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Preparation of nano-sized TiN coated α-Si_3N_4 particles

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α-Si_3N_4 particles coated with 10 and 25 vol% nano-sized TiN were prepared by coating the surface of the Si_3N_4 particles with TiO_2, followed by nitridation. Coating by TiO_2 was accomplished by dispersing α-Si_3N_4 powders (0.16 and 1.6 g l^{-1}) in a solution of $TiCl_4$, urea and aqueous HCl, and heating at 105 °C for 130 and 190 min. The success of the coating procedure was confirmed by TEM observation with electron diffraction and EDX analysis. Zeta potential measurements suggest that the TiO_2 coating on the surface of Si_3N_4 particles occurs at a pH between 3.7 and 4.3 by the attractive force of opposite charges. When the TiO_2 on the surface of the Si_3N_4 is nitrided with NH_3 gas at 1000 °C, it is completely changed to TiN of uniform particle size (20 nm).

Introduction

Si_3N_4 ceramics are promising high temperature structural materials[1,2] but are difficult to mechanically form into complex shapes because of their toughness and hardness. Si_3N_4–matrix ceramics containing highly electrically conductive TiN[2,3] can be machined to desired shapes by electric discharge machining. These Si_3N_4–matrix ceramics containing TiN were fabricated by sintering mechanically mixed Si_3N_4 or Si and TiN or TiO_2 powders,[4–7] but the mixtures contained an inhomogeneous distribution of TiN, necessitating an increased amount of TiN. It is known that coating dispersed particles with other materials constitutes a method for homogeneous mixing, leading to several reports dealing with the coating of Si_3N_4 by sintering oxide additives such as Al_2O_3, Y_2O_3, La_2O_3 or MgO,[8–10] to reduce the amount of oxide needed to promote full densification. If Si_3N_4 could be coated by fine TiO_2 particles in a controlled manner, the composite powders would be densified at TiN contact without sintering additives, since monolithic nano-sized TiN is sintered by field-assisted sintering.[11] Thus, Si_3N_4–matrix ceramics with continuous TiN networks, which exhibit high electrical conductivities, should be obtained from the tailored composite powders. However, the preparation of TiN coated Si_3N_4 particles has been reported only by Narula and coworkers[12] whose TiN coated Si_3N_4 composite particles were obtained by direct deposition of TiN through the pyrolysis of $(CH_3)_3SiNHTiCl_3$ with Si_3N_4 at 600 °C. According to this report, the yield of the precursor of $(CH_3)_3SiNHTiCl_3$ was low and the composite particles contained Si, Cl and C impurities. It would be interesting to fabricate TiN coated Si_3N_4 composite particles from TiO_2-coated Si_3N_4 by subsequent nitridation of the TiO_2, to obtain samples of good purity and controlled TiN particle size. Although alkoxides such as $Ti(OC_2H_5)_4$ and $Ti(OC_3H_7)_4$ are well known starting materials for the formation of TiO_2,[13–17] they are expensive and sensitive to atmospheric moisture. An additional disadvantage is the retention of carbon impurities in the TiO_2 product. The preparation of TiO_2 particles through the thermal hydrolysis of $TiCl_4$ by urea[18] has the advantage that $TiCl_4$ is cheap and easily handled in air.

In coating the matrix Si_3N_4 particles with a second phase (TiO_2) from solution, it is important to know the zeta potential[8,9,19–21] of both particles, since the success of the coating depends on the surface charge of the two particles. Changes in the zeta potential of the particles with pH should indicate the pH at which the coating by TiO_2 of Si_3N_4 should occur.

The purpose of this study was to prepare nano-sized TiN coated α-Si_3N_4 particles by depositing TiO_2 on the surface of Si_3N_4 particles by thermal hydrolysis of $TiCl_4$ with urea, followed by nitridation of the TiO_2 by NH_3 gas. The coating process is discussed on the basis of zeta potential measurements for Si_3N_4 and TiO_2 and TEM observation of the coated particles.

Experimental procedure

Preparation of TiO_2 coated α-Si_3N_4 composite particles

A flow chart of the experimental procedure for preparing TiN coated Si_3N_4 particles is shown in Fig. 1. The starting materials were Si_3N_4 ($\alpha > 95\%$) with a mean particle size of 0.5 μm (UBE Industries, Tokyo, Japan), $TiCl_4$ (KANTO Chemical, Co., Inc., Tokyo, Japan) and urea (KANTO Chemical, Co., Inc., Tokyo, Japan). The Si_3N_4 powder was added to a solution of HCl, $TiCl_4$ and urea (79.9 g), and ultrasonically dispersed for 15 min. The amount of $TiCl_4$ with respect to Si_3N_4 was adjusted to 10 and 25 vol% of the reduced volume of TiN in Si_3N_4. For example, the amount of $TiCl_4$ needed for 25 vol% TiN is 0.025 and 0.25 ml at Si_3N_4 contents of 0.16 and 1.6 g l^{-1}, respectively. The suspension was heated at 105 °C for 130 or 190 min in flowing N_2 gas. For comparison, $TiCl_4$ was slowly dropped into a dispersion of Si_3N_4 in aqueous NH_3 solution (28 vol.%) (KANTO Chemical, Co., Inc., Tokyo, Japan), omitting the urea and without heating. The TiO_2-coated Si_3N_4 particles from both methods were washed several times with distilled water and dried at 60 °C. The dried particles were observed by TEM and identified by XRD. The existence of TiO_2 on the Si_3N_4 surface was ascertained by electron diffraction and EDX analysis.

The zeta potentials of the Si_3N_4 powder and the TiO_2 precipitate prepared from $TiCl_4$ by thermal hydrolysis were measured using a Zeta plus apparatus (Brookhaven Instrument Corporation) in distilled water adjusted to a pH range of 3 to 7 with HCl solution. KCl solution (0.01 mol l^{-1}) was added to the solvent to keep the ion strength constant.

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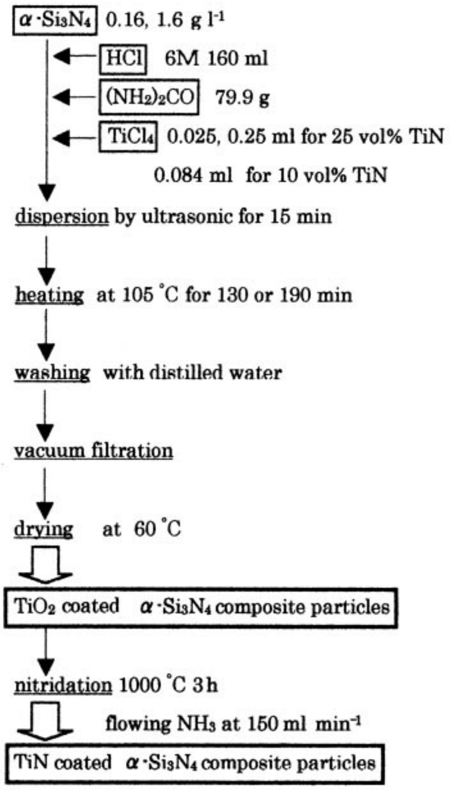

Fig. 1 Flow chart of the experimental procedure.

Nitridation

In the preliminary experiments, TiO_2 obtained by thermal hydrolysis of $TiCl_4$ for 190 min was nitrided in flowing NH_3 gas (150 ml min^{-1}) at 900 and 1000 °C for 180 min. Based on these results, the TiO_2 coated Si_3N_4 composite particles were nitrided at 1000 °C for 180 min. The TiN coated Si_3N_4 composite particles were identified by XRD and the lattice constant (a_0) of TiN was determined from the 311 diffraction peak. The size and shape of these particles were determined by TEM observation. The electrical resistivity of the compact composite powder containing 25 vol% TiN at a uniaxial pressure of 20 MPa was measured by the two-probe method.

Results and discussion

Preparation of TiO_2 coated α-Si_3N_4 composite particles

$TiCl_4$ in the HCl solution containing Si_3N_4 and urea was hydrolyzed by NH_3 generated by the decomposition of urea on heating at 105 °C, during which the pH value increased from 1 to 7. A time of about 130 min was needed for the formation of TiO_2 by this method. Fig. 2 shows TEM photographs of the TiO_2 coated Si_3N_4 particles obtained after thermal hydrolysis for 130 and 190 min of the $TiCl_4$ solution containing 0.16 and 1.6 g l^{-1} Si_3N_4, equivalent to 25 vol% of TiN. It is seen that the large particles are covered with nano-particles irrespective of the concentration of $TiCl_4$ and Si_3N_4 or the hydrolysis time. Rings in the electron diffraction patterns of the fine particles in Fig. 2(c) (see arrow) indicate the formation of TiO_2 (anatase). EDX analysis showed that the larger particles were composed of Si and N containing a trace of Ti with the fine particles containing Ti and O (Fig. 3). XRD analysis also indicates the appearance of broad TiO_2 peaks due to anatase. The nanometer sized particles are thus shown to be TiO_2 and the larger particles are α-Si_3N_4, indicating the successful preparation of composite particles of Si_3N_4 with a fine coating of TiO_2. Few TiO_2 particles are detected by TEM observation, suggesting that most of the TiO_2 formed from $TiCl_4$ is coating the Si_3N_4. With increasing hydrolysis time from 130 to 190 min, the size of the TiO_2 particles on the surface of Si_3N_4 grew from 3 to 7 nm. Agglomerated TiO_2 particles (see arrows) were observed in the samples obtained after 130 min, but tended to disappear after 190 min. TiO_2 coated Si_3N_4 particles were similarly prepared from the suspension containing 0.084 ml $TiCl_4$ and 1.6 g l^{-1} Si_3N_4 corresponding to 10 vol% TiN with a hydrolysis time of 190 min (Fig. 4). It is obvious that the amount of TiO_2 covering the Si_3N_4 particles is less than for the corresponding 25 vol% TiN sample (Fig. 2). This

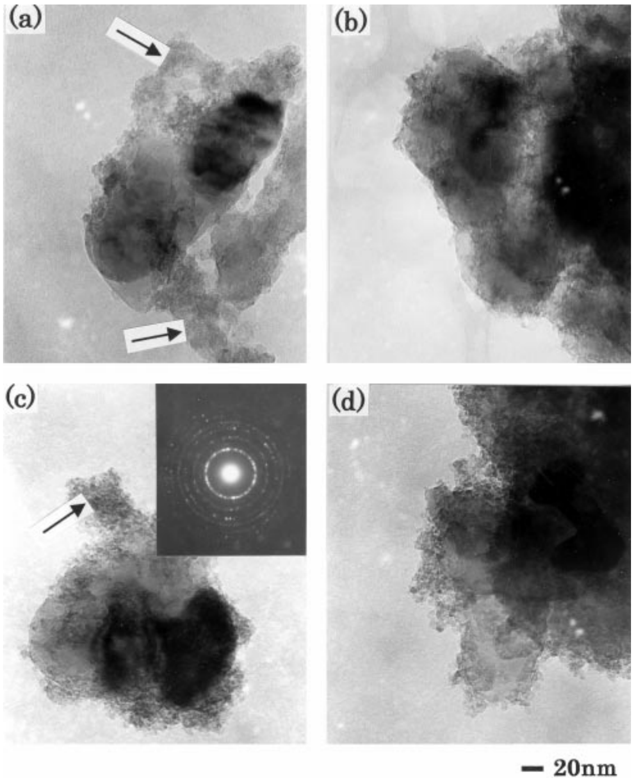

Fig. 2 TEM images of TiO_2 coated α-Si_3N_4 particles at 25 vol% TiN. Concentration/g l^{-1} and hydrolysis time/min: (a) 0.16 and 130, (b) 0.16 and 190, (c) 1.6 and 130, (d) 1.6 and 190.

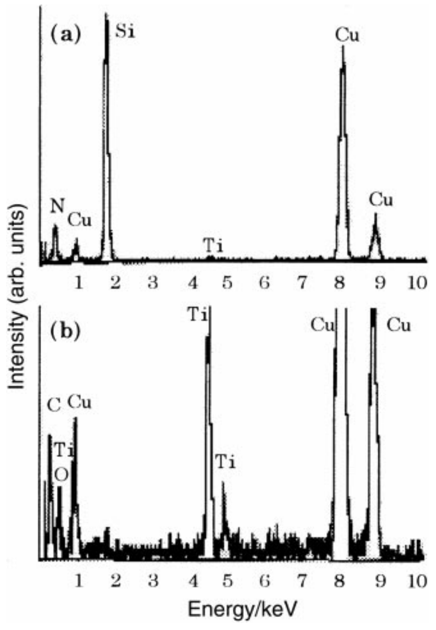

Fig. 3 EDX spectra for the particles shown in Fig. 2(c): (a) larger particle, (b) fine particle. Cu peaks are derived from the mesh and C from PVD carbon which provided the sample conductivity.

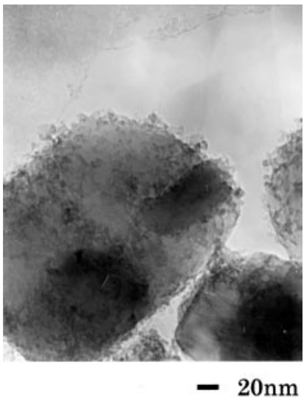

Fig. 4 TEM image of TiO_2 coated α-Si_3N_4 particles from 10 vol% TiN.

indicates that the coating of Si_3N_4 surfaces with the desired amount of TiO_2 is achieved simply by controlling the amount of $TiCl_4$.

Fig. 5 shows the change of the zeta potential with pH in a solution containing Si_3N_4 and TiO_2 particles. The signs of the zeta potential of Si_3N_4 and TiO_2 are opposite at pH values between 3.7 and 4.3. It is anticipated that the deposition of TiO_2 on the surface of the Si_3N_4 particles occurs in this pH region by attractive forces between the two types of particles with opposite charges. For comparison, coating of TiO_2 on Si_3N_4 was attempted by direct precipitation from $TiCl_4$ in aqueous NH_3 solution at pH 13.7 without urea, but scarcely any reaction was observed. It is concluded that the coating of TiO_2 on the surfaces of Si_3N_4 particles from $TiCl_4$ solution occurs at a pH between 3.7 and 4.3, which is achieved by increasing the pH as a result of the decomposition of the urea.

Nitridation

Preliminary experiments showed that TiO_2 particles produced by the thermal hydrolysis of $TiCl_4$ were not completely nitrided by NH_3 gas at 900 °C, but were fully converted to TiN at 1000 °C. When the TiO_2 coating on the surface of Si_3N_4 particles was nitrided at 1000 °C for 180 min, complete conversion to TiN was observed, as shown by XRD (Fig. 6). Compared with the lattice constant value ($a_0 = 0.424$ nm) of pure TiN, the a_0 value of TiN obtained atfter a hydrolysis time of 190 min ($a_0 = 0.422$ nm) was smaller, indicating the dissolution of a small amount of oxygen in the TiN. As shown by the TEM images (Fig. 7), the Si_3N_4 particles are coated with TiN particles of a uniform size (20 nm), independent of the hydrolysis time (130–190 min) or the TiN content (10 or 25 vol%). The electrical resistivity of the compact powder containing 25 vol% TiN was measured to be 0.1 Ω cm. Although the electrical resistivity was not as low as for the bulk TiN sample, the result suggested that electrical conductive paths provided by TiN coating should be formed through the powder compact.

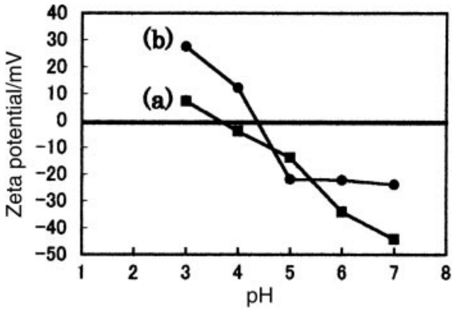

Fig. 5 Zeta potentials as a function of the pH: (a) α-Si_3N_4, (b) TiO_2.

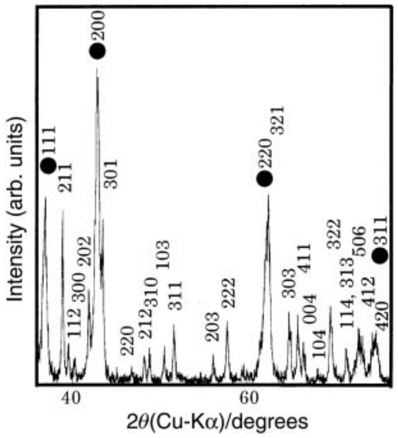

Fig. 6 XRD pattern of TiN coated α-Si_3N_4 particles: (●) TiN, (○) α-Si_3N_4.

Conclusion

Fine TiO_2 (anatase) particles were deposited on the surface of Si_3N_4 particles by thermal hydrolysis of $TiCl_4$ by the decomposition of urea in the suspension. The result was confirmed by TEM, EDX and XRD. The TiO_2 particles grew from 3 to 7 nm on increasing the hydrolysis time from 130 to 190 min. Zeta potential measurements suggested that TiO_2 coating on the surface of Si_3N_4 occurs at a pH between 3.7 and 4.3. When the TiO_2 coated Si_3N_4 composite particles were nitrided in NH_3 gas at 1000 °C, the coating was converted to TiN particles of uniform 20 nm size.

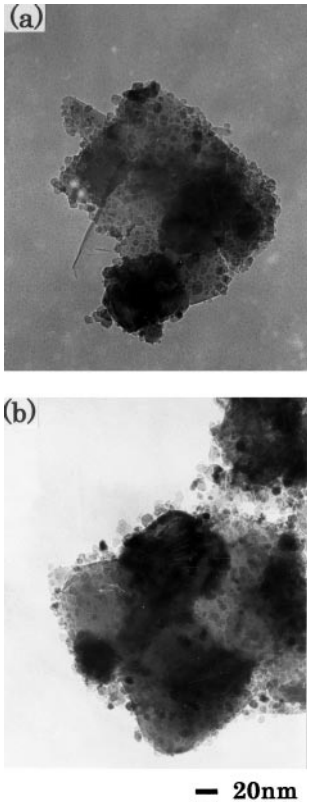

Fig. 7 TEM images of TiN coated α-Si_3N_4 particles: TiN content (vol%): (a) 10, (b) 25.

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