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MICROWAVE SINTERING OF ZrO_2 -12 MOL% CeO_2

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ABSTRACT

Sintering of ZrO_2 -12 mol% CeO_2 was accelerated by microwave processing at 2.45 GHz as compared with conventional firing. However, the size of the "microwave effect" was significantly smaller than that which was previously observed for microwave sintering of ZrO_2 -8 mol% Y_2O_3 . The difference in the effect that the microwave field had on the two zirconia systems is interpreted in terms of their ionic conductivities.

INTRODUCTION

Microwave sintering of yttria-doped zirconia has been shown to reduce significantly the temperature required to achieve full density.^{1,2} Samuels and Brandon² further claim evidence for a reduction in the activation energy for sintering of zirconia by microwave firing. This reduction in processing temperature or activation energy is commonly called the "microwave effect".

Study of the sintering of ceria-doped zirconia allows examination of a system similar in chemistry to yttria-doped zirconia, but with significantly lower ionic conductivity.³ It is hypothesized that the lower ionic conductivity of the ZrO_2 -12 mol% CeO_2 should lead to a smaller microwave effect for this material.

Research sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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EXPERIMENTAL PROCEDURE

This study was performed using commercial powders with composition ZrO_2 -12 mol% CeO_2 .^{*} All samples were formed by uniaxial pressing at 35 MPa (5 kpsi) in a 2.9 cm (1 1/8 in.) diam die, followed by isopressing at 210 MPa (30 kpsi). Samples for conventional firing weighed ~12g. Samples for microwave firing were significantly larger, typically 75g. Using a larger sample is related to the ability to heat the sample using microwaves and to the ability to measure temperature accurately. Small samples do not couple efficiently to the microwave field and it is more difficult to measure their temperature. (Detailed discussions regarding the issues of sample size and temperature measurement in a microwave furnace can be found in references 4-9.) The microwave samples were made in two pieces, a top part (50g) and a bottom part (25g). A channel (~5mm wide x 5 mm deep) was cut into the top part using a ball-end mill to act as a thermocouple well. An alumina protection tube was placed around the thermocouple sheath to reduce the microwave field concentration at the thermocouple tip. A schematic view of the preferred arrangement for the sample and insulation is shown in Figure 1.

Both microwave and conventional furnaces were used in this investigation. The microwave furnace used in this study was built in-house. It consisted of a water-cooled aluminum microwave vessel, 70 cm (28 in.) diam by 120 cm (48 in.) long, with integral mode stirrer, forward and reflected power meters, microwave safety interlocks, ports for air and N_2 -4% H_2 gas feeds, and thermocouple penetrations. Power was supplied by a 6 kW, continuously variable, 2.45 GHz microwave generator[‡]. A computer data acquisition and control program[†] was used to regulate the furnace and to log the temperature and power. Conventional furnace runs in air were made in a molybdenum disilicide element furnace.[#]

DEVELOPMENT OF THE MICROWAVE FIRING TECHNIQUE

To be successful, the microwave firing technique used in this investigation had to fulfill at least three requirements: (1) provide indirect heating to the zirconia sample at low temperature; (2) provide a reasonable match between the dielectric properties of the insulation and the sample; and, (3) prevent contamination of the sample.

Developing a technique to uniformly sinter the ZrO_2 -12 mol% CeO_2 composition and meet the firing requirements outlined above was extremely challenging. Table 1 summarizes several of the different insulation and heating systems that were investigated. Fig. 2 shows four samples (Exs. 2, 3, 5, and 6) that resulted from microwave firing runs using the different insulation systems; Fig. 3 shows the heating curves (power and temperature vs. time) for these four samples.

One of the primary requirements for the insulation system was that it not contaminate the ZrO_2 -12 mol% CeO_2 composition of the samples. The first approach to this situation used a primary insulation that had the same composition as the sample. (The primary insulation is the material directly in contact with the

Figure 1. The preferred arrangement for firing ceria-doped zirconia at 2.45 GHz placed the sample within a porous alumina crucible, enclosed in yttria-doped zirconia bulk fiber insulation inside an alumina fiberboard crucible.

Figure 2. Examples of samples fired with different types of insulation systems described in Table 1. (a) Ex. 2; (b) Ex. 3; (c) Ex. 5; (d) Ex. 6.

sample, Fig. 1.) Specifically, the primary insulation consisted of granulated ZrO_2 -12 mol% CeO_2 powder, Table 1, Ex. 2. Fig. 2a shows that the result of this approach was less than satisfactory. The sample was conical in shape, having densified more on the top than on the bottom, which led to severe cracking caused by differential sintering. Apparently, a "hot spot" developed on the top side of the sample or in the insulation around the sample. The second approach was to blend the ZrO_2 -12 mol% CeO_2 powder with alumina bulk fiber insulation, Table 1, Ex. 3. Using the blend of alumina fiber and ZrO_2 -12 mol% CeO_2 powder resulted in somewhat more uniform heating but still did not produce a good pellet, Fig. 2b. The sample was convex in shape having bent toward the back side of the sample away from the thermocouple tip. In addition, a crack formed at the thermocouple well. At this point in the development of the insulation system it was thought that the insulation was not absorbing enough microwave energy. Hence, it might not be acting as a good "electric blanket"¹² to heat the sample to a temperature where it would couple on its own. In an attempt to increase the coupling of the fiber/powder blend, SiC grit was admixed with the insulation, Table 1, Ex. 5. This approach was disastrous, Fig. 2c. A large hot spot appeared on the bottom of the sample, which led to severe cracking. The insulation on the bottom of the sample actually fused, which indicated that the temperature was high enough to form a zirconia - alumina - silica glass in the insulation.

There were two keys to developing a workable insulation system for firing the ZrO_2 -12 mol% CeO_2 samples. The first was to use yttria-doped zirconia bulk fiber (ZYBF) as the primary insulation around the sample. The second was to put the sample inside an alumina refractory crucible. ZYBF insulation couples strongly with the microwave field at temperatures above $\sim 400^\circ\text{C}$. Therefore, it acted as a good "electric blanket" to provide secondary heating to the sample at temperatures between ~ 400 and 700°C , which was in addition to that provided by the picket fence below $\sim 400^\circ\text{C}$. The auxiliary heating provided by the ZYBF insulation allowed the samples to be heated uniformly. Hot spots in the insulation package that might lead to nonuniform sintering of the sample were thereby avoided. The alumina crucible provided a physical barrier between the sample and the zirconia bulk fiber insulation, which prevented contamination of the samples by yttria, Ex. 6 in Table 1, and Fig 2d. It also provided a more even thermal barrier at the sample surface, which helped to keep the temperature more uniform. A schematic of the preferred experimental setup is shown in Figure 1.

RESULTS AND DISCUSSION

Sintering curves for conventional and 2.45 GHz microwave firing in air and N_2 -4% H_2 are shown in Figure 3. The samples that were microwave fired reached higher densities at a given temperature than those that were conventionally fired. The samples are completely in the tetragonal zirconia phase, as determined by x-ray diffraction. Normal microstructures were obtained for both the conventional and the microwave fired samples.

Figure 3. Sintering curves for ZrO_2 - 12 mol% CeO_2 in air, conventional and 2.45 GHz microwave furnaces. Sintering curves for ZrO_2 - 8 mol% Y_2O_3 included for comparison. Curves for the yttria-doped samples were offset by 10% in density.

(a)

(b)

Figure 4. The average grain size, d , for ZrO_2 - 12 mol% CeO_2 sintered in air was larger for conventional sintering than for microwave sintering. Polished section; thermal etch 1h at 1150°C to reveal grain boundaries; SEM micrograph; (a) conventional firing, $p=97.4\%$ td, $d=0.93\ \mu\text{m}$, $T_{\text{sinter}} = 1450^\circ\text{C}$; (b) microwave firing at 2.45 GHz using procedure of Ex. 6, $p=97.5\%$ td, $d=0.77\ \mu\text{m}$, $T_{\text{sinter}} = 1400^\circ\text{C}$. Grain size was determined using the lineal intercept method.¹³

For the ZrO_2 -12 mol% CeO_2 samples, there was a shift in the sintering curves of about 50°C for the microwave fired samples as compared with the conventionally fired samples over the entire range of densification. The average grain size for the conventionally fired sample ($d = 0.93 \mu\text{m}$ @ 97.4% td) was larger than that for the microwave-fired sample ($d = 0.77 \mu\text{m}$ @ 97.5% td) when compared at the same densities. Grain sizes were determined using the lineal intercept method.¹⁰ Both of these observations are consistent with the presence of a microwave effect for the sintering of ceria-doped zirconia. If no microwave effect existed, there should be no differences in the sintering curves or in the microstructures.

This shift in the sintering curves for microwave and conventional sintering of ZrO_2 -12 mol% CeO_2 was much smaller than that observed for the sintering of ZrO_2 -8 mol% Y_2O_3 examined in a previous study.¹ As is shown in Fig. 4, the difference in sintering temperature between the microwave and conventionally fired yttria-doped zirconia samples was $\sim 100^\circ\text{C}$ over most of the range of density and increased to as much as 175°C at the highest densities. In addition, the differences in grain size between conventional and microwave firing was different for the ceria- and yttria-doped systems. The ratio of conventional to microwave grain size in the ceria-doped system was 1.2 to 1; for the yttria-doped system it was 1.6 to 1. Thus the ceria-doped zirconia exhibited a smaller microwave effect than the yttria-doped system both in terms of densification enhancement and grain size reduction.

The reason for the difference in the magnitude of the microwave effect for these two zirconias is thought to be the differences in their ionic conductivity. The ionic conductivity of the ZrO_2 -8 mol % Y_2O_3 samples is >100 times that of the ZrO_2 -12 mol% CeO_2 samples over a wide range of temperature.³ The higher conductivity is caused by the substitution of the Y^{+3} ion onto the Zr^{+4} site in the zirconia lattice, which creates oxygen vacancies to balance the charge in the lattice. This increase in the concentration of oxygen vacancies in the lattice increases the ionic conductivity. In the case of Ce^{+4} substituting for Zr^{+4} , no additional vacancies are created and the ionic conductivity is not significantly increased. The predominant mechanism by which microwaves interact with an oxide ceramic is through defects in the structure of that material.¹¹ Therefore, it is reasonable to expect that a material with a higher concentration of defects should absorb more microwave energy and should heat more readily than one with a lower concentration of defects. This was indeed observed: the ceria-doped zirconia was more difficult to heat than the yttria-doped zirconia.

DISCLAIMER

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CONCLUSIONS

A "microwave effect" was observed for the sintering of ZrO_2 -12 mol% CeO_2 at 2.45 GHz. This manifested itself as a shift in the sintering curve to lower temperature for microwave heating as compared with conventional heating. The grain size of the microwave fired samples was smaller than that of the conventionally fired samples. The magnitude of the microwave effect observed for ceria-doped zirconia in this study was substantially smaller than that observed previously for yttria-doped zirconia. The shift in sintering curves in the present study was only $\sim 50^\circ\text{C}$ as compared with $\sim 100^\circ\text{C}$ in the previous study. Also, there was a smaller difference in the ratio of grain sizes of conventional to microwave samples in the present study (1.2:1) as compared with the previous study (1.6:1).

ACKNOWLEDGEMENTS

The authors would like to acknowledge the following people for their help and support: J.O. Kiggans for discussions relating to experimental design; P.F. Becher for discussions relating to interpretation of results; G.C. Marsh for metallography; C.T. Wilson for design of the microwave furnace control system; R.R. Steele for SEM microscopy; J.W. Nave for photography; O.B. Cavin for x-ray diffraction; and J.O. Kiggans and O.O. Omatete for critical review of the paper.

NOTES

* TOSOH U.S.A., Inc., Atlanta.

‡ Cober Electronics, Stamford, Conn.

† LabVIEW®, National Electronics, Inc., Dallas.

Keith Co., Inc., Pico Rivera, CA.

REFERENCES

1. M.A. Janney, C.L. Calhoun, and H.D. Kimrey, "Microwave Sintering of Solid Oxide Fuel Cell Materials, I: Zirconia - 8 mol % Yttria," *J. Am. Ceram. Soc.*, **75** [2] 341-6 (1992).
2. J. Samuels and J.R. Brandon, "Effect of Composition on the Enhanced Microwave Sintering of Alumina-Based Ceramic Composites," *J. Matls. Sci.*, **27**, 3259-65 (1992).
3. B.-S. Chiou, H.-T. Dai, and J.-G. Duh, "Electrical Behavior of Ceria-Stabilized Zirconia with Rare-Earth Oxide Additives," *J. Am. Ceram. Soc.*, **73** [4] 866-71 (1990).

4. M.A. Janney, H.D. Kimrey, M.A. Schmidt, and J.O. Kiggans, "Alumina Grain Growth in a Microwave Field," *J. Am. Ceram. Soc.*, **74** [7] 1675-81 (1991).
5. J.O. Kiggans, C.R. Hubbard, R.R. Steele, and H.D. Kimrey, "Characterization of Silicon Nitride Synthesized by Microwave Heating," in **Microwaves: Theory and Applications in Materials Processing**, D.E. Clark, F.D. Gac, and W.H. Sutton, eds., *Ceram. Trans.*, **21**, 403-410 (1991).
6. M.A. Janney, H.D. Kimrey, and J.O. Kiggans, "Microwave Processing of Ceramics: Guidelines Used at the Oak Ridge National Laboratory," in **Microwave Processing of Materials, III**, R.L. Beatty, W.H. Sutton, and M.F. Iskander, eds., *MRS Symp. Proc.*, **269**, 173-85 (1992).
7. D.J. Grellinger and M.A. Janney, "Temperature Measurement in a 2.45 GHz Microwave Furnace," to be published in **Microwaves: Theory and Applications in Materials Processing, II**, D.E. Clarke, ed., *Ceramic Transactions*, 1993.
8. J.R. Brandon, J. Samuels, and W.R. Hodgkins, "Microwave Sintering of Oxide Ceramics," in **Microwave Processing of Materials, III**, R.L. Beatty, W.H. Sutton, and M.F. Iskander, eds., *MRS Symp. Proc.*, **269**, 237-43 (1992).
9. C.E. Holcombe and N.L. Dykes, "Importance of 'Casketing' for Microwave Sintering of Materials," *J. Matl. Sci. Lett.*, **9**, 425-8 (1990).
10. R.L. Fullman, "Measurement of Particle Sizes in Opaque Bodies," *Trans. Met. Soc. AIME*, **197**, 447-52 (1953).
11. W.W. Ho, "High-Temperature Dielectric Properties of Polycrystalline Ceramics," in **Microwave Processing of Materials**, W.H. Sutton, M.H. Brooks, and I.J. Chabinsky, eds., *MRS Symp. Proc.*, **124**, 137-48 (1988).

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