Comparison of physical and mechanical properties in ceramics composites
$\text{Si}_3\text{N}_4$–CTR–AlN and $\text{Si}_3\text{N}_4$–$\text{Y}_2\text{O}_3$–AlN

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ABSTRACT. The important factor to consider for a successful ceramics composites development is the need of to match the whiskers and matrix characteristics, taking into account the chemical compatibility of the sintering aids utilized. The purpose of this work was to analyze and compare to use of the rare earth concentrate (CTR) and yttrium oxide, as sintering aids, in the densification and physical/mechanical properties of hot pressing $\text{Si}_3\text{N}_4$-$\text{SiC}_{(w)}$ sintered. The CTR powder materials present high yttrium oxide percentage and its production cost is cheaper than the additive usually utilized in ceramic materials, such as $\text{Y}_2\text{O}_3$. For physical and mechanical properties, specific mass, crystalline phases, micrographs analysis, microhardness and fracture toughness were evaluated, showing results similar properties between sintering aids. Therefore, this study shows the possibility to obtain products of the low processing cost with the utilization of the rare earth concentrate. Meanwhile, more characterization steps are necessary for analyze its behavior at elevated temperature.

I. INTRODUCTION

Processing and characterization steps at room and high temperature are the main field of study in ceramics composites, considering this potential application such as structural materials, including turbine components, cutting tools, among others, due to excellent thermal and mechanical properties [1-3].

The incorporation to second phase, such as whiskers, platelets or fibers, into to the ceramics matrix has been utilized aiming to improve the mechanical properties of these materials [2-3]. Silicon carbide in the form whiskers has been most widely used as reinforcing agents for silicon nitride [4-5] or oxides ceramics such as $\text{Al}_2\text{O}_3$ and $\text{Zr}_2\text{O}_3$ [6-7], due to high strength, high elastic modulus and chemical inertness at elevated temperature, obtaining substantial improvements in fracture toughness and slow-crack-growth resistance [8].

However, due to high degree of covalent bonding and low self-diffusivity of $\text{Si}_3\text{N}_4$ and $\text{SiC}$, densification of the monolithic ceramics and their composites is difficult. Several papers have been published, trying to achieve fully densified samples through the addition of oxides as sintering aids. The additives are effective to promote densification by mechanism of liquid phase sintering at elevated temperature [9-10].

The important factor to consider for a successful ceramics composites development is the need of to match the whiskers and matrix characteristics, taking into account the chemical compatibility of the sintering aids utilized. For the silicon nitride matrix based, the additive more effective are $\text{Y}_2\text{O}_3$, AlN, $\text{Al}_2\text{O}_3$ and MgO [11-12]. The utilization of the $\text{Y}_2\text{O}_3$ and AlN as sintering aids showed excellent results of the physical and mechanical properties in $\text{Si}_3\text{N}_4$-$\text{SiC}_{(w)}$ [13].
There are reports of the monolithic ceramics materials containing rare earth oxides [14-15], but the ceramics composites containing rare earth concentrate require more studies. The purpose of this work was to analyze the viability of use of the rare earth concentrate (CTR), as sintering aids, in the densification and physical/mechanical properties of Si$_3$N$_4$-SiC$_{(w)}$ sintered and compare with properties obtained to yttrium oxide.

II. METHODS AND MATERIALS

In this work, the compositions of materials evaluated are given in Table 1. Silicon nitride, yttrium oxide and aluminum nitride powders were obtained from H. C. Starck. Rare earth concentrate was acquired by Nuclemon. All powders presented mean particles size less than 1 µm. Silicon carbide whiskers (ICD Group) used as reinforcements, presented the diameter and length about 0.3-0.6 µm and 5-15 µm, respectively, providing the higher aspect ratio.

Table 1- Compositions used in this work.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Matrix (% weight)</th>
<th>Whiskers (% vol.)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Si$_3$N$_4$</td>
<td>AlN</td>
</tr>
<tr>
<td>A</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>90</td>
<td>5</td>
</tr>
</tbody>
</table>

The SiC$_{(w)}$ were incorporate directly into silicon nitride matrix based and ball-milled for 24 h period, using high purity alumina milling balls and dry ethanol. The slurry was dried and each composition die pressed at 50 MPa, using steel dies, followed by cold isostatic pressing at 300 MPa.

Hot uniaxial pressed sintering was performed in nitrogen atmosphere, at 1750 ºC during 30 min. and heating rate off 15 ºC/min, under 20 MPa pressure. This processing parameters utilized in this work were performed due to excellent results obtained in other works realized for same research group [13;16-17].

The specific mass of the sintered materials was determined by the Archimedes method and relative density was calculated according to mixture rule. The crystalline phases were identified by X-ray diffraction with CuKα radiation and the micrographs analysis of polished surface were taken using scanning electron microscope (SEM) after etching in a 1:1 mixture of NaOH and KOH at 500 ºC.

Microhardness and fracture toughness values, from the formula give by [18], were determined on the polished sections, at room temperature, using Vickers indentation with 29.4 N load and taking an average from ten indentations for each composition.

III. RESULTS AND DISCUSSIONS

III.1 Density

The specific mass and relative density results, showed in Table 2, presents similar for both sintering aids, obtaining densification rate near theoretical. The liquid phase sintering, operative for silicon nitride ceramics, has a resulting solution, diffusion re-precipitation mechanism, where the rate controlling step was more effective for sintering parameters used in this work.

The important factor to high densification is related to use of pressure during the sintering process, which accelerate densification kinetics due increase particle contacts and higher grains rearrangements [19]. In this case, pressure associated with high temperature increased the driving force for densification, contributing to higher values of the specific mass obtained.
Table 2 – Specific mass and relative density values.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Specific mass (g/cm³)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3,20</td>
<td>98,40</td>
</tr>
<tr>
<td>B</td>
<td>3,16</td>
<td>97,20</td>
</tr>
<tr>
<td>C</td>
<td>3,18</td>
<td>98,00</td>
</tr>
<tr>
<td>D</td>
<td>3,15</td>
<td>97,00</td>
</tr>
</tbody>
</table>

On the other hand, observed that while increase SiC\((w)\) content, the densification rate decreased, related to whiskers interference on matrix grains rearrangement and volumetric retraction of ceramics composites, promoting a small decrease in the specific mass for both sintering aids.

### III.2 X-ray diffraction analysis

Crystalline phases identified by X-ray diffraction are show in Figure 1.

![Crystalline phases identified by X-ray diffraction](image)

(a) composition A  
(b) composition B  
(c) composition C  
(d) composition D

Fig. 1–Crystalline phases identified by X-ray diffraction.
For yttrium oxide sintering aids compositions, the principal phases detected were $\beta$-Si$_3$N$_4$ (predominantly), $\alpha$-Si$_3$N$_4$ remnant, SiC (related to whiskers) and some traces of the Y$_2$Si$_3$O$_3$N$_4$ phases. On the other hand, for CTR sintering aids compositions, the crystalline phases were $\alpha$-Si$_3$N$_4$ remnant, $\beta$-Si$_3$N$_4$, SiC and some traces of the Er$_2$O$_3$ and Y$_2$Si$_3$O$_3$N$_4$ phases.

The presence of $\alpha$-Si$_3$N$_4$ remnant phase, detected in all compositions, is related to the sintering process parameters. Sintering holding time (30 min) was not, in these cases, sufficient to allow complete $\alpha \rightarrow \beta$ transformation.

The Er$_2$O$_3$ and Y$_2$Si$_3$O$_3$N$_4$ phases are related to the grains boundary phases, due to the sintering aids and its reactions with Si$_3$N$_4$ and liquid phase formed during sintering process. The presence of these phases in the grain boundaries, triple junction and matrix/whiskers interface results in beneficial effects to the mechanical properties at room temperatures, as a consequence of the acicular grain growth and the reduction of the inherent flaw size. However, these phases deteriorate the high temperature mechanical properties and also affect the oxidation behavior of ceramics composites. The high temperature performance depends primarily on the composition of intergranular phase and its distribution [20-21].

Analyzing the peaks intensity of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$, observed that the $\alpha \rightarrow \beta$ transformation was inhibited with the increase of SiC$_{(w)}$ content. It is inferred, in this case, that the $\alpha$-Si$_3$N$_4$ grains wetting was reduced, resulting in a solubility decrease of $\alpha$-Si$_3$N$_4$ in liquid phase and a consequent $\beta$ transformation delay.

### III.3 Mechanical properties

For both sintering aids, the mechanical properties were similar. The Table 3 shows of the microhardness and fracture toughness ($K_{1c}$) values obtained by Vickers indentation method.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Microhardness (GPa)</th>
<th>$K_{1c}$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.60 ± 0.25</td>
<td>8.33 ± 0.23</td>
</tr>
<tr>
<td>B</td>
<td>15.52 ± 0.21</td>
<td>10.36 ± 0.38</td>
</tr>
<tr>
<td>C</td>
<td>16.48 ± 0.72</td>
<td>8.17 ± 0.14</td>
</tr>
<tr>
<td>D</td>
<td>15.37 ± 0.24</td>
<td>10.16 ± 0.22</td>
</tr>
</tbody>
</table>

Observed that microhardness values presented low dispersion in the results, maintaining practically constant in the surface than nucleus. This factor associated the SEM analysis, supposed the homogeneity good of the powders involved. The microhardness values are related, principally, to densification rate, observing its decrease while increase of SiC$_{(w)}$ content. The presence of $\alpha$-Si$_3$N$_4$ remnant phase, detected by X-ray diffraction, contributed also to higher microhardness results. Second literature [22], this phase is more hard that $\beta$-Si$_3$N$_4$.

The utilization of whiskers as reinforcements improved significantly the fracture toughness when compared to monolithic materials, around 5 MPa.m$^{1/2}$ [23-24]. Observed that increasing of the SiC$_{(w)}$ content into a Si$_3$N$_4$ matrix and the presence of elongated $\beta$-Si$_3$N$_4$ grains significantly improved fracture toughness. Indeed, the introduction of whiskers to silicon nitride based matrix strongly inhibits grain growth and composite cannot be tailored with a matrix containing large grains. Thus, the toughness of the composite is resultant of the competition between a toughness decrease of the matrix and toughening due to whiskers.

Toughening mechanisms in ceramics composites were studied and analyzed by Rice [25] and Shetty [26]. For the SiC$_{(w)}$ as reinforce in silicon nitride matrix based, only a small amount of whiskers pull-out was observed, indicating that this mechanisms was not principal responsible for the improve of fracture toughness. We believe that crack deflection and crack bridging were toughening mechanisms operative in the present case.
III.4 Scanning electron microscopy (SEM)

The micrographs analysis, showed in Figure 2, presented microstructures based on equiaxial $\alpha$-$\text{Si}_3\text{N}_4$ grains, elongated $\beta$-$\text{Si}_3\text{N}_4$ grains and whiskers homogeneously distributed on the matrix grains, indicating that the grinding/homogenization, utilized in this work, step was efficient.

The homogeneous microstructure between whiskers and matrix grains is fundamental to the successful toughening of ceramics composites reinforced by SiC$_{(w)}$. The inhomogeneous mixture may be responsible for a decrease of mechanical properties [27].

SEM observations indicated the small-preferred orientation of the whiskers, tending to align along the normal plane to the pressing axis, due the sintering process utilized. This behavior can be produce the anisotropy of the mechanical properties, principally, the fracture toughness [28-29].

Other aspect important observed, principally to CTR sintering aids compositions, was related the whiskers interference on matrix grains, that occasioned the reduction of growing of $\beta$-grains. This reduction will promote an decrease of fracture toughness, because the toughening mechanisms require high aspect ratio than whiskers as $\beta$-grains, serving of the obstacle for crack propagation.

![Photomicrographs obtained by SEM in polished and etched surfaces.](image-url)

(a) composition A   
(b) composition B

(c) composition C   
(d) composition D

Fig. 2 – Photomicrographs obtained by SEM in polished and etched surfaces.
IV. CONCLUSIONS

The use of rare earth concentrate (CTR) as additive during silicon nitride sintering gives rise to materials with similar physical and mechanical properties characteristics in relation to yttrium oxide-added silicon nitride, at room temperature, showed quite small differences.

The crystalline phases identified and microstructural analysis showed dependent of the sintering aids, sintering parameters and SiC\(_{(w)}\) content utilized in this work.

By X-ray diffraction analysis observed the crystalline phases present, related to powder involved and its reactions with liquid phase formed during sintering. The existence in conjunction of the \(\alpha\)-Si\(_3\)N\(_4\) and \(\beta\)-Si\(_3\)N\(_4\) phases is attractive, because can associate the high hardness of \(\alpha\)-phase with better toughness of \(\beta\)-phase.

By SEM analysis and microhardness values was possible observed the homogeneity good between whiskers and matrix grains, contributing to higher mechanical properties values obtained.

Observed the increasing of the SiC\(_{(w)}\) content occasioned a small decrease the densification rate and, consequently, in microhardness values. On the other hand, the higher fracture toughness values improved with increase SiC\(_{(w)}\) content, showed the importance of the reinforce use in this materials, improvement the reliability to structural application.

Therefore, from these excellent physical and mechanical properties results obtained, the use of the rare earth concentrate (CTR), as sintering aids, showed viable and efficient, can be obtain products with low processing cost. Therefore, more characterization steps are necessary for analyze its behavior at elevated temperature, such as creep test, due the presence glassy phase formed during sintering process, occasioned by sintering aids.

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REFERENCE