Influence of the substitution of Y_2O_3 for CeO_2 on the mechanical and microstructural properties of silicon nitride

(Influência da substituição de Y_2O_3 por CeO_2 nas propriedades mecânicas e microestruturais do nitreto de silício)

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Abstract

This work investigated the substitution of Y_2O_3 for CeO_2 in liquid-phase sintered silicon nitride ceramics. Cost reduction as well as good physical, mechanical and microstructural properties are the main objectives of the present study. Two powder mixtures were prepared, varying the contents of α-Si_3N_4, Al_2O_3, AlN, Y_2O_3 and CeO_2. The mixtures were homogenized in ethanol, dried in a rotating evaporator and kiln, respectively, and then uniaxially (100 MPa) and cold isostatically pressed (300 MPa). The samples were sintered at 1850 ^{o}C for 1 h in a graphite resistive furnace under nitrogen atmosphere. After sintering the density of the samples was higher than 97% of the theoretical value. The fracture toughness and hardness were higher than 5.28 MPa.m$^{1/2}$ and 17.12 GPa, respectively. Phase analysis by X-ray diffraction and scanning electron microscopy revealed the presence of α-SiAlON and β-Si_3N_4.
Keywords: Si_3N_4, liquid-phase, Y_2O_3, CeO_2, fracture toughness, hardness.

Resumo

Este trabalho foi proposto com objetivo de analisar a possibilidade da substituição de Y_2O_3 por CeO_2 na sinterização via fase líquida de nitreto de silício (Si_3N_4), visando obter um material com boas propriedades físicas, mecânicas e microestruturais, além da redução de custos de produção desta cerâmica. Para o desenvolvimento deste trabalho foram preparadas duas misturas de pós, variando-se as proporções entre α-Si_3N_4, Al_2O_3, AlN, Y_2O_3 e CeO_2. As misturas de pós foram homogeneizadas em etanol, secas em evaporador rotativo e estufa, respectivamente. Em seguida, prensadas uniaxialmente (100 MPa) e isostaticamente a frio (300 MPa). As amostras foram sinterizadas à 1850 ^{o}C durante 1 h, em forno com elemento resistivo de grafite sob atmosfera de nitrogênio. Após sinterização, as amostras apresentaram densidades relativas superiores a 97% do valor teórico. A tenacidade à fratura e a dureza foram superiores a 5,28 MPa.m$^{1/2}$ e 17,12 GPa, respectivamente. As análises de fases por difração de raios X e microscopia eletrônica de varredura mostraram a presença das fases α-SiAlON e β-Si_3N_4.
Palavras-chave: *Si_3N_4, fase líquida, Y_2O_3, CeO_2, tenacidade à fratura, dureza.*

INTRODUCTION

Due to its excellent properties, silicon nitride (Si_3N_4) is a promising material for several structural applications, such as: combustion gas exhaust valve, sealing, piston and combustion chambers and others. Such inherent properties of Si_3N_4 result from strong and directional covalent bonding between Si and N, resulting in a material with low self-diffusion coefficient, but difficult to sinter without additives [1]. In the last decades, dense Si_3N_4 ceramics have been obtained by liquid-phase sintering using small amounts of sintering additives to enhance diffusion, decrease porosity and, consequently, improve densification and mechanical properties of dense Si_3N_4. Y_2O_3 is one of the most often used additives in the liquid phase sintering of silicon nitride. However, due to the high cost of the material, other alternatives have been researched, including CeO_2, which is about twenty times cheaper than Y_2O_3 [2, 3].

Si_3N_4 shows low resistance to oxidation and creep if compared to other covalent ceramics, such as silicon carbide (SiC) [2, 3]. A way of improving such properties involves the use of additives rich in Al, Y and O ions, which enter the crystalline structure of Si_3N_4, resulting in substitutional and/or interstitial solid solutions called SiAlONs. Upon sintering these materials, α-Si_3N_4 grains are formed in the liquid phase rich in Al, Y and O ions. Al and O substitute Si and N, respectively. Meanwhile, Y ions occupy interstitial positions of the structure, stabilizing the α phase at high

sintering temperatures [2, 4, 5].

The objective of this study was to investigate the substitution of Y_2O_3 by CeO_2 in silicon nitride liquid phase sintering, obtaining ceramics with high densification, good mechanical properties and relatively low production costs.

EXPERIMENTAL PROCEDURE

The materials used in this study were: α-Si_3N_4 (99.9 % - H. C. Starck - Germany), Y_2O_3 and AlN (Fine grade - H. C. Starck – Germany); CeO_2 (high purity – H. C. Starck – Germany), Al_2O_3 (AS 250K – Baikalox) and nitrogen gas (Type 4.6 – White Martins).

The powder batches were prepared in a planetary mill for 3 h using isopropanol as vehicle. The suspensions were dried and subsequently sieved. The compositions of

Table I - Compositions of the prepared powder mixtures.
[Tabela I - Composições das misturas preparadas de pós.]

Label	Composition (wt %)				
	α-Si_3N_4	Al_2O_3	AlN	CeO_2	Y_2O_3
SNAYA	78.50	3.50	12.00	-	6.00
SNACA				6.00	-

the different powder mixtures are represented in Table I.

Rectangular green bodies (16.36 x 16.36 x 7.5 mm) were uniaxially pressed under 100 MPa and subsequently isostatically pressed under 300 MPa. After compaction, the green density was geometrically estimated. The samples were involved in a powder bed consisting of 70% Si_3N_4 and 30% BN and then sintered in a furnace with graphite heating elements (Thermal Technology Inc. type 1000-4560-FP20) under nitrogen. The heating and cooling rate were 25 ^{o}C/min up to the maximum sintering temperature of 1850 ^{o}C. The holding time was 1 h.

The relative density of the sintered samples was determined by immersion in distilled water. The weight loss was determined before and after sintering. Phase analysis was carried out by X-ray diffraction using Cu-Kα radiation and scanning speed of 0.02^o/s. Polished samples were submitted to chemical etching in NaOH:KOH (1:1 at 500 ^{o}C/10 min) to reveal the microstructure. Scanning electron micrographs of the sintered samples were obtained. Vickers hardness values were measured applying a load of 20N for 30 s. For statistical reasons, 20 indentations were made in each sample. The fracture toughness was determined by measuring the crack length created during the hardness tests. The values of the fracture toughness were calculated using the relationship proposed by Evans and valid for Palmqvist type cracks [6].

RESULTS AND DISCUSSION

The values of green density, final density and weight loss of the samples are shown in Table II. The results revealed relative densities above 97% of the theoretical density (%TD) for both samples. However, sample labeled SNAYA showed a higher value of the relative density with lower weight loss, suggesting the efficiency of the liquid phase formed in this system, which probably allowed good wettability of α-Si_3N_4 particles, assisting the liquid phase sintering mechanisms. The high weight loss observed for the SNACA samples was probably due to volatilization of CeO_2 during sintering.

Table II - Green density, final density and weight loss of sintered samples.
[Tabela II - Densidade a verde, densidade final e perda de massa das amostras sinterizadas.]

Sample	Green Density (% TD)	Final Density (% TD)	Weight loss (%)
SNAYA	60.06	98.18	2.62
SNACA	62.94	97.40	5.86

The X-ray diffraction patterns of the sintered samples are shown in Table III, along with the relative contents of α-SiAlON to β-Si_3N_4 phases. In SNACA samples, only α-SiAlON was observed, showing the good efficiency of this system in the stabilization of α-Si_3N_4, allowing solid solution and holding the transformation from α-Si_3N_4 to β-Si_3N_4 during sintering. For SNACA samples, α-SiAlON was the predominant phase. A small amount of β-Si_3N_4 was also noticed, revealing limited transformation from α-Si_3N_4 to β-Si_3N_4.

Table III - X-ray diffraction patterns and α-SiAlON: β-Si_3N_4 ratio.
[Tabela III - Difratogramas de raios X e razão entre as fases α-SiAlON e β-Si_3N_4.]

Sample	Phases	α-SiAlON:β-Si_3N_4
SNAYA	α-SiAlON	100:00
SNACA	β-Si_3N_4, α-SiAlON	19:81

The microstructures of sintered samples are shown in Fig. 1. Elongated grains with high aspect ratio (length/diameter), characteristic of α-Si_3N_4 and β-Si_3N_4 can be seen. SNAYA samples (Fig. 1a) depicted homogeneous dispersion of relatively small grains compared to SNACA samples (Fig 1b), whose microstructure clearly consisted of a mixture of fine α-SiAlON and coarse β-Si_3N_4 grains.
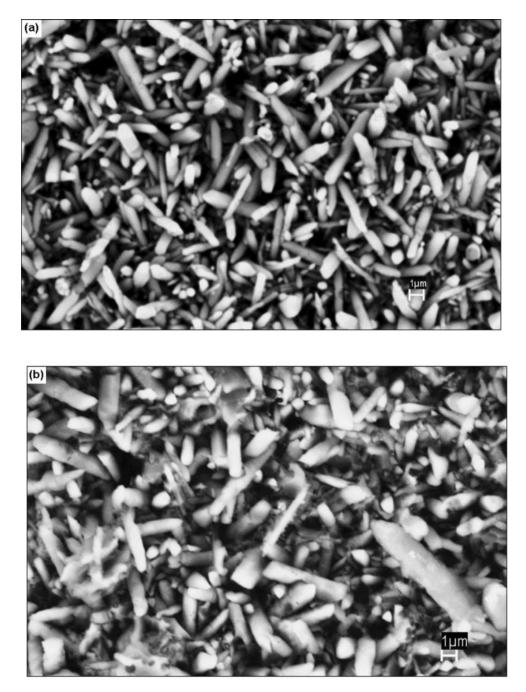
Figure 1: SEM micrographs of chemically etched (a) SNAYA and (b) SNACA surfaces.
[Figura 1: Micrografias de amostras atacadas quimicamente (a) SNAYA e (b) SNACA.]

The hardness and fracture toughness of SNAYA and SNACA sintered samples are listed in Table IV. The results showed that SNAYA samples depicted higher hardness values, mainly due to the predominance of α-SiAlON, inherently harder than β-Si_3N_4. Conversely, the same samples presented fracture toughness values lower than those of SNACA samples because of the larger aspect ratio and mixed microstructure, as it could be seen from the corresponding micrographs.

Table IV - Hardness and fracture toughness of SNAYA and SNACA sintered samples.
[Tabela IV - Dureza e tenacidade à fratura de amostras sinterizadas SNAYA e SNACA.]

Sample	Hardness (GPa)	Fracture Toughness (MPa.m$^{1/2}$)
SNAYA	19.86 ± 0.32	5.28 ± 0.15
SNACA	17.12 ± 0.54	6.34 ± 0.41

CONCLUSIONS

It is possible to obtain dense Si_3N_4 with good mechanical properties at low cost, replacing Y_2O_3 by CeO_2. The densification of Si_3N_4 containing $AlN:CeO_2$ was nearly identical to that of the composition containing $AlN:Y_2O_3$. However, $AlN:CeO_2$ stabilized the β-Si_3N_4 phase whereas $AlN:Y_2O_3$ stabilized α-SiAlON. Therefore, distinct mechanical properties were observed. The former was tougher whereas the latter was harder.

ACKNOWLEDGEMENTS

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