PROCEEDINGS

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FABRICATION OF TRANSFORMATION TOUGHENED CERAMICS
BY MICROWAVE PROCESSING

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ABSTRACT

Various ceramic-matrix composites containing partially stabilized zirconia (tetragonal) were sintered by
microwaves at 2.45 GHz. Microwave enhancement in the densification of these composites was evaluated. The
enhancement up to 46% over conventional sintering was observed, and the greater microwave effect was found in the
low zirconia content compositions. As zirconia content increases, the microwave enhancement diminishes. This result
is due to the higher sinterability of zirconia over that of the matrices.

INTRODUCTION

Ceramics are usually brittle and transformation toughening is adopted to improve fracture toughness of various
ceramics. Partially stabilized zirconia in tetragonal phase is a toughening agent popularly used, and a high density is
critically important to achieve the desired transformation toughening.

Microwave sintering of ceramic materials is different from conventional sintering in its heating mechanism[1].
In microwave sintering, the work piece is directly heated as a whole by heat generated through microwave-material
interaction. The wave-material interaction, or microwave absorption, of a material directly depends on the dielectric
loss factor of that material.

It is the objective of this study to see if microwaves can enhance the densification of certain composites.
Microwave sintering of ceramic composites of zirconia and four matrices, including alumina, mullite, calcium
strontium zirconium phosphate (CSZP), C40,5Sr0,5Zr4P4O24, and barium zirconium phosphosilicate (BS25),
Ba0,25Zr4P4O22, was carried out in the current study. For comparison, conventional sintering of the duplicate
samples was also carried out in a high capacity, low thermal inertia furnace at the heating rates comparable to those in
the microwave processing.

EXPERIMENTAL PROCEDURES

An amorphous alumina powder (RhOne-Poulenc, France) of -325 mesh (45 μm opening) was used as a starting
material for alumina matrix. The mullite precursor was prepared by a diphasic xerogel method by mixing sols of
boehmite (A1O2OH) and silica (Ludox) at a molar ratio of 3:2. The CSZP powder was also prepared by a sol-gel
method[2]. The BS25 powder was synthesized by a solid-state reaction method using dry oxide precursors[3]. The
zirconia powder (HSY-3.0, Zirconia Sales, Inc., Atlanta, GA) used in this study was partially stabilized in tetragonal
form by Y2O3 (5.4%), in which monoclinic zirconia was detected as a minor phase. The average particle size of this
zirconia powder was about 0.1 μm.

Each matrix powder was mixed with zirconia in various proportions. An appropriate amount of 2% PVA
solution was used as a binder during mixing. The mixture was homogenized by hand mixing with an agate mortar.
The alumina/zirconia and BS25/zirconia mixtures were compacted into pellets of either 0.5 or 0.25 inch in diameter.
The compaction was uniaxially carried out at 350 MPa. The relative green densities of the as-compacted pellets of
various systems were in the range of 39-53% for alumina/zirconia, 46-51% for mullite/zirconia, 53-58% for
CSZP/zirconia, and 60-67% for BS25/zirconia, respectively. No sintering aid was used in this study.
Microwave sintering was carried out in a multimode microwave cavity at 2.45 GHz, which was modified from a 900 W microwave oven with a rotating plate. Multi-pellet run was adopted in the sintering. The pellets were placed in the center of a sintering packet. The sample pile was vertically surrounded by a porous zirconia cylinder, which acted as a microwave absorber to preheat the specimens, and as a thermal insulator to keep heat from dissipation. The sintering packet was placed on a rotating plate, which keeps all the samples under the same irradiation conditions and provides uniform heating.

Temperature in the microwave sintering was measured using a platinum-sheathed S-type (Pt-Pt10Rh) thermocouple inserted from the top of the microwave cavity and properly grounded. In this way, microwave interference to the temperature measurement was completely avoided during microwave processing. The heating rates and soaking temperatures were controlled by adjusting the power input with a variac.

Conventional sintering was carried out by following the heating schedule of the corresponding microwave processing. Temperature was also measured with the same S-type thermocouple as in the microwave sintering, but no platinum sheath. The samples were placed in a platinum crucible which was in contact with the tip of the thermocouple.

The sintering of the composites based on alumina, mullite, and CSZP, was conducted at 1500°C. Composites of BS25 were sintered at 1550°C. All samples were soaked at the peak temperatures for 20 min. Since the sintering of the biphasic mullite gel is a reaction-sintering process and the densification of gels through viscous deformation is far more efficient than that of the related crystalline materials through ordinary solid diffusion, step sintering was adopted for the composites based on the mullite gel, in which the samples were first heated to and then soaked at 1200°C for 30 min. for densification, and finally heated to 1500°C for Mullitization.

RESULTS AND DISCUSSION

After both microwave and conventional sintering, all the composites showed an increase in sintered density as increasing zirconia content, but higher densities were achieved by microwave sintering. The sintered densities for our systems containing 40vol.% zirconia were 72% for the alumina system, 96% for the mullite system, 91% for the CSZP system, and 98% for the BS25 system. Even higher densities were achieved by further increasing zirconia content, but the microwave enhancing effect diminished as zirconia content increased. The net microwave enhanced densities are listed in the following table as a percentage of the densities of correspondent conventional sintering. As can be seen, in the compositions containing up to 40 vol.% zirconia, the microwave enhancement in the composites based on alumina, mullite, CSZP, and BS25 was 20-46%, 24-34%, 1-2%, and 4-13%, respectively.

<table>
<thead>
<tr>
<th>ZrO₂ Vol.%</th>
<th>1500°C/20 min</th>
<th>1200°C/30 min</th>
<th>1500°C/20 min</th>
<th>1550°C/20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>48.69</td>
<td>40.29</td>
<td>1.00</td>
<td>13.36</td>
</tr>
<tr>
<td>2</td>
<td>40.29</td>
<td>34.46</td>
<td>1.12</td>
<td>7.68</td>
</tr>
<tr>
<td>5</td>
<td>40.29</td>
<td>32.45</td>
<td>0.64</td>
<td>11.16</td>
</tr>
<tr>
<td>10</td>
<td>46.40</td>
<td>30.52</td>
<td>1.97</td>
<td>13.40</td>
</tr>
<tr>
<td>20</td>
<td>38.55</td>
<td>26.85</td>
<td>1.00</td>
<td>9.91</td>
</tr>
<tr>
<td>30</td>
<td>32.41</td>
<td>25.61</td>
<td>1.23</td>
<td>3.86</td>
</tr>
<tr>
<td>40</td>
<td>19.82</td>
<td>23.75</td>
<td>2.04</td>
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</table>

Significantly higher sintered density was produced in the microwave sintered specimens of alumina/zirconia system. The difference between microwave and conventional sintering in the low-zirconia-content composites is more significant. This is due to the fact that the sintering temperature of zirconia is lower than the matrix. The same is true for the rest of the systems. The relatively low sintered densities of this system were due to the coarse starting powder, low green density, low processing temperature, and short processing time. Furthermore, no sintering aid was used. Microwave frequency might also be partly responsible for the lower densities, as Kimrey and coworkers have shown that the alumina/zirconia system couples better with microwaves at 28 GHz than at 2.45 GHz[4].

In the mullite/zirconia system, no significant difference in sintered density was found after sintering at 1500°C. A comparison of the densities after the first-stage sintering (1200°C x 30 min.), however, clearly showed the
microwave effect. As shown in the above table, the densities after the 30 min. microwave heating at 1200°C were much higher than those of the samples conventionally sintered. Obviously, microwave irradiation efficiently promoted the densification of the diphasic mullite gel. This is in good agreement with the earlier observation of Roy et al.[5, 6] that the alumina and silica gels absorb microwave energy and get heated very quickly. Once the crystalline mullite is formed, the sintering mechanism changes and there is no more viscous deformation. Further densification can only rely on the boundary diffusion and related factors as in ordinary solid state sintering. Since the solid state diffusion of ions in mullite is very low, conventional sintering of mullite is usually carried out at 1600-1700°C for many hours. Due to the limit in processing temperature and time, and more importantly, the transparency of the crystalline mullite to microwaves, the microwave sintering of the mullite system after multilization, under the current experimental conditions, did not show much advantage over conventional method.

In the BS25/zirconia system containing up to 30% zirconia, the microwave enhancement was also obvious. The increase in density of the CSZP/zirconia system, however, was not as significant. This is probably due to the high processing temperature. When processing temperature is sufficiently high, the solid state diffusion of ions under conventional conditions might also have been substantially accelerated to allow the microwaves to lose their effectiveness. The results of the previous study [7] showed that pure CSZP could be sintered to a relative density of 94% by microwave processing at 1300°C for 30 min. which was about 24% higher than that achieved in conventional sintering under the conditions of same temperature and duration. This may explain why the CSZP/zirconia system sintered at 1500°C did not show as obvious microwave enhancement.

Powder XRD study showed that zirconia in the sintered composites based on alumina, mullite, and BS25 remained tetragonal, with monoclinic zirconia in trace amount. In the CSZP system, however, zirconia had completely transformed to monoclinic phase. Further study is needed to explain this phenomenon. All the amorphous or low crystallinity matrices turned to be highly crystalline after sintering. The diphasic mullite gel remained amorphous after the first sintering stage at 1200°C for 30 min., but crystallized after 1500°C. No decomposition was found in any of these systems. SEM observation indicated that the microstructures of the composites were fairly homogeneous.

Because duplicate green samples were used, the heating rates in the microwave and conventional sintering were comparable, temperature measurement was the same, and sintering time and temperatures were identical, the enhanced densification in the microwave processed samples could be certainly attributed to the microwave effect. Although some of the composites were not very dense, we believe that it is only a problem of optimization of processing parameters.

CONCLUSIONS

Microwave sintering studies of various ceramic composites containing zirconia were carried out along with parallel conventional sintering studies. The results show that microwave processing significantly enhanced the densification of these composites. The observed enhancement was up to 46%, varying with the system and zirconia content. Increasing zirconia content decreased microwave effect. This is due to the relatively higher sinterability of zirconia over that of the matrix materials.

ACKNOWLEDGEMENT

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REFERENCES