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Influence of Microstructural Characteristics on the Mechanical Properties of Silicon Nitride with Al_2O_3, Y_2O_3 and Nd_2O_3 as Sintering Aids

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Abstract: Silicon nitride based ceramics have attracted considerable attention as good candidates for structural applications due to their excellent mechanical properties including strength, hardness, fracture toughness, and high temperature strength. These properties are strongly influenced by grain size and morphology, and by the degree of crystallinity and chemistry of grain boundary phases. In this work, the microstructure of Si_3N_4 densified with Nd_2O_3, Y_2O_3 and Al_2O_3 sintering additives was studied. Sintered samples were polished and plasma etched for microstructural analysis using scanning electron microscope. Quantitative evaluation of materials microstructure was accomplished using Quantikov software. Fracture toughness was measured by Vickers indentation method. The observed microstructure is typical of silicon nitride based materials and is characterized by high aspect ratio .-Si_3N_4 grains embedded into a matrix formed by sintering additives. The grain size distribution was shown to depend on the alumina content. Fracture toughness increase with the increase of average grain diameter.

Introduction

Silicon nitride based ceramics are considered to be one of the most promising groups of materials for high temperature structural applications, due to a unique combination of properties such as good flexural strength, fracture toughness, hardness maintained in a wide temperature range, high thermal shock resistance and good hot corrosion resistance [1].

However, it is difficult to densify silicon nitride due to its high degree of covalent bonding (˜70%) and low self diffusion coefficient. The only way to densify silicon nitride without pressure is by liquid phase sintering using sintering aids. At high temperature, silica, which is always present as a surface oxide film on silicon nitride particles, reacts with the oxide additives to form an oxide melt and, with increasing temperature, an oxynitride melt by dissolving Si_3N_4. After the .-Si_3N_4 particles dissolve and supersaturate the liquid phase, .-Si_3N_4 is reprecipitated. Metal oxides such as MgO, Al_2O_3 and rare earth oxides have been found to be effective sintering aids for silicon nitride [2]. The final .-silicon nitride grain size and shape distribution in the material are controlled by the silicon nitride powder characteristics, the metal oxide sintering additives, and the processing conditions [2,3].

It is generally agreed that for superior mechanical properties a fine microstructure with a high proportion of elongated . grains is necessary [3].

One of the main factors favoring elongated grains formation is the viscosity of the liquid phase formed during sintering which depends on the type of the metal oxides [3,4].

The purpose of this study is to verify the influence of different combinations of Al_2O_3, Y_2O_3, and Nd_2O_3 on microstructure and mechanical properties of silicon nitride based ceramics.

Experimental Procedure

.-Si_3N_4 powder (H.C.Starck – M11 with 92,7 of .-Si_3N_4), Al_2O_3 (Alumalux – 39SG Alcoa Chemicals), Y_2O_3 (Aldrich Chemical Company) and Nd_2O_3 (calcined from Nd_2CO_3 - Nuclemon) were used as starting materials. The formulations of studied compositions are presented in Table 1.

Table 1 – Studied compositions

Sample	Si_3N_4 (wt%)	Al_2O_3 (wt%)	Y_2O_3 (wt%)	Nd_2O_3 (wt%)
90-2Y2Nd	90	6	2	2
90-3Y1Nd	90	6	3	1
90-1Y3Nd	90	6	1	3
90-4Y	90	6	4	-
90-4Nd	90	6	-	4
90-3Y3Nd	90	4	3	3
90-6Y	90	4	6	-
90-6Nd	90	4	-	6

The compositions were milled in an attrition mill with Si_3N_4 milling media in isopropanol for 4h at 300rpm. The slurry was dried for 12h in a drying box at 100°C and subsequently, in the form of water slurry, passed through a spray-dryer for granulation.

The powder agglomerates were compacted into cylindrical specimens 14mm in diameter and then cold isostatically pressed under a pressure of 200 MPa.

In order to obtain high density, heat treatment was carried out for 1h at 1750°C in atmosphere of nitrogen and heating rate of 20°C/min. The densities of the sintered samples were determined by the Archimedes method. The microstructure was analyzed by scanning electron microscope (SEM) (Philips XL 30). The phase composition was studied by means of X-ray diffraction (XRD). Samples for microstructural investigation were prepared by standard ceramographic procedure of multistep diamond polishing with subsequent plasma etching (SF_6). Microstructural parameters, such as grain size distribution and grains aspect ratio of .-Si_3N_4 were estimated using the Quantikov image analyzer [5].

Fracture toughness of the ceramics was measured by Vickers indentation method under 60N. In the literature there are numerous empirical expressions for correlating the crack length to the fracture toughness, K_{Ic}. In this work, the Anstis' equation (Eq.1) was used [6]. Ten indentations were evaluated for each sample.

$$K_{Ic} = 0.016\left(\frac{E}{H_v}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \qquad \text{(Eq.1)}$$

Where $\mathbf{K_{Ic}}$ is the fracture toughness (MPa.m$^{1/2}$), **E** is the elastic modulus of silicon nitride (GPa), $\mathbf{H_v}$ is the Vickers hardness (GPa), **P** is the test load (N) and c is the crack length (m), measured from the indentation centre.

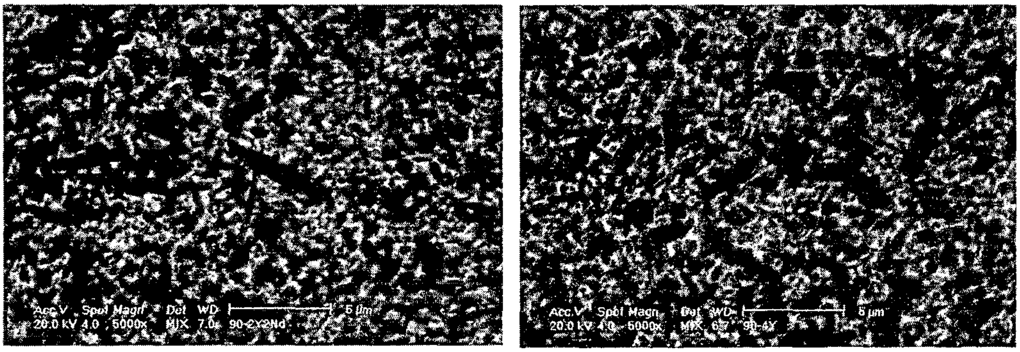
Results and Discussion

The values of green and sintered densities of the investigated materials are presented in Table 2. The samples were analyzed before and after plasma etching with SF_6. The plasma etching is a very sensitive technique regarding small chemical changes in the material. The etching rate strongly depends on the aluminum content of the Si_3N_4 grains [3]. A higher aluminum concentration in the solid solution results in a lower plasma-etching rate. The samples, before plasma etching, exhibit good homogeneity of phase distribution.

Table 2 – Density of the samples before and after sintering at 1750°C/1h

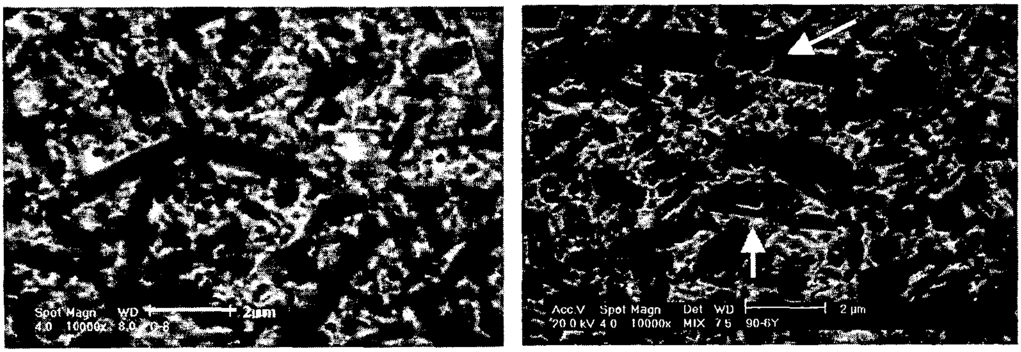
Sample	· theoretical (g/cm^3)	· green (% theoretical)	· apparent (%theoretical)
90-2Y2Nd	3.30	55	97
90-3Y1Nd	3.30	56	97
90-1Y3Nd	3.31	57	97
90-4Y	3.29	56	97
90-4Nd	3.31	57	97
90-3Y3Nd	3.32	57	98
90-6Y	3.30	57	97
90-6Nd	3.34	56	95

The microstructure of the samples doped with Al_2O_3, Y_2O_3 and Nd_2O_3, and plasma etched is presented in Fig.1 and Fig.2. The microstructure was a typical one of a liquid phase sintered silicon nitride, consisting of elongated .-Si_3N_4 grains of prismatic shape embedded into a secondary vitreous phase formed by the oxide sintering aids.



(a) (b)

Fig. 1 – Microstructure of samples polished and plasma etched (a) 90-2Y2Nd; (b) 90-4Y.



(a) (b)

Fig. 2 – Microstructure of samples polished and plasma etched (a) 90-3Y3Nd; (b) 90-6Y.

Some grains exhibit an internal structure (Fig.2), indicated by arrows, with a core in the middle visible after plasma etching. In accordance with Petzow and Hoffman [7], during densification, three possible mechanisms for the "nucleation" of .-crystals have to be considered: i) a homogeneous nucleation of .-grains in the supersaturated oxynitride glass; ii) a heterogeneous nucleation of .-Si_3N_4 on .-grain, and iii) assuming that there is no nucleation at all, the growth of preexisting .-grains in the initial Si_3N_4 powder. It was concluded that neither a homogeneous nor a heterogeneous nucleation of .-Si_3N_4 has a significant influence on the microstructural development. Only preexisting .-particles of the starting powder seem to grow [3]. Therefore, the core represents the .-nucleus of the inner crystal. All the samples exhibit a core-rim structure of the number of grains, coherent with the amount of . phase in the starting powder.

The determination of grain size distribution was carried out using the software Quantikov 1.7. The results of average grain size, aspect ratio and fracture toughness are shown in Table 3.

Table 3 – Grain size , aspect ratio and fracture toughness (K_{Ic}) of the studied samples

Samples	· average (.m)	Aspect Ratio	K_{Ic} (MPa.m$^{1/2}$)
90-2Y2Nd	5.0.2.9	0.71	4.8.0.2
90-3Y1Nd	4.8.3.2	0.73	5.1.0.3
90-1Y3Nd	3.8.2.9	0.74	4.9.0.3
90-4Y	5.3.3.3	0.76	5.1.0.2
90-4Nd	4.3.2.8	0.73	4.8.0.2
90-3Y3Nd	3.2.2.4	0.73	4.8.0.2
90-6Y	3.2.2.6	0.76	4.7.0.1
90-6Nd	2.7.2.1	0.70	4.6.0.2

It was observed that the samples with 6wt% Al_2O_3 have higher average grain compared to size that with 4wt% Al_2O_3. The grain size depends mostly on the viscosity of the liquid phase during sintering. Low viscosity liquid phase promotes the grain growth by facilitating diffusion processes. Certain amount of alumina are known to lower the viscosity of oxynitride liquid phases formed during sintering which explains the higher average grain size observed in the samples with 6 wt% of Al_2O_3 [3].

Earlier studies confirm that an appreciable toughening effect can be achieved in silicon nitride based ceramics due to the *in situ* development of elongated .-Si_3N_4 grains. This effect can be further enhanced by the use of appropriate sintering aids producing liquid phase of high viscosity during sintering [3].

Comparing the fracture toughness and average grain size, it can be observed that the samples with 6wt% Al_2O_3 (and larger grain size) show fracture toughness slightly higher than the samples with 4wt% Al_2O_3. This behavior was expected in accordance with Kawashima *et al* [8] and Mitomo [9]. In two independent experiments it was shown that the fracture toughness of silicon nitride increases with the increase of diameter of the most elongated grains.

The crack propagation paths induced by the indentation are shown in Fig.3. It can be observed in these micrographs that the crack path has a "zig-zag" shape. It occurs when the crack approaches the .-grain and is deflected by it. This behavior was observed for all studied samples. Crack deflection is mostly related to .-Si_3N_4 grains with the diameter exceeding 1 .m [10]. According to Rat *et al* [11] transcrystalline fracture occurs mainly when the longitudinal axis to the grain is at an angle of more than 45° to the crack. If the angle is less than 45°, the crack will propagate through the glass phase along the grain boundary, and the shape of individual grains determines the shape of the crack path. Fig.3 shows an example of a transcrystalline crack.

Secondary phase with high Al_2O_3 and N content, results in .’-SiAlON formation on the surface of .-Si_3N_4 grains. The formation of .’-SiAlON represents a change in the nature of the atomic bonding across the interface. Although isostructural with .-Si_3N_4, .’-SiAlON contains Al-N, Al-O, and Si-O bonds in addition to the Si-N bonds. Because the major atomic bonds in the Si-Al-Y oxynitride glasses are Si-O, Si-N, Al-N, and Al-O, similar chemical bonds can be established across the .’-SiAlON/glass interface as well as within the two phases. Thus, the .’-SiAlON/glass interface has a potential to be more strongly chemically bonded than the Si_3N_4/glass interface. In some cases, this new interface can cause the shift of the crack propagation mode from intergranular to transgranular and consequently lower the fracture toughness.

Another factor that influences the crack deflection mechanism is the tensile stress in the material. The fracture toughness can be lower if on cooling or after post-sintering treatment tensile stress is induced in the material due to the thermal expansion coefficient mismatch between silicon nitride and the secondary phase or due the volume changes upon phase transformation [12].

In the latter case, a mixed crack propagation mode can be observed, i.e., both the inter- and transgranular fracture occur simultaneously. Thus, in Fig.3a the overall crack path is observed to have a “zig-zag” shape typical for intergranular fracture and crack deflection mechanism, while some grains, indicated by arrows and presented in details in Fig. 3b, undergo transgranular fracture.

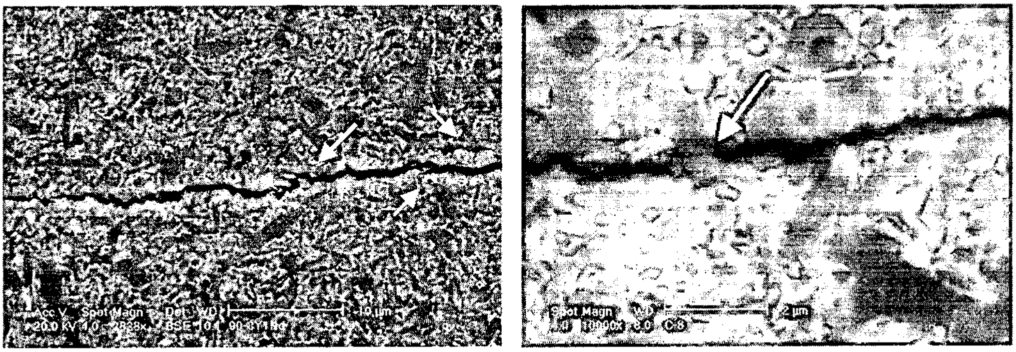


Fig. 3 – Crack propagation profile of Si_3N_4: (a) 90-3Y1Nd and (b) 90-3Y3Nd. Interaction between the crack and the grains.

Conclusions

The microstructure and mechanical properties of silicon nitride sintered with Al_2O_3, Y_2O_3 and Nd_2O_3 were investigated.

The increase of the average grain diameter was attributed to the alumina content. Alumina is believed to lower the viscosity of the liquid phase formed during sintering which results in the higher average grain diameter for the samples with 6 wt % of Al_2O_3 than for the ones with 4 wt % of Al_2O_3.

The observed increase in fracture toughness was mainly attributed to the variation of grain size, microstructure modifications and second phase characteristics.

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