ANALYSIS OF PROPERTIES MECHANICAL IN Si₃N₄ - SiCₜ(w) :
GAS-PRESSURE AND HOT UNIAXIAL PRESSING SINTERING

Sandro Aparecido Baldacim
Olivério Moreira Macedo Silva
Kátia Celina da Silva Richetto
Carlos Alberto Alves Cairo
Cosme Roberto Moreira da Silva

CTA-IAE-AMR - Divisão de Materiais
Pça. Marechal do Ar Eduardo Gomes, 50 - Vila das Acáciás
São José dos Campos – SP Cep: 12228-904
e-mail : sandrobaldacim@bol.com.br

Keywords: Gas-pressure sintering, hot uniaxial pressing, ceramics composites, silicon nitride

ABSTRACT. The purpose of the present work was to study the fabrication of Si₃N₄-SiCₜ(w) ceramics composites containing 10 - 20 vol.% SiCₜ(w) via gas-pressure and hot uniaxial pressing sintering. The compositions were ball milled (wet) for a 6 hours period and the whiskers addition to the powder mixture was made before wet milling. After the grinding/homogenization step, the powders were cold pressed with load of 50 MPa, using steel dies, followed by cold isostatic pressing at 300 MPa. Both sintering process were performed under nitrogen atmosphere, at 1750 °C and heating rate off 20 °C/min. For physical properties was determined the specific gravity according to ASTM C20-87, crystalline phases were identified by X-ray diffraction and microstructural analysis were performed using scanning electron microscope. For properties mechanical, the microhardness and fracture toughness were evaluated by Vickers indentation method taking an average of five measurements.

I. INTRODUCTION

The hot pressing sintering method offers the ability to fabricate dense and strong products with small amount of sintering aids. However, fabrication is limited to simples shapes. This factor coupled with high cost of machining makes silicon nitride products very expensive and, hence, of limited application [1-2]. In order to eliminate the high cost of machining, combining with high mechanical properties, gas-pressure sintering has been utilized for silicon nitride based ceramics materials, but to ceramics composites few researches has been studied and analyzed [3].

The fracture toughness of Si₃N₄ increases on raising the sintering temperature because the grain morphology changes from granular to needle like according to the $\alpha \rightarrow \beta$ transformation [4] and it can be also increased by adding second phases [5]. The silicon carbide of different sizes, morphologies and types has been introduced to strengthen and toughen the Si₃N₄ matrix, such as whiskers, fibers or platelets [6-8]. Regarding platelets, give better fracture resistance then whiskers although they reduce the strength. On the other hand, whiskers give better fracture toughness, but the difficult are to achieve uniform dispersion, specially in high volume content.

Among the existing fracture toughness mechanism that can be activated, there are crack deflection, microcracking, crack bridging and whisker pull-out [9]. Another important aspect to consider, for a successful composite production is the need of to match the whisker and matrix characteristics, taking into account the thermal expansion and elastic modulus difference between whiskers and matrix, and their chemical compatibility, during the densification process at high temperature [10]. The length, volumetric fraction, particle size distribution and surface characteristics of whiskers will determinate the microstructure development [11].
The aim of the present work was to investigate the fabrication and properties of Si₃N₄-SiC₍w₎ ceramics composites compacted by different densification methods, i.e., gas-pressure sintering and hot uniaxial pressing, varying the volumetric fraction of SiC₍w₎. The effects of these two sintering methods in microstructure development, such as matrix grains size, and mechanical properties at room temperature were studied.

II. EXPERIMENTAL PROCEDURE

The Si₃N₄ (H.C. Starck; average diameter, 0,85 µm; α-phase content greater > 90%) with 5 wt% AlN (H.C. Starck; average diameter, 1,20µm) and 5 wt% Y₂O₃ (H.C. Starck; average diameter, 0,28µm), as sintering aids, were reinforced with silicon carbide whiskers (ICD Group Inc.) at 10 and 20 vol%, with the diameter and length about 0,3-0,6 µm and 5-15 µm, respectively.

The starting materials were mixed by wet ball milling with ethanol in a plastic bottle for 6 h. After ball milling, the slurries were dried and then sieved to particle size smaller than 100 µm. These mixtures were compacted by cold pressed at 50 MPa followed by cold isostatic pressed at 300 MPa.

The densification process was conducted in a gas-pressure sintering furnace that permitted a maximum nitrogen pressure at 1 MPa. On the other hand, hot uniaxial pressed sintering used pressure at 20 MPa. Both sintering process were performed under nitrogen atmosphere, at 1750 °C for 30 min. with heating rate off 20 °C/min.

With respect of the physical properties, the phases identification was realized by conventional X-ray diffraction (XRD) and densities were measurements of the according to ASTM C20-87. For microstructure characterization, surfaces etched by molten NaOH and KOH were observed by scanning electron microscopy (SEM).

For the mechanical properties, the fracture toughness and microhardness were measured on polished surfaces by the indentation technique using a Vickers hardness tester, with a 19,6 N load, taking a mean of five measurements.

The Figure 1 present the all of the processing and characterization steps utilized in development in this work.

Figure 1 – Schematic drawing of the processing and characterization steps utilized in this work.
III. RESULTS AND DISCUSSIONS

III.1 – Physical properties

The Figure 2 indicate the phases that were detected via X-ray diffraction (XRD) in all composition by both sintering process. Basically observed the presence of the $\alpha$-Si$_3$N$_4$, $\beta$-Si$_3$N$_4$ and SiC phases.

The $\alpha$-Si$_3$N$_4$ remnant and $\beta$-Si$_3$N$_4$ phases are related to sintering parameters used in this work, indicating that sintering time was insufficiently to promote $\alpha \to \beta$ transformation complete. The SiC phase is related to whiskers utilized as reinforcement.

Figure 2 – XRD analysis of the Si$_3$N$_4$-SiC(w) ceramics composites obtained for both sintering process utilized in this work.
Observed that $\alpha \rightarrow \beta$ transformation was inhibited, more significantly for the compositions gas-pressure sintered, by an increasing SiC$_{(w)}$ content, due probably to decreasing of wetting degree of the $\alpha$- Si$_3$N$_4$ grains, that can decrease solubility of the solid phase in liquid phase, retarding the transformation.

The other difference was related of the grain boundary phases, where by gas-pressure sintering detected the Y$_2$O$_3$ phase, while by hot uniaxial pressed detected the Y$_2$Si$_3$O$_3$N$_4$ phase, related as the reactions products of the Si$_3$N$_4$ with sintering aids.

Observed that the densities values, Table 1, decrease gradually with increasing SiC$_{(w)}$ content, due to whiskers interference on matrix grains rearrangement and volumetric retraction. Meanwhile, this interference is extremely attenuate by the pressure use during the hot uniaxial pressed, obtained better results of the densities. The use of pressure accelerate densification kinetics due increase particle contacts and higher grains rearrangements.

On the other hand, in compositions by gas-pressure sintering the interference was more significantly, obtained low densification for composition with high SiC$_{(w)}$ content, that makes impossible to realize microstructure analysis and mechanical properties characterization.

Table 1 – Densities and theoretical densities values obtained.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Gas-pressure sintering</th>
<th>Hot uniaxial pressed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Densities (g/cm$^3$)</td>
<td>Theoretical densities (%)</td>
</tr>
<tr>
<td>Si$_3$N$<em>4$ – 10 vol.% SiC$</em>{(w)}$</td>
<td>3,16</td>
<td>97,00</td>
</tr>
<tr>
<td>Si$_3$N$<em>4$ – 20 vol.% SiC$</em>{(w)}$</td>
<td>2,92</td>
<td>90,00</td>
</tr>
</tbody>
</table>

The micrographs analysis, Figures 3 and 4, showed that the compositions has a distinctly microstructure with respect to sintering process, where the growth of the $\beta$-grains during densification was reduced more significantly by gas-pressure sintering, decreasing the aspect ratio and size of the $\beta$-Si$_3$N$_4$ grains. This factors are related to smaller $\alpha \rightarrow \beta$ transformation, due the sintering parameters utilized, and presence of the SiC$_{(w)}$.

![Figure 3](image_url) – SEM images showing microstructure of Si$_3$N$_4$ – 10 vol%. SiC$_{(w)}$ gas-pressure sintered.
Si₃N₄ – 10 vol.% SiC(w)                                                              Si₃N₄ – 20 vol.% SiC(w)

Figure 4 - SEM images showing microstructure of compositions hot uniaxial pressing sintered.

III.2 – Mechanical properties

The Table 2 presented fracture toughness and microhardness values obtained in this study by Vickers indentation for both sintering process utilized.

Table 2 – Fracture toughness and microhardness values obtained in this study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Gas-pressure sintering</th>
<th></th>
<th>Hot uniaxial pressed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microhardness (GPa)</td>
<td>$K_{1c}$ (MPa.m$^{1/2}$)</td>
<td>Microhardness (GPa)</td>
<td>$K_{1c}$ (MPa.m$^{1/2}$)</td>
</tr>
<tr>
<td>Si₃N₄ – 10 vol.% SiC(w)</td>
<td>15,14 ± 0,19</td>
<td>7,86 ± 0,15</td>
<td>16,60 ± 0,25</td>
<td>8,33 ± 0,23</td>
</tr>
<tr>
<td>Si₃N₄ – 20 vol.% SiC(w)</td>
<td>*</td>
<td>*</td>
<td>15,52 ± 0,21</td>
<td>10,36 ± 0,38</td>
</tr>
</tbody>
</table>

* No determined due a low densification

For all compositions, by both sintering process, was observed that increasing of the SiC(w) content into a Si₃N₄ matrix significantly improved fracture toughness, compared to monolithic materials (4 – 5 MPa.m$^{1/2}$) [12]. This increase is probably related to activation of crack bridging and crack deflection mechanisms on ceramics composites.

Due higher aspect ratio of β- Si₃N₄ grains, that can be also acting as reinforcement, in couple of the SiC(w) content, the better fracture toughness results were obtained to hot uniaxial pressing Si₃N₄ – SiC(w) sintered.

The higher microhardness values showed dependents of the two factors. The first, and more important, is the densification rate, influenced by sintering process and SiC(w) content, presenting the better results by hot uniaxial pressed sintering. The second factor is the presence of α- Si₃N₄ remnant phase, more hard than β- Si₃N₄ phase, second to literature [13].
IV. CONCLUSIONS

We reached the following conclusions from the results obtained of this investigation, for the processing parameters used in this work:

- The hot uniaxial pressing Si$_3$N$_4$-SiC$_{(w)}$ sintered presented better results of the physical and mechanical properties, due higher densification and microstructural aspects. Such results are related to use of the pressure during sintering, that increased particle contacts and higher grains rearrangements, and the presence in couple of the higher aspect ratio for β- Si$_3$N$_4$ grains (more toughness) and α- Si$_3$N$_4$ grains (more hard).

- The gas-pressure Si$_3$N$_4$-SiC$_{(w)}$ sintered showed excellent results of the density and mechanical properties only for composition to 10 vol.% SiC$_{(w)}$. The increasing of the SiC$_{(w)}$ content, the densification and consequently the mechanical properties were significantly affected. On the other hand, we believe that modifying the processing parameters utilized in this process, such sintering time and temperature, the improve the density and mechanical properties for compositions to higher SiC$_{(w)}$ are expected.

AKNOWLEDGEMENTS

FAPESP – Fundação de Amparo a Pesquisa do Estado de São Paulo
CTA/IAE/AMR – Divisão de Materiais

REFERENCE