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Evaluation of the Reliability of Si_3N_4-Al_2O_3-CTR_2O_3 Ceramics through Weibull Analysis

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The objective of this work has been to compare the reliability of two Si_3N_4 ceramics, with Y_2O_3/Al_2O_3 or CTR_2O_3/Al_2O_3 mixtures as additives, in regard to their 4-point bending strength and to confirm the potential of the rare earth oxide mixture, CTR_2O_3, produced at FAENQUIL, as an alternative, low cost sinter additive for pure Y_2O_3 in the sintering of Si_3N_4 ceramics. The oxide mixture CTR_2O_3 is a solid solution formed mainly by Y_2O_3, Er_2O_3, Yb_2O_3 and Dy_2O_3 with other minor constituents and is obtained at a cost of only 20% of pure Y_2O_3. Samples were sintered by a gas pressure sintering process at 1900 °C under a nitrogen pressure of 1.5 MPa and an isothermal holding time of 2 h. The obtained materials were characterized by their relative density, phase composition and bending strength. The Weibull analysis was used to describe the reliability of these materials. Both materials produced presented relative densities higher than 99.5%t.d., β-Si_3N_4 and $Y_3Al_5O_{12}$ (YAG) as cristalline phases and bending strengths higher than 650 MPa, thus demonstrating similar behaviors regarding their physical, chemical and mechanical characteristics. The statistical analysis of their strength also showed similar results for both materials, with Weibull moduli m of about 15 and characteristic stress values σ_o of about 700 MPa. These results confirmed the possibility of using the rare earth oxide mixture, CTR_2O_3, as sinter additive for high performance Si_3N_4 ceramics, without prejudice of the mechanical properties when compared to Si_3N_4 ceramics sintered with pure Y_2O_3.

Keywords: *Si_3N_4, rare earth oxides, mechanical properties, Weibull analysis*

1. Introduction

Silicon nitride based ceramics possess great potentials for structural applications and, therefore, the reliability of their mechanical properties is very important for successful aplications. The characteristics of the liquid phase formed during the sintering such as viscosity, dihedral and contact angles are important for a successfull sintering and, consequently, for the mechanical properties of the sintered body[1-3].

Several additives have been investigated in order to optimize the sintering process and to adapt the microstructural characteristics to the intended properties. Yttrium oxide (Y_2O_3) is one of the most frequently used sintering additive due to the characteristics of the intergranular phase formed. The use of additive mixtures based on the Y_2O_3/Al_2O_3 system presented higher bending strengths and fracture toughness than other systems[4-6].

At the Department of Materials Engineering of the Faculty of Chemical Engineering of Lorena, a process has been developed producing a mixed concentrate of Yttrium and rare

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earth oxides, CTR_2O_3, by the alkaline fusion of the ore Xenotime, abundantly found in Brazilian soils. The final product is an oxide solid solution of yttrium and rare earth (Er^{+3}, Yb^{+3}, Dy^{+3}, Ho^{+3}) elements occupying Y^{+3} positions in the Y_2O_3 structure. The relative cost of this concentrate is only 20% of pure Y_2O_3, as demonstrated in previous studies[3].

One of the main problems encountered in the use of ceramics for structural components is the great dispersion of their mechanical strength, reducing the reliability. Obtaining consistent data about the mechanical strength of ceramic materials is more complex than for ductile materials, because of their inherent brittleness and the statistical nature of the distribution of defects, ultimately causing the failure of the components. Therefore, the mechanical behaviour must be described by statistical methods. The statistical approach by Weibull is frequently used to describe the variation of the mechanical properties in ceramic materials[7-10].

The objective of the present work was the comparison of the reliability in terms of the bending strength by the Weibull analysis of two Si_3N_4 based ceramic materials, using mixtures of Y_2O_3/Al_2O_3 or CTR_2O_3/Al_2O_3 as additives, and demonstrating the possibility of the substituion of pure Y_2O_3 by CTR_2O_3, produced at DEMAR, as sintering additive without prejudice of the mechanical properties.

2. Experimental

Si_3N_4-CTR_2O_3-Al_2O_3 mixtures (*SNTRA*) were prepared using 86 vol.% of Si_3N_4 and 14 vol.% of Al_2O_3/CTR_2O_3 in the stoichiometry of the phase $Y_3Al_5O_{12}$, YAG[11]. For comparison, another mixture based on Si_3N_4-Y_2O_3-Al_2O_3 (*SNYA*) was prepared, in the same proportions as the previous mixture. The sample compositions are resumed in Table 1. Samples were prepared by isostaticaly pressing under 300 MPa and subsequent sintered at 1900 °C, for 2 h, under 1.5 MPa of N_2, and further heat treatment at 1400 °C, for 24 h under 0.1 MPa of N_2. The samples were characterized by the relative density, using the immersion method, the phase composition determined by X-ray diffractometry, and the mechanical properties by 4-point bending strength and Weibull analysis.

Table 1. Characteristics and compositions of the materials studied in this work.

Material	Characteristics Chemical Composition (%)	Composition (wt.%)	
		SNYA	SNTRA
Silicon Nitride (Si_3N_4)	92 - α phase	81.4	78.8
Alumina (Al_2O_3)	99.99 - α phase	8.0	7.6
Yttrium oxide (Y_2O_3)	99.98 - α phase	10.6	--
Concentrate (CTR_2O_3)	Y_2O_3 - 45%, Yb_2O_3 - 18%, Er_2O_3 - 15%, Dy_2O_3 - 12%, other R.Earth10%	13.6	--

Microstructural analysis was executed by scanning electronic microscopy (SEM). Prior to analysis the samples were polished and plasma etched, using a mixture of CF_4/O_2 in a proportion of 4:2 for 2 min, and covered with a fine gold layer.

For the accomplishment of the bending tests, batches of 21 samples were grinded and polished, obtaining bars of 4 × 3 × 45 mm, according ASTM C 1116 - 94. The tests were conducted using a 4-point bending device with outer and inner spans of 40 and 20 mm, I_1 and I_2, respectively, as shown in Fig. 1. The speed of the crosshead displacement has been 0.5 mm/s. The bending strength of the samples was calculated by Eq. 1.

$$\sigma_f = \frac{3}{2} F_A \times \frac{(I_1 - I_2)}{b \times h^2} \quad (1)$$

where:

σ_f: Bending strength (MPa);
F_a: Rupture load (N);
b: Width of the samples (mm);
h: Height of the samples (mm);
I_1: Outer span distance (mm);
I_2: Inner span distance (mm).

For the statistical evaluation of the fracture strength the

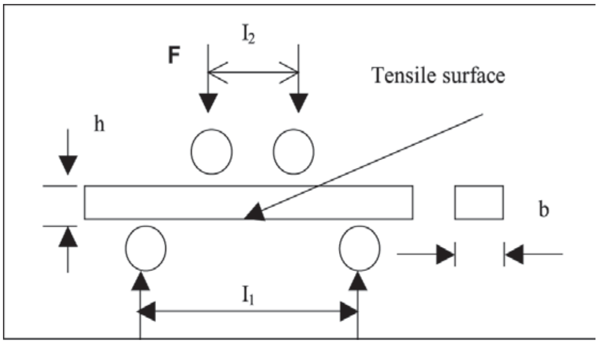


Figure 1. Schematic illustration of the 4-point bending test, with b: sample width (mm), h: sample height (mm), I_1: outer span distance (mm), I_2: inner span distance (mm).

two-parameter Weibull distribution function[9] has been used, according Eq. (2):

$$P = 1 - \exp\{[-\frac{\sigma}{\sigma_0}]^m\} \tag{2}$$

where:
P: Failure probability;
m: Weibull modulus;
σ_0: Characteristic strength;
σ: Bending strength.

The Weibull parameters *m* and σ_0, are obtained transforming Eq. 2 in Eq. 3 and plotting ln ln [1/(1-P)] *vs*. ln σ.

$$\ln \ln \frac{1}{(1/P)} = m.\ln \sigma - m.\ln \sigma_0 \tag{3}$$

The stress value for 50% of rupture probability was estimated as reference and also for direct comparison with the average fracture stress. The Weibull parameters m were determined using a factor of correction of 0.938, corresponding to 21 samples, in agreement with the German norm DIN-51-110[12].

3. Results and Discussion

3.1. Sintering

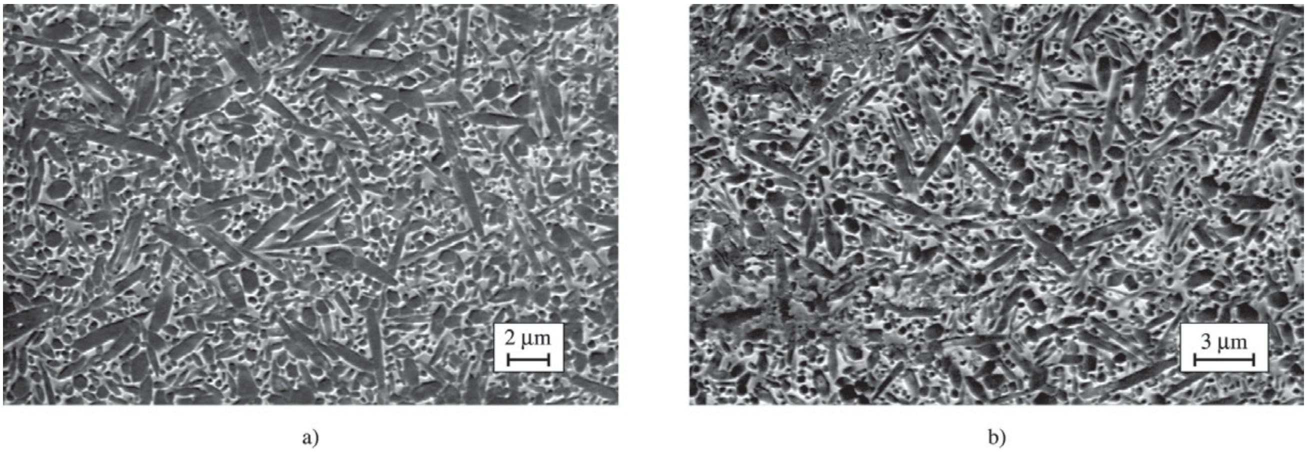
Table 2 presents the results of phase composition, relative density and weight loss of the sintered samples. Both compositions studied resulted in almost completely densified materials exhibiting only small weight losses during sintering, indicating a possible substitution of Y_2O_3 by CTR_2O_3 as sinter additive without decrease of the sintering activity in these systems. Furthermore, in both materials β-Si_3N_4 and YAG have been identified as the only cristalline phases, giving further evidence for a possible substitution of Y_2O_3 by CTR_2O_3.

Table 2. Phase composition, relative density and weight loss of sintered samples.

System	Phases	Relative density (%)	Weigth loss (%)
Si_3N_4-Y_2O_3-Al_2O_3	β-Si_3N_4, YAG	99.7 ± 0.2	2.4 ± 0.3
Si_3N_4-CTR_2O_3-Al_2O_3	β-Si_3N_4, YAG	99.5 ± 0.2	2.3 ± 0.4

Table 3. 4-point bending strength of sintered samples.

Specimen type	Number of specimens	Average bending strength, σ_f (MPa)	Standard deviation $\Delta\sigma_f$ (MPa)
Si_3N_4+CTR_2O_3-Al_2O_3 (14 vol.%)	21	670	45
Si_3N_4+Y_2O_3-Al_2O_3 (14 vol.%)	21	690	45



a) b)

Figure 2. SEM micrographs of polished and plasma etched surfaces of sintered samples: a) SNYA; b) SNTRA.

3.2. Microstructure

Figure 2 presents the microstructures of the sintered and heat treated samples. In general, the presence of a great amount of elongated grains with a high aspect ratio is observed in both samples, SNYA and SNTRA. Grains with high aspect ratios are decisive for the improvement of the bending strength and fracture toughness of these materials[3-6]. The microstructural aspects observed take us to believe that the use of CTR_2O_3 as additive results in a similar microstructure compared to Si_3N_4 sintered with Y_2O_3, which will contemplate in similar mechanical behaviors for both materials.

3.3. Mechanical Properties

The results of the bending strength are shown in Table 3. The properties presented by the sintered samples were promising for structural applications, comparable to other results reported in the literature using similar amounts and types of additives and sinter conditions[3-6]. It was verified that the use of the additive mixtures proposed in this work, allied to the employed sintering conditions, resulted in elevated bending strengths. The good mechanical strength of the produced materials is a consequence of the high final densities, or low porosity and microstructures composed of fine and elongated β-Si_3N_4 grains, leading also to the high fracture toughness of the Si_3N_4 ceramics.

3.4. Weibull Analysis

Figure 3 presents a comparison between failure probability of the SNYA and SNTRA samples, as function of the bending strength.

It is observed that in spite of SNTRA samples possess smaller average strengths than SNYA samples, the curves are similar, indicating a similar behavior of failure probability. These results are confirmed by the Weibull analysis, whose results are presented in Table 4 and Fig. 4.

The Weibull analysis was applied to the 4-point bending strength values. In the Table 4 the values for the Weibull moduli (m), characteristic strength (σ_0) and the correlation coefficient (R) of the interpolation are listed. The correlation coefficients present values tending to 1, indicating that the rupture stress data are very well adjusted according to Weibull´s analysis[9].

In general, the parameter *m*, observed in a vast range of ceramic materials, depends strongly on processing, the microstructure, pore distribution and of the surface finishing degree. These values are, typically, between 3 and 15, meaning that a material with $m = 15$ presents less scattering of the fracture strength than a material with $m = 3$[10,13]. Quinn[10] reports that a *m* value exceeding 10 indicates a "good" ceramic material. Considering that the specimens were sintered under the same conditions and that the relative densities are similar for SNYA and SNTRA, the predominant factors for this resistance behavior are the characteristics of the microstructure and the intergranular phase formed. The same values of $m = 15$ determined for both materials (SNYA and SNTRA) demostrate that they contain similar defects and also similar defect size distributions. Therefore, the reliability of both materials studied are almost identical, and both are suited for high performance mechanical applications.

4. Conclusions

In this work, two Si_3N_4 based ceramic materials with mixtures of Y_2O_3/Al_2O_3 or CTR_2O_3/Al_2O_3 as additives have been prepared by gas pressure sintering. The high final den-

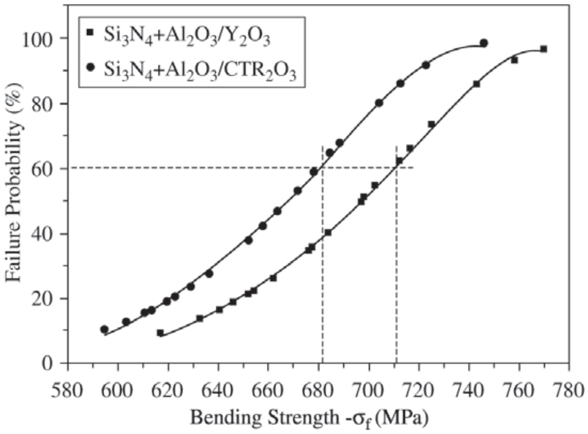


Figure 3. Comparative Failure Probability between SNYA and SNTRA samples.

Table 4. Weibull parameters m and σ_0 of sintered samples.

Specimen type specimens	Number of modulus, *m*	Weibull coeficient (R)	Correlation stress (σ_0)	Characteristic
$Si_3N_4+CTR_2O_3-Al_2O_3$ (14vol.%)	21	15.5	R = 0.986	683
$Si_3N_4+Y_2O_3-Al_2O_3$ (14vol.%)	21	15.3	R = 0.969	713

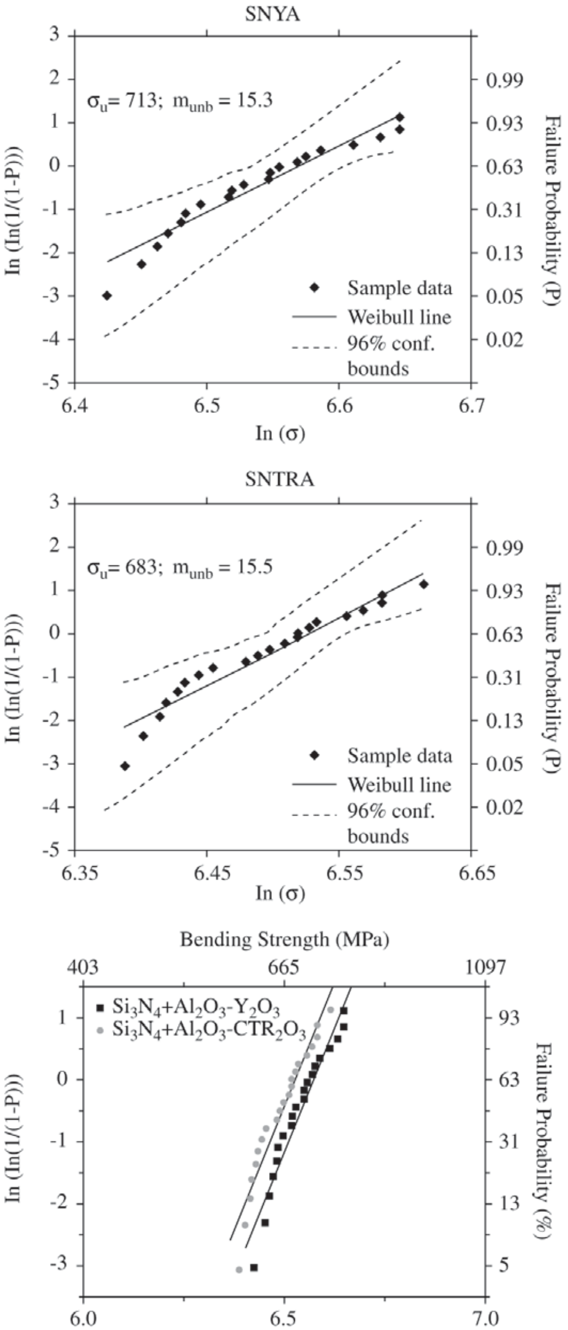


Figure 4. Weibull diagrams for the Si_3N_4-Y_2O_3-Al_2O_3 (SNYA) and Si_3N_4-CTR_2O_3-Al_2O_3 (SNTRA).

sities and small weight losses during sintering of both compositions, as well as the similar microstructures and phase composition, indicate similar sintering behavior and therefore confirm the possibility of substitution of pure Y_2O_3 by the lower cost rare earth oxide mixture, CTR_2O_3, produced at DEMAR-FAENQUIL, resulting ultimately in a cost reduction of these Si_3N_4 ceramics. The average bending strengths of these materials exceeding 670 MPa turns them suitable for structural applications. Furthermore, the elevated Weibull moduli *m* of 15 and characteristical stresses σ_0 of 700 MPa, demonstrate the high reliability of these ceramics, and also that similar defect populations must have been present in both materials. This observation represents further support for a possible substitution of pure Y_2O_3 by the rare earth oxide mixture, CTR_2O_3, without causing significant reduction of the mechanical properties.

Acknowledgements

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