

Si₃N₄–ZrO₂ composites with small Al₂O₃ and Y₂O₃ additions prepared by HIP

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Si₃N₄–ZrO₂ composites have been prepared by hot isostatic pressing at 1550 and 1750 °C, using both unstabilized ZrO₂ and ZrO₂ stabilized with 3 mol % Y₂O₃. The composites were formed with a zirconia addition of 0, 5, 10, 15 and 20 wt %, with respect to the silicon nitride, together with 0–4 wt % Al₂O₃ and 0–6 wt % Y₂O₃. Composites prepared at 1550 °C contained substantial amounts of unreacted α-Si₃N₄, and full density was achieved only when ≥ 1 wt % Al₂O₃ or ≥ 4 wt % Y₂O₃ had been added. These materials were generally harder and more brittle than those densified at the higher temperature. When the ZrO₂ starting powder was stabilized by Y₂O₃, fully dense Si₃N₄–ZrO₂ composites could be prepared at 1750 °C even without other oxide additives. Densification at 1750 °C resulted in the highest fracture toughness values. Several groups of materials densified at 1750 °C showed a good combination of Vickers hardness (HV10) and indentation fracture toughness; around 1450 kg mm⁻² and 4.5 MPa m^{1/2}, respectively. Examples of such materials were either Si₃N₄ formed with an addition of 2–6 wt % Y₂O₃ or Si₃N₄–ZrO₂ composites with a simultaneous addition of 2–6 wt % Y₂O₃ and 2–4 wt % Al₂O₃.

1. Introduction

It was recognized in the mid 1970s that ZrO₂ or other Zr-based additions such as zircon, ZrSiO₄, could be used successfully as sintering aids to obtain dense Si₃N₄ ceramics by hot pressing (HP) at high temperatures [1, 2]. At about the same time, the positive effect of additions of unstabilized ZrO₂ on the fracture toughness of Al₂O₃-based ceramics was discovered, and the underlying mechanisms have later been well summarized by Rice [3]. Claussen and Jahn [4] measured mechanical properties of Si₃N₄–ZrO₂ composites (with 2.5 wt % Al₂O₃ milled in) using samples prepared by HP. They reported a clear increase in fracture toughness with increasing ZrO₂ content; from 5.5 MPa m^{1/2} for “pure” Si₃N₄ to a maximum of 8.5 MPa m^{1/2} at around 20 vol % ZrO₂ in the composite material. Several subsequent investigations have confirmed the positive effect on mechanical properties of Si₃N₄ achieved by ZrO₂ additions [5–10]. More recent investigations have shown that the fracture toughness of Si₃N₄ composites can be improved also by additions of 10–30 vol % Y₂O₃-stabilized ZrO₂ [11, 12]. In fact, composites formed with 30 wt % ZrO₂ together with 4.1 mol % Y₂O₃ added as separate colloidal solutions have shown a room-temperature flexural strength of 1170 MPa and a fracture toughness of 6.7 MPa m^{1/2} [12]. It has also been demonstrated that a post-sintering heat treatment may increase the apparent toughness and strength of some ceramics formed in the Si₃N₄–ZrO₂ system [12, 13].

Generally, a tetragonal structure of the ZrO₂ grains in the Si₃N₄–ZrO₂ composite is preferred. However, it may be a difficult task to obtain this during densification of the ceramic. A reaction between Si₃N₄ and ZrO₂ may occur at high temperatures, which produces less desirable phases such as Zr-oxynitride and ZrN [11, 13–16]. The Zr-oxynitrides are easily oxidized, which is associated with a molar volume increase [13]. At initial stages in the oxidation process this introduces surface compressive stresses which could be of advantage in a subsequent low-temperature application. Prolonged oxidation will, however, result in a build up of radial tensile stresses below the oxidized surface. Depending on the microstructure of the ceramic, this may cause severe spalling [11, 13]. The formation of these N-containing phases during densification may be suppressed by the use of Y₂O₃-stabilized ZrO₂ starting powder. It has been suggested that 4.1 mol % Y₂O₃ in the ZrO₂ was sufficient to prevent nitrogen uptake during sintering [11]. In addition, it has also been found that sintering at lower temperatures makes it possible to avoid ZrN and Zr-oxynitride formation [14, 19]. Weiss *et al.* [15] studied the possible reactions by thermodynamic calculations and concluded that the preparation of dense Si₃N₄ bodies containing only ZrO₂ would be difficult due to the absence of a liquid phase and to a chemical reaction between the components which would produce a gas phase giving porosity. They suggested that an addition of Al₂O₃ would overcome this, since Si₃N₄ may form a β sialon phase via a transient liquid.

This would result in fast densification, and a β sialon ceramic composite with ZrO_2 dispersions. Addition of Al_2O_3 has later been used by Bellosi *et al.* [18] and they found that the oxidation resistance of the obtained material was significantly better than that of other $\text{Si}_3\text{N}_4\text{-ZrO}_2$ composite materials.

The $\text{Si}_3\text{N}_4\text{-ZrO}_2$ ceramic composites are interesting engineering materials not only because of an improved toughness behaviour, but also due to improved chemical inertness [5, 18]. The oxidation behaviour of such composites has been studied in several investigations [e.g. 10–11, 17]. The aim of the present study has been to investigate the effect of preparing dense $\text{Si}_3\text{N}_4\text{-ZrO}_2$ composites by glass encapsulated hot isostatic pressing (HIP), without or with only small additions of Al_2O_3 and/or Y_2O_3 . The phase compositions of the materials have been related to room-temperature fracture toughness and hardness.

2. Experimental procedure

The selected compositions in this study were based on Si_3N_4 as parent material with additions of 0, 5, 10, 15 and 20 wt % ZrO_2 or $\text{ZrO}_2(+3 \text{ mol } \% \text{ Y}_2\text{O}_3)$. 0–4 wt % Al_2O_3 and/or 0–6 wt % Y_2O_3 was also added to the powder mixtures. The source materials were silicon nitride (H. C. Starck–Berlin, grade LC1), zirconium oxide (Chema Tex, grade SC16), zirconium oxide stabilized with 3 mol % Y_2O_3 (TOSOH, grade TZ–3Y), aluminium oxide (Alcoa, grade A16SG) and yttrium oxide (H. C. Stark–Berlin, grade Finest). The analysed oxygen content of the silicon nitride powder corresponds to 2.9 wt % SiO_2 . The starting powders were carefully weighed (the total batch size was 500 g for each composition), mixed in water-free propanol and milled in a vibratory mill for 17 h with a sialon milling medium. After drying and agglomeration, the powder mixtures were dry-pressed (125 MPa) into compacts of size 16 mm \times 16 mm \times 6 mm. The samples were glass-encapsulated and HIP at 1550 °C (2 h) or 1750 °C (1 h) using an argon pressure of 200 MPa. Before encapsulation, the samples were covered with a BN layer in order to prevent direct contact between the glass and the specimens.

The density of the as-HIPed samples was characterized both by density measurements using Archimedes principle and by porosity levels determined from polished cross sections examined in an optical microscope. The materials were prepared for physical characterization using standard techniques. Hardness (HV 10) and indentation fracture toughness (K_{IC}) at room temperature were obtained by use of a Vickers diamond indenter applying a 98 N (10 kg) load. The fracture toughness was evaluated by the formula given by Anstis *et al.* [20], assuming a value of 300 GPa for Young's modulus. The accuracy, determined by repeated measurements on the same sample, was $\pm 0.2 \text{ MPa m}^{1/2}$. Phase analysis was based on X-ray diffraction patterns obtained from polished cross-sections of the specimens using a Rigaku diffractometer with a rotating Cu anode working at 10 kW and equipped with a graphite monochromator. The

z -values of the β sialon phase $\text{Si}_{6-2z}\text{Al}_z\text{O}_2\text{N}_{8-2z}$ were evaluated from the lattice parameters, using the equations $a = 0.7603 + 0.00297 z \text{ nm}$ and $c = 0.2907 + 0.00255 z \text{ nm}$ [21]. An internal standard for peak positions, TiN (cubic, $a = 0.4240 \text{ nm}$) was dusted on to the surface prior to X-ray recording. The accuracy of z -values obtained in this way is normally better than ± 0.05 . For determination of the abundance ratio, Q , of $\alpha\text{-Si}_3\text{N}_4$, by the formula $Q = \alpha/(\alpha + \beta)$, integrated intensities of the (102) and (210) peaks of the α phase and the (101) and (210) peaks of the β phase were used. Similarly, the relative amount of $\text{Si}_2\text{N}_2\text{O}$, denoted S , was calculated by the formula $S = \text{Si}_2\text{N}_2\text{O}/(\text{Si}_2\text{N}_2\text{O} + \alpha + \beta)$ and the relative amount of tetragonal ZrO_2 , denoted T , by the formula $T = \text{tetragonal ZrO}_2/(\text{tetragonal} + \text{monoclinic}) \text{ ZrO}_2$. The (111), (202) peaks and the (111), (11–1) peaks were used for the tetragonal and monoclinic modifications of ZrO_2 , respectively. The tetragonal ZrO_2 was clearly identified by peak splitting and the presence of extra peaks not allowed in an X-ray pattern from the cubic phase.

3. Results

3.1. Densification process

Materials with poor density were obtained only at the lower HIP temperature 1550 °C, using a single addition of Y_2O_3 , ZrO_2 or $\text{ZrO}_2(+\text{Y}_2\text{O}_3)$. Similar results were obtained for the two types of zirconia addition, and the relative density stayed fairly constant at around 85% theoretical independent of amount zirconia added to the silicon nitride composite, Fig. 1. An addition of $\geq 1 \text{ wt } \% \text{ Al}_2\text{O}_3$ or $\geq 4 \text{ wt } \% \text{ Y}_2\text{O}_3$ to these composites promoted densification, and resulted in fully dense materials, i.e. $\geq 99.5\%$ theoretical. When ZrO_2 was not added, fully dense Si_3N_4 materials were formed only in the presence of Al_2O_3 .

Materials formed at 1750 °C using the $\text{ZrO}_2(+3 \text{ mol } \% \text{ Y}_2\text{O}_3)$ starting powder had a porosity level of 0.2 vol %, i.e. they had 99.8% theoretical density. These materials can be regarded as virtually fully

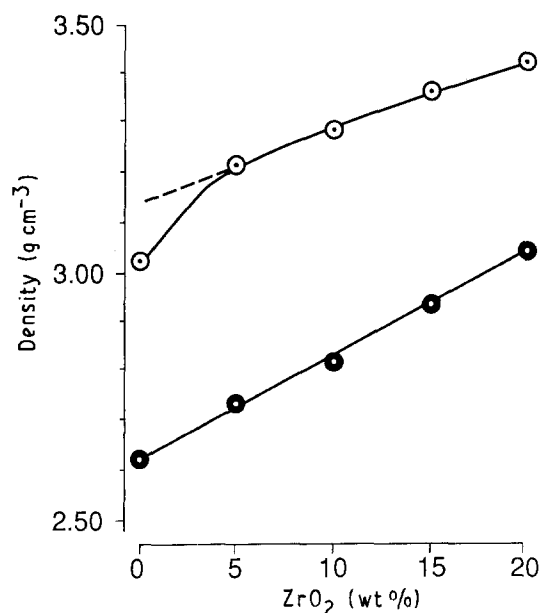


Figure 1 Densities of the $\text{Si}_3\text{N}_4\text{-ZrO}_2$ or $\text{Si}_3\text{N}_4\text{-ZrO}_2(+3 \text{ mol } \% \text{ Y}_2\text{O}_3)$ composites after HIP at (●) 1550 °C or (○) 1750 °C.

dense, as it can not be excluded that some crystals had been pulled out during the final polishing step. The use of unstabilized ZrO₂ produced, however, somewhat less dense materials at this temperature; a porosity between 0.6 and 1 vol %, was observed in these materials. A further addition of ≥ 1 wt % Al₂O₃ or ≥ 2 wt % Y₂O₃ to the Si₃N₄-ZrO₂ composites resulted in densities above 99.5% theoretical. Si₃N₄ materials formed at 1750 °C with different additions of Y₂O₃ and Al₂O₃, but without ZrO₂, were all fully dense.

3.2. X-ray diffraction analysis

After processing at 1750 °C, a majority of the samples contained Si₂N₂O, Tables I-III. X-ray diffraction analysis of the Si₃N₄-ZrO₂ and Si₃N₄-ZrO₂ (+ Y₂O₃) composites formed with up to 2 wt % Al₂O₃, showed that the amount of Si₂N₂O was relatively constant with increasing ZrO₂ addition. However, Table I indicates that the Si₂N₂O content was slightly lower when the ZrO₂ starting powder had been prereacted with Y₂O₃. Larger, separate, additions of Y₂O₃ did, in general, suppress the Si₂N₂O formation, Tables II and III.

As shown by the *Q*-values in Tables I-III, the α - to β -Si₃N₄ transformation was complete in most ZrO₂ containing samples densified at 1750 °C. When the ZrO₂ was added as unstabilized powder and together with a separate Y₂O₃ addition, the zirconia phase appeared fully tetragonal in the X-ray diffractograms. However, without the simultaneous addition of Y₂O₃, the ZrO₂ was only partly in the tetragonal form (40%-60%). Zirconia added as Y₂O₃-stabilized ZrO₂ powder resulted always in the tetragonal phase.

X-ray diffraction results obtained from samples densified at 1550 °C were similar to the phase compositions after densification at 1750 °C discussed above. The major difference was that a considerable amount of α -Si₃N₄ remained after processing at the lower temperature - between 45% and 85%. This clearly demonstrates the incomplete α - β -Si₃N₄ transformation at this low processing temperature.

Additions of Al₂O₃ made it possible for β sialon Si_{6-z}Al₂O₂N_{8-z} to form, and a β sialon phase with a low *z*-value, i.e. very low Al-O substitution, was found in materials where the amount of Y₂O₃ added was low, see Table III. The observed trend was, that for a constant addition of Al₂O₃ the *z*-value decreased towards zero with increasing Y₂O₃ addition.

TABLE I Phase analysis of Si₃N₄-ZrO₂ and Si₃N₄-ZrO₂(+ 3 mol % Y₂O₃) composites formed by HIP at 1750 °C for 1 h using additions of Al₂O₃ only

Oxide additives (wt %)			Phase composition	Relative amounts		
ZrO ₂	ZrO ₂ (Y ₂ O ₃)	Al ₂ O ₃		<i>Q</i>	<i>T</i>	<i>S</i>
0	0	0	α , β , SNO	0.80	-	0.06
0	0	1	α , β , SNO	0.04	-	0.05
0	0	2	α , β , SNO	0.08	-	0.05
5	0	0	β , ZrO ₂ , SNO	0	0.70	0.08
5	0	1	β , ZrO ₂ , SNO	0	0.54	0.06
5	0	2	β , ZrO ₂ , SNO	0	0.52	0.06
10	0	0	β , ZrO ₂ , SNO	0	0.72	0.08
10	0	1	β , ZrO ₂ , SNO	0	0.62	0.06
10	0	2	β , ZrO ₂ , SNO	0	0.55	0.06
15	0	0	β , ZrO ₂ , SNO	0	0.69	0.08
15	0	1	β , ZrO ₂ , SNO	0	0.58	0.07
15	0	2	β , ZrO ₂ , SNO	0	0.64	0.06
20	0	0	β , ZrO ₂ , SNO	0	0.63	0.09
20	0	1	β , ZrO ₂ , SNO	0	0.64	0.07
20	0	2	β , ZrO ₂ , SNO	0	0.62	0.06
0	5	0	α , β , ZrO ₂ , SNO	0.04	1	0.05
0	5	1	β , ZrO ₂ , SNO	0	1	0.05
0	5	2	α , β , ZrO ₂ , SNO	0.04	1	0.05
0	10	0	β , ZrO ₂ , SNO, (ZrN)	0	1	0.05
0	10	1	β , ZrO ₂ , SNO	0	1	0.03
0	10	2	α , β , ZrO ₂ , SNO	0.06	1	0.05
0	15	0	β , ZrO ₂ , SNO	0	1	0.04
0	15	1	β , ZrO ₂ , SNO	0	1	0.05
0	15	2	β , ZrO ₂ , SNO	0	1	0.04
0	20	0	β , ZrO ₂ , SNO	0	1	0.05
0	20	1	β , ZrO ₂ , SNO	0	1	0.03
0	20	2	β , ZrO ₂ , SNO	0	1	0.04

α = α -Si₃N₄, β = β -Si₃N₄ and SNO = Si₂N₂O.

Q = $\alpha/(\alpha + \beta)$ Si₃N₄.

T = tetragonal ZrO₂/(tetragonal + monoclinic)ZrO₂.

S = Si₂N₂O/(Si₂N₂O + α + β).

TABLE II Phase analysis of $\text{Si}_3\text{N}_4\text{-ZrO}_2$ and $\text{Si}_3\text{N}_4\text{-ZrO}_2(+3\text{ mol \% Y}_2\text{O}_3)$ composites formed by HIP (1750 °C, 1 h) using Y_2O_3 additions only

Oxide additives (wt %)			Phase composition	Relative amounts		
ZrO ₂	ZrO ₂ (Y ₂ O ₃)	Y ₂ O ₃		Q	T	S
0	0	0	α, β, SNO	0.80	0	0.06
0	0	2	α, β, SNO	0.08	0	0.04
0	0	4	α, β, SNO	0.03	0	0.05
0	0	6	α, β,	0.04	0	0
5	0	0	β, ZrO ₂ , SNO	0	0.70	0.08
5	0	2	β, ZrO ₂ , SNO	0	1	0.05
5	0	4	β, ZrO ₂	0	1	0
5	0	6	β, ZrO ₂ , SNO	0	1	0.02
10	0	0	β, ZrO ₂ , SNO	0	0.72	0.08
10	0	2	β, ZrO ₂ , SNO	0	1	0.04
10	0	4	β, ZrO ₂ , SNO	0	1	0.05
10	0	6	β, ZrO ₂ , SNO	0	1	0.03
0	5	0	α, β, ZrO ₂ , SNO	0.04	1	0.05
0	5	2	α, β, ZrO ₂ , SNO	0.05	1	0.04
0	5	4	β, ZrO ₂ , SNO	0	1	0.04
0	5	6	β, ZrO ₂ , SNO	0	1	0.05
0	10	0	β, ZrO ₂ , SNO	0	1	0.04
0	10	2	β, ZrO ₂ , SNO	0	1	0.03
0	10	4	β, ZrO ₂ , SNO	0	1	0.04
0	10	6	β, ZrO ₂	0	1	0

α = α-Si₃N₄, β = β-Si₃N₄ and SNO = Si₂N₂O.

Q = α/(α + β) Si₃N₄.

T = tetragonal ZrO₂/(tetragonal + monoclinic) ZrO₂.

S = Si₂N₂O/(Si₂N₂O + α + β).

TABLE III XRD analysis of $\text{Si}_3\text{N}_4\text{-ZrO}_2$ and $\text{Si}_3\text{N}_4\text{-ZrO}_2(+3\text{ mol \% Y}_2\text{O}_3)$ composites formed by HIP at 1750 °C for 1 h using simultaneous additions of Al₂O₃ and Y₂O₃. The same notation is used as in Tables I and II. The z-value refers to the β sialon formula Si_{6-z}Al₂O₂N_{8-z}

Oxide additives (wt %)				Phase composition	Relative amounts		β sialon z-value
ZrO ₂	ZrO ₂ (Y ₂ O ₃)	Al ₂ O ₃	Y ₂ O ₃		Q	S	
0	0	2	0	α, β, SNO	0.08	0.05	0.10
0	0	2	2	α, β, SNO	0.03	0.04	0
0	0	2	4	β, SNO	0	0.04	0
0	0	2	6	α, β	0.07	0	0.01
0	0	4	2	α, β, SNO	0.07	0.04	0.12
0	0	4	4	β, SNO	0	0.04	0
0	0	4	6	α, β	0.02	0	0.02
5	0	2	2	β, ZrO ₂	0	0	0
5	0	2	6	β, ZrO ₂	0	0	0.12
10	0	2	2	β, ZrO ₂ , SNO	0	0.05	0
10	0	4	2	β, ZrO ₂ , SNO	0	0.08	0.08
10	0	4	4	β, ZrO ₂ , SNO	0	0.04	0.05
10	0	4	6	β, ZrO ₂	0	0	0.07
0	10	2	2	α, β, ZrO ₂ , SNO	0.05	0.03	0.08
0	10	2	4	β, ZrO ₂ , SNO	0	0.02	0
0	10	2	6	β, ZrO ₂	0	0	0
0	10	4	2	β, ZrO ₂ , SNO	0	0.04	0.10
0	10	4	4	β, ZrO ₂	0	0	0.07
0	10	4	6	β, ZrO ₂	0	0	0.01

3.3. Mechanical properties

Vickers hardness, HV10, and indentation fracture toughness, K_{IC}, are given in Figs 2–6. When the hardness and toughness values of the ceramics formed at the two different temperatures are compared, two general trends can be noted in these figures.

The hardness was much higher after processing at 1550 °C, whereas the fracture toughness was higher when the material was formed at 1750 °C. Without other additions, the $\text{Si}_3\text{N}_4\text{-ZrO}_2$ and $\text{Si}_3\text{N}_4\text{-ZrO}_2\text{-Y}_2\text{O}_3$ composites showed similar decreases in hardness with increasing zirconia content, Fig. 2a. The

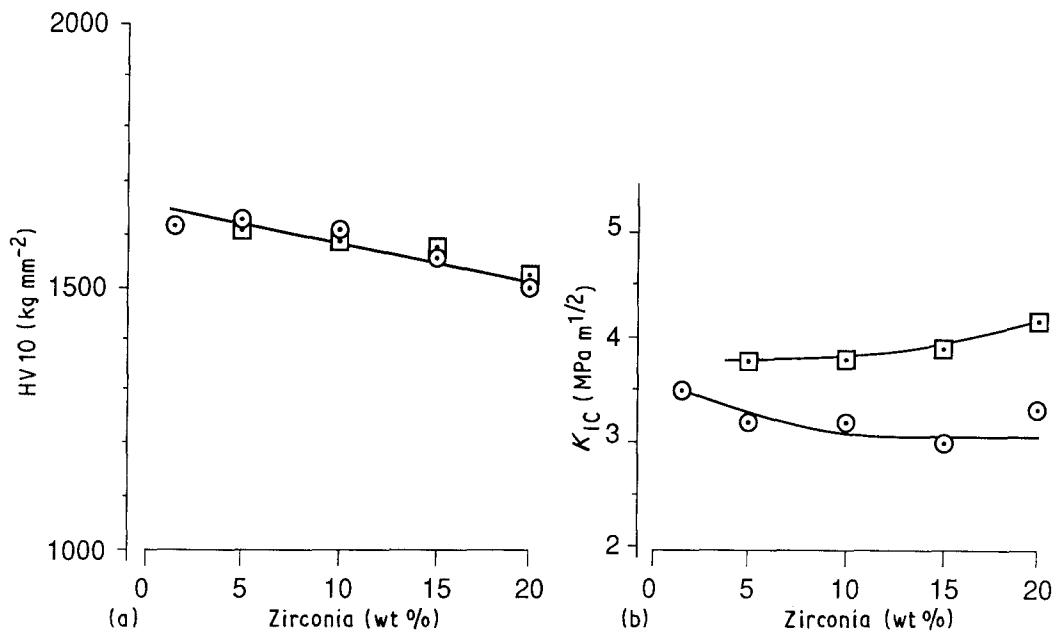


Figure 2 (a) Vickers hardness HV_{10} , measured using a 98 N (10 kg) load, and (b) indentation fracture toughness measured on the Si_3N_4 -zirconia composites formed by HIP at 1750 °C. (○) ZrO_2 , (□) $\text{ZrO}_2(\text{Y}_2\text{O}_3)$.

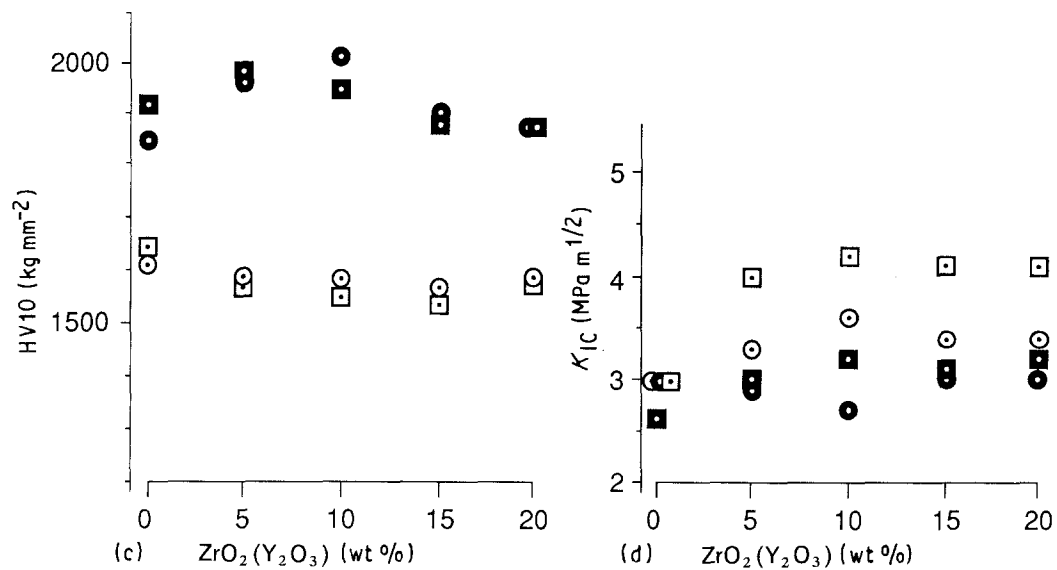
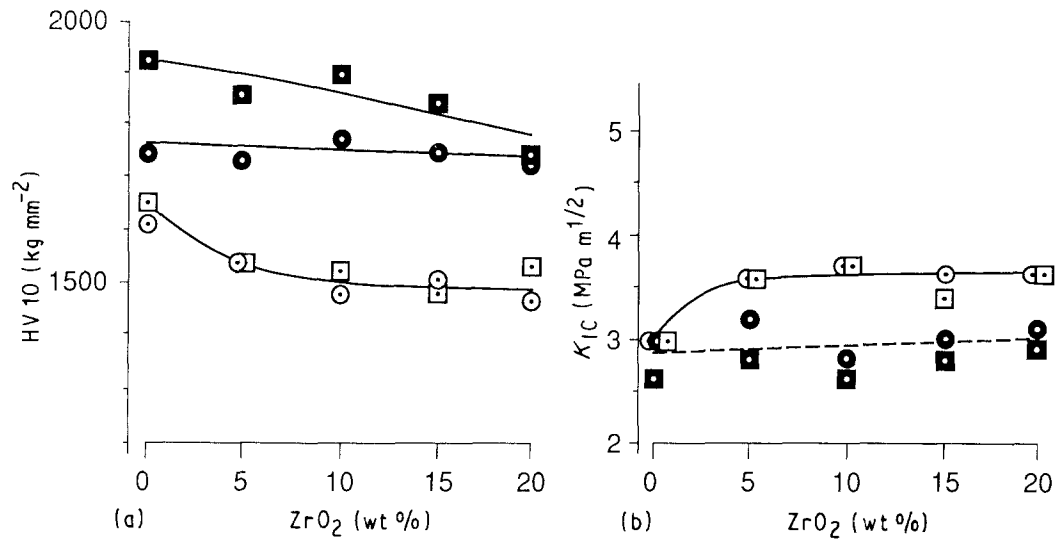


Figure 3 (a, c) Vickers hardness and (b, d) fracture toughness of Si_3N_4 -zirconia composites formed with additions of (●, ○) 1 or (■, □) 2 wt % Al_2O_3 only. Results are shown for additions of (a, b) unstabilized ZrO_2 and (c, d) ZrO_2 with 3 mol % Y_2O_3 . (●, ■) 1550 °C, (○, □) 1750 °C.

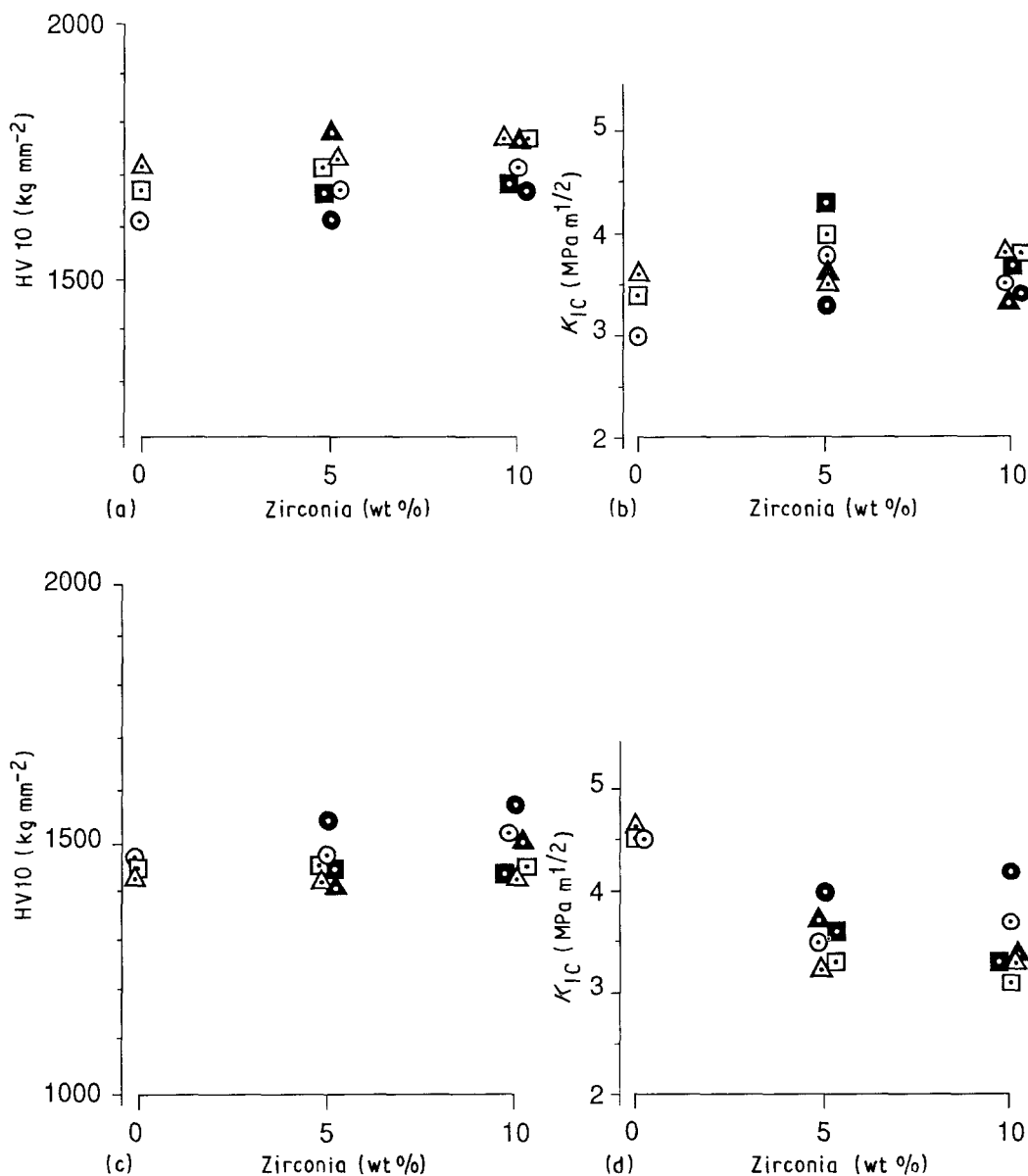


Figure 4 (a, c) Vickers hardness and (b, d) fracture toughness of Si₃N₄-zirconia composites formed with additions of (●, ○) 2, (■, □) 4 or (▲, △) 6 wt % Y₂O₃. Results are shown for a densification temperature of (a, b) 1550 °C and (c, d) 1750 °C. (○, □, △) Composites made from unstabilized ZrO₂, (●, ■, ▲) composites made from ZrO₂ stabilized with 3 mol % Y₂O₃.

fracture toughness showed, however, a different behaviour as can be seen in Fig. 2b. When additions of unstabilized ZrO₂ were used instead of ZrO₂ (+ 3 mol % Y₂O₃), the K_{1C} values were significantly reduced.

The differences between materials with the same composition densified at the two temperatures are well illustrated in Fig. 3. In these diagrams, small differences between samples formed with additions of either ZrO₂ or ZrO₂(Y₂O₃) can be noted. Addition of both zirconia variants seemed to have a slightly positive effect on the fracture toughness of materials formed at 1750 °C. However, together with 2 wt% Al₂O₃, the ZrO₂(Y₂O₃) material showed a significantly higher increase, cf. Fig. 3d. The hardness of these ceramics showed the same general trend as that described above; the hardness decreased with increasing zirconia content. The hardness of composites densified at 1550 °C, was more scattered and showed no obvious trend.

The mechanical properties of Si₃N₄-ZrO₂ composites formed with additions of Y₂O₃ are summarized in Fig. 4. The measured hardness did not show the decrease with increasing zirconia content shown in Fig. 3, and remained fairly constant, although at different levels, for both the 1550 and 1750 °C samples. Y₂O₃ containing silicon nitride materials formed without zirconia at 1750 °C had the highest toughness values and increasing the addition of zirconia gave a small increase in fracture toughness, Fig. 4.

The observed mechanical behaviour of Si₃N₄ materials formed with simultaneous additions of Y₂O₃ and Al₂O₃ was fairly complex, see Figs 5 and 6. Generally, it can be said that the fracture toughness of the samples formed at 1750 °C was high; around 4 or slightly higher. The addition of ZrO₂ or ZrO₂(Y₂O₃) had no clear effect on the K_{1C} values, and a similar situation was found for the hardness of the materials. Some interesting details might be noted; a harder

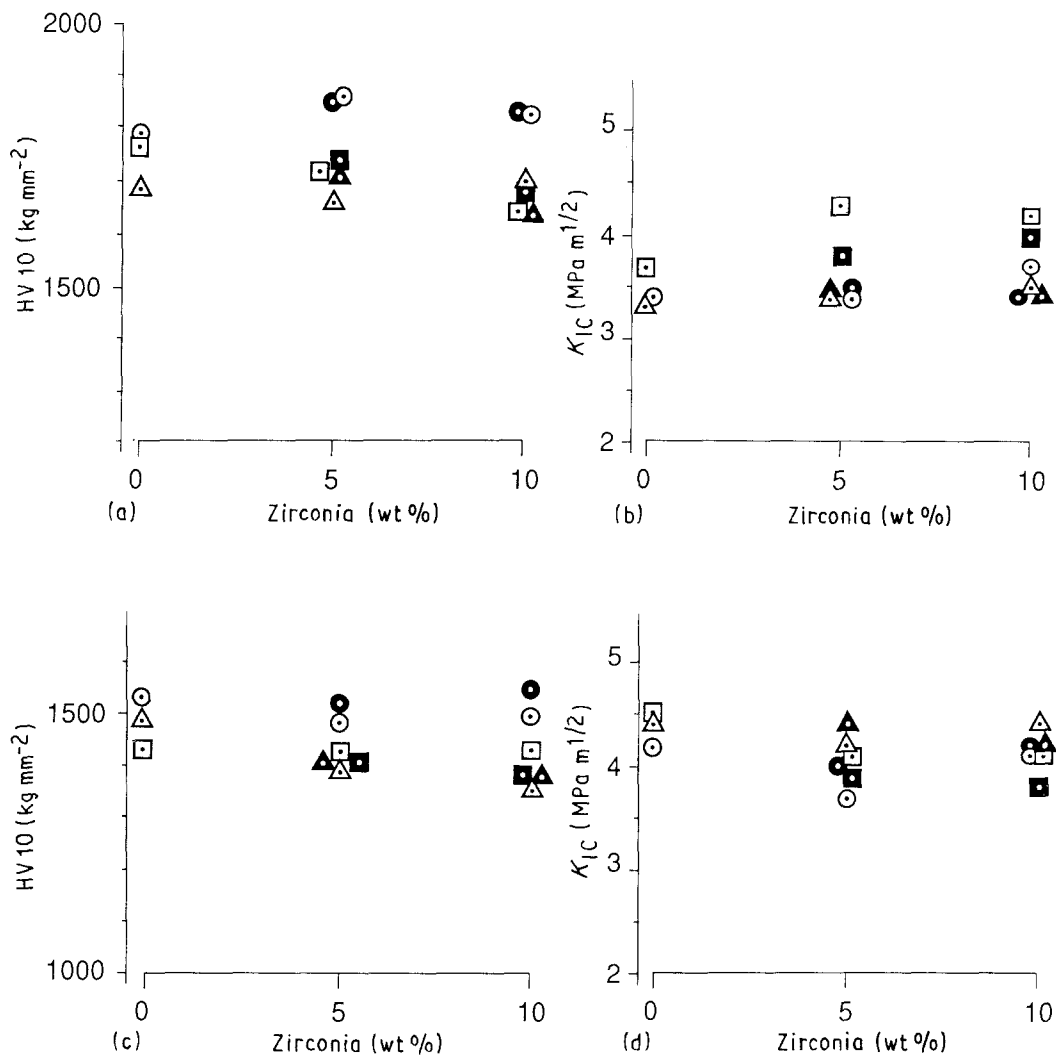


Figure 5 (a, c) Vickers hardness and (b, d) fracture toughness of Si_3N_4 -zirconia composites formed with additions of (●, ○) 2, (■, □) 4 or (▲, △) 6 wt% Y_2O_3 together with 2 wt% Al_2O_3 . Results are shown for densification temperatures of (a, b) 1550°C and (c, d) 1750°C. (○, □, △) Composites made from unstabilized ZrO_2 , (●, ■, ▲) composites made from ZrO_2 stabilized with 3 mol% Y_2O_3 .

material was formed when 4 wt % Al_2O_3 was added together with 2 wt % Y_2O_3 , than when 4 wt % Al_2O_3 was added together with 4 or 6 wt % Y_2O_3 . As can be seen from Table III, the latter materials had significantly lower Q value. The use of simultaneous additions of Y_2O_3 and Al_2O_3 for the formation of Si_3N_4 -based ceramics is considered to be of special interest because that might allow pressureless sintering to full density [22].

4. Discussion

4.1. Densification process

The observed densification behaviour during processing of the different materials, and the role of the sintering aids, can well be explained by the formation of a liquid phase between the metal oxides added and the silica adhering to the Si_3N_4 powder particles. The lowest reported eutectic temperatures in the systems Al_2O_3 - SiO_2 , Y_2O_3 - SiO_2 and ZrO_2 - SiO_2 are 1595, 1650 and 1640°C, respectively, and when the Si_3N_4 itself starts to dissolve in the liquid, the nitrogen content lowers the eutectic temperatures further to 1470, 1480 and 1590°C [23, 24]. In this study it was clearly seen that additions of ZrO_2 or $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ alone to

silicon nitride at the lower temperature (1550°C) did not promote densification when compared with "pure" silicon nitride, i.e. a density around 85% theoretical was achieved. This confirms that only a limited volume fraction of eutectic liquid was formed at 1550°C and that no significant amount of Y_2O_3 was released from the $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ grains to form a quaternary Y-Zr-Si-O liquid.

As indicated previously, the effective densification of composites formed with additions of Y_2O_3 stabilized ZrO_2 powder at 1750°C might, to some extent, be caused by Y_2O_3 diffusing out from the ZrO_2 [8, 11, 25]. It was shown by analytical transmission electron microscopy that a glassy phase, rich in cations from the metal oxide additives, was present in Si_3N_4 - ZrO_2 (+ Y_2O_3) composites formed both with and without Al_2O_3 . At a densification temperature of 1750°C, liquid-phase formation in these systems does not require the presence of Y_2O_3 , however, the presence of this oxide would affect the volume fraction and viscosity of the liquid which forms. The porosity observed in the Si_3N_4 - ZrO_2 composites made from unstabilized ZrO_2 and densified at 1750°C could therefore either reflect a reaction between the Si_3N_4 and the ZrO_2 resulting in formation of gaseous species, as predicted

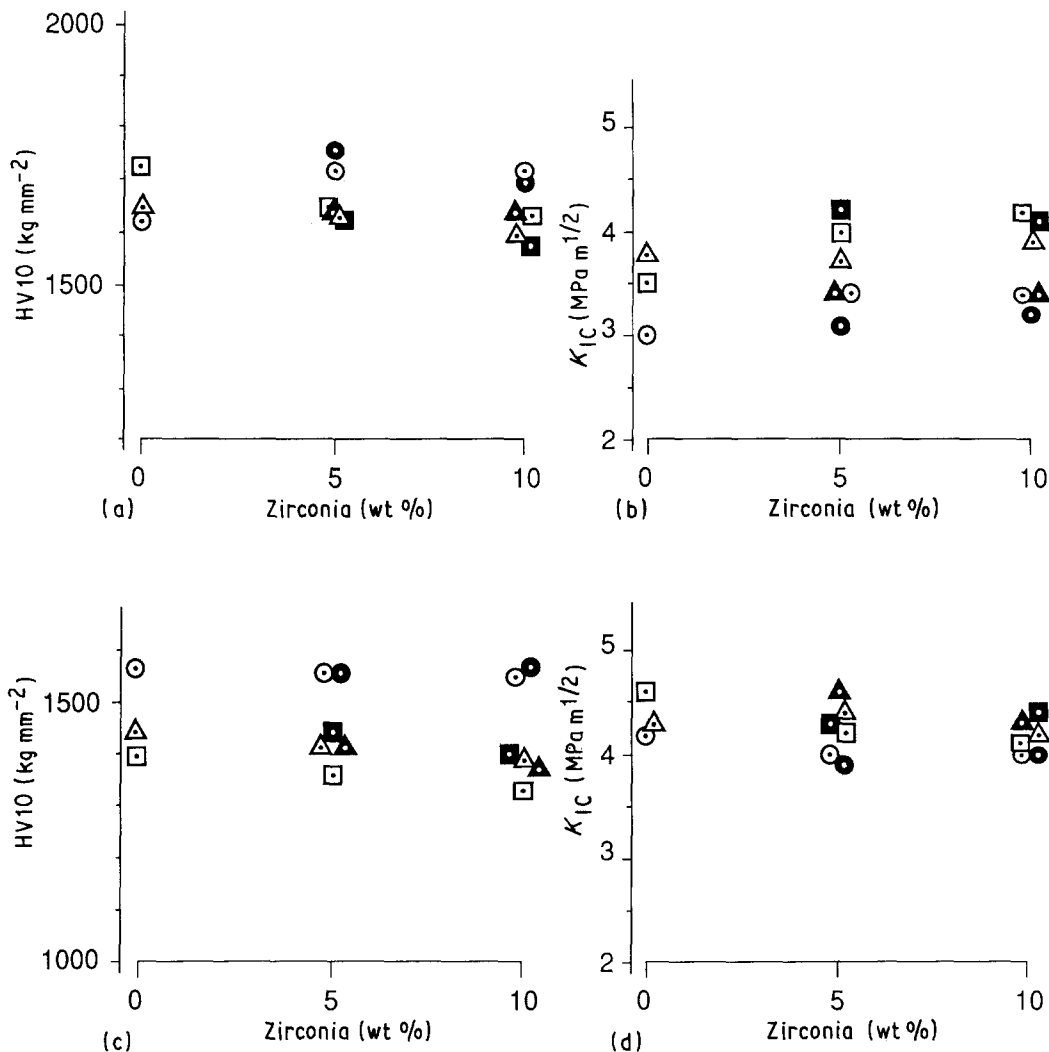


Figure 6 (a, c) Vickers hardness and (b, d) fracture toughness of Si_3N_4 -zirconia composites with additions of (●, ○) 2, (■, □) 4 or (▲, △) 6 wt % Y_2O_3 together with 4 wt % Al_2O_3 . Results are shown for densification temperatures of (a, b) 1550°C and (c, d) 1750°C. (○, □, △) Composites made from unstabilized ZrO_2 , (●, ■, ▲) composites made from ZrO_2 stabilized with 3 mol % Y_2O_3 .

by Weiss *et al.* [15], or an insufficient volume fraction of liquid phase present in the compact during densification. The formation of fully dense bodies when $\text{ZrO}_2(+3 \text{ mol } \% \text{ Y}_2\text{O}_3)$ powder was added instead, could possibly be explained by the dissolved Y_2O_3 which has been suggested to inhibit nitrogen uptake of the ZrO_2 phase [11]. This would suppress the reaction causing gas formation. One other possibility would be that a larger volume fraction of liquid phase forms in the Y-Zr-Si-O-N system at this temperature, which promotes densification. The observed densities of the Si_3N_4 - ZrO_2 composites in this study are in good agreement with those reported for similar composites formed by HIP by Terao *et al.* [7].

Additions of Al_2O_3 and/or Y_2O_3 always resulted in fully dense materials at 1750°C. Even a comparatively low amount of these sintering aids (1–2 wt %) formed a sufficient volume fraction of low-viscosity liquid through reaction with the surface silica on the Si_3N_4 powder particles, which facilitated solidification at the applied high external pressure (200 MPa). Processing at the lower temperature, however, did not result in dense bodies without an addition of either 1 wt % alumina or at least 4 wt % Y_2O_3 . The solubility of zirconia at low temperatures in these liquids is not

known, but it is generally expected that the solubility in pure silicate liquids is low, because zirconia can be used as a nucleating agent in glass ceramics. At higher sintering temperatures a fair amount of zirconia might dissolve. This was shown by Cheng and Thompson who studied Y_2O_3 - Al_2O_3 - SiO_2 liquids containing additions of ZrO_2 [26]. They observed that the solubility of ZrO_2 is around 10 wt % at 1700°C, but that dissolved zirconia will precipitate during cooling from the sintering temperature. This is in agreement with work carried out on composite ceramics formed in the Si_3N_4 - $\text{ZrO}_2(+\text{Y}_2\text{O}_3)$ system with additions of Al_2O_3 , which indicated that the ZrO_2 underwent a solution-precipitation process during densification [17]. Even when alumina is absent, zirconia probably has a high solubility at high temperatures as shown by Falk *et al.* [25] in a previous electron microscopy study on Si_3N_4 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ composites. They noted that the ZrO_2 grains often had irregular shapes and filled up space between Si_3N_4 grains, which strongly implies that ZrO_2 grains grew from the liquid during cooling. Similar microstructural observations have been made on the 1750°C materials in the present study, but these results will be presented in detail elsewhere [27].

A considerable portion of the ZrO_2 grains in the $\text{Si}_3\text{N}_4\text{-ZrO}_2$ composites had tetragonal structure, Tables I and II. This implies that size and composition of these grains allowed retention of the high temperature tetragonal form by mechanical constraints imposed by the surrounding matrix. Materials formed with Y_2O_3 -stabilized ZrO_2 as well as with a separate addition of Y_2O_3 contained only tetragonal ZrO_2 . It could be expected that some of the Y_2O_3 from a separate addition is incorporated into the ZrO_2 grains during densification which would contribute to a stabilization of the tetragonal structure [25]. In addition, it has previously been suggested that the tetragonal ZrO_2 structure present in some composites formed in the $\text{Si}_3\text{N}_4\text{-ZrO}_2(+\text{Y}_2\text{O}_3)$ system was stabilized by nitrogen [17]. This could, also in these materials, be a stabilizing agent, and affect the crystal structure of the ZrO_2 grains in the composites.

Significant amounts of residual $\alpha\text{-Si}_3\text{N}_4$ was present after densification at 1550°C , whereas only a very small volume fraction could be detected in some of the samples densified at 1750°C . The general trend was that increasing amounts of sintering aids appeared to promote the α to β transformation. This can be understood from the fact that the formation of $\beta\text{-Si}_3\text{N}_4$ is a solution-precipitation process (i.e. solution of $\alpha\text{-Si}_3\text{N}_4$ from the starting material in the liquid followed by precipitation of $\beta\text{-Si}_3\text{N}_4$). The high pressure during HIP will, as described above, give fully dense materials even if equilibrium is not attained in the solution-precipitation process. Densification with Al_2O_3 will result in formation of an Y-Si-Al-O-N liquid, and this opens up a possibility for some Al-O to enter the β phase structure with subsequent formation of β sialon, $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$. This was observed in some of the materials.

4.2. Mechanical properties

It is well known that a large quantity of pores in a ceramic material will reduce the measured hardness value, but increase the apparent toughness. The fracture toughness and hardness values in the present investigation have, therefore, been measured only on materials with a density of at least 99% theoretical.

The generally observed high hardness values of materials formed at 1550°C are believed to be caused by the substantial amount of unreacted $\alpha\text{-Si}_3\text{N}_4$ because it is known that the α form is harder than the β form of silicon nitride. Additions of zirconia could be expected to lower the hardness, as this constituent phase is fairly soft (about 1000 kg mm^{-2}). However, the hardness values of the 1550°C materials are scattered and such a trend is not obvious. One reason for the scatter in the observed hardness values might be the varying $\alpha\text{-Si}_3\text{N}_4$ content. In the samples formed at 1750°C , however, where little or no $\alpha\text{-Si}_3\text{N}_4$ is observed in the materials, it is clearly found that additions of zirconia lower the microhardness, see e.g. Fig. 2. Similar hardness behaviour is also reported by others [7]. It should be stressed, however, that the hardness does not decrease with increasing zirconia content in the composite as a general rule. Together with a separate

addition of Y_2O_3 , the hardness stays at about the same magnitude regardless of zirconia content, and this is roughly the case also for $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ additions, cf. Figs 4–6. This shows that other factors, such as grain size, or amount and hardness of the intergranular phase, also affect the measured value.

Silicon nitride densified without or with only very small additions of sintering aids had typically a fracture toughness of around $3\text{ MPa m}^{1/2}$ in the present investigation. Most of the materials in this study, especially when formed at 1750°C , showed a fracture toughness which was clearly increased above this value. There may be two different origins of this effect. A growth of elongated $\beta\text{-Si}_3\text{N}_4$ grains during densification would result in a fibrous microstructure and thereby an increased fracture toughness [28]. The observed increase in toughness of materials containing additions of ZrO_2 may, together with the duplex microstructure, be caused by mechanisms such as transformation toughening and ferroelasticity [29, 30]. In composites where only zirconia was added to the silicon nitride, the fracture toughness was clearly higher for $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ additions than for unstabilized ZrO_2 additions. In $\text{Si}_3\text{N}_4\text{-ZrO}_2$ composites containing Y_2O_3 , either originating from the stabilized ZrO_2 starting powder or from a separate Y_2O_3 addition, the ZrO_2 was present only with the tetragonal structure, whereas composites formed without Y_2O_3 contained substantial amounts of monoclinic ZrO_2 . This indicates that, apart from the Si_3N_4 matrix morphology, a ferroelastic or transformation toughening mechanism may possibly contribute to the toughness of these composites. On the other hand, when Y_2O_3 or $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ were added to the composites densified at 1750°C , high fracture toughness values could always be noted, and additions of zirconia did not seem to improve the toughness further. An increase in toughness of Si_3N_4 and β sialon materials with additions of ZrO_2 has previously been reported in a number of investigations [6, 7, 10, 31–34]. This phenomenon has frequently been explained by a transformation-toughening mechanism [6, 7, 10, 31, 32].

5. Concluding remarks

Composites prepared at 1550°C contained substantial amounts of residual $\alpha\text{-Si}_3\text{N}_4$ which made them harder and more brittle than composites formed at 1750°C .

Dense $\text{Si}_3\text{N}_4\text{-ZrO}_2(+\text{Y}_2\text{O}_3)$ composites could be prepared by HIP at 1750°C , but some porosity remained in the microstructure when the ZrO_2 starting powder was not stabilized by Y_2O_3 .

$\text{Si}_3\text{N}_4\text{-ZrO}_2$ composites formed with a separate addition of Y_2O_3 and/or Al_2O_3 were fully dense after densification at both 1550 and 1750°C .

Composites prepared at 1750°C had the highest fracture toughness values, and ZrO_2 transformation-toughening, ferroelasticity or the formation of elongated $\beta\text{-Si}_3\text{N}_4$ grains are suggested to be underlying causes.

Several materials densified at 1750°C had a good combination of hardness and fracture toughness: about 1450 kg mm^{-2} and $4.5\text{ MPa m}^{1/2}$, respectively.

Examples of such materials were either Si_3N_4 with additions of 2–6 wt % Y_2O_3 alone, or Si_3N_4 – ZrO_2 composites with simultaneous additions of 2–6 wt % Y_2O_3 and 2–4 wt % Al_2O_3 .

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