–7 μm-sized TiN grains (white particles) [Fig. 4(b)], which exist separately from the Si_3N_4 grains. It is apparent that these ceramics have not sintered. By contrast to the TiN-coated Si_3N_4-derived materials, the surface of the N-mixture ceramic [Fig. 4(c)] shows isolated TiN particles of around 1–2 μm size and Si_3N_4 particles. The mechanical mixtures of TiN and Si_3N_4 do not form of continuous TiN networks, which are necessary to make the Si_3N_4 matrix electrically conducting.

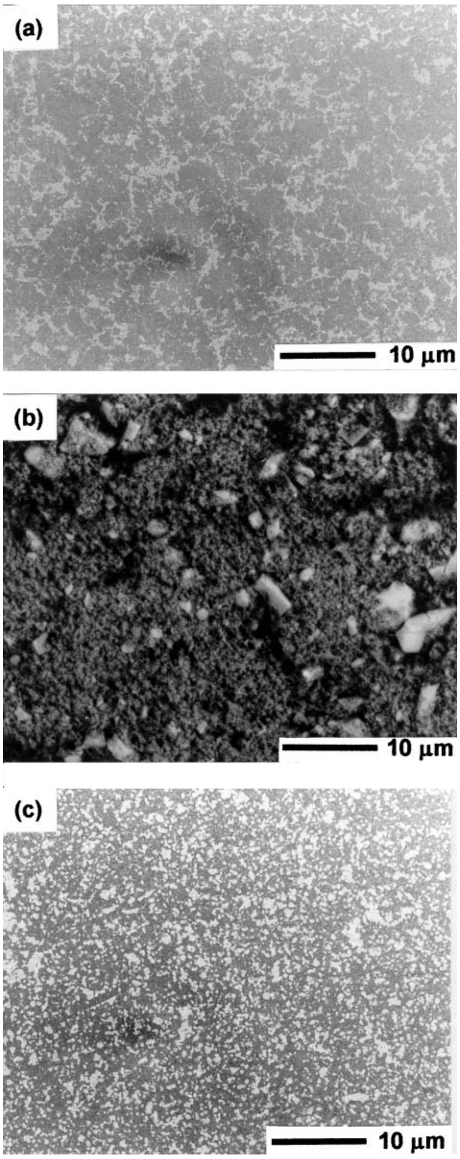

Fig. 4 Backscattered SEM images of polished TiN/Si_3N_4 ceramics containing 25 vol.% TiN prepared from (a) TiN-coated Si_3N_4 particles, (b) a mechanical mixture of commercial TiN and Si_3N_4 (L-mixture), (c) a mechanical mixture of nano-sized TiN and Si_3N_4 (N-mixture).

Fig. 5 shows that the relative densities of the TiN-coated Si_3N_4 ceramic measured as a function of the TiN content increase sharply from 64% (17.5 vol.% TiN) to 91% (25 vol.%), respectively, followed by a gradual increase to 97% for single phase TiN. On the other hand, ceramics containing 25 vol.% TiN derived from the L- and N-mixtures in which the TiN particle sizes were 1.43 and 20 nm, respectively, showed relative densities of 50 and 98%, respectively.

Fig. 6 shows the TEM image of the lattice fringes in a representative region of Si_3N_4 and TiN, including their phase boundaries. The lattice fringe spacings of 0.67 and 0.39 nm in Fig. 6(a) and (b) correspond to the (100) and the (110) spacings of α-Si_3N_4, respectively, whereas the spacing of 0.24 nm in Fig. 6(b) and (c) corresponds to the (111) spacing of TiN. As seen in Fig. 6(a), the grain boundary phase between the α-Si_3N_4 grains is amorphous, suggesting a glassy phase of *ca.* 1 nm thickness. This thin glassy layer may contain the oxygen remaining on the surfaces of the Si_3N_4 particles since no oxide sintering additives were added to this system. The boundary phase between the Si_3N_4 and TiN grains is also amorphous, but thicker (*ca.* 2 nm) [Fig. 6(b)]. This increase of grain boundary thickness may be due to the reaction of Si_3N_4 with the oxygen swept out from the TiN during SPS. In contrast, no glassy layer is observed between the TiN grains [Fig. 6(c)], suggesting that TiN–TiN connections can be produced without an intervening glassy phase. The interfacial images and microstructure (Fig. 4) show that the compact derived from TiN-coated Si_3N_4 particles may be densified by the formation of the glassy layer between the TiN and Si_3N_4 interface, whereas the sample derived from the N-mixture is sintered not only *via* the glassy layer but more predominantly by TiN–TiN contacts, as in single phase TiN.

The Vickers hardness values of the Si_3N_4/TiN composites containing >25 vol.% TiN are shown in Table 1. The hardness of sample containing 100 vol.% TiN is 1850 kg mm^{-2}, comparable to the reported value for pure TiN (2000 kg mm^{-2}),[21] whereas the hardness of the 25 and 32.5 vol.% TIN ceramics derived from the TiN-coated Si_3N_4 particles and the N-mixture is about 1400 kg mm^{-2} for all. This decreased hardness is probably due to the presence of pores and/or the existence of a glassy layer in the ceramics.

The change of electrical resistivity of the composites is shown as a function of the TiN content in Fig. 7. The resistivity rapidly decreases from 2×10^6 Ω cm in the 10 vol.% TiN sample to *ca.* 10^{-4} Ω cm in the 25 and 32.5 vol.% TiN samples. This rapid decrease is related to the formation with TiN networks as shown in Fig. 4(a). The resistivity finally decreases to

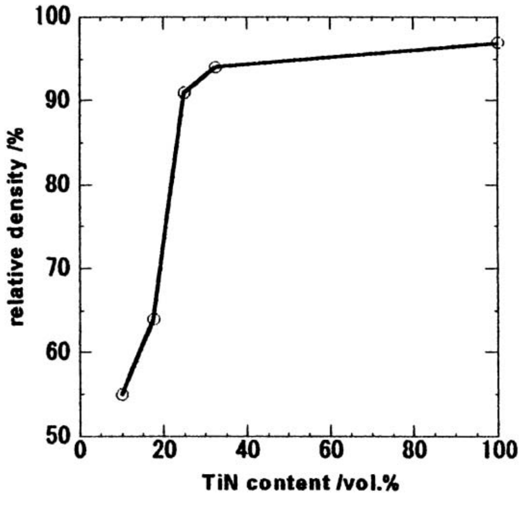

Fig. 5 Change in the relative density of the composites with TiN content.

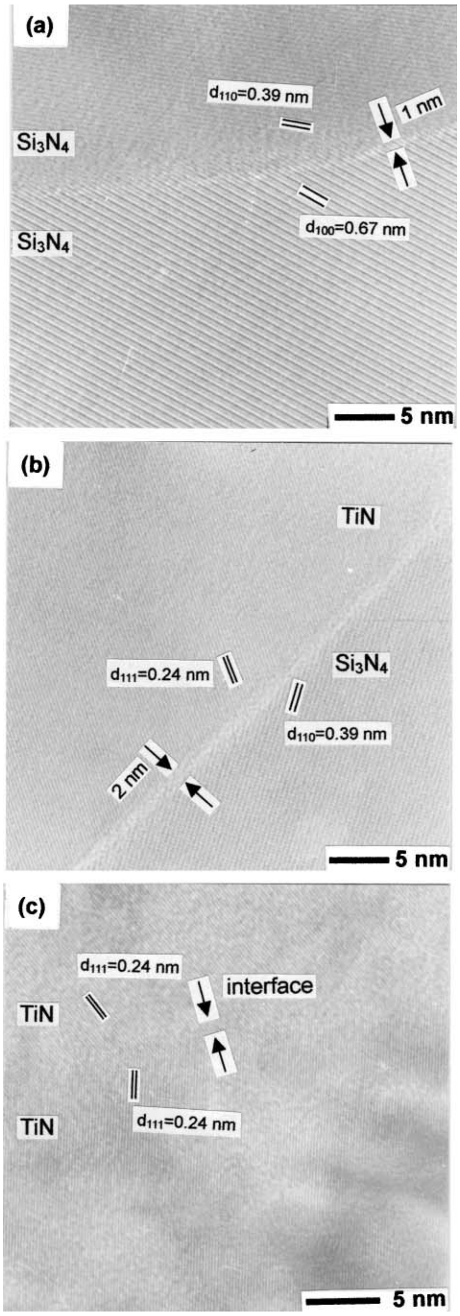

Fig. 6 Interface images of (a) Si_3N_4-Si_4N_4, (b) Si_3N_4–TiN, (c) TiN–TiN.

Table 1 Vickers hardness of TiN/Si_3N_4 composites

TiN content/vol.%	Vickers hardness/kg mm^{-2}
25 (coated)	1390 ± 110
32.5 (coated)	1430 ± 90
25 (N-mixture)	1460 ± 130
100	1850 ± 50

1×10^{-5} Ω cm in the 100% TiN sample, comparable with the reported value for pure TiN (2.5×10^{-5} Ω cm).[21] The amount of TiN required to fabricate TiN/Si_3N_4 ceramics by EDM was found here to be a maximum of 23 vol.% (Fig. 7), a reduction of 10 vol.% from the previously-reported value (33 vol.%).[3–5] The electrical resistivity of the ceramic prepared at 1600 °C from the N-mixture containing 25 vol.% TiN was 1 Ω cm, higher by a factor of 10^4 than the composites prepared from TiN-coated Si_3N_4 particles. This is because continuous TiN networks do not exist in the N-mixture composite [Fig. 4(c)].

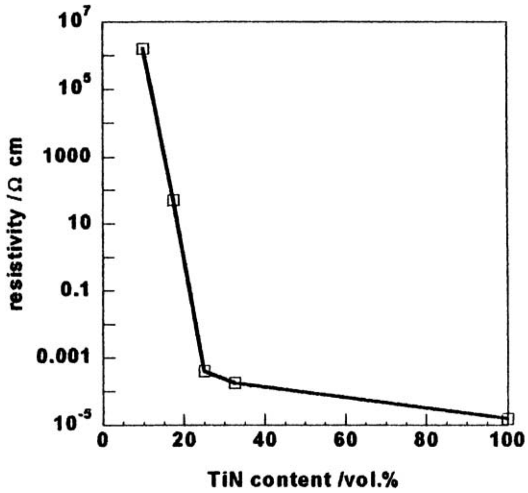

Fig. 7 Change of electrical resistivity of the composites with TiN content.

Thus, it is concluded that the TiN coating on the Si_3N_4 particles greatly reduces the amount of TiN needed to provide a low enough electrical resistivity for EDM processing of Si_3N_4 composites.

Conclusion

TiN/Si_3N_4 composite ceramics have been fabricated from Si_3N_4 particles coated with 20 nm sized TiN particles at 1600 °C using SPS with a controlled current. The ceramic product containing 25 vol.% TiN has a relative density of 91%, which increases with the TiN content to 97% at 100 vol.% TiN. At the Si_3N_4/Si_3N_4 and Si_3N_4/TiN grain boundaries, glassy layers a few nm thick are observed by TEM. These may play a role in the densification of the composites. By contrast, no interfacial glassy layer is observed at the TiN/TiN grain boundaries, indicating direct connection between the TiN particles.

The electrical resistivity of the composite ceramic containing 25 vol.% TiN (4×10^{-4} Ω cm) was found to be much lower than for ceramics obtained from a mechanical mixture of the component (1 Ω cm), indicating that coating the Si_3N_4 particles with TiN particles is effective in producing a continuous TiN network at lower TiN contents. By this means, the amount of TiN in TiN/Si_3N_4 composites needed for EDM can be reduced by 10 vol.%, compared with the previously reported values.

Acknowledgements

The use of the multi beam high voltage electron microscope (HREM) in Hokkaido University is gratefully acknowledged. The authors thank Dr H. Takahashi and Dr K. Sugawara (CARET, Hokkaido University, Sapporo, Japan) for useful advice and discussions on TEM and HREM observations, Dr K. Kurokawa (Hokkaido University, Sapporo, Japan) for using the SPS apparatus, and Dr K. J. D. MacKenzie (Industrial Research, Lower Hutt, New Zealand) for reviewing our manuscript.

References

1 C. K. Naurula, J. E. Allison, D. R. Bauer and H. S. Gandhi, *Chem. Mater.*, 1996, **8**, 984.
2 A. W. Weimer, *Carbide, Nitride and Boride Materials Synthesis and Processing*, Chapman & Hall, London, 1997, pp. 5, 7 .
3 C. Martin, B. Cales, P. Vivier and P. Mathieu, *Mater. Sci. Eng. A*, 1989, **109**, 351.
4 E. Kamijo, M. Honda, M. Higuchi, H. Takeuchi and T. Tanimura, *Sumitomo Electr. Tech. Rev.*, 1985, **24**, 183.

5 A. Bellosi, S. Guricciardi and A. Tampieri, *J. Eur. Ceram. Soc.*, 1992, **9**, 83.
6 Yu. G. Gogotsi and F. Porz, *Corros. Sci.*, 1992, **33**, 62.
7 B.-T. Lee, Y.-J. Yoon and K.-H. Lee, *Mater. Lett.*, 2001, **47**, 71.
8 W. Lin, J.-M. Yang, S.-J. Ting, A. Ezis and C. J. Shin, *J. Am. Ceram. Soc.*, 1992, **75**, 945.
9 J. Yang, J. M. F. Ferreira and W. Weng, *J. Colloid Interface Sci.*, 1998, **206**, 274.
10 F. Bertoni, C. Galassi, S. Ardizzone and C. L. Bianchi, *J. Am. Ceram. Soc.*, 1999, **82**, 2653.
11 A. K. Garg and L. C. D. Jonghe, *J. Mater. Res.*, 1990, **5**, 136.
12 C. K. Narula, B. G. Demczyk, P. Czubrow and D. Seyferth, *J. Am. Ceram. Soc.*, 1995, **78**, 1247.
13 S. Kawano, K. Tsukurimichi, J. Takahashi and S. Shimada, *J. Mater. Chem.*, 2001, **11**, 2625.
14 S. W. Wang, L. D. Chen and T. Hirai, *J. Mater. Res.*, 2000, **15**, 982.
15 G. J. S. Hohg, H. Miyamoto and S. D. D. L. Torre, *J. Eur. Ceram. Soc.*, 2000, **20**, 2149.
16 N. Murayama and W. Shin, *J. Ceram. Soc. Jpn.*, 2000, **108**, 799.
17 W. Li. L. Gao, *J. Eur. Ceram. Soc.*, 2000, **20**, 2441.
18 M. Omori, *Mater. Sci. Eng., A*, 2000, **287**, 183.
19 J. Takahashi, S. Kawano, S. Shimada and K. Kageyama, *Jpn. J. Appl. Phys.*, 1999, **38**, 5493.
20 ASTM 38-1420.
21 L. E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York & London, 1971, pp. 7, 188.