REACTION BETWEEN SILICON NITRIDE AND MAGNESIUM OXIDE DURING HOT PRESSING

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The density of materials based on silicon nitride (Si₃N₄) can be increased by the addition of various activators [1], in particular oxides of alkaline earth metals [2-5]. Of these, the most effective is magnesium oxide, MgO. The densification kinetics characterizing the hot pressing of Si₃N₄ with a MgO addition has been investigated by a number of authors, who have attributed the influence exerted by this activator on the densification process to various causes: the formation of magnesium silicate [2-5], a solid solution of MgO in β-Si₃N₄, and the ternary compound MgSiN₂ [3, 4].

In the present work a study was made of the reaction between magnesium oxide and silicon nitride in a hot-pressed material containing 5 wt% MgO and in model systems containing equal amounts of the two components in powder form as well as MgO in the form of a single crystal in Si₃N₄ powder. As starting materials, powdered technical silicon nitride (to VTU 3SNKh No. 002-60 specification) and ultra-light magnesium oxide (to TU MKhP 1985-49 specification) were used. The starting Si₃N₄, the hot-pressed material produced from it, and the model systems were investigated by subjecting them to microscopical examinations, chemical, x-ray diffraction, mass spectrometric analyses, electron probe microanalyses, and weight loss determinations.

The hot pressing of the material and the model systems, which was performed in a graphite die, consisted in induction heating to temperatures in the range 1500-1800°C. The pressing pressure was 300 kgf/cm² and the pressing time, 30 min. To prevent the charge from reacting with the graphite pressing tool, the latter was coated with a paste based on boron nitride.

The main impurities in the technical Si₃N₄ were as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>57.2</td>
<td>35.3</td>
<td>1.2</td>
<td>0.5</td>
<td>4.5</td>
<td>0.65</td>
<td>0.5</td>
<td>1.5</td>
<td>0.02</td>
<td>0.13</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Microscopical and x-ray diffraction studies of the starting Si₃N₄ powder showed that these elemental impurities formed in the silicon nitride the following compounds: silicon carbide (SiC), silicon dioxide (SiO₂), silicon oxynitride (Si₄O₅N₂), and Fe, Al, and Ca silicates. Because of the lack of reliable methods for the chemical analysis of materials of the Si–O–N system, data on the SiO₂ and Si₂ON₂ contents of technical Si₃N₄ powder - 4 and 14 wt.%, respectively - were taken from [6].

An x-ray diffraction analysis of the hot-pressed material (charge composition 95% Si₃N₄ + 5% MgO, pressing temperature 1700°C) showed that the main β-Si₃N₄ phase had remained unchanged, and revealed also the presence of an oxynitride (~ 10 wt.%) and free silicon (~ 5 wt. %). Specimens of the material of this composition pressed at various temperatures were subjected to chemical analyses, which yielded the data given in Table 1. It will be seen from the table that with rise in hot-pressing temperature the total amount of magnesium steadily fell. Apart from this, the relative amounts of magnesium in the silicates and magnesium oxide changed: The amount of enstatite (MgSiO₃) decreased and that of forsterite (Mg₂SiO₄) increased, both changes being in accord with the MgO–SiO₂ constitution diagram.

A petrographic study of a ground sample of the hot-pressed material showed that it contained crystalline silicates - forsterite and enstatite - and variable-composition glasses (xMgO·ySiO₂) with values of refractive index (n) ranging from 1.50 to 1.52. Now for the majority of glasses investigated the index n varies linearly with composition, and consequently, using the known values of n for quartz glass (1.455) and SiO₂·MgO (1.581), it...
proved possible to determine the composition of the glasses formed during hot pressing. The mole fraction of MgO in these glasses varied from 0.35 to 0.52.

To determine the precise form of the silicates and glasses forming in the material, a study was made of a model Si$_3$N$_4$-MgO-SiO$_2$ system with a component ratio of 1:1:1, which was subjected to hot pressing under the same conditions as the material itself. Forsterite and enstatite were found in small amounts, in the form of a finely divided phase. The small particle size of these compounds combined with the low resolving power of the microscope could have resulted in low values being obtained in determination of their amounts. Because of this, no attempt was made to determine the relative amounts of the crystalline and amorphous phases.

In order to eliminate the effect of Si$_3$N$_4$ on the crystallization process and on the chemical reaction between SiO$_2$ and MgO, a mixture of equal parts of powders of these compounds was hot pressed under the conditions of preparation of the material. Both amorphous silica and quartz sand were used. In both cases the main phase forming in the course of hot pressing was coarse-crystalline forsterite and enstatite (50-150 μ). The vitreous binder in the specimens constituted thin interlayers between the grains.

The phase composition of inclusions in the hot-pressed material was studied in detail by subjecting them to quantitative local electron probe microanalyses for individual elements. The metallic inclusions proved to be mutual solid solutions of silicon and iron (the Fe:Si ratio varied from 1:1 to 2.5:1). Coarse light-gray inclusions contained silicon (~ 66 wt. %) and carbon. As the theoretical silicon content of SiC is 70%, it is reasonable to assume that the inclusions were the silicon carbide present in the starting technical Si$_3$N$_4$ powder.

To discover the nature of the reaction between Si$_3$N$_4$ and MgO, a model experiment was carried out in which a sample of silicon nitride powder with a magnesium oxide single crystal embedded in it was hot-pressed. The specimen was then sectioned along a diameter, and a microsection was prepared (Fig. 1). Around the single crystal there was a dark zone, the color of the material gradually becoming lighter with increasing distance from the crystal. A metallographic examination gave the same results as for an ordinary specimen pressed hot from Si$_3$N$_4$ with 5% MgO. Visually, the dark and light regions differed only in the amount of pores.

The diffusion zone around the magnesium oxide single crystal was subjected to local electron probe microanalysis for magnesium and silicon. Use was made also of the method of photography in characteristic x-ray radiation. The probe traversed a linear distance of 1675 μ, over which the magnesium content fell to the background level. The intensities of magnesium lines at various points, obtained by automatic recording over the whole distance investigated, starting from the edge of the single crystal, were converted into magnesium contents using data on the line intensities of appropriate reference standards.

To discover the overall pattern of magnesium and silicon distribution in a macrovolume of the material, the data obtained were processed statistically, which involved constructing confidence intervals with the aid of Student's number (at a confidence level α = 0.95) in 17 chosen intervals. The magnesium concentration curve obtained is shown in Fig. 2a. It will be seen that the maximum magnesium content was 6.8 wt. %, which corresponded to 11.0 wt. % of magnesium oxide.