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Coating and spark plasma sintering of nano-sized TiN on alumina particles of different size, shape and structure

Shiro SHIMADA, Anongsack PASEUTH and Hajime KIYONO

Graduate School of Engineering, Hokkaido University, West-8, North-13, Kita-ku, Sapporo 060−8628

TiN-coated Al_2O_3 particles of different size, shape and crystal structure were prepared by depositing nano-size TiO_2 on the Al_2O_3 surfaces from $Ti(O–i–C_3H_7)_4$ solution (TiO_2 precursor) by controlled hydrolysis, then nitrided with NH_3 at 1000°C. Irrespective of the source of Al_2O_3 particles, a homogeneous TiO_2 coating was achieved by heating from 10 to 40°C an ultrasonic suspension of the Al_2O_3 particles containing the precursor with 1.0 vol% H_2O. After nitridation, the Al_2O_3 grains were coated with 10–20 nm TiN particles. Spark plasma sintering of the TiN/Al_2O_3 particles at 1500°C and 1600°C yielded the composite ceramics with a relative density of 94–97%. Composite TiN/Al_2O_3 ceramics with an electrical resistivity of ~10^{-2} Ω cm were obtained at 25 vol% TiN composition.

Key-words : Coating, Spark plasma sintering, Nano-sized TiN, Alumina, Composites

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1. Introduction

Al_2O_3 ceramics are an excellent high-temperature material, but are difficult to shape by mechanical methods because of their high brittleness and hardness. TiN exhibits very low electrical resistivity, a high melting point (> 3000 K) and high hardness. Therefore, if highly electroconductive TiN/Al_2O_3 ceramics could be fabricated, they could be used to make complex-shaped Al_2O_3 ceramics by electric discharge machining (EDM). For this purpose, the TiN content in the TiN/Al_2O_3 ceramics should be as small as possible without degradation of the electrical and mechanical properties, because TiN is readily oxidized at < 600°C.

TiN/Al_2O_3 composite ceramics are usually fabricated by sintering mechanically mixed powders of TiN and Al_2O_3. For example, Bellosi et al. have densified Al_2O_3-based composites containing 30 vol% TiC, TiN and TiB_2 from the mechanical mixture by hot pressing.[1] Rak and Czechowski have densified mixed powders of Al_2O_3 with 5–25 vol% TiN by spark plasma sintering (SPS).[2] Electoconductive ceramics of Al_2O_3–AlN–42 wt% TiN were fabricated from the mixed powders by hot-pressing.[3] Shen et al. have fabricated TiN/Al_2O_3 composite ceramics by SPS from a mixture of TiN and α-Al_2O_3 powders treated in a high-speed planetary mill.[4] Apart from these composite ceramics, TiN/Al_2O_3 laminate composites have been fabricated from Al_2O_3 and TiN slurries.[5] Such mechanical mixing method leads to an inhomogeneous distribution of the second phase (TiN in the TiN/Al_2O_3 composite) and agglomerates in the mixture. In this respect, homogeneous precipitation of Al_2O_3 and TiO_2 from $Al(NO_3)_3$ and $Ti(OBu)_4$ is useful for the preparation of a starting source for electroconductive Al_2O_3/TiN composites.[6] For homogenous precipitates to be prepared, in-situ processing of a TiO_2 second phase in a matrix of Al_2O_3 is interesting as a possibility.

For the fabrication of electroconductive TiN–Al_2O_3 nanocomposites, nano-size TiO_2 particles have been deposited on the surface of α-Al_2O_3 by hydrolysis of tetra-butyl titanate and nitrided with NH_3.[7] Wang et al. have synthesized TiN–Al_2O_3 nanocomposite ceramics by SPS using a mixture of TiO_2, AlN and Ti powder as the starting material.[8] However, there have been no reported studies of the homogenous coating of TiN on the surface of Al_2O_3 grains of different particle sizes/shapes and crystal structures.

The present author (S. S.) has established a novel method, called the precursor-containing method, for successful coating Si_3N_4-based particles (Si_3N_4, α-SiAlON, β-SiAlON) with nano-size TiO_2 by controlled hydrolysis of a precursor solution containing $TiCl_4$ or $Ti(O–i–C_3H_7)_4$.[9)–13)] Subsequent nitridation of TiO_2 with NH_3 gas resulted in the homogeneous coating on Si_3N_4-based particles with nano-sized TiN, followed by SPS that produced TiN/Si_3N_4 composite ceramics with low electrical resistivity (~10^{-4} Ω cm). It was demonstrated that such a TiN/Si_3N_4 composite ceramic can have a ϕ 0.54 mm hole bored in it by EDM. However, these studies have been limited to Si_3N_4-based materials such as Si_3N_4, α-SiAlON, and β-SiAlON. It is of interest to investigate the application of the precursor-containing method to the formation of a homogeneous coating of TiO_2 particles on an oxide rather than a nitride. The present study reports a method for forming a homogenous coating of nano-size TiO_2 particles on the surfaces of Al_2O_3 by controlled hydrolysis of $Ti(O–i–C_3H_7)_4$ using ultrasonic dispersion. Five kinds of Al_2O_3 particles with different structures (α- and θ-Al_2O_3), shapes (angular and spherical) and sizes (0.3–10 μm) were used. As are the previous studies, nitridation and SPS of the nano-sized TiO_2/Al_2O_3 composites were carried out to fabricate densified TiN/Al_2O_3 composite ceramics with low electrical resistivity.

2. Experimental procedure

2.1 Coating of TiO_2 on Al_2O_3 particles

The five kinds of Al_2O_3 particles used in this study had different sizes (0.3–10 μm), shapes (spherical and angular) and structures (α- and θ-Al_2O_3) (**Table 1**). The Al_2O_3 samples labeled CA were from the Kojundo Chemical Lab., Ltd., while those labeled AO were provided by Admatechs Company Ltd., Japan. The complete process for the preparation of the TiO_2/Al_2O_3 composite particles and their densification is shown in **Fig. 1**. The Al_2O_3

Table 1. Al_2O_3 Powders Used for Preparation of TiO_2/Al_2O_3 Composites

	CA–0.3	CA–2	AO–0.7	AO–6	AO–10
Particle size/μm	0.3	2.0	0.7	6.1	9.9
Shape	angular	angular	spherical	spherical	spherical
Crystal structure	α-type	α-type	θ-type	θ-type	θ-type

CA-type alumina (purity 3N) was purchased from Kojundo Chemical Lab., Ltd. (Saitama), AO-type alumina (purity > 99.9 wt%) was supplied from Admatechs Co. Lit. (Miyoshi-cho, Aichi).

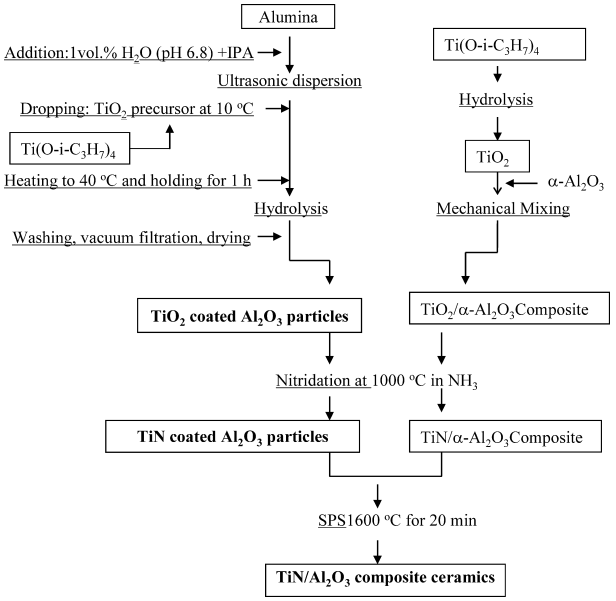

Fig. 1. Flow chart for the fabrication of TiN/ Al_2O_3 composites from TiO_2/ Al_2O_3 particles prepared by both chemical route and mechanical mixing.

powder was ultrasonically dispersed in a solution of 1 vol% H_2O with isopropyl alcohol (IPA) (Wako Pure Chemical Ind.), to which the TiO_2 precursor solution was added dropwise, maintaining the temperature at 10°C. The TiO_2 precursor solution was prepared from $Ti(O\text{–}i\text{–}C_3H_7)_4$ (99.999% purity; Kojundo Chemical Lab., Ltd.) as described previously.[11] The precursor of 13, 15, 18, 23, and 28 mL was added to Al_2O_3, corresponding to 15, 17, 20, 25, and 30 vol% TiN, respectively. The precursor-containing Al_2O_3 dispersion was heated from 10 to 40°C and held for 1 h in flowing N_2, during which fine TiO_2 particles were precipitated onto the Al_2O_3. The TiO_2-containing Al_2O_3 product was washed, vacuum-filtered, and dried at 60°C. In other experiments, pure TiO_2 particles were also precipitated by hydrolysis from the TiO_2 precursor according to the same method and mechanically mixed with each of the five different Al_2O_3 powders.

2.2 Coating of TiN on Al_2O_3 particles

TiO_2-coated Al_2O_3 particles obtained as above were nitrided at 1000°C for 3 h in NH_3 flowing at 150 mL min^{-1}. The mechanically mixed TiO_2/Al_2O_3 particles also were nitrided at 1000°C in NH_3. The TiO_2 or TiN coating on the Al_2O_3 surface was examined by TEM with energy-dispersive X-ray analysis (EDX). The phases were identified by XRD and the lattice constant (a_o) of the TiN was determined using silicon powder as an internal standard.

2.3 Densification of TiN/ Al_2O_3 composites by SPS

A 0.25 g powder aliquot of TiN-coated Al_2O_3 composite was formed into a pellet (6 mm diameter × 4 mm high) by uniaxial pressing (75 MPa), followed by cold isostatic pressing (100 MPa). This TiN/Al_2O_3 composite was densified by SPS (SPS–501L, Sumitomo Coal Mining Co.) at 1500 and 1600°C in N_2. The details of the sintering condition have been reported elsewhere.[10] The temperature on the graphite die surface was measured using an optical pyrometer.

The densities of the sintered TiN/Al_2O_3 composites were measured with distilled water at room temperature by the Arc-

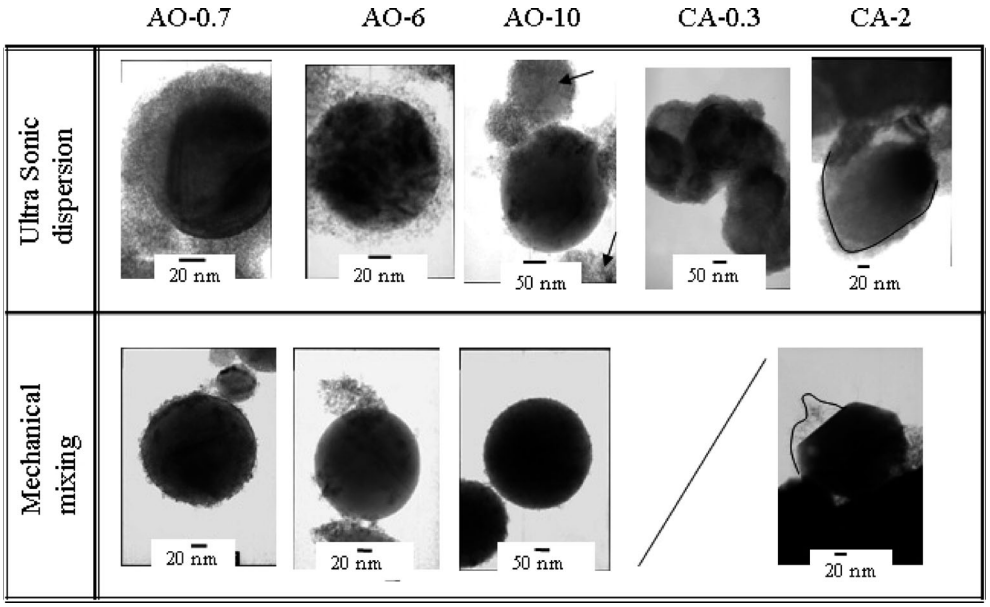

Fig. 2. SEM image of TiO_2 coated Al_2O_3 particles of different size, shape and structure prepared from both the TiO_2 precursor and mechanical mixtures. TiO_2 content corresponds to 25 vol% TiN.

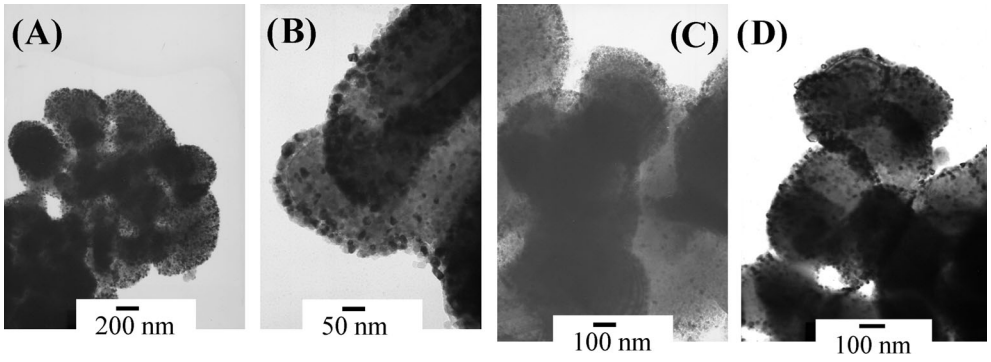

Fig. 3. TEM images of TiN/ Al_2O_3 composite particles with various TiN contents. Vol%: (A) 15, (B) 17, (C) 20, (D) 25.

himedes method. The phase identification of the ground powder was made by XRD. The polished surface microstructures of the sintered TiN/Al_2O_3 composites were observed by scanning electron microscopy (SEM). The Vickers hardness of the TiN/Al_2O_3 ceramics containing 25 vol% TiN was measured using a load of 200 g for 15 s.

3. Results and discussion

3.1 Preparation of TiO_2-coated Al_2O_3 particles

When the TiO_2 precursor-containing Al_2O_3 dispersion was ultrasonically mixed in an IPA solution with 1.0 vol% H_2O and gradually heated from 10 to 40°C (controlled hydrolysis), it became opaque at 35–40°C, suggesting the precipitation of TiO_2. **Figure 2** shows TEM images of TiO_2/Al_2O_3 composite particles with a Ti content corresponding to 25 vol% TiN when nitrided. Very fine TiO_2 particles about 20 nm thick homogeneously cover the surface of each of the different types of Al_2O_3. It should be noted that this homogeneous coverage by TiO_2 particles on both the AO- and CA-type Al_2O_3 occurred at the Ti content corresponding to 15–30 vol% TiN. Some aggregated TiO_2 particles were seen in the vicinity of the 10 μm size Al_2O_3 particles (AO–10) (see arrows). When TiO_2 precursor-containing Al_2O_3 was not dispersed ultrasonically, only partial coating of TiO_2 on Al_2O_3 occurred. Mechanical mixing gave a sparse covering of TiO_2 on the surface of the AO- and CA-type Al_2O_3 particles. The TiO_2 coating on the CA–0.3 Al_2O_3 was not carried out. The TiO_2 obtained by controlled hydrolysis of the TiO_2 precursor was identified as anatase by SAD. It is clear that ultrasonic dispersion of the TiO_2 precursor is effective in a homogeneous coating the Al_2O_3 particles, irrespective of their size, shape and crystal structure, in contrast to mechanical mixing that produced only a partial coating of TiO_2 on the Al_2O_3 particles.

3.2 Preparation of TiN-coated Al_2O_3 particles

TiO_2/Al_2O_3 composite particles prepared from the CA–2 type Al_2O_3 corresponding to 15 to 25 vol% TiN were nitrided at 1000°C in flowing NH_3. The influence of the TiN content on the coating is shown in **Fig. 3**, indicating that a uniform coating of 10–20 nm TiN particles is achieved on the surfaces of the Al_2O_3, irrespective of the TiN content. **Figures 4**A and 4B show the XRD patterns of TiN-coated Al_2O_3 particles from the CA–2 and AO–0.7. Relatively strong TiN peaks are observed in the former sample, indicating that the TiO_2 is completely converted to TiN by reaction in NH_3 at 1000°C. The lattice constant (a_o) of this TiN is 0.4230 nm, smaller than that the literature value (0.4242 nm),[14] suggesting the presence of a small amount of oxygen in the TiN. The AO-sample (θ-Al_2O_3) was partially transformed to

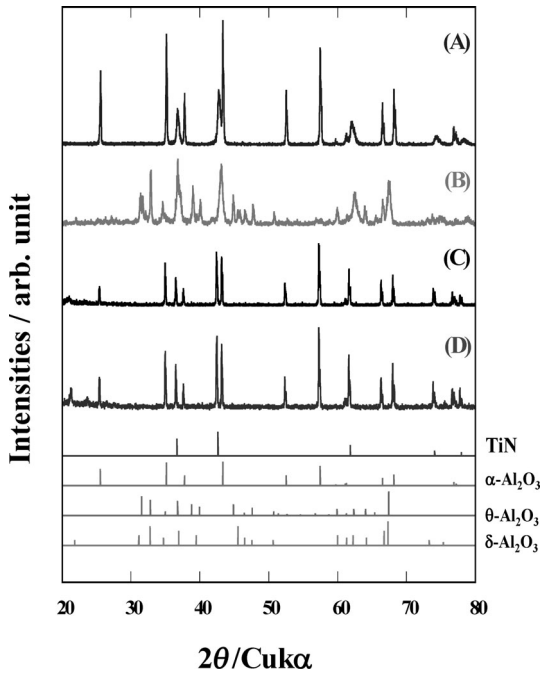

Fig. 4. XRD patterns of 25 vol% TiN/Al_2O_3 composite particles and ceramics derived from CA–2 and AO–0.7 samples. (A) and (B), composite particles; (C) and (D) composite ceramics formed by SPS at 1600°C. (A) and (C), CA–2 sample; (B) and (D) AO–0.7 sample.

the δ-phase, but not to α-phase in NH_3 at 1000°C. **Figure 5** shows TEM images of the 25 vol% TiN/Al_2O_3 composite particles formed from the different CA– and AO–Al_2O_3. TiN particles of 20 nm size occur homogeneously on the surfaces of the CA–0.3/–2 and AO–0.7 Al_2O_3 grains. On the contrary, the TiN coverage of the larger AO–6 and –10 alumina particles is incomplete, probably because of their larger surface area per individual particle (6.1 and 9.9 μm diameter). It is summarized that a homogeneous coating of TiN is formed on the surfaces of Al_2O_3 particles, irrespective of their size, shape and crystal structure, by controlled hydrolysis of a TiO_2 precursor derived from $Ti(O–i–C_3H_7)_4$ in an ultrasonic dispersion of Al_2O_3 and subsequently nitrided.

3.3 Densification of TiN/Al_2O_3 composites by SPS

The 25 vol% TiN/Al_2O_3 composite powders obtained from the AO– and CA–Al_2O_3 were sintered by SPS at 1500 and 1600°C.

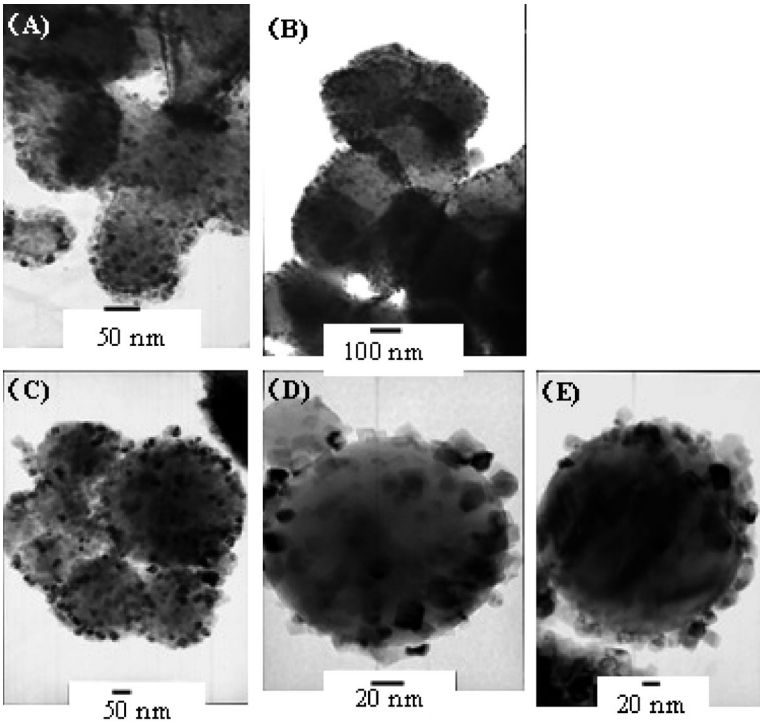

Fig. 5. TEM images of TiN-coated Al_2O_3 of different size, shape and structure at 25 vol% TiN content. (A) CA–0.3, (B) CA–2, (C) AO–0.7, (D) AO–6, (E) AO–10.

The phases formed on the surface of densified TiN/Al_2O_3 ceramics from the CA–2 and AO–0.7 samples are determined by XRD (Figs. 4 C and D) to be only α-Al_2O_3 and TiN. The a_o value of the TiN increased from 0.4230 to 0.4239 nm after SPS, approaching that of pure TiN, probably reflecting the removal of oxygen in the TiN lattice and the replacement by nitrogen during SPS at 1600°C. **Table 2** shows the relative density, Vickers hardness and electrical resistivity of the composite TiN/Al_2O_3 ceramics with 25 vol% TiN. The relative density ranges from 94 to 97%. The AO sample gave the well densified ceramics (~97%), probably because the transformation of θ- to α-Al_2O_3 promotes the densification of the composite. The Vickers hardness value from the CA samples was about 2200 kg mm^{-2}, while that from

Table 2. Relative Density, Electrical Resistivity, and Vickers Hardness of Ceramics Formed by SPS at 1600°C of TiN/Al_2O_3

Sample	Relative density /%	Vickers hardness /MPa	Electrical resistivity /Ω cm
CA–0.3	94	2200 ± 100	2.5×10^{-3}
CA–2	94	2100 ± 100	3.0×10^{-3}
AO–0.7	97	1760 ± 150	7.2×10^{-2}
AO–6	93	1740 ± 300	3.2×10^{-3}
AO–10	96	1770 ± 140	1.6×10^{-3}

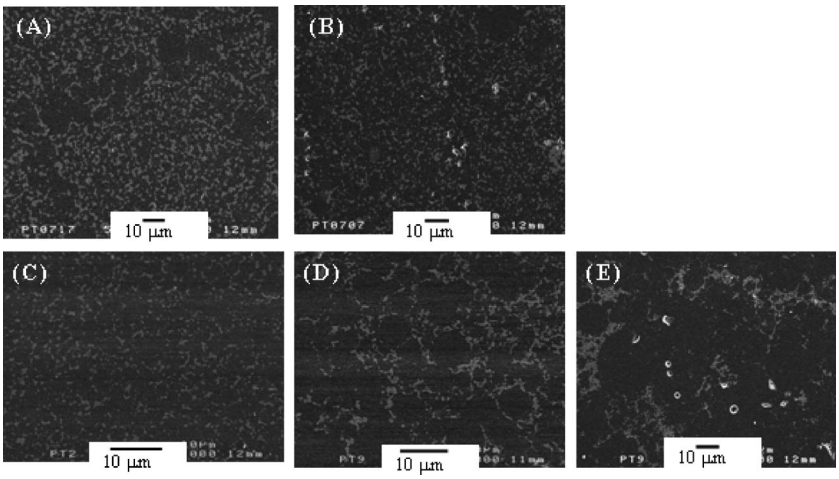

Fig. 6. SEM images of polished surface of 25 vol% TiN/Al_2O_3 composite ceramics. The labels are as for Fig. 5.

the AO samples was about 1750 kg mm^{-2}. Although the TiN/Al_2O_3 ceramics derived from the AO-samples showed relatively higher densities, their Vickers hardness was smaller. The reason for this is unknown. Composite TiN/Al_2O_3 ceramics with an electrical resistivity of ~10^{-2} Ω cm were obtained at 25 vol% TiN composition, which is appropriate for EDM (< 10^{-2} Ω cm) a dotted line in Fig. 7.

Figure 6 shows SEM images of the microstructure of the polished surface of the TiN/Al_2O_3 ceramics formed by SPS at 1600°C. The white and dark regions correspond to TiN and Al_2O_3, respectively. The surfaces of all the ceramics show a compact structure in spite of the presence of a few pores together with homogeneously distributed TiN networks of micrometer thickness. The AO–6 and –10 samples produce ceramics with the larger Al_2O_3 grains (10–20 μm), reflecting the larger grain sizes of the starting sample.

The change of electrical resistivity and density with TiN content of the TiN/Al_2O_3 ceramics formed from the CA–2 sample by SPS at 1500 and 1600°C is shown in **Fig. 7**. The densities of the ceramics sintered at 1600°C are slightly higher than those sintered at 1500°C. The electrical resistivity is decreased sharply with TiN content of the TiN/ Al_2O_3 ceramics formed at 1500 and 1600°C, becoming ~10^{-2} Ω cm at a TiN content ≥ 25 vol% TiN.

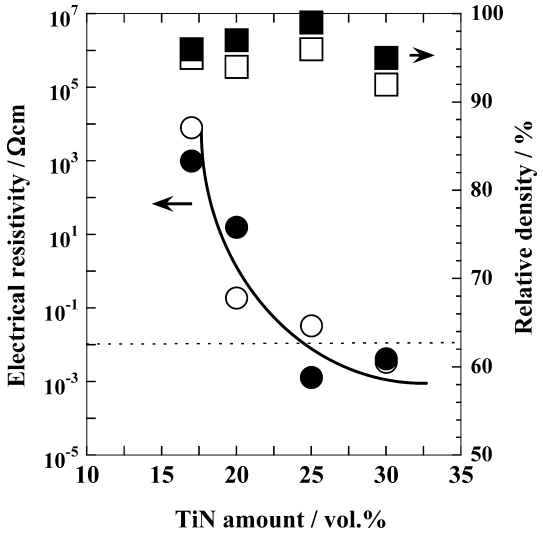

Fig. 7. Electrical resistivity (circles) and density (cubic) of 25 vol% TiN/Al_2O_3 composite ceramics as a function of TiN content. Al_2O_3, CA–2 sample; open and closed marks correspond to 1500 and 1600°C, respectively.

4. Conclusion

Nano-sized TiO_2-coated Al_2O_3 particles were prepared by ultrasonically suspending the precursor solution derived from $Ti(O–i–C_3H_7)_4$ containing Al_2O_3 powders of different size, shape and crystal structure. When this suspension containing 1.0 vol% H_2O was heated from 10 to 40°C, the surfaces of the Al_2O_3 particles were covered with unagglomerated TiO_2. Nitridation of TiO_2-coated Al_2O_3 particles with NH_3 gas at 1000°C produced nano-sized TiN-coated Al_2O_3. The particle size and lattice constant of the resulting TiN were 10–20 nm and 0.419 nm, respectively. Spark plasma sintering of 25 vol%TiN/Al_2O_3 at 1500°C and 1600°C produced the composite ceramics with a relative density ranging from 94 to 98% and the electrical resistivity of ~10^{-2} Ω cm.

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