Materials Research, Vol. 12, No. 2, 145-150, 2009

Influence of Additive System (Al_2O_3-RE_2O_3, RE = Y, La, Nd, Dy, Yb) on Microstructure and Mechanical Properties of Silicon Nitride-Based Ceramics

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Received: September 11, 2008; Revised: April 7, 2009

Silicon nitride based ceramics have been widely used as structural ceramics, due mainly to their thermo-mechanical properties such as high density, high thermal shock resistance, corrosion resistance and chemical stability. The aim of this study was to determine the influence of rare earth and aluminum oxide additions as sintering aids on densification, microstructure and mechanical properties of silicon nitride. Silicon nitride mixtures with 91 wt. (%) Si_3N_4 and 9% wt. (%) additives were prepared and sintered. The density, microstructure and mechanical properties of the sintered specimens of these mixtures were determined. In most specimens, scanning electron microscopic examination and X ray diffraction analysis revealed elongated grains of β-Si_3N_4 with aspect ratio of about 2.0 and dispersed in a glassy phase. The density of the sintered specimens was higher than 94% of the theoretical density (td) and specimens with La_2O_3 and Al_2O_3 additions exhibited the highest value. The results of this investigation indicate that the rare earth ion size influences densification of silicon nitride, but this correlation was not observed in specimens containing two different rare earth oxides. The hardness values varied in direct proportion to the density of the specimens and the fracture toughness values were influenced by the composition of the intergranular glassy phase.

Keywords: *silicon nitride, sintering, rare earth additives, mechanical properties*

1. Introduction

Silicon nitride based ceramics have been used as structural materials in a wide range of applications due to their high hardness, high heat resistance, high fracture toughness and excellent wear resistance. These applications include heat exchangers, turbine and automotive engine components, valves and cam roller followers for gasoline and diesel engines, insulators, electronic substrates, high Tc superconductors, tool bits, wear surfaces, etc[1,2,3]. Even though silicon nitride ceramics have found a variety of applications, a number of issues still remain to be addressed for it to reach its full potential. This includes optimization of processing routes, choice of additives and sintering parameters.[4,5,6,7,8]

Recent studies on silicon nitride include fabrication of near-net-shaped specimens[9] and development of porous ceramics with several rare earth additives[10]. It has been suggested that porous ceramics with tailored microstructures are potential structural component materials[11]. Silicon nitride is considered to be a promising biomaterial as it is non-cytotoxic[12]. Moreover, total hip arthroplastic bearings have been successfully manufactured from silicon nitride powder[13]. Despite these studies, a suitable additive to increase the density of silicon nitride based ceramics is still being sought. It is well known that silicon nitride has two polymorphic states, α and β, with differences in the sequence of Si-N stacking layers. Besides the Si-N covalent bond and the low diffusion coefficient, additives are required to promote densification[14]. These additives are in general oxides, such as alumina, yttria, magnesia and rare earth oxides[15] that react with the silica layer on the silicon nitride powder surfaces to form a liquid phase. Liquid phase sintering involves α-Si_3N_4 particle rearrangement, dissolution of the α-phase, diffusion of Si and N atoms and precipitation of the β-phase[16], followed by grain growth[17].

The type and total amount of additives used can be adjusted to optimize the process and to increase the desired properties of the final silicon nitride-based ceramics, depending on the application. These modifications render controlled microstructures that are composed of elongated grains. Because most rare earth additives do not form a solid solution with Si_3N_4, the liquid phase, after cooling, forms at grain boundaries as an amorphous or partially crystalline phase[18]. In other words, the silicon nitride grains are surrounded by an intergranular glass or an intergranular film containing the rare earth element[3]. It has been mentioned that the glassy phase deteriorates high temperature creep and strength of the ceramics[19].

Changes in microstructure are closely related to mechanical properties. In this context, increase in fracture toughness of such materials has been reported[17]. One way to improve mechanical properties is to control the formation of elongated grains through anisotropic grain growth during sintering[17]. This can be circumvented by using different sintering additives, especially rare earth elements[20].

According to Becher et al.[21], the aspect ratio of silicon nitride grains is influenced by the size of the rare earth element used as an ad-

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ditive, and this effect is valid for a wide range of rare earths. However, studies so far have not produced a clear relationship. While some studies have shown that an increase in ionic radius of such elements causes an increase in the aspect ratio of silicon nitride grains[22], others have concluded the opposite, i.e. additions of rare earth elements with larger ionic radii tend to reduce the liquid viscosity, which in turn decreases the aspect ratio of the silicon nitride grains[23]. Moreover, since the rare earth ion acts as a network modifier in glasses, a decrease in its radius increases the bond strength between the rare earth ion and the surrounding oxygen[24].

Hence, the objective of this investigation was to evaluate the effect of alumina and rare earth oxide additions on the densification, microstructure and mechanical properties of silicon nitride ceramics.

2. Materials and Methods

The following starting materials were used: powders of Si_3N_4 (M11, Hermann C. Starck; with 92.7% α-Si_3N_4 and 1.14% wt oxygen), Y_2O_3 (Hermann C. Starck; purity > 99.9%) and other rare earth oxides (Sigma–Aldrich, purity > 99.9%) – La_2O_3, Nd_2O_3, Dy_2O_3 and Yb_2O_3.

Silicon nitride mixtures containing 9 wt. (%) additives (Table 1) were prepared using an attritor mill with silicon nitride spheres and isopropyl alcohol as the liquid media.

The milled and homogenized powder mixtures were dried at 90 °C and uniaxially compacted at 50 MPa followed by cold isostatic pressing at 200 MPa. The samples were then sintered at 1750 °C for 60 minutes in a furnace (Astro 1000, 4560, FP 20, Thermal Technology Inc.) with graphite heating elements and a nitrogen atmosphere. A powder bed of silicon nitride mixed with the same oxides used as additives was prepared to avoid evaporation of the oxide and decomposition of the silicon nitride.

Density measurements were performed using the Archimedes method and the final densities of the samples were expressed in terms of the theoretical density for each mixture composition. The theoretical densities were determined using the rule of mixtures.[25]

Sintered samples were analyzed using X ray powder diffraction analysis (XRD; Siemens® D5000 X ray powder diffractometer, Cu K_α) to identify the crystalline phases. To observe the crystal shapes and grain sizes as well as their distribution, scanning electron microscopy (SEM, XL 30, Philips®) was used. The sample surfaces were polished and plasma-etched using SF_6 and O_0 in a 3:1 ratio (Polotron, PT, 7160). The aspect ratio was estimated using the Quantikov software[26].

The mechanical properties of the different silicon nitride samples were determined from Vickers hardness tests. The fracture toughness was then obtained from the hardness indents (Zwick & Co., KG), using a 100 N load. Ten indents were made on the surfaces of samples corresponding to every silicon nitride composition. The hardness indents were observed in an optical microscope and lengths of the diagonals measured using an Image Tool software[27]. Vickers hardness (Hv) was determined using Equation 1. The crack propagation behavior of silicon nitride based ceramics was also evaluated from the scanning electron micrographs of the indents.

The Poisson's ratio (ν) and Young's modulus (E) were determined using a 200 MHz ultrasonic pulser-receiver (Panametrics, USA, 5900 PR), 20 MHz longitudinal pulses, as described by Yoshimura et al.[28] The measured bulk density, longitudinal velocity and shear velocity were used as the parameters. Ten measurements at both velocities were made on polished samples with composition corresponding to the different mixtures.

The fracture toughness was evaluated from Equation 2, using the method proposed by Anstis et al.[29]

$$Hv = 1.8544.\frac{P}{d^2} \quad (1)$$

P = load applied, d = diagonal impression

$$K_{IC} = \varepsilon\left(\frac{E}{Hv}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \quad (2)$$

ε = constant of deformation geometry, 0.016, c = crack dimension (from centre indents).

3. Results and Discussion

The densities of the different silicon nitride samples are summarized in Table 2. It can be seen that the theoretical density values are dependent on the additive used. The final densities were between 94 and 98.5% of the theoretical density (td), indicating the importance of silicon nitride as a structural material.

The results obtained with samples containing alumina and a single rare earth oxide (SN-Y, SN-La, SN-Nd, SN-Dy and SN-Yb) suggest that the density values tend to increase with increasing ionic radius of the rare earth (ionic radii of the rare earth elements are sequenced in Equation 3). As a result, the SN-La sample (with 98.5% td) had the highest density and the SN-Yb sample (with 94% td), the lowest.

$$R_{La} > R_{Nd} > R_Y > R_{Dy} > R_{Yb} \quad (3)$$

The results obtained in this study are in agreement with Becher et al.[30]. They showed that the viscosity of bulk Si–RE–Al oxynitride glasses with specific compositions and in the 800-1100 °C range, increased with decrease in rare earth ion radius. Thus rare earth cations with larger radii (La^{3+}) contribute towards decrease in the eutectic temperature of the mixture. According to Murakami et al.[31], the energy of formation of a solid phase (H) that coexists with the liquid is dependent on the ionic radius of the RE element. SN-La exhibited

Table 1. Composition of the different silicon nitride-based ceramics (wt. (%)).

Sample identification	Al_2O_3	Y_2O_3	Nd_2O_3	Dy_2O_3	Yb_2O_3	La_2O_3
SN-Y	4.5	4.5	-	-	-	-
SN-La	4.5	-	-	-	-	4.5
SN-Nd	4.5	-	4.5	-	-	-
SN-Dy	4.5	-	-	4.5	-	-
SN-Yb	4.5	-	-	-	4.5	-
SN-Y/La	3	3	-	-	-	3
SN-Y/Yb	3	3	-	-	3	-
SN-Nd/Dy	3	-	3	3	-	-

Table 2. Density of the silicon nitride-based ceramic samples.

Sample identification	Density (%td)
SN-Y	95.00 ± 1.18
SN-La	98.38 ± 0.44
SN-Nd	94.86 ± 0.36
SN-Dy	94.91 ± 0.63
SN-Yb	94.11 ± 0.51
SN-Y/La	96.63 ± 0.56
SN-Y/Yb	95.00 ± 0.87
SN-Nd/Dy	96.21 ± 0.49

the lowest temperature for liquid formation, due to the large radius of La^{3+}, and this implies a liquid with lower viscosity. This lower viscosity aids mass transport, which in turn increased densification of silicon nitride-based materials. On the other hand, SN-Yb revealed the highest temperature for liquid formation, due to the small radius of Yb^{3+}. This implied a liquid with higher viscosity, hindered mass transport and consequent reduction in densification.

When two rare earth oxides are used simultaneously, the final density results require careful analysis as these mixtures (SN-Y/La, SN-Y/Yb and SN-Nd/Dy) contain a lesser amount of alumina compared to those containing a single rare earth oxide. This observation suggests that the sintering behavior of such materials cannot be directly related to the ionic radius of the rare earth elements used as additives. The higher amounts of rare earth oxides in these mixtures probably modify the viscosity and amount of the liquid at the sintering temperature[32], resulting thereby in changes in the densification process and consequently, the microstructure of the silicon nitride-based materials. The density of SN-Y/La is in between those observed for SN-Y and SN-La. The density of SN-Y/Yb is close to that of SN-Y, even though SN-Yb exhibited a slightly lower density. The density of SN-Nd/Dy was higher than that observed for SN-Nd and SN-Dy.

The X ray diffraction patterns of the silicon nitride samples are shown in Figure 1. The β-Si_3N_4 phase can be observed in all the samples indicating dissolution of the α-Si_3N_4 phase and re-precipitation of the β-Si_3N_4 phase during sintering. This is a typical behavior in liquid phase sintering mechanisms[33]. Secondary crystalline phases did not form during cooling, indicating that the secondary phase is amorphous in the grain boundary regions.

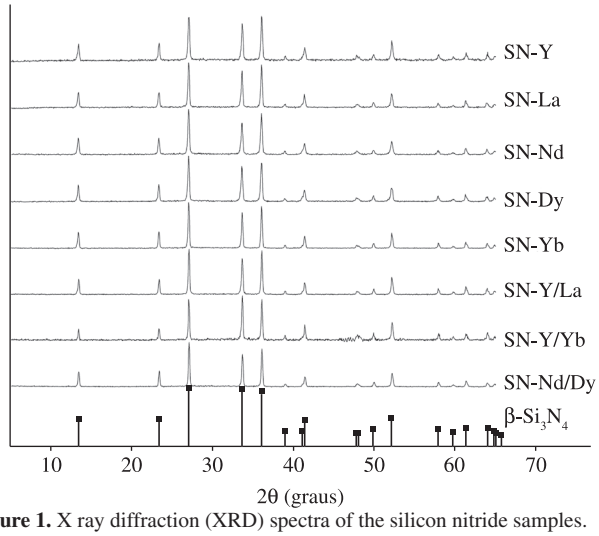


Figure 1. X ray diffraction (XRD) spectra of the silicon nitride samples.

The mechanical properties determined from the indents on the different polished silicon nitride samples are summarized in Table 3. Vickers hardness values were estimated to be between 11.5 and 15 GPa (Table 3). In general, higher density samples reveal higher Vickers hardness values. As expected, SN-La had the highest Vickers hardness. No significant differences were found among SN-Nd, SN-Dy and SN-Yb, but these had lower hardness values than SN-La and SN-Y.

The Young's modulus values were between 298 and 264 GPa (Table 3), slightly lower than the typical value for silicon nitride of 300 GPa[34]. The Young's modulus is closely related to the final density and Vickers hardness of silicon nitride. Moreover, a decrease in ionic radius implies a decrease in Young's modulus. The Poisson ratios varied between 0.26 and 0.31 (Table 3) without revealing any pattern, and in accordance with data in the literature[35].

The fracture toughness values were estimated to be between 4.17 and 4.83 $MPa.m^{1/2}$. The values are similar to each other when only one rare earth oxide is used as a sintering aid. The same behavior was also observed when two oxides were used simultaneously, but the fracture toughness values were higher, compared to that of samples with a single rare earth oxide.

The microstructures of polished and plasma-etched cross-sections of sintered silicon nitride with different additives are shown in Figure 2 and these reveal uniformly distributed elongated grains of β-Si_3N_4. No significant differences in features were noticed when different oxides were used as additives. The estimated aspect ratio was approximately 2 for all the samples (Table 3).

The slightly lower fracture toughness of the silicon nitride samples can be attributed to the low volume fraction of needle-like grains (Figure 2). Moreover, this property is also dependent on the grain-boundary phase, which is similar in all the samples. As reported by[36] Becker et al., increase in interfacial de-bonding between the grains should result in high fracture toughness.

To study the crack propagation behavior in silicon nitride based ceramics, the Vickers indent (a) and the crack path (b) (shown in the example in Figure 3) were considered. It can be seen from the intergranular crack path, in all samples, that crack deflection occurred at the grain boundaries, resulting in the observed Si_3N_4 grain pullout. Similar toughening mechanisms tend to operate in the materials that have been studied here, independent of the additives.

As summarized by Rosenflaz[37], not only the microsctructure, composed of bimodal silicon nitride grain diameter distribution[38], but characteristics of the glass/grain interface, as determined by bond matching, are important to have a material with high fracture toughness. They showed that the decrease in rare earth ion size

Table 3. Mechanical properties and aspect ratio of the silicon nitride-based ceramics.

Sample identification	Vickers hardness (GPa)	Young's modulus (GPa)	Poisson's ratio	Fracture toughness ($MPa.m^{1/2}$)	Aspect ratio
SN-Y	14.18 ± 0.38	280.13 ± 7.81	0.28 ± 0.02	4.39 ± 0.36	1.94 ± 0.94
SN-La	15.06 ± 0.40	298.71 ± 5.24	0.27 ± 0.01	4.17 ± 0.12	1.98 ± 0.89
SN-Nd	11.51 ± 0.37	285.95 ± 2.74	0.27 ± 0.01	4.32 ± 0.22	2.01 ± 1.03
SN-Dy	12.14 ± 0.25	273.09 ± 3.74	0.31 ± 0.01	4.21 ± 0.51	1.94 ± 0.87
SN-Yb	11.61 ± 0.26	264.70 ± 1.89	0.26 ± 0.01	4.19 ± 0.12	2.01 ± 0.96
SN-Y/La	12.29 ± 0.22	291.68 ± 4.44	0.31 ± 0.01	4.58 ± 0.15	1.91 ± 0.80
SN-Y/Yb	12.46 ± 0.38	282.43 ± 3.87	0.29 ± 0.02	4.83 ± 0.16	1.87 ± 0.74
SN-Nd/Dy	12.74 ± 0.24	288.17 ± 2.01	0.26 ± 0.01	4.61 ± 0.20	1.96 ± 0.88

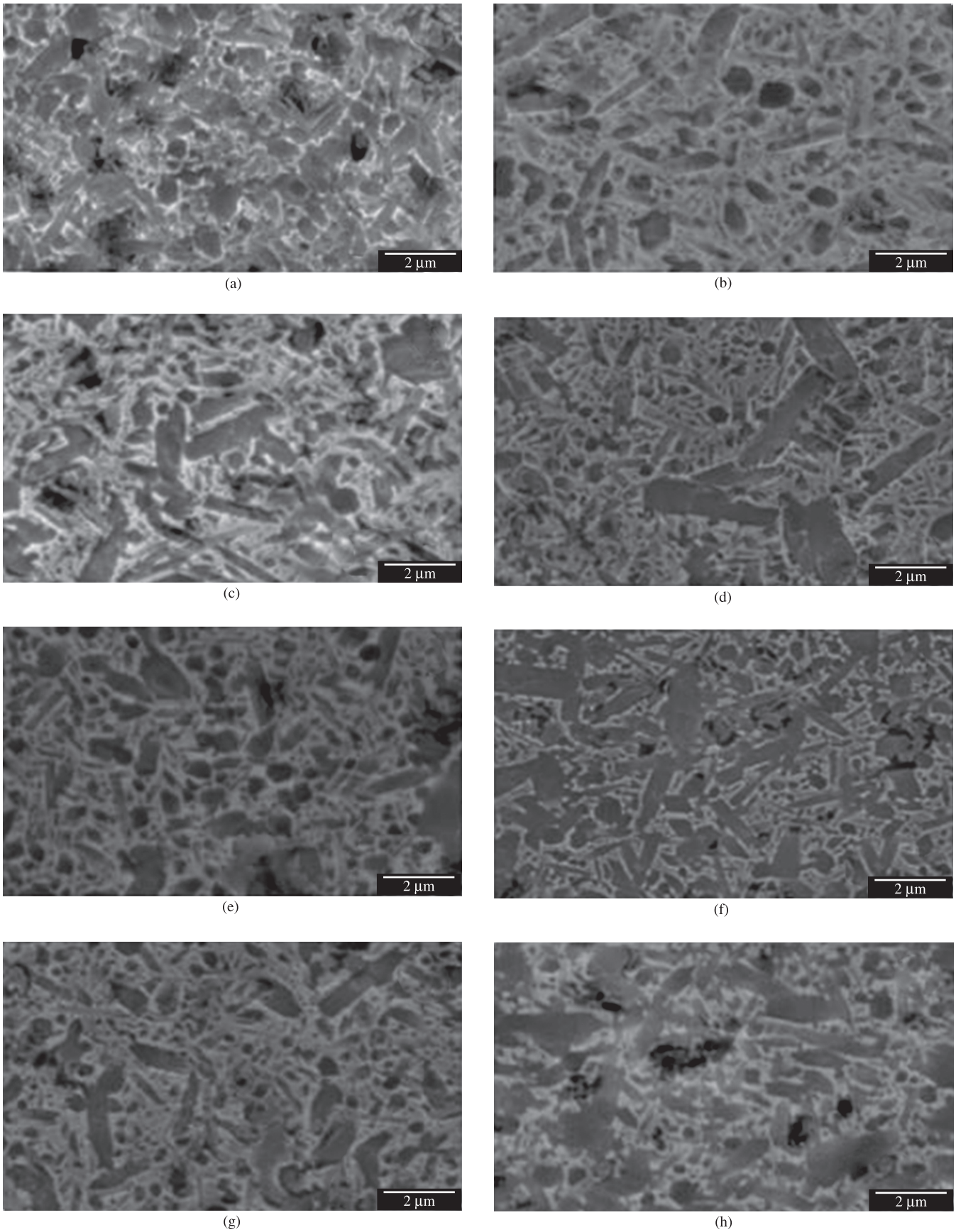
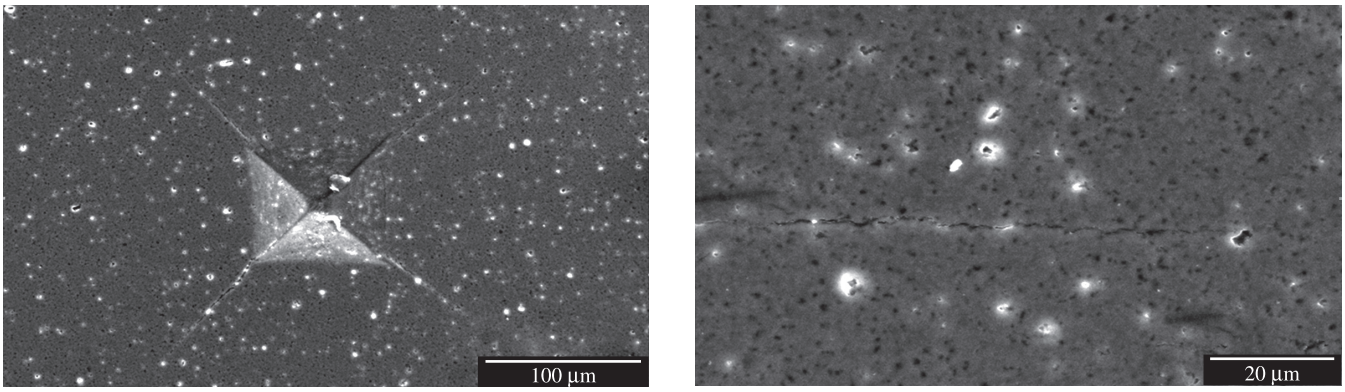


Figure 2. Scanning electron micrographs of plasma-etched silicon nitride-based ceramics with different additives (9 wt. (%)): a) SN-Y; b) SN-La; c) SN-Nd; d) SN-Dy; e) SN-Yb; f) SN-Y/La; g) SN-Y/Yb; and h) SN-Nd/Dy.



(a) (b)

Figure 3. Typical scanning electron micrographs of: (a) Vickers indent; (b) propagating crack in silicon nitride based ceramics.

leads to a decrease in crack bridging (in terms of debonding length), and consequent lower fracture resistance. We did not observe this behavior, due probably to the method used to estimate the fracture toughness values.

Our results demonstrate the influence of intergranular phase composition on fracture toughness of silicon nitride-based ceramics. Samples with lower alumina content, i.e. samples containing two rare earth oxides, present a brittle interface compared with those with higher alumina content. A brittle interface induces intergranular fracture due to enhanced detachment between grains and the intergranular phase, promoting higher fracture toughness values[22].

The aspect ratio is an important parameter to discuss the mechanical properties of silicon nitride based ceramics[39]. Amongst rare earths, as shown by Hoffman et al.[40], there is an increase in the aspect ratio of silicon nitride grains (that grow dispersed in a Si-Al-RE oxynitride glass) with increase in the ionic radius of the rare earth used as the additive. However, additions of alumina have a limited effect on this relationship, because the opposite behavior is observed[5]. These observations explain the similarity in aspect ratios observed in this study, amongst samples with different rare earth additives (~2, Table 3). Similar microstructure features amongst samples with different oxide additives can also imply similar aspect ratio values.

4. Conclusions

It can be concluded that the pressureless sintering conditions, associated with the amount and composition of additives, used in this study were adequate to obtain high density silicon nitride-based ceramics with relatively good mechanical properties. The results are related to the morphological features of several samples and especially to the aspect ratio of β-Si_3N_4 grains.

Comparison of the effects produced by the different additives revealed that the highest densification and Vickers hardness results were obtained in samples containing Al_2O_3 and La_2O_3. The use of two rare earth oxides simultaneously as sintering additives in combination with a lower alumina content increased the fracture toughness of the silicon nitride-based ceramics. The influence of the intergranular phase composition on fracture toughness of silicon nitride-based ceramics was also evaluated.

This revealed that the size of the rare earth ion can affect densification and, consequently, the mechanical properties. However, when rare earth oxides are used together and in combination with a lower alumina content, other factors are involved which hinder a direct correlation.

Acknowledgements

The authors would like to thank FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and PRONEX/CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for their financial support.

The experimental work performed at the X ray laboratory (Laboratório de Difração de Raios X do Departamento de Mineralogia e Geotectônica do Instituto de Geociências da Universidade de São Paulo) and the Mechanical Laboratories (Laboratório de Ensaios Mecânicos do Departamento de Metalurgia e Materiais da Escola Politécnica da Universidade de São Paulo and Laboratório de Metalurgia e Materiais Cerâmicos do Instituto de Pesquisas Tecnológicas – LMMC-IPT), are greatly appreciated. The authors also thank Catia Frederici and Marcelo Mendes Pinto for their help with the Young's Modulus experiments

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