Available online at www.sciencedirect.com

Journal of the European Ceramic Society 24 (2004) 309–312

www.elsevier.com/locate/jeurceramsoc

The preparation and spark plasma sintering of silicon nitride-based materials coated with nano-sized TiN

Shuichi Kawano, Junichi Takahashi, Shiro Shimada*

Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Abstract

TiN coating on β-sialon ($z=2$) and Si_3N_4 was performed by depositing TiO_2 on their particle surfaces through controlled hydrolysis of $Ti(O\text{–}i\text{–}C_3H_7)_4$, and subsequent nitridation with NH_3 gas. TiN particles covering β-sialon and Si_3N_4 were 10–20 nm in size. Spark plasma sintering of TiN/β-sialon composite particles produced ceramics with TiN networks of 0.1–0.5 μm wide at 1500 °C, but with TiN grains of 0.1–2.0 mm sizes isolated in the sialon matrix at 1600 °C. SPSed TiN/sialon ceramics at 1500 °C had $>95\%$ density of the theoretical one, irrespective of the TiN amount. TiN/sialon ceramics (25 vol.%) showed a lower electrical resistivity ($\sim 10^{-3}$ Ω cm) making these ceramics suitable for electric discharge machining.

Keywords: Composites; Electrical conductivity; Sialons; Nitrides; Spark plasma sintering; TiN; Si_3N_4

1. Introduction

Silicon nitride-based materials such as silicon nitride (Si_3N_4)[1] and sialon ($Si_{3-z}Al_zO_zN_{4-z}$)[2,3] are high temperature materials with high mechanical strength and hardness, which make them difficult to mechanically shape a complex form. Titanium nitride (TiN) shows a very low electrical resistivity[4] and a high hardness.[5] Therefore, if highly electroconductive silicon nitride-based materials with TiN could be fabricated, it would be possible to make desired shaped ceramics by electric discharge machining (EDM). For this purpose, the added TiN amount should be as small as possible, because TiN is readily oxidized at 600 °C,[6] leading to degradation of the electrical and mechanical properties. For the TiN addition to be decreased, it is effective to use Si_3N_4 and sialon particles coated with TiN. The present authors have reported that TiN-coating on Si_3N_4 surfaces is successfully achieved by thermal hydrolysis of $TiCl_4$ with urea and subsequent nitridation with NH_3 gas.[7] Spark plasma sintering (SPS) of these particles yielded composite ceramics with a lower electrical resistivity ($\sim 10^{-4}$ Ω cm) at 25 vol.% TiN,[8] smaller than the reported amount (30 vol.%) fabricated from a mechanical mixture.[9]

Hydrolysis of titanium alkoxide would be useful for homogeneous TiO_2-coating on silicon nitride-based particles, since the hydrolysis species Ti-OH are expected to react with Si-OH existing on the silicon nitride-based particles.[10] Since rapid hydrolysis of alkoxide generally occurs to coat agglomerated particles on matrix particles surfaces,[11,12] the careful control of alkoxide hydrolysis is required to achieve homogeneous coating. The purpose of the present study is to prepare TiN-coated β-sialon ($z=2$) and Si_3N_4 particles by controlled hydrolysis of $Ti(O\text{–}i\text{–}C_3H_7)_4$, followed by nitridation with NH_3 gas. TiN/Si_3N_4 and TiN/sialon composites are densified by SPS, and their relative density and electrical resistivity are compared.

2. Experimental procedure

2.1. Preparation of silicon nitride-based particles coated with TiO_2 and TiN

$Ti(O\text{–}i\text{–}C_3H_7)_4$ (the purity, 5N; Kojundo chemical lab Co., Ltd. Japan) was used as the starting source of TiO_2. TiO_2 precursor (0.1 mol l^{-1}) was prepared by adding 2-methoxyethanol (4.8 ml) (Kanto chemicals, Co., Inc., Japan) and $Ti(O\text{–}i\text{–}C_3H_7)_4$ (4.5 ml) at a mole ratio of 4:1 to dehydrated isopropyl alcohol (IPA 160 ml) (Wako pure chemical industries, Ltd., Japan) and refluxing the solution at 82 °C for 180 min in flowing N_2 gas.

---

* Corresponding author. Tel./Fax: +81-11-706-6576.
E-mail address: shimashi@eng.hokudai.ac.jp (S. Shimada).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00229-2

The experimental procedure for TiO_2 coating was shown in Fig. 1. 0.244 g β-sialon ($z=2$; mean particle size, 0.5 μm) or 0.250g Si_3N_4 particles (α-phase >95%; mean particle size, 0.5 μm) were ultrasonically dispersed for 15 min in IPA (160 ml) containing 1.0 vol.% H_2O at 15 °C, to which the TiO_2 precursor was dropwise added. The amount of precursor added was 7.6, 14.5, 22.8, and 37.6 ml, corresponding to 10, 17.5, 25 and 32.5 vol.% TiN, respectively. When the precursor-containing suspension was gradually heated to 40 °C and held for 60 min in flowing N_2 gas, it changed to that containing the TiO_2 colloids, which was then washed, vacuum-filtered, and dried at 60 °C. The resulting TiO_2/sialon and TiO_2/Si_3N_4 composite particles were nitrided at 800 °C for 180 min in flowing NH_3 gas (150 ml min^{-1}).

The coating state of TiO_2 and TiN on the sialon and Si_3N_4 surfaces was examined by transmission electron microscopy (TEM) with electron diffraction (ED) and energy dispersive X-ray analysis (EDX). Phases were identified by X-ray diffraction (XRD) and the lattice constant (a_0) of the TiN was determined using silicon powder as an internal standard.

2.2. Densification of TiN/sialon and TiN/Si_3N_4 composites by SPS

SPS of the composite particles of 0.250 g was carried out at 1400–1700 °C in N_2 under a uniaxial pressure of 39 MPa according to our previous report.[8] The temperature was increased with a controlled electric current and measured on the graphite die surface with an optical pyrometer. When the sintering temperature was reached, the current was immediately switched off. A typical healing schedule at 1600 °C was current; 740 A, heating rate; 20 °C min^{-1}, and total time; 14.5 min.

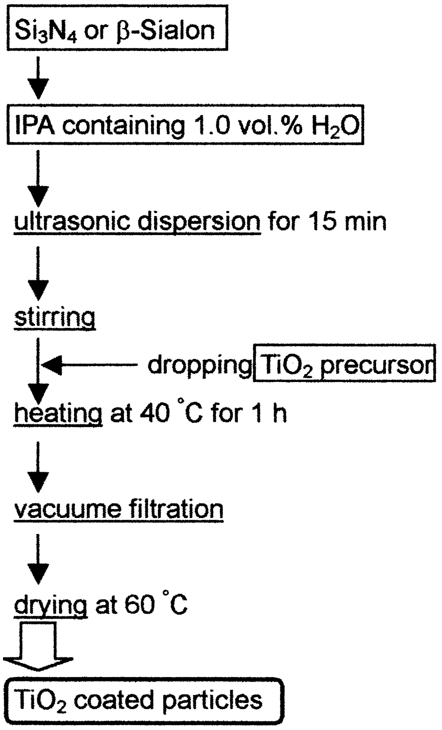

Fig. 1. Flow chart for preparing TiO_2-coated composite particles.

The densities of the sintered TiN/sialon and TiN/Si_3N_4 composites were measured by the Archimedes method using CCl_4 at room temperature. Phase identification of TiN and its lattice constant were determined by XRD as the described above. The Vickers hardness of TiN/sialon and TiN/Si_3N_4 composite ceramics was measured using a load of 200 g for 15 s. The microstructure of the polished sintered composites surface was observed by scanning electron microscopy (SEM). The electrical resistivities of the composite ceramics containing 10–32.5 vol.% TiN were measured by a two-probe and/or four-probe method at room temperature.

3. Results and discussion

3.1. Preparation of silicon nitride-based particles coated with TiO_2 and TiN

A TEM image of TiO_2/sialon composite particles obtained by heating to 40 °C the TiO_2 precursor-containing suspension, corresponding 25 vol.% TiN, is shown in Fig. 2(a). Amorphous TiO_2, which was confirmed by EDX and ED (see inserted diffraction figure), homogeneously covers sialon particles with <50 nm thick. Similarly Si_3N_4 coated with TiO_2 also was obtained. Fig. 2(b) shows a TEM image of TiN/sialon composite particles obtained after nitridation of TiO_2/sialon particles with NH_3 gas at 800 °C. TiN particles grow to 10–20 nm sizes on sialon particles; the formation of TiN was confirmed by the ED pattern (see an inserted figure) at a location indicated by an arrow. Therefore, it is found that sialon particles are successfully coated with nano-sized TiN. The lattice constant (a_0) of TiN was 0.420 nm, smaller than the pure value (0.424 nm),[13] meaning that TiN contains a small amount of oxygen.

3.2. Densification of TiN/sialon and TiN/Si_3N_4 composites by SPS

TiN/Sialon particles (25 vol.%) were sintered without any additives by SPS at 1400–1700 °C. The XRD pattern of the ground composite ceramics revealed that starting β-sialon and TiN phases were not changed without any reaction. The a_0 value of TiN increased with increasing SPS temperature and reached the pure value at 1500 °C. The electrical resistivity of the SPSed ceramics showed a lower value ($\sim 10^{-3}$ Ω cm) at 1500 °C, but very high ($\sim 10^6$ Ω cm) at 1600 °C. Fig. 3(a) and (b) show the surface texture of the ceramics SPSed at 1500 and 1600 °C, respectively. The former ceramics possess TiN networks (white contrasts) of 0.1–0.5 µm wide, which provide a path for high electrical conductivity and the latter ones indicate TiN grains of 0.1–2.0 µm sizes isolated in the sialon matrix. This isolated texture may be formed by liquid phase sintering derived from sialon particles and explains why an electrical resistivity of the ceramics prepared at 1600 °C is very high.

The relative density is shown in Fig. 4 as a function of TiN amount in the sialon and Si_3N_4 composite ceramics obtained at 1500 and 1600 °C, respectively. Sialon-matrix composites have a relative density of 95% (solid line), irrespective of the TiN amount. Liquid glass phase produced during SPS should be responsible for such a high relative density of the sialon ceramics. In contrast, the Si_3N_4 composite ceramics show a high relative density (dotted line) only containing >25 vol.% TiN. A correlation between the relative density of the TiN/Si_3N_4 ceramics and the TiN amount is very similar to that for the TiN/Si_3N_4 ceramics obtained from thermal hydrolysis of urea.[8] The Vickers hardness of TiN/Sialon and TiN/Si_3N_4 ceramics containing 25 vol.% TiN was

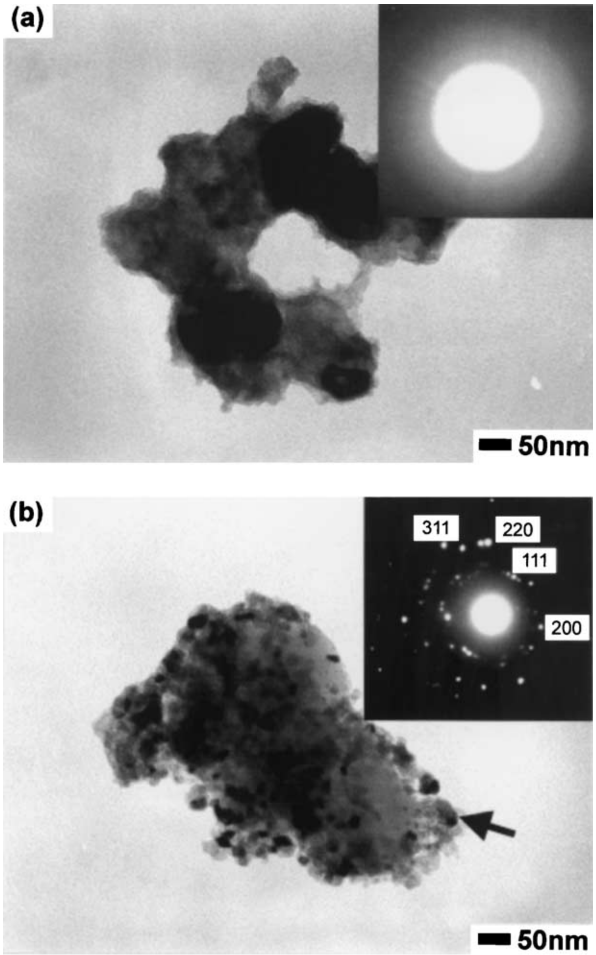

Fig. 2. TEM image of (a) TiO_2/Sialon particles, (b) TiN/Sialon particles.

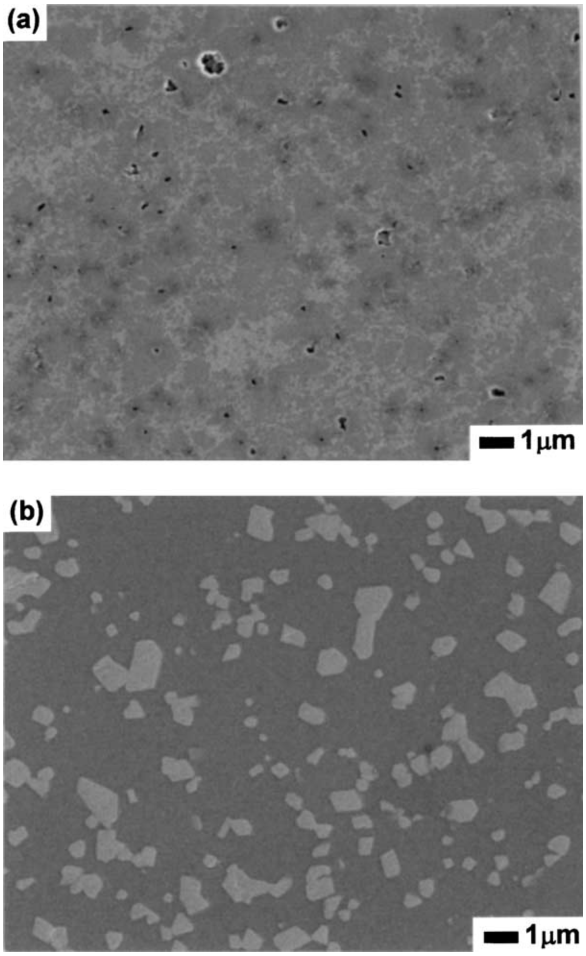

Fig. 3. SEM images of polished surfaces of 25 vol.% TiN/Sialon composite SPSed at (a) 1500 °C and (b) 1600/bk7C.

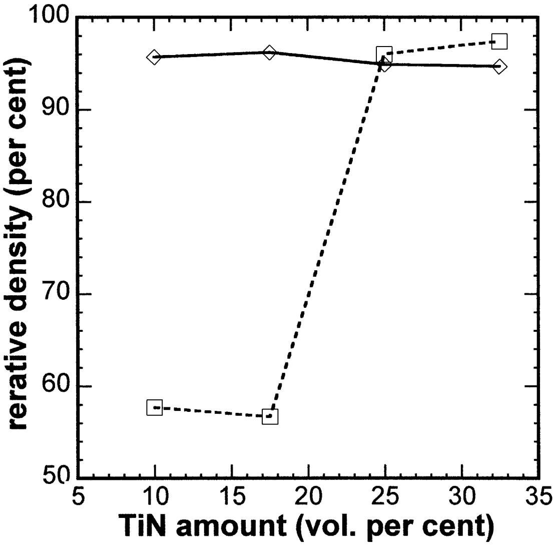

Fig. 4. Change of the relative density of (◇) Sialon composites and (□) Si_3N_4 composites with TiN content.

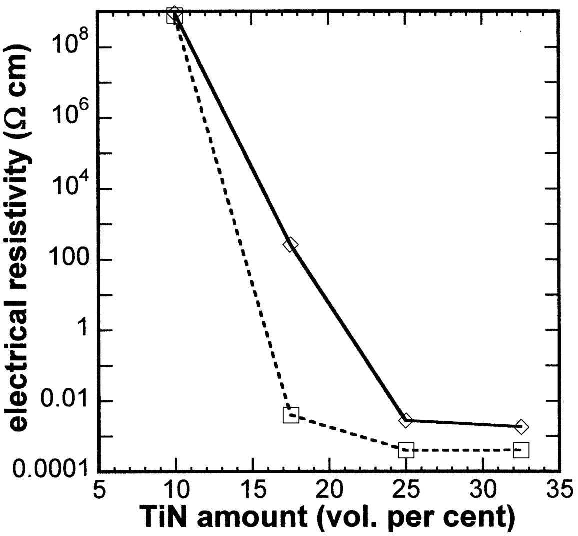

Fig. 5. Change of the electrical resistivity of (◇) Sialon composites and (□) Si_3N_4 composites with TIN content.

1600 ± 200 and 1200 ± 200 kg mm^{-2}, respectively. Fig. 5 shows a relationship between the electrical resistivity and the TiN amount in the composite ceramics. The resistivity for TiN/sialon (solid line) is higher than for TiN/Si_3N_4 (dotted line), which may be due to the presence of glass phase in TiN–TiN interface in TiN/sialon ceramics. The TiN amount necessary to provide EDM-applicable resistivity ($< 5 \times 10^{-3}$ Ω cm) was 25 and 17.5 vol.% for sialon and Si_3N_4, respectively.

4. Conclusion

Nano-sized TiN was coated on β-sialon ($z = 2$) and Si_3N_4 by depositing TiO_2 on their particle surfaces, and subsequent nitridation with NH_3 gas. TiO_2-coating was successfully achieved by mixing the matrix particles and $Ti(O–i–C_3H_7)_4$ in isopropyl alcohol containing 1.0 vol.% H_2O at 15 °C, followed by heating to 40 °C. Nitridation yielded 10–20 nm TiN particles covering β-sialon and Si_3N_4. Spark plasma sintering of TiN/sialon composite particles produced the ceramics with TiN networks of 0.1–0.5 μm wide at 1500 °C, but with isolated TiN grains of 0.1–2.0 μm in the matrix at 1600 °C. The former ceramics had a relative density of <95%, irrespective of the TiN amount. Electrical resistivity of TiN/sialon and $TiNSi_3N_4$ ceramics decreased steeply to a lower electrical resistivity ($\sim 10^{-3}$ Ω cm) with increasing TiN amount, making these ceramics suitable for electric discharge machining at 25 and 17.5 vol.% TiN, respectively.

Acknowledgements

The authors wish to express hearty thanks to Professor K. Kurokawa (Hokkaido University, Sapporo, Japan) for using the SPS apparatus. This research was financially supported by the Sasagawa Science Research Grant from The Japan Science Society.

References

1. Naurula, C. K., Allison, J. E., Bauer, O. R. and Gandhi, H. S., Materials chemistry issue related to advanced materials applications in the automotive industry. *Chem. Mater.*, 1996, **8**, 984–1003.
2. Jack, K. H., Sialons and related nitrogen ceramics. *J. Mater Sci.*, 1976, **11**, 1135–1158.
3. Ekström, T. and Nygren, M., Sialon ceramics. *J. Am. Ceram. Soc.*, 1992, **75**, 259–276.
4. Weimer, A. W., *Carbide, Nitride and Boride Materials Synthesis and Processing*. Chapman & Hall, London, 1997.
5. Groza, J. R., Curtis, J. O. and Kramer, M., Field-assisted sintering of nanocrystalline titanium nitride. *J. Am. Ceram. Soc.*, 2000, **83**, 1281–1283.
6. Gogotsi, Yu. G. and Porz, F., The oxidation of particulate-reinforced Si_3N_4–TiN composites. *Corrosion Sci.*, 1992, **33**, 627–640.
7. Kawano, S., Takahashi, J. and Shimada, S., Preparation of nano sized TIN-coated Si_3N_4 particles. *J. Mater. Chem.*, 2001, **11**, 2625–2628.
8. Kawano, S., Takahashi, J. and Shimada, S., Highly electroconductive TiN/Si_3N_4 composite ceramics fabricated by spark plasma sintering of Si_3N_4 particles coated nano-sized with TiN. *J. Mater. Chem.*, 2002, **12**, 361–365.
9. Bellosi, A., Guicciardi, S. and Tampieri, A., Development and characterization of electroconductive Si_3N_4-TiN composites. *J. Euro. Ceram. Soc.*, 1992, **9**, 83–93.
10. Hirano, S., Yogo, T. and Kikuta, K., Processing of functional ceramics by metallorganic route. *J. Ceram. Soc. Jpn.*, 1991, **99**, 1026–1035.
11. Wang, C. M., Microstructural homogeneity improvement in Si_3N_4 by a powder coating method. *J. Mater. Sci.*, 1996, **31**, 4709–4718.
12. Takahashi, Y. and Chizaki, J., Titania coating of alumina powders. *J. Ceram. Soc. Jpn.*, 1988, **96**, 240–246.
13. *JCPDS* 38-1420.