Porous glass was crushed into small particles (20 to 35 mesh), etched with 5% HF for 2 min to remove surface contaminants, and dried in an oven at 80°C. Different weights of porous glass were immersed in 100 mL of NaOH solutions with various concentrations. Calcium chloride (0.001 mol) was added to each solution and the solution was oven-heated at 80°C for 2 h; a preliminary experiment showed that 2 h were sufficient to reach equilibrium.

The calcium concentration remaining in the solution after treatment was determined by atomic absorption analysis. The deposition, indicated by the ratio of calcium content remaining in a solution (C) to the initial calcium content (C₀), is shown in Fig. 2. Even without alkali solution, a small amount of calcium is deposited; this deposition probably comes from the nature of porous glass as a trace ion getter. In alkaline solutions, the calcium deposition increases as the weight or surface area of porous glass increases. Also, the higher the alkalinity of a solution, the more calcium is deposited, suggesting that the reaction between calcium and silica is accelerated in more alkaline environments. When the higher calcium concentration or the larger amount of porous glass was used, a process. The precipitate is probably a reaction product of calcium deposited, suggesting that the reaction between calcium and silica is calcium silicate hydrates; CaCO₃ may be a by-product in the drying process. Taylor, with other peaks identified as CaCO₃ and other types of silicate compound peaks and an X-ray diffraction pattern similar to the silica slide glass.

The precipitate was separated and dried in an oven. Measuring it by infrared analysis showed a fleecy precipitate appeared in the solution. This precipitate was accelerated in more alkaline environments. When the higher calcium concentration or the larger amount of porous glass was used, a process. The precipitate is probably a reaction product of calcium deposited, suggesting that the reaction between calcium and silica is calcium silicate hydrates; CaCO₃ may be a by-product in the drying process. Taylor, with other peaks identified as CaCO₃ and other types of silicate compound peaks and an X-ray diffraction pattern similar to the silica slide glass.

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The System Si₃N₄-SiO₂-ZrN-ZrO₂

J. WEISS,∗ L. J. GAUCKLER,* and T. Y. TIEN∗

Zirconium dioxide has been reported to be an effective additive for hot-pressing silicon nitride ceramics. However, the reaction between these two compounds has not been studied. The present note reports the reactions between two pairs of compounds: Si₃N₄+ZrO₂ and SiO₂+ZrN.

Appropriate amounts of chemicals were weighed and mixed for 1 h in a hard metal mill under acetone. After drying, the mixtures were pressed under a uniaxial pressure of 35 MPa. The pressed specimens were fired in BN-lined graphite crucibles in a graphite resistance-heated furnace. A mild flow of nitrogen was introduced during firing. Weight change after firing was recorded and the phases present were analyzed by X-ray diffraction (XRD). The relative amounts of different phases were compared with standard mixtures using XRD peak heights.

A mixture of 50 mol% Si₃N₄ and 50 mol% ZrO₂ was heated-treated at 1400°C, 1600°C, and 1700°C for different lengths of time. No reaction was observed at 1400°C. The phases present after heat treatment were identified by XRD analysis.

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treatment at 1600° and 1700°C are given in Fig. 1. Weight loss was considered as the gas species in the figure. These results indicate that Si₃N₄ and ZrO₂ reacted, giving ZrN and gaseous species; Si₂N₂O was the intermediate phase.

Mixtures of 50 mol% SiO₂ and 50 mol% ZrN were prepared in the same way and heat-treated at 1400°, 1600°, and 1700°C. No reaction was observed at 1400°C. The results for 1600° and 1700°C heat treatments are given in Fig. 2. The reaction at 1600°C was slow; it

Fig. 1. Time dependence of phases present after sintering of Si₃N₄-ZrO₂ mixtures at (A) 1600° and (B) 1700°C.

Fig. 2. Time dependence of phases present after sintering of SiO₂-ZrN mixtures at (A) 1600° and (B) 1700°C.
was not completed after 40 h. However, from the trend it may be concluded that ZrO, forms an intermediate phase and ZrN will be the solid end product when fired in flowing nitrogen. These results suggest that the following reactions take place:

\[
\begin{align*}
\text{Si}_3\text{N}_4 + 3/2 \text{ZrO}_2 &= 3/2 \text{ZrN} + 3\text{SiO} + 3/2 \text{N}_2 \\
2\text{SiO} + \text{ZrN} &= \text{ZrO}_2 + 2\text{SiO} + 1/2 \text{N}_2
\end{align*}
\]

However, the actual reactions would be more complicated.

A computer program is being set up to calculate all gaseous species present in equilibrium with the condensed phase under a given condition in this system, using known free energy data. The program is used the same as that suggested by Eriksson, with modifications to suit local computers.


**Effect of Carbon Impurity on the Thermal Degradation of an Si,\textsubscript{3}N\textsubscript{4}-Y\textsubscript{2}O\textsubscript{3} Ceramic**

H. KNOCH* and G. E. GAZZA*

ALTHOUGH Y\textsubscript{2}O\textsubscript{3}-doped Si\textsubscript{3}N\textsubscript{4} exhibits improved high-temperature ( \(>1300^\circ\text{C}\) ) properties, as compared with MgO-doped Si\textsubscript{3}N\textsubscript{4}, severe degradation of Y\textsubscript{2}O\textsubscript{3}-doped Si\textsubscript{3}N\textsubscript{4} occurs in an oxidizing environment at intermediate temperatures ( \(\approx 1000^\circ\text{C}\) ). This effect has been shown to be related to the existence of certain quaternary compounds in the material, e.g., Si\textsubscript{3}Y\textsubscript{2}O\textsubscript{6}N\textsubscript{2}, SiO\textsubscript{2}Y\textsubscript{2}O\textsubscript{2}N\textsubscript{2}, and Y\textsubscript{2}Si\textsubscript{2}O\textsubscript{6}N\textsubscript{2} (N-melilite, K, H, and J phase, respectively). To alleviate this problem for an Si\textsubscript{3}N\textsubscript{4} material containing 13 wt% Y\textsubscript{2}O\textsubscript{3}, Gazza et al. reported a method involving post-heat treatment of specimens in a nitriding environment. Further studies with Si\textsubscript{3}N\textsubscript{4}-Y\textsubscript{2}O\textsubscript{3} compounds suggest that the instability of these compounds, principally Si\textsubscript{3}Y\textsubscript{2}O\textsubscript{6}N\textsubscript{2} in air at \(\approx 1000^\circ\text{C}\), is greatly influenced by the presence of carbon in the material.

Two commercial Si\textsubscript{3}N\textsubscript{4} powders were used for producing the Si\textsubscript{3}N\textsubscript{4}-Y\textsubscript{2}O\textsubscript{3} compounds (Table I). Both powders were individually mixed with Y\textsubscript{2}O\textsubscript{3} in a 1:1 molar ratio and ball-milled in ethanol for 20 h using polyethylene containers and WC balls. Chemical analysis of the milled powder showed only 0.8 wt% tungsten in the samples. Therefore, the maximum amount of carbon introduced by milling is <0.06%.

The milled and dried powders were hot-pressed in graphite dies for 90 min at 1750°C in N\textsubscript{2} with an applied pressure of 30 MN/m\textsuperscript{2}. Some test bars for oxidation measurements were cut leaving as-pressed surfaces on opposite faces, whereas all faces were ground on the remaining specimens. The oxidation behavior was studied at 700° to 1400°C in air. During the oxidation treatment the samples rested on hot-pressed SiC pedestals with sharp edges.

X-ray analysis showed that all the hot-pressed materials studied were principally Si\textsubscript{3}Y\textsubscript{2}O\textsubscript{6}N\textsubscript{2} (N-melilite) with weak traces of YSiO\textsubscript{2}N (K phase) present. The X-ray diffraction data obtained were in good agreement with those reported by H. Knoch. Initial oxidation experiments were conducted with specimens hot-pressed from powders A and B with Y\textsubscript{2}O\textsubscript{3} added (materials A and B1). Specimens tested had two as-cut and two as-pressed surfaces. Visually, the as-cut test specimens after oxidation at 1000°C in air appeared similar to that previously reported. However, there was a peculiarity in the oxidation effect on the B1 material (Fig. 1(A)); only the surfaces which were in contact with the graphite die during hot-pressing showed signs of volume expansion and cracking. This result suggests that a reaction layer produced during hot-pressing strongly influences the oxidation behavior. The tests were repeated with A and B1 specimens in which the as-pressed surfaces were ground prior to testing. Specimens of material

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**Table I. Impurity Concentrations of Starting Si\textsubscript{3}N\textsubscript{4} Powders**

<table>
<thead>
<tr>
<th>Impurities in unmilled powders</th>
<th>(\text{Si}_3\text{N}_4)*A</th>
<th>(\text{Si}_3\text{N}_4)*B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (ppm)</td>
<td>1800</td>
<td>30</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>1200</td>
<td>30</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>1.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Free Si (%)</td>
<td>&lt;2</td>
<td></td>
</tr>
</tbody>
</table>

*H. C. Starck; **GTE Sylvania, Inc.