Densification and mechanical properties of mullite–SiC nanocomposites synthesized through sol–gel coated precursors

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Abstract. Mullite–SiC nanocomposites are synthesized by introducing surface modified sol–gel mullite coated SiC particles in the matrix and densification and associated microstructural features of such precursor are reported. Nanosize SiC (average size 180 nm) surface was first provided with a mullite precursor coating which was characterized by the X-ray analysis and TEM. An average coating thickness of 120 nm was obtained on the SiC particles. The green compacts obtained by cold isostatic pressing were sintered in the range 1500–1700°C under pressureless sintering in the N₂ atmosphere. The percentage of the theoretical sintered density decreases with increase in SiC content. A maximum sintered density of 97% was achieved for mullite–5 vol.% SiC. The fractograph of the sintered composite showed a highly dense, fine grained microstructure with the SiC particles uniformly distributed along the grains as well as at the grain boundaries inside the mullite. The Vicker's microhardness of mullite–5 vol.% SiC composite was measured as 1320 kg/mm² under an applied indentation load of 500 g. This value gradually decreased with an increase in SiC content.

Keywords. Mullite–SiC nanocomposites; sol–gel; microstructure; Vicker's microhardness.

1. Introduction

The ceramic matrix nanocomposites, which involve a uniform dispersion of nanometer size second phase particles in a ceramic matrix, are a class of special materials, widely used for engineering applications (Niihara 1991; Komerneni 1992). Such composites are reported to have high strength and toughness due to the dissipation of the applied strain energy to several orders of magnitude (Hu and Rahaman 1992) and minimize the fracture surface energy, g_c . The dispersed second phase is believed to control the inherent flaws, especially at the grain boundaries and thus reduces the residual stresses at the interfaces of the matrix (Choa *et al* 1994). The alumina dispersed with nano SiC is extensively studied by many researchers (Thompson *et al* 1995; Bhaduri and Bhaduri 1998). Alumina containing 5 vol.% SiC particles showed an increase of fracture strength (σ) from 320 MPa to 1050 MPa and fracture toughness (K_{IC}) from 3.2 MPa·m^{1/2} to 4.7 MPa·m^{1/2} (Mitchell and De Jonghe 1995). The proposed mechanism for such an improvement of fracture strength and toughness are (i) particle bridging, (ii) crack pinning and crack deflection and (iii) stress induced micro cracking (Warrier *et al* 1996). The most important criteria for such properties are uniform distribution of the second phase particles in the matrix and minimum agglomeration of the dispersed phases, which will reduce the heterogeneity, which may lead to partial densification (Hu and Rahaman 1993). The conventional methods of processing

are hot pressing and hot isostatic pressing, that are mostly used and widely reported (Kapolnek and De Jonghe 1991). Although, the hot pressed alumina–SiC ceramics have much narrower flaw size population, during mechanical operations, the morphology and flaw size rapidly changes and produce crack like voids due to SiC agglomeration (Wang *et al* 1996). Recently, the pressureless sintering of alumina–SiC nanocomposites is reported in which a thin layer of alumina precursor coating is achieved by hybrid polymer–powder processing which resulted in a highly dense microstructure with reduced flaws (Kanpuri *et al* 1996). Other important ceramic–matrix nanocomposites reported are alumina–SiC, MgO–SiC and mullite–SiC (Pezzotti and Saki 1994; Saka *et al* 1995; Wang 1996).

In the present work, a sol–gel synthesis of mullite–SiC nanocomposite is reported and the densification analysed by its microstructural features are presented. The room temperature microhardness is also studied and compared with sol–gel mullite without SiC reinforcement.

2. Experimental

2.1 Activation of SiC powder

As received SiC powder (~180 nm size), Ibiden, Ogaki (Japan) was washed with dilute 1% HF solution to remove possible traces of silica associated with the powder. The HF treated powder was then washed thoroughly with double distilled water, finally with acetone and dried. Further,

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this powder was thermally activated at 250°C for 3 h in air. This activated SiC powder was used for the synthesis of mullite–SiC nanocomposite precursors.

2.2 Preparation of mullite coated SiC nanocomposite precursor

Boehmite sol prepared by the hydrolysis of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and tetraethylorthosilicate (TEOS) were used as alumina and silica sources respectively. Four different mullite–SiC nanocomposite precursors were prepared by varying the amount of SiC loading in the mullite matrix i.e. precursor containing 5 vol.% SiC, 10 vol.% SiC, 15 vol.% SiC and 20 vol.% SiC. In a typical experiment for the preparation of 30 g mullite 5 vol.% SiC composite, 1.5 g of SiC was dispersed in 200 ml of ethanol–water mixture (1 : 1). This was then ball milled for ~ 5 h in a PVC container with alumina as the grinding media to get a good dispersion of SiC particles in the medium. The mullite precursor sol was prepared by mixing boehmite sol and TEOS. 1024 ml of boehmite sol was taken and to this 27.6 ml of TEOS was added dropwise with vigorous stirring. The mixture was stirred for about 5 h to result in a homogeneous distribution of alumina and silica species (to get 23.5 g mullite phase). To this mixture a SiC suspension was added, stirred for 1 h and the whole suspension with the dispersed SiC particles were flocculated to pH 7.5 by the addition of dilute ammonia solution. The coated powders were filtered, washed and dried in an air oven at 80°C. Similar experimental procedure was repeated for the preparation of 10 vol.%, 15 vol.% and 20 vol.% SiC–mullite composites.

The characterization of the mullite coating on the green samples as well as those calcined at 600° and 800°C were carried out using a transmission electron microscope (TEM, Model: JEOL 100 CX). The TEM samples were prepared as follows:

A suspension containing coated SiC particles (0.5 wt%) was made in a percentage ethanol–isopropanol medium. A drop of the suspension was deposited on to a carbon coated TEM grid and dried under vacuum. The grid was observed under TEM. The composite precursors containing SiC particles were calcined at 1000°C in N_2 atmosphere for 2 h with a heating rate of 5°C/min. The calcined powders were then ball milled in ethanol for 12 h and the hard agglomerates were removed by sedimentation and dried in an air oven at 50°C. The dried powders were then compacted into bars of dimensions 40 × 5 × 4 mm by uniaxial pressing at 25 MPa followed by cold isostatic pressing (CIP) at 500 MPa. The bars were then subjected to gas pressure sintering at 1550°, 1650° and 1700°C for a period of 1 h under N_2 atmosphere in a graphite crucible over SiC powder bed. A gas pressure of 60 bar was applied at the sintering temperature. The sintered densities of the fired samples were measured by Archimedes' method with water as the reference liquid. The thermo-

mechanical analysis of the samples was done (after calcining the coated powder at 1000°C in nitrogen atmosphere) in Netzsch dilatometer at a heating rate of 10°C/min up to 1000°C and up to 1700°C at a heating rate of 30°C/min in N_2 atmosphere. XRD of samples were recorded in Philips PW-1710 diffractometer. The sintered composites were mounted in a polymer matrix and polished to get a smooth, crack free surface. The Vicker's microhardness was determined by indentation with varying load using Shimadzu microhardness tester.

3. Results and discussion

3.1 Characterization of coating

The coating on the SiC particles with the mullite precursor was first identified through analysing the intensities of the peaks in the XRD patterns of the uncoated SiC and mullite gel coated SiC. The XRD patterns of the uncoated SiC and mullite gel coated SiC, and the same calcined at 600°C are presented in figure 1. The intensities of the SiC

Figure 1. XRD patterns of sol-gel mullite coated SiC nanocomposites: a. SiC as received, b. mullite 5 vol.% SiC, c. mullite 15 vol.% SiC, d. mullite 20 vol.% SiC, e. sol-gel mullite 600°C, f. mullite 5 vol.% SiC–600°, g. mullite 15 vol.% SiC–600° and h. mullite 20 vol.% SiC–600°C.

peaks were found to decrease on coating with the mullite precursor. However, the reduction in intensity decreased with increase in concentration of SiC particles from 5–20 vol.%, which could have been due to the increase in SiC particle per unit area. TEM observation of the coated mullite-SiC precursor is presented in figure 2.

The starting gel particle size of mullite precursor was about 100 nm and the coating was built up of 2–3 layer stacking over the SiC particles. This coating also appeared to be microporous. The gel crystallites were elongated in shape with a maximum length of ~250 nm and thickness of 80–100 nm. On calcination at 600°C, there was a uniform shrinkage of the coating to an average size of 70 nm. The coating also appeared to be denser. In any case, the method of the coating adopted in this procedure had been successful in obtaining fully coated SiC particles.

3.2 Densification features

The green compact densities were found to be ~50% of the theoretical. The sintering behaviour of the sol-gel mullite coated SiC composite precursor was followed by dilatometry (figure 3).

The coated SiC precursor was preheated to 1000°C before subjecting it to the dilatometric measurements. The typical heating cycle followed for dilatometric analysis

Figure 2. TEM image of sol-gel mullite coated SiC.

was 10°C/min up to 1000°C and 30°C/min up to 1700°C in a N₂ atmosphere and soaking for 1 h at that environment. The extent of densification decreased with increasing vol.% SiC. The composite containing 5 vol.% SiC showed no change up to 1000°C and no shrinkage was observed. The shrinkage started approximately around 1200°C and proceeded faster in the range 1270–1300°C.

Mullitization of the precursor phase was expected at such sintering temperatures. The maximum shrinkage occurred in this narrow range which indicated a fast rate of sintering. In the case of 10 vol.% SiC, the densification started at 1220°C and the rate of densification was maximum between 1300 and 1350°C. The mullite SiC nanocomposite precursor with high vol.% SiC required additional driving force for complete densification. Mullite-10 vol.% SiC had a maximum shrinkage of 17.5% in the range 1000–1350°C. The maximum shrinkage in a sample with 15 vol.% and 20 vol.% SiC was less than 15%. Qualitative observations indicated very low level of oxidation of the SiC phase. Since the thermal expansion coefficient of mullite and SiC is nearly identical, the interface mismatch between mullite-SiC was avoided. The reactive alumina present in the coating reacted only with the silica which formed a liquid phase at lower temperatures that favoured the densification process. The sintered densities of the coated nanocomposite samples at different temperatures are presented in table 1. The results indicated that the densities of the composite were strongly dependent on the volume fraction of the particulate dispersions.

In all the cases sintering had been carried out under N₂ atmosphere mainly to avoid the oxidation of SiC. The original property of the composite could have been lost due to oxidation of SiC. Considering the sintered densities of the samples, there was a decrease in density with the increase in vol.% of SiC. This could be due to the clustering of the reinforcing particles to form networks, which hindered the densification of the composite (Kanpuri *et al* 1996).

Figure 3. Dilatometric curve of mullite-SiC nanocomposites.

Table 1. % Theoretical sintered density of mullite–SiC composite at various temperatures.

Sample no.	Samples	% Theoretical sintered density		
		1550°C	1650°C	1750°C
1.	Mullite–5 vol.% SiC	92.72	94.66	96.93
2.	Mullite–10 vol.% SiC	91.49	93.31	93.98
3.	Mullite–15 vol.% SiC	89.39	92.36	92.78
4.	Mullite–20 vol.% SiC	86.78	88.96	89.04

Figure 4. SEM fractograph of mullite–5 vol.% SiC nanocomposites.

3.3 Microstructural features

The fractograph of the 5 vol.% SiC incorporated mullite composite is presented in figure 4. The coated precursor route had shown excellent dispersion characteristics with 5 vol.% SiC. Silicon carbide particles of sizes around 200 nm appeared to have dispersed in mullite having grain size about 1–2 μm and a high density. Random closed pores of submicron size were also seen. Under the present conditions of preparation the silicon carbide particle appear to get preferentially distributed at the grain boundaries and this could be a feature of the coated precursors. The dispersoid also exhibited a very good interface property. The fracture was often seen around the SiC particles, thus deciding the fracture mode. There appeared a strong influence for SiC particles in controlling the grain growth in the mullite, especially when placed at two opposite ends of a mullite grain. However, as the vol.% of SiC dispersion increased, an increasing tendency for the segregation of the coated SiC particles was observed. The size of such aggregates varied in the range 1–2 μm . This could have occurred due to the localized flocculation of the gel at the early stages of blending of the precursor. The room temperature microhardness in table 2 showed a decrease in the microhardness values with an increase in the percentage of SiC volume fractions. However, the

Table 2. Vicker's microhardness of mullite SiC nanocomposite.

Sl. no.	Samples	V_H at 500 g (kg/mm^2)
1.	Mullite	965
2.	Mullite–5 vol.% SiC	1330
3.	Mullite–10 vol.% SiC	1165
4.	Mullite–15 vol.% SiC	965
5.	Mullite–20 vol.% SiC	999

incorporation of SiC increased the hardness value which was found to have almost doubled from 965 kg/mm^2 to 1330 kg/mm^2 .

4. Conclusions

A well dispersed nanosized SiC in mullite composite by a coating technique was achieved. The sintered densities of the composites were found to decrease with increased volume % of SiC at all sintering temperatures from 1550–1750°C, although qualitative observations indicated low levels of oxidation of the SiC phase. The Vicker's microhardness however, showed a maximum hardness of 1330 kg/mm^2 of the composite having only 5 vol.% SiC. At a higher vol.% of SiC, the SiC particles were found to have dispersed at the grain boundaries, with agglomeration that had inhibited the grain growth.

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