USING CONDUCTING NANOPARTICLES TO REDUCE THE SURFACE CHARGING OF CERAMICS*

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Abstract

Ceramics used in vacuum for various purposes suffer from the problem of surface charging in the presence of energetic free electrons. A novel technique has been proposed to reduce the charging effects by filling pores in the ceramic with conductive nanoparticles. Pores in ceramics can be formed in a chain with varying depths depending on sintering temperatures and methods for creating the pores. We report on the preparation and measurements of ceramic matrix pre-forms prior to the capillary infiltration of nanoparticles.

INTRODUCTION

The charging of insulating ceramics in a vacuum is a common problem in the presence of energetic electrons due to secondary electron emission with ratios of about 7:1 from the ceramic. Typically this problem is addressed by adding a surface coating to the ceramic of materials such as TiN (titanium nitride) or other suitable material with low secondary electron yields. The thickness (~15 angstroms) of the TiN coating on RF windows, high voltage ceramics, and lossy dielectrics must be carefully controlled to minimize losses and heating of the ceramic. RF absorbing materials such as used in particle accelerator environments may have DC conductivities that decrease when cooled to cryogenic temperatures [1]. The chemistry of these materials must be carefully formulated and controlled specifically for cryogenic applications to eliminate charging. However, various manufacturers of lossy ceramics may not control the manufacturing process of their products "specifically" for cryogenic applications.

The time and temperature chosen for sintering powders to form a solid ceramic are typically chosen based upon two material considerations: densification and grain growth. Densification is the reduction of pore volumes and grain size dominates the mechanical properties. Most ceramics used in vacuum systems are sintered for maximum strength with high densification even though the final end use of the ceramic may not benefit from the elimination of pores.

There are three types of pores found in ceramics: open, closed, and thru pores. Open pores are open to a surface and can be filled with liquids through capillary action. Closed pores are not accessible and are essentially trapped volumes of the sintering atmosphere. Thru pores are passageways through the bulk of a ceramic. Examples of pores and grain structures are shown in Figure 1 for sintered Al_2O_3.

In this paper we report on the work to date in preparing ceramic matrix pre-forms prior to the capillary infiltration of nanoparticle slurry. The chemistry of these pre-forms is designed so that the resultant ceramic is useful as a lossy ceramic at cryogenic temperatures.
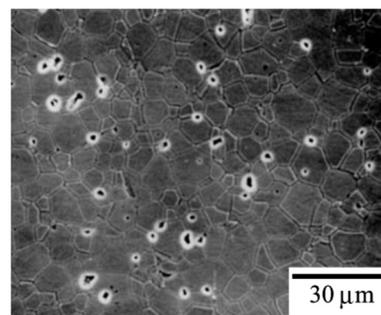
Figure 1: Typical microstructure of sintered Al_2O_3 showing pores and grain structure [2].

TECHNICAL APPROACH

Carbon loading of ceramics by several manufacturers has been found to be adequate for lossy ceramics at cryogenic temperatures [3]. But to use the carbon in any form, the sintering atmosphere for the ceramic matrix must be a non-reducing atmosphere. Otherwise, the formation of CO and CO_2 at temperatures of about 1100-1600°F will volatilize the carbon from the matrix and leave behind open pores of the size of the individual carbon particles or their agglomerates. This may be a problem if the carbon is the only form of loss within the ceramic matrix.

In the studies designed for this research, the volatilization of the carbon in the pre-load leaves behind open pores to be filled by a slurry of copper nanoparticles. In addition, some percentage of the carbon particles will remain in the closed pores because they are trapped from the sintering atmosphere by the surrounding ceramic matrix.

Initially GS-4827 nano-graphite powder will be used with a particle size distribution from 0.10μm to 10μm. It is designed specifically for void formation in dense ceramic materials among other uses. Based upon our examination and use of the ceramic preforms made from this mixture of carbon and alumina dominant powders we may choose to reduce the particle size distribution of the carbon in further experiments.

For copper nanoparticles we will use Applied Nanotech's copper nanoparticle ink, Cu-IJ70-30, made for printable electronics. We will experiment with various

concentrations, measure infiltration rates, and perform single frequency measurements of the complex dielectric constant of the ceramic pre-forms in a cavity pillbox measurement. Based upon these measurements, the variables of the pre-form sintering time and temperature, carbon particle size distribution, and copper ink concentration will be adjusted.

Sintering Time and Temperature

In general, as the ceramic is being sintered, the pores are being reduced in volume and densification occurs. There is also a reduction in surface volume and consequently a reduction in surface energy. Models of sintering processes are relatively complex and described in detail in the book cited in reference [2]. Grain size is determined by many different variables, based upon the chemistry of the sintered material both as additives and contaminants. These variables will also be studied in the Phase I effort latter in the program. For now we will concentrate on porosity as a function of sintering temperature and the addition of the carbon to the ceramic mixture.

Measurements of Porosity and Density

The measurement of porosity is important because it will tell us how much of the nanoparticle slurry will be consumed by capillary action into the open pores. Weighing the ceramic before and after immersion into water provides a good simple estimate of the porosity. The added weight of the water in grams is the cubic centimetres of pore volume in the preform.

Density is approximately 1-porosity, and Table 1 is an example of "density" measurements made with carbon and a ceramic mixture sintered at various temperatures. What is missing in this calculation is the closed pore volume, so it is imperfect for a measurement of true density.

Table 1: "Density" Measurements

% by weight of Carbon	Sintering Temperature		
	1007C	1119C	1222C
0.22%	86.95%	92.67%	99.79%
0.52%	84.75%	90.91%	99.79%
1.50%	84.90%	88.93%	99.75%

With this information a sintering temperature for the preforms is chosen for the addition of the nanoparticles. From Table 1, the optimum temperature appears to be 1119C. At 1007C, the sintering of the ceramic appears to be incomplete compared to the 1119C sintering temperature where the change in density is approximately linear with respect to the amount of carbon added to the mixture. At the higher temperature, 1222C, the density is so high that there may not be enough pores to fill with the nanoparticles. These early conclusions may change as further experimentation is performed during this Phase I period of the project.

Measurements of Open Pore Length

One can also determine an average depth of the open pores by dividing the volume of all pores by the surface area of the preform times the porosity. (This assumes the porosity percentage is the same for surface area as it is for volume, and that the pores are cylinders of constant diameter.) This is not exact, but gives a figure of merit one can use to compare various chemistries.

This is shown in Table 2 for porosity measurements made with SiC as the additive in a ceramic mixture. (We will perform these types of measurements for preforms made with carbon as the additive.) This data can also be used to determine an optimum thickness for a ceramic that could be used in an application where the thru pores, filled with nanoparticles, provide a path to ground for removing charge build-up.

In this particular mixture, the porosity is quite high, and the average depth is 5mm. A direct measurement of the impact of this depth will be made during Phase I, where the resistivity of the preforms will be determined as a function of the thickness. This will be done by making a measurement, removing material, and making a subsequent measurement.

Table 2: Pore Depth in Ceramics with % of SiC

grams of SiC	% SiC	V (cm^3)	water weight (g)	dry weight (g)	volume of water (g,cc)	min % porosity	avg depth of penetration (mm)	total surface area (cm^2)
100	6%	43.52	83.7	70.7	13	29.9%	5.211	83.52
200	11%	39.46	80.5	68.4	12.1	30.7%	5.009	78.78
300	17%	46.51	91.2	77.9	13.3	28.6%	5.177	89.84
400	22%	47.71	97.3	83.6	13.7	28.7%	5.379	88.7
500	28%	54.84	111	96.3	14.7	26.8%	5.552	98.76

Microwave Measurements and Process Steps

Currently preforms of the mixtures shown in Table 1 are out at ceramic grinders making cylinders that will be used to test samples at the JLab. These cylinders are 1.5cm in diameter and 1cm long to fit within a 1.5 GHz cavity. Measurements will be made of the complex dielectric constant without the addition of nanoparticles.

The ceramics will then be loaded with copper nanoparticles and a second set of dielectric measurements will be taken. In addition to a dielectric measurement, a resistivity measurement will also be made. From this we can then determine some of the other variables that will need to be evaluated; for example, the density of the nanoparticle slurry used for the capillary action pulling the slurry into the open pores.

Nickel nanoparticle slurry is also available to infuse into the ceramic preforms. Measurements of the complex dielectric constant will be used to determine if the material of the nanoparticle is significant in making this type of dielectric.

After the infusion of the nanoparticles is completed a second firing will be made. This firing is to be done in a reducing atmosphere at the same temperature that was used for sintering. This means that in the case of copper there will be melting of the nanoparticles, and in the case of nickel there will not be. Again, after this process step, dielectric and resistivity measurements will be made.

CONCLUSION

At this stage of the Phase I, materials have been identified and procured, initial experiments performed to define process steps for the various processes identified and controls established for a successful conclusion to a process for developing a new class of ceramic matrix.

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