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13. ABSTRACT (Maximum 200 words)  
Two different methods were used to prepare tough glass-ceramics containing ZrO2.  
One was to melt ZrO2-containing Li2O-Al2O3-SiO2 glasses and transform them by control-
led crystallization. The other was to sinter BaO-SiO2-Al2O3 glass powder together  
with ZrO2 powder. In both materials, some toughness improvement by the transformation  
of zirconia during fracture was observed. However, unexpectedly, the greater tough-
ness improvement was realized when the zirconia particles in the glass-ceramics were  
transformed prior to the fracture by cooling to a lower temperature, e.g., liquid  
nitrogen temperature. This drastic increase of the fracture toughness was attributed  
to the deflection of the propagating crack by the large stress fields around the trans-
formed (monoclinic) zirconia. The examination of the fracture surface demonstrated  
clearly that the crack deflection is taking place in the specimen with transformed  
zirconia.  
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HIGH-TOUGHNESS GLASS-CERAMICS

FINAL REPORT

MINORU TOMOZAWA

August 31, 1994

U.S. ARMY RESEARCH OFFICE

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STATEMENT OF THE PROBLEMS STUDIED

Glasses and ceramics have many desirable characteristics such as light weight and refractoriness. But in general they lack toughness, or the ability to resist crack propagation. Tougher glass and ceramics are desired in many applications. Addition of ZrO$_2$ at high temperature is one of the effective ways to increase the toughness of glasses and ceramics. A high temperature form of zirconia, tetragonal zirconia, transforms upon cooling at ~1000°C to monoclinic zirconia and expands. When ZrO$_2$ powder is dispersed in a glass or ceramic matrix, this transformation is shifted to lower temperature or suppressed until the time of fracture. Transformation during fracture reduces the crack tip tensile stress, thus making the crack propagation difficult. This mechanism of toughening, called transformation toughening, has been applied to a variety of different ceramics. Application of this toughening process to glass-ceramics has been investigated in this research program. Glass-ceramics with zirconia have been prepared by two different methods: (i) melting of glass containing zirconia and crystallizing the glass by controlled heat-treatment, (ii) glass powder is sintered together with zirconia powder and crystallized. The former is simpler in operation, but it usually requires a high temperature for glass melting, especially when the incorporation of a large amount of ZrO$_2$ is desired. In the latter, a larger quantity of ZrO$_2$ can be incorporated more easily but the process is more complicated and the product usually contains pores.
SUMMARY OF THE MOST IMPORTANT RESULTS

I. Fracture Toughness of ZrO$_2$-containing Glass-Ceramics

(A) Melting method.

Up to 15 wt% ZrO$_2$ was added to the Li$_2$O-Al$_2$O$_3$-SiO$_2$ system which, upon heat-treatment, produced $\beta$-eucryptite (Li$_2$OAl$_2$O$_3$2SiO$_2$) phase. While the fracture toughness was observed to increase with ZrO$_2$ addition, primarily because of the large thermal expansion anisotropy of the $\beta$-eucryptite phase, extensive spontaneous cracking occurred when the grain size of this phase becomes larger than ~1 $\mu$m.

(B) Sintering method.

A BaO-SiO$_2$-Al$_2$O$_3$ glass which produced the best sintering characteristic was melted and pulverized. To this glass powder, various amounts of 10 vol% CeO$_2$-stabilized tetragonal ZrO$_2$ powder were added and sintered. The fracture toughness increase by more than 100% was possible by choosing the grain size of tetragonal zirconia powder. Even greater increase of fracture toughness was realized by transforming tetragonal zirconia to monoclinic zirconia by cooling the specimen to liquid nitrogen temperature prior to the mechanical testing at room temperature. Selected fracture toughness results are shown below.

<table>
<thead>
<tr>
<th>Description</th>
<th>Fracture Toughness (MPa$\sqrt{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) BaO-SiO$_2$-Al$_2$O$_3$ glass-ceramics</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>(b) BaO-SiO$_2$-Al$_2$O$_3$ + 10 vol% ZrO$_2$</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
<td>(c) sample (b), after cooling to liq. N$_2$</td>
<td>3.0 ± 0.6</td>
</tr>
</tbody>
</table>

Apparently, several different mechanism are operating in
ZrO₂-containing glass-ceramics. The following toughness processes appear to be involved.

(i) ZrO₂ transformation toughening.

This involves the stress-induced transformation of tetragonal ZrO₂ to monoclinic ZrO₂. This was the originally intended mechanism.

(ii) residual stress toughening.

Thermal expansion mismatch of two phases or two directions of single phases produces residual stress. This can cause toughening in some Li₂O-Al₂O₃-SiO₂ systems.

(iii) crack deflection by inclusion.

When tetragonal ZrO₂ transforms into monoclinic ZrO₂ in a glass-ceramic matrix, an extremely large stress is produced around the transformed particle. This causes crack deflection and leads to toughening.

Of particular interest in this research is the greater toughness improvement realized when the zirconia particles in the glass-ceramics transformed prior to the fracture. The accompanying figures demonstrate the crack deflection mechanism. The cooled specimens with transformed (monoclinic) zirconia exhibit tortuous path for cracks. For example, figure (a) and (b), which show the fracture surfaces, reveal a rougher surface for sample cooled to liquid nitrogen temperature. Correspondingly, figure (c) and (d), which show zirconia on the fracture surface, reveal more zirconia after cooling, even though the zirconia content remains unchanged, indicating that the cracks are deflected towards zirconia particles.
II. Crystallization of Lithium-Disilicate Glass

In the course of crystallization study of glasses, an interesting phenomenon was observed. Usually, lithium disilicate glasses crystallize into lithium silicate, Li₂O·2SiO₂, without changing composition. Some reported that metastable lithium metasilicate crystals (Li₂O·SiO₂) precipitated first and then disappeared by a longer heat-treatment. It was discovered that the lithium metasilicate crystal precipitated from lithium silicate glasses predominantly when the glass was heat-treated in a LiNO₃ melt near the glass transition temperature. Apparently, the lithium oxide is incorporated into the glass from the LiNO₃ melt at the treatment temperature. This is contrary to the commonly accepted notion that at the glass transition temperature, only Li is mobile but not oxygen.
List of Publications


PARTICIPATING SCIENTIFIC PERSONNEL

Minoru Tomozawa, Principal Investigator, Professor of Materials Engineering.

Richard D. Sarno, Research Assistant, earned Ph.D. in December, 1993.

Sridharan Srinivasan, Research Assistant, earned Ph.D. in December, 1993.

Jeffrey R. Jacquin, Research Assistant, earned Master’s Degree, December, 1993.
Secondary electron image of the fracture surface.
(a) before cooling, (b) after cooling.
Energy dispersive x-ray mapping of Zr on the fracture surface.
(c) before cooling, (d) after cooling.