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Pressureless Sinterability of Slip Cast Silicon Nitride Bodies Prepared from Coprecipitation-coated Powders

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Abstract

The sinterability of compositions from different powder preparation methods (coprecipitation-coating of Si_3N_4 powder or mechanical mixing of Si_3N_4 with Y_2O_3 and Al_2O_3) and compaction routes (dry pressing or slip casting) was compared. Both the coating method and the slip casting process improved silicon nitride sinterability over the mechanical mixing method and dry pressing route. However, the minimisation of powder agglomeration in the green bodies achieved by slip casting is more determinant to the sintering behaviour than the homogeneous distribution of the sintering additives around the Si_3N_4 offered by the coated powder. The coating powder method in combination with the slip casting process is the most favourable processing route, leading to a homogeneous and fully dense microstructure by pressureless sintering at a relatively low temperature of 1750°C. This technique produced materials with hardness of 15·2 GPa, fracture toughness of 7 MPa $m^{1/2}$ and flexural bending strength of 910 MPa. © 1999 Elsevier Science Limited. All rights reserved

Keywords: Si_3N_4, slip casting, sintering, pressing, powder preparation.

1 Introduction

The full densification of Si_3N_4-based ceramics is difficult to obtain due to the covalent character of the chemical bonding involved in this compound. With pressure assisted approaches such as hot-pressing, hot isostatic pressing and gas pressure sintering, using several sintering additives (Y_2O_3, Al_2O_3, La_2O_3, CeO_2, etc.) dense materials are easily obtained. However, these methods are only applicable for simple shapes and are very expensive for mass production. Pressureless sintering, hereafter designated sintering, as an alternative processing method, usually requires a high processing temperature at which Si_3N_4 would decompose,[1,2] and a considerable amount of sintering additives, which degrade the high temperature mechanical properties. Both these disadvantages can be partially alleviated by using Si_3N_4 powder with a uniform distribution of sintering additives. Methods for uniformly coating powders, with interesting advantages, were originally used for applications such as pigments, catalysts and some other chemical raw materials.[3] Recently, these methods have been increasingly used in materials processing to obtain a homogeneous incorporation of additives within the matrix powders, in order to improve the sinterability of the composites. For example, Hu *et al.*[4] reported that the sinterability of ZrO_2 and ZnO composites is remarkably improved by using coating coarse ZrO_2 inclusion particles with a cladding of fine-grained crystalline ZnO powder. Yang *et al.*[5] showed that the coating of SiC platelets with Al_2O_3 could produce a highly dense composite by sintering. They concluded that the network formation between the particles, and the inhomogeneous packing of the matrix phase were key detrimental factors to the full densification of the composites. Agglomerates occurring in dried powders, which remain in the resulting compact bodies prepared by dry pressing are likely to retard sintering and to degrade the mechanical properties and reliability of silicon nitride based materials. Colloidal processing (slip casting, pressure filtration, etc.), allowing both complex shape forming and the obtaining of a homogeneous green compact, has been widely used to prepare the Si_3N_4-based materials in the past two decades.[6–10] However, most of these studies involved the mechanically mixed Si_3N_4 powder processing (Si_3N_4, Y_2O_3 and

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Al_2O_3, etc.). Shaw *et al.*[6] used metal hydroxide precipitation reactions to prepare and mixing fine particles of the sintering additives with silicon nitride in an attempt to obtain homogeneous green compacts. Albano *et al.*[9] developed a concentrated aqueous slurry of Si_3N_4 powder with sintering additives and concluded that a higher density of slip cast compacts could produce a higher sintered density.

The study of colloidal processing of coated Si_3N_4 powder, which provides a homogeneous distribution of sintering additives around Si_3N_4 particles, followed by pressureless sintering of the powder compacts has seldom been reported. The objective of the present work is to evaluate the potential improvement in the sintering behaviour and ultimate material properties by the use of a coated Si_3N_4 powder in combination with the slip casting process. The microstructure and the mechanical properties of the pressureless sintered samples derived from the Si_3N_4 powder coated with Y_2O_3 and Al_2O_3 were investigated. The sinterability of samples from the coated and mechanically mixed powders, shaped by slip casting and dry pressing techniques, was compared. The influence of the powder treatment and the processing method on the sintering was also discussed.

2 Experimental Procedure

2.1 Preparation and sintering of green bodies

Si_3N_4-sintering aids compositions (1) and (2) were selected for the following Si_3N_4:SiO_2:Y_2O_3:Al_2O_3 molar ratios: (1)-49:4·5:2·5:3 and (2)-49:4·5:3:3·6. These compositions were chosen based on the SiO_2–Al_2O_3–Y_2O_3 phase diagram,[11] so that different liquidus temperatures of 1550°C for (1) and 1625°C for (2) were obtained. Glassy phase amounts were estimated from data of the Hyatt and Day work on yttria-alumina-silica glasses[12] and are 12·6 vol% and 14·1 vol% for compositions (1) and (2), respectively.

Two powder preparation methods were used. The first one, involving coating of Si_3N_4 particles with the sintering aids by a precipitation method described elsewhere,[13] is termed CO. The as prepared powders, CO-1 and CO-2, were calcined at 500°C for 1 h before shaping. The second one, a mechanically mixed system, named MM, and with the same composition of the CO-1 powder, was also used in order to compare the influence of the powder preparation procedure on the sinterability. The mechanically mixing process consisted of ball-milling the commercial Al_2O_3 (A-16, SG, Alcoa Chemicals, USA), Y_2O_3 and Si_3N_4 M11 powders (H.C. Starck GmbH, Germany) in absolute isopropanol for 4 h, using Al_2O_3 balls, followed by drying the suspensions at 70°C.

In order to evaluate the relative influence of the powder treatment on the extent of agglomeration, a well-dispersed slurry of the MM powder was rolled for 24 h before drying. The powder obtained was labelled as MM* and used in dry pressing. The sinterability of this powder was compared with those of the MM and CO powders.

Powder compacts were obtained by slip casting (SC) and dry pressing (DP) methods. A suspension for slip casting was prepared by adding a suitable amount (0·4 wt% relative to the solid content) of a dispersant based on a polycarboxylic acid, Dolapix CE64 (Zschimmer & Schwarz, Germany) to distilled water. The powders were then dispersed by simultaneous mechanical stirring and ultrasonic agitation. The as-obtained slurries were rolled in polyethylene bottles using Al_2O_3 balls for 24 h. Subsequently, a de-airing and conditioning step was performed for a further 24 h by rolling the slips in the milling container without balls. The pressed compacts were shaped by pressing uniaxially in a die (20 MPa) and then isostatic pressing (about 200 MPa) to form green bodies. The powder compacts obtained by both methods were then placed inside a powder bed composed by 50 wt% BN + 50% of starting powder, i.e. the powder used to produce the compacts, and sintered in a graphite furnace under 0·1 MPa atmosphere. They were initially heated to 1000°C at a rate of 10°C/min, and then to 1750°C at a rate of 5°C/min, and were maintained at this temperature for 2 h. After cooling down the samples to 1000°C at a rate of 10°C/min, a natural cooling followed by switching-off the power.

2.2 Characterisation techniques

The coated powder was characterised by thermogravimetric analysis (Linseis L18) in air at a heating rate of 10°C/min. Electrophoretic measurements of the particles of the different powders were performed on a Zetasizer (Malvern AZ 6004, Malvern Instrument, UK). An electrolyte solution (0·001 M KCl) was used as a dispersion medium in order to maintain a constant ionic strength. The microstructure of the polished surfaces of sintered bodies was observed by Scanning Electron Microscopy, SEM/EDS (Hitachi S-4100). X-ray diffraction (D/MAX-C, Rigaku, Japan), was also used for phase identification. The final density was measured by the Archimedes methods in mercury. Vickers indentation with 98 N load was used to measure hardness. Indentation fracture toughness was also calculated by measuring the lengths of the four cracks emanating from the corners of each indentation, according to the equation given by

Anstis *et al.*[14] The bending strength measurements were performed by three-point bending with the span of 20 mm at a cross head speed of 0·5 mm/min. Specimen surfaces were ground and polished to a 1 μm finish prior to testing.

3 Results and Discussion

3.1 Characterisation of the coated powder

Figure 1 shows the DTA-TG curves of the CO-1 powder. An endothermic band between 100 and 200°C and an exothermic band between 300 and 500°C were observed. The endothermic band corresponds to the evaporation of the water, while the exothermic one can be attributed to oxidation of some organic compounds associated with the coating of sintering additives. No significant weight loss is observed for temperatures exceeding 500°C. Based on this result, the coated powders were calcined at 500°C for 1 h, since a calcination at higher temperature would probably produce an oxidation layer of SiO_2 around the Si_3N_4 particles. The XRD results of the coated powder after calcination at 500°C indicated the amorphous nature of the Al and Y components. The formation of an amorphous coated layer of Al and Y components around the Si_3N_4 particle was already shown in a previous work.[13]

3.2 Characterisation of the sintered bodies

Figures 2–4 show the microstructures of the sintered samples obtained from different powders and shaping methods, under back scattering observation. It can be observed that all the samples were composed of elongated and interlocked β-Si_3N_4 grains, surrounded by a small amount of glassy phase. No strong preferred orientation of β-Si_3N_4 grains, which usually occurs in the hot-pressed sintered samples, is observed. X-ray diffraction spectra showed that β-Si_3N_4 is the main phase, in compositions (1) and (2) although in the coated and slip cast samples of the first composition, CO-1-SC, significant amounts of yttrium α-sialon appeared. This could be due to the nanometric size and amorphous nature of the particles in the coating layer, and the intimate mixing of the reactants, achieved by the colloidal processing. This allowed Y to enter the sialon structure more easily and explains why the other combinations of processing methods do not yield any α-sialon phase. Whenever this phase is not present, β-Si_3N_4 and another phase identified as $Y_2Si_3N_4O_3$, present in all samples, are the stable phases upon cooling. The presence of these phases indicates that the hardness and high temperature properties could be improved by appropriate tailoring of the compositions.[15] Beyond the above common features observed in the microstructures of the samples, there are some differences in the porosity and

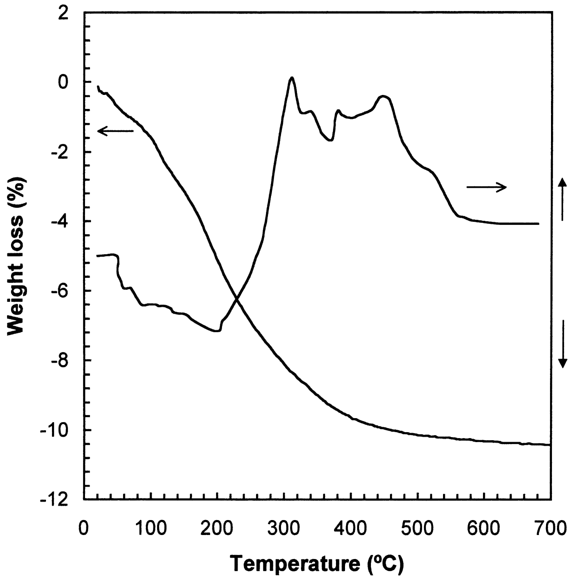
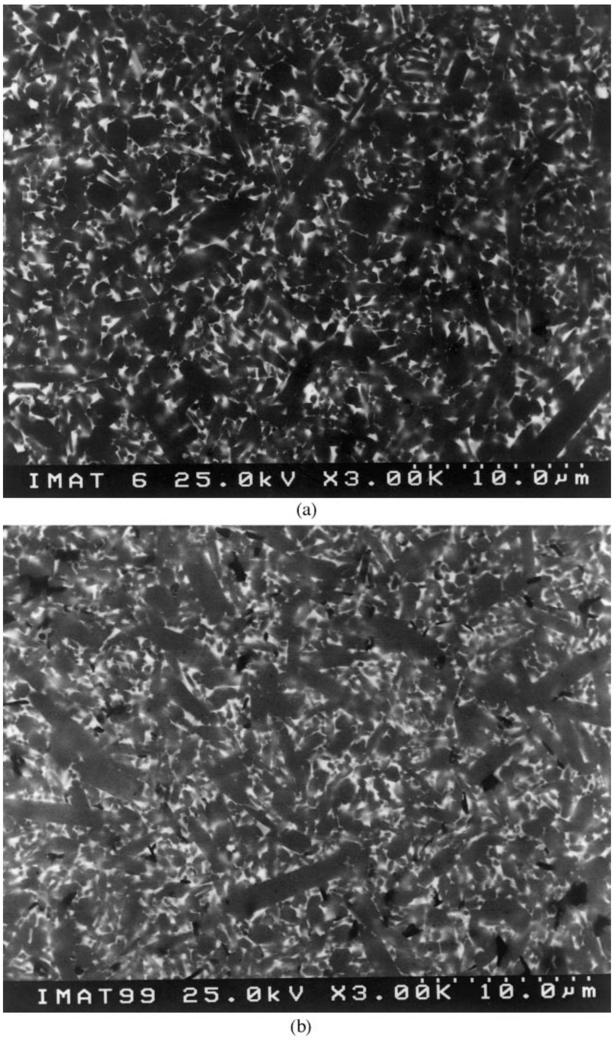


Fig. 1. DTA-TG curves of the CO-1 powder.



(a)

(b)

Fig. 2. SEM morphology of the sintered samples derived from CO-1 powder and shaped by (a) slip casting; (b) dry pressing.

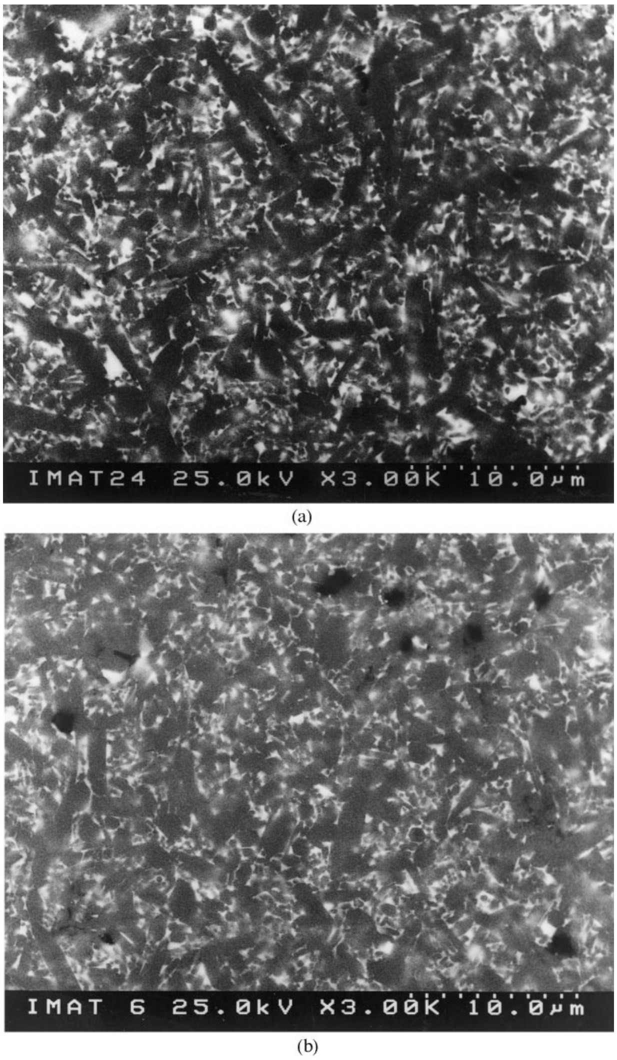


Fig. 3. SEM morphology of the sintered samples derived from MM powder and shaped by (a) slip casting; (b) dry pressing.

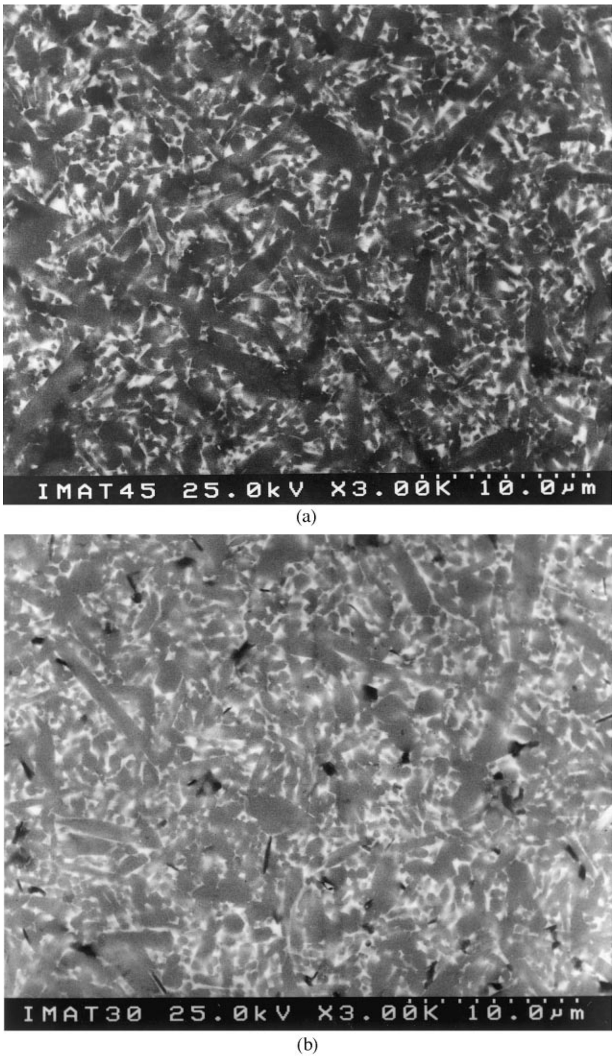


Fig. 4. SEM morphology of the sintered samples derived from CO-2 powder and shaped by (a) slip casting; (b) dry pressing.

homogeneity. First of all, the samples from the coated powders show highly homogeneous microstructures, as can be seen in Figs 2 and 4. Coarse and elongated β-Si_3N_4 grains, regions containing fine grains, as well as the grain boundary phase are uniformly distributed in these samples. Conversely, in the sample obtained from mixed powder, the larger white pools in Fig. 3 indicate that the distribution of the grain boundary phase is inhomogeneous. Secondly, the effect of the shaping method on the sintering can be observed by comparing Figs 2–4. The samples prepared by slip casting (Figs 2(a), 3(b) and 4(a)) have higher density than their counterparts from the dry pressing process (Figs 2(b), 3(b) and 4(b)), Table 1, this being valid for both CO and MM systems. In the slip casting process, the preparation of a well-dispersed suspension is a key factor to obtain reliable materials.[16] This process will minimise the agglomeration and possible formation of network between particles, allowing the formation of a homogenous green body, which is favourable to dense sintering.

Table 1 shows the density and mechanical properties of the samples prepared from CO and MM powders by the different shaping methods. In all cases, the slip casting method produced samples with higher values of density, hardness and fracture toughness than those obtained by dry pressing. For the slip cast samples, the comparison between the different powder treatments, only reveals small differences between the CO and MM systems.

Table 1. Properties of the sintered bodies. CO: Coating method; MM: mechanical mixing; SC: slip casting; DP: dry pressing; 1: composition (1); 2: composition (2)

Sample	*Density (g/cm^3)*	*Hardness (GPa)*	*Fracture toughness ($MPa\ m^{1/2}$)*
CO-1-SC	3·25	15·2 ± 0·5	6·9 ± 0·1
CO-1-DP	3·23	14·5 ± 0·5	6·7 ± 0·2
MM-1-SC	3·26	15·1 ± 0·5	7·1 ± 0·2
MM*-1-DP	3·26	14·6 ± 0·5	6·9 ± 0·2
MM-1-DP	3·24	13·4 ± 0·5	6·4 ± 0·2
CO-2-SC	3·29	15·1 ± 0·6	7·1 ± 0·2
CO-2-DP	3·27	14·9 ± 0·4	6·2 ± 0·1

The comparison between dry pressed samples prepared from the MM and MM* powders, clearly suggests that the de-agglomeration step is very important. The formation of a well-dispersed suspension enabled a high degree of homogeneity to be achieved. Although the drying of the suspension would lead to a partial re-agglomeration of particles,[16] the extent of particle–particle association in the MM* system seems less important than that achieved in MM powder prepared in isopropanol. As a consequence, the samples derived from the former powder show a more homogeneous microstructure and less porosity, as well as better properties (including density, hardness and toughness) than the latter one.

The above results (Table 1 and Figs 2–4) show that the kind of starting powder (coated or mixed) has not a significant effect on the properties of the sintered bodies shaped by slip casting. The differences are somehow enhanced in the case of dry pressing, in which the CO powder exhibits better sinterability than the MM powder. Obviously, the slip casting seems to be a very promising process, which allows the MM sintered bodies to possess comparable properties to that of the CO sintered body herein. The advantage of the slip casting lies in the formation of homogeneous green bodies and a uniform distribution of the sintering additives. Therefore, the sintered bodies derived from either CO-1 or MM, and prepared by slip casting do exhibit better sinterability than the pressed ones, as seen in Table 1 and Figs 2–4.

It was already reported[13,17] that Dolapix is an anionic dispersant that shifts the zeta potential curves of all the powder components used in this work towards lower pH values, when compared with the situation in absence of deflocculant. At the pH of the slurries, $\approx 8{\cdot}5$, all the component particles in the MM powders are negatively charged. In this conditions heteroflocculation by charge neutralisation is not expected to occur as in the case reported by Lidén *et al.*[18] They referred that Y_2O_3 could be electrostatically adsorbed onto the surface

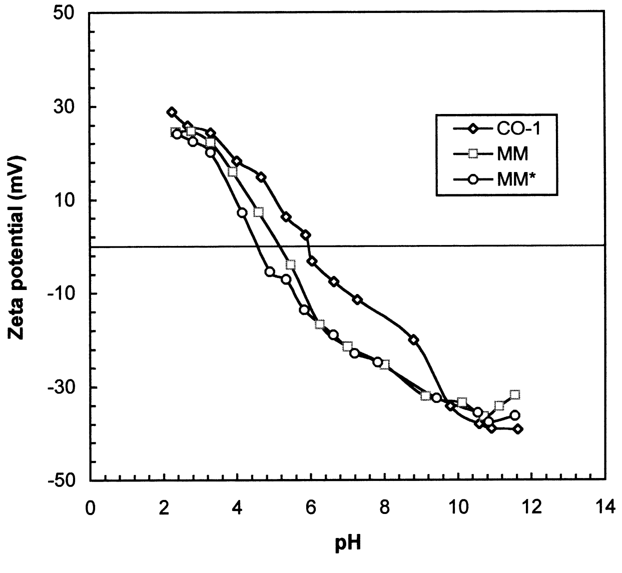


Fig. 5. Evolution of zeta potential versus pH value for the various powders in the presence of 0·4 wt% Dolapix CE 64.

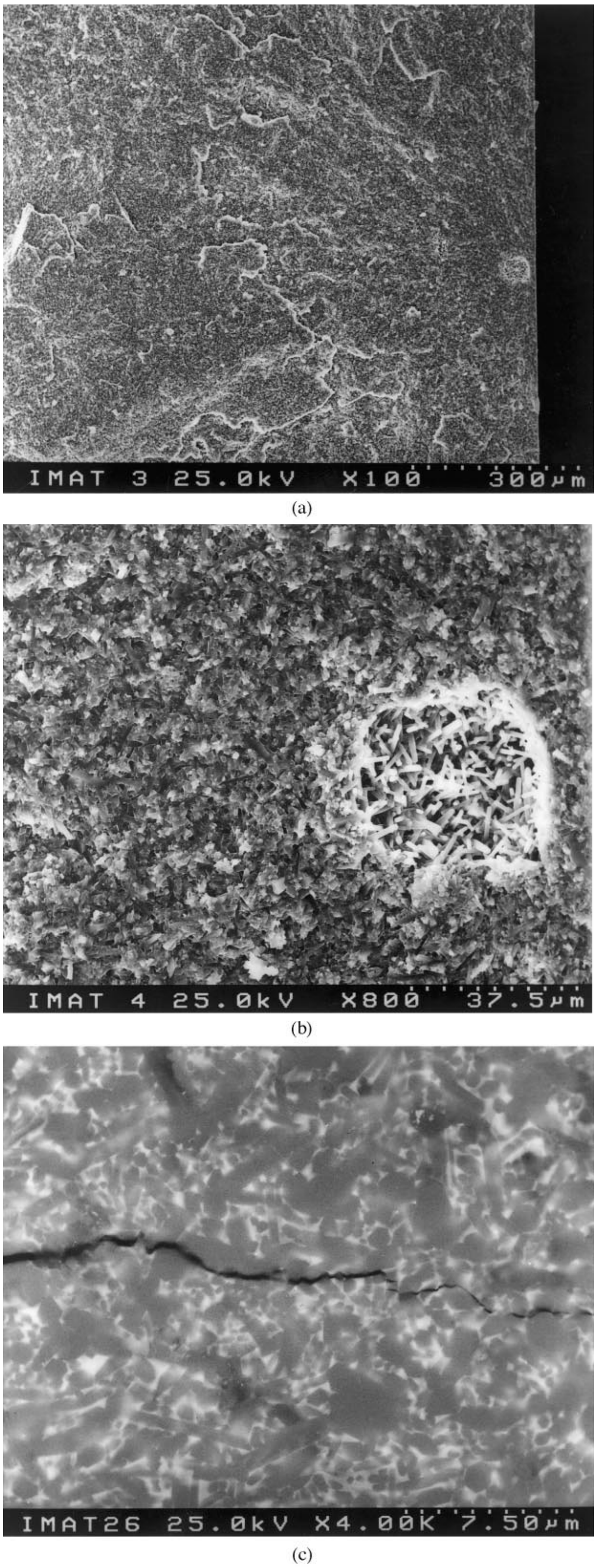


Fig. 6. SEM micrographs of CO-2-SC samples. (a) Low magnification of the fracture surface; (b) detail of the defect at the origin of fracture; (c) path of an indentation crack in a polished surface.

of Si_3N_4 particles, what is expectable in absence of a surface-active agent. Figure 5 compares the electrophoretic behaviour of the CO powder, and the mixed powder as obtained, (MM) and after rolling for 24 h (MM*) in the presence of Dolapix. The CO powder, with Al_2O_3- or Y_2O_3-like surface charge properties, has an isoelectric point (IEP) at around pH 6, which is about 2 pH units lower than in absence of deflocculant.[13] The IEPs of the mixed powders are close to that of Si_3N_4, the major component in the mixture. However, a small shift to lower pH values is observed for the MM*, that has been rolled for 24 h. This suggests that an enrichment of Si_3N_4 surface particles in silanol groups has occurred during the conditioning process.[19] These results show that for all the systems, the particles of all components at pH 8·5 are negatively charged, and exhibit a zeta potential high enough to enable the formation of homogeneous suspensions which, in turn, lead to slip cast bodies with uniform microstructures. It can be concluded that the combination of the colloidal processing with the homogeneous distribution of the sintering additives around the Si_3N_4 powder provided by coated powder enhances the sinterability of the Si_3N_4-based ceramics. In fact, it enables to obtain fully dense materials at a temperature as low as 1750°C by pressureless sintering.

Figure 6 shows SEM micrographs of the fracture surface of a sample derived from the coated powder CO-2-SC. The intergranular fracture surface with sharp grain shapes accompanied by rough surfaces, and the transgranular fracture surface with flat cleavage planes, are seen in Fig. 6(a). These two paths for crack propagation are also observed in Fig. 6(c). It can be observed that the failure was originated from a defect of about 50 μm size, as shown in Fig. 6(b). The fracture strength at room temperature was 910 ± 100 MPa. Some elongated β-Si_3N_4 grains can be seen inside the pore, without any Y or Al containing compounds. The average fracture strength could be improved if efforts are made to obtain the minimum amount of glassy phase that allow fully dense materials to be obtained, for these glass compositions.

4 Conclusions

From the above discussion, the following conclusions can be drawn:

1. The sintered bodies prepared by slip casting exhibit higher density, better mechanical properties and microstructural homogeneity than those obtained by dry pressing.
2. The sintered bodies derived from the coprecipitation-coated powder have more homogeneous microstructures than those derived from the mixed powder, for the same compaction methods. No appreciable differences could be observed between the sintered bodies properties derived from CO and MM powder when shaped by slip casting.
3. The coprecipitation-coating in combination with the slip casting can produce more homogeneous microstructure and dense materials without any residual porosity by pressureless sintering under a relatively low temperature (1750°C).
4. The materials obtained by CO-SC possess hardness, fracture toughness and fracture strength comparable to the values of other materials obtained by pressure assisted sintering techniques.
5. The optimisation of room temperature and high temperature properties depends on the minimisation of the glassy phase amount at the sintering temperature and on the phases in equilibrium upon cooling.

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