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Effects of ZrO_2 and Y_2O_3 dissolved in zyttrite on the densification and the α/β phase transformation of Si_3N_4 in Si_3N_4–ZrO_2 composite

JAE RYONG KIM, CHONG HEE KIM
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

In Si_3N_4–ZrO_2 composite, the effects of zirconia and Y_2O_3 dissolved in zyttrite on the densification and the α/β phase transformation of Si_3N_4 were studied using hot-pressing of Si_3N_4 with the addition of pure, 3, 6, and 8 mol% Y_2O_3-doped zirconia. Reaction couples between Si_3N_4 and ZrO_2 of zyttrite were made to observe the reaction phenomena. The addition of pure zirconia was not effective to obtain full density of the Si_3N_4–ZrO_2 composite. However, Y_2O_3 diffused from the added zyttrite promoted densification; the density of Si_3N_4 with 5 vol% pure ZrO_2 composite was 71% theoretical, and nearly full density (> 97%) could be obtained in Si_3N_4 with 5 vol% 6, 8 mol% Y_2O_3-doped ZrO_2 composite. On the basis of observations of the Si_3N_4-pure ZrO_2 reaction couple, the reaction between Si_3N_4 and ZrO_2 resulted in the formation of Si_2N_2O phase, and the α/β phase transformation of Si_3N_4 occurred via this Si_2N_2O phase. From the XRD analysis of the reaction layer between Si_3N_4 and zyttrite, it is suggested that the reaction products, $Y_2Si_2O_7$ and $Y_2Si_3N_4O_3$ phases, play an important role in the densification of Si_3N_4–zyttrite composite.

1. Introduction

Silicon nitride is a well-known candidate material for heat engine and cutting tools, because of its good thermal-shock resistance, high-temperature strength and oxidation resistance. Generally, a dense silicon nitride body is fabricated by pressureless sintering, hot-pressing or hot isostatic pressing processes with the addition of sintering aids, such as MgO, Y_2O_3, CeO_2, etc. Since 1975, a few workers have studied hot-pressed Si_3N_4 with the addition of mono-zirconia or zyttrite (yttria-stabilized zirconia) [1–9]. These Si_3N_4–ZrO_2 composites were shown to be superior to hot-pressed Si_3N_4 with MgO with regard to room- and high-temperature strength, oxidation resistance and capability as cutting tools [6–8]. Lange [4] reported that toughness could be increased by compressive surface stress resulting from the oxidation of Si_3N_4–ZrO_2 composite.

Previously, workers were primarily concerned about the effects of added zirconia on the beneficial properties of Si_3N_4 ceramics, thus little is known about the details of the effects of zirconia on the densification and the α/β phase transformation of Si_3N_4 [4–10]. Moreover, the behaviour of Y_2O_3 dissolved in zyttrite has been almost neglected in Si_3N_4–zyttrite composite.

In the present work, the effects of ZrO_2 and Y_2O_3 dissolved in zyttrite on the densification and the α/β phase transformation of Si_3N_4 were studied using pure 3, 6, and 8 mol % Y_2O_3-doped zirconia powder without any other sintering aids. In order to observe the reaction phenomena between Si_3N_4 and ZrO_2 (pure or zyttrite), reaction couples were made. Specimens for this study were made by hot-pressing.

2. Experimental procedure

Commercially available Si_3N_4 powder (LC-12, H. C. Starck, Berlin, West Germany; ratio of α and β is 94 to 3 and contained less than 0.1 wt % free silicon) and 0, 3, 6, 8 mol % Y_2O_3-doped zirconia (TZ-0 and TZ-3Y, 6Y, 8Y, respectively, Toyo Soda Co., Tokyo, Japan; for convenience, Y_2O_3-doped zirconia powders are expressed as a zyttrite in this article) (denoted 0Y, 3Y, 6Y, and 8Y, respectively) powders were used to prepare the mixtures of Si_3N_4 and 5, 10, 15, 20, and 30 vol % of various zirconia. The mixtures were centrifugally mixed in acetone for 2 h using zirconia balls and jar (Pulverisette 6, Fritsch, West Germany). For more uniform mixing of Si_3N_4 and zirconia powders, these mixtures were again vibration mixed (Spex 8000 mixer/mill, Edison, New Jersey, USA) for 10 min in a teflon-coated container with zirconia balls, and then dried in an oven.

The dried mixture screened to -60 mesh, was hot-pressed in a tungsten mesh heater furnace (Model 60 series, Centorr Associate, Inc., Suncook, New Hampshire, USA) using BN coated graphite die (2 cm i.d.). 1 atm N_2 atmosphere was maintained during hot-pressing, and the temperature and pressure were 1750° C and $35\,MN\,m^{-2}$, respectively. Temperature was measured pyrometrically to ± 5° C.

For the reaction couples between Si_3N_4 and pure ZrO_2(0Y) or zyttrite, as-received Si_3N_4 powder was

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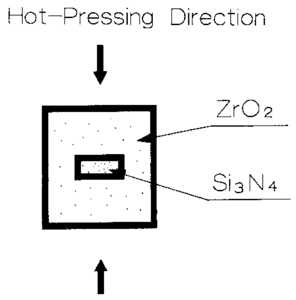

Figure 1 Schematic diagram of Si_3N_4–ZrO_2 reaction couple.

die-pressed to form discs (1 cm i.d.) and subsequently cold isostatically pressed at 150 MN m^{-2}. These compacts were, then embedded in 0Y, 3Y and 8Y zirconia powder as shown in Fig. 1. These reaction couples were hot-pressed under the same conditions described above.

Microstructural characterization of the interface of reaction couples, was made by optical microscopy (Zeiss, West Germany) and scanning electron microscopy (SEM, ETEC Autoscan Co., Hayward, California, USA), and phase identification was performed by X-ray diffraction (XRD, Rigaku, Japan). Transmission electron microscopy (TEM, Model 200 CX, Jeol, Tokyo, Japan) was used to distinguish cubic and tetragonal zirconia phase in Si_3N_4 matrix. The electron transparent specimen for TEM was obtained by argon-ion bombardment technique (MIN, Technics, Inc., USA). The specimen was thinned from both sides with an incident angle of 15° with an average voltage of 5 kV. The density of the hot-pressed body was determined by Archimedes method, and the theoretical density was calculated by the rule of mixture.

3. Results and discussion

3.1. Si_3N_4–ZrO_2 composites

3.1.1. Effect of added zirconia on the densification

Pure Si_3N_4 and the mixtures of Si_3N_4 and 5 vol % 0Y, 3Y, 6Y, and 8Y ZrO_2 were hot-pressed to investigate the effect of zirconia on the densification. Fig. 2 shows the final densities obtained by hot-pressing pure Si_3N_4, mixtures of Si_3N_4 and various zirconia. The addition of only 5 vol % 6Y and 8Y zirconia increased the density up to 97% and 99% theoretical, respectively. However, the density of pure Si_3N_4 was low (57%). Therefore, densification did not take place in hot-pressed pure Si_3N_4. The density of Si_3N_4 with 5 vol % 0Y ZrO_2 composite (71%) was higher than that of pure Si_3N_4. From these results, Y_2O_3 in zyttrite affected the densification dominantly rather than ZrO_2 phase.

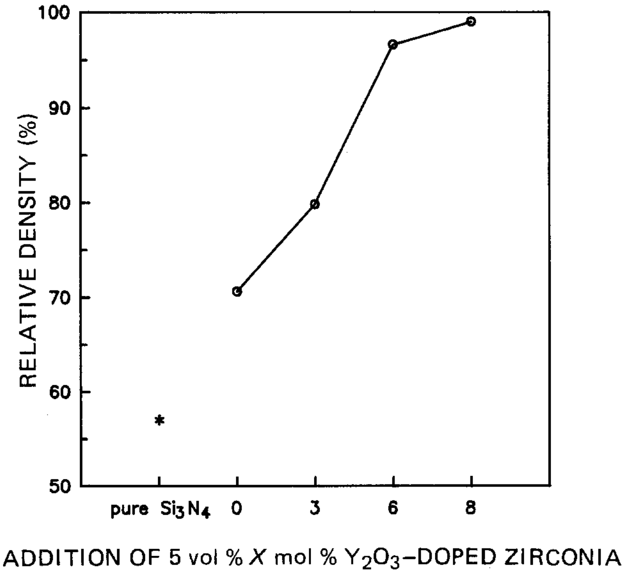

Figure 2 Variations of relative density of hot-pressed Si_3N_4 with 5 vol % ZrO_2 composite with the addition of various zirconia (pure, 3, 6, 8 mol % Y_2O_3-doped zirconia) and hot-pressed pure Si_3N_4.

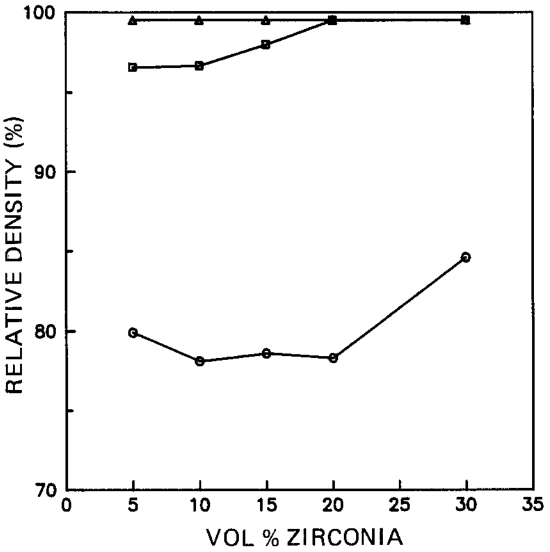

Figure 3 Variations of relative density of hot-pressed Si_3N_4 with (○) 3, (□) 6, (△) 8 mol % Y_2O_3-doped zirconia composite with the amount of added zirconia.

Fig. 3 shows the variations in density of hot-pressed Si_3N_4–zyttrite composite with the amount of added 3Y, 6Y, 8Y zirconia. Si_3N_4 with 6Y and 8Y zirconia composites show high densities (97%) regardless of the amount of added zirconia, but densities of Si_3N_4 with 3Y ZrO_2 composite cannot exceed 80% theoretical up to 20 vol % zirconia. These results support the fact that densification of these composites is mainly affected by the content of Y_2O_3 in zyttrite. According to Fick's first law, the total amount of Y_2O_3 diffused from zyttrite depends on the ΔC (concentration gradient of Y_2O_3 between zyttrite and the matrix) and temperature. Therefore, significant densification could not occur when 3Y ZrO_2 was added to Si_3N_4, because ΔC of 3Y ZrO_2 was lower than that of 6Y and 8Y ZrO_2. Moreover, nearly full density (98%) was obtained in Si_3N_4 with 5 vol % 3Y ZrO_2 composite by raising the hot-pressing temperature up to 1850° C i.e. increasing D: diffusivity, D, is exponentially proportional to the temperature. So, it is concluded that Y_2O_3 diffused from zyttrite promotes the densification of Si_3N_4–zyttrite composite. But the Si_3N_4 and zyttrite system involves various chemical reaction processes; the diffusion process is not simply expressed as described above. Thus, to explain fully the density variations with the addition of 3Y ZrO_2, further work is required to complement the diffusion process.

3.1.2. Phase identification

In order to evaluate the role of the zirconia on the α/β

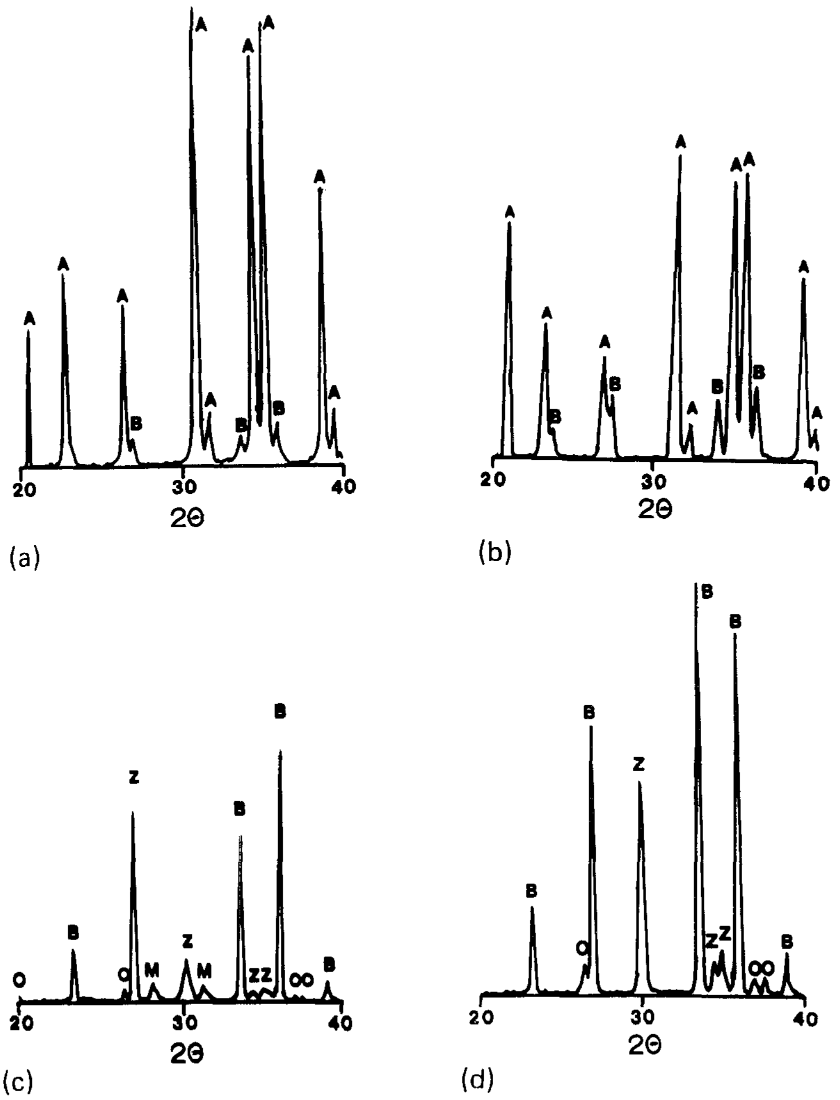

Figure 4 XRD pattern of (a) as-received Si_3N_4 powder, (b) hot-pressed pure Si_3N_4, (c) hot-pressed Si_3N_4 with 5 vol % 3 mol % Y_2O_3-doped zirconia composite, and (d) hot-pressed Si_3N_4 with 5 vol % 6 mol % Y_2O_3-doped zirconia composite: (A) α-Si_3N_4, (B) β-Si_3N_4, (O) Si_2N_2O, (Z) cubic or tertragonal zirconia, (M) monoclinic zirconia peaks.

phase transformation of Si_3N_4, X-ray analysis was performed (Fig. 4). A significant α/β ratio change could not be detected in hot-pressed pure Si_3N_4 composite* compared to the starting powder (0.044), Figs 4a, b. However in Si_3N_4–0Y ZrO_2 composite, β-Si_3N_4 and Si_2N_2O (silicon oxynitride) peaks were detected together (Fig. 4c). Therefore, ZrO_2 phase seems to be concerned with the formation of Si_2N_2O phase, and the α/β phase transformation of Si_3N_4 also seems to be caused by this Si_2N_2O phase; this will be discussed in detail in a later section. With this, it is conceivable that the density of Si_3N_4 with 0Y ZrO_2 composite, compared with that of the hot-pressed pure Si_3N_4, is slightly increased by Si_2N_2O phase. On the basis of these suggestions, Si_2N_2O phase influences the phase transformation rather than the densification of Si_3N_4; the phase transformation of Si_3N_4 is not always accompanied by densification [12]. Also, zirconia existing in this composite as a mono and cubic phase, was reported by Claussen as a "nitrogen stabilized zirconia" [10]. For this cubic phase, Lange also reported the $ZrO_{2-2x}N_{4x/3}$ $0.25 \leqslant x \leqslant 0.43$ (zirconium oxynitride) in Si_3N_4–ZrO_2 composite [4].

The XRD pattern of Si_3N_4 with 3Y ZrO_2 composite was composed of cubic or tetragonal ZrO_2, β-Si_3N_4 and Si_2N_2O peaks (Fig. 4d); the XRD patterns of Si_3N_4 with 6Y and 8Y ZrO_2 composite were similar to those of Si_3N_4 with 3Y ZrO_2 composite. As described earlier, if Y_2O_3 in zyttrite mainly acted as a sintering aid rather than a stabilizer for zirconia, it might be expected that yttria-stabilized cubic zirconia would be transformed to tetragonal phase which had a lower Y_2O_3 content [13]. From TEM works, the presence of the tetragonal ZrO_2 in Si_3N_4 with 8Y ZrO_2 composite was confirmed as shown in Fig. 5. This result indicates that the zirconia which is stable in the cubic region is moved to the low Y_2O_3 content region, i.e. tetragonal + cubic region, by diffusion of Y_2O_3 from zyttrite during hot-pressing.

3.2. Si_3N_4–ZrO_2 reaction couples

3.2.1. Microstructures of reaction couples

To investigate the reaction product of Si_3N_4–ZrO_2, reaction couples were used. Fig. 6 shows optical micrographs of the interfaces between Si_3N_4 and 0Y, 3Y, and 8Y zirconia. In the Si_3N_4–0Y ZrO_2 reaction

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*β fraction was determined by comparing the intensities of $\alpha(2\,1\,0)$ and $\beta(2\,1\,0)$ diffraction peaks, in a manner described by Gazzara and Messier [11]. In this case, β fraction was 0.203.

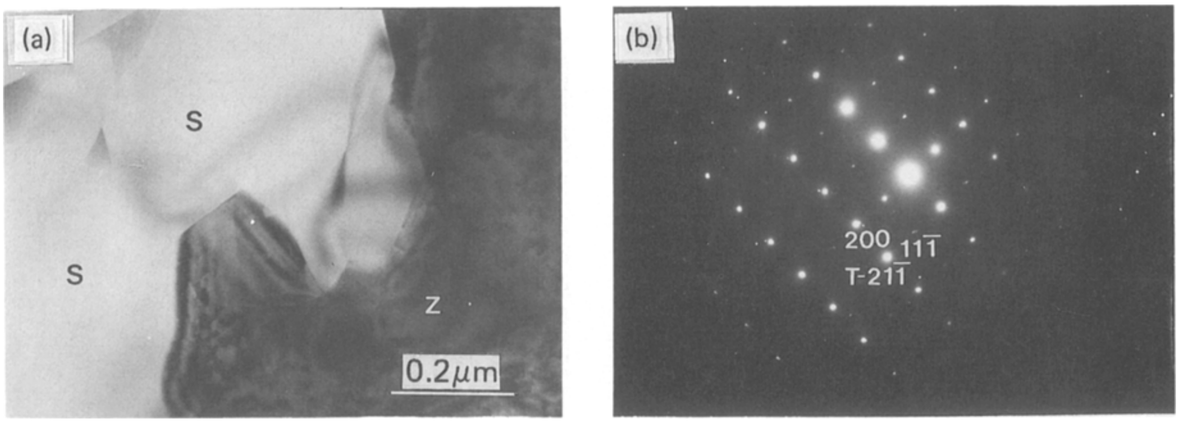
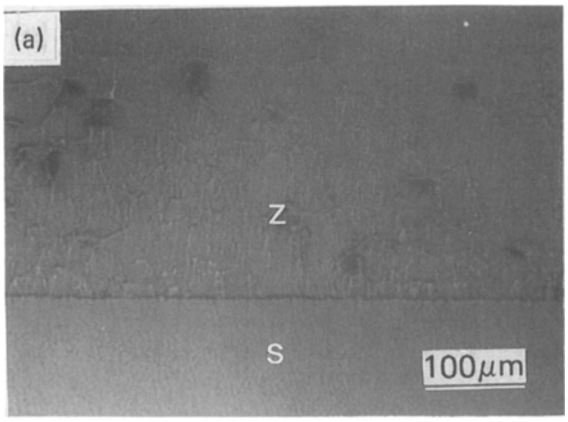


Figure 5 Transmission electron micrographs of hot-pressed Si_3N_4 with 30 vol % 8 mol % Y_2O_3-doped zirconia: (a) bright-field image and (b) selected-area diffraction pattern of Z region in (a); $B = [0\,1\,1]$c,t (S, Si_3N_4; Z, ZrO_2).

couple, no significant reaction layer could be shown and the interface is flat (Fig. 6a). Recently, in the α/β phase transformation of Si_3N_4, β-Si_3N_4 phase was precipitated via silicon melts [12, 14, 15]. A similar change in morphology was observed in the reaction layer between Si_3N_4 and zyttrite. Both interfaces of the Si_3N_4–3Y and 8Y ZrO_2 reaction couples are rough, and a bright reaction layer containing a large precipitated phase can be seen (Fig. 6b, c). At the interface between Si_3N_4 and the bright reaction layer (marked by arrows), a fine precipitated phase is observed. The interface between ZrO_2 and the bright reaction layer was easily separated because of their large thermal expansion mismatch (Si_3N_4: $\simeq 3.5 \times 10^{-6}$, ZrO_2: $\simeq 8$ to 10×10^{-6} °C^{-1}). Scanning electron micrographs of Si_3N_4–3Y ZrO_2 reaction couple show glassy phase (Fig. 7a) and elongated β-Si_3N_4 (Fig. 7b) at the reaction layer; these micrographs were obtained from the viewing angle which was vertical to the reaction layer and parallel to the hot-pressing direction. However, the central part of Si_3N_4 in the reaction couple contains equi-axed β-Si_3N_4 of initial morphology (Fig. 7c), and spherical zirconia grains (2 to 6 μm) (Fig. 7d) exist in the outer part of the reaction layer. On the basis of observation of the above microstructure, it is considered that Y_2O_3 diffuses from the zyttrite reacts with Si_3N_4 during hot-pressing and forms a glass phase. Accompanying this, the α/β phase transformation of Si_3N_4 can occur via this phase.



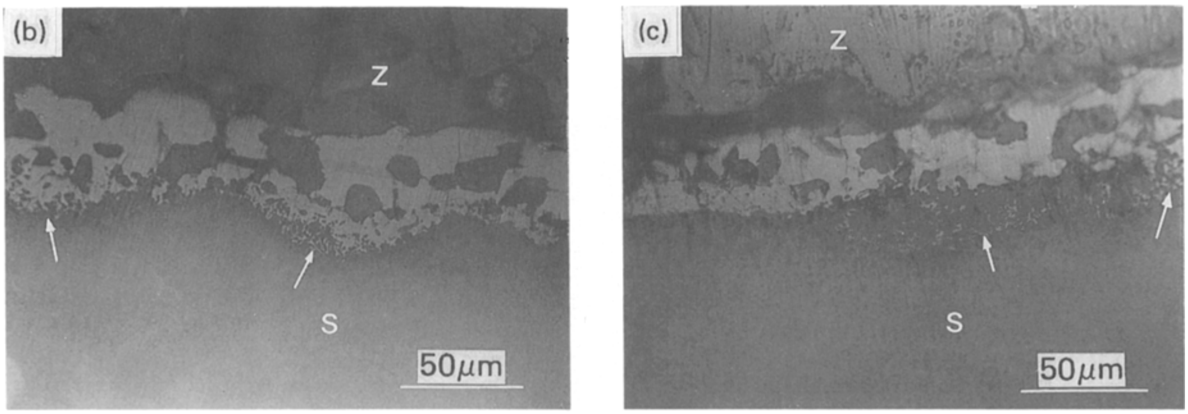


Figure 6 Optical micrographs of the interface of Si_3N_4 and (a) pure zirconia, (b) 3 mol % Y_2O_3-doped zirconia, (c) 8 mol % Y_2O_3-doped zirconia reaction couple (S, Si_3N_4; Z, ZrO_2, bright phase in (b), (c), reaction layer).

3.2.2 Reaction products of Si_3N_4–ZrO_2 reaction couples

α,β-Si_3N_4 and strong Si_2N_2O peaks could be detected in the Si_3N_4–0Y ZrO_2 reaction couple (Fig. 8a). This result provides strong evidence for the formation of Si_2N_2O phase resulting from the reaction between Si_3N_4 and ZrO_2. Gauckler *et al.* [16] reported that the Si_2N_2O phase could be related to the reaction between Si_3N_4 and ZrO_2, and Terao [9] reported that the Si_2N_2O phase increased with the amount of added ZrO_2 in hot isostatically pressed-Si_3N_4. In the previous section, β-Si_3N_4 and Si_2N_2O peaks were detected together in hot-pressed Si_3N_4 with 0Y ZrO_2 composite. If cubic zirconia in Si_3N_4 is present in the

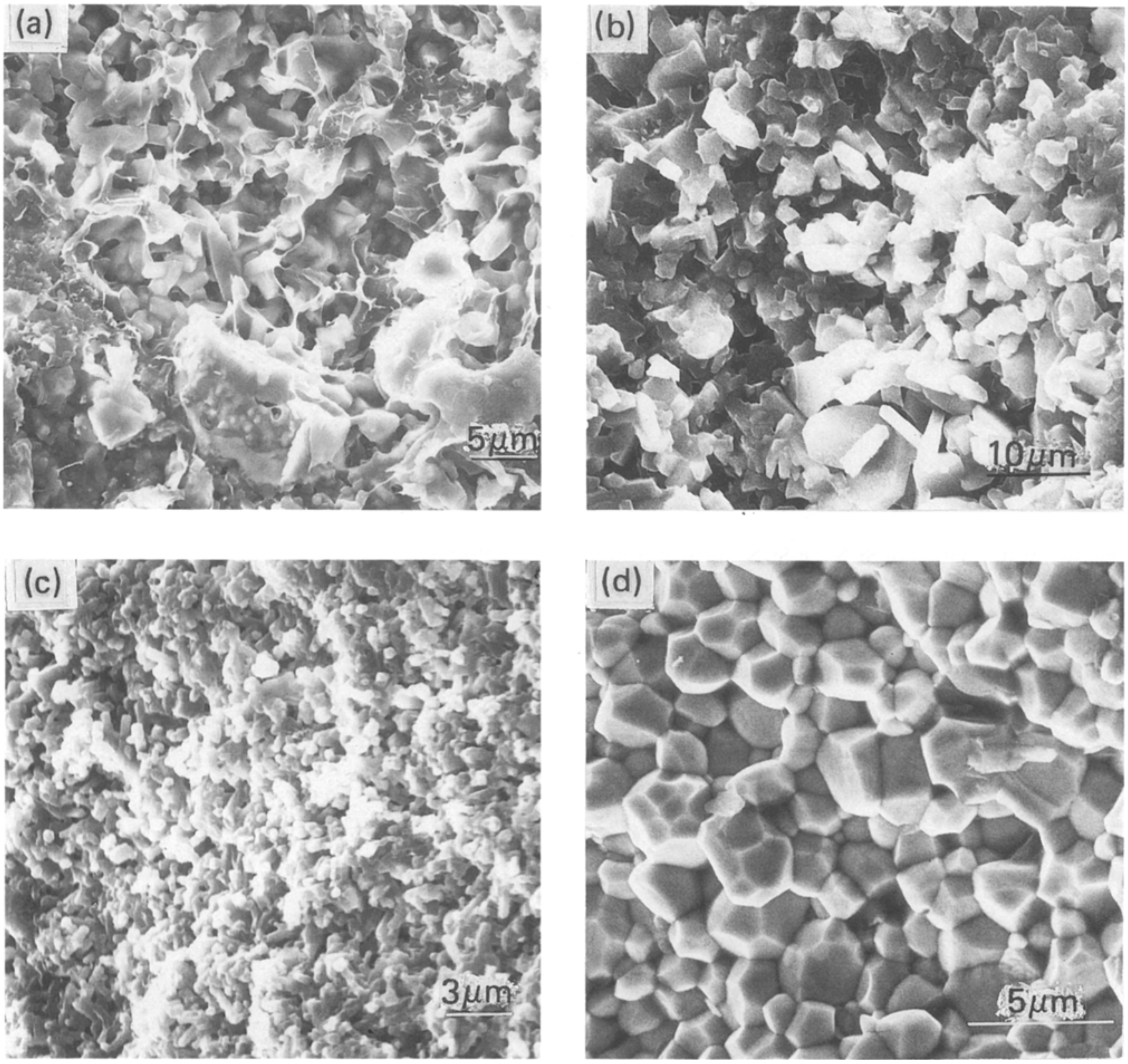


Figure 7 Scanning electron micrographs of Si_3N_4 and 3 mol % Y_2O_3-doped zirconia reaction couple: (a) and (b) at interface region, (c) at central part of Si_3N_4 and (d) at zirconia region.

form of zirconium oxynitride [4, 10], therefore, the formation of silicon oxynitride can be considered as follows

$$A\mathrm{Si_3N_4} + B\mathrm{ZrO_2} \rightarrow C\mathrm{ZrO}_{2-2x}\mathrm{N}_{3x/4} + D\mathrm{Si_2N_2O}$$

where A, B, C, D are constant. Oxygen atoms in ZrO_2 are substituted by nitrogen atoms, and can form a silicon oxynitride phase. Subsequently, α/β phase transformation of Si_3N_4 occurs via Si_2N_2O glass during hot-pressing. Here, although the possibility of

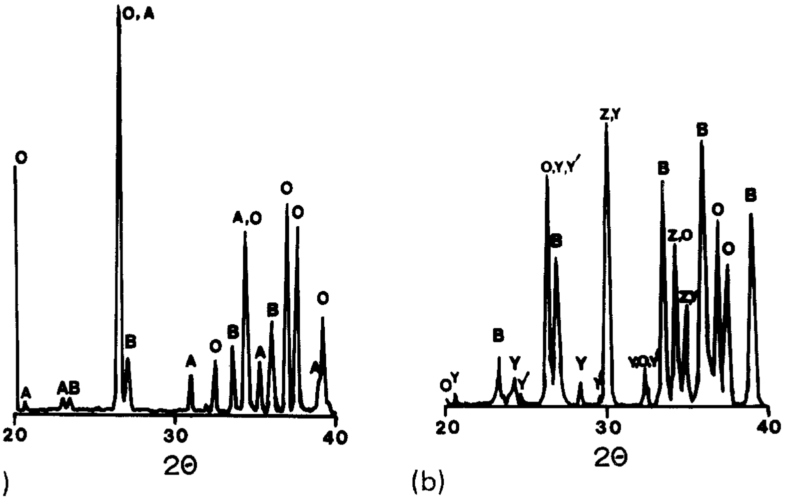


Figure 8 XRD pattern of the interface of Si_3N_4 and (a) pure zirconia, (b) 3 mol % Y_2O_3-doped zirconia reaction couple: (A) α-Si_3N_4, (B) β-Si_3N_4, (O) Si_2N_2O, (Z) cubic or tetragonal zirconia, (Y) $Y_2Si_2O_7$, (Y′) $YY_2Si_3N_4O_3$ peaks.

the reaction of Si_3N_4 and surface silica to form a silicon oxynitride is not ruled-out, it seems that this reaction does not actively occur in this system; if Si_2N_2O phase was actively formed by this reaction, a significant phase transformation would occur in the hot-pressed pure Si_3N_4.

In the case of the Si_3N_4–zyttrite reaction couple, β-Si_3N_4, Si_2N_2O, $Y_2Si_3N_4O_3$ (silicon yttrium oxynitride), and $Y_2Si_2O_7$ (yttrialite) peaks were detected (Fig. 8b). For the $Y_2Si_2O_7$ phase, Clark [17] reported that the α/β phase transformation and the densification of Si_3N_4 could occur via the $Y_2Si_2O_7$ phase. Also, the $Y_2Si_3N_4O_3$ phase was frequently observed in Si_3N_4 sintered with Y_2O_3 [18–20]. Therefore, in this system, the phase transformation can take place via Si_2N_2O, $Y_2Si_3N_4O_3$, and $Y_2Si_2O_7$ phases. However, it is not possible to determine the phase which affects the phase transformation dominantly rather than the others. It is suggested that the major reaction products of the reaction between Si_3N_4 and zyttrite are $Y_2Si_3N_4O_3$ and $Y_2Si_2O_7$ phase, which can play an important role in the densification of Si_3N_4–zyttrite composites.

Conclusions

1. The role of pure ZrO_2 on densification was not effective in obtaining full density of Si_3N_4–ZrO_2 composite, but most α-Si_3N_4 phase was transformed to β-Si_3N_4, resulting from the formation of Si_2N_2O phase.

2. In Si_3N_4–zyttrite composite, nearly full density ($> 97\%$) could be obtained by the addition of 5 vol % 6Y or 8Y ZrO_2, but the densification did not occur sufficiently in the case of the addition of 3Y ZrO_2. From these results, it is suggested that Y_2O_3 diffused from the added zyttrite promotes the densification of the Si_3N_4–zyttrite composite, and the densification depends on the content of Y_2O_3 in the zyttrite. Related to this, a tetragonal zirconia phase stable in the cubic + tetragonal region was observed.

3. In the Si_3N_4–pure ZrO_2 reaction couple, the reaction between Si_3N_4 and ZrO_2 resulted in the formation of Si_2N_2O phase, and the α/β phase transformation of Si_3N_4 occurred via this Si_2N_2O phase. In the Si_3N_4–zyttrite reaction couple, a bright reaction layer containing large and fine β-Si_3N_4 precipitates was observed. From the XRD analysis of this reaction layer, it is suggested that the reaction products of the reaction between Si_3N_4 and zyttrite, $Y_2Si_3N_4O_3$ and $Y_2Si_2O_7$ phases, play an important role in the densification of Si_3N_4–zyttrite composite.

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