LA-UR 95-1459

Conf-950401--1

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

TITLE: DIELECTRIC PROPERTY MEASUREMENT OF ZIRCONIA FIBERS AT HIGH TEMPERATURES

AUTHOR(S): Gerald J. Vogt, Wayne R. Tinga, and Ross H. Plovnick

SUBMITTED TO: David E. Clark
Symposium Chair
Dept. of Materials Science & Engineering
136 MAE
P.O. Box 116400
Gainesville, FL 32611

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO 836 R4
ST NO 2629 5/81

DIELECTRIC PROPERTY MEASUREMENT OF ZIRCONIA FIBERS AT HIGH TEMPERATURES

Gerald J. Vogt
Los Alamos National Laboratory, P.O. Box 1663
Los Alamos, New Mexico 87545

Wayne R. Tinga
Dept. of Electrical Engineering, University of Alberta
Edmonton, Canada T6G 2G7

Ross H. Plovnick
3M Ceramic Technology Center, 3M Center, Building 201-4N-01
St. Paul, Minnesota 55144

ABSTRACT

Using a self-heating, electronically tunable microwave dielectrometer, the complex dielectric constant of zirconia-based filaments was measured at 915 MHz from 350° to 1100°C. This fibrous material cools rapidly to near room temperature within several seconds due to a large surface area to volume ratio. Such rapid sample cooling necessitates the use of a self-heating technique to measure the complex dielectric constant at temperatures up to 1100°C. Sample temperature was measured with optical fiber thermometry. The effect of sample temperature measurement on data accuracy is discussed.

INTRODUCTION

Successful application of microwave heating for ceramic fibers will require knowledge of the temperature-dependent dielectric properties of the desired ceramic filament. These dielectric properties can greatly affect the design and performance of the microwave process system, since they can change by several orders of magnitude with increasing temperature. Furthermore, the dielectric

properties can significantly change due to chemical or structural changes in the ceramic during processing. Process modeling will naturally need the same data to produce realistic numerical results.

Because these properties are generally unknown, the dielectric properties must be measured over the range of possible process temperatures. Typically, fibrous material cools rapidly from a high temperature (>1000°) to near room temperature within several seconds due to a large surface area to volume ratio. Also, test samples cannot be consolidated into high-density bulk because this will significantly alter the dielectric properties of the ceramic fibers. Dielectric measurements under these sample constraints were performed with the self-heating, electronically tunable microwave dielectrometer developed at the University of Alberta [1-3]. Measurements were made for zirconia-based filaments.

EXPERIMENTAL

The theory and operation of the self-heating, electronically tunable microwave dielectrometer has been described in earlier work [1-3]. Dielectric properties were measured at 915 MHz over a 350°-1100°C temperature range. Sample temperature was controlled with a Luxtron/Accufiber Optical Fiber Thermometer (OFT) unit, operating at a single-wavelength band of 0.3-1.12 μm to measure temperate over a 300°-1200°C range. A second OFT unit, operating with dual-wavelength bands near 800 nm and 950 nm over a 550°-2000°C range, was added to the system for dual-wavelength temperature measurements. Each OFT unit used an open-ended sapphire lightpipe to monitor the sample temperature. The lightpipe tips were positioned, as shown in Figure 1, outside the measuring gap in the dielectrometer, ~15 mm away for the control OFT and ~12 mm away for the second OFT. The spectral emissivity of the zirconia-based filaments was 0.17 at 800 nm and 0.18 at 950 nm, as measured by the ripple technique [4]. Data from the dual-wavelength OFT were recorded as single-wavelength temperature values during measurement, which were later converted to dual-wavelength temperature values.

Test samples of 3M zirconia-based filaments were packed into a 7-mm OD x 5-mm ID x 10-cm long fused quartz tube with one closed end. The organic sizing on the filaments was removed by firing in air for 1 hour. Two sample groups with significant different packing densities were prepared from chopped fibers in one group and from coarse powder in the second group. Filaments were chopped

under a 1 w% aqueous solution of poly(ethylene oxide) (~5MW) in a food blender. Chopped filaments were dried and then fired in air at 600°C for 1 hour to burn off the poly(ethylene oxide). The coarse powder was prepared by lightly grinding filaments in a porcelain mortar and pestle. The mean packing densities of the chopped filament samples and the powder samples were typically 1.5 g/ml and 2.8 g/ml. The mean packing density was calculated from initial sample weight and initial sample volume which was measured by water displacement after removing the heated test sample.

Dielectric properties were measured at two different locations along each tubular sample. The two measured segments along a sample were sufficiently spaced apart to avoid overlapping heating between the first and second measurements. Each location was measured either one, two or three times before moving to a new location or to a new sample.

RESULTS AND DISCUSSION

Dielectric Properties

Figures 2 and 3 show temperature-dependent dielectric data measured for a powder sample and for a chopped fiber sample. Above 600°C the dielectric constant ε' for each sample increased rapidly. In the first measurement for the chopped sample, the dielectric constant ε' at 975°C is approximately three times greater than at 350°C. Similarly for the powder sample, the dielectric constant ε' at 900°C in the first measurement is approximately five times the value measured at 350°C. Even larger increases are seen the dielectric loss data, approximately 100 times or more.

Interestingly, in Figures 2 and 3, the dielectric properties from a second measurement on the same sample volume yield even greater values than those from the first measurement indicating a change in the material caused by the first measurement. Dielectric data from a third measurement in Figure 3 closely agree with those in the second measurement.

The heated volumes for all samples were partially sintered, as evident from the presence of a weakly sintered piece found in the core of each heated volume. Each sample was probably sintered during the first heating and measurement cycle with possible further sintering with each repeat measurement. The sintered core was also found in a sample that was measured only once. The increase in

dielectric properties in a second measurement in Figures 2 and 3 is likely caused by partial sintering of the sample during the first measurement.

Temperature Measurement

Figure 4 shows the temperature values for the powder sample in Figure 2 as measured by the control OFT (OFT1) and the dual-wavelength OFT (OFT2). The ratio temperatures in Figure 4 were calculated using the single-wavelength temperatures from the dual-wavelength OFT. In both measurements, the single-wavelength temperatures from OFT2 were significantly greater than the temperatures from OFT1. From OFT2, the temperature measured at the 800 nm band was always greater than the temperature measured at the 950 nm band, although each was corrected with a measured emissivity. The OFT2-OFT1 difference is ~100°-150°C at the beginning of the test and ~200°C at the end of the test. The three single-wavelength temperatures show a continuous rise through the course of the measurement, where the slope of the OFT2 temperature curves is greater than that for the OFT1 temperature curve.

Ratio temperature data from OFT2 display a very different behavior. In both tests, these ratio temperatures are substantially greater than the three single-wavelength temperatures. In fact, the ratio temperature is greater than the OFT1 temperature by ~500°C in the beginning and by ~400°C at the end. More surprisingly, the ratio temperature is nearly constant in the middle of both tests, although the single-wavelength temperatures show continuous increase. Since the ratio temperature is largely unaffected by targeting error, the ratio temperature might represent a hot spot temperature from non-uniform sample heating. Conversely, because the sample's 2.5-mm gap target area only fills a fraction of the OFTs' conical field of view, the single-wavelength temperatures are probably low, but increase with microwave input power.

Potential Sources of Temperature Error.

Large temperature variations in the measurements can be attributed to several experimental error sources. These errors might contribute to temperature variation between sensors and to general error in the temperature measurements as discussed below.

Targeting Error: The Accufiber lightpipe sensor tip collects the emitted light over an optical cone angle of ~52°. If the emitting source does not fill the conical

view of sensor tip, the measured temperature will be less than the source temperature in proportion to the fraction of view not filled by the source. The amount of light collected by the sensor is filtered and then measured as a photodiode current by a detector. Temperature is then computed from a calibration table of temperature and photodiode current values. If the source does not fill the conical view, the measured photodiode current will be lower than the expected current, producing a low temperature reading.

The control OFT1 will likely be affected by targeting error because the sensor tip was located ~15 mm back from heated sample surface. The visible heated sample is ~2.5 mm high by ~5 mm wide surrounded by a 7-mm OD quartz tube. The 52° optical cone of the sensor tip allows the sensor to view a circular spot with a diameter approximately equal to the distance between the source and the sensor tip. Both control OFT1 and OFT2 were probably viewing part of the dielectrometer inner brass surface as well as the heated sample.

Absorption Error from the Quartz Tube: The quartz tube in which the samples are packed will absorb and reflect a fraction of the emitted light from the heated sample. The corresponding amount of light gathered by the OFT sensor will be reduced by the absorption and reflection at the quartz tube. The resulting photodiode current will be less than expected, yielding a low temperature reading. At room temperature quartz has a large, constant spectral transmittance of >0.9 for 1-mm thickness over the 0.3-1.1 μm band [5]. This error will certainly affect the single-wavelength temperature measurements. The dual-wavelength measurement will be affected if the spectral transmittances at 800 nm and 950 nm are significantly different.

Other sources of error caused by the quartz tube may be the curvature of the tube, the fogging by devitrification on the inner surface of the tube, and the changes in light transmission through the quartz wall due a large thermal gradient across the tube wall. Localized fogging of the quartz tube by devitrification at the inner surface was observed for some, but not all, of the samples. Fogging is expected to produce large temperature errors due to a significant decrease in the transmittance of the quartz wall. Fogging would result in still lower temperature readings.

Emissivity Error: Using an incorrect emissivity can induce a large error in temperature measurement [6]. The constant emissivity values used in this study were measured at temperatures below 800°C. A change in emissivity at higher temperatures would result in a temperature reading error for the single-wavelength

measurements. This error will yield either lower or higher temperatures, depending on whether the emittance increases or decreases. The ratio temperatures would be affected if the ratio of the two emittances at 800 and 950 nm changed from the low temperature value. The OFT1 measurement could have the greater chance for emissivity error because the OFT1 detector was measuring the collected light over a broad band of 0.3 to 1.1 μm, certainly broad compared to the much smaller ±50 nm bands at 800 and 950 nm.

Error from non-uniform heating: The OFT1 and OFT2 lightpipes viewed different portions of the heated samples, as evident from Figure 1. If the sample volume was not uniformly heated, the temperatures measured by OFT1 and OFT2 could differ significantly. While this is not strictly a temperature measurement error, it will introduce an unaccountable different between OFT1 and OFT2. We suspect that the samples may not heat uniformly because the quartz tubes for several samples were not uniformly fogged by devitrification. Typically, these quartz tubes were visibly fogged at one spot on the inner wall, but not uniformly in a band around the tube.

Error from self-insulation: The test samples consisted of loosely packed chopped fiber and powder. Thermal conduction across the zirconia-based samples will then be proportionally lower than what is already expected from the low thermal conductivity of zirconia. Microwave heating will naturally produce an inverse thermal gradient across the sample diameter. We would expect that the surface temperature of loosely packed samples was measurably lower than the core temperature in the sample. Self-insulation will produce a low-temperature error that will be typical of all surface temperature measurement methods.

Interpretation of Experimental Data

The dielectric measurements with temperatures as measured by the single-wavelength method, as shown in Figure 2 with OFT1 temperatures, exhibit the anticipated continuous increase in ε' and ε'' with increasing temperature. We believe that the OFT2 temperatures are probably closer to the actual sample temperatures than the OFT1 temperatures. However, both sets of temperatures are probably significantly lower than the actual temperatures due to targeting error and absorption error by the quartz tube. The ratio temperatures measured by OFT2 are probably a better measure of the true sample temperature during the dielectric measurement as the ratio temperature measurement is not affected by

targeting error. Just how accurate the ratio temperatures are in this experiment is not known without further experimental study.

The experimental picture for the dielectric measurements as seen from the ratio temperature measurements is quite different from what is expected. In Figure 5 both the ε' and ε'' curves in the first measurement contain an abrupt step change at 1140°C, followed by gradual increases with increasing temperature. This step change is not seen in the ε' and ε'' curves for the repeat measurement. Apparently, the sample properties were significantly altered during the first measurement. Presumably, that change in sample dielectric properties is associated with the sintering that was observed in the first measurement.

CONCLUSIONS

During the first dielectric measurement, the dielectric properties of the zirconia-based samples were changed due to the heating of the sample. Sintering of the test sample was observed during removal of the samples from the quartz sample holder. Sample sintering probably occurs during the first dielectric measurement. Significant experimental uncertainty exists in the temperature measurement by a single-wavelength optical fiber thermometry. Temperature measurement can be significantly improved by eliminating targeting error with the lightpipe sensor and by using the dual-wavelength optical fiber thermometry.

ACKNOWLEDGMENTS

This work at Los Alamos was supported by the Department of Energy, Office of Industrial Technologies, Advanced Industrial Materials Program.

REFERENCES

1. W.R. Tinga, "Microwave System Design and Dielectric Property Measurements," **Microwave Processing of Materials IV**, Materials Research Society Symposium Proceedings, Vol. 347, pp. 427-440, (1994).
2. W.R. Tinga and W. Xi, "Design of a New High-Temperature Dielectrometer System," Journal of Microwave Power & Electromagnetic Energy, 28(2), pp. 93-103, (1993).
3. W. Xi and W.R. Tinga, "Error Analysis and Permittivity Measurements with Re-entrant High-Temperature Dielectrometer," Journal of Microwave Power & Electromagnetic Energy, 28(2), pp. 104-112, (1993).

4. Private communication with Chuck Schietinger, Luxtron Accufiber.
5. Y.S Touloukian and D.P. DeWitt, **Thermophysical Properties of Matter, Vol. 8, Thermal Radiative Properties - Nonmetallic Solids**. (IFI/Plenum, New York, 1972), p. 392.
6. T.D. McGee, **Principles and Methods of Temperature Measurement**, (John Wiley & Sons, New York, 1988), pp364-367.

DISCLAIMER

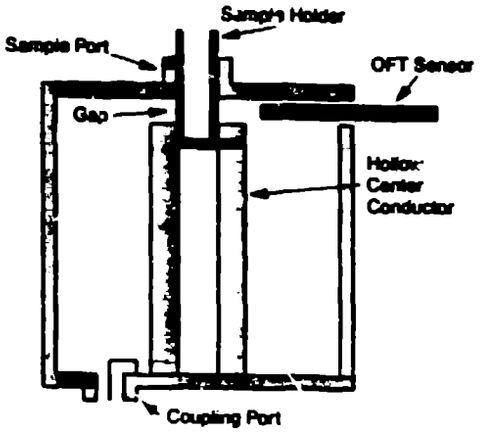

Figure 1a. Positioning of the OFT lightpipe sensors shown in sideview.

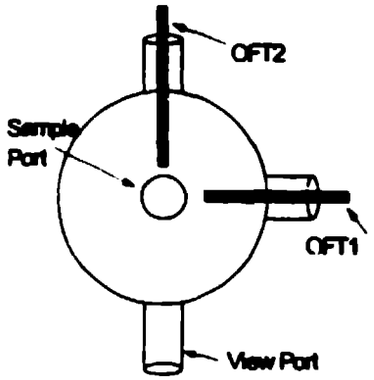

Figure 1b. Positioning of the OFT lightpipe sensors in topview. OFT1 is the control OFT and OFT2 is the dual-wavelength OFT.

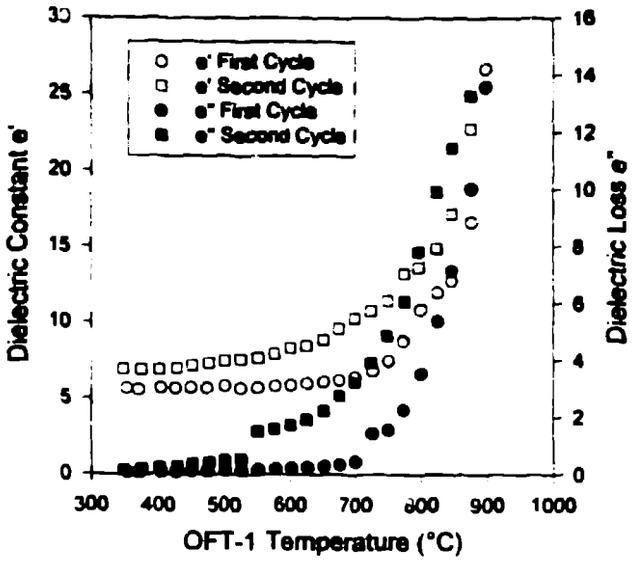

Figure 2. Measured dielectric constants for a zirconia-based powder sample versus temperature measured by the control OFT. Mean sample density is 2.78 g/ml. Data for two measurement cycles are given.

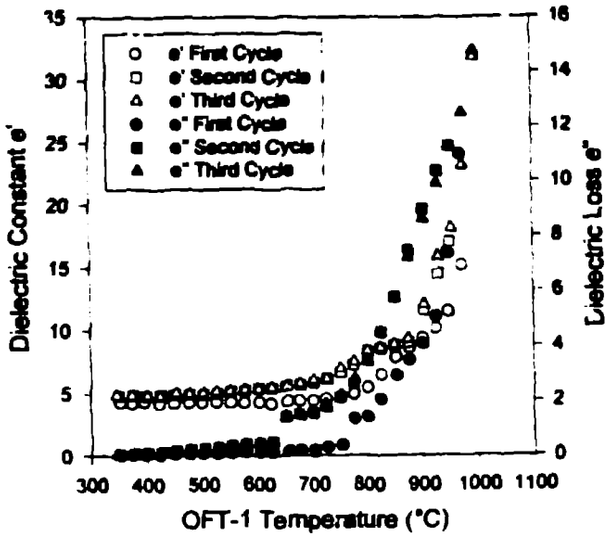

Figure 3. Measured dielectric constants for a zirconia-based chopped fiber sample versus temperature measured by the control OFT. Mean sample density is 1.82 g/ml. Data for three measurement cycles are given.

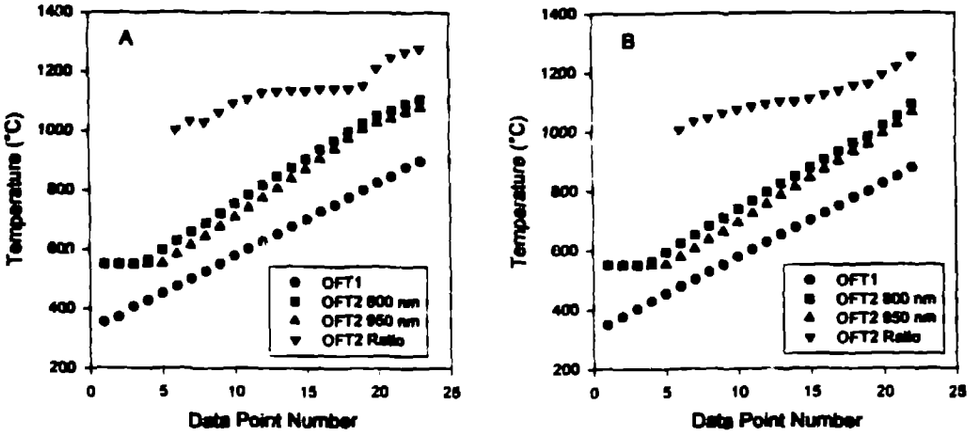

Figure 4. Measured temperatures for the zirconia-based powder sample in Figure 2 for the first (A) and second (B) measurement cycles at the same position. Data is plotted against its data point number in each measurement cycle.

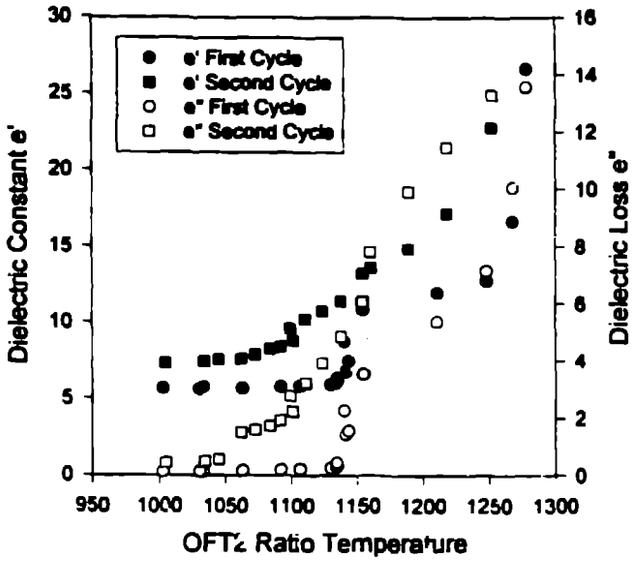

Figure 5. Dielectric constants for powder sample in Figure 2 versus the OFT2 ratio temperature.