

SILICON NITRIDE CERAMICS OBTAINING FOR ALTERNATIVE SINTERING ADDITIVE

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Abstract. Due to its physical and thermomechanical properties, silicon nitride ceramics (Si_3N_4) are materials promising to be used in structural applications. However, factors group endears the manufacture this material, such as: type and cost of additive. This paper is proposed with the objective to manufacture silicon nitride (Si_3N_4) ceramics by liquid phase sintering with good physical and mechanical properties, above all the reduction of production costs. To development of the same were prepared different powder mixtures varying proportions among $\alpha\text{-Si}_3\text{N}_4$, AlN, Y_2O_3 , Al_2O_3 , Cr_2O_3 , CeO_2 , that were homogenized, compacted and sintered at 1900°C for 1h. After sintering, samples showed relative densification, hardness and fracture toughness varying of 97 to 98 of theoretical, hardness and fracture toughness between 16.8 to 20.7 GPa and 4.4 to 5.1 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. The phase analysis by x-ray diffraction and scanning electron microscopy (SEM) showed presence of $\alpha\text{-SiAlON}$ and $\beta\text{-Si}_3\text{N}_4$ phases. The results obtained to demonstrated that is possible to obtain Si_3N_4 ceramics with good properties and lower costs.

Keywords: Si_3N_4 , alternative additives, sintering, mechanical properties, microstructure.

1. Introduction

Because of its excellent properties, silicon nitride (Si_3N_4) is a promising material to several structural applications, such as: combustion gas exhaust valve, sealing, piston and combustion chambers and others. Such inherent properties of Si_3N_4 occur due to the strong covalent bonding between Si and N, resulting in a material with directional chemical bonding and low self-diffusion coefficient, which is difficult to obtain dense Si_3N_4 ceramics by solid state sintering (Dressler, 1997).

In recent decades, dense Si_3N_4 ceramics have been obtained by liquid phase sintering using AlN, Al_2O_3 and Y_2O_3 or mixtures of these (Ribeiro, 2000). Such sintering additives facilitate the diffusion phenomena, decreasing the porosity of the material and consequently, improving the densification and mechanical properties of the Si_3N_4 (Santos, 2004).

The change in the sintering parameters, such as additives amount and type, it can influence straight on densification, microstructure and consequently properties of Si_3N_4 ceramics (Ribeiro, 1997, Santos, 2004). For example, rich liquid phase in Al, Y and O, during the sintering of Si_3N_4 appeases the formation of a solid solution called SiAlONs, which improve oxidation, hardness and creep resistance of the Si_3N_4 ceramics at high temperatures. SiAlONs shows two crystalline phases, α and β , resultants in α and $\beta\text{-Si}_3\text{N}_4$ phases, respectively; by replacement of Si and N by Al and O, and occupation the interstitial void to Y (Ruiz, 2000, Santos, 2003).

Among the factors that influence in the manufacture process this ceramic detach for raw materials costs (as of the additives: Al_2O_3 , Y_2O_3 , Ce_2O_3 , CRE_2O_3 etc). The yttrium oxide (Y_2O_3) has been the additive more employed in Si_3N_4 liquid phase sintering (LPS- Si_3N_4), but the high costs this material make unfeasible to use of same, having need in finding others alternative materials to LPS- Si_3N_4 , as cerium oxide (CeO_2) and CRE_2O_3 , because of its lower costs. The CeO_2 powder costs about twenty times cheaper that Y_2O_3 (H. C. Starck, site). Whereas, the CRE_2O_3 is an oxide manufactured in DEMAR-Faenquil, starting from the Xenotima mineral, that is rich in rare earth oxides (Y, Yb, Dy, Er, etc), costing about ten times cheaper than Y_2O_3 (Santos, 2004).

The goal this paper was: to obtain Si_3N_4 ceramics by liquid phase process with high densification and good mechanical properties, to make possible the use of CeO_2 and CRE_2O_3 in substitution to the Y_2O_3 , and application those materials in several knowledge areas (engineering materials machining, aerospace, aeronautic and others).

2. Experimental procedure

2.1 Materials

The materials used in this paper were: $\alpha\text{-Si}_3\text{N}_4$ (99.9 % - H. C. Starck - Germany), Y_2O_3 and AlN (Grade C - H. C. Starck - Germany), Al_2O_3 (Fine grade - H. C. Starck - Germany), CeO_2 (H. C. Starck), CRE_2O_3 (yttrium and rare earth mixed oxide) produced at DEMAR-FAENQUIL and nitrogen (Type 4.6 - White Martins). The chemical analysis of the yttrium and rare earth oxide mixture, CRE_2O_3 are listed in **Tab. 1**.

Table 1. Chemical analysis of the yttrium and rare earth mixed oxide.

CRE_2O_3	Composition (wt %)	CRE_2O_3	Composition (wt %)
Y_2O_3	44.60	Gd_2O_3	1.17
Yb_3O_3	19.71	Tb_2O_3	0.82
Er_2O_3	13.94	Sm_2O_3	0.38
Dy_2O_3	10.25	Ce_2O_3	0.09
Ho_2O_3	3.27	Eu_2O_3	0.02
Tm_2O_3	2.83	Nd_2O_3	0.12
Lu_2O_3	2.62	La_2O_3	0.01

2.2 Method

The powder batches were prepared in a planetary mill for 3 hours using isopropilic alcohol as a vehicle. The suspensions were dried and subsequently sieved. The overall compositions of the different powders mixtures, as well as their designations are represented in **Tab. 2**.

Table 2. Code and Composition of the powder mixture prepared.

Code	Composition (wt %)					
	$\alpha\text{-Si}_3\text{N}_4$	AlN	CeO_2	CRE_2O_3	Al_2O_3	Y_2O_3
A	77.40	14.00	-	-	-	8.60
B			-	8.60	-	-
C			3.00	-	2.60	3.00
D			8.60	-	-	-

The green bodies were fabricated by uniaxial pressing under a 100 MPa pressure and subsequent isostatic pressing under a 300 MPa pressure. After compaction, samples had 13.36x13.36x7.5 mm dimensions and green density of 60 % density theoretical. The green densities of the compacts were determined geometrically. Before sintering, the samples were involved in 70% Si_3N_4 + 30% BN as powder bed, and then introduce in a furnace with a graphite heating element (Thermal Technology Inc. type 1000-4560-FP20) in nitrogen atmosphere. The heating rate employed was 25°C/min up to a maximum sintering temperature of 1900°C, with a holding time for 1 hour. The cooling rate was the same as heat-up rate.

The density of the sintered samples was determined by the immersion method in distilled water. The weight loss was determined before and after sintering measurements. The phase analysis was determined for X-ray diffraction with Cu-K α radiation and scanning speed equal to 0.02°/s.

Smoothed and polished samples were submitted to chemical etching in a NaOH:KOH mixture (1:1 at 500°C/10 minutes) to reveal the microstructure. The micrographs of the sintered samples were obtained by the use of Scanning Electron Microscopy (SEM).

The hardness was determined by Vicker's indentations under an applied load of 20N for 30 s. To statistical reasons, 20 indentations were made to each sample. The fracture toughness has been determined by the measurement of crack length created by indentations. The calculation of the fracture toughness values was done by relation proposed by Evans et al., valid for Palmqvist type cracks, conform equation (1) (Silva, 1992).

$$K_{IC} = 0.16(E/H)^{1/2} \cdot F \cdot b^{-3/2} \quad (1)$$

Where: K_{IC} = fracture toughness [$\text{MPa} \cdot \text{m}^{1/2}$]; E = Young modulus of material [GPa]; HV = Vickers hardness [GPa]; b = crack size [μm] and F = applied load [N].

Fracture toughness values were revised, considering influence of the porosity in growth and propagation of crack during indentation, conform equation (2) (Silva, 1992).

$$K_{IC} = K_{IC0} \cdot e^{-bP} \quad (2)$$

Where: K_{IC} = real fracture toughness of material [$\text{MPa} \cdot \text{m}^{1/2}$]; K_{IC0} = fracture toughness obtained for indentation; b = proportionality constant ($\beta\text{-Si}_3\text{N}_4 = 7,1$) (Silva, 1992). P = porosity of material.

3. Results and discussions

3.1. Relative density and linear shrinkage

Relative density, linear shrinkage and weight loss of sintered samples has been shown in **Tab. 3**. The samples additived with $\text{AlN}/\text{Y}_2\text{O}_3$ and $\text{AlN}/\text{CRE}_2\text{O}_3$ showed the better densification, linear shrinkage and weight loss results. Such characteristics can be explained because good chemical stability and properties inherent to liquid formed, such as viscosity, which influence directly in LPS- Si_3N_4 mechanisms, particle rearrangement and solution-reprecipitation mainly, responsible by decrease of the porosity and consequent increase of relative density. The weight loss observed at sample utilizing AlN/CeO_2 probable is due to lower volatilization of CeO_2 and organics material, utility to compaction. Hence, this weight is possible because the high temperature in the sintering process.

Table 3. Green density, final density and loss weight results of the sintered samples.

Code	Physical properties		
	Final density (% of theoretical)	Linear shrinkage (%)	Weight loss (%)
A	98.52 ± 0.15	16.34 ± 0.34	2.10 ± 0.20
B	98.04 ± 0.20	15.96 ± 0.23	3.92 ± 0.31
C	97.98 ± 0.43	15.38 ± 0.18	4.08 ± 0.45
D	97.21 ± 0.36	15.14 ± 0.10	5.86 ± 0.58

3.2. Phase analysis of the sintered samples

The results the x-ray diffraction of the sintered samples is shown in **Fig.1**. The samples additived for $\text{AlN}/\text{Y}_2\text{O}_3$ (**Fig. 1a**) $\text{AlN}/\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3/\text{CeO}_2$ (**Fig. 1c**) and $\text{AlN}/\text{CRE}_2\text{O}_3$ (**Fig. 1b**) showed predominant presence of $\alpha\text{-SiAlON}$ phase, because the characteristics of liquid formed in this samples together with the sintering parameters, that probably allowed the stabilization of $\alpha\text{-Si}_3\text{N}_4$ and transformation to $\alpha\text{-SiAlON}$. Whereas, only $\beta\text{-Si}_3\text{N}_4$ phase has been noted in the samples additived AlN/CeO_2 (**Fig. 1d**), because of the full α into $\beta\text{-Si}_3\text{N}_4$ transformation.

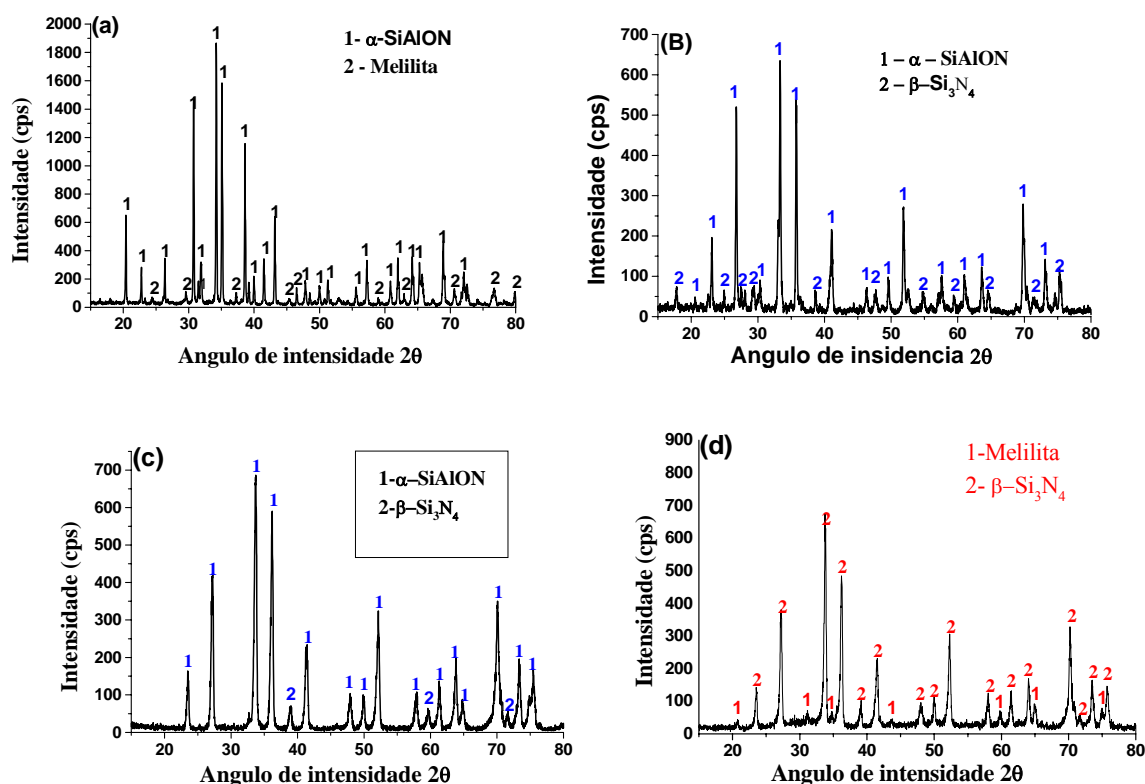
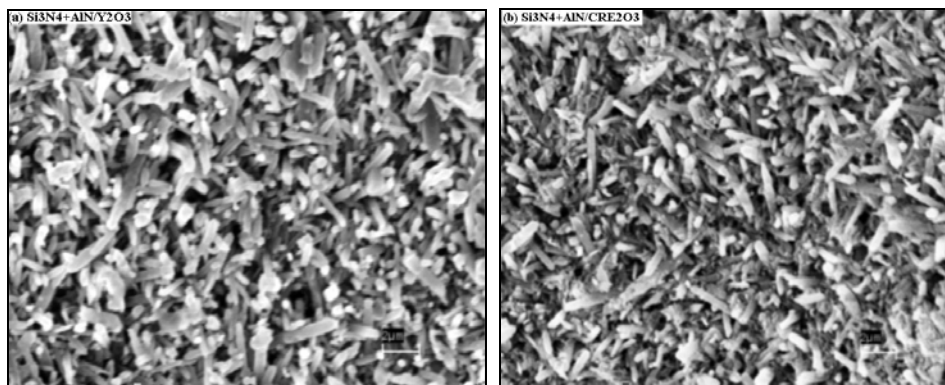


Figure 1. X-ray diffraction patterns samples sintered.

3.3. Microstructural analysis of the sintered samples

The micrographs of the sintered sample are shown in **Fig. 2**. Analyzing the results, observe microstructures with elongated grain morphology, characteristics of α -SiAlON and β -Si₃N₄ phases, have been shown for different samples. A tendency homogeneous microstructure is noted in all samples. whereas in (**Fig. 2a and 2b**) the samples shows similar microstructure due probably the great influence of yttrium oxide, that is presents in higher amount on yttrium and rare earth mixed oxide, such as already shown **Tab.1**. To others samples (**Fig. 2c and 2d**) it is observed different microstructure, because maybe of the distribution of additives on ceramic matrix or same sintering conditions used during LPS-Si₃N₄, that can have influenced in the viscosity of liquid phase and consequently on sintering mechanisms. In sample added to AlN/Al₂O₃/CeO₂/Y₂O₃ (**Fig. 2c**), a more fine microstructure has been shwon when compared to the others systems, condition that can be related to the characteristics inherent to the liquid formed.



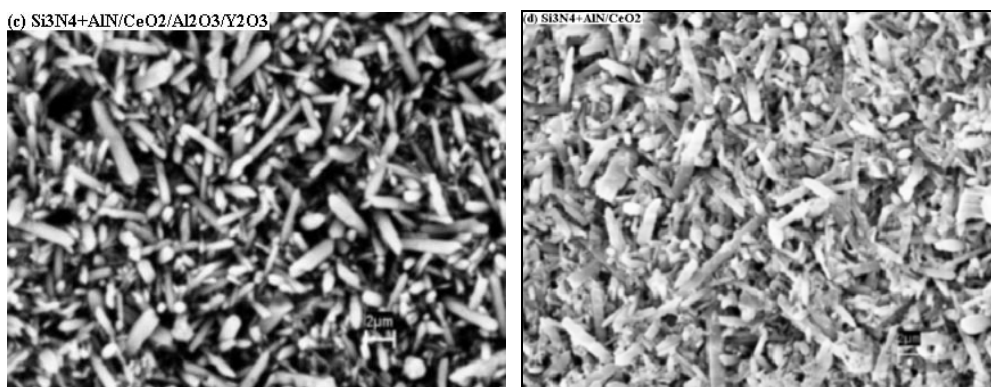


Figure 2. Micrograph of samples sintered.

3.4. Hardness and fracture toughness

Fracture toughness and hardness of the sintered samples are shown in **Tab. 4**. The samples additived for AlN/Y₂O₃ and AlN/CRE₂O₃ showed the largest hardness values, because of α -SiAlON phase. The same samples too showed the lowest fracture toughness values, because probably of microstructure or same of high hardness, that it is inversely proportional to the fracture toughness, as shown in equation (1) (Silva, 1992). Whereas, for the samples additived for AlN/Al₂O₃/CeO₂/Y₂O₃ and AlN/CeO₂ has been noted inverse behavior.

Table 4. Hardness and fracture toughness of sintered samples.

Code	Mechanical properties	
	Hardness (GPa)	Fracture toughness (MPa.m ^{1/2})
A	20.75 ± 0.21	4.41 ± 0.15
B	19.72 ± 0.14	4.45 ± 0.23
C	17.60 ± 0.32	4.89 ± 0.32
D	16.80 ± 0.43	5.09 ± 0.25

3.5 Preliminary costs analysis for manufacture of the samples

In this paper only costs of raw materials (such as: α -Si₃N₄, AlN, Al₂O₃, CeO₂, Y₂O₃ and CRE₂O₃) has been considered in LPS-Si₃N₄ manufacture, considering this mode that other costs, such as: preparation, compactation and sintering has been same to different powder mixtures. The costs of raw materials are shown in **Tab. 5**. The estimated cost of the yttrium oxide and rare earth mixed oxide (CRE₂O₃) has been obtained by literature (Santos, 2004), whereas, the costs of the others raw materials (α -Si₃N₄, AlN, Y₂O₃, Al₂O₃ and CeO₂) is supplied by the manufacturer (Hermann C. Starck, site). The AlN, Al₂O₃, CRE₂O₃ and CeO₂ costs are the lowest when compared to the α -Si₃N₄ and Y₂O₃ costs.

Table 5. Price per kilogram of raw materials used in this paper (H. C. Starck, site).

Raw material	Price (US\$/kg)
Alpha-Silicon nitride (α -Si ₃ N ₄)	140.00
Aluminum nitride (AlN)	43.00
Yttrium oxide (Y ₂ O ₃)	200.00
Aluminum oxide (Al ₂ O ₃)	1.74
Yttrium and rare earth mixed oxide (CRE ₂ O ₃)	20.00
Cerium oxide (CeO ₂)	9.50

The costs to manufacture, of different mixtures, studied in this paper has been listed in **Tab. 6**. The powder mixtures containing α -Si₃N₄ plus AlN/CRE₂O₃ (code B), α -Si₃N₄ plus AlN/Al₂O₃/CeO₂/Y₂O₃ (code C) and α -Si₃N₄ plus AlN/CeO₂ (code D) showed the lowest costs when compared to another powder mixture. In agreement with the costs analysis and results shown previously has been possible to substitute Y₂O₃ by CRE₂O₃ and CeO₂, particularly for CRE₂O₃, whose samples additived to AlN/CRE₂O₃ exhibited physical, mechanics and microstructural characteristics similar to the additived for AlN/Y₂O₃.

Table 6. Price per kilogram of the different mixtures studied in this work.

Raw material	Price (US\$/kg)			
	Code			
	A	B	C	D
α -Si ₃ N ₄	108.36	108.36	108.36	108.36
AlN	6.02	6.02	6.02	6.02
Al ₂ O ₃	-	-	0.045	-
Y ₂ O ₃	17.20	-	6.00	-
CrE ₂ O ₃	-	1.72	-	-
CeO ₂	-	-	0.28	0.817
Total price	131.58	116.10	120.70	115.19

4. Conclusions

The results in this paper shown to be possible substitute the yttrium oxide (Y₂O₃) by yttrium and rare earth mixed oxide (CrE₂O₃) and cerium oxide (CeO₂), mainly by CrE₂O₃, because that samples additived with AlN/CrE₂O₃ showed properties physical, mechanical and microstructural similar to additive AlN/Y₂O₃. This behavior can be justified by the great Y₂O₃ amount present in the CrE₂O₃.

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