CONF-8906135--2

DE89 014769

MICROWAVE SINTERING OF CERAMICS*

W. B. Snyder

*Research sponsored by the Office of Conservation of Renewable Energy and the Office of Defense Programs, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

MICROWAVE SINTERING OF CERAMICS

W. B. Snyder

INTRODUCTION

Since the invention of the microwave oven by Raytheon in 1945, microwave processing has revolutionized industrial and home food preparation and replaced conventional heating in a variety of applications such as the vulcanization of rubber, recycling of asphalt, curing of epoxies, and the drying of grains, paper, textiles, and wood products. The unique benefits of uniform, rapid heating have been realized in all of these applications [1]. While these commercial processes have all been carried out at temperatures less than 500°C, research has pushed microwave processing temperatures as high as 2300°C opening the possibilities for high-temperature processing of advanced ceramics [2].

BACKGROUND

Microwave heating differs substantially from conventional heating techniques. Figure 1 shows a conventional resistively heated furnace and a microwave furnace. In the conventionally heated furnace, electrons (in the form of alternating current at 60 Hz) are passed through a resistive element producing heat which can be either radiantly or convectively transferred to the workpiece. In order to produce a uniform temperature distribution in the furnace, the furnace is by necessity "hot walled." In the case of microwave radiation, electrons are first accelerated and subsequently decelerated to produce photons in the 1-300 GHz frequency range. The electromagnetic energy is transmitted to the furnace chamber by use of a waveguide or coaxial cable. Radiation is reflected from the furnace walls until it is absorbed by the workpiece. With proper design the furnace can be a "cold walled" device.

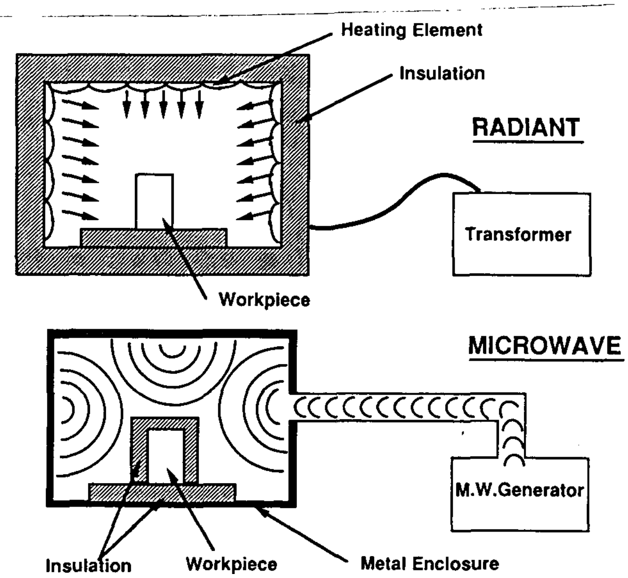

Figure 1. Illustration of conventional radiant and microwave furnace configurations.

Microwave heating has several unique benefits over conventional heating techniques. When using microwave radiation, heating occurs volumetrically. If proper insulation is employed, heat is generated uniformly throughout the workpiece thus minimizing thermal stresses. With proper furnace design controlled heating rates approaching 1000°C/minute can be achieved.

BASICS OF MICROWAVE SINTERING

The use of microwave energy to densify or sinter ceramic materials at high temperatures requires consideration of four principal factors: (1) The dielectric absorption characteristics of the material, (2) Consideration of internal versus external heating, (3) Electric field uniformity, and (4) Chemical compatibility.

Dielectric Absorption

The power dissipated per unit volume in the workpiece is approximated by the following equation:

$$\frac{\text{Power}}{\text{Volume}} \approx \frac{\omega}{2} \tan\delta \; \varepsilon |E|^2$$

where ω is the frequency, ε is the dielectric constant, tan δ is the dielectric loss, and E is the peak electric field strength. The attenuation of power follows Lambert's Law according to

$$P = P_o e^{-\alpha x}$$

where P_o is the incident power, P is the power at distance, x, into the material, and α is the linear absorption coefficient. The linear absorption coefficient is directly proportional to frequency (ω), relative dielectric constant (ε_r'), and loss tangent (tanδ) according to

$$\alpha = \frac{\omega \sqrt{\varepsilon_r'} \tan\delta}{c}$$

where c is the speed of light [3]. Higher frequencies, greater loss tangents, and larger dielectric constants therefore result in greater power attenuation rates within a material. While frequency is known and the relative dielectric constant can normally be approximated, the loss tangent is an extrinsic material property and is therefore a function of many variables such as frequency, temperature, purity, and particle size. Figure 2 shows the variation of loss tangent for 99.5 percent alumina as a function of temperature (at 35 GHz) and frequency (at room temperature). Thus the

*Based on work performed at Oak Ridge National Laboratory, operated for the U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

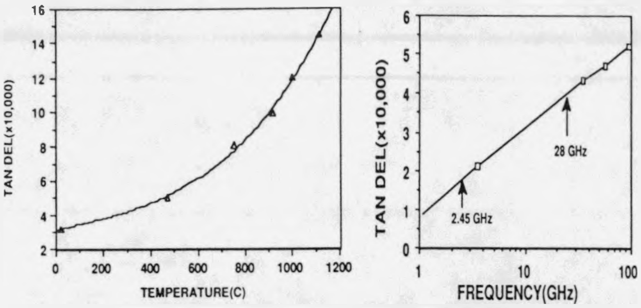

Figure 2. The effects of temperature and frequency on the loss tangent of Coors AD995 alumina.

variation in loss tangent is perhaps the most important variable to consider when heating a material. Unfortunately, the database available for dielectric properties of materials contains very little information on the effects of purity, sintered density, etc. on loss tangent, and therefore, the heating behavior of most materials must be determined experimentally.

Internal versus External Heating

The absorption of microwave radiation generates heat internally. The difference in thermal gradient that is generated in an uninsulated part is the inverse of that observed for radiant heating. Figure 3 shows what might be typical thermal stress distributions generated from the two types of heating. Microwave heating creates a reversal of the thermal stress distribution generated from radiant heating. With proper use of nonmicrowave absorbing insulation, it is possible to create a uniform temperature distribution through the workpiece (Figure 4). Careful balance of applied power, workpiece container, and insulation characteristics will allow very rapid heating rates with minimal thermal stresses.

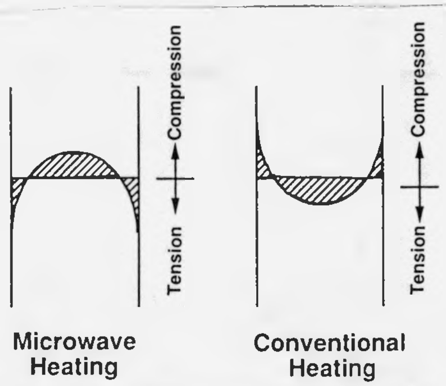

Figure 3. Thermal stress distributions generated from microwave and conventional heating.

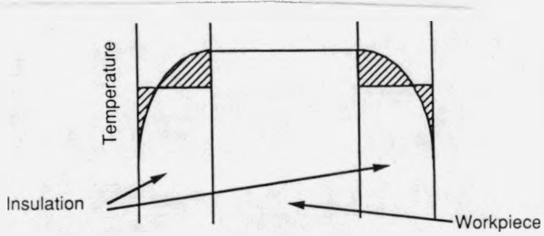

Figure 4. Technique for reducing thermal gradient in microwave sintered part.

Electromagnetic Field Uniformity

Uniform heating of a load in a microwave furnace is also a function of the electric field uniformity in the furnace. Kimrey [1,4] has shown that a worst case field uniformity of ±4 percent can be achieved in a vessel which has an average dimension of approximately 100 wavelengths (1 meter at 28 GHz). Equivalent uniformity at the more commonly used 2.45 GHz frequency would require a vessel that was 12.2 meters in average dimension. The importance of heating uniformity is illustrated by the two discs in Figure 5. The zirconia-3 mole percent yttria medallions were green processed at the same time by die pressing the bodies to 8.2 mm thickness by 57.5 mm diameter (42 percent of theoretical density) and sintering for one hour at 1150°C. The left disc was sintered in a 2.45 GHz furnace having low field uniformity while the other disc was sintered in a 28 GHz furnace having high field uniformity. The disc sintered in the 28 GHz unit is essentially theoretically dense and translucent. It is believed that the disc sintered at 2.45 GHz experienced a very high electric field at a single point. Because zirconia has very poor thermal conductivity and its loss tangent increases rapidly with temperature, the temperature at the point of high field intensity increased very rapidly to the sintering temperature. The shrinkage stresses resulting from sintering caused separation of an initial piece from the body. Radiation continued to heat adjacent pieces until they also experienced separation. Final sintered densities of the numerous pieces varied from 100 to 67 percent of theoretical density. The illustration shown here should be considered a worst case scenario for heating of materials using microwave radiation. Although the 28 GHz device clearly produces a more uniform field, 2.45 GHz radiation can be very successfully used to sinter a wide range of materials if one properly considers the nonuniformity of electric field.

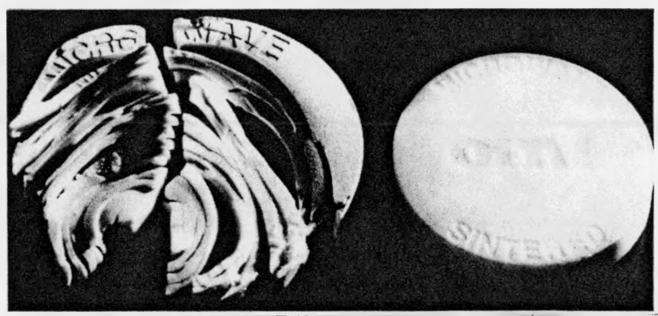

Figure 5. Zirconia-3 mole percent yttria discs sintered at 2.45 GHz (left) and 28 GHz (right). Right disc is 6.4 mm thick by 44.5 mm diameter.

Chemical Compatibility

The microwave sintering furnace offers a wide range of flexibility in operation since different atmospheres and materials may be used on alternate furnace runs. Radiantly heated furnaces must be designed to account for the chemical compatibility of the sintering atmospheres with heating elements and heat shields. During microwave sintering, chemical compatibility must also be considered to prevent reactions generated between the atmosphere, workpiece, and insulation.

SINTERING RESULTS

In a recent review, Sutton has discussed many potential applications of microwave processing of ceramics including sintering, calcining, and joining [4]. At Oak Ridge we have focused on determining the microwave sintering behavior of materials. We have examined alumina, zirconia-toughened alumina, zirconia, lithium hydride, silicon nitride, 1-2-3 superconductor, silicon, titanium diboride, boron carbide, and SiAlON.

Alumina

Microwave sintering of alumina at 28 GHz has shown that microstructural evolution and densification are inherently different for microwave versus conventionally sintered alumina [5]. Figure 6 shows the densification behavior of alumina sintered for one hour at each temperature. Note that equivalent densities can be obtained at temperatures 300-400°C lower using microwave radiation rather than conventional heating. An Arrhenius plot of this data and similar data taken for other time periods shows that the apparent activation energy for microwave sintering is roughly one third of that for conventional sintering (Figure 7). A thorough search of the literature has failed to identify a mechanism which explains why the presence of an electromagnetic field would significantly enhance the densification of alumina.

Pore distributions determined by mercury intrusion porosimetry, Figure 8, were also found to differ between microwave and

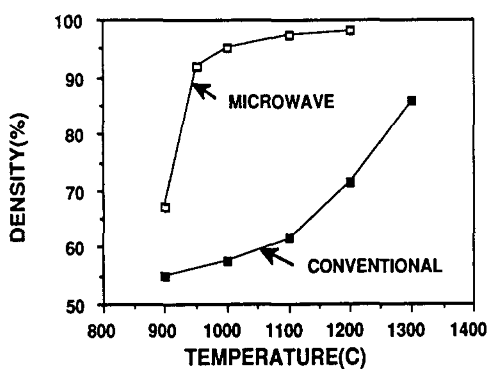

Figure 6. Density as a function of temperature for 99.9 percent alumina sintered conventionally and at 28 GHz. Data is for a one hour hold at temperature.

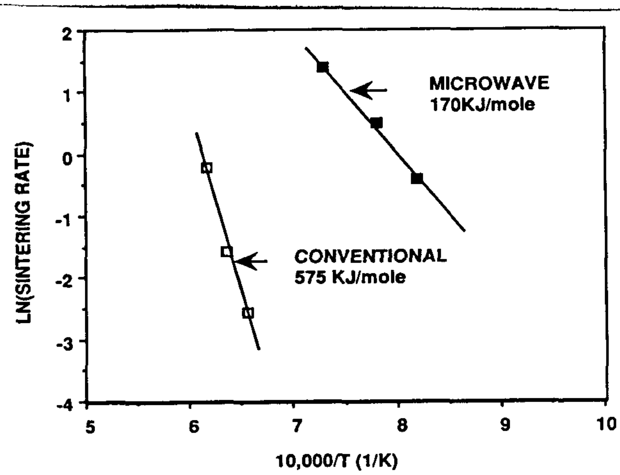

Figure 7. Arhennius plot of log sintering rate versus reciprocal absolute temperature for 28 GTHz microwave and conventionally sintered alumina.

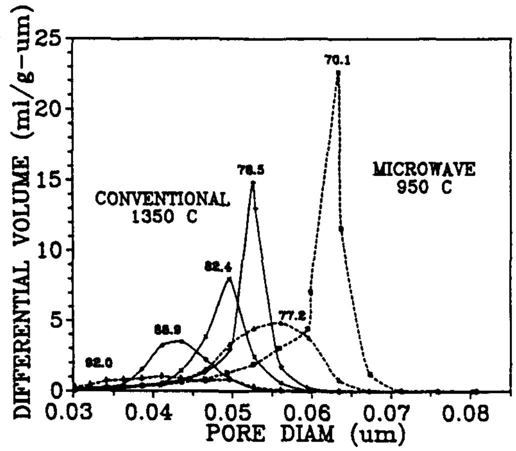

Figure 8. Pore size distributions for microwave and conventionally sintered alumina.

conventionally sintered alumina. Note the broad distribution of pore volume for the microwave sintered specimen at 77.2 percent of density (dotted line) versus the sharper distribution for the conventionally fired specimen at 78.5 percent of density. At a given density the pore necks are larger for microwave sintered alumina. We interpret this observation to mean that microwave sintering favors mechanisms which lead to densification (i.e., bulk or grain boundary diffusion) rather than coarsening (i.e., surface or vapor transport) of the structure.

Though the mechanisms responsible for the differences in densification, grain growth, and pore distribution between microwave and conventionally sintered alumina are not well known, the implications of the results are clear. Using microwave radiation, it is possible to densify and maintain a fine grain size in alumina at temperatures 300-400°C lower than conventional sintering. With the lower processing temperatures allowed by microwave heating, it will be possible to cofire previously incompatible materials such as alumina/copper composites for electronic applications. Unique pore structures may also be possible in porous materials used for filtration, etc.

1-2-3 Superconducting Ceramic

Yttrium oxide, barium carbonate, and copper oxide were calcined and comminuted three times to produce powder of the 1-2-3 superconducting compound [6]. Compacts of the superconducting powder were annealed in oxygen at various times and temperatures in both radiant and microwave furnaces. In order to avoid arcing, the microwave furnace contained a segmented silicon carbide susceptor and therefore produced both radiant and microwave components of heating (mixed mode heating). Sintered density of the superconducting compacts is shown in Figure 9. Note that the mixed mode heated specimens attained a density of 95 percent of theoretical while the radiantly heated specimens had a maximum density of 85 percent. Zero field critical current measurements on these specimens are given in Figure 10 as a function of sintered density. Although the peak current densities for radiant and mixed mode heating are essentially the same, the maxima occur at 62 percent of theoretical density for radiant and 85 percent for mixed mode. Using mixed mode heating it is therefore possible to produce a much stronger superconducting ceramic with equivalent current density to conventionly sintered material.

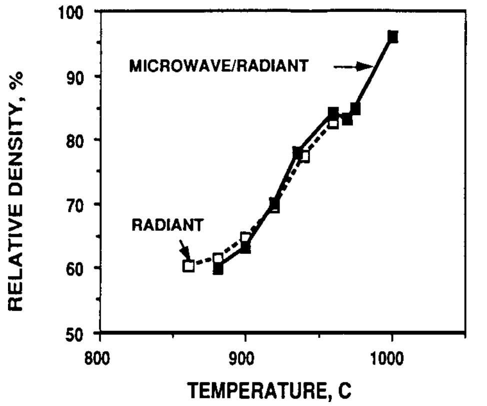

Figure 9. Sintered density as a function of temperature for conventionally and mixed mode (radiant/microwave) heated specimens of 1-2-3 superconductor powder. Data is for 10 hour soak in pure oxygen.

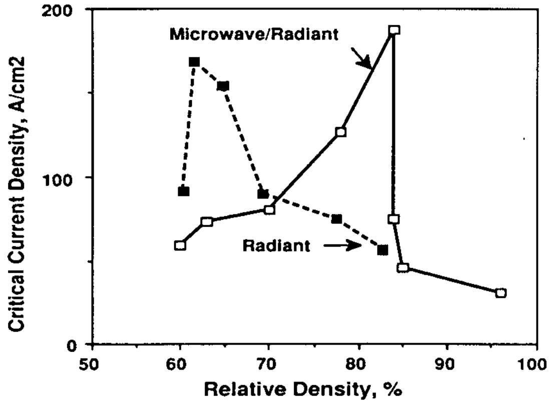

Figure 10. Critical current density at zero field for 1-2-3 superconductor versus sintered density. Data is for 10 hour soak in pure oxygen.

Titanium Diboride

Titanium diboride is a ceramic material of interest for armor, corrosion, and wear applications. Using a commercially available powder of titanium diboride-3 weight percent chromium diboride, we have conducted a microwave sintering feasibility experiment with a 6 kW, 2.45 GHz furnace [2]. By surrounding pressed pellets of the diboride with yttria contained in a boron nitride crucible, it was possible to achieve temperatures up to 2300°C as measured by an optical pyrometer. Densification curves in Figure 11 show that 98 percent of theoretical density can be achieved in 15 minutes at 2100°C. The rapid increase in sintering rate between 1800°C and 1900°C is indicative of formation of a liquid phase. These data clearly show that titanium diboride-3 weight percent chromium diboride can be rapidly microwave sintered to nearly full density.

SUMMARY

Successful adaptation of microwave heating to the densification of ceramic materials requires a marriage of microwave and materials technologies. Using an interdisciplinary team of microwave and materials engineers, we have successfully demonstrated the ability

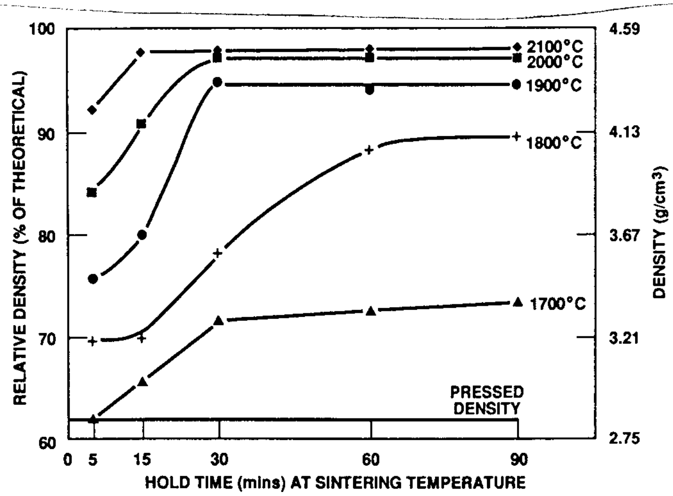

Figure 11. Density versus time for titanium diboride-3 weight percent chromium diboride.

to densify ceramic materials over a wide range of temperatures. Microstructural evolution during microwave sintering has been found to be significantly different from that observed in conventional sintering. Our results and those of others indicate that microwave sintering has the potential to fabricate components to near net shape with mechanical properties equivalent to hot pressed or hot isostatically pressed material.

ACKNOWLEDGMENTS

The results reported in this paper were obtained by Dr. M. A. Janney and Mr. H. D. Kimrey for alumina, Dr. H. E. Kim for the 1-2-3 superconductor, and Mr. C. E. Holcombe for titanium diboride. Drs. Janney and Kim are members of the Metals and Ceramics Division of the Oak Ridge National Laboratory. Mr. Kimrey is a member of the Fusion Energy Division of the Oak Ridge National Laboratory. Mr. Holcombe is a member of the Development Division of the Oak Ridge Y-12 Plant.

REFERENCES

1. W. H. Sutton, M. H. Brooks, and I. J. Chabinsky, (eds), *Microwave Processing of Materials*, Volume 124, Materials Research Society, 1988.

2. C. E. Holcombe, paper presented at American Ceramic Society 1989 Spring Meeting, Indianapolis, Indiana.

3. H. D. Kimrey, Reference 1, p. 367.

4. W. H. Sutton, "Microwave Processing of Ceramic Materials," *American Ceramic Society Bulletin*, Vol. 68, No. 2, 1989, p. 376.

5. M. A. Janney and H. D. Kimrey, "Microstructure Evolution in Microwave Sintered Alumina," *Advances in Sintering*, American Ceramic Society, in press.

6. H. E. Kim, paper presented at American Ceramic Society 1989 Spring Meeting, Indianapolis, Indiana.