Effects of TiN Particle Size on Mechanical Properties of $\text{Si}_3\text{N}_4/\text{TiN}$ Particulate Composites

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$\text{Si}_3\text{N}_4/\text{TiN}$ 複合セラミックスの機械的性質に及ぼす TiN 粒子径の効果

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$\text{Si}_3\text{N}_4/10 \text{ vol}\% \text{TiN}$ particulate composites with six TiN particle size distributions (average size: 0.3–13.6 μm) were sintered at 1850°C for 4 h in 0.9 MPa N_2 atmosphere, and Young's modulus, fracture toughness and microstructure of the composites were examined. Although all the composites were densified up to >98% theoretical density, Young's modulus of the composites with larger TiN particles decreased due to the pre-existing microcracks. Fracture toughness of the composites showed a maximum value at the particle size of TiN of about 4 μm , which is smaller than the predicted critical size. It is suggested that the presence of the grain-boundary phases in the composite favors the formation of microcracks at smaller TiN particles.

Key-words: Si_3N_4 , TiN, Composite, Young's modulus, Fracture toughness, Microcrack

1. Introduction

Silicon nitride (Si_3N_4) is one of promising engineering ceramics for high-temperature applications because of their excellent properties such as high strength, oxidation resistance and thermal shock resistance. Recently, considerable attention has been denoted on further improvement of fracture toughness and high-temperature strength of Si_3N_4 ceramics by means of particle and/or whisker reinforcement. Among various types of composites, toughening effect available in particulate composites is not so high in comparison with that in other composites. However, particle toughening has a potential for fabricating complicated shape by easier processing.

The effect of SiC or TiC dispersion on the mechanical properties of Si_3N_4 ceramics have been studied,^{1)–4)} but particle size effect has not been well clarified. In this study, 10 vol% of TiN powders with six grades of particle size range was dispersed in Si_3N_4 matrix, and the effect of particle size on the mechanical properties of $\text{Si}_3\text{N}_4/\text{TiN}$ particulate composites were studied.

2. Experimental procedure

TiN powders (Nippon Shin-Kinzoku Co.) were dis-

persed in a mixture of water and methanol (1 : 1 in weight), and separated into six grades of particle size range by using elutriation technique. Their average particle sizes were 0.3, 1.0, 1.8, 3.7, 7.3 and 13.6 μm . In each range of particle sizes, the average size (d_{50}) was determined from the particle size distribution (in Fig. 1) measured with a particle size analyzer (Seishin Enterprise Co., SK Lazer Micron Sizer PRO-7000 s) except for the powders smaller than 1.5 μm . For such smaller particles, scanning electron microscopy (SEM) was used to estimate d_{50} .

High purity Si_3N_4 powder (Denki Kagaku Co., SNP21C3 grade; S. S. A. : 11.2 m^2/g , α -phase content : 92.2%, oxygen content : 1.57 wt%) was mixed with 5 wt% Y_2O_3 , 2 wt% Al_2O_3 (Hokko Chem. Co., Ltd.) and 2 wt% MgO (Iwatani Chem. Ind. Co.) as additives in a vibratory mill using methanol, and followed by drying. In order to prepare a homogeneous powder mixture, the Si_3N_4 powder with additives and 10 vol% of TiN powders were dispersed in water at pH $\approx$ 10 by means of ultrasonication. The mixed slurry was washed with acetone and filtered off on the funnel. Then the obtained powder cake was dispersed again in toluene, and residual water was removed by utilizing azeotropy between water and toluene. After drying in N_2 -5% H_2 atmosphere, the powders were cold-isostatically-pressed (CIP'ed) at 490 MPa and was sintered at 1850°C for 4 h in a 0.9 MPa N_2 atmosphere. In order to confirm the dispersion effect, the Si_3N_4 specimen

Fig. 1. Particle-size distributions of graded TiN powders. Average particle sizes are (a) 0.3, (b) 1.0, (c) 1.8, (d) 3.7, (e) 7.3 and (f) 13.6 μm .

without TiN particles was prepared using the same procedure.

The bulk density was measured by an Archimedes technique using distilled water. The phase identification was performed by X-ray diffraction (XRD). Young's modulus was measured by a pulse echo method. The fracture toughness (K_{IC}) was determined using an indentation fracture (IF) method with a load of 20 kg. The fracture surface of the composites was observed by using a SEM.

3. Results

According to the XRD analyses, all the sintered materials were mainly composed of β -Si₃N₄ and TiN. Trace of unknown peaks, which are possibly assigned to grain-boundary phases, was also observed. Figure 2 shows the change of relative density and Young's modulus of the composites with dispersed TiN particle size. Relative density of the composites

Fig. 2. Change of relative density (R.D.) and Young's modulus (E) of Si₃N₄/TiN particulate composites with average TiN particle size. Dashed line indicates the predicted value of E

Fig. 3. Change of average crack length (Av. c. l.) and fracture toughness (K_{IC}) of Si₃N₄/TiN particulate composites with average TiN particle size.

showed almost constant value higher than 98% theoretical density regardless of TiN particle size. Young's modulus of the composites with smaller particle sizes were higher than that of monolithic Si₃N₄. However, it drastically decreased at larger particle sizes, and showed lower value than that of specimen without TiN particles.

Influence of average TiN particle size on average crack length induced by diamond indenter and on fracture toughness are shown in Fig. 3. The crack length of the composites was diminished by TiN addition, in comparison with that of monolithic Si₃N₄. The crack length showed a minimum value at TiN particle size of about 4 μm. K_{IC} also varied with TiN particle size, and showed a maximum value at about 4 μm.

4. Discussion

It is well-known that Young's modulus of the composite depends on volume fraction and Young's modulus of each constituent phases. According to a rule of mixture, all the moduli in the present composites should be on the predicted line (dashed line in Fig. 2). However, Young's modulus for the composites containing larger TiN particles shifted toward lower values, and did not follow the rule of mixture. One of the reasons is possibly due to the pre-existing microcracks which were observed around larger TiN particles (Fig. 4). The microcracks are considered to be caused by highly localized stresses around the particles, set up by thermal expansion mismatch between matrix and particles.⁵⁾ Moreover, the formation of microcracks in such composites is affected by the dispersed particle size.⁵⁾ On the basis of an energy balance concept, the critical particle size (R_c) for the formation of microcracks was estimated from the equation proposed by Davidge and Green:⁶⁾

$$R_c > 8 \gamma_s / \{P^2 [(1 + \nu_m)/E_m + 2(1 - 2\nu_p)/E_p]\} \quad (1)$$

where

$$P = \frac{(\alpha_m - \alpha_p) \Delta T}{[(1 + \nu_m)/2E_m + (1 - 2\nu_p)/E_p]}$$

and γ_s is the value of fracture surface energy evaluated for the material without inclusion, ΔT is the cooling range, ν is Poisson's ratio and E is Young's modulus; the subscript m and p refer to the matrix and particle, respectively. The critical particle size in the Si₃N₄/TiN particulate composite was estimated to be 10–25 μm using Eq. 1. The material properties used for this calculation are $\gamma_s = 30\text{--}70 \text{ J/m}^2$,⁷⁾ $E_m = 320 \text{ GPa}$, $\nu_m = 0.26$ and $\alpha_m = 3 \times 10^{-6}/^\circ\text{C}$ for Si₃N₄ and $E_p = 400 \text{ GPa}$, $\nu_p = 0.22$ and $\alpha_p = 9.4 \times 10^{-6}/^\circ\text{C}$ for TiN.

As shown in Fig. 4, the microcracks were already formed around TiN particles as smaller size as about 4 μm. The discrepancy between the observed and calculated R_c values may be partly due to the estimation of γ_s , to which R_c is directly proportional. The γ_s values used for R_c calculation are those of sintered

Fig. 4. SEM photographs of the fracture surface of $\text{Si}_3\text{N}_4/\text{TiN}$ particulate composites with average TiN particle sizes of (a) $0.3\ \mu\text{m}$, (b) $3.7\ \mu\text{m}$ and (c) $13.6\ \mu\text{m}$.

Si_3N_4 body. However, it is considered that the microcracks are formed in the glassy and/or partially crystallized grain-boundary phase, which might have the lower γ_s than that of Si_3N_4 matrix. Therefore, it is suggested that the presence of the grain-boundary phases in the composite enable to form microcracks at smaller TiN particles.

Crack bowing, crack deflection, crack blunting and microcracking and so on as the mechanisms which account for toughening of particulate composites were reported.⁸⁾⁻¹⁰⁾ In the case of the composite with large difference in thermal expansion between the particle and matrix, the improvement mechanisms for toughening were reported to be due to the energy absorption caused by microcracking.¹¹⁾ In the present work, the fracture toughness of $\text{Si}_3\text{N}_4/\text{TiN}$ particulate composites was improved by the addition of TiN, whose thermal expansion is larger ($9.4 \times 10^{-6}/^\circ\text{C}$) than that of Si_3N_4 ($3 \times 10^{-6}/^\circ\text{C}$) and therefore its mechanism is considered to be due to the microcracking. Moreover, it was reported that the fracture toughness of particulate composite was significantly influenced by pre-existing microcracks when the inclusion size is almost equal to critical particle size.^{12),13)} In this work, the fracture toughness of the composites showed maximum value at about $4\ \mu\text{m}$ TiN particles, and the microcracks were observed around TiN particles as shown in Fig. 4. This result is similar to the results reported by Claussen et al.^{12),13)} On the other hand, in the case of larger TiN particles, the fracture toughness of the compo-

sites decreased. This can be accounted for by the high density of microcracks, which will make it easier to propagate the primary crack by the microcrack-microcrack and primary crack-microcrack coalescence mechanism.¹¹⁾

5. Conclusions

$\text{Si}_3\text{N}_4/10\ \text{vol}\%\text{TiN}$ particulate composites with various TiN particle sizes were fabricated in order to clarify the effects of the dispersed particle size on mechanical properties of the composites. The following results were confirmed.

(1) The fracture toughness of the composites was improved by addition of TiN particles. The addition of the particles with $4\ \mu\text{m}$ average gave a maximum toughness value.

(2) Young's modulus of the composites decreased at large TiN particles, because of the formation of pre-existing microcracks caused by the mismatch in thermal expansion between Si_3N_4 matrix and TiN particles.

(3) The discrepancy between the observed and calculated R_c values suggested that the presence of the grain-boundary phases in the composite enable to form microcracks at smaller TiN particles.

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