PHASE COMPOSITION AND MECHANICAL PROPERTIES OF A ZIRCONIUM DIOXIDE BASED CERAMIC OBTAINED BY HIGH TEMPERATURE SINTERING IN A VACUUM

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Changes in phase composition and mechanical properties of sintered ZrO$_2$ + 3\% (mole) Y$_2$O$_3$ specimens were examined after annealing in air and after various mechanical operations. Compacted ceramic specimens containing T and T' phase were obtained by sintering in a vacuum at 1800°C. Ceramics containing T and T' phases have excellent toughness ($K_{lc}$ up to 15 MPa-m$^{1/2}$), bend strength up to 800 MPa and HV hardness up to 13 GPa.

Data concerning the influence of a nonoxygen-containing sintering atmosphere on the structure and properties of a ZrO$_2$ based ceramic are scarce and uncoordinated. It is accepted [1, 2] that sintering or annealing ZrO$_2$ at a very low oxygen partial pressure ($10^{-6}$ Pa) results in improved stabilization of the high temperature ZrO$_2$ phases. The addition of oxides such as CaO, MgO, Y$_2$O$_3$ and so on have a similar effect. Despite the fact that a number of references [2-4] have reported better mechanical properties for a ZrO$_2$ based ceramic that was sintered in the absence of oxygen as compared with a similar material composition that was sintered in air, the influence of nonoxygen sintering on the tendency to transformation of high temperature ZrO$_2$ phases and thus on the mechanical properties, has remained virtually unresearched.

This present paper has examined the phase composition and mechanical properties of a zirconia ceramic that was vacuum sintered.

Powdered ZrO$_2$ + 3\% (mole) Y$_2$O$_3$ was obtained by dissociating an aqueous solution of zirconium and yttrium nitrates in a high frequency plasma discharge. The zirconium oxide was present in the original powder as the tetragonal modification, and had a 20-nm mean particle size.

After semidry pressing at 200 MPa pressure, the specimens, which weighed about 5 g, were sintered in an SShV type furnace having tungsten heaters at a residual oxygen pressure of 5·10$^{-5}$ mm Hg. The specimens were heated to the sintering temperature at 300°C/h, and the cooling rate after sintering was 1600°C/h. Specimen density was determined by hydrostatic weighing. X-ray phase analysis on a DRON-3 diffractometer with CuK$_\alpha$ radiation was used to identify the phase on the specimens surface both after sintering and after mechanical and thermal treatments. The quantitative ratio of the phases was determined using the methods described in [5, 6]. The mean particle size of the sintered specimens were calculated from transverse optical photographs of the thermally etched surface. Fracture investigations were carried out on a Tesla BS-500 transmission electron microscope using carbon replicas. Polished specimens measuring 4 × 3 × 40 mm were used to determine the three point bend strength. The fracture toughness was calculated on a basis of indentation values on the polished specimen surface obtained with a Vickers pyramidal indenter at a 10 kg loading using an equation suggested by the workers in [7].

After sintering, the specimens were gray or black in color. Sintering at 1600°C resulted in three phases being formed: tetragonal and a small amount of cubic and monoclinic (Table 1), this being in total agreement with the phase diagram for ZrO$_2$−Y$_2$O$_3$ [8]. Beginning at 1700°C, it appears to be possible to obtain specimens that are totally tetragonal zirconium dioxide. However, these contain two phases with variable tetragonality. The T' phase has already been identified by many workers [9], and was recorded among the additional (004) and (400) T phase diffraction reflections. It is recognized that the T' phase is formed as a result of the nondiffusive K→T transformation during rapid cooling and is characterized by a reduced...
TABLE 1. Characteristics of ZrO$_2$ + 3% (mole) Y$_2$O$_3$ Ceramic Sintered in a Vacuum

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>Phase concentration</th>
<th>Particle size, $\mu$m</th>
<th>$\rho$, g/cm$^3$</th>
<th>$\sigma_b$ (bend strength, MPa)</th>
<th>$H_V$, GPa</th>
<th>$K_{IC}$, MPa$\cdot$m$^{1/2}$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600 1 83T, 10K, 5M</td>
<td>85%</td>
<td>0.8</td>
<td>5.65</td>
<td>450±100</td>
<td>10.0</td>
<td>17.0±0.5</td>
<td>Grey</td>
</tr>
<tr>
<td>1700 1 83T, 17T'</td>
<td>83%</td>
<td>1.5</td>
<td>5.9</td>
<td>500±100</td>
<td>11.0</td>
<td>10.2±1.0</td>
<td>Black</td>
</tr>
<tr>
<td>1800 3 70T, 30T'</td>
<td>70%</td>
<td>2.5</td>
<td>6.0</td>
<td>680±120</td>
<td>13.2</td>
<td>15.3±1.3</td>
<td>Black</td>
</tr>
</tbody>
</table>

Fig. 1. Microstructure of ZrO$_2$ + 3% (mole) Y$_2$O$_3$ ceramic sintered at 1800°C

The cooling rate (1600°C/h) after sintering in our experimental work was the same as in [10], and was adequate to form the T' phase. Hence, the zirconium based ceramic phase composition was controlled by the vacuum sintering temperature.

Increasing the sintering temperature resulted in an increased particle size up to 2.5 $\mu$m (Table 1, Fig. 1) above the critical value of 1 $\mu$m for ZrO$_2$ + 3% (mole) Y$_2$O$_3$ [11], followed by the spontaneous T $\rightarrow$ M transformation.

A characteristic feature of the T' phase is its nontransformability [9]. The absence of this spontaneous T $\rightarrow$ M transformation at a 2.5 $\mu$m tetragonal phase particle size is in accordance with [1], and may be due to increased tetragonal ZrO$_2$ stabilization by oxygen vacancies that occur as a result of stoichiometry failure during vacuum sintering. It is accepted that the tetragonal phase lattice parameters are strongly dependent on the amount of Y$_2$O$_3$ that is dissolved in the lattice. In [12, 13], it was established that an increased Y$_2$O$_3$ concentration results in an increase in the tetragonal phase cell volume and a simultaneous decrease in the tetragonality factor almost to unity for cubic ZrO$_2$.

The data in Table 2 show that the lattice cell volume $V$ and the tetragonality factor $c/a$ for the T phase ZrO$_2$ after sintering in a vacuum at 1600 and 1700°C corresponds to the same characteristics for a ceramic containing 3% (mole) Y$_2$O$_3$ and which was air treated. At the same time, $c/a$, $a$ and $V$ differ from the corresponding values for the T phase ZrO$_2$ containing this specified Y$_2$O$_3$ concentration at 1800°C. Under these conditions, the $a$ value decreases as the temperature rises and results in a significant drop in the lattice cell volume to a value even lower than that of the T phase ZrO$_2$ containing no stabilizing additions.

Such a significant reduction in the volume of the T phase lattice cell cannot be solely attributed to the inherent redistribution of the yttrium from the tetragonal to the cubic phase during high temperature sintering in accordance with the constitution diagram [8]. The fact that the lattice cell volume is less than is the case for ZrO$_2$ without any stabilizing additions cannot account for this effect and yttrium volatilization from the specimen surface which takes place during vacuum sintering [6]. It is natural to assume that the volume reduction in the ZrO$_2$ lattice cell after high temperature sintering in a vacuum is controlled by the presence of a large quantity of oxygen vacancies due to significant failure in T phase stoichiometry. According to [1], the concentration of oxygen vacancies (in cubic ZrO$_2$ stabilized with CaO), which occur due to nonoxygen sintering at 1900°C, is 17%. The decrease in the cell lattice volume for such material was 0.3%. Assuming a similar reduction in the T phase volume, the amount of dissolved Y$_2$O$_3$ may be calculated. In our experimental work, this was 1% (mole), which is very much the expected results.

Results from air annealing specimens for 1 h at 1300°C specimens sintered in a vacuum serve to confirm the additional stabilizing effect due to oxygen vacancies on the tetragonal phase. At the same time, a recovery took place in the lattice cell.