Journal of the European Ceramic Society 16 (1996) 535-543

0955-2219/96/$15.00
0955-2219(95)00126-3

Si_2N_2O–ZrO_2 Composites Prepared by Hot Isostatic Pressing

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(Received 17 February 1995; revised version received 26 June 1995; accepted 14 July 1995)

Abstract

Fully dense Si_2N_2O–ZrO_2 composites have been prepared by glass-encapsulated hot isostatic pressing at 1600 and 1700°C by two different routes. Firstly, from reacting powder mixtures of equimolar amounts of Si_3N_4 plus SiO_2 with 0, 5 and 20 wt% ZrO_2 or ZrO_2 (3 mol% Y_2O_3), and secondly by an in-situ reaction from equimolar mixtures of Si_3N_4 and $ZrSiO_4$ to form a Si_2N_2O composite with 36 wt% ZrO_2. The effects of small additions of Al_2O_3 or Y_2O_3 in the two different preparation routes were also studied. It was found that the reaction of Si_3N_4 with SiO_2 was strongly influenced by the addition of sintering aids and temperature, whereas the reaction with $ZrSiO_4$ was mainly temperature controlled and proceeded rapidly at 1700°C.

Addition of zirconia or stabilized zirconia did not appear to have any positive effect on the toughness, and the materials prepared were in general brittle with a fracture toughness of ~3 MPa $m^{1/2}$. The observed hardness was typically 12–14 GPa for the composites. The composites which consisted of more or less unreacted starting materials had a very fine-grained microstructure. In the fully reacted samples which had the highest fracture toughness the zirconia grains had increased in size compared to the more brittle samples.

1 Introduction

Improving high-temperature chemical resistance and mechanical properties, in particular of engineering ceramics, has been an important focus for some time. Oxide based ceramics are often chemically inert but are more brittle than the silicon nitride based ceramics, for instance. Non-oxide ceramics, on the other hand, are generally not very oxidation resistant when heated to high temperatures in oxidizing environments, but exceptions are found for silicon based ceramics, which develop a protective silica film on the surface, e.g. silicon carbide, silicon nitride and silicon oxynitride. From among these compounds silicon oxynitride (Si_2N_2O) has been shown to be very oxidation resistant and materials based on the oxynitride have therefore been considered as very promising candidates for high temperature engineering purposes.[1–5]

In a number of previous studies silicon oxynitride ceramics have, therefore, received attention, but it was found that formation of the Si_2N_2O phase by conventional sintering of equimolar mixtures of Si_3N_4 and SiO_2 powders at high temperatures is difficult in the absence of added sintering aids.[6–8] The Si_2N_2O phase forms and the flake-like crystals precipitate through a transient melt of silica in which the Si_3N_4 initially added dissolves. The kinetics of this process are very slow in a pure silica melt because of its extreme viscosity, even at high temperatures. Additions of small amounts of a number of metal oxides which initially react with the silica melt and thereby reduce the overall viscosity have been shown to greatly facilitate both the formation and the densification of silicon oxynitride ceramics.[9–12]

Composite ceramic materials based on Si_2N_2O with additions of pure ZrO_2 or ZrO_2 stabilized by Y_2O_3 (typically 3 mol%) have also gained attention in the past.[10,13–15] The motivation for adding zirconia to the Si_2N_2O ceramics originates from the assumption that ZrO_2 might have potential as a toughening and strengthening agent in these fairly brittle ceramics, in a similar way as has been observed for the addition of ZrO_2 to oxide matrices. Zirconia additions may also act as an effective sintering aid at preparation temperatures above 1750°C, which are normally used for nitride ceramics (see, for example, Refs 16–20). The formation of silicon oxynitride at 1700°C by hot pressing of silicon nitride and silica with ZrO_2 and ZrO_2(2·8 mol% Y_2O_3) was, for instance, studied by Ohashi and co-workers.[10] However, the dispersed particles of zirconia were not found to contribute to toughening of the oxynitride ceramics and the indentation fracture toughness was ~3 MPa $m^{1/2}$.

The observed lack of a transformation toughening effect of zirconia in silicon oxynitride ceramics has been proposed by Cheng and co-workers[15] to be the result of dissolution of nitrogen into the zirconia structure. This N-substitution results in further stabilization of the high-temperature tetragonal ZrO_2 crystal form and thus prevents the martensitic transformation to the monoclinic form under mechanical stress. This hypothesis is in agreement with similar findings in the Si_3N_4–ZrO_2 composites where the fracture toughness at room temperature remained essentially unchanged.[20]

Two major preparation routes have been used in the past to prepare Si_2N_2O–ZrO_2 composites. The first and most well-known is from powder mixtures of equimolar amounts of Si_3N_4 and SiO_2, with ZrO_2 or $ZrO_2(Y_2O_3)$ added separately. An alternative route is via the *in-situ* reaction involving sintering of equimolar mixtures of Si_3N_4 and $ZrSiO_4$ to form a Si_2N_2O composite with 36 wt% ZrO_2.[21,22] The advantage of using the second route is the 'freedom' of preparing the materials with no or only minor additions of sintering aids, but a drawback is the substantial amount of ZrO_2 that is formed (~24 vol%). Also, there is a risk that oxidation of these materials may occur when used in air at temperatures above 1000°C. A porous oxide scale containing silica and $ZrSiO_4$ is formed and, especially at temperatures above 1250°C, a severe degradation of the materials has been observed as this oxide scale provided poor protection against further oxidation.[14] At these high zirconia contents it might also be expected that the surface stresses which result from the large volume expansion during oxidation will become significant, leading to cracking and spalling.[23]

In the present study the effects of starting materials, reaction route and overall composition on the properties of fully dense $Si_2N_2O + ZrO_2$ composite ceramics prepared by glass-encapsulated hot isostatic pressing (HIP) have been explored. The effects of small amounts of sintering aids (yttria or alumina) have also been studied. The results from phase analysis and microstructure characterization will be presented and discussed in relation to the observed mechanical properties.

2 Experimental Procedures

Table 1. Characteristics of the materials prepared and the densities obtained after glass-encapsulated HIP for 2 h, 200 MPa, at 1600 (HIP1600) and 1700°C (HIP1700). In series A equimolar mixtures of Si_3N_4 and SiO_2 were used as the starting materials to form Si_2N_2O and zirconia; sintering aids were added separately. In series B equimolar mixtures of Si_3N_4 and $ZrSiO_4$ were used in a sintering reaction to form an Si_2N_2O–ZrO_2 composite with 36 wt% ZrO_2

Sample series	*Additives (wt%)*				*Density (g cm⁻³)*	
	ZrO_2	*$ZrO_2(Y_2O_3)$*	*Al_2O_3*	*Y_2O_3*	*HIP1600*	*HIP1700*
A	—	—	—	—	2·827	2·829
A	5	—	—	—	2·897	2·898
A	—	5	—	—	2·896	2·893
A	5	—	2	—	2·880	2·892
A	—	5	2	—	2·875	2·891
A	20	—	—	—	3·082	3·087
A	—	20	—	—	3·075	3·078
A	20	—	2	—	3·050	3·045
A	—	20	2	—	3·042	3·042
A	—	20	5	—	3·040	3·029
B	(36)	—	—	—	3·387	3·382
B	(36)	—	1	—	3·379	3·393
B	(36)	—	2	—	3·384	3·380
B	(36)	—	4	—	3·371	3·341
B	(36)	—	8	—	3·362	3·390
B	(36)	—	—	1	3·429	3·437
B	(36)	—	—	2	3·440	3·441
B	(36)	—	—	4	3·462	3·432
B	(36)	—	2	1	3·399	3·349
B	(36)	—	2	4	3·460	3·445

Selected $Si_2N_2O + ZrO_2$ compositions were prepared by two reaction routes from different starting materials. Firstly, equimolar mixtures of Si_3N_4 and SiO_2 were used (series A), with additions of 0, 5 and 20 wt% ZrO_2 or 0, 5 and 20 wt% ZrO_2(3 mol% Y_2O_3), and with 0–5 wt% Al_2O_3 added (cf. Table 1). And secondly, equimolar mixtures of Si_3N_4 and $ZrSiO_4$ (series B) were taken, which after reaction form an Si_2N_2O composite containing 36 wt% ZrO_2. With the latter materials 0–8 wt% Al_2O_3 and 0–4 wt% Y_2O_3 were added as sintering aids.

The source materials used were silicon nitride (H.C. Starck-Berlin, grade LC1), silicon dioxide (analytical purity), zirconium dioxide (Chema Tex, grade SC16), zirconium silicate (Ventron), aluminium oxide (Alcoa, grade A16SG), yttrium oxide (H.C. Stark-Berlin, finest grade) and yttrium oxide stabilized with 3 mol% Y_2O_3 (TOSOH, grade TZ-3Y). The starting powders were carefully weighed, mixed in water-free propanol and milled in a vibratory mill for 17 h with sialon milling media. After drying, the powder mixes were dry-pressed (125 MPa) into compacts of size 16 × 16 × 6 mm. The samples were glass-encapsulated and hot isostatically pressed at 1600 and 1700°C for 2 h with an argon pressure of 200 MPa.

Density measurements using Archimedes principle were made on the as-sintered samples. Hardness (HV_{10}) and indentation fracture toughness (K_{IC}) at room temperature were obtained by a

Vickers diamond indenter using 98 N (10 kg) load. The fracture toughness was evaluated by the formula given by Anstis *et al.*,[24] using a value of 290 GPa for Young's modulus, and the precision of repeated measurements on the same sample was ± 0·2. The phase analysis was based on X-ray powder patterns recorded by Guinier–Hägg cameras. Scanning electron microscopy (SEM) was performed on carbon-coated materials, using a Jeol JSM 6400 microscope equipped with Tracor System EDS and WDS analysers.

3 Results

3.1 Densification

HIPed materials from both preparation routes (series A and B) sintered at two temperatures (1600 and 1700°C) were examined by optical microscopy or SEM on polished cross-sections and were found to be virtually pore-free, i.e. fully dense. Thus densification took place even if the reaction of the starting materials to yield silicon oxynitride was sometimes poor (cf. below). It can be noted in Table 1 that the density of the equimolar $Si_3N_4 + SiO_2$ mix was found to be 2·83 g cm^{-3}, which at first looked surprisingly close to the theoretically calculated density of the silicon oxynitride structure, 2·82 g cm^{-3},[6] despite the observation that a reaction had not taken place. The mixture of equal volumes of silicon nitride (density ~3·2 g cm^{-3}) and silica (density ~2·6 g cm^{-3}) would, however, theoretically yield ~2·9 g cm^{-3} for a fully dense body, even when the oxynitride is not formed.

It was found that the measured density of the HIPed materials of series A increased as expected with increasing ZrO_2 additions (density ~5·9 g cm^{-3}) from 2·83 to 3·08 g cm^{-3} for 20 wt% ZrO_2. In series B the amount of zirconia formed by the *in-situ* reaction was considerably higher (36 wt%) and therefore the densities were higher and varied somewhat from 3·38 to 3·46 g cm^{-3} depending on the amount of sintering aid added. Small additions of alumina generally lowered the density slightly, whereas additions of yttria gave rise to a small increase in observed density.

3.2 X-ray diffraction phase analysis

The formation of the silicon oxynitride phase from silicon nitride and silica (series A) was strongly dependent on the addition of sintering aids and sintering temperature. The X-ray diffraction results are summarized in Table 2. Without any alumina or yttria added prior to sintering, no oxynitride phase were formed even at the higher temperature, and the crystalline content of the sample mainly reflected the Si_3N_4 initially added, where the α-Si_3N_4/β-Si_3N_4 ratio determined by X-ray diffraction (XRD) was 96:4. This phase ratio is unchanged at 1600°C, whereas at 1700°C some formation of the β-phase took place during sintering.

Table 2. Results of X-ray diffraction analysis of series A, where equimolar mixtures of Si_3N_4 and SiO_2 were used as the starting materials to form the parent Si_2N_2O-matrix and zirconia and/or sintering aids were added separately

Preparation temperature (°C)	*Additives (wt%)*			*XRD results*			
	ZrO_2	$ZrO_2(Y)$	Al_2O_3	*Phase analysis**	*Q*	*T*	*S*
1600	—	—	—	α, β	0·96	—	—
1600	5	—	—	α, β, ZrO	0·98	0·39	—
1600	—	5	—	α, β, ZrO,	0·92	1	—
1600	5	—	2	α, β, ZrO,	0·86	—	—
1600	—	5	2	α, ZrO, SNO	1	0·14	0·27
1600	20	—	—	α, ZrO	1	1	—
1600	—	20	—	α, β, ZrO	0·95	1	—
1600	20	—	2	α, ZrO, SNO	1	—	0·76
1600	—	20	2	α, ZrO, SNO	1	—	0·90
1600	—	20	5	α, ZrO, SNO	1	—	0·90
1700	—	—	—	α, β	0·91	—	—
1700	5	—	—	α, β, ZrO	0·92	1	—
1700	—	5	—	α, β, ZrO, SNO	0·73	0·45	0·86
1700	5	—	2	α, ZrO, SNO	1	—	0·88
1700	—	5	2	α, ZrO, SNO	1	0·50	0·91
1700	20	—	—	α, ZrO	1	0·34	—
1700	—	20	—	α, ZrO, SNO	1	—	0·89
1700	20		2	α, ZrO, SNO	1	0·33	0·92
1700	—	20	2	α, ZrO, SNO	1	—	1
1700	—	20	5	ZrO, SNO	—	0·10	1

*α and β denote α- and β-Si_3N_4, respectively, and ZrO and SNO denote ZrO_2 and Si_2N_2O, respectively.
Q= $\alpha/(\alpha + \beta)$–Si_3N_4 phase ratio.
T= Tetragonal /(tetragonal + monoclinic + cubic)–ZrO_2 phase ratio.
S= $Si_2N_2O/(\alpha\text{-}Si_3N_4 + \beta\text{-}Si_3N_4 + Si_2N_2O)$ phase ratio.

At the lower sintering temperature only yttria-doped ZrO_2 combined with alumina addition supported formation of the silicon oxynitride phase in series A. The added zirconia was found to be present as the monoclinic and tetragonal forms in the sintered materials and the relative amount of each phase was roughly estimated by comparison of peak height ratios. Small amounts of cubic ZrO_2 present simultaneously with the tetragonal phase are difficult to detect because of extensive peak overlap. Occasionally a few very weak peaks occurred in the X-ray spectra, which were not possible to identify with any certainty. However, some of the weak peaks indicate the presence of the phases ZrN and $Zr_7O_{11}N_2$.

At the higher sintering temperature (1700°C) the composites of series A formed more silicon oxynitride, but only in the material with the highest amount of alumina added to an yttria-doped zirconia was complete reaction of the starting materials to Si_2N_2O achieved. At this temperature the yttria-doped zirconia itself also promoted a fair degree of oxynitride formation, whereas addition of pure zirconia had no observable positive effect (cf. Table 2). Again weak peaks occurred indicating the presence of small amounts of additional phases.

The phase analysis of the materials formed by reaction of silicon nitride with zirconium silicate (series B) is summarized in Table 3. At the lower temperature (1600°C) the reaction is mostly incomplete, as greater or lesser amounts of silicon nitride were identified in HIPed materials. Residual $ZrSiO_4$ is, however, only found in the materials with no addition of sintering aids or with only 1 wt% alumina added. The amount of silicon oxynitride formed seems to be relatively independent of the amounts of alumina or yttria added, and even with both sintering aids added simultaneously complete reaction was not obtained at this temperature. Weak additional X-ray peaks were also found in these samples.

The results obtained for series B at 1700°C are quite different and complete reaction to form $Si_2N_2O + ZrO_2$ has occurred for all materials. The zirconia identified in these preparations by XRD was sometimes present as either monoclinic or tetragonal ZrO_2, but often as a mixture of the two crystal modifications.

3.3 Mechanical properties

The use of the HIP technique assured that all materials were fully dense even if the formation of silicon oxynitride was not always complete. In this way the mechanical properties of the ceramics could still be evaluated. Thus, the room temperature Vickers hardness (HV_{10}) and indentation fracture toughness (K_{IC}) were measured on all materials and the results are summarized for series A and B in Tables 4 and 5, respectively.

It can be seen that in both series the hardness is ~12–14 GPa and the fracture toughness is typically between 2·2 and 3·5 MPa $m^{1/2}$. No improvement

Table 3. Results of X-ray diffraction analysis of series B, where equimolar mixtures of Si_3N_4 and $ZrSiO_4$ were used in sintering reaction to form a Si_2N_2O composite with 36 wt% ZrO_2

Preparation temperature (°C)	*Additives (wt%)*		*Phase analysis**	*XRD results*		
	Al_2O_3	*Y_2O_3*		*Q*	*T*	*S*
1600	—	—	α, ZrO, SNO, $ZrSiO_4$	1	—	0·55
1600	1	—	α, ZrO, SNO, $ZrSiO_4$	1	—	0·69
1600	2	—	α, ZrO, SNO	1	—	0·71
1600	4	—	ZrO, SNO	—	0·02	1
1600	8	—	α, ZrO, SNO	1	0·31	0·83
1600	—	1	α, ZrO, SNO	1	0·92	0·42
1600	—	2	α, ZrO, SNO	1	1	0·73
1600	—	4	α, ZrO, SNO	1	1	0·45
1600	2	1	α, ZrO, SNO	1	0·03	0·67
1600	2	4	α, ZrO, SNO	1	1	0·95
1700	—	—	ZrO, SNO	—	0·10	1
1700	1	—	ZrO, SNO	—	0·03	1
1700	2	—	ZrO, SNO	—	0·2	1
1700	4	—	ZrO, SNO	—	—	1
1700	8	—	ZrO, SNO	—	0·03	1
1700	—	1	ZrO, SNO	—	1	1
1700	—	2	ZrO, SNO	—	1	1
1700	—	4	ZrO, SNO	—	0·26	1
1700	2	1	ZrO, SNO	—	0·27	1
1700	2	4	ZrO, SNO	—	1	1

*α and β denote α- and β-Si_3N_4, respectively, and ZrO and SNO denote ZrO_2 and Si_2N_2O, respectively.
Q= α/(α + β)–Si_3N_4 phase ratio.
T= Tetragonal /(tetragonal + monoclinic + cubic)-ZrO_2 phase ratio.
S= Si_2N_2O/(α-Si_3N_4 + β-Si_3N_4 + Si_2N_2O) phase ratio.

Table 4. Room temperature hardness (HV_{10}) and indentation fracture toughness (K_{IC}) of series A. Equimolar mixtures of Si_3N_4 and SiO_2 were used as the starting materials to form the parent Si_2N_2O-matrix and zirconia and/or sintering aids were added separately

Preparation temperature (°C)	*Additives (wt%)*			HV_{10} *(GPa)*	K_{IC} *(MPa $m^{1/2}$)*
	ZrO_2	*$ZrO_2(Y)$*	*Al_2O_3*		
1600	—	—	—	13·0	3·5
1600	5	—	—	12·6	4·0
1600	—	5	—	12·4	2·9
1600	5	—	2	12·7	2·8
1600	—	5	2	13·9	2·3
1600	20	—	—	12·4	2·9
1600	—	20	—	12·5	2·9
1600	20	—	2	14·0	2·3
1600	—	20	2	14·4	2·2
1600	—	20	5	13·8	2·5
1700	—	—	—	12·6	2·7
1700	5	—	—	13·1	2·3
1700	—	5	—	13·8	2·1
1700	5	—	2	13·2	2·0
1700	—	5	2	12·5	2·1
1700	20	—	—	12·3	2·8
1700	—	20	—	13·1	2·3
1700	20	—	2	13·4	2·3
1700	—	20	2	14·1	2·2
1700	—	20	5	13·8	2·2

of the fracture toughness of series A seems to occur when increasing amounts of zirconia are added. In series B, which contains a considerable amount of zirconia, the ceramics are still brittle and only addition of alumina seems to have some small positive effect on the toughness. In the latter series addition of yttria alone gives a slightly higher hardness. The magnitude of the properties, however, are low compared with a typical silicon nitride based ceramic and more nearly resemble values typical for oxide ceramics. This will be discussed below as these values are correlated to either incomplete chemical reaction or the nature of the phases present.

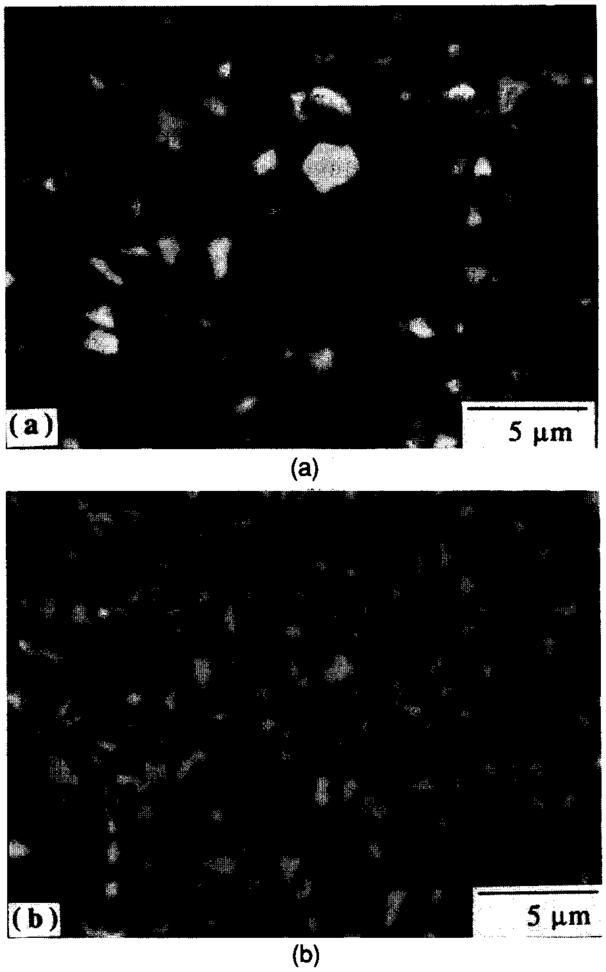
Table 5. Room temperature hardness (HV_{10}) and indentation fracture toughness (K_{IC}) of series B, where equimolar mixtures of Si_3N_4 and $ZrSiO_4$ were used in a sintering reaction to form a Si_2N_2O composite with 36 wt% ZrO_2

Preparation temperature (°C)	*Additives (wt%)*		HV_{10} *(GPa)*	K_{IC} *(MPa $m^{1/2}$)*
	Al_2O_3	*Y_2O_3*		
1600	—	—	13·1	2·7
1600	1	—	12·5	2·6
1600	2	—	12·4	2·9
1600	4	—	12·0	3·4
1600	8	—	12·4	2·9
1600	—	1	12·4	3·0
1600	—	2	12·7	2·3
1600	—	4	12·3	2·5
1600	2	1	11·6	2·8
1600	2	4	13·4	2·6
1700	—	—	12·9	2·6
1700	1	—	13·0	2·8
1700	2	—	12·8	3·1
1700	4	—	12·5	3·5
1700	8	—	12·3	3·4
1700	—	1	13·2	2·6
1700	—	2	13·6	2·3
1700	—	4	14·1	2·2
1700	2	1	12·6	2·8
1700	2	4	12·9	2·6

3.4 Microstructure

Generally, the materials which consisted of more or less unreacted starting powders have a very small grain size, ≤ 1 μm, and only the phases rich in zirconium were easy to distinguish. This was especially true for many of the samples HIPed at 1600°C (see Fig. 1).

For series A sintered at 1700°C all samples are very brittle (see above) and thus have not been studied in detail. However, as an example of such a structure, the sample containing 20 wt% yttria-doped zirconia is shown in Fig. 2. The structure is seen to be very fine grained. Many of the zirconia grains are smaller than 0·2 μm. A few larger α-Si_3N_4 grains can also be seen.



(a)

(b)

Fig. 1. SEM image of sample in series A containing 20 wt% ZrO_2 (a) and sample in series B containing 8 wt% Al_2O_3 as sintering aid (b), sintered at 1600°C. The bright areas correspond to the zirconia grains, whereas the dark area is a mixture of the other phases which formed.

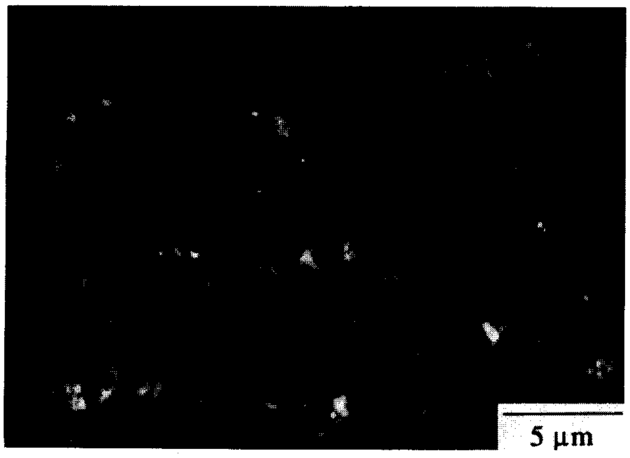


Fig. 2. SEM image of sample in series A containing 20 wt% yttria-stabilized zirconia as sintering aid.

In series B sintered at 1700°C the maximum fracture toughness was achieved when only alumina was used as sintering aid (see above). When comparing the sample containing no sintering aid [Fig. 3(a)] with the one containing 8 wt% alumina [Fig. 3(c)], it can be seen that the addition of alumina increases the size of the zirconia grains. Without any sintering aid the zirconia grains are very small (< 1 μm), whereas the size of the grains has increased to ~4 μm in the alumina-containing sample. When comparing the size of the zirconia grains as the amount of alumina added increases gradually, i.e. including the sample containing 4 wt% alumina [Fig. 3(b)], it can be seen that the size of the zirconia grains is dependent on the alumina content. The composition does not, however, affect the size of the Si_2N_2O grains as much. The grains are needle-shaped with a length of ~4 μm and a short axis of ~0·5 μm. This is also true for the remaining samples in this series.

Also seen in Figs 3(a)–(c) is the effect of the zirconia grain size on the shape of the various crack paths. In the sample with the smallest grains [Fig. 3(a)] the crack path is fairly straight and transgranular and only weakly influenced by the zirconia grains. In the samples with the largest zirconia grains [Figs 3(a) and (b)] the crack path is much more winding and seems to develop in both a trans- and intragranular way.

4 Discussion

For both preparation routes, as expected, an increase in sintering temperature was found to affect the reaction to form silicon oxynitride. However, the dissolution of the starting material in the transient liquid and the transport of species by diffusion will in these cases also be important rate controlling steps. This is clearly seen for the reaction of silicon nitride with silica (series A), where additions of sintering aids to lower the viscosity is crucial. At 1600°C addition of both alumina plus yttria (released from the zirconia) was needed to lower the viscosity of the silica melt

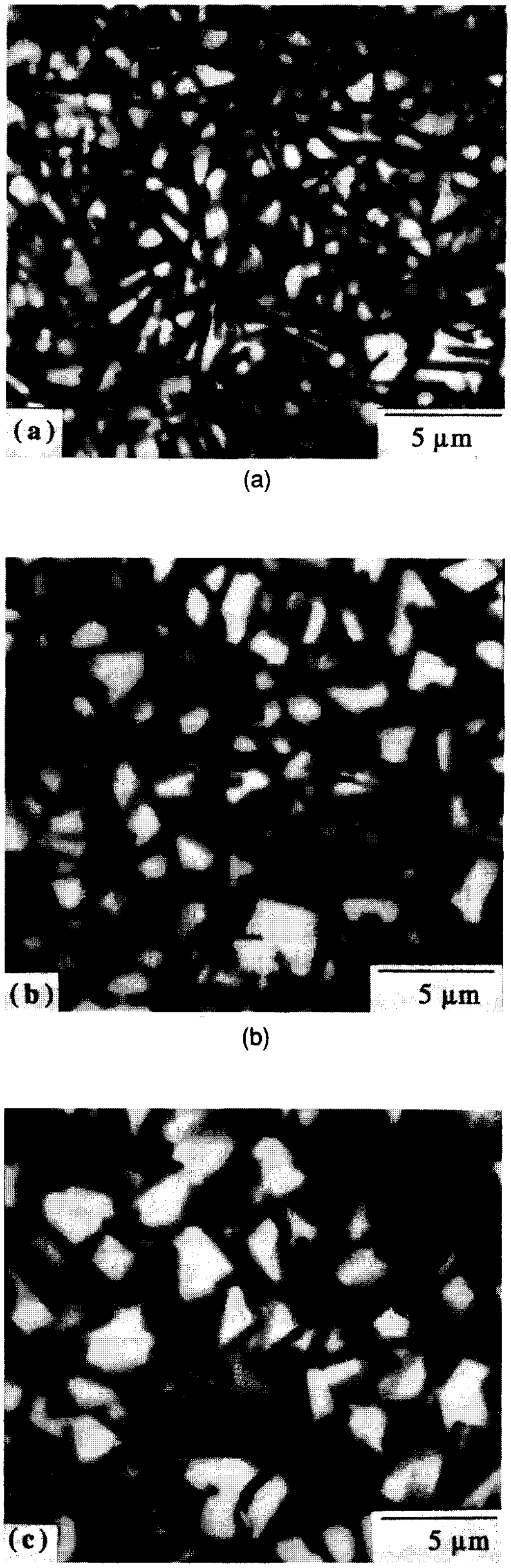


Fig. 3. SEM images showing the microstructure and representative crack deflection profiles of the undoped sample (a) and samples containing 4 wt% (b) and 8 wt% alumina (c) in series B, sintered at 1700°C.

to an extent where a sufficiently rapid diffusion occurred, whereas at the higher temperature both alumina addition or yttria from $ZrO_2(Y_2O_3)$ can achieve this effect. It should be stressed, however, that addition of pure zirconia did not help even at the higher temperature used (1700°C).

These observations are in agreement with earlier findings where silicon nitride and silica mixtures with additions of ZrO_2 or ZrO_2(2·8 mol% Y_2O_3) were hot-pressed at 1700°C.[10] It was found that the reaction rate for the Si_2N_2O formation was slow for the pure ZrO_2 additions, whereas Y_2O_3 released from ZrO_2(2·8 mol% Y_2O_3) additions increased the reaction rate considerably. The previous authors suggested that this behaviour was caused by the fairly high eutectic temperature of 1590°C found for the ZrO_2–SiO_2–Si_3N_4 system, whereas some yttrium released from the yttria-stabilized zirconia would lower both the eutectic temperature and the viscosity of the liquid significantly.

When silicon nitride reacts with zirconium silicate the decomposition of this phase will become important. As $ZrSiO_4$ is not stable at temperatures above 1675°C,[25] this will stimulate the reaction at the higher sintering temperature, and indeed all materials HIPed at 1700°C were found to be fully reacted. At the lower temperature, however, the reaction to form silicon oxynitride is surprisingly unaffected by sintering additives, which indicates that diffusion through a transient liquid is less important in determining the reaction rate. The results thus imply that the dissolution of the zirconia silicate into the liquid may be the rate controlling step in this case.

The solubilities of zirconia or zirconium silicate at 'low' temperatures in silica or silicon oxynitride liquids are not well known, but it is generally expected that the solubility is low because zirconia additions can be used as nucleation agents in glass ceramics. At higher temperatures, however, a fair amount of these zirconium compounds may dissolve as shown by Cheng and Thompson.[26] They observed that the solubility of ZrO_2 increases to ~10 wt% at 1700°C. The dissolved zirconia will, however, precipitate rapidly during cooling from this temperature. Rapid solidification of zirconia that has been partly dissolved and has acted as an sintering aid also seems to take place for Si_3N_4–ZrO_2 composites prepared at 1750°C.[20] This can schematically be illustrated in a Jänecke prism for two temperatures below and above the decomposition of $ZrSiO_4$ and is shown as the increasing solubility of Zr in the liquid in Fig. 4. The reaction of silicon nitride with zirconium silicate at the lower temperature proceeds slowly due to limited Zr solubility, whereas at the higher temperature the silicate will dissociate into zirconia + silica and the Zr solubility is drastically increased and thus opens a path for rapid reaction. Addition of up to 4 wt% yttria to the starting mix at the lower temperature does not appear to improve the degree of reaction significantly. Other sintering aids such as Sm_2O_3, however, have been reported to have a remarkably positive effect for such small additions.[21,22] Sintering temperatures of 1500–1550°C could be used, which is well below the dissociation temperature of zirconium silicate, and dense materials were obtained.

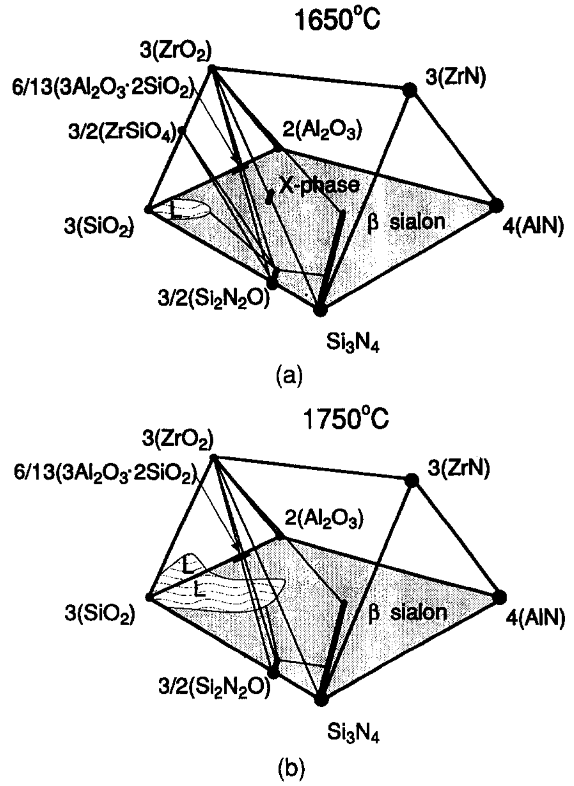


Fig. 4. Zr–Si–Al–O–N system at (a) 1650°C and (b) 1750°C, represented as Jänecke prisms.

The hardness values obtained in this study were of the order of 12–14 GPa, which can be compared with 15·2 and 15·0 GPa reported for dense Si_2N_2O and O'sialon ceramics, respectively.[6,7] The reaction to the oxynitride was incomplete in many of the silicon nitride/silica preparations and the observed hardness is affected negatively by the fairly soft silica glass. In addition, zirconia does not form very hard ceramics (~10 GPa) and when present in large amounts in the composites this will lower the hardness value. In series B HIPed at 1700°C, for instance, the materials have reacted to Si_2N_2O containing ~24 vol% ZrO_2 and the expected hardness is about 13–14 GPa, in fair agreement with the observed values.

The reported fracture toughness of dense Si_2N_2O and O'sialon ceramics is of the order of 3·1–3·5 MPa $m^{1/2}$.[6,7] In this study, however, the materials are generally more brittle, with the exception of the ceramics of series B sintered at 1700°C containing only alumina as sintering aid, which reaches this level. Since there is only a very small amount of tetragonal zirconia present ($T < 0{\cdot}03$), transformation toughening is not responsible for this. However, in these samples the size of the zirconia grains has increased compared with the other samples. It thus appears that this influences the fracture toughness in a positive manner. This can be seen when comparing the different crack paths in the different samples. In the samples containing the largest zirconia grains the crack path is more irregular compared to the samples with the smallest zirconia grains. The cracks develop in both a trans- and intragranular way. Since there are a number of factors influencing the crack deflection pattern, i.e. the composition of the intergranular phase, the strength of the interfacial bonding and the different thermal expansion coefficients of the different phases (none of which has been determined), it is not easy to determine the crack growth mechanism or why the fracture toughness increases in these samples. However, it should be stressed that the addition of zirconia or stabilized zirconia does not appear to have any positive effect on the fracture toughness. This is perhaps unexpected, but similar findings have been reported previously for zirconia added to silicon nitride.[20] This phenomenon has been discussed in depth by Cheng *et al.*[15] They concluded that by dissolution of nitrogen into the zirconia, which simultaneously created oxygen vacancies in the crystal lattice, the non-transformable tetragonal zirconia (t') phase forms. No transformation toughening will therefore be possible, although a tetragonal phase might be confirmed to be present by XRD.

The preparation of Si_2N_2O–ZrO_2 composites is less straightforward and the observed mechanical properties are lower than those obtained for the O'sialon ceramics.[7] In addition, the oxygen resistance of the former materials has been reported to be inferior at high temperatures,[14] especially compared with pure Si_2N_2O.[3–5]

5 Conclusions

The reaction of Si_3N_4 with SiO_2 is strongly dependent on the addition of sintering aids, and is also affected by temperature, whereas the reaction of Si_3N_4 with $ZrSiO_4$ was mainly temperature controlled and proceeded rapidly at 1700°C. Addition of zirconia or stabilized zirconia did not appear to have any positive effect on the toughness and the prepared materials were, in general, brittle with a fracture toughness of ~3 MPa m$^{1/2}$. The observed hardness was typically 12–14 GPa for the composites. Generally, the composites which consisted of more or less unreacted starting materials had a very fine-grained microstructure. In the fully reacted samples which had the highest fracture toughness the zirconia grains had increased in size compared to the more brittle samples.

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