Sintering and fracture toughness of alumina-zirconia composites

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Microstructure, grain growth and fracture toughness of alumina-zirconia composites prepared from commercial grade technical alumina and imported zirconia were studied. Ostwald ripening and coalescence of ZrO$_2$ and Al$_2$O$_3$ grains were observed. Fracture toughness of the composites having different phase assemblages seemed to be controlled by the transformation toughening and microcracking toughening mechanisms. Highest fracture toughness of the order of 5.5 MN m$^{-3/2}$ was found for the composite prepared from a batch of Al$_2$O$_3$ + 29.5% ZrO$_2$ + 1.5% Y$_2$O$_3$.

Alumina-zirconia composites (AZC) or zirconia-toughened alumina (ZTA) find application as cutting tools, metal pouring nozzles, high temperature refractories by virtue of their high fracture toughness, wear resistance and thermal-shock resistance. Sintering and grain growth in this system take place mainly by solid state diffusion process. Alexander et al. measured activation energies and obtained grain growth exponent of $n=3.45$ which suggested boundary diffusion controlled mechanism for grain growth. The growth occurred by ripening and coalescence processes. Kibbel and Heuer observed predominance of coalescence over Ostwald ripening. Smaller particles dissolved more than the larger particles in the matrix. The difference in solubility of particles of different sizes caused matter to be transported down the concentration gradient from the smaller to the larger particles. Larger particles have, therefore, grown at the expense of smaller ones which ultimately disappeared. During coalescence, ZrO$_2$ particles at Al$_2$O$_3$ corners were dragged by migrating Al$_2$O$_3$ boundaries and met other ZrO$_2$ particles.

The toughness of ZTA is higher than that of alumina by virtue of several toughening mechanisms. These are transformation toughening (TT), microcracking strengthening toughening (MT), crack deflection toughening, elastic matrix constraint of Al$_2$O$_3$ on ZrO$_2$, pinning or bowing of the crack front by the second phase transformation. Surface strengthening or grinding induced compressive surface layer strengthening in the Al$_2$O$_3$-ZrO$_2$ ceramics is also important.

Rajendran et al. obtained 3.5 to 6 MN m$^{-3/2}$ $K_{IC}$ value ($K_{IC}$ symbolises fracture toughness) for Al$_2$O$_3$ + Y-TZP (5-30 wt%) (Y-TZP means Y$_2$O$_3$ stabilized tetragonal zirconia phase) composites prepared by Hipping coprecipitated powder at 1500°C (toughness of alumina is 3 MN m$^{-3/2}$). Others obtained even higher $K_{IC}$ for AZC.

The present communication deals with densification, microstructure, grain growth and fracture toughness of alumina-zirconia composites.

**Experimental Procedure**

**Sample preparation**

A commercial grade technical alumina of 97.35 wt% Al$_2$O$_3$ content and median particle diameter 1.18 μm was used. An imported monoclinic zirconia having 95.19 wt% ZrO$_2$ and 2.25 wt% SiO$_2$ with median particle diameter 12.30 μm was used. Analytical reagent grade Y$_2$O$_3$ and MgCO$_3$ were employed. The particle size distribution of the main raw materials (Al$_2$O$_3$ and ZrO$_2$) are shown in Fig.1. Batch compositions shown in Table 1 were pot milled for 30 h, sieved and dried. Bar specimens (78 mm × 18 mm × 4-5 mm) were prepared by dry pressing at 650 kg/cm$^2$ pressure and isostatic pressing at 3,165 kg/cm$^2$. These were sintered at 1560-1580°C, surface ground with 220 and 400 mesh SiC powders, annealed at 1140°C for 1.5 h and subsequently heat-treated at 1200°C for 15 h.
Sintering, annealing and heat-treatment of the composites were conducted in an electric furnace in air. Green density of dry pressed samples and sintered densities were determined in the usual manner. Per cent theoretical density was also calculated.

**Mechanical properties**

Flexural strength in three point bending was obtained from Instron. For the determination of fracture toughness, bigger samples were cut by diamond wheel. The samples of 50 mm × (3-4.5) mm × (3-4) mm dimension were ground by SiC powders (-200, -400 and -600 mesh B.S.S.) and finally polished with 3 μm Al₂O₃ powder and then notched with 0.1 mm thick diamond blade (100 mm dia.).

The notched dimensions were:
- notch length, \( a = 0.7-1.2 \) mm
- notch width = 0.11-0.14 mm
- sample width, \( w = 3-3.7 \) mm,

\[
\left( \frac{a}{w} \right) = 0.14 - 0.5
\]

The notched samples were loaded in three point bending jig with 16 mm span at room temperature. The breaking load was recorded. The fracture toughness (\( K_{IC} \)) was calculated utilising the following equation

\[
K_{IC} = \frac{Y.3pL}{2bw^2}\sqrt{a}\sqrt{\alpha m} \text{ or } \text{MN m}^{-3/2}
\]

where \( p \) is the breaking force, \( L \) is the bearing spacing or span length, \( b, w \) and \( a \) are thickness and width of the sample and length of the notch, respectively.

\[
Y = a \text{ geometric factor }
\]

\[
= 1.93 - 3.07 \left( \frac{a}{w} \right) + 13.66 \left( \frac{a}{w} \right)^2 - 23.98 \left( \frac{a}{w} \right)^3
\]

\[
+ 25.22 \left( \frac{a}{w} \right)^4
\]

(2)

At least four samples were tested for each composition.

**Constitution**

**X-ray diffraction**

X-ray diffraction analysis of samples for identification of phases, determination of their relative concentration and measurement of size of the crystals of different ZrO₂ phase in them was done in Philips PW-1730 X-ray diffractometer with CuKα radiation. Crystal size of \( m \)-ZrO₂ and \( t \)-ZrO₂ was measured by the X-ray line broadening technique employing the following equation:

\[
D_{hkl} = \frac{0.9\lambda}{\beta_{1/2} \cos \theta}
\]

(3)

where \( \lambda \) is the wave length of the X-ray beam, \( \beta_{1/2} \) is the pure diffraction broadening of the peak at half the height, and \( \theta \) is the glancing angle of the selected reflection.

Crystal size of ZrO₂ in as sintered samples, samples annealed at 1140°C for 1.5 h and samples heat-treated at 1200°C for 15 h were measured.

**Electron microscopy**

Fractured surfaces of as sintered and heat-treated samples were optically polished by grinding-polishing with SiC powders of 200, 400, 600 mesh B.S., 3 μm Al₂O₃, 1 μm Al₂O₃ and diamond pastes of S-4, S-2, S-0.5 grades successively. The polished surface was etched by 20% HF. These were viewed under scanning electron microscope (Cambridge Stereoscan-250)
Results and Discussion

X-ray diffraction

The low angle portion of the X-ray diffractograms of samples are shown in Fig.2. Phase compositions of composites derived from X-ray diffractometry are presented in Table 2. Crystal sizes of ZrO$_2$ obtained by X-ray diffraction

Table 2—Crystalline phases in the composites

<table>
<thead>
<tr>
<th>Crystalline phase</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$-ZrO$_2$</td>
<td>**</td>
<td>+</td>
<td>**</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>$t$-ZrO$_2$</td>
<td>+</td>
<td>**</td>
<td>*</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>$c$-ZrO$_2$</td>
<td>-</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

A = Matrix

$m$-ZrO$_2$ = monoclinic zirconia, $t$-ZrO$_2$ = tetragonal zirconia, $c$-ZrO$_2$ = cubic zirconia, A = alumina which is the matrix phase.

Table 3—Size of ZrO$_2$ crystals in as sintered, annealed and heat-treated composites

<table>
<thead>
<tr>
<th>Composite conditions</th>
<th>Composite</th>
<th>ZrO$_2$ crystal size (µm) in composite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>As sintered</td>
<td>0.12</td>
<td>0.37</td>
</tr>
<tr>
<td>Annealed at 1140°C for 1.5 h</td>
<td>0.65</td>
<td>0.27</td>
</tr>
<tr>
<td>Heat-treated at 1200°C for 1.5 h</td>
<td>0.34</td>
<td>2.20</td>
</tr>
</tbody>
</table>

with secondary electrons and back-scattered electrons. Grain sizes of ZrO$_2$ and Al$_2$O$_3$ were measured from the enlarged micrographs.

Results and Discussion

X-ray diffraction

The low angle portion of the X-ray diffractograms of samples are shown in Fig.2. Phase compositions of composites derived from X-ray diffractometry are presented in Table 2. Crystal sizes of ZrO$_2$ obtained by X-ray diffraction

Fig. 3—Microstructure of alumina-zirconia composites (a) Secondary electron image for as sintered sample, (b) backscattered electron image for as sintered sample, and (c) backscattered electron image for samples subjected to heat-treatment at 1200°C/15 h
technique are given in Table 3. The crystal size varied from 0.12-0.4 μm in as sintered samples. On annealing at 1140°C for 1.5 h the crystal size apparently decreased due to removal of strain in the crystals. On subsequent heat-treatment of the samples at 1200°C for 15 h the crystal sizes increased appreciably in all the cases. So, heat-treatment resulted in the growth of crystals. This growth is the result of grain boundary diffusion or Ostwald ripening even at this temperature.

**Electron microscopy**

Figs 3a and 3b reveal the secondary electron image and back scattered electron images, respectively of as sintered alumina-zirconia composites. Fig. 3c is the back scattered electron image of the composite after heat-treatment at 1200°C for 15 h. The grains were differentiated on the basis of black and white colour contrast. While the ZrO₂ phase was white, alumina was grey, the pores and crevices appeared to be black. The colour contrast of Al₂O₃ and ZrO₂ grains in the back scattered mode was due to the difference in electron scattering coefficients of the elements.

Grain to grain bonding, sealed pores, coalescence of zirconia grains in the microstructure of the composites are seen in the electron micrographs. After heat-treatment grain bonding remained coherent. The ZrO₂ grain size increased and coalescence of ZrO₂ grains had taken place. The Al₂O₃ grains also suffered similar changes. The alumina-zirconia composites contained hardly any liquid phase. However, some glassy phase may form from the impurities and the additives but most of it got absorbed into alumina. This absorption took place in the final stage of sintering. As a result insignificant amount of residual glassy phase may be present. So, liquid phase sintering was not important in the Al₂O₃-ZrO₂ system. The additives, e.g., Y₂O₃ can enter the ZrO₂ grains in solid solution. However, in composite E with 4.4 wt % Y₂O₃, a liquid phase was formed which later on got absorbed in ZrO₂ grains as well as covered their surface also. The existence of the liquid phase was confirmed during etching of the sample (composite E). The grains were not properly viewed under the electron microscope without etching which implied that the grains were musked by a very thin glassy layer. The etching by 20% HF removed the glassy layer to expose the grains. The mutual solid solubility of Al₂O₃ and ZrO₂ is low, to the extent of maximum 0.1 wt % and for this reason, solid state diffusion is very sluggish in the Al₂O₃-ZrO₂ system.

Initially, pores were reduced and densification occurred by surface, grain-boundary and vacancy diffusion processes. In the final stage of sintering grain growth started by Ostwald ripening and coalescence processes for both Al₂O₃ and ZrO₂. The results summarised in Table 3, confirmed the growth of crystals on heat-treatment by the above processes. In Fig. 2c, coalescence of ZrO₂ and Al₂O₃ grains are observed.

**Density**

Green density of the dry pressed composites varied from 2.43 to 2.50 g/cc. The sintered density of each composite and the percentage of the theoretical density are presented in Table 4.

**Fracture toughness**

The fracture toughness values were 3.5, 4.5, 3.7,
5.5 and 4.35 MN m$^{-3/2}$ for composites A, B, C, D and E, respectively (Table 4). The fracture toughness of $Y_2O_3$ stabilised composite B was higher than that of A and C. Composite B contained $t$-$ZrO_2$ phase which transformed into monoclinic form under applied stress, thereby some part of the stress was absorbed and the critical stress intensity required for crack initiation and propagation increased. So, transformation toughening had taken place in composite B. Composite D and E, like composite B contained higher amount of transformable $t$-$ZrO_2$ phase (Table 2). Consequently, this explained high fracture toughness of composites B, D and E. The variation in grain growth of $ZrO_2$+Al$_2$O$_3$ grains as evidenced by the micrographs of the composites had been the most probable cause of different fracture toughness of the composites. In addition to this the composites C, D and E had higher $ZrO_2$ content as compared to that of A and B. The high fracture toughness of D and E was originated from the bigger size of $ZrO_2$ ($t$- and $m$-) grains developed therein. However, the fracture toughness of composite C did not attain the same value as that of D and E in spite of high $m$-$ZrO_2$ content and its big size. This revealed that transformation toughening due to $t$-$ZrO_2$ contributed far more to the fracture toughness than that contributed by the microcracking toughening by $m$-$ZrO_2$. Comparison of fracture toughness values of composites A and C and also B and E showed a marginal increase in C (3.5 in A, 3.7 in C) and a marginal decrease in E (4.5 in B, 4.35 in E). Although the $ZrO_2$ content of C was twice that of A, the former had $ZrO_2$ grains of about 3 times the size of $ZrO_2$ grains in the latter. Similarly, the $ZrO_2$ grain size in E was about 4 times less than that in B while E contained twice the amount of $ZrO_2$ as B. The marginal change in fracture toughness of these composites was, therefore, mainly due to large variation in the grain size of $ZrO_2$ in these composites.

Conclusion

1. The pressureless sintering of Al$_2$O$_3$-$ZrO_2$ composites produced Al$_2$O$_3$ matrix embedded with $ZrO_2$ grains.

2. Heat-treatment of the composites caused increase in the size of $ZrO_2$ grains.

3. The amount of $t$-$ZrO_2$ and $m$-$ZrO_2$ being same in the composites, the contribution of transformation toughening due to $t$-$ZrO_2$ on their fracture toughness was more than that of microcracking toughening due to $m$-$ZrO_2$.

4. Provided $m$-$ZrO_2$ to $t$-$ZrO_2$ transformation was small in the composites with equal $ZrO_2$ content, the fracture toughness of the composites was more influenced by the microcracking toughening due to $m$-$ZrO_2$ than by the transformation toughening due to $t$-$ZrO_2$.

5. Irrespective of the existence of $t$-$ZrO_2$ and $m$-$ZrO_2$ in the composites, the bigger size of the $ZrO_2$ grains ensured higher fracture toughness of the composites.

References