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Mechanical Properties of TiO_2-coated ZrO_2/Si_3N_4 Composite

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Abstract

TiO_2-coated ZrO_2/Si_3N_4 composite was fabricated by hot-press sintering. Room-temperature mechanical properties of the TiO_2-coated ZrO_2/Si_3N_4 composites were investigated as a function of the coating amount of TiO_2, as well as of the incorporated amount of TiO_2-coated 3Y-ZrO_2. The densification was promoted, and the Vicker's hardness of the composite was improved remarkably with the increase in TiO_2. The fracture toughness was enhanced nearly linearly with increasing the fraction of TiO_2-coated 3Y-ZrO_2. The toughening mechanism was analysed according to the evolution of microstructure. © *1998 Elsevier Science Limited. All rights reserved*

Keywords: mechanical properties, Si_3N_4, composite, coating, hot pressing.

1 Introduction

Si_3N_4-based ceramics are the more attractive and promising structural materials at high temperature applications. However, the intrinsic low fracture toughness has impeded their widespread applications. In general, the fracture toughness of hot-pressed Si_3N_4 ceramics is typically 3–5 MPa. m.[1,2] It has been reported that the fracture toughness can be improved by incorporation of a proper amount of ZrO_2 into Si_3N_4 matrix.[1–3] However, undesired ZrN and Zr-oxynitride phases might be generated during sintering.[4] To suppress the formation of these phases, TiO_2 is coated on 3Y-ZrO_2 before incorporation into Si_3N_4 matrix.[5] It has been demonstrated that the TiO_2 coating can take a suppressive effect on the reaction of Si_3N_4 and ZrO_2 to a large degree. In the present study, the room-temperature mechanical properties of the TiO_2-coated ZrO_2/Si_3N_4 composites will be investigated.

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2 Experimental

Starting materials were Si_3N_4 (Ube,E10), 3Y-ZrO_2 (Tosoh, stabilized by 3 mol% Y_2O_3), Titanium alkoxide (Wakou), and Y_2O_3 (Wakou, purity >99·99%). The 3Y-ZrO_2 was first coated with TiO_2 by using sol–gel method described in reference.[5] The as-received and the TiO_2-coated 3Y-ZrO_2 powders were blended with Si_3N_4 by two-step ball-milling, respectively. Y_2O_3 was chosen as sintering additive, the doped amount was based on the content of Si_3N_4 in the composites. After drying, the blended powders were hot-pressed at 1725°C for 1 h under 20 MPa in a flowing nitrogen atmosphere. The hot-pressed discs were ground, cut and polished for measuring the bending strength, the fracture toughness, and the microstructure observation. The bulk density were determined by the water immersion method. The three point bending strength test was conducted. The fracture toughness and Vicker's hardness was measured using the indentation method with a load of 10 kg. The microstructure and crack propagating path were examined by SEM. The grain boundary was observed by TEM.

3 Results and Discussion

3.1 Effect of TiO_2 coating on densifying behavior and mechanical properties of the ZrO_2/Si_3N_4 composite

The samples were composed of 80 wt% Si_3N_4 and 20 wt% 3Y-ZrO_2 coated with 5, 10, and 15 wt% TiO_2, respectively, together with 1 wt% Y_2O_3 as sintering additive. Figure 1 shows the variation of bulk density and bending strength of these composites

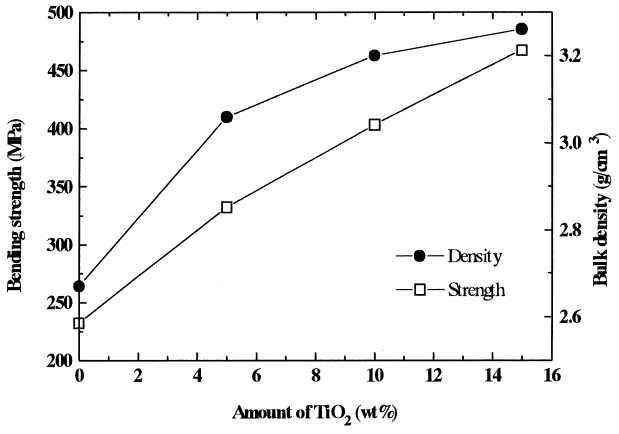

Fig. 1. Bulk density and bending strength of the composite doped with 1 wt% Y_2O_3 versus the coating amount of TiO_2.

with the coating amount of TiO_2. Obviously, with the rise in TiO_2 coated on 3Y-ZrO_2, the bulk density was enhanced. It has proved that the reaction between Si_3N_4 and TiO_2 occurring at low temperatures results in the formation of some amorphous SiO_2.[5,6] Therefore, with increasing the amount of TiO_2, more amorphous SiO_2 formed, causing relatively more transient liquid phase which is considered to be beneficial to the densification process. Consequently, the densifying process in the sample with more TiO_2 was prompted, and hence the bending strength increased as a result of the higher densification. However, all the samples with 1 wt% Y_2O_3 did not get fully densified.

When the samples were doped with 4 wt% Y_2O_3, and were hot-pressed at the same conditions, all the samples got nearly completely densified. The variation of bending strength, fracture toughness, and Vicker's hardness of these samples with the coating amount of TiO_2 is illustrated in Fig. 2 Apparently, compared to the monolithic Si_3N_4, the Vicker's hardness was improved, and the fracture toughness was slightly enhanced with increased TiO_2, but the bending strength of the sample with the 3Y-ZrO_2 coated with more TiO_2 decreased. SEM observation (Fig. 3) revealed that the elongated grains with higher aspect ratio about 3–10 were developed in the sample with the 3Y-ZrO_2 coated with 15 wt% TiO_2, on the other hand, the aspect ratio of elongated grains was only about 2–5 in the sample with the 3Y-ZrO_2 coated with 5 wt% TiO_2. This implies that a little more TiO_2 can promote the development of elongated grains with high aspect ratio, which, in general, is contributed to the improvement of the fracture toughness of Si_3N_4-based ceramics. From this point of view, therefore, the little higher fracture toughness of the sample containing the 3Y-ZrO_2 coated with 15 wt% TiO_2 is correspondent to the development of the high aspect ratio elongated grains.

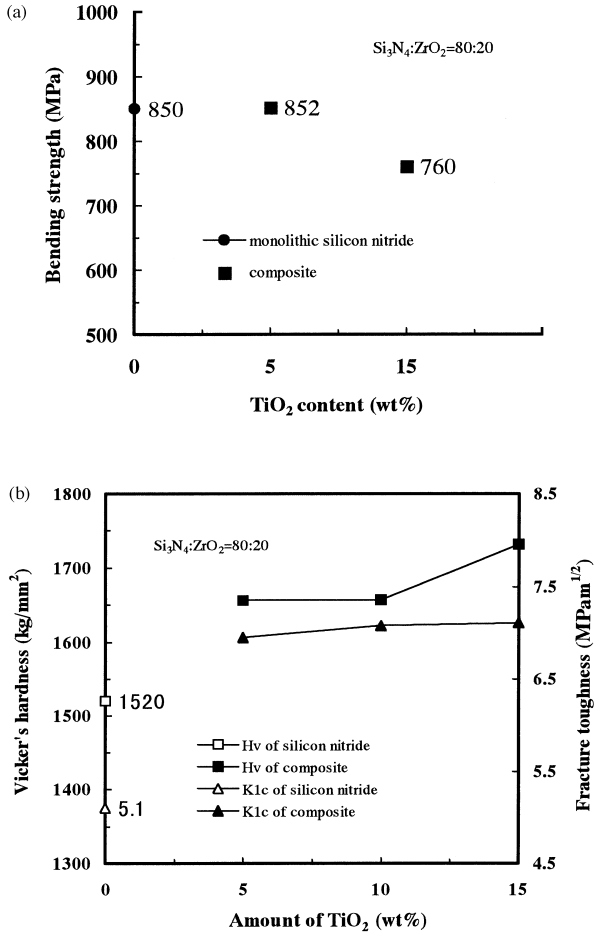

Fig. 2. Bending strength (a), Vicker's hardness, and fracture toughness (b) of the composite doped with 4 wt% Y_2O_3 versus the coating amount of TiO_2.

During sintering, TiO_2 reacted with Si_3N_4 to give the high hardness TiN[5] (1900 kg/mm^2); in addition, TEM observation on the sample with the 3Y-ZrO_2 coated with 15 wt% TiO_2 revealed that the thickness of the grain boundary was about 2–3 nm, and it seems that the lattice fringe existed between ZrO_2 and Si_3N_4, where the composition was Si, Zr, O, and N analysed by EDS (Fig. 4) Therefore, it is possible that all these factors might contribute to the high hardness of the TiO_2-coated ZrO_2/Si_3N_4 composite.

3.2 Effect of 3Y-ZrO_2 amount on room-temperature mechanical properties of the TiO_2-coated ZrO_2/Si_3N_4 composite

Figure 5 illustrates the bending strength and the fracture toughness of the composite as a function of the amount of 3Y-ZrO_2 coated by 10 wt% TiO_2, also together with 4 wt% Y_2O_3. The fracture toughness was enhanced linearly with the increase in the amount of 3Y-ZrO_2. On the other hand, a peak at 30 wt% 3Y-ZrO_2 exists for bending strength. With 30 wt% 3Y-ZrO_2 incorporation, the bending strength reached 840 MPa, nearly the same as that of the monolithic Si_3N_4.

SEM observation revealed that the incorporation of 3Y-ZrO_2 took an effect on the microstructure evolution of the TiO_2-coated ZrO_2/Si_3N_4 composite. Figure 6 shows the micrographs of molten NaOH-etched polished surfaces of the samples with 20 and 30 wt% the TiO_2-coated 3Y-ZrO_2, respectively. Obviously, some coarse elongated grains with diameter from 0·5 to 1·0 μm were developed in the sample with 30 wt% 3Y-ZrO_2, while there were few coarse grains developed in the samples with 10 and 20 wt% 3Y-ZrO_2. It has proved that the development of some of coarse grains in ceramic microstructure can improve the fracture energy.[7,8]. Therefore, the improvement of the fracture toughness of the composite with the increased the TiO_2-coated ZrO_2 is corresponding to its microstructure development.

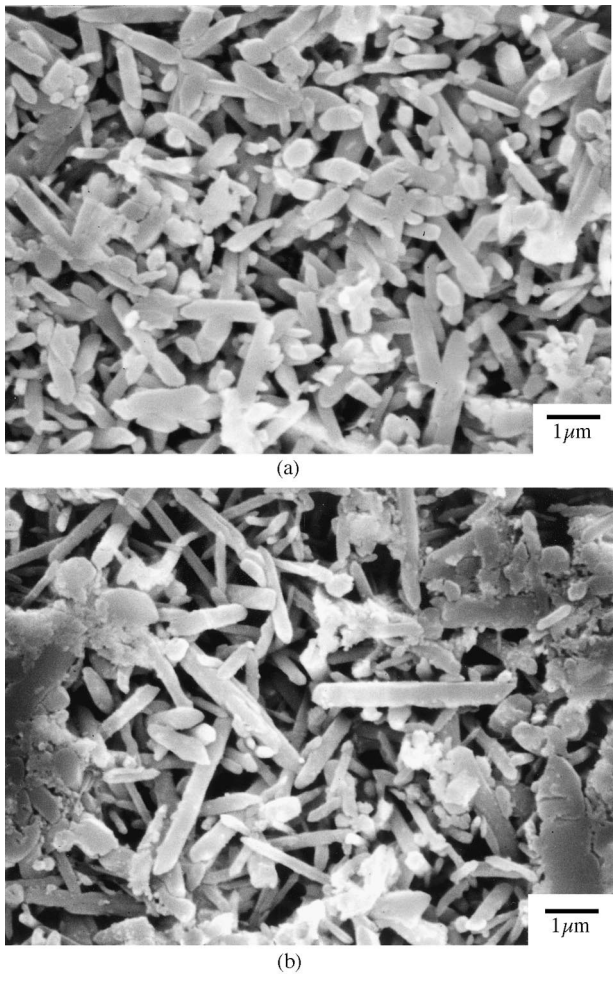

Fig. 3. Micrographs of the molten NaOH-etched polished surfaces of the composites with 5 (a) and 15 wt% (b) TiO_2 coating, respectively.

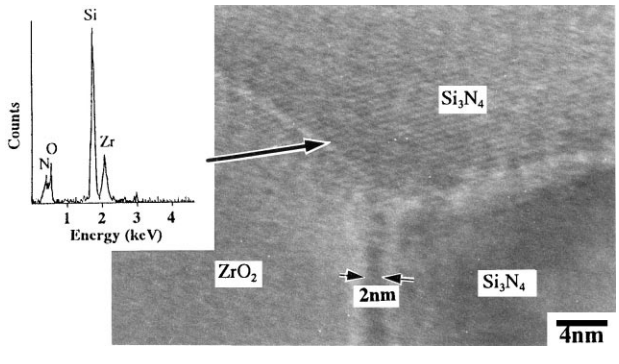

Fig. 4. TEM micrograph, showing the existence of lattice fringe between ZrO_2 and Si_3N_4, and some grain boundary thickness between them.

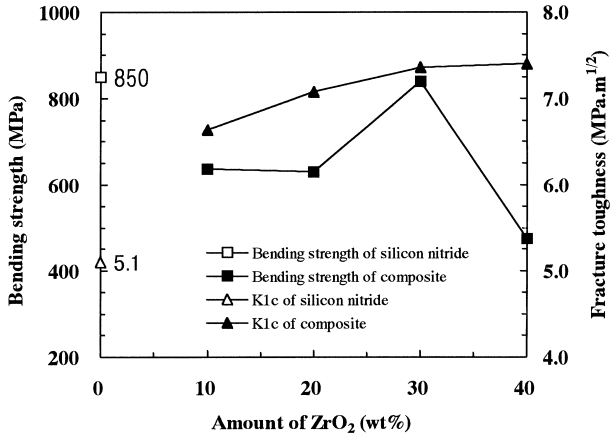

Fig. 5. Bending strength and fracture toughness of TiO_2-coated ZrO_2/Si_3N_4 versus the amount of 3Y-ZrO_2 coated by 10 wt% TiO_2.

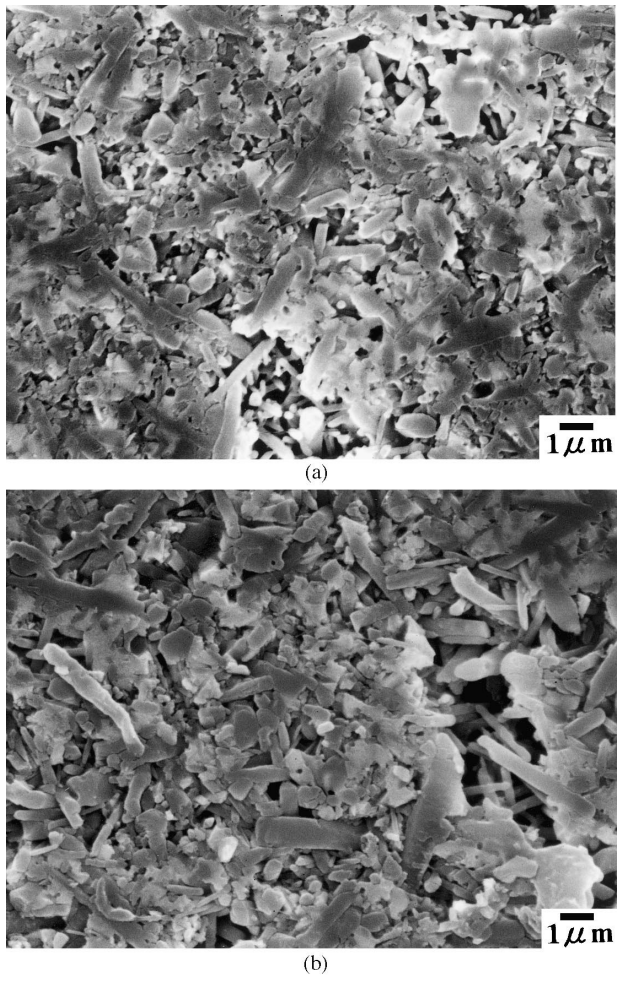

Fig. 6. Micrographs of the molten NaOH-etched polished surface of the composites with 20 (a) and 30 wt% (b) TiO_2-coated ZrO_2, respectively.

It has been reported that thermal expansion coefficient and elastic modulus, as well as the bonding strength between the matrix and grain boundary can affect the crack propagating path, and the needle-like grains can only reinforce the materials in the case of a predominantly intergranular fracture mode.[9,10] Because of the different thermal expansion coefficients of TiN($10\times10^{-6}K^{-1}$), ZrO_2 ($9{\cdot}4\times10^{-6}K^{-1}$), and Si_3N_4 ($3{\cdot}5\times10^{-6}K^{-1}$) in the temperature range from 20 to 1000°C, and of the different elastic moduli of these phases (TiN: 400 GPa, ZrO_2: 210 GPa, and Si_3N_4: 300 GPa), thermal stress must be generated in the composite. Tensile stresses existed inside the TiN and ZrO_2 grains, and tangential compressive stresses, as well as radial tensile stresses in the surrounding of Si_3N_4 grains. As a result, the intrinsic thermal residual stresses probably resulted in the formation of some microcracks, and made the relief of the constraints on ZrO_2 grains easy, thereby facilitating the transformation of t-ZrO_2 to m-ZrO_2. Both the microcracks and the transformation of t-ZrO_2 to m-ZrO_2 can increase the energy consumption during fracture process in the ZrO_2/Si_3N_4 composite, which has proved in the reference.[3] In addition, the observation on crack propagation (introduced by indentation method) by BEI demonstrated the crack deflected preferentially along the interfaces of these phases (Fig. 7) and the fracture of the composite was predominantly in intergranular mode (Fig. 8) Moreover, crack bridging and pull-out of the elongated grains which provided another energy dissipation mechanisms were also observed, especially in the sample with 30 wt% ZrO_2 (arrow-marked in Figs 7 and 8). Therefore, all the factors mentioned above improved the fracture energy and then resulted in the increase in the bending strength and fracture toughness. The decrease of the bending strength of the sample with 40 wt% the TiO_2-coated 3Y-ZrO_2 might be related to much more microcracks in its microstructure.

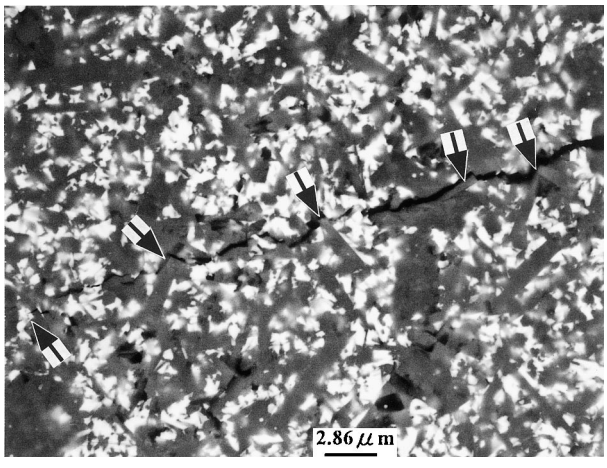

Fig. 7. Crack propagation in the composite with 30 wt% TiO_2-coated 3Y-ZrO_2.

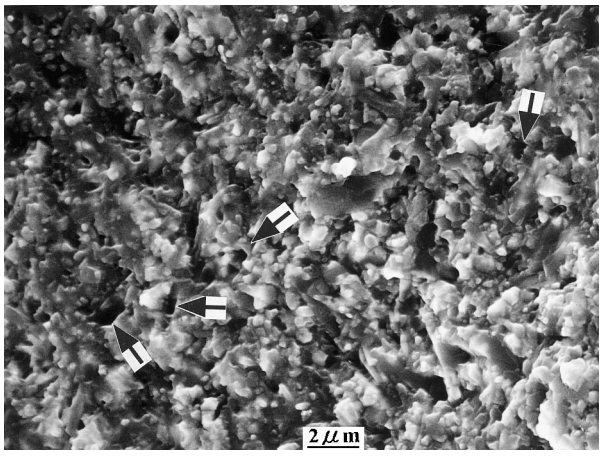

Fig. 8. Fracture surface of the composite with 30 wt% TiO_2-coated 3Y-ZrO_2 coated by 10 wt% TiO_2.

4 Summary

Room-temperature mechanical properties of the TiO_2-coated ZrO_2/Si_3N_4 composites were investigated as a function of the coating amount of TiO_2, as well as of the incorporated amount of the TiO_2-coated 3Y-ZrO_2. The densification of ZrO_2/Si_3N_4 composite was promoted, and the hardness of the composite was enhanced remarkably with the increase in the coating amount of TiO_2. In addition, the fracture toughness of the composite was improved linearly with increasing the fraction of the TiO_2-coated 3Y-ZrO_2. The fracture of the composite was predominantly in the intergranular mode. Crack deflection, crack bridging, and grain pull-out might be considered to contributed to the improvement of fracture toughness.

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