Wetting behaviour of SiC ceramics
Part II—Y\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and Sm\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}

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Received 8 December 2003; received in revised form 19 April 2004; accepted 2 May 2004
Available online 20 June 2004

Abstract

Wettability is the most significant phenomenon in SiC liquid phase sintering. The wetting of Y\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and Sm\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} on SiC was analysed by the “Sessil drop” method. The wetting of liquid on solid during liquid phase sintering is very important. The behaviour of the additive on the SiC plate was observed using an imaging system with a CCD camera, and the contact angle measurements were analysed by Qwin Leica software. The samples were cut transversally and characterized by scanning electron microscopy and X-ray spectrometry (SEM/EDS). The wetting was found to be strongly influenced by the temperature; the SiC/additive contact angle decreased with increasing temperature. The YA and SA additives presented low contact angle values, indicating their good wetting on SiC in the argon atmosphere. The contact angle could not be measured when the test was performed in the nitrogen atmosphere because bubbles formed in the liquid during the test. The best atmosphere for this sintering was found to be argon, which allows uniform spreading.

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Keywords: Wettability; Liquid phase sintering; Silicon carbide; Y\textsubscript{2}O\textsubscript{3}; Al\textsubscript{2}O\textsubscript{3}; Sm\textsubscript{2}O\textsubscript{3}

1. Introduction

The SiC ceramics are obtained by solid phase or liquid phase sintering. The use of metallic oxide additives in liquid phase sintering leads to homogeneous microstructures with morphologies suitable to achieve high toughness values [1–7]. However, the use of oxides to form the liquid phase also involves disadvantages because they may evaporate or react with SiC, leading to the formation of volatile composites, and consequently, weight loss [2,4,6,7]. Thermodynamic studies have demonstrated the probability of chemical reactions between SiC and several oxides at 2147 °C. The most stable additives, in increasing order, are Al\textsubscript{2}O\textsubscript{3}, BeO, HfO\textsubscript{2}, ThO\textsubscript{2}, Sm\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3} and Ce\textsubscript{2}O\textsubscript{3} [8].

Wetting of the additive on SiC is crucial in liquid phase sintering. The behaviour of the liquid on the solid surface is generally indicated by the contact angle $\theta$, which is expressed as a function of the surface energies solid–liquid, liquid–vapour, solid–vapour ($\gamma_{\text{SL}}$, $\gamma_{\text{LV}}$, $\gamma_{\text{SV}}$), as shown in Eqs. (1) and (2) [9–14]:

$$\gamma_{\text{SL}} - \gamma_{\text{SV}} = -\gamma_{\text{LV}} \cos \theta$$

(1)

$$\Delta G = -\gamma_{\text{LV}} (1 + \cos \theta)$$

(2)

where $\Delta G$ is the Gibbs energy change.

In wetting studies of different Y\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} compositions on Si\textsubscript{3}N\textsubscript{4} using the “Sessil drop” method, the final contact angle was found to decrease as the Y\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} ratio increased [15]. This finding led to the conclusion that the additive composition and the temperature significantly influence the wetting process [9,10,15]. Lower final contact angle values also result from decreased viscosity arising from increased in temperature [15,16].

Lee et al. [17] conducted wetting experiments of MgO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} glass on SiC in alumina tube and graphite tube furnaces in argon atmosphere at 1500 °C. The wetting test performed in the alumina tube furnace resulted in perfect wetting, $\theta \equiv 0^\circ$. However, the test performed in graphite tube furnace produced a contact angle of $\theta \equiv 45^\circ$, indicating intermediate wetting. This difference was attributed to the
formation of carbon monoxide in the furnace. Changes in composition of the atmosphere alter the wetting behaviour, owing to the influence of surface energies (liquid–gas and gas–solid). The surface energies of oxynitride glasses are about twofold higher than those of glass oxides due to the incorporation of nitrogen from the atmosphere, resulting in augmented viscosity in the liquid phase [15]. Therefore, wetting is influenced strongly by the atmosphere [10,17].

<table>
<thead>
<tr>
<th>Code</th>
<th>Al₂O₃</th>
<th>Y₂O₃</th>
<th>Code</th>
<th>Al₂O₃</th>
<th>Sm₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>mol%</td>
<td>wt.%</td>
<td>mol%</td>
<td>wt.%</td>
<td>mol%</td>
</tr>
<tr>
<td>YA1</td>
<td>80.24</td>
<td>90</td>
<td>19.76</td>
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<td>64.35</td>
<td>80</td>
<td>35.65</td>
<td>20</td>
<td>SA2</td>
</tr>
<tr>
<td>YA3</td>
<td>40.37</td>
<td>60</td>
<td>59.63</td>
<td>40</td>
<td>SA3</td>
</tr>
</tbody>
</table>

The purpose of this work was to study the wetting of Y₂O₃/Al₂O₃ and Sm₂O₃/Al₂O₃ additives on SiC. The first additive system was chosen because according to the literature, in combination with SiC it forms a ceramic with good mechanical properties, serving as a reference for comparison with other systems. The second additive system, which is relatively new in the literature [18], displays good thermodynamic stability with SiC [8].

2. Experimental

The materials used for the wettability study were SiC plates (10.0 × 10.0 × 4.0 mm³) with a 98.9% T.D., manufactured by Wacker-Chemie, Germany. These plates were ground and polished with 1-μm diamond paste.

The additives used were Al₂O₃ (CR6, AS 250 KC supplied by Baikalox), Y₂O₃ (Grade C, HCST–Hermann C. Starck) and Sm₂O₃ (donated by INB–Indústrias Nucleares do Brasil). The additive mixtures are listed in Table 1. The YA2 and SA2 samples had a eutectic composition, as illustrated in Fig. 1.

![Fig. 1. Phase diagram of (a) Y₂O₃/Al₂O₃ [19] and (b) Sm₂O₃/Al₂O₃ systems [18].](image)

![Fig. 2. Variation of contact angle of (a) YA and (b) SA with temperature.](image)
The materials were prepared as described in Part I [19]. The additive/SiC set was placed in a graphite resistance furnace (Astro) and heated at a rate of 10 °C/min to the additive sphere melting point in argon or nitrogen atmospheres. The wetting test was concluded when the contact angle remained constant and/or the maximum experimental temperature was 2000 °C.

The additive behaviour on the SiC plate was observed by means of an imaging system using a CCD camera, and the contact angle measurements were analyzed using the Qwin Leica software program. The presence of crystalline phases of melted additive was identified by X-ray diffraction analysis (XRD, Rich Seiferst & Co. Isso-Debeyefflex 1001) with Cu-κα radiation. The samples were cut transversally and their microstructures were characterized by scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS).

3. Results and discussion

The wettability of the two systems, Y₂O₃/Al₂O₃ and Sm₂O₃/Al₂O₃, on SiC substrates was investigated in both argon and nitrogen atmospheres; however, measurement of the contact angle was only possible in the test using argon due to the formation of bubbles in the additive during the test, which hindered taking these measurements.

The changes in contact angle according to the temperature are shown in Fig. 2(a) for the YA samples and in Fig. 2(b) for the SA samples.

The contact angle decreased in all systems as the temperatures increased. The initial spreading temperatures of liquids lie close to the liquid’s melting points, as indicated in the phase diagram [20] (Fig. 1), which correspond to 1760 and 1755 °C to YA and SA, respectively. All the compositions showed low final contact angle values below 10°, indicating good wetting.

Composition YA3, which showed the highest Y₂O₃/Al₂O₃ ratio, exhibited a lower decrease in the contact angle rate than did the YA1, YA2, SA1, SA2 and SA3 compositions. This was probably because the YA3 composition is a eutectic of higher melting point, as indicated in Fig. 1(a).

The eutectic molar composition (%) of both 20Y₂O₃/80Al₂O₃ and 24Sm₂O₃/76Al₂O₃ additives presented better contact angle rate results. This behaviour was expected because mixtures with eutectic compositions form less viscous liquids at given temperatures than do other compositions of the same system in which the solid and liquid phases exist simultaneously. Another factor that interferes strongly in the wetting is the surface energies [21,22] (Eqs. 87x559).
so that when the compositions of additive systems change, the superficial energies (solid–liquid and liquid–gas) are altered.

Fig. 3 shows a cross section of samples after the wettability test, representing the behaviour of additive on SiC, in argon and nitrogen atmospheres. All the tests in the argon atmosphere, see Fig. 3(a), displayed a fine layer of additive containing some porosity but no bubbles, and the additive did not infiltrate into the SiC. The tests in the nitrogen atmosphere, see Fig. 3(b), showed a layer of additive with a few pores and bubbles, and most of the additive compositions in both systems infiltrated into the SiC slightly. The nitrogen atmosphere likely increased the additive’s viscosity [23–25], decreasing the gas diffusion in the liquid and modifying the additive’s microstructure formed upon cooling.

Figs. 4 and 5 depict the additives’ microstructures after the wettability test in argon and nitrogen atmospheres, respectively. An EDS analysis was performed at different points of each sample to identify the supposed phases by comparison with the respective diagram phases and X-ray diffraction (Table 2).

The wetting test conducted in the nitrogen atmosphere produced fragile microstructures and modified phases. The nitrogen also modified the liquid’s viscosity, leading to the formation of bubbles. Therefore, the nitrogen atmosphere is not recommended for sintering SiC with additives from the YA and SA systems.

### 4. Conclusions

(a) The wettability proved to be strongly influenced by the temperature; the contact angle of SiC/additive decreased with increasing temperature.

(b) The atmosphere used in the wetting test affected the systems’ superficial energies, modifying the behaviour of the contact angle rate. The YA and SA additives displayed low contact angle values, indicating the satisfactory wetting of these additives on SiC in the argon atmosphere.

(c) The contact angle was immeasurable in the tests in nitrogen atmospheres because of the formation of bubbles in the liquid during the test. The atmosphere used for sintering should preferably be argon, which allows uniform spreading.

(d) The best contact angle rate results were achieved with the eutectic composition due to the large amounts of liquid formed. It can be suggested that the liquid phase sintering of SiC with Y2O3/Al2O3 or Sm2O3/Al2O3...
systems should be performed with the eutectic composition of additives because they exhibited relatively fast spreading and because the final contact angle was smaller than $10^\circ$.

(e) The wettability curves of the YA and SA systems displayed a sharp decline indicative of good spreading. The single exception was sample YA3, which spread more slowly than the other samples. The increase in the $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio led to a slower contact angle rate.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian research funding institutions FAPESP (Grants 01/10664-6 and 01/11339-1), CNPq, CAPES and INB.

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