Hot pressing of SiC additivated with Al$_2$O$_3$ and Y$_2$O$_3$

Prensagem a quente de SiC aditivado com Al$_2$O$_3$ e Y$_2$O$_3$

Prensado en caliente de SiC aditivado con Al$_2$O$_3$ y Y$_2$O$_3$

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ABSTRACT
This work investigated the sintering of silicon carbide (SiC) with alumina (Al₂O₃) and yttria (Y₂O₃) additives by hot pressing. Mixtures of SiC with 1% and 5% Al₂O₃ and Y₂O₃ were used, pressed at 1800 °C and 1850 °C, resulting in specimens that were characterized in terms of density, microstructure, Vickers hardness and fracture toughness. The addition of 5% oxide additives provided greater densification and better mechanical properties. The temperature of 1800 °C proved to be the most effective for sintering due to the microstructure presented. The analysis revealed a homogeneous distribution of additives and grains, concluding that the 5% additive is considerably superior for increasing the densification and mechanical strength of SiC.

Keywords: SiC, Al₂O₃, Y₂O₃, hot Pressing, Liquid Phase Sintering.

RESUMO
Este trabalho investigou a sinterização do carbeto de silício (SiC) com aditivos de alumina (Al₂O₃) e ítria (Y₂O₃) por prensagem a quente. Foram utilizadas misturas de SiC com 1% e 5% de Al₂O₃ e Y₂O₃, prensadas a 1800 °C e 1850 °C, resultando em corpos de prova que foram caracterizados em função da densidade, microestrutura, dureza Vickers e tenacidade à fractura. A adição de 5% de aditivos óxidos proporcionou maior densificação e melhores propriedades mecânicas. A temperatura de 1800 °C mostrou-se mais eficaz para sinterização em função da microestrutura apresentada. A análise revelou uma distribuição homogênea dos aditivos e grãos, concluindo que a aditivação de 5% é consideravelmente superior para o incremento da densificação e resistência mecânica do SiC.

Palavras-chave: SiC, Al₂O₃, Y₂O₃, Prensagem a Quente, Sinterização em Fase Líquida.

RESUMEN
En este trabajo se investigó la sinterización de carburo de silicio (SiC) con aditivos de alúmina (Al₂O₃) e ítria (Y₂O₃) mediante prensado en caliente. Se utilizaron mezclas de SiC con 1% y 5% de Al₂O₃ y Y₂O₃, prensadas a 1800 °C y 1850 °C, obteniéndose probetas que se caracterizaron en términos de densidad, microestructura, dureza Vickers y tenacidad a la fractura. La adición de un 5% de aditivos de óxido proporcionó una mayor
densificación y mejores propiedades mecánicas. La temperatura de 1800 °C resultó ser la más eficaz para la sinterización debido a la microestructura presentada. El análisis reveló una distribución homogénea de aditivos y granos, concluyendo que el aditivo al 5% es considerablemente superior para aumentar la densificación y la resistencia mecánica del SiC.

**Palabras clave:** SiC, Al₂O₃, Y₂O₃, Prensado en Caliente, Sinterización en Fase Líquida.

1 INTRODUCTION

Silicon carbide (SiC) is widely recognized as a remarkable semiconductor due to its characteristics, such as a wide bandgap, exceptional magnetic properties, extraordinary chemical inertness, as well as high thermal, mechanical, optical and electronic properties. These characteristics make SiC widely used in solid-state lighting and power electronics, due to its low intrinsic carrier concentration and high thermal conductivity under conditions of high power, high temperature, high voltage or other adverse environments. However, it is important to note that the biocompatibility and other recent applications of SiC have been little explored by researchers, despite the broad potential for studies in this area (Xu et al., 2021).

Several methods have been reported for the synthesis of SiC, such as carbon-silica carbothermic reduction (C-SiO₂), chemical vapor deposition (CVD), mechanical milling (MM) or liquid phase sintering (LPS), physical vapor deposition (PVD) and sol-gel methods (Abderrazak, 2011). Saleiro et al. (2018) produced Al₂O₃ and Y₂O₃ powders by Self-Sustaining High Temperature Combustion Synthesis (SHS) and used them as additives for sintering SiC in the presence of a liquid phase, achieving good mechanical properties as a result.

The aim of this study was to produce silicon carbide specimens with high densification and good mechanical properties, using oxide additives (Al₂O₃ and Y₂O₃), for pressure sintering in liquid phase.
2 MATERIALS AND METHODS

2.1 MATERIALS

For this work, we used silicon carbide (β-SiC) from Sky Spring Nanomaterials Inc. With an average particle size of 40 nm and purity of over 99%, alumina with an average size of 0.5 μm, produced by Almatis do brasil ltda. And yttria with a size between 50 and 70 nm, from Alfa Aesa.

2.2 PROCESSING METHOD

Two mixtures of SiC with 1% and 5% additions of alumina and yttria were prepared. The mixture is made wet, using deionized water or isopropyl alcohol as solvents, and processed in a ball mill for periods of 3 to 6 hours (Liu, 2013; Ribeiro, 2014). In this study, a suspension in isopropyl alcohol with 5% powder by volume proved to be the most appropriate. The suspension was homogenized using a mechanical stirrer in a beaker, in order to avoid possible contamination in a mill, applying moderate speed for a period of 4 hours. After this period, the mixture was dried in an oven at 80 °C for 48 hours, until the alcohol had completely volatilized and the moisture had been removed. The result of this process was an agglomerate which, after being macerated with a grater and pistil, was sieved through a 0.180 mm mesh coupled to an agitator, thus obtaining a powder with a fine and uniform granulometry.

From the mixtures, 12 mm cylindrical specimens were prepared and uniaxially pressed at 33 MPa. The load applied during the process was 620 N (20 MPa), in order to maintain a slight compressive stress. The sintering was also carried out in an inert atmosphere of argon (Ar) at 68.9 Pa (10 psi) for threshold temperatures of 1800 and 1850 °C, for a time of 30 min, at a heating rate of 10 °C/min up to 1100 °C and 20 °C/min up to the threshold (DE CARVALHO, 1999). Cooling was carried out inside the furnace for a total of six hours for each cycle. These samples were named S1PQA, S1PQB, S5PQA and S5PQB. Numbers 1 and 5 refer to the percentage amount of additives. The indices A
and B refer to the temperatures of 1800 and 1850 °C, respectively.

Figure 1 shows the Thermal Technology Inc hot press used in this work. The samples were placed one on top of the other in the graphite crucible, i.e. two pads for each sintering cycle. To facilitate disassembly and avoid reaction with the mold, each disk was coated with boron nitride powder (De Carvalho, 1999).

Figure 1 - Hot pressing: a) general view of the equipment; b) positioning of the samples in the crucible

Source: Authors

2.3 CHARACTERIZATIONS OF PHYSICAL PROPERTIES

The material produced was characterized in terms of its density by the archimedes method, the phases formed by x-ray diffraction, its microstructure by scanning electron microscopy of the fracture surface, vickers hardness and fracture toughness.

2.3.1 Archimedes Method

Density determination was made possible with the regulatory support of ASTM C20 and ABNT NBR 6220, which are based on Archimedes' principle. A Gehaka BK 300 analytical Gehaka BK 300 analytical balance was used, with a resolution of 0.001 g, and accessories suitable for measuring density.

All the samples were submerged in water in a beaker and boiled for 2 hours. The cooled to room temperature, and then the immersed mass (mi) was read. Then, to measure the saturated mass (mu), the excess water on the surface was removed using a
damp cloth. Surface using a damp cloth. Afterwards, the samples were placed in an oven where they remained for 17 hours at 75 °C, for complete drying and measurement of the dry mass (ms).

The calculation of the apparent specific mass (Mea), in g/cm³, is expressed mathematically by eq. 1, which means the ratio of the dry mass to the sum of the volume of the open and where magua represents the specific mass of water (1 g/cm³). As a function of Mea and theoretical density (ρtheoretical) determined by the rule of mixtures, the total porosity (Ptotal) is calculated using eq. 2. From Ptotal, it is also possible to obtain the percentage of of densification (D%) using eq. 3.

\[
Mea = \frac{m_s}{m_{agua} + m_i} m_{water}
\]  
(1) 

\[
P_{total} = \frac{\rho_{theoretical} - Mea}{\rho_{theoretical}} \times 100
\]  
(2) 

\[
D\% = 100 - P_{total}
\]  
(3)

2.3.2 X-Ray Diffraction (XRD)

The S5PQA e S5PQB sintered bodies were analyzed using a diffractometer X’pert Pro from Panalytical, with CuKα radiation, 40 kV acceleration voltage and 40 mA current. The scan took place with a 2θ between 20 and 100°, a step of 0.05° and a collection time of 150 s on the surface of the samples. The quantitative analysis of the phases found was carried out by the Rietveld method using the TOPAS Academic v4.1 software, as in the powder analysis.

2.3.3 Scanning Electron Microscopy (SEM)

The morphology of the hot-pressed samples was evaluated using a FEI Company Quanta FEG 250 field emission SEM. Acceleration voltages of 15 and 30 kV were used,
with working distances ranging from 2.0 to 4.0 mm, scanning times of 30 μs. For the S1PQA and S1PQB groups (1 %), was used magnifications of 5000 x. For S5PQA and S5PQB groups (5 %), a magnification of 30000 x was used due to its higher densification.

2.3.4 Vickers Hardness and Fracture Toughness

This stage of the work was carried out in accordance with ASTM C1327-15, which deals with the Vickers hardness test for advanced ceramics. A Shimadzu HMV-G with Vickers penetrator was used, accredited by INMETRO in accordance with ABNT NBR ISO 17025. Only the S5PQA and S5PQB groups were evaluated, since the obtained sufficient densification to produce a specular surface after ceramography.

The samples were tested in a total of four indentations for 15 seconds, loads of 2.942 N (HV0.3), 4.903 N (HV0.5) and 9.807 N (HV1) were used in order to evaluate the effect of the load on the hardness value measured.

The ceramographic preparation required for the hardness test was carried out following the route developed by Gonçalves et al. (2017). To calculate fracture toughness, this work used the models of Niihara (1983) and Liang (1990), just as Lima (2006) applied these two equations to characterize SiC sintered with Al₂O₃ and Y₂O₃.

3 RESULTS AND DISCUSSION

3.1 ARCHIMEDES METHOD

The densification and total porosity results for the hot-pressed samples are shown in Figure 2. Table 1 shows the apparent specific mass (Mea), densification percentage and total porosity values for each condition analyzed.

The groups with the best densification were S5PQA and S5PQB, with a densification percentage above 90 % and total porosity below 10 % (Figure 2a and Figure 2b). In this case, the amount of additives had a major influence on the increase in density. The
addition of 5% by weight of Al₂O₃ and Y₂O₃ proved to be significantly more efficient in sintering than 1%. It was also found that the temperature of 1800 °C, in principle, is ideal, since at 1850 °C there was no increase in density for both the group with 1% and 5% additives.

Figure 2 – a) Densification percentage as a function of sintering temperature for samples obtained by hot pressing; b) Total porosity as a function of sintering temperature for samples obtained by hot pressing.

![Figure 2](image)

Source: Authors

Table 1. Results of apparent specific mass, densification percentage and total porosity for each condition.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Mea (g/cm³)</th>
<th>Density (%)</th>
<th>Total porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1PQA</td>
<td>2.11 ± 0.06</td>
<td>65.57 ± 1.87</td>
<td>34.43 ± 1.87</td>
</tr>
<tr>
<td>S1PQB</td>
<td>2.14 ± 0.00</td>
<td>33.65 ± 0.08</td>
<td>66.35 ± 0.08</td>
</tr>
<tr>
<td>S5PQA</td>
<td>3.14 ± 0.15</td>
<td>95.90 ± 4.62</td>
<td>4.10 ± 4.62</td>
</tr>
<tr>
<td>S5PQB</td>
<td>3.03 ± 0.05</td>
<td>92.78 ± 1.46</td>
<td>7.42 ± 1.46</td>
</tr>
</tbody>
</table>

Source: Prepared by the authors.

3.2 X-RAY DIFFRACTION

The S5PQA and S5PQB groups were chosen for XRD characterization due to the high percentage of densification obtained compared to the others and the diffractograms are shown in Figure 3. Peaks referring to 2H graphite were identified in all groups analyzed from contamination with the furnace crucible. The relative amount of each phase calculated by Rietveld is shown in Table 2.
Figure 3 – Phases formed in S5PQA and their relative quantity calculated by Rietveld.

Table 2. Phases formed in S5PQA and S5PQB and their quantity calculated by Rietveld

<table>
<thead>
<tr>
<th>Phases</th>
<th>Percentage (%)</th>
<th>Phases</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC 3C</td>
<td>92.74</td>
<td>SiC 3C</td>
<td>75.39</td>
</tr>
<tr>
<td>AlY3</td>
<td>2.53</td>
<td>AlY3</td>
<td>1.99</td>
</tr>
<tr>
<td>BN</td>
<td>1.19</td>
<td>BN</td>
<td>1.75</td>
</tr>
<tr>
<td>Graphite 2H</td>
<td>3.55</td>
<td>Graphite 2H</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiC 4H</td>
<td>4.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiC 6H</td>
<td>5.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si</td>
<td>10.13</td>
</tr>
</tbody>
</table>

Source: Prepared by the authors.

In hot pressing with 5 % additives, in addition to 2H graphite, boron nitride contamination was identified as it was deposited on the surface of the green body. The pressure, together with the temperature and the presence of boron nitride, modified the phases formed by the additives, preventing the occurrence of YAG, YAP and YAM, but favoring the appearance of AlY3.

The increase in temperature of 50 °C was sufficient for the formation of new phases. While only SiC 3C was formed in S5PQA, polytypes 3C, 4H and 6H were formed
in S5PQB. At 1850 °C, peaks were also identified for elemental silicon. Above all, it is possible that there is an oxide rhombohedral phase that fits better in place of Si.

3.3 SCANNING ELECTRON MICROSCOPY

The morphology of the sintered samples differed depending on the sintering process and the amount of additives. The structure of the grains and existing pores was observed, as was the distribution of the sintering additives.

The hot-pressed samples differed greatly from each other only in terms of the amount of additives, which promoted greater densification. The increase in temperature from 1800 °C to 1850 °C only led to an increase in grain size. The 5,000 x micrographs in Figure 4 show the S1PQA and S1PQB groups.

![Figure 4](image_url)

With 5 % additives, the microstructure was better observed at 30,000 x magnification, due to the greater densification. Figure 5 shows that there is no microstructural difference between the temperatures of 1800 °C and 1850 °C.
3.4 VICKERS HARDNESS AND FRACTURE TOUGHNESS

The vickers test was suitable for characterizing hardness in accordance with literature, and there was no need to explore knoop hardness. The hardness indentations could be measured and evaluated in accordance with ASTM C1327-15, as shown in Figure 6, a micrograph taken immediately after the test. The red square corresponds to the diagonal measurements.

Figure 6 – Valid indentation according to ASTM C1327-15 of S5PQA.
A complete characterization of hardness includes measurements over a wide range of loads, as the hardness of ceramics tends to drop with increasing force or indentation size. This effect is known as the indentation size effect (ISE). The most correct measurement value to consider is in the load range where there is no further variation in hardness with increasing force (ASTM, 2015). The graph in Figure 7 shows the influence of the load on the hardness values measured in the hot-pressed samples. It can be seen that the plateau begins to stabilize at 9.807 N.

Table 3 shows the fracture toughness values obtained in comparison with authors who used the same methods used in this research. The equation developed by Liang (1990) is the most reliable for comparing results, as it is independent of load and crack system.
Table 3. Fracture toughness of S5PQA and S5PQB compared to literature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fracture toughness (MPa. $\sqrt{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_c$ Niihara</td>
</tr>
<tr>
<td>S5PQA</td>
<td>6.12 ± 0.08</td>
</tr>
<tr>
<td>S5PQB</td>
<td>4.92 ± 0.23</td>
</tr>
<tr>
<td>(LIMA, 2006)</td>
<td>7.40 ± 0.27</td>
</tr>
<tr>
<td>(RIBEIRO, 2014)*</td>
<td>-</td>
</tr>
<tr>
<td>(RIBEIRO, 2014)**</td>
<td>-</td>
</tr>
</tbody>
</table>

* SiC + 10% ($Y_2O_3 + Al_2O_3$)
** SiC + 10% ($Dy_2O_3 + Al_2O_3$)

Source: Prepared by the authors.

Lima (2006) evaluated SiC mixed with 5% Al$_2$O$_3$ and Y$_2$O$_3$ sintered without pressure at 1900 °C, while Ribeiro (2014) compared SiC sintered with alumina and rare earths at 1950 °C. The correlation in Table 3 shows that the toughness of the hot-pressed silicon carbide obtained in this work is lower than that produced by Lima (2006) and Ribeiro (2014).

The load of 9.807 N (HV1) was the most suitable for producing a measurable indentation size, free of distortion and for better propagation of the radial cracks. As the l/a ratio was 1.63 ± 0.06, the crack system can be characterized as Palmqvist, as found for SiC at low loads (LIMA, 2006). When observing the polished surface after the S5PQA hardness test in Figure 8, some cracks were found that were disconnected from the vertex of the indentation. Therefore, the equation developed by Niihara (1983) is valid.
4 CONCLUSIONS

The study of hot pressing at 1800 and 1850 °C aimed to evaluate the influence of the percentage of additives (1 and 5%) on the SiC sintering. Considering the evaluation of physical properties (density and apparent porosity), mechanical properties (hardness and fracture toughness) and microstructural properties, it was found that the addition of 5% by weight is significantly superior to 1% in providing densification, due to the greater formation of the liquid phase.
The microstructural characterization by SEM, in addition to showing the degree of densification, showed the grain growth associated with the increase from 1800 to 1850 °C in hot pressing.

The ceramography procedures adopted proved to be efficient in preparing SiC samples for the correct measurement of Vickers hardness, and for determining fracture toughness by propagating radial cracks from the indentation.

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