

Phase Composition of TiO₂-Coated ZrO₂/Si₃N₄ Composite

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(Received 20 May 1998; accepted 14 August 1998)

Abstract

The effect of TiO₂ coating on the phase composition of ZrO₂/Si₃N₄ composites was investigated both with pressureless-sintered samples and with hot-pressed ones. The formation of ZrN could be suppressed by increasing in the amount of TiO₂ coated on 3Y-ZrO₂. However, the existence of TiO₂ did little to accelerate the transformation of α- to β-Si₃N₄. When combined with small addition of Y₂O₃, the formation of ZrN could be further suppressed and the α to β-Si₃N₄ transformation could also be improved. The compositional variation of TiN grains with a rise in temperature was analyzed by using TEM and EDS. There was some solubility of zirconium ion into the TiN lattice. It increased with sintering temperature and caused the XRD peaks of TiN towards lower angles. © 1999 Elsevier Science Limited. All rights reserved

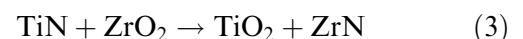
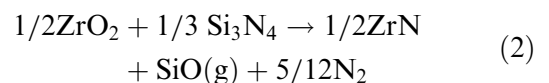
Keywords: TiO₂, ZrO₂, Si₃N₄, composites, coating.

1 Introduction

To improve the densification and mechanical properties of Si₃N₄-based ceramics, the addition of ZrO₂ stabilized by suitable oxides, such as Y₂O₃, CaO, or MgO into the Si₃N₄ matrix has proved to be one of the more effective methods.^{1–5} However, the reaction between Si₃N₄ and ZrO₂ which occurs above 1600°C according to thermodynamic analysis⁶ might result during the sintering process in the formation of zirconium nitride and/or zirconium oxynitride, these phases are easily oxidized at the intermediate temperatures (500–800°C) with a large molar volume increase which can generate cracks

and subsequently degrade the mechanical properties. To suppress the formation of ZrN and/or Zr-oxynitride, a number of approaches have been reported in the literature,^{4,5,7,8} such as lowering the densification temperature by adding sintering aids combined with hot-pressing or HIP sintering. It has also been demonstrated⁷ that more than 4.1 mol% Y₂O₃ in ZrO₂ can reduce nitrogen intake in the ZrO₂ lattice and suppress the formation of ZrN and/or Zr-oxynitride to some degree. This implied that more oxygen vacancies can inhibit the nitrogen absorption in the ZrO₂ lattice.

It has been reported⁹ that different reaction mechanisms occur in the systems Zr–Si–O–N and Ti–Si–O–N. The reaction between TiO₂ and Si₃N₄ can occur at temperatures as low as 1000°C according to reaction (1), where SiO₂ is present in the amorphous state; even at 1400°C, however, no reactions occur in the system Zr–Si–O–N. At much higher temperature, the reaction between ZrO₂ and Si₃N₄ can happen by reaction (2).



On the other hand, TiN is not oxidized by ZrO₂ in the Ellingham diagram calculated by Koji Watari *et al.*,¹⁰ i.e. the Gibbs free energy for reaction (3) is positive. Therefore, preparing a TiO₂ coating on ZrO₂ before incorporation into Si₃N₄ can prevent physical contact between ZrO₂ and Si₃N₄; the in-situ formed TiN and the amorphous SiO₂ produced on the surface of ZrO₂ by reaction (1) at low temperatures during sintering might then serve as a diffusion barrier to retard the reaction between ZrO₂ and Si₃N₄.

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Therefore, the objective of the present work is to investigate how a TiO_2 coating on ZrO_2 affects the phase composition of $\text{ZrO}_2/\text{Si}_3\text{N}_4$ composites prepared by pressureless and hot-press sintering.

2 Experimental Procedure

Starting materials were $\alpha\text{-Si}_3\text{N}_4$ (Ube Industries, Japan, grade E10), 3Y- ZrO_2 (Tosoh, Japan, stabilized by 3.0 mol% Y_2O_3), Ti-tetraisopropoxide (Wakou Chemical Industry, Japan) and Y_2O_3 (Wakou Chemical Industry, Japan, purity > 99.99%). The 3Y- ZrO_2 powder was first dispersed into iso-propanal containing the desired amount of Ti-tetraisopropoxide by using ultrasonic stirrer for 10 min; then water was added up to a molar ratio of water to Ti-tetraisopropoxide of 20:1. After drying, the 3Y- ZrO_2 powder coated by titanium hydroxide was calcined in air at 550°C for 2 h to produce TiO_2 -coated 3Y- ZrO_2 powder. The coating amount of TiO_2 on 3Y- ZrO_2 was 5, 10, and 15 wt%, respectively. The as-received and the coated 3Y- ZrO_2 powders were then blended with Si_3N_4 by two-step ball-milling. Y_2O_3 was chosen as sintering additive. The blended powders were either die-pressed and pressureless-sintered in a flowing nitrogen atmosphere at the desired temperature for 2 h or hot-pressed under 20 MPa at the desired temperature for 1 h. The phase compositions were analyzed by XRD, and microstructures were observed by TEM-EDS.

3 Results and Discussion

3.1 Effect of TiO_2 coating on the phase composition of pressureless-sintered samples

Figure 1 shows the XRD profiles of samples composed of 80 wt% Si_3N_4 and 20 wt% 3Y- ZrO_2 coated by 0, 5 and 15 wt% TiO_2 , respectively, and

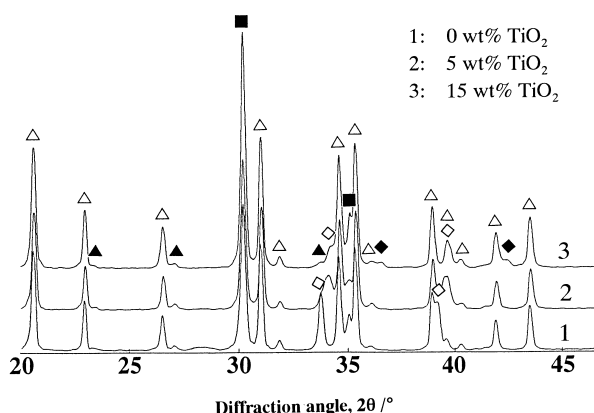


Fig. 1. XRD profiles of the samples coated by different amounts of TiO_2 and pressurelessly sintered at 1600°C. (Δ : $\alpha\text{-Si}_3\text{N}_4$ \blacktriangle : $\beta\text{-Si}_3\text{N}_4$ \blacksquare : t- ZrO_2 \blacklozenge : TiN, \diamond : ZrN).

pressureless-sintered at 1600°C. It can be noticed that the intensity of ZrN decreased with increasing TiO_2 , and that TiN was detected in the sample with 15 wt% TiO_2 . According to XRD analysis, TiN could form by the reaction of TiO_2 and Si_3N_4 at 1250°C, a temperature at which no liquid occurs in the system $\text{TiO}_2\text{-SiO}_2$. As a result, the migration of TiN from the surface of the ZrO_2 grains remains difficult (as shown in Fig. 5). This implies that the in-situ formed TiN and SiO_2 can prevent direct contact between ZrO_2 and Si_3N_4 . If the amount of TiO_2 coated on ZrO_2 is very small, the amounts of TiN and amorphous SiO_2 are insufficient to inhibit the reaction between ZrO_2 and Si_3N_4 . Additionally, the shift of the 2θ angles of ZrN towards higher values from XRD (Fig. 1) indicates that some TiN was possibly consumed by entering the ZrN lattice to form a Zr-rich solid solution. Consequently, in the sample with little TiO_2 coating there was still some ZrN formed, and no TiN detected by X-ray diffraction. With an increase in the amount of TiO_2 , more TiN and amorphous SiO_2 formed, thereby serving as a diffusion barrier for the reaction between ZrO_2 and Si_3N_4 . As a result, the TiN peak was strong and the formation of ZrN was suppressed. Figure 2 shows the relative intensity of t- ZrO_2 , ZrN, and TiN in the above samples.

From Fig. 1, it seems that the effect of TiO_2 on the transformation of α to $\beta\text{-Si}_3\text{N}_4$ is not obvious according to the XRD data. Therefore, to improve the transformation of α - to $\beta\text{-Si}_3\text{N}_4$ and the densifying behaviour, and to further inhibit the reaction between ZrO_2 and Si_3N_4 , a small amount of Y_2O_3 , which was 1, 2, and 4 wt% of the Si_3N_4 content in the composites, respectively, was added to the above samples. It was found that ZrN disappeared completely and the 2θ value of ZrO_2 moved slightly towards lower angles with increased Y_2O_3 (as illustrated in Fig. 3), implying that more yttrium dissolved into the ZrO_2 lattice, causing more oxygen

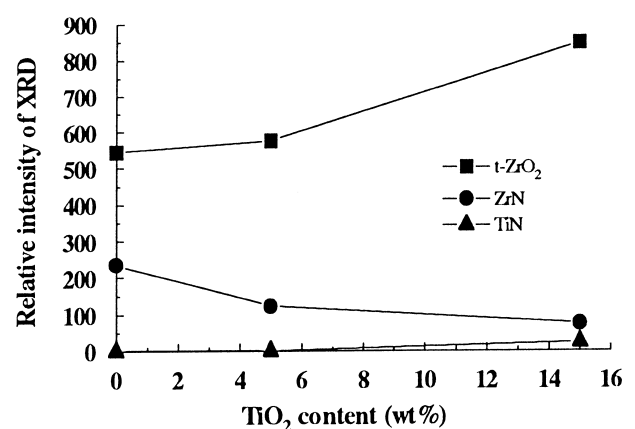


Fig. 2. Relative intensity of XRD peaks of t- ZrO_2 , ZrN and TiN versus TiO_2 coating on 3Y- ZrO_2 .

vacancies and then suppressing nitrogen intake in the ZrO₂ lattice (it was rather difficult by using EDS in the present experiment to discriminate between Y₂O₃ and ZrO₂ because of the small amount of Y₂O₃ in ZrO₂). Moreover, β -Si₃N₄ became the main phase with increase in Y₂O₃ from 0 to 4 wt%.

The effect of the TiO₂ coating on suppressing the formation of ZrN was also observed in the samples doped by 2 wt% Y₂O₃, as shown in Table 1. This

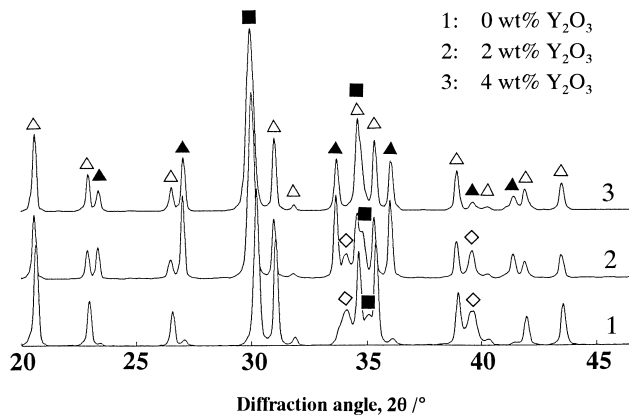


Fig. 3. XRD profiles of the 5 wt% TiO₂-coated 3Y-ZrO₂/Si₃N₄ composite doped with different amounts of Y₂O₃ and pressurelessly sintered at 1600°C (Δ : α -Si₃N₄ \blacktriangle : β -Si₃N₄ \blacksquare : t/c-ZrO₂ \blacklozenge : TiN, \diamond : ZrN).

Table 1. Effect of TiO₂ content on the formation of ZrN in the sample with 2Wt% Y₂O₃

TiO ₂ content (wt%)	5	10
Relative intensity of ZrN (%)	9.6	5.1

indicates that the combination of Y₂O₃ with the TiO₂ coating enhanced the suppressive effect on the formation of ZrN and still improved the transformation of α - to β -Si₃N₄.

3.2 Phase composition in the hot-pressed samples

To achieve a densified composite and to evaluate the effect of TiO₂ coating on the mechanical properties, samples were hot-pressed at 1750°C for 1 h under 20 MPa. However, TiN was not detected by X-ray diffraction even in the sample with 15 wt% TiO₂ coating on 3Y-ZrO₂. As mentioned above,

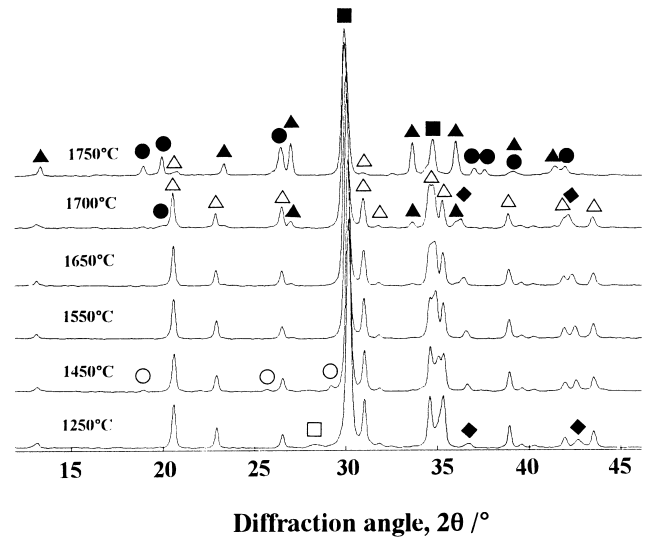


Fig. 4. XRD profiles of 15 wt% TiO₂-coated 3Y-ZrO₂/Si₃N₄ composite (ZrO₂:Si₃N₄ = 40:60) doped with 4 wt% Y₂O₃ and hot-pressed at different temperatures. (\bullet : Si₂N₂O, \circ : Y₂Si₂O₇, Δ : α -Si₃N₄, \blacktriangle : β -Si₃N₄, \blacksquare : t/c-ZrO₂ or Y_{0.15}Zr_{0.85}O_{1.93}, \blacklozenge : TiN, \square : ZrO₂).

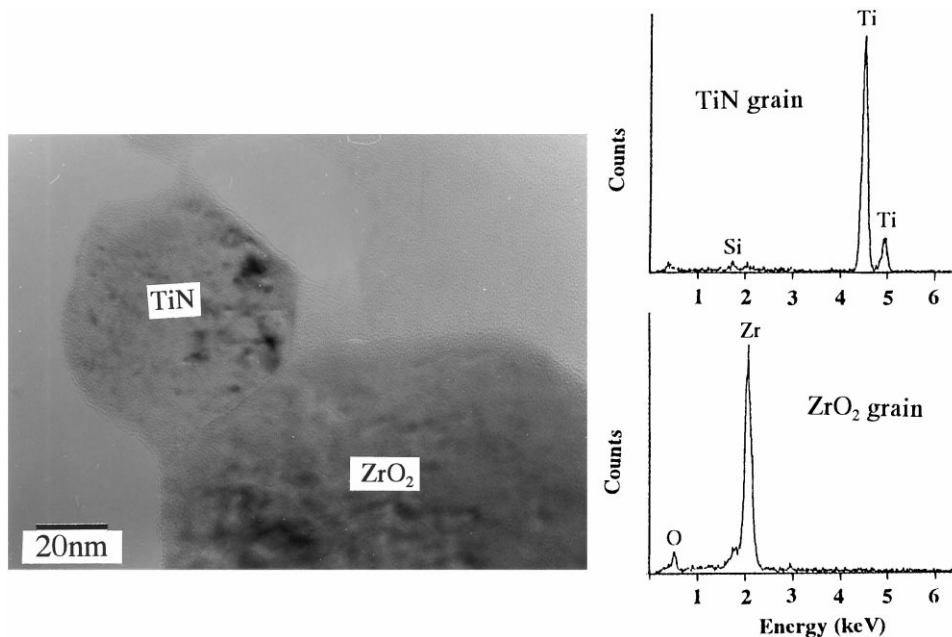


Fig. 5. TEM image of TiN and ZrO₂ grains, and EDS analysis of TiN and ZrO₂ grains hot-pressed at 1450°C.

TiN can be compatible with ZrO_2 , i.e. ZrO_2 does not oxidize TiN. Therefore, in order to clarify the absence of TiN at higher temperature, a study was made on 15 wt% TiO_2 -coated ZrO_2 /

Si_3N_4 composite, together with 4 wt% Y_2O_3 additive. The sample was hot-pressed at different temperatures, and subsequently characterized by X-ray diffraction and observed by TEM with EDS.

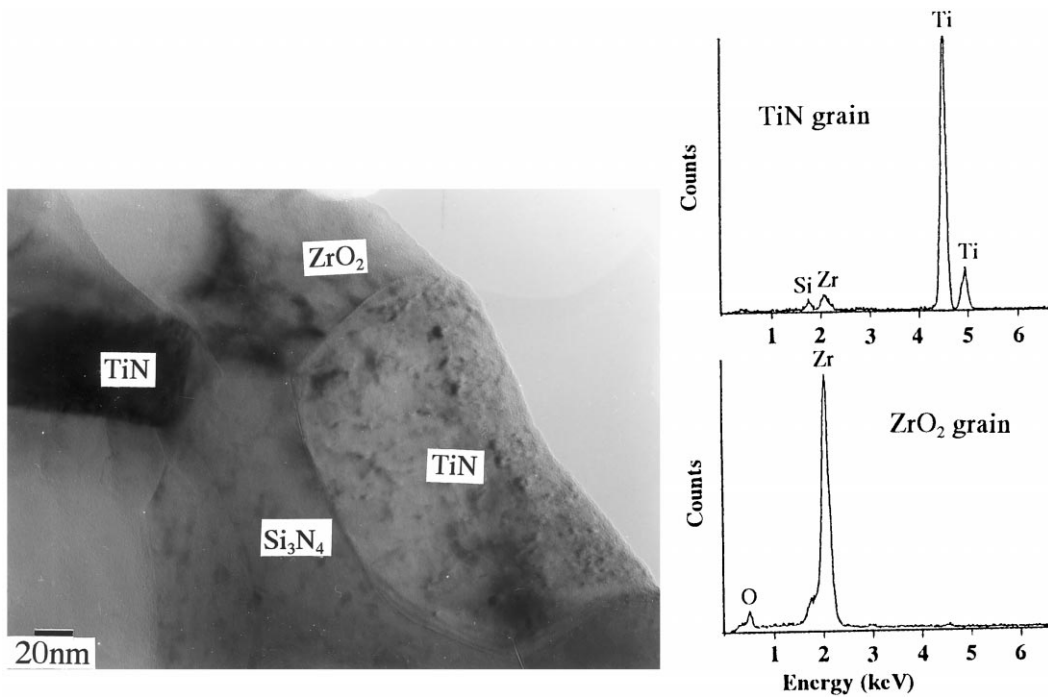


Fig. 6. TEM microstructure of the composite hot-pressed at 1650°C, and EDS analysis of TiN and ZrO_2 grains, showing some zirconium was dissolved into TiN lattice.

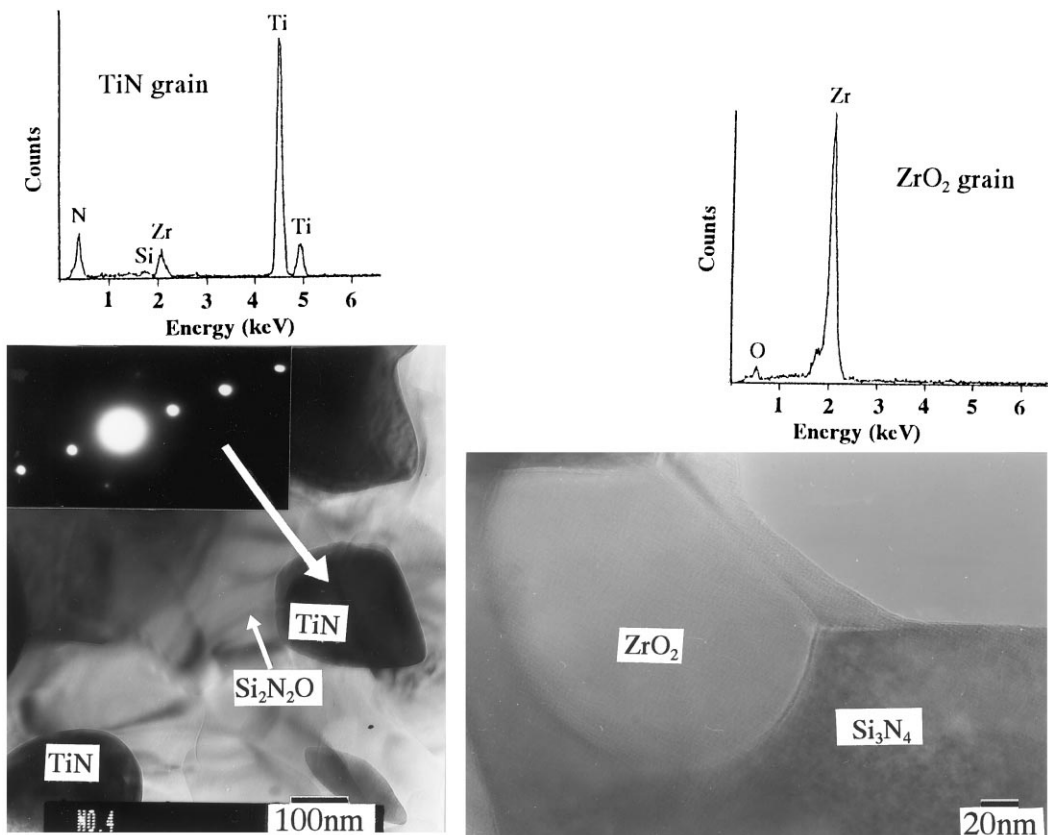


Fig. 7. TEM micrograph of the composite hot-pressed at 1750°C, and EDS analysis of TiN and ZrO_2 grains, showing much more zirconium was dissolved into TiN lattice, two times higher than that hot-pressed at 1650°C.

Figure 4 illustrates the X-ray profiles of these samples. It can be seen that TiN was formed even at 1250°C, where no eutectic liquid exists in the system TiO₂-SiO₂. As a result, it might be inferred that TiN was possibly formed through solid phase reaction other than via the solution-precipitation process reported in some references.¹¹ At 1450°C, γ -Y₂Si₂O₇, formed, suggesting that some SiO₂, formed by the reaction of the TiO₂ coating with Si₃N₄, reacted with Y₂O₃ to give γ -Y₂Si₂O₇. EDS analysis of the TiN grains by TEM (probe-size: 15 nm) revealed that a little Si⁴⁺, arising from the amorphous SiO₂, was taken into the TiN grains located on the surface of the ZrO₂, as demonstrated in Fig. 5. At 1550°C, γ -Y₂Si₂O₇ disappeared. At 1650°C, the peak of β -Si₃N₄ became strong, and the peaks of TiN shifted towards low angles, possibly implying that some Ti³⁺, was replaced by zirconium ion in the TiN lattice. EDS analysis of TiN grains proved that the concentration of zirconium dissolved into the TiN grains was about 4% (calculated from the energy intensity of titanium and zirconium), as shown in Fig. 6. Additionally, TEM observation revealed that some fine-grained Si₂N₂O existed around the TiN grains.

When the composite was hot-pressed at 1700°C, a small amount of Si₂N₂O was detected by XRD and the peaks of β -Si₃N₄ became much stronger. However, there still remained a small amount of α -Si₃N₄. The sample hot-pressed at 1750°C showed that most α -Si₃N₄ was transformed into β -Si₃N₄; and no ZrN, or Zr-oxynitride was detected. TEM observation demonstrated that TiN grains neighboring with Si₂N₂O grains still existed in the microstructure of the composite, (Fig. 7), and EDS analysis revealed that the TiN grains absorbed as much as ca. 8% of zirconium in their lattice. No nitrogen was detected in ZrO₂ grains (Fig. 7), implying there might be no reaction between ZrO₂ and Si₃N₄.

4 Summary

The formation of ZrN could be suppressed in Si₃N₄/ZrO₂ composite by TiO₂ coated on 3Y-ZrO₂. The combination of the TiO₂ coating with Y₂O₃ addition could suppress the formation of ZrN completely and still enhance the transformation of α into β -Si₃N₄. There was some solubility of zirconium ion in the lattice of TiN, and it increased with sintering temperature resulting in the XRD peaks of TiN towards lower angles.

Acknowledgements

The authors would like to give their appreciation to Mr. Hayasi, Mr. Kubotsu, and Mrs. Fujiwara who provided help with observing the microstructures and analyzing the compositions by using TEM.

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