

**Titanium Casting Molds via Selective Laser Sintering**  
Nicole Harlan, David Bourell, Joe Beaman  
The University of Texas at Austin

**Abstract**

A mold material system has been developed that can be SLS processed and used to cast titanium alloys. Stabilized zirconia, chosen for its low reactivity with molten titanium, has been sintered into mold shapes. The molds have been infiltrated with a colloidal solution of unstabilized zirconia and fired to create a partially stabilized structure. SEM analysis shows that the unstabilized zirconia forms bridges between the larger stabilized zirconia particles that provide strength to the mold.

**Introduction**

Titanium has interested designers for years because of its light weight, high strength, corrosion resistance and its abundance as a natural resource. Difficulties in room-temperature machining and forming have prevented wider spread use of titanium. Near-net-shape fabrication processes such as casting are the most commonly used methods to produce titanium parts since they require minimal post machining.

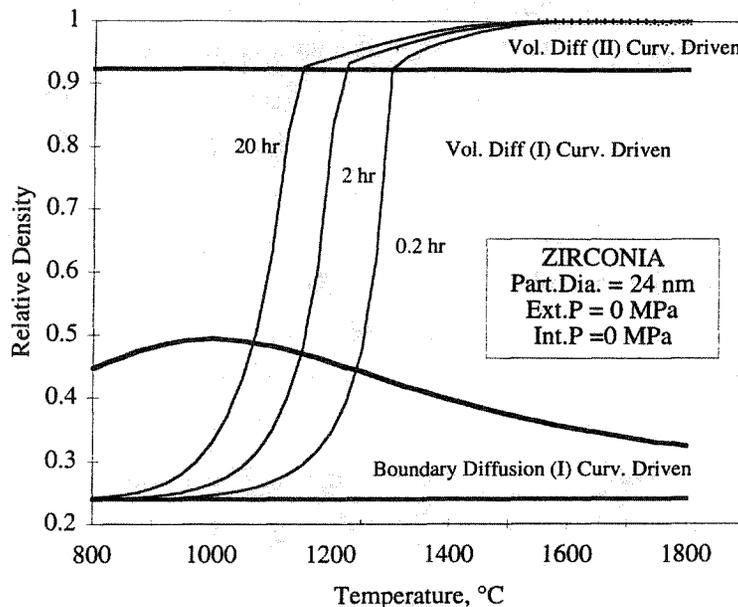
Investment casting is a conventional way to produce titanium parts. Because molten titanium reacts with most solids, liquids and gases, specific mold materials and casting environments are used to minimize contamination of the final part. Rammed graphite molds are widely used because of the low cost and availability of graphite. However, the carbon reacts with titanium and forms a hardened titanium shell on the cast part that must be machined off. When casting parts in small quantities, a less reactive, more expensive mold material can be cost efficient by reducing the post-machining costs.

Several studies show that zirconia is one of the least reactive materials with molten titanium [1,2]. However, zirconia undergoes a destructive phase transformation at 1100°C that can crack the mold during casting. It converts from a monoclinic to a tetragonal atomic structure, resulting in a 7 percent volume shrinkage. The addition of a small amount of yttria stabilizes the zirconia in a cubic structure that does not change phase at 1100°C [3]. If a cubic phase zirconia mold is fabricated and infiltrated with unstabilized monoclinic zirconia, a "partially stabilized" structure is created. The partially stabilized zirconia structure has better thermal shock resistance than either the unstabilized or fully stabilized structures [4].

Selective laser sintering (SLS) has been used to build partially stabilized zirconia molds for titanium casting. Prototype titanium parts have applications in the aerospace and automotive fields and as customer specific biomedical implants.

### Experimental Procedure

Granulated yttria-stabilized zirconia powder from TOSOH Ceramic Corporation was used as the base material for the casting mold. The average zirconia crystallite size was 24 nm; the average granulate size was approximately 50  $\mu\text{m}$ . To prevent post SLS shrinkage, the granulated particles were presintered for one hour at 500°C followed by two hours at 1250°C to burn off the binder and densify each particle. The sintering schedule was determined from a sintering map generated by Bourell, shown below [5].



**Figure 1.** Zirconia sintering map

The pre-sintered powder density was measured using a Quantachrome Ultrapycnometer 1000.

The SLS binder, an 80:20 molar blend of methylmethacrylate and butylmethacrylate, respectively, was produced by methods discussed elsewhere [6]. This particular copolymer binder was chosen because it completely “unzips” during firing, leaving no contaminating residue [7]. The copolymer binder was spray dried into fine particles using an Anhydro Laboratory 1 Model Spray Drier. The resulting powder was on

the order of 5  $\mu\text{m}$ . Copolymer powder density was measured using the same Quantachrome gas pycnometer mentioned earlier. The melt flow index, ASTM D1238, of the copolymer was measured at 200°C using a Kayeness Galaxy I capillary rheometer. Copolymer flexural properties were tested per ASTM D790 using a three point bend apparatus. Ten samples were used for each measurement.

Preliminary blends of pre-sintered stabilized zirconia powder and 10 to 40 vol% copolymer powder, in increments of 5 vol%, were heated to 175°C in a furnace. Based on visual inspection, it was determined that at least 20 vol% copolymer was needed to bind the zirconia together in a solid mass, and blends containing 30 vol% copolymer possessed sufficient handling strength. Hence, 20 vol% and 30 vol% copolymer-zirconia blends were tested for SLS processing. The appropriate amounts of copolymer and zirconia were weighed out and mixed together in a rolling mill for 24 hours.

An SLS Model 125 Workstation was used to build bend test specimens. A layer thickness of 0.005 inches, scan spacing of 0.003 inches and CO<sub>2</sub> laser power of 5 watts were used. Laser scan speed was 16 in/s. The fabricated bend specimens, at least five in each set, were tested per ASTM D790 using a four point bend apparatus. Open porosity of the samples was measured using Archimedes density measurements.

A set of 20 vol% and 30 vol% copolymer SLS samples were infiltrated using Nyacol Zr100/20 colloidal zirconia. The Zr100/20 colloidal solution is 20 wt% unstabilized zirconia suspended in water by a nitrate counter ion. The zirconia crystallite size is 100 nm. The colloidal solution would not infiltrate the samples in its original concentration, so it was blended in 3:2 and 1:1 ratios with methanol to decrease viscosity and facilitate infiltration. The SLS samples were infiltrated with solution and dried until no further solution absorption was observed, typically after four infiltrations. Weight gain during infiltration was measured to determine a) whether the 20 or 30 vol% samples absorbed more infiltrant and b) which colloidal zirconia:methanol ratio resulted in more solid weight gain. At least five specimens were tested in each experiment. Sample weight was measured initially, after the specimens were dried 24 hours following the final infiltration, and after a 60 minute cure cycle at 100 and 150°C.

The following schedule was used to fire the infiltrated specimens. It was designed to burn off the copolymer binder and sinter the infiltrated zirconia to the base particle structure:

Heat Schedule	Desired Effect
Ramp 1°C/min to 500 °C	Slow ramp to prevent cracking
Dwell 60 minutes	Copolymer burn off
Ramp 20°C/min to 1000°C	
Ramp 10°C/min to 1400°C	
Dwell 480 minutes	Zirconia sintering and grain growth
Ramp 10°C/min to 25°C	

The change in the ramp rate from 20 to 10°C/min at 1000°C was due to furnace limitations. SEM micrographs were taken on the final specimens to determine the effectiveness of the zirconia infiltrant as a binder for the stabilized zirconia particles. No mechanical testing has been done.

### Results and Discussion

Specimen preparation and SEM analysis show the TOSOH granulated particles were sintered to full density during the 1250°C thermal cycle. This agrees with the sintering map prediction shown earlier.

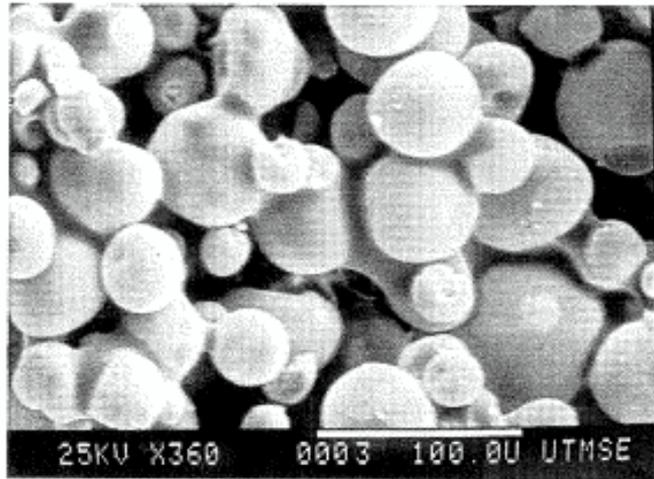
Pycnometer Density	Theoretical Density
6.05 +/- 0.01 g/cc	5.9 g/cc

The 80:20 methylmethacrylate butylmethacrylate copolymer had comparable material properties to the same copolymer produced by Vail, shown in the following table [8]. Copolymer powder density was measured as 1.24 g/cc.

#### *Copolymer Material Testing*

	Melt Flow Index g/10 min	Flexural Strength [Pa] x 10 <sup>4</sup>	Flexural Modulus [Pa] x 10 <sup>6</sup>
80/20	17.9	2.6 +/- 0.2	2.20 +/- 0.04
80/20, Vail	15	2.6 +/- 0.1	2.37 +/- 0.08

Figure 2 shows a close up of the copolymer binder tacking the stabilized zirconia particles together after SLS processing.



**Figure 2.** Zirconia + 30 vol% copolymer after SLS processing

The coupons produced with 30 vol% copolymer were easier to handle than those with 20 vol% copolymer. The latter chipped and broke during transport and handling. The following two tables show open porosity and mechanical testing data for the 20 vol% and 30 vol% copolymer samples.

***Archimedes Density Measurements***

	Open Porosity vol%
zirconia + 20 vol% copolymer	35
zirconia + 30 vol% copolymer	23

***Four Point Bend Testing***

	Flexural Strength [Pa] x 10 <sup>2</sup>
zirconia + 20 vol% copolymer	8.0 +- 0.6
zirconia + 30 vol% copolymer	14.6 +- 0.6

The lower amount of copolymer binder and higher open porosity resulted in lower strength for the 20 vol% samples. Strength decreased by almost a factor of 2 from the 30 vol% samples.

During infiltration, a colloidal solution with the highest possible solid weight percent should be used to deposit the maximum amount of material in the green part. However, colloidal solutions with high solid weight percentages can be viscous and may not penetrate the entire sample. The original concentration of the colloidal zirconia (20 wt%  $ZrO_2$ ) could not be used because it did not penetrate the samples at room temperature. Testing showed that diluting the colloidal solution with methanol in a 3:2 ratio caused immediate sample infiltration. No advantage was seen when the colloidal solution was diluted below a 3:2 colloid-methanol ratio, as shown in Figure 3. Weight gain is given as a ratio of the original dry weight to the cured weight of the sample.

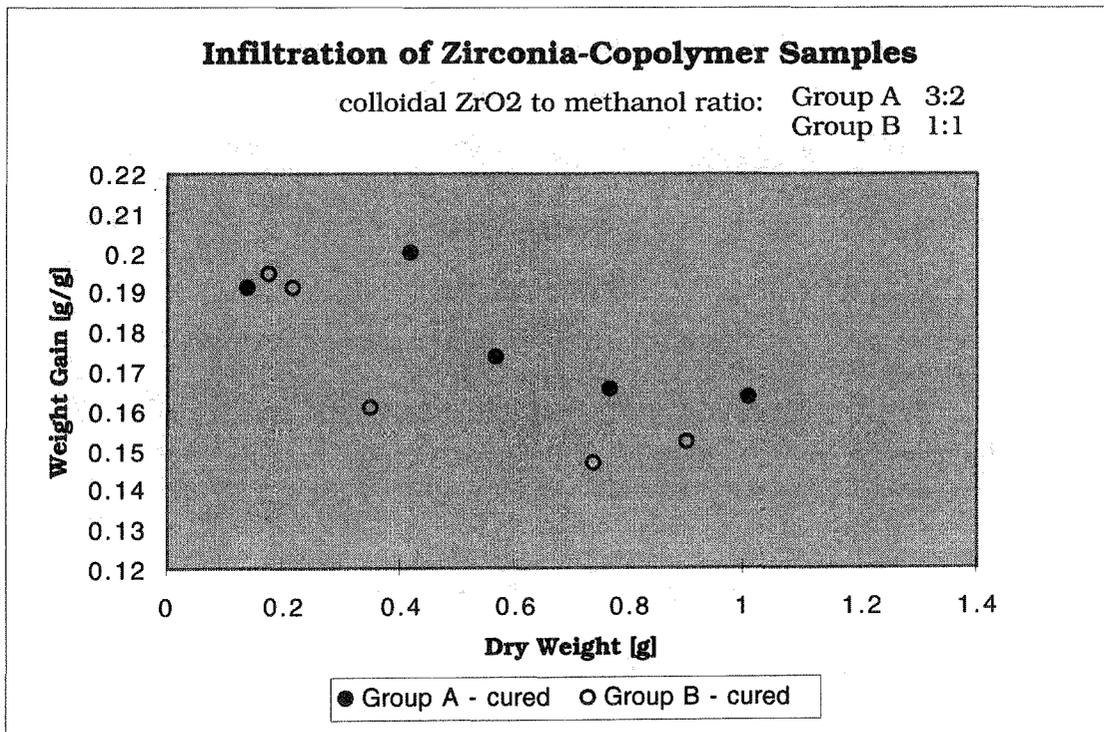
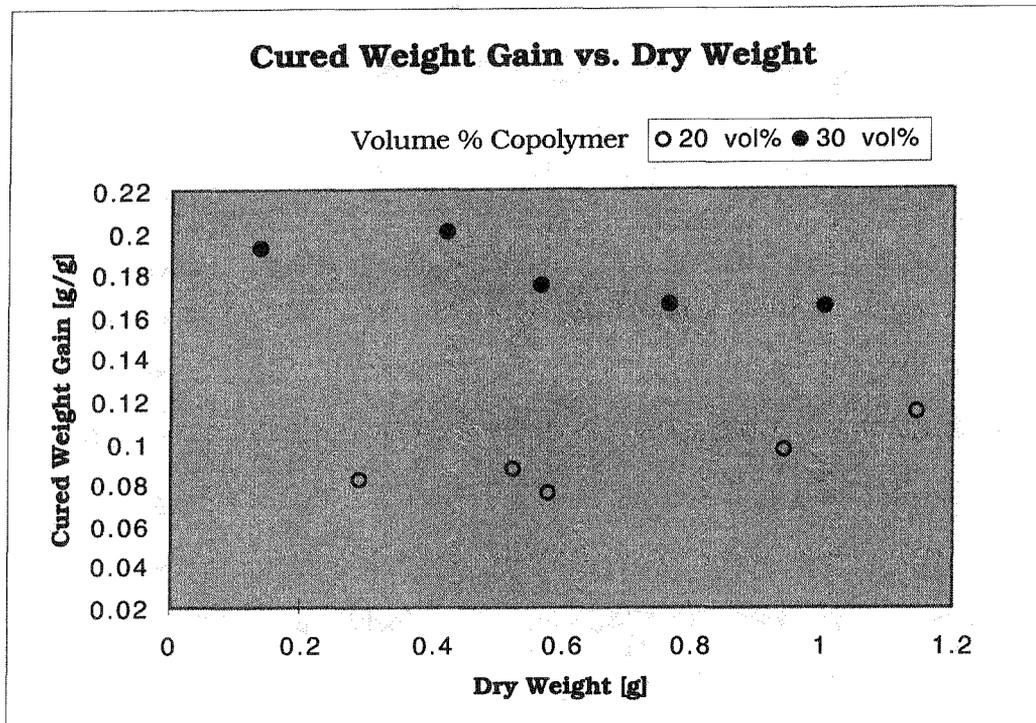


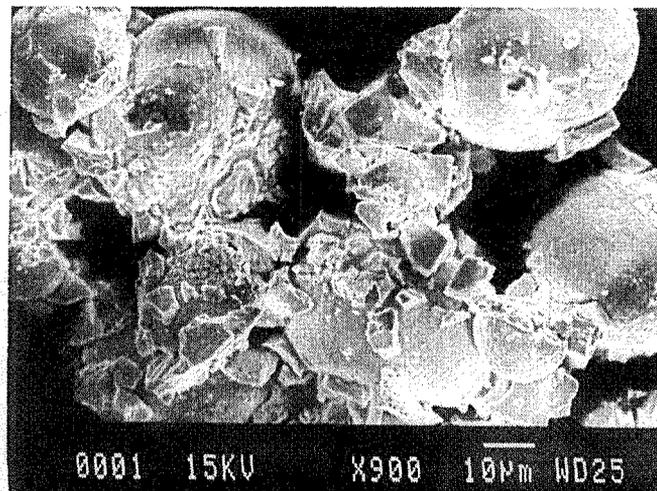
Figure 3. Weight Gain Based on Infiltrant Concentration

The 3:2 ratio resulted in more weight gain after curing than the 1:1 solution. Weight gain measurements also show that the 30 vol% copolymer specimens absorbed more infiltrant than the 20 vol% copolymer samples, shown in Figure 4.



**Figure 4.** Weight Gain in 20 vol% and 30 vol% Copolymer Samples

An SEM micrograph of a specimen fired at 1400 °C for 8 hours, Figure 5, shows that the copolymer binder has burnt off and that the infiltrated zirconia, identified by its irregular shape, has formed bridges between the spherical zirconia particles



**Figure 5.** Zirconia + infiltrated zirconia

This result is promising because the infiltrated zirconia has replaced the copolymer bridges and can provide strength in the mold.

## Conclusion

Mixtures of stabilized zirconia powder and a 80:20 PMMA-BMA copolymer binder have been selective laser sintered to form casting mold green shapes. Parts made from a 30 vol% copolymer - zirconia powder blend were found to have higher green strength than those made from a 20 vol% copolymer - zirconia blend. A solution of colloidal zirconia (3 parts) and methanol (2 parts), infiltrates the porous green shapes at room temperature. The 30 vol% copolymer green parts experience a higher weight gain than 20 vol% copolymer green parts when infiltrated. After binder burn out and firing at 1400°C, bridges of unstabilized zirconia from the colloidal solution remain as structural bonds between the stabilized zirconia particles.

## Acknowledgments

I would like to acknowledge Dr. Neal Vail and Dr. Joel Barlow for their guidance in this project and for their assistance in preparing the copolymer.

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