

Electroconductivity of sintered bodies of α -Al₂O₃-TiN composite prepared by CVD reaction in a fluidized bed

KEIICHI TSUGEKI, TAKAFUMI KATO, YOSHIHIRO KOYANAGI,
KATSUKI KUSAKABE, SHIGEHARU MOROOKA*

*Department of Chemical Science and Technology, Kyushu University, 6-10-1 Hakozaki,
Higashi-ku, Fukuoka 812, Japan*

α -Al₂O₃ particles whose primary size is ca. 450 nm are smoothly fluidized by forming agglomerates of ca. 200 μ m and are coated with TiN crystallites generated by a chemical vapour deposition (CVD) reaction of TiCl₄ and NH₃ at 973 K. The α -Al₂O₃-TiN composite particles and those obtained by mechanically mixing constituent particles are sintered at 1873 K in a nitrogen atmosphere, and the electroconductivity of sintered bodies is measured at 298 K. The electroconductivity of the CVD-hybridized composites is higher than that of mechanically mixed ones. This shows the effectiveness of fluidized-bed CVD processing in the preparation of composite ceramic particles.

1. Introduction

Particles used for ceramics are in the size range of 1 μ m or smaller, and are classified as Group C powders which are hard to fluidize [1]. However, a few kinds of submicrometre particles are found to be fluidizable [2, 3]. The fluidization is maintained because agglomerates are spontaneously and steadily formed in the bed and behave like Group A particles. Morooka *et al.* [2] reported that powders of Ni, Si₃N₄, SiC, Al₂O₃ and TiO₂ of 20–400 nm in diameter were well fluidized by forming agglomerates of 70–700 μ m. Pacek and Nienow [4] also found that tungsten carbide particles of 4–5 μ m were also fluidizable via self-agglomeration. On the other hand, particles such as ZrO₂ and CaCO₃ were very cohesive and formed a bulk structure in the bed [2].

As indicated by Morooka *et al.* [2], Chaouki *et al.* [3] and Kono *et al.* [5], the agglomeration phenomena in the fluidized bed are in dynamic equilibrium between integration, mainly due to van der Waals force among adjacent particles, and disintegration due to the shearing force generated by bubble movement.

Morooka *et al.* [6] fluidized fine Al₂O₃ particles and coated them uniformly with TiO₂ crystallites formed by the oxidation of TiCl₄. Toda and Kato [7] introduced mixed tetraethyloxysilane-ethanol-water vapour with air or nitrogen into a fluidized bed of MgO particles at 473–673 K and coated the particles with non-crystalline SiO₂ film. The resistance of the SiO₂-coated MgO particles against acid increased with increasing film thickness. Yan *et al.* [8] protected electroluminescent particles of 18 μ m in size with a

moisture-resistant thin film of amorphous silicon nitride. This processing was carried out by the reaction of SiH₄ and N₂ in an r.f. plasma atmosphere. Other recent work on CVD processing in fluidized beds has been reviewed by Morooka *et al.* [9].

Aluminium oxide is an excellent high-temperature material but is not electroconductive. If sintered Al₂O₃ bodies can be made electroconductive, the electrospark technique can be applied to manufacturing [10]. In this study, α -Al₂O₃ crystallites are coated with TiN crystallites formed by the reaction of TiCl₄ with NH₃ in a fluidized-bed reactor. Composite particles obtained are sintered, and the electroconductivity of the sintered bodies is evaluated. Titanium nitride is chosen as the electroconductive phase because it is a typical high-temperature material. The CVD coating is compared with mechanical mixing of the components, α -Al₂O₃ and TiN.

2. Experimental procedure

Fig. 1 shows the experimental apparatus used in this work. The fluidized-bed reactor, made of a mullite tube (35 mm i.d. and 1 m long), was heated by an external electric furnace. NH₃ gas, dried by passing through a sodium hydroxide column, was introduced via a mullite tube of 4 mm i.d., while TiCl₄ vapour was diluted with nitrogen and then fed through a layer of 1 mm aluminium oxide particles packed in the annular space of the reactor. Nitrogen was deoxidized by passing through an activated copper column and was dried by passing through a silica gel column and a dry ice-ethanol trap. The mole fraction of TiCl₄ in the bed

* To whom all correspondence should be addressed.

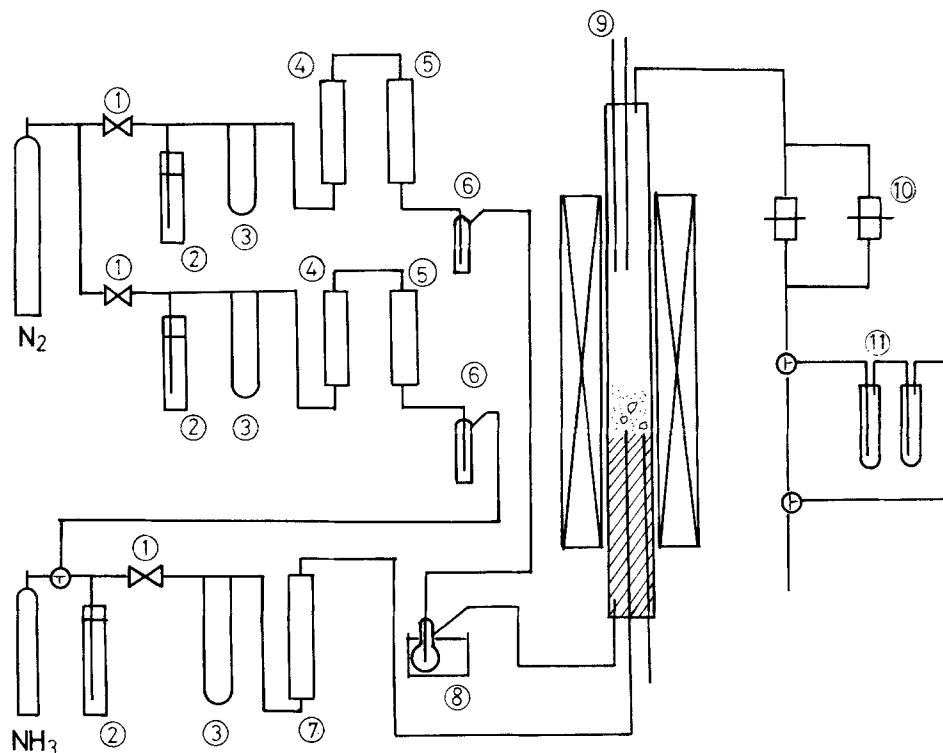
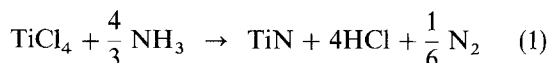


Figure 1 Schematic diagram of experimental apparatus: (1) gas valve, (2) pressure controller, (3) manometer, (4) activated copper column, (5) silica gel column, (6) dry ice-ethanol trap, (7) NaOH column, (8) TiCl_4 evaporator, (9) thermocouple, (10) filter, (11) absorption bottle.

was 0.005–0.014, and was controlled by changing the temperature of the TiCl_4 evaporator.

TiN crystallites were formed by the following CVD reaction:



The reaction in the present study was carried out at 973 K, at which TiCl_4 was completely consumed in the reactor. The reaction rate was estimated from the previous result [6]. HCl was absorbed at the exit, and its concentration was determined by titration with 0.1 M NaOH.

The matrix particles were $\alpha\text{-Al}_2\text{O}_3$ crystallites (Sumitomo Chemical Co. Ltd, purity 99.99%, density 3.8 Mg m^{-3}). Fig. 2 shows a TEM image of primary

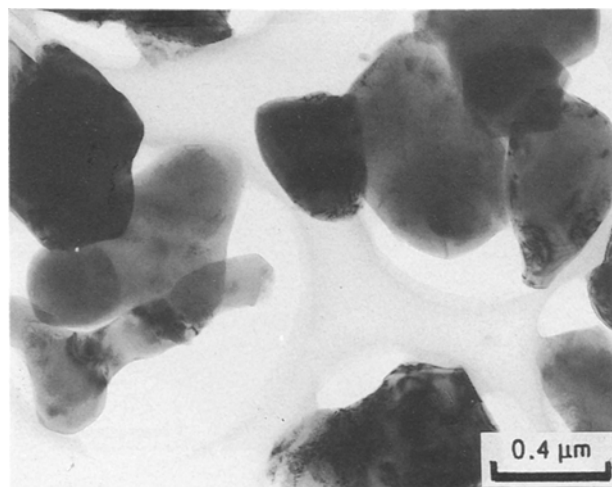


Figure 2 Transmission electron micrograph of $\alpha\text{-Al}_2\text{O}_3$ primary particles used.

$\alpha\text{-Al}_2\text{O}_3$ particles. The average size was 450 nm by TEM and is in agreement with the value calculated from the BET area. Fig. 3 is an SEM image of the agglomerates formed spontaneously in the bed. Agglomerates were crushable by the pressure of a fingernail, and the density and porosity were ca. 200 μm and 0.50–0.53, respectively.

20 g of $\alpha\text{-Al}_2\text{O}_3$ was put into the reactor at a settled bed height of 2–3 cm. The fluidizing gas velocity was in the range of 12–17 cm s^{-1} at 0.1 MPa and 973 K. The reaction period was in the range of 0.5–4 h, and the content of TiN in the composite agglomerates formed was dependent on reaction period and TiCl_4 concentration. Self-decomposition of NH_3 was negligible compared to the reaction with TiCl_4 at this temperature and residence time.

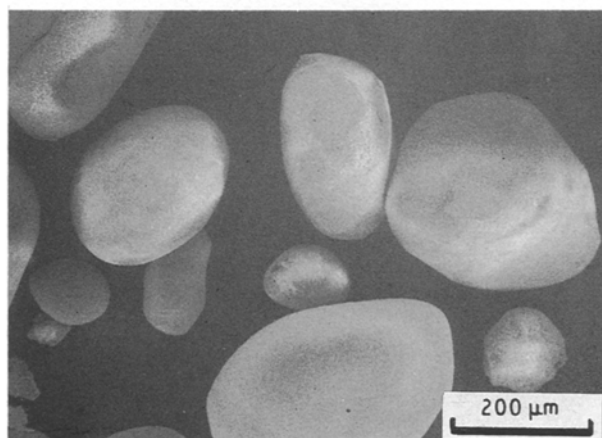


Figure 3 Scanning electron micrograph of $\alpha\text{-Al}_2\text{O}_3$ agglomerates formed in a bed.

Sintered bodies of $\alpha\text{-Al}_2\text{O}_3\text{-TiN}$ composites were prepared by the following methods:

1. Using as-formed $\alpha\text{-Al}_2\text{O}_3\text{-TiN}$ agglomerates by CVD hybridization.
2. Using distintegrated $\alpha\text{-Al}_2\text{O}_3\text{-TiN}$ agglomerates by CVD hybridization.
3. Using mechanically mixed $\alpha\text{-Al}_2\text{O}_3$ and TiN particles.

The crystalline TiN powder used in method 3 was purchased from Tokyo Tekko Co. Ltd. The average size was 20 nm by TEM, and the density was 5.21 Mg m^{-3} . Each sample was shaped by cold-pressing at 5 MPa into tablet discs of 10 mm diameter and 1–2 mm thickness, which were then sintered at 1873 K for 1 h in a nitrogen atmosphere. The temperature was raised at a rate of 400 K h^{-1} between 293 and 1473 K and 200 K h^{-1} between 1473 and 1873 K.

Characterization of particles and sintered bodies was performed by an analytical transmission electron microscope (Jeol JEM-2000FX) equipped with an energy-dispersive X-ray analyser (EDXA, Tracor Northern TN-2000) and a scanning electron microscope (SEM, Hitachi S-2300) equipped with an EDXA

(Kevex delta class). Crystallites were characterized by X-ray diffraction, X-ray fluorescence and BET adsorption analysis as well as TEM and SEM observation. The electroconductivity of the sintered bodies was measured by the four-terminal method.

3. Results and discussion

TEM images of composite particles with TiN mass fractions of 0.097 and 0.37 are shown in Fig. 4a and b, respectively. Ultimate analysis of cubic crystallites in Fig. 4b by TEM-EDXA shows a sharp peak of Ti, as seen in Fig. 5. The XRD analysis indicates that the titanium compound formed is crystalline TiN. The size of crystallites increased with increasing titanium content and was in the range 30–100 nm by TEM and 53–76 nm by XRD with $\text{CuK}\alpha$.

Fig. 6 is a two-dimensional dot map of Ti in the sectioned area of the CVD-hybridized agglomerates, showing a localization of Ti in the peripheral region.

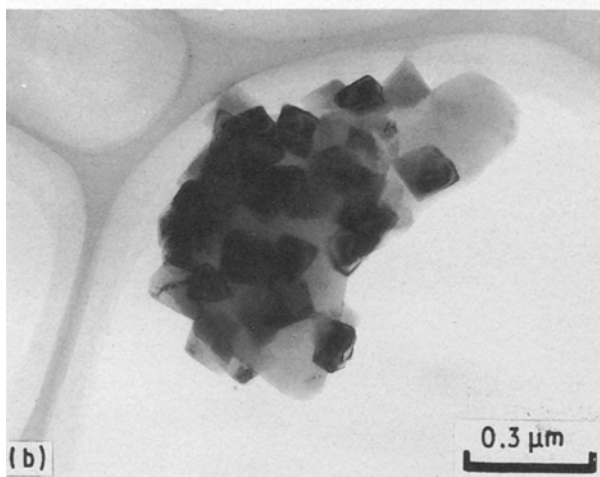
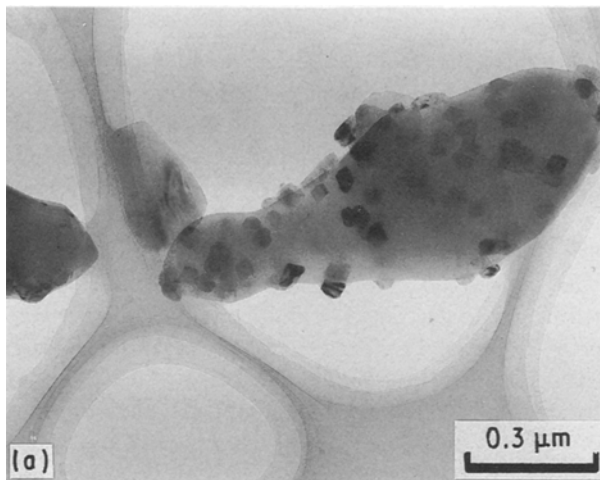


Figure 4 (a) TiN crystallites deposited on the surface of $\alpha\text{-Al}_2\text{O}_3$ particles. Reaction period, 2 h; TiN mass fraction in composite particles, 0.097. (b) TiN crystallites deposited on the surface of $\alpha\text{-Al}_2\text{O}_3$ particles. Reaction period, 4 h; TiN mass fraction in composite particles, 0.37.

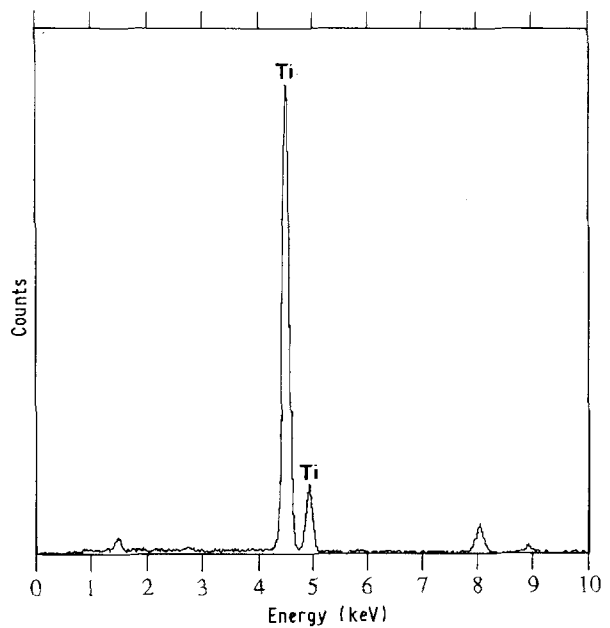


Figure 5 TEM-EDXA spectrum of a cubic crystallite.

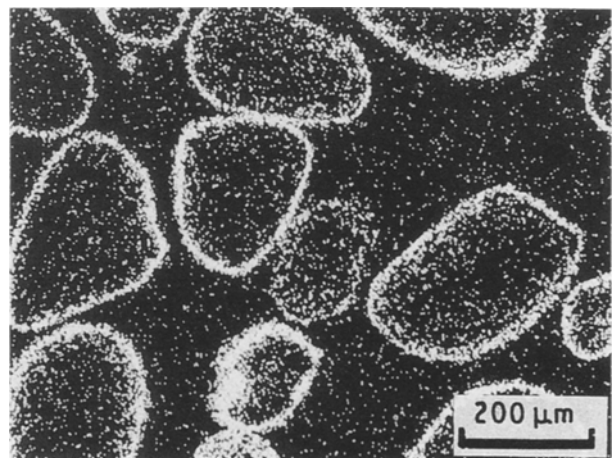


Figure 6 Dot map of Ti in composite agglomerates formed in a bed. $\alpha\text{-Al}_2\text{O}_3$ particles were fluidized for 1 h prior to reaction. Reaction period, 2 h; TiN mass fraction, 0.097.

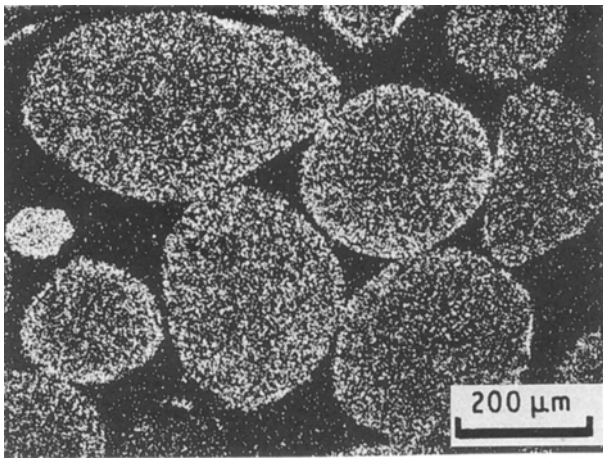


Figure 7 Dot map of Ti in composite agglomerates formed in a bed. Reaction was started soon after α - Al_2O_3 particles were fed into the bed. Reaction period, 2 h; TiN mass fraction, 0.17.

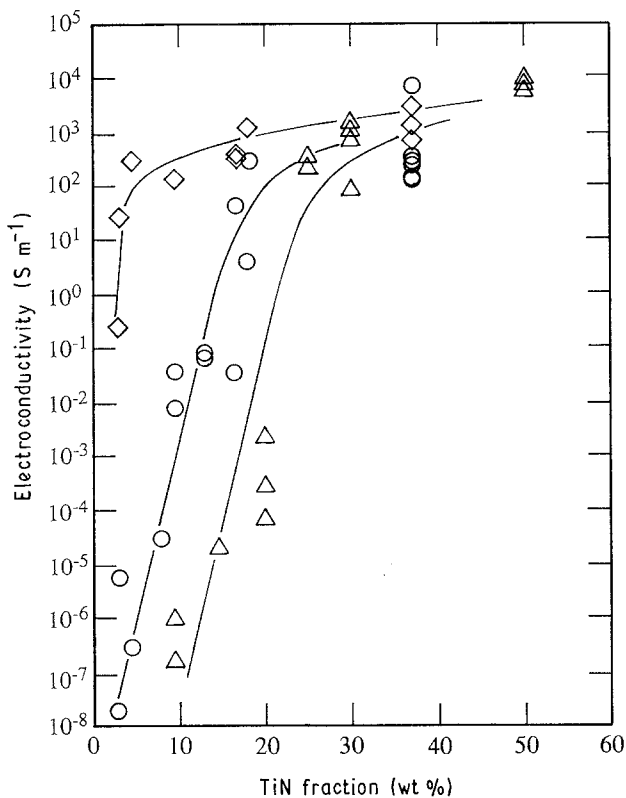


Figure 8 Relationship between mass fraction of TiN and electroconductivity of sintered body: (◇) method 1, (○) method 2, (△) method 3.

Before the start of the CVD reaction, the agglomerates were stabilized by being fluidized for 1 h with a nitrogen flow at the reaction temperature. This procedure probably densified the outer part of agglomerates, which became a diffusion barrier to CVD gases. When we started the reaction just after introducing raw α - Al_2O_3 powder into the reactor, on the other hand, we obtained agglomerates coated homogeneously with TiN. Fig. 7 shows a dot map of Ti in the sectioned area of the agglomerates.

Fig. 8 illustrates the relationship between the electroconductivity of a sintered body of α - Al_2O_3 -TiN composite particles and the TiN content. The relative

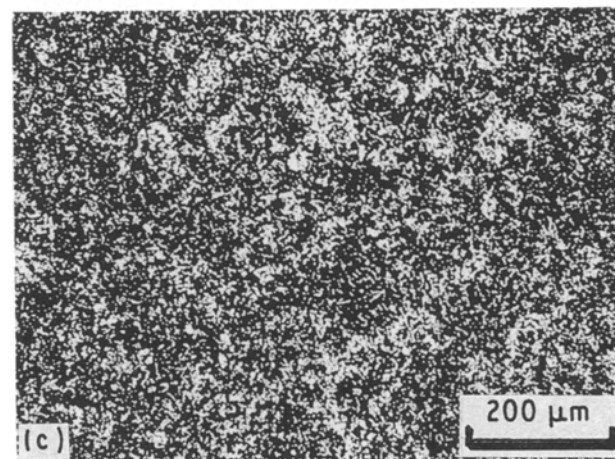
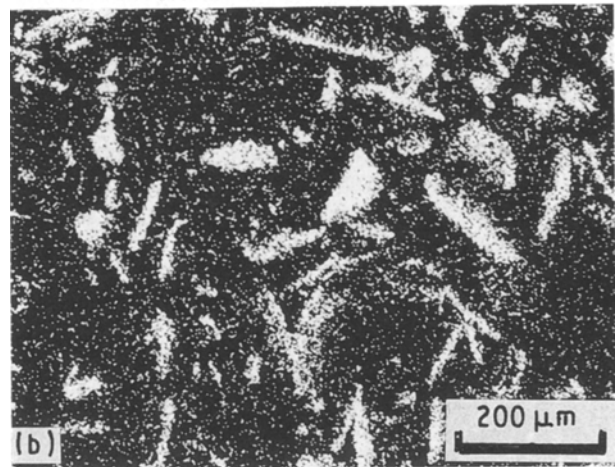
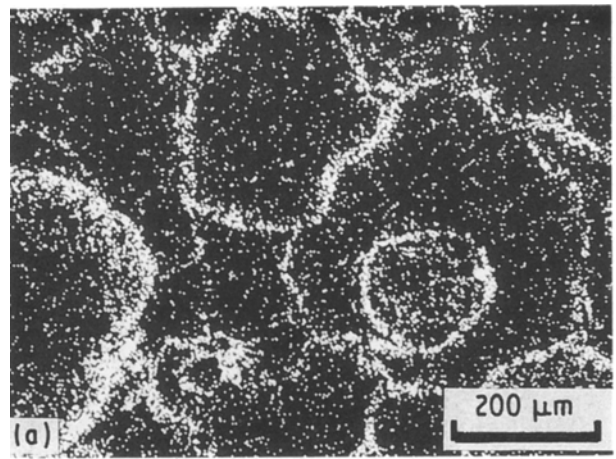


Figure 9 Distribution of Ti in sintered body. (a) Prepared with as-formed agglomerates shown in Fig. 6. Relative density, 0.89; TiN fraction, 0.097; conductivity, $1.5 \times 10^2 \text{ S m}^{-1}$. (b) Prepared by roughly crushing agglomerates of Fig. 6. Relative density, 0.90; TiN fraction, 0.097; conductivity, $4.1 \times 10^{-2} \text{ S m}^{-1}$. (c) Prepared by finely crushing agglomerates of Fig. 7. Relative density, 0.90; TiN fraction, 0.17; conductivity, 3.7 S m^{-1} .

density of the sintered bodies was 0.85–0.88 for the mixture prepared by method 1, 0.88–0.92 by method 2, and 0.92–0.95 by method 3. The conductivity of the sintered bodies prepared from composite agglomerates of method 1 was much higher than those by method 3.

Fig. 9a, b and c are respectively dot maps of Ti in sintered bodies prepared by method 1 with agglomer-

ates having the heterogeneous Ti distribution of Fig. 6, by method 2 with those having the distribution of Fig. 6 as well, and method 2 with those having the homogeneous Ti distribution of Fig. 7. The TiN mass fraction in the composite samples was 0.097 for Fig. 6 and 0.17 for Fig. 7. Fig. 9a shows a three dimensional network whose domain size is similar to that of the original agglomerates. The formation of this network is prevented in the case of method 2, but the electroconductivity of sintered bodies is still higher than that of sintered bodies prepared with the mechanically mixed particles. The electroconductivity of the structure shown in Fig. 9c is roughly equal to that of the structure shown in Fig. 9b. The above results suggest the formation of a micro-scale conductive network in a sintered body when CVD-hybridized agglomerates are used.

Highly electroconductive sintered bodies can be obtained if agglomerates are coated in the peripheral region with many TiN crystallites. However, these agglomerates are difficult to sinter. The optimum TiN content should be decided on the basis of the thermal resistance and mechanical strength of the sintered bodies.

4. Conclusion

α -Al₂O₃-TiN composite particles were synthesized by a CVD reaction in a fluidized-bed reactor. Sintered bodies made with the CVD-hybridized agglomerates had a conductivity much higher than did those made with mechanically mixed powders. The high electroconductivity was caused by three-dimensional TiN networks having dual scales of elemental grains and agglomerates. The above results suggest the effect-

iveness of fluidized-bed CVD processing in the preparation of composite ceramic particles.

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