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Microstructure and mechanical properties of nanoscale SiC/Ca α-SiAlON composites

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Ceramic composites comprising nanoscale (less than 200 nm) silicon carbide particles distributed in a matrix of calcium α-SiAlON (α′) have been prepared by uniaxial hot pressing, and the reaction sequence, during densification of a sample containing 20 wt% SiC, has been investigated in the temperature range 1400–1800 °C. Samples containing up to 20 wt% SiC were produced to near full density by pressure sintering at temperatures as low as 1600 °C for 1 h. For samples with higher SiC contents subjected to a similar treatment, there was residual porosity which was detrimental to the mechanical properties. The SiC was preferentially distributed intergranularly within the α-SiAlON and was effective in controlling grain growth of the α-SiAlON during processing. There was an increase in the uniformity of the grain structure and a significant refinement of the grain size of the composite microstructures with increasing SiC content. The hardness and the three-point bending strength of the composite samples increased markedly with increasing SiC content up to a level of 20 wt%. For a sample containing 20 wt% SiC, the bending strength was about ~ 1.5 times that of single-phase α-SiAlON. For samples with higher SiC contents, the rate of increase in hardness was diminished and the bending strength decreased because of incomplete densification. The initial improvement in fracture strength with increasing SiC content is plausibly attributable to the uniform refined grain structure of the composite materials, assuming that the maximum flaw size scales with the grain size.

1. Introduction

Ceramics based on silicon nitride (Si_3N_4) exhibit an excellent combination of high strength, hardness, and wear and corrosion resistance, and there remains sustained interest in the development of Si_3N_4-based ceramics and ceramic composites combining high strength and toughness for structural engineering applications at elevated temperatures [1–3]. Within this family of materials SiC–Si_3N_4 composites have attracted particular attention because of the potentially favourable combination of the properties of the individual components [4, 5]. Silicon carbide has been added to Si_3N_4-based ceramics in a variety of different sizes and shapes, including continuous fibres [6], whiskers [7, 8], platelets [9] and, most recently, nanoscale (less than 200 nm) dispersoids [10]. Those materials prepared using additions of nanoscale SiC to Si_3N_4 have been reported [11] to exhibit remarkable increases in strength compared with monolithic Si_3N_4 at both room temperature and elevated temperatures and thus appear worthy of further evaluation.

It has been suggested [11] that the improvements in strength observed in these nanoscale composites may be attributed to the residual microstresses surrounding dispersed SiC particles and arising from the difference between the thermal expansion coefficients of the dispersed SiC and the surrounding Si_3N_4 matrix. However, it has also been noted [12] that the addition of as little as 10 wt % SiC can modify the morphology of the silicon nitride and promote significant changes in the aspect ratio of individual grains. Aside from these tentative suggestions, the mechanism by which the dispersed SiC improves the properties of these refined composites has received little detailed attention and there remains a need for improved understanding.

In the present work, the reaction sequence occurring during the densification of hot-pressed nanoscale SiC–Ca α-SiAlON ceramic composites has been studied, and the effects of the SiC particles on the microstructure and mechanical properties of the resulting composites examined through comparison of samples with SiC contents ranging from 0 to 40 wt %. The Ca α-SiAlON was chosen as a matrix for the composite samples because it has been established [13] that, in the absence of SiC, the Ca α′ forms with a uniform fine-scale (300–400 nm) grain structure that is predominantly equiaxed and contains a minimum of residual glassy phase. It is to be anticipated that such a matrix microstructure would minimize any effects that added SiC might have on the aspect ratio of the SiAlON grains. It is also to be noted that it

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is possible to complete reaction and to achieve full density in the Ca α-SiAlON at relatively low temperatures (1550–1600 °C) [14], which may offer additional advantages in constraining matrix grain growth and limiting coarsening and/or transformation of the nanoscale SiC particles.

2. Experimental procedures

The SiC/Ca α-SiAlON composites were prepared from starting powders of Si_3N_4 (UBE-10; α phase, more than 90%), AlN (laboratory prepared; 32.5 wt % N), nanoscale β-SiC and $CaCO_3$. The nominal Ca α-SiAlON composition was designed to be equivalent to $CaO{\cdot}3Si_3N_4{\cdot}3AlN$ [13, 15], and composite samples were prepared with additions of 0, 10, 20, 30 and 40 wt % β-SiC particles. The powder mixtures were initially stirred ultrasonically and then milled 24 h in ethanol using sintered silicon nitride grinding media. After drying, the powders were cold pressed in a steel die and then placed in a graphite die for hot pressing. The die surface was coated with boron nitride to inhibit interaction between specimen and die. The samples were calcined for 1 h at 1000 °C, heated to the sintering temperature (1400–1800 °C) and hot pressed for 1 h at 25 MPa. The heating rate was $30\,^{\circ}C\,min^{-1}$, and the natural cooling rate was approximately $60\,^{\circ}C\,min^{-1}$.

The bulk density of the final samples was measured using the water immersion method. Bulk crystalline phases were identified using a Rigaku Geigerflex diffractometer with Ni-filtered Cu Kα radiation. A JEOL JSM840A scanning electron microscope and a Philips EM420 transmission electron microscope operating at 120 kV were used to investigate the microstructures. Specimens for transmission electron microscopy (TEM) were prepared by diamond cutting thin composite slices, grinding and polishing these slices to a thickness of about 120 μm in the form of discs 3 mm in diameter, dimpling the discs mechanically and finally ion milling the centre of these discs to electron transparency. Perforated foils were coated with a thin carbon film to prevent charge accumulation.

The bending strength of each of the composites was determined by conventional three-point bend testing using polished bars 3 mm × 4 mm × 38 mm in dimensions. At least three bars were tested for each composite and the results reported represent average values for these three tests. The hardness of each sample was also measured using a Vickers diamond indenter under a force of 98 N (HV 10).

3. Experimental results

3.1. Reaction sequence

To investigate the reaction sequence during densification, composite samples of Ca α-SiAlON containing 20 wt % of nanoscale SiC were hot pressed at temperatures at 100 °C intervals between 1400 and 1800 °C for 1 h under a pressure of 25 MPa. The dominant crystalline phases present in each of the as-fired samples were identified by powder X-ray diffraction, and representative X-ray diffractometer traces from samples prepared at the different temperatures are compared in Fig. 1. The relative fractions of these phases were estimated on the basis of the relative intensities of prominent diffraction peaks and the results of these measurements are presented in Fig. 2 as a function of the hot-pressing temperature.

Since the surfaces of the starting nitride powders are inevitably covered by an oxide layer, such as alumina in the case of aluminium nitride and silica or silicon oxynitride in the case of silicon nitride, it is not surprising that the first reaction that is observed with

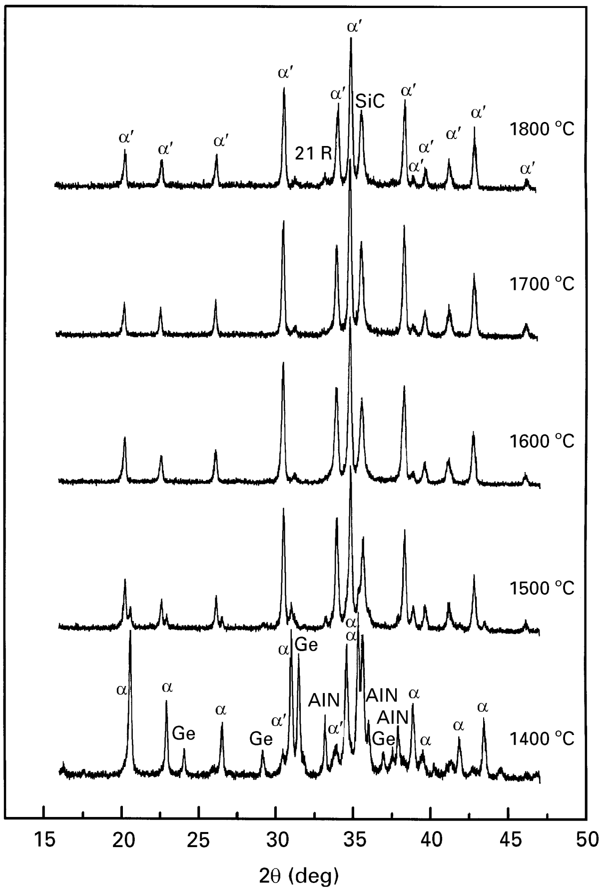

Figure 1 X-ray diffraction patterns of Ca α-SiAlON composites containing 20 wt % SiC hot pressed at different temperatures.

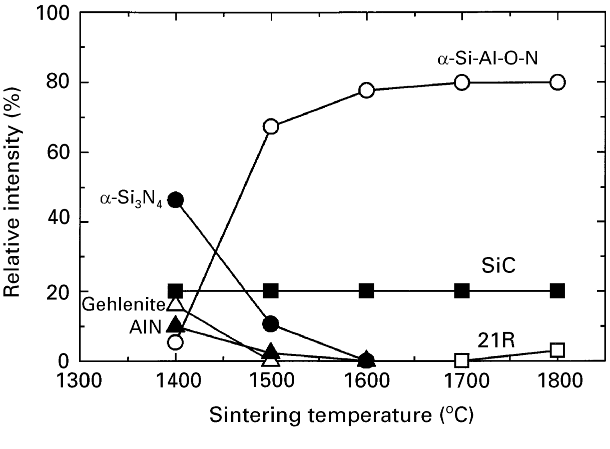

Figure 2 The relative fractions of the phases detected using X-ray diffraction analysis of the samples containing 20 wt % SiC as a function of the hot-pressing temperature.

increasing temperature appears to involve a combination of CaO, Al_2O_3 and SiO_2. The product is a Ca-containing silicate, namely gehlenite ($2CaO{\cdot}SiO_2{\cdot}Al_2O_3$), which appears as an intermediate oxide phase in the sample fired at 1400 °C. Both the AlN and the α-Si_3N_4 in the starting powder remain unreacted at this stage. Above 1400 °C, the calcium aluminosilicate is a liquid phase, and the Si_3N_4 and AlN dissolve in this liquid oxide, while Ca α-SiAlON begins to precipitate from the liquid phase. The Ca^{2+} cations available in the liquid phase are incorporated into the SiAlON structure to stabilize the α' phase.

The diffractometer trace from the sample hot pressed at 1500 °C indicates a major proportion of α-SiAlON after 1 h, but there remain significant unreacted fractions of both α-Si_3N_4 and AlN. The dissolution of Si_3N_4 and AlN, and the precipitation of Ca α-SiAlON, continue with increasing temperature. After sintering for 1 h under pressure at 1600 °C, the reaction appears essentially complete and the microstructure consists of a matrix of Ca α-SiAlON containing the SiC additions. A small fraction of the AlN polytypoid 21R phase was detectable in the sample hot pressed at the upper end of the temperature range (1800 °C), but in those samples prepared at temperatures of 1600–1800 °C the dominant phases were α-SiAlON and β-SiC. It is noteworthy that the fraction of SiC remains constant throughout this reaction sequence and there is no evidence in the X-ray diffraction results of transformation within the SiC.

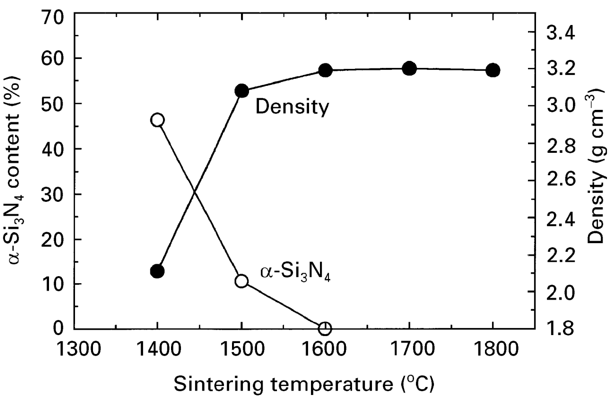

Figure 3 The variation in the bulk density of samples hot pressed for 1 h as a function of temperature, compared with the change in Si_3N_4 during the densification.

3.2. Densification

The densification of the composite samples was followed by combining these observations of the reaction sequence with measurements of the bulk density and examination of the fracture surfaces of pressure-sintered specimens. Fig. 3 shows the change in measured bulk density as a function of the sintering temperature compared with the reduction in the initial α-Si_3N_4 content with increasing reaction temperature for a 1 h exposure. Figs 4a, b and c contains scanning electron micrographs recorded from the fracture surfaces of samples containing 20 wt % SiC, hot pressed for 1 h at 1400 °C, 1500 °C and 1600 °C, respectively, and fractured in three-point bending. It is noted that there is only limited densification at 1400 °C and the fraction of retained α-Si_3N_4 remains high. The eutectic temperature in the $CaO{\cdot}Al_2O_3{\cdot}SiO_2$ system is approximately 1350 °C and thus one would expect a liquid phase at 1400 °C that would assist in particle rearrangement and consolidation. The fracture surface of the sample pressed at 1400 °C, (Fig. 4a) has a smooth featureless appearance consistent with the presence of liquid phase at the processing temperature. However, the structure remains of a coarse scale and there is little evidence of the emergence of fine-scale crystalline α-SiAlON compounds. It is believed that the precipitation of the calcium aluminosilicate gehlenite at this temperature (Fig. 1) restricts the fraction of liquid phase available and thus retards consolidation and formation of α-SiAlON.

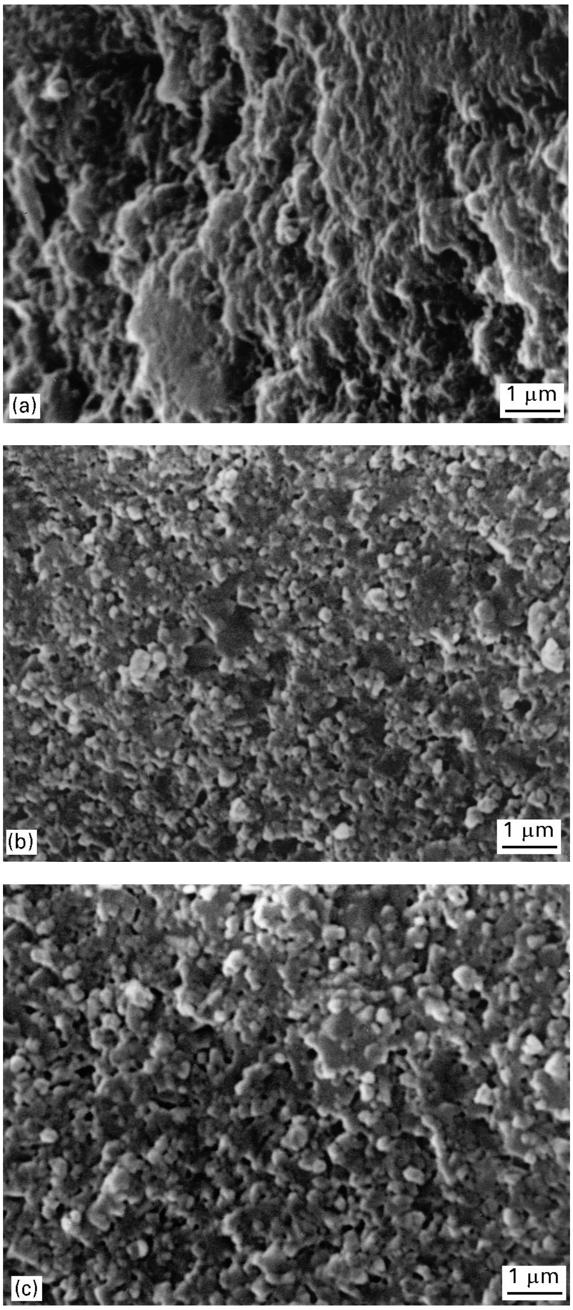

Figure 4 The fracture surfaces of the samples hot pressed at (a) 1400 °C, (b) 1500 °C and (c) 1600 °C.

When the sintering temperature is increased above 1400 °C, there is an approach to full density within the 1 h exposure time. This increase in densification rate is attributed to the melting of the gehlenite which, accompanied by the dissolution of Si_3N_4 and AlN, increases the fraction of liquid phase available to aid consolidation. The fracture surface of the sample hot pressed at 1500 °C (Fig. 4b) is now fully intergranular and there is clear evidence of fine-scale equiaxed crystals of α-SiAlON dominating the microstructure. However, the material has not achieved full density in 1 h and there remains significant porosity. In contrast, the reaction sequence is completed within the sample sintered for 1 h at 1600 °C and the density of the material exceeds 99% of the theoretical density. The exposed fracture surface (Fig. 4c) suggests a uniform equiaxed grain structure that is slightly coarser than that produced at 1500 °C and there is little evidence of residual porosity.

The densities of the composite samples hot pressed for 1 h at 1700 °C under 25 MPa are recorded in Table I as a function of SiC content. It is noteworthy that, for the given processing treatment, the density of the samples decreases significantly for SiC contents in excess of 20 wt %. This suggests that, at higher concentrations, the SiC retards densification perhaps by reducing the effective fraction of liquid phase available during sintering.

3.3. Microstructure

Figs 5a, b and c compare secondary-electron images of the fracture surfaces of three-point bending specimens containing 0 wt %, 20 wt % and 40 wt % SiC respectively, all hot pressed for 1 h at 1700 °C under a pressure of 25 MPa. In each case, the fracture surface is approximately parallel to the original direction of hot pressing and the mode of fracture is predominantly intergranular, which permits a direct comparison of grain size. For the SiC-free single-phase α-SiAlON sample, the scale of the structure is relatively coarse and there is considerable variability in the grain size. The majority of the equiaxed grains have a diameter in the range 500–600 nm, comparable with the grain size reported to be typical of the yttrium– and rare-earth–(SiAlON) systems [16, 17]. However, it is notable that there is also a small fraction of coarse grains of the Ca α-SiAlON which exceed 1 μm in diameter (Fig. 5a).

In comparison, there are two features which distinguish the microstructures of those samples containing nanosized SiC additions and processed under similar conditions; the microstructures become more uniform in terms of grain size distribution and the grain size of the Ca α-SiAlON matrix is refined. For the sample with 20 wt % SiC, the grain diameter typically varies in the range 300–400 nm (Fig. 5b), while that in the sample with 40 wt % SiC is further refined and spans the range from 200 to 300 nm (Fig. 5c). The composite samples are particularly noteworthy for their uniformly fine-grained microstructures.

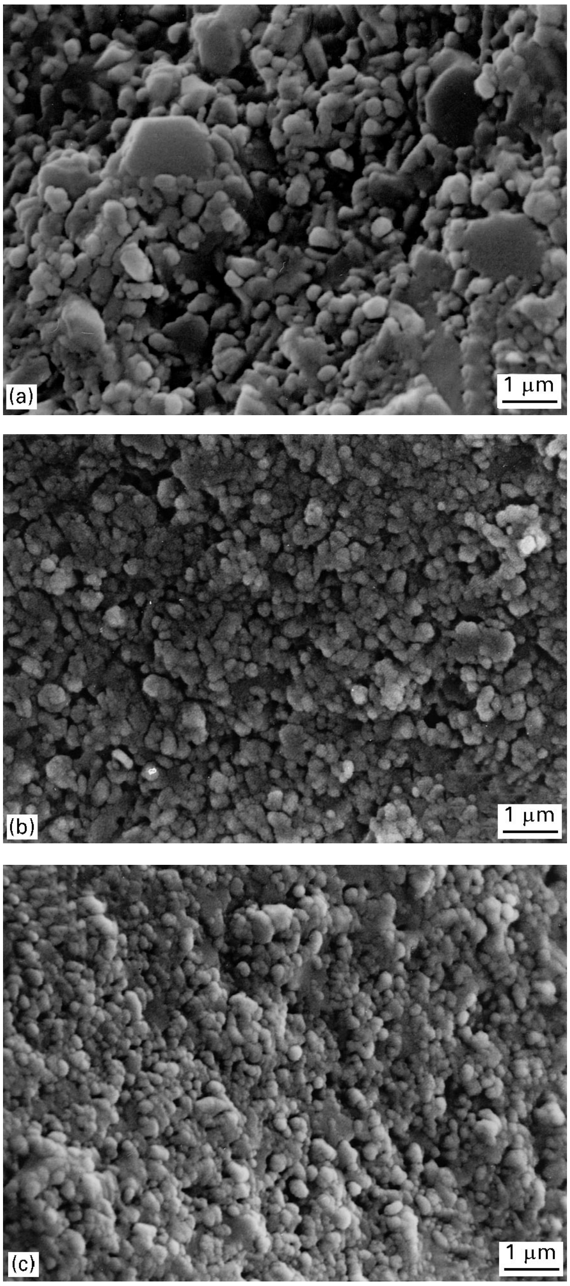

Figure 5 The secondary-electron images of the fracture surfaces of Ca α-SiAlON containing (a) 0 wt % (b) 20 wt % and (c) 40 wt % SiC. All samples were hot pressed for 1 h at 1700 °C under a pressure of 25 MPa.

A combination of TEM and electron microdiffraction was used to confirm that the microstructures of the as-sintered composite samples consisted of the crystalline phases α-SiAlON and β-SiC, and a minor fraction of amorphous intergranular phase distributed principally at grain and interphase boundary junctions. Fig. 6 includes transmission electron micrographs recorded from a sample containing 20 wt% SiC and hot pressed at 1700 °C; the section is approximately perpendicular to the direction of hot pressing. The α-SiAlON grains have a predominantly equiaxed polygonal form and a relatively uniform distribution, with the grain size ranging from 300 to 400 nm. The distributed SiC particles were typically in the range 50–200 nm in scale and reasonably uniformly dispersed throughout the composite microstructure. Occasional fine-scale particles (less than 100 nm) were observed within individual α-SiAlON grains, but

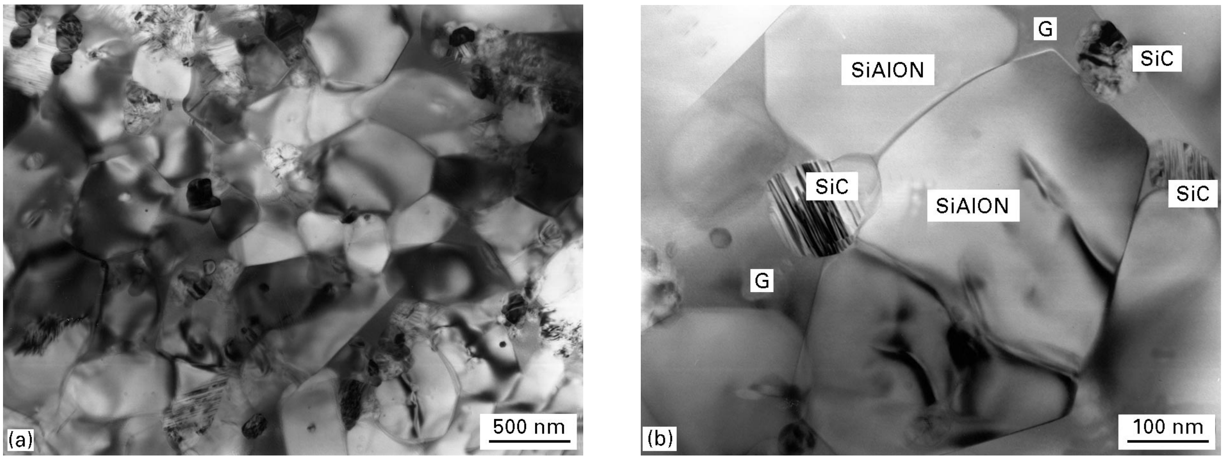

Figure 6 Transmission electron micrographs of the SiC–(Ca α-SiAlON) composite. The sample contained 20 wt % SiC and was hot pressed at 1700 °C. SiC is predominantly distributed between the α-SiAlON grains and often found in the amorphous phase regions G.

TABLE I Density, fracture strength and hardness of SiC–(Ca α-SiAlON) composites

Samples	Density ($g\,cm^{-3}$)	Relative density (%)	Three-point bending strength (MPa)	Vickers hardness (HV 10)
α-SiAlON	3.21	99.4	500 ± 57	1759
α′ + 10 wt % SiC	3.21	99.4	525 ± 54	1809
α′ + 20 wt % SiC	3.20	99.2	786 ± 33	1904
α′ + 30 wt % SiC	3.19	98.9	663 ± 40	1917
α′ + 40 wt % SiC	3.17	98.3	524 ± 31	1939

the SiC was predominantly distributed between the grains of α-SiAlON, often in association with regions of intergranular amorphous phase (Fig. 6b).

3.4. Mechanical properties

The results of measurements of the Vickers hardness (load, 10 kgf) and three-point bending strength of the SiC–Ca α-SiAlON composites are summarized in Table I. The single-phase α-SiAlON itself had an intrinsically high hardness (about 17.5 GPa) and the addition of SiC produced a significant increase in this hardness. The hardness of the composite samples increased continuously with increasing SiC content up to a concentration of 40 wt % SiC, with the most significant gains being achieved for those samples containing 10 and 20 wt % SiC. The fracture strength in bending was also initially improved significantly by the addition of the dispersed carbide. For a SiC content of 20 wt %, the bending strength was about 786 MPa and approximately 1.5 times that of SiC-free single-phase α-SiAlON. However, with further increase in the SiC additions, the bending strength was observed to decrease and, for the sample containing 40 wt % SiC, the fracture strength was similar to that of carbide-free Ca α-SiAlON to within reasonable experimental error.

4. Discussion

Preparation of Ca α-SiAlON is a liquid-phase sintering process, with the oxides present as sintering additives or as impurities in the mixture reacting to form a transient liquid phase which promotes initial consolidation. Densification proceeds through dissolution of α-Si_3N_4 and AlN in this liquid phase and the subsequent precipitation of Ca α-SiAlON. At intermediate temperatures in the range 1200–1400 °C, this process may be retarded by the formation of the calcium aluminosilicate gehlenite [14], but at temperatures above 1400 °C the gehlenite itself is liquid and densification proceeds rapidly. At 1600 °C, the reaction sequence is essentially complete and in excess of 99% theoretical density is achieved within a 1 h hot-pressing treatment. In the present composite samples containing 0–40 wt % SiC, it is noteworthy that the fraction of SiC remains constant throughout the reaction sequence (Fig. 2) and the SiC appears to play little or no role in the reaction responsible for formation of the α′. Excluding the SiC, the reaction sequence that is represented in Fig. 2 for the composite containing 20 wt % SiC is essentially identical with that reported for preparation of single-phase Ca α-SiAlON [14].

The present work has demonstrated the feasibility of generating composite SiC/Ca α-SiAlON materials in which the SiC is randomly and uniformly dispersed by simple uniaxial hot pressing of pre-mixed powders. In samples containing up to 20 wt % SiC, it is possible to complete reaction and to achieve in excess of 99% theoretical density in 1 h at temperatures as low as 1600 °C. This relatively low processing temperature arises from the choice of CaO as a sintering additive and its effectiveness in reducing the melting temperature of the oxide-based liquid phase. The choice of Ca α-SiAlON as the matrix for these composite samples and the resulting low formation temperatures has also proven effective in avoiding significant decomposition of the body-centered cubic β-SiC during processing. The transformation from β-SiC to one or more of the hexagonal α-SiC polymorphs may be accompanied by anomalous grain growth [18] and in the case of the present composites would probably prove detrimental to the integrity of the composite microstructures.

Both the hardness and the three-point bending strength of the composite samples increased markedly with increasing SiC content up to a level of 20 wt % SiC. Microstructural examination revealed that the SiC was preferentially distributed at grain boundaries of the α-SiAlON and in association with residual pockets of amorphous phase and was apparently effective in controlling grain growth of the α-SiAlON during processing. A feature of the microstructures of the composites was an increase in the uniformity of the grain size distribution and a refinement of the grain size with increasing SiC content. It is likely that the increase in strength associated with initial increases in SiC content may be largely attributed to this refinement in the scale of the composite microstructure.

If the composite samples were to behave as ideal brittle solids, we would expect the fracture strength to be given by a relationship of the form

$$\sigma = \left(\frac{2E\gamma}{\pi c}\right)^{1/2} \qquad (1)$$

where E is the elastic modulus, γ is the fracture surface energy per unit area and c is a critical flaw size. In strong, covalently bonded ceramics, failure is commonly associated with grain-boundary decohesion, or the presence of flaws at the grain boundaries arising from incomplete densification or thermal expansion mismatch between an intergranular amorphous phase and the crystalline matrix. In either case, it is to be expected that the critical flaw size would be influenced directly by the grain size, and that a refined and more uniform grain size distribution would lead to a commensurate decrease in flaw size. In the present samples, the α-SiAlON grain size was reduced from 500 to 600 nm in the carbide-free material to some 300–400 nm in the material containing 20 wt % SiC sintered to nearly full density, and in both samples the mode of fracture was almost exclusively intergranular. If the flaw size was assumed to scale as the grain size and was correspondingly reduced to approximately half its initial value, then according to Equation 1 we would expect an increase to approximately 1.3 times the initial fracture stress. This is consistent with measurements which indicated that the strength of the 20% SiC sample was approximately 1.5 times that of the carbide-free α-SiAlON and demonstrates that it is plausible to attribute the improvement in strength of the composite to the refinement in microstructure.

For SiC contents in excess of 20 wt % in those samples hot pressed for 1 h at 1700 °C, the rate of increase in hardness decreased and the fracture strength actually decreased with increasing SiC content. In those samples containing 30 and 40 wt % SiC, the SiC content was apparently sufficient to retard densification and these materials achieved less than 99% theoretical density in the standard hot-pressing treatment (Table I). Since the SiC does not participate directly in the reaction sequence, it may be that its role is to reduce the effective fraction of liquid phase available to aid consolidation. An increase in residual porosity and in the effective flaw size would be sufficient to explain qualitatively both the reduced rate of increase in hardness and the decrease in fracture strength in those samples of higher SiC content.

5. Conclusions

1. Ceramic composites containing up to 20 wt % nanoscale (less than 200 nm) SiC particles distributed in a fine-grained polycrystalline Ca α-SiAlON matrix may be prepared to in excess of 99% theoretical density by uniaxial hot pressing of pre-mixed powders at temperatures as low as 1600 °C for 1 h. For samples with higher SiC contents, subjected to similar treatment, there is residual porosity which is detrimental to mechanical properties.
2. The SiC is preferentially distributed at grain boundaries of the α-SiAlON and in association with residual pockets of amorphous phase and is effective in controlling grain growth of the α-SiAlON during processing. There is an increase in the uniformity of the grain structure and a significant refinement of the grain size of the composite microstructures with increasing SiC content.
3. The hardness and the three-point bending strength of the composite samples increase markedly with increasing SiC content up to a level of 20 wt %. For a sample containing 20% SiC, the bending strength is about 1.5 times that of single-phase α-SiAlON. For samples with higher SiC contents, the rate of increase in hardness is diminished and the bending strength decreases because of incomplete densification.
4. The initial improvement in fracture strength with increasing SiC content is attributable to the more uniform refined grain structure in the composite materials, if it is assumed that the maximum flaw size in the composite microstructures scales as the grain size.

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