Tailored Powder Composites by Freeze Drying, Electrophoretic Deposition and Sintering

Eugene A. Olevsky and Xuan Wang

San Diego State University, College of Engineering, Powder Technology Laboratory
5500 Campanile Dr, San Diego, CA 92182-1323, USA
eolevsky@mail.sdsu.edu

Abstract

Two approaches for the fabrication of tailored powder composites with specially distributed pore-grain structure and chemical composition are investigated. Electrophoretic Deposition (EPD) followed by microwave sintering is employed to obtain functionally graded materials (FGM) by in-situ controlling the deposition bath suspension composition. Al_2O_3/ZrO_2 and zeolite FGM are successfully synthesized using this technique. In order to fabricate an aligned porous structure, unidirectional freezing followed by freeze drying and sintering is employed. By controlling the temperature gradient during freezing of powder slurry, a unidirectional ice-ceramic structure is obtained. The frozen specimen is then subjected to freeze drying to sublimate the ice. The obtained capillary-porous ceramic specimen is consolidated by sintering. The sintering of the graded structure is modeled by the continuum theory of sintering.

Keywords : sintering, freeze-drying, functionally-graded, capillary-porous

1. Introduction

In the present research, functionally graded and directional green powder composites are produced by electrophoretic deposition and freeze drying. The fabricated tailored green components are subjected to microwave sintering with the purpose of rapid densification with grain size retention.

2. Experiments

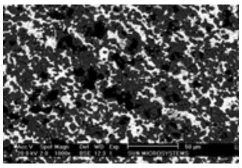
For heterogeneous materials, the solution of the inverse sintering problem will indubitably lead to the request for some complex shape functionally structured (in particular, graded) initial green specimen. How can such a specimen be produced?

The first green pre-sintering specimen's assembly approach considered in the project is the electrophoretic deposition (EPD): assembling powder particles from suspensions under the influence of an electric field. Using this methodology, FGM disks with varying along their axes concentrations of alumina and zirconia have been produced.

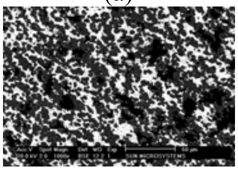
During microwave sintering, in order to avoid rapid heating and cooling, stepwise strategy was employed. The total sintering time was 1 hour. After sintering, the FGM specimens were characterized by SEM. Figure 1 shows the microstructure of one of the FGM samples. The white area is ZrO_2 while the gray area is Al_2O_3, and the black areas are pores. It is clear that the composition of ZrO_2 changes from one side to the other from Figure 1 (a) to (c).

The second green specimen assembly approach is freeze drying. Here the ultimate goal is to be able to fabricate functional multi-phase composite materials with functional gradient structures including unidirectional aligned pores. Freeze drying is a process in which the water in materials is first frozen into ice and then been converted directly into water vapor under special temperature and pressure. The ZrO_2 preforms with aligned channels used in this work were prepared based on the process introduced by Fukasawa [1]. The slurry was poured into a cylindrical mold made of fluorocarbon. There was an aluminum rod under the slurry with the other end dipping into liquid nitrogen. The ZrO_2 slurry was poured into the mold. After the entire slurry was frozen, it was removed from the mold and dried in a freeze-dryer (Labconco FreeZone 1) for 24 hours to sublimate the ice.

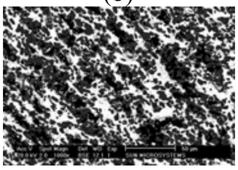
The dried sample was sintered in a tube furnace in air at 1400°C for 2 hours. The heating rate was 10°C/min. After sintering, the preform was cooled at the rate of 10 °C/min down to room temperature. The sintered ZrO_2 has aligned channels parallel to the direction of solidification of ice. Figure 2 shows the sintered specimen with aligned porosity. The white area is the ZrO_2 skeleton; while the black area is the epoxy for mounting. The specimens are 0.5 inch in diameter and 0.5 inch in height. The sintered specimen was highly porous because of the presence of aligned channels.



(a)



(b)



(c)

Fig. 1. Microstructure of disk-shape FGM (a) Al_2O_3 rich layer (b) Intermediate layer (c) ZrO_2 rich layer

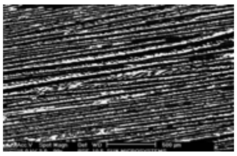


Fig. 2. Sintered ZrO_2 aligned porous structure

The aligned pores are opened extending along the solidification direction. The unidirectional solidification generates temperature gradient in the slurry. As a result, the ice dendrite grows along the temperature gradient direction. Because ZrO_2 particles are insoluble in water, they were repelled from the ice dendrites and trapped in between the columnar ice dendrites to form the aligned porous structure. It can be seen from Figure 5 (b) that there were some protruded ceramic agglomerates on the walls of the pores. These ceramic agglomerates could be formed because they were trapped by the second dendrite arms during freezing.

3. Modeling

The sintering of an FGM disk, which is made of Al_2O_3 and ZrO_2, was simulated using the results obtained by Maximenko *et al*. [2] based on the continuum theory of sintering [3]. The disk is partitioned into four layers; each layer was assigned a material property. It was assumed that the porosity remains the same at each layer, only the composition changes along the thickness direction. In the simulation, the alumina and zirconia particle sizes were taken as 5.0 and 0.5 micron respectively. The simulation results are shown in Fig. 3. It is clear that the upper layer, which contains more zirconia, densifies faster than the bottom layer. The initial porosity of the specimen was set to be θ=0.35. In the end of sintering, the top layer has a porosity of 0.09, the bottom layer has a porosity of 0.15.

This is because the top layer has more zirconia powder, whose particle size is ten times smaller than that of alumina powder. Smaller particles cause higher densification rates.

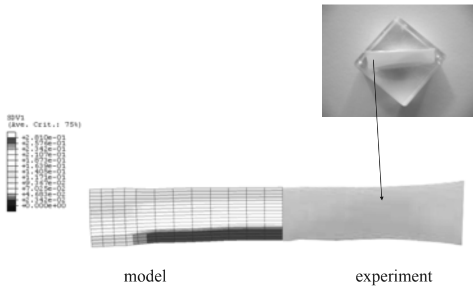


Fig. 3. FEM modeling of shape change and distortion

The results of modeling agree satisfactorily with the experimental results (see Fig. 3). The next step is the solution of the inverse problem of sintering, when the initial specimen's shape before sintering is optimized in such a way that the specimen assumes the desired final shape after sintering. The authors are currently carrying out the research work dedicated to this problem's model solution and its experimental verification.

4. Summary

Al_2O_3/ZrO_2 3-D FGM structure (obtained by electrophoretic deposition) and alumina capillary-porous structure (obtained by freeze-drying) were successfully densified by microwave sintering. A stepwise heating regime was adopted in order to avoid cracking. The sintered specimens were characterized by SEM and showed clearly the graded/textured structure. The continuum theory of sintering has been employed for modeling the shape changes of the graded specimen during sintering. The modeling results agree satisfactorily with the experimental data.

5. Acknowledgements

The support of the National Science Foundation, Division of Civil and Mechanical Systems (Grant CMS-030115), Division of Materials Research (Grant DMR-0313346), and Division of Manufacturing and Industrial Innovations (Grant DMI-0354857) are gratefully appreciated.

6. References

[1]. T. Fukasawa, Z.-Y. Deng, and M. Ando, *J. Am. Ceram. Soc*., 85 (9), 2151 (2002).

[2]. A. L. Maximenko, O. Van Der Biest, and E. A. Olevsky, Prediction of Initial Shape of Functionally Graded Ceramic Pre-Forms For Near-Net-Shape Sintering, *Sci. Sintering*, 35, 5-12 (2003).

[3]. E. Olevsky, Theory of sintering: from discrete to continuum. Invited Review, *Mater. Sci. & Eng. R. Reviews*, 23, 41-100 (1998).