Processing of Alumina-Toughened Zirconia Composites

Narottam P. Bansal
Glenn Research Center, Cleveland, Ohio

Sung R. Choi
Ohio Aerospace Institute, Brook Park, Ohio

May 2003
Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA’s mission.

Specialized services that complement the STI Program Office’s diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at http://www.sti.nasa.gov
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301–621–0134
- Telephone the NASA Access Help Desk at 301–621–0390
- Write to: NASA Access Help Desk NASA Center for AeroSpace Information 7121 Standard Drive Hanover, MD 21076
Processing of Alumina-Toughened Zirconia Composites

Narottam P. Bansal
Glenn Research Center, Cleveland, Ohio

Sung R. Choi
Ohio Aerospace Institute, Brook Park, Ohio
Acknowledgments

The authors are grateful to John Setlock for materials processing, Bob Angus for hot pressing, Ralph Pawlik for mechanical testing, and Ralph Garlick for x-ray diffraction analysis. This work was funded by the Zero CO$_2$ Emission Technology (ZCET) project of the Aerospace Propulsion and Power Program.

The Propulsion and Power Program at NASA Glenn Research Center sponsored this work.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov
Processing of Alumina-Toughened Zirconia Composites

Narottam P. Bansal
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Sung R. Choi*
Ohio Aerospace Institute
Brook Park, Ohio 44142

Dense and crack-free 10-mol%-yttria-stabilized zirconia (10YSZ)-alumina composites, containing 0 to 30 mol% of alumina, have been fabricated by hot pressing. Release of pressure before onset of cooling was crucial in obtaining crack-free material. Hot pressing at 1600 °C resulted in the formation of ZrC by reaction of zirconia with grafoil. However, no such reaction was observed at 1500 °C. Cubic zirconia and α-alumina were the only phases detected from x-ray diffraction indicating no chemical reaction between the composite constituents during hot pressing. Microstructure of the composites was analyzed by scanning electron microscopy and transmission electron microscopy. Density and elastic modulus of the composites followed the rule-of-mixtures. Addition of alumina to 10YSZ resulted in lighter, stronger, and stiffer composites by decreasing density and increasing strength and elastic modulus.

Introduction

Solid oxide fuel cells (SOFC) are being developed for various applications in the automobile, power generation, aeronautic, and other industries. More recently, NASA has explored the possibility of using SOFCs for aero-propulsion under its Zero Carbon Dioxide Emission Technology (ZCET) Project in the Aerospace Propulsion and Power Program. Yttria-stabilized zirconia (YSZ) is a very good anionic conductor at high temperatures, and is therefore used as an oxygen solid electrolyte in SOFC. It has high thermal expansion coefficient, low thermal shock resistance, low fracture toughness and poor mechanical strength, which may be sufficient for land-based power generation SOFC systems without thermal cycling. However, for aeropropulsion applications, the thin ceramic electrolyte membrane of the SOFC needs to be stronger and tougher as it would be subjected to thermal cycling and severe vibration forces during take off and landing. We are currently investigating the possibility of reinforcement of YSZ with alumina in order to enhance the strength and fracture toughness of the electrolyte, without degrading its electrical conductivity to an appreciable extent. This concept would also find applications in other industries such as the oxide ceramic cutting tools. Alumina is known to be an effective additive for scavenging the resistive SiO₂ phase, present as impurities in the starting YSZ material, by removing it from grain boundaries. A limited solubility of alumina in YSZ results in substitution of Al³⁺ for Zr⁴⁺ in the lattice and assists in sintering. Additions of alumina also inhibit the grain growth in YSZ.

*NASA Senior Resident Research Scientist at Glenn Research Center.
The primary objective of this study was to develop the processing of 10YSZ composites reinforced with various concentrations of alumina. Dense and crack free 10YSZ-alumina composites, containing 0 to 30 mole percent of alumina, were fabricated. Microstructure, density, and room temperature mechanical properties of these composites are also reported here.

**Experimental**

The starting materials used were alumina powder (Baikalox CR-30, 99.99% purity, average particle size 0.05 µm, specific surface area 25 m²/g) from Baikowski International Corporation, Charlotte, NC and 10 mol% yttria fully-stabilized zirconia powder (HSY-10, average particle size 0.41 µm, specific surface area 5.0 m²/g) from Daiichi Kigenso Kagaku Kogyo Co., Japan. Various steps involved during processing of the composite panels are shown in the flow chart of Fig. 1. Appropriate quantities of alumina and zirconia powders were slurry mixed in acetone and ball milled for ~24 h using zirconia milling media. Acetone was evaporated and the powder dried in an electric oven. The resulting powder was loaded into a graphite die and hot pressed in vacuum under 30 MPa pressure either into 1-in.-diameter discs using a mini-hot press or into 6 in. by 6 in. plates using a large hot press. Grafoil was used as spacers between the specimen and the punches. Various hot pressing cycles were tried in order to optimize the hot pressing parameters, which would result in dense and crack free ceramic samples. The hot pressed plates were machined into bend bars for flexure strength measurements. The sharp edges of test specimens were chamfered to reduce spurious premature failure emanating from those sharp edges.

![Flow chart showing various steps in the processing of dense and crack-free 10YSZ-alumina composites](image)

**Figure 1.** Flow chart showing various steps in the processing of dense and crack-free 10YSZ-alumina composites
X-ray diffraction (XRD) patterns were recorded at room temperature using a step scan procedure (0.02°/2θ step, time per step 0.5 or 1 s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing Cu Kα radiation. Density was determined from weight and volume of each specimen. Elastic modulus was measured at room temperature using an impulse excitation method (Grindosonic) in accordance with ASTM test standard C-1259. Room temperature flexure strengths of the YSZ/alumina composites were determined in air using 50 by 4.0 by 3.0 mm bend bars in accordance with ASTM test standard C-1161. Stress-strain curves were recorded using a four-point bend fixture having 40 mm outer span and 20 mm loading span, in conjunction with an electromechanical testing machine (Model 8562, Instron, Canton, MA). A fast stress rate of 50 MPa/s was applied in load control to reduce slow crack growth effect of the materials. A total of 10 test specimens were tested for each composite. A limited fractographic analysis was performed optically to examine fracture origins and their nature. Microstructures of the polished cross-sections were observed in a JEOL JSM-840A scanning electron microscope (SEM). Thin foils for transmission electron microscopy (TEM) were prepared using a procedure that involved slicing, polishing, and argon ion beam milling. The thin foils were examined in a Philips EM-400T operating at 120 keV. A thin carbon coating was evaporated onto the TEM thin foils and SEM specimens for electrical conductivity prior to analysis. X-ray element analyses of the phases were carried out using a Kevex Delta thin window energy dispersive spectrometer (EDS) and analyzer.

Results and Discussion

XRD patterns from zirconia discs hot pressed for 1 h at 1500 or 1600 °C are shown in Fig. 2. The material hot pressed at 1500 °C shows the presence of only cubic-ZrO₂ whereas small amount of ZrC is also detected in the 1600 °C hot-pressed material. Formation of ZrC occurs from the reaction between zirconia and grafoil during hot pressing:

\[ \text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO} \]  

(1)

To avoid this reaction, all further hot pressing was done at 1500 °C. During initial runs, the pressure was released after the panel had cooled to ambient temperature. This resulted in badly cracked composite panels. On cooling from 1500 °C to room temperature under applied load, large residual stresses are produced due to large CTE of cubic zirconia which result in cracking. However, modification of the hot pressing cycle, where applied load was released before onset of cooling, alleviated the cracking problem.
Figure 2. X-ray diffraction patterns of 10YSZ material hot pressed at 1500 °C and 1600 °C. Z and ZC indicate cubic-zirconia and zirconium carbide, respectively.

Figure 3. X-ray diffraction patterns for 10YSZ reinforced with different alumina contents. “Z” and “A” indicate cubic-zirconia and α-alumina, respectively.
X-ray diffraction patterns from various 10YSZ-alumina composites containing 0 to 30 mol% alumina are shown in Fig. 3. Cubic zirconia and α-alumina were the only phases present indicating the absence of any reaction between the materials during hot pressing at elevated temperatures. Typical SEM micrographs taken from polished cross-sections of various YSZ/alumina composites are shown in Figure 4. Alumina particulates are uniformly dispersed throughout the material. The dark areas represent alumina while the light areas indicate the

![SEM micrographs showing polished cross-sections of 10YSZ-alumina composites containing various alumina mol%: (a) 0 mol%; (b) 5 mol%; (c) 10 mol%; (d) 20 mol%; (e) 30 mol%.](image)

10YSZ matrix, as confirmed from EDS analysis (Fig. 5). TEM micrograph and dot maps for various elements for the composite containing 30 mol% alumina are shown in Fig. 6. The average equiaxed grain size is less than 1.0 µm for either YSZ matrix or alumina. The high magnification TEM micrographs showing grain boundaries and triple junctions for the 0 and 30 mol% alumina composites are presented in Fig. 7 and 8, respectively. The grain boundaries as well as the triple junctions are clean for either the 0 or 30 mol% composite. Presence of any amorphous phase was not detected. No appreciable deformation or microcracks of adjacent
Figure 5. SEM micrograph and EDS analysis of 10YSZ-alumina composite containing 10 mol% alumina; dark area (A): alumina, light area (B): zirconia.

Figure 6. TEM micrograph showing zirconia and alumina grains and dot maps of different elements for 10YSZ-alumina composite containing 30 mol% alumina.
grains in the composites, which might occur due to thermoelastic mismatches between the YSZ matrix and the alumina particulates, was observed from the analysis of TEM micrographs.

Densities of 10YSZ-alumina composites as a function of mol% of alumina are presented in Table I and Fig. 9. Density, $\rho$, decreased with alumina content, as expected. The measured values were in agreement with those calculated from the rule-of-mixtures:

$$
\rho_c = \rho_z V_z + \rho_A V_A
$$

(2)
where \( V \) is the volume fraction and the subscripts \( c, z, \) and \( A \) refer to the composite, zirconia and alumina, respectively. Values of \( \rho_z = 5.84 \text{ g/cm}^3 \) and \( \rho_A = 3.85 \text{ g/cm}^3 \) were used. Values of room temperature elastic modulus for various composites are listed in Table I and also shown in Fig. 10.

### Table I. Room Temperature Properties of 10YSZ-Alumina Composites

<table>
<thead>
<tr>
<th>Composite No.</th>
<th>Composition (mol%)</th>
<th>Density, ( \rho ) (g/cm(^3))</th>
<th>Elastic modulus ( E ) (GPa)</th>
<th>Flexure strength ( \sigma ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2-0</td>
<td>100 0</td>
<td>5.839 ± 0.008</td>
<td>219 ± 2</td>
<td>280 ± 23</td>
</tr>
<tr>
<td>A2-5</td>
<td>95 5</td>
<td>5.740 ± 0.012</td>
<td>225 ± 2</td>
<td>288 ± 57</td>
</tr>
<tr>
<td>A2-10</td>
<td>90 10</td>
<td>5.642 ± 0.007</td>
<td>233 ± 1</td>
<td>319 ± 64</td>
</tr>
<tr>
<td>A2-20</td>
<td>80 20</td>
<td>5.437 ± 0.005</td>
<td>250 ± 1</td>
<td>358 ± 42</td>
</tr>
<tr>
<td>A2-30</td>
<td>70 30</td>
<td>5.178 ± 0.042</td>
<td>262 ± 1</td>
<td>393 ± 38</td>
</tr>
</tbody>
</table>

Figure 9. Density of 10YSZ-alumina composites as a function of alumina content. Solid line is prediction from rule-of-mixtures.
Elastic modulus, $E$, increased with alumina content and the experimental values followed those calculated from the rule-of-mixtures

$$E_c = E_z V_z + E_A V_A$$

where $V$ is the volume fraction and the subscripts $c$, $z$, and $A$ refer to the composite, zirconia and alumina, respectively. Values of $E_z = 220 \text{ GPa}$ and $E_A = 370 \text{ GPa}$ were used.

Room temperature flexure strength as a function of alumina (mol%) content for the 10YSZ-alumina composites are listed in Table I and also shown in Figure 11. The strength increased with increasing alumina content. The 30 mol% alumina composite showed 40% higher strength than the 10YSZ baseline material. The number of test specimens, 10 for each composition, was not sufficient to obtain the reliable Weibull statistical parameters such as Weibull modulus and characteristic strength. Weibull modulus that was estimated with 10 specimens, however, was found to be in the range of 5 to 15, typical of many commercial ceramics.

Typical examples of fracture surfaces of 10YSZ-alumina composites containing 0 and 30 mol% alumina, tested at ambient temperature, are shown in Figure 12. Fracture originated distinctly from surface-connected defects (“surface flaws”), associated with voids in conjunction
Figure 11. Room temperature flexure strength of 10YSZ-alumina composites as a function of alumina content in air. Error bars indicate ±1.0 standard deviation. The line represents the best fit.

Figure 12. Typical examples of fracture surfaces showing fracture origins (surface flaws indicated with arrows) for 10YSZ-alumina composites reinforced with (a) 0 mol% and (b) 30 mol% alumina.
with machining. Voids, contaminations and severity of machining were found to be dominant
strength controlling surface flaws, independent of alumina content. Overall flaw sizes seemed to
range from 20 to 40 \( \mu \text{m} \). Some other zirconia/alumina composites exhibited a strength decrease
with increasing alumina content.\(^7\) The strength decrease would be more significant for larger
alumina particulates since they may act as strength-controlling flaws. On the contrary, fracture
toughness in this case would be increased due to more enhanced crack deflection/bridging.

Temperature dependence of strength, fracture toughness, elastic modulus, coefficient of
thermal expansion, thermal conductivity, and electrical ionic conductivity of zirconia-alumina
composites will be reported elsewhere.\(^8\)

Summary and Conclusions

Dense and crack free 10YSZ-alumina composites containing 0 to 30 mol\% alumina have
been fabricated by hot pressing. Cubic zirconia and \( \alpha \)-alumina were the only phases present in
hot pressed composites indicating no chemical reaction between the constituent materials during
high temperature processing. Microstructure analysis of the composites was done using x-ray
diffraction, SEM, TEM, and EDS. Density, elastic modulus and flexure strength of the
composites were measured. Addition of alumina to 10YSZ resulted in lighter, stronger, and
stiffer composite materials.

References

Secondary-Ion Mass Spectroscopy Observation of the Scavenging of Siliceous Film from
8-mol\%-Yttria-Stabilized Zirconia by the Addition of Alumina,” \textit{J. Am. Ceram. Soc.}, \textbf{83}
3. E.M. Levin and H.M. McMurdie (Eds.), Phase Diagram for Ceramists, Volume III,
Fig. 4378, The Am. Ceram. Soc., Westerville, OH; p. 136 (1975).
4. R.V. Wilhelm and D.S. Howarth, “Iron Oxide-Doped Yttria-Stabilized Zirconia Ceramic:
(1979).
5. ASTM C 1161 “Test Method for Flexural Strength of Advanced Ceramics at Ambient
Temperature,” \textit{Annual Book of ASTM Standards}, Vol. 15.01, American Society for Testing
7. F.F. Lange, “Transformation Toughening, Part 4: Fabrication, Fracture Toughness and
8. S.R. Choi and N.P. Bansal, “Strength, Fracture Toughness, and Slow Crack Growth of
Zirconia/Alumina Composites at Elevated Temperature,” NASA/TM—2003-212108
(2003).
Processing of Alumina-Toughened Zirconia Composites

Narottam P. Bansal and Sung R. Choi

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio  44135–3191

Available electronically at http://gltrs.grc.nasa.gov
This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

May 2003

NASA TM—2003-212451

Processing; Ceramic composites; Zirconia-alumina; Microstructure; Strength; Mechanical properties

Dense and crack-free 10-mol%-yttria-stabilized zirconia (10YSZ)-alumina composites, containing 0 to 30 mol% of alumina, have been fabricated by hot pressing. Release of pressure before onset of cooling was crucial in obtaining crack-free material. Hot pressing at 1600 °C resulted in the formation of ZrC by reaction of zirconia with grafoil. However, no such reaction was observed at 1500 °C. Cubic zirconia and α-alumina were the only phases detected from x-ray diffraction indicating no chemical reaction between the composite constituents during hot pressing. Microstructure of the composites was analyzed by scanning electron microscopy and transmission electron microscopy. Density and elastic modulus of the composites followed the rule-of-mixtures. Addition of alumina to 10YSZ resulted in lighter, stronger, and stiffer composites by decreasing density and increasing strength and elastic modulus.