EVALUATION OF GRAIN BOUNDARY PHASES OF β-SIALON
BY CRYOGENIC SPECIFIC HEAT MEASUREMENTS

TOYOKAZU KURUSHIMA *, KOZO ISHIZAKI ** AND TOYOHIRO HAMASAKI **
* INAX Corporation, Tokoname, Aichi 479, JAPAN
** Nagaoka University of Technology, Nagaoka, Niigata 940-21, JAPAN

ABSTRACT

Fully densified β-SIALON ceramics (Si₆Al₂O₅Nₓ), were prepared by a normal sintering and a post-sintering HIP (hot isostatic pressing) treatment. After exposure to corrosion by molten copper oxide (CuO) at 1200°C in air for 1 hour, both samples were evaluated by measuring their specific heat at cryogenic temperatures. Due to the fast cooling rate during sintering, the HIPed sample contained more grain boundary glassy phases than the normally sintered one. This was evaluated by a newly developed copper oxide etching method. Cryogenic specific heat is a powerful and a sensitive property for evaluating the grain boundary glassy phases of β-SIALON ceramics. The copper oxide etching method used was found to be an effective method for observing ceramic structures with siliceous grain boundary glassy phases.

INTRODUCTION

β-SIALON ceramics are considered one of the best refractory materials for containing molten metals such as steel [1,2], but they are easily corroded by molten copper oxide [3]. However, they are not corroded to any extent by steel slag. It is possible that their corrosion by copper oxide could be caused by the presence of grain boundary glassy phases.

Watari et al. have proposed that the abnormal specific heat at cryogenic temperatures of silicon nitride ceramics could be used to evaluate glassy phases [4]. Hamasaki et al. showed that this is also an extremely sensitive method for evaluating the amount of grain boundary glassy phases in silicon nitride ceramics [5].

This study uses cryogenic specific heats to compare the relative amounts of glassy phases in HIPed and normally sintered β-SIALON ceramics (Si₆Al₂O₅Nₓ). The relation of the amount of grain boundary glassy phases present in β-SIALON ceramics to their rate of corrosion by molten copper oxide is discussed.
TABLE 1 shows the grain sizes and chemical compositions of the starting materials for B-SIALON ceramics. The raw materials were pressed uniaxially at 20 MPa, and CIPed (cold isostatic pressing) at 100 MPa.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Grain Size</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-SIALON</td>
<td>0.6 μm</td>
<td>99 wt%</td>
</tr>
<tr>
<td>(Si₄Al₂O₂N₆)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>3 μm</td>
<td>1 wt%</td>
</tr>
</tbody>
</table>

The sintering schedules are shown in Figure 1. Normal sintering is indicated by a solid line. The HIPed samples were first sintered normally following the solid line in this figure, and then HIPed at 100 MPa of nitrogen gas following the dashed line. Using a diamond cutter, the samples were cut into rectangular shapes about 10 mm x 10 mm x 7 mm. The density was calculated by Archimedes' principle after weighing in water and air.

Figure 2 is a schematic diagram of the corrosion test. The samples were heated in molten copper oxide at 1200°C for 1 hour. The alumina lid of the heating vessel was kept slightly open to maintain the oxygen partial pressure at ambient pressure. Samples before and after the corrosion test were studied by scanning electron microscopy (SEM).

The specific heats of the B-SIALON samples were measured at temperatures between 10K and 40K using equipment developed by Hamasaki et al. [5].

RESULTS

The normally sintered and the HIPed B-SIALON ceramics were fully densified to the densities of 99.5% and 100% respectively.

Figure 3 shows photographs of B-SIALON samples before and after the corrosion test. A marked reduction in dimensions occurred, particularly for the HIPed sample.

Figure 4 shows the specific heats of the normally sintered and the HIPed B-SIALON samples at temperatures between 10K and 40K. For reference, the solid line indicates the specific heat of silicon nitride ceramics calculated from the Debye theory for temperatures of Ñ=1100 K [4]. The difference between the specific heats of the HIPed B-SIALON and the normally sintered sample is mainly due to the amount of grain boundary glassy phases present. One can observe that the HIPed sample contains more grain boundary glassy phases.

Figure 5 shows the SEM micrographs of polished surfaces of the corrosion tested B-SIALON samples. Pores are located along the grain boundaries. More pores are present in the HIPed sample than in the normally sintered one.