Selective Laser Sintering of Zirconia with Micro-Scale Features

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Abstract

Recent work in Selective Laser Sintering of ceramics at the University of Texas at Austin demonstrates the capability to produce zirconia parts with fine features. Zirconia powder was pre-processed into spherical particles, laser sintered with a sacrificial polymer binder, infiltrated and post-sintered to higher density. Optical micrographs show that hole sizes of 180 μm are possible in fully ceramic components.

1 Introduction

Selective laser sintering (SLS) was limited initially to low temperature material. Recent work utilizing metals, ceramics and cermets has created new applications for SLS produced components [1, 2]. Studies show that blends of stabilized and unstabilized zirconia powder are resistant to thermal cycling through the monoclinic to tetragonal transformation temperature and exhibit a lower thermal expansion than fully stabilized zirconia [3, 4]. An investigation of indirect ceramic SLS processing has shown the potential to produce micro-scale features in "partially stabilized" zirconia. In addition to micro-scale features and high operating temperature, part impermeability was identified as a desirable feature of the ceramic components. Porosity and liquid surface tension are factors in the part impermeability, as given by the Washburn equation,

$$P = 2\gamma \cos\theta / d \tag{1}$$

where γ is the surface tension of the liquid, θ is the contact angle between the liquid and the solid, d is the pore diameter and P is the pressure head [5]. A liquid will infiltrate to a capillary restriction equal to d for a given pressure, based on the wetting characteristics of the liquid. As the pore size decreases, more pressure is needed to permeate the part.

A series of experiments have been done to characterize the SLS produced zirconia parts and quantify the minimum hole size that may be produced using an SLS Model 125 Workstation. A micro-feature part was built to demonstrate the potential of this processing technique.

2 Experimental Procedure

Granulated yttria-stabilized zirconia powder (Tosoh TZ-8Y) was de-bound and sintered at 1250°C for 2 hours. The pre-sintered powder was mixed with a copolymer and roll-milled for 24 hours. The zirconia-copolymer mixture was SLS processed using an SLS Model 125 Workstation with a CO_2 laser energy density between 10 and 13 J/cm^2, calculated from the

Andrew number formula [6]. The laser spot size was approximately half of a millimeter. SLS green shapes were infiltrated with a colloidal solution of amorphous zirconia (Nyacol Zr100/20). Wetting of the green shapes was improved by adding a surfactant to the colloid. After several infiltration cycles, the green shapes were pyrolyzed to burn off the copolymer binder, crystallize the infiltrated zirconia and densify the parts. The heating schedule consisted of a slow ramp to 500°C, a faster ramp to 1500°C and a 10 hour soak. Infiltration and firing cycles were repeated until adequate strength was achieved.

A thin plate (0.015 inches thick) containing a series of small holes was built to determine the minimum hole size that could be produced using the processing method described above. Hole sizes were measured in the green state and after firing using an optical microscope. A micro-scale nozzle was built with holes of similar size. Green and post-fire dimensions were measured to quantify the amount of shrinkage that occurred during post-processing. Density was measured using the Archimedes method with ethanol. Bend coupons were produced and broken per ASTM C1161-94 to measure flexural strength. After each firing step, roughness was measured using a Surfanalyzer 5000. Pore size was measured via mercury porosimetry using a Micromeritics AutoPore 3000.

3 Result and Discussion

The spherical shape of the granulated zirconia powder was maintained during the de-binding and sintering step. The spherical particle shape improves powder bed packing, thereby increasing the initial density of the SLS part. The pre-sintering step prevents the particles from dissolving in the colloidal zirconia solution during infiltration and eliminates a small amount of shrinkage during post-processing. The average particle size of the pre-sintered powder was 50 μm, determined from SEM micrographs. The smallest hole size that was produced in the thin plate was 180 μm. The size of the holes did not change significantly during firing. An optical micrograph of one of the larger holes is shown in Figure 1. Spherical zirconia particles are surrounded by a crystallized matrix of infiltrated zirconia.

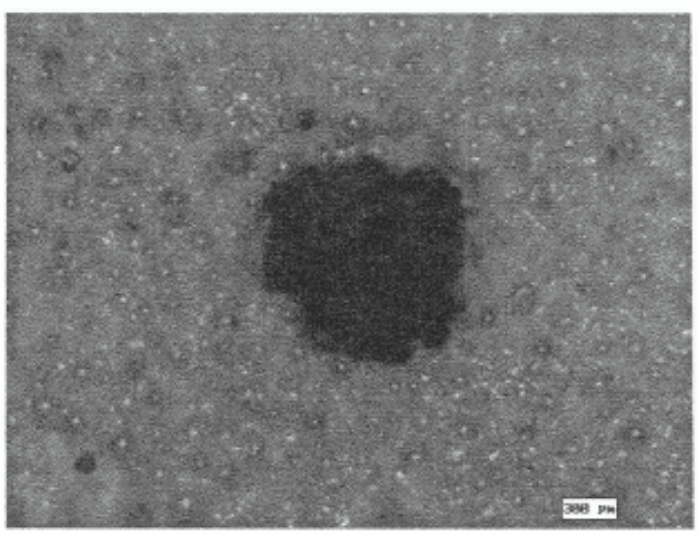

Figure 1: Hole in thin zirconia plate, post fire.

It is encouraging that such small holes can be created from a powder with an average particle size of 50 μm and using a laser spot size not much finer than 500 μm. A photo of the micro-scale nozzle is shown in Figure 2. The holes are close to the same size as that shown in Figure 1. The length of the nozzle is less than 3/4 of an inch.

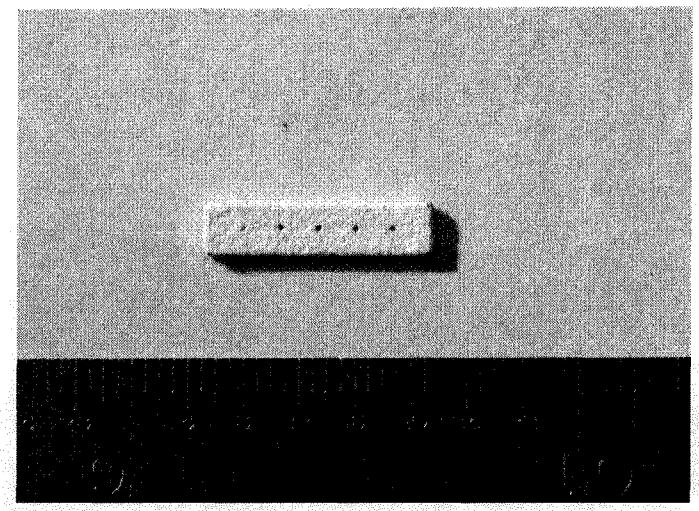

Figure 2: Zirconia Test Coupon with Features

Shrinkage measurements in the x, y and z directions are shown in Figure 3. The extent of shrinkage is not significantly different for samples fired once than for samples fired three times. Hence, the majority of the shrinkage occurred during the first firing cycle. This can be attributed to the rearrangement of the zirconia particles that occurs during intial stage sintering after copolymer burn-out. An average of 13% shrinkage occurred in each direction. No cracking was observed in the fired samples.

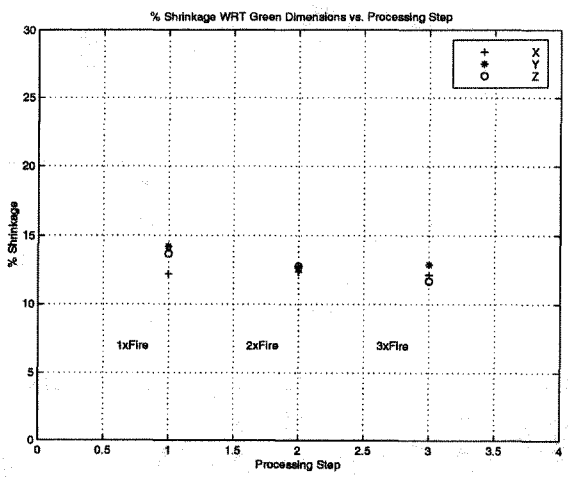

Figure 3: Shrinkage during Post Processing

The density of the SLS parts increased with colloidal zirconia weight gain. The plot in

Figure 4 shows the density of the zirconia parts versus the weight gain of infiltrated zirconia (with respect to the initial Tosoh zirconia weight). A theoretical density of 5.9 g/cm^3 was assumed. Flexural strength also increased with weight gain, as was expected. A plot of the four-point bend strength of green and ceramic specimens is shown in Figure reffig:plot3.

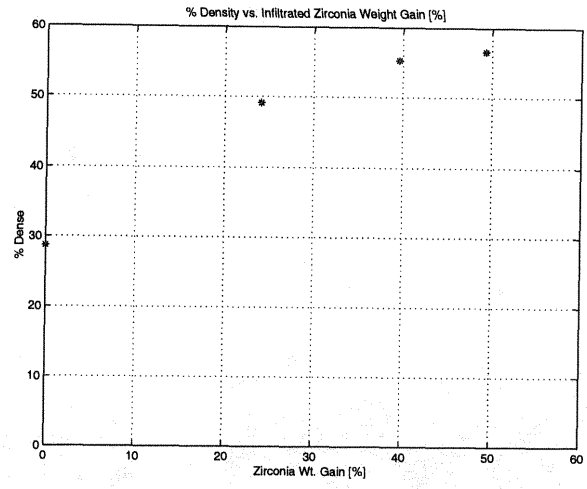

Figure 4: Density vs. Zirconia Weight Gain

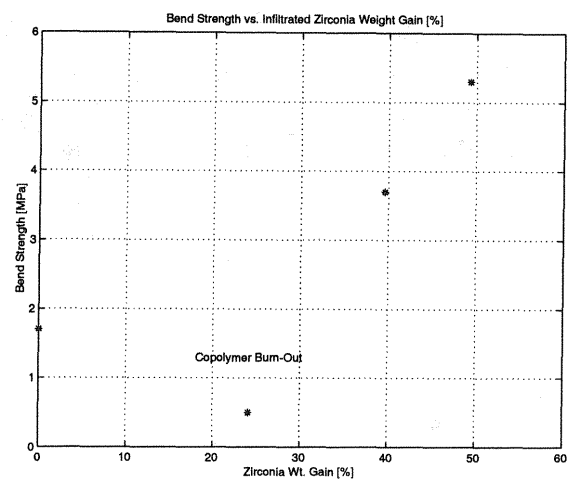

Figure 5: Bend Strength vs. Zirconia Weight Gain

Multiple colloidal infiltration steps smoothed the surface of the SLS part. The roughest surface of an SLS green part is on its side, where the stair-stepping effect is prominent. The average roughness, Ra, of the side of a zirconia SLS green part was 14 μm. After multiple infiltrations, the average roughness decreased to 9 μm on all surfaces.

Mercury porosimetry was used to measure the median pore size based on volume. Figure 7 shows the decrease in size of the largest pores with colloidal zirconia weight gain.

Final pore size was less than 5 μm, corresponding to an infiltrant weight gain of 50%. The pore size can be used to calculate the impermeability of the part to a specific liquid. If we

assume that a pressurized fluid has similar surface energy and wetting characteristics to those of mercury, then a pressure of 50 psia would be necessary to permeate this part through its largest pores according to the Washburn model and experimental porosimetry data.

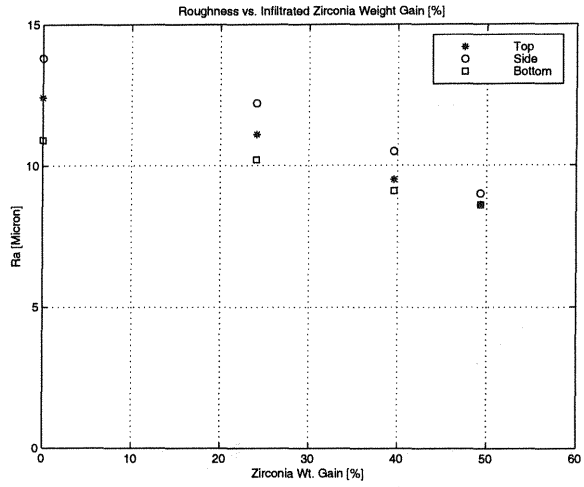

Figure 6: Roughness vs. Zirconia Weight Gain

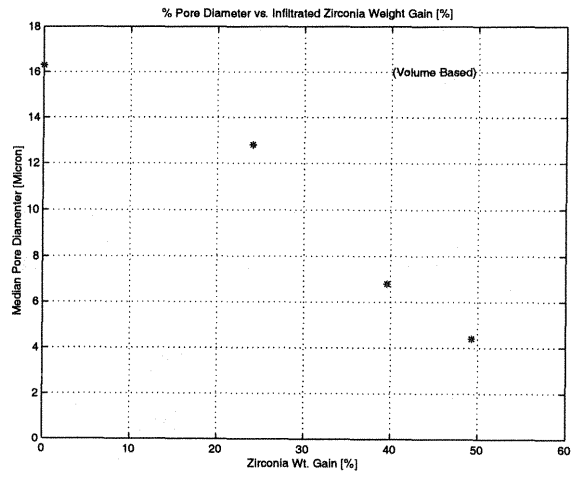

Figure 7: Pore Size vs. Zirconia Weight Gain

4 Conclusion

The work done shows that indirect processing of micro-scale zirconia ceramics via selective laser sintering is feasible. A minimum hole size of 180 μm was produced. With repeated infiltration, an average roughness of 9 μm was achieved on all surfaces, and the median pore size was reduced to less than 5 μm. The small pore size supports pressures up to 50 psia before mercury permeates the part. No cracking was observed in pieces that went through multiple

firing cycles. To produce components with finer features, future experiments could incorporate a smaller laser spot size and a reduced particle size.

References

[1] S. Das, et al., *Direct SLS Processing for Production of Cermet Composite Turbine Sealing Components*, Materials and Manufacturing Processes, Vol. 13, No. 2, pp. 241-261, (1998).

[2] J.W. Barlow and N.K. Vail, *Method of Producing High-Temperature Parts by Way of Low-Temperature Sintering*, U.S. Patent 5,284,695, (1994).

[3] E.D. Calvert, *An Investment Mold for Titanium Casting*, U.S. Bureau of Mines Report of Investigations, n. 8541, (1981) p.20.

[4] N. Harlan, D. L. Bourell, J.J. Beaman, *Titanium Casting Molds via Selective Laser Sintering*, Solid Freeform Fabrication Proceedings, (UT Austin), Aug. 1998.

[5] G. de With, *Process Control in the Manufacture of Ceramics*, Materials Science and Technology - A Comprehensive Treatment, Vol. 17A, p. 45, (1996).

[6] N.K. Vail, *Preparation and Characterization of Microencapsulated Finely Divided Ceramic Materials for SLS*, Ph.D. Disseration, The University of Texas at Austin, 1994.