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Lost Mold Rapid Infiltration Forming of Mesoscale Ceramics: Part 1, Fabrication

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Abstract

Free-standing mesoscale ($340\ \mu\text{m} \times 30\ \mu\text{m} \times 20\ \mu\text{m}$) bend bars with an aspect ratio over 15:1 and an edge resolution as fine as a single grain diameter ($\sim 400\ \text{nm}$) have been fabricated in large numbers on refractory ceramic substrates by combining a novel powder processing approach with photoresist molds and an innovative lost-mold thermal process. The colloid and interfacial chemistry of the nanoscale zirconia particulates has been modeled and used to prepare highly concentrated suspensions. Engineering solutions to challenges in mold fabrication and casting have yielded free-standing, crack-free parts. Molds are fabricated using high-aspect-ratio photoresist on ceramic substrates. Green parts are formed using a rapid infiltration method that exploits the shear thinning behavior of the highly concentrated ceramic suspension in combination with gelcasting. The mold is thermally decomposed and the parts are sintered in place on the ceramic substrate. Chemically aided attrition milling disperses and concentrates the as-received 3Y-TZP powder to produce a dense, fine-grained sintered microstructure. Initial three-point bend strength data are comparable to that of conventional zirconia; however, geometric irregularities (e.g., trapezoidal cross sections) are present in this first generation and are discussed with respect to the distribution of bend strength.

I. Introduction

As microfabrication technology expands outside the realm of silicon, ceramics are gaining popularity in microdevices due to their high-temperature capability, chemical stability, electronic properties, and attractive mechanical properties, especially elastic modulus and strength. Recent applications include microchemical reactors,¹ microturbines,² gas sensors,³ and microactuators.⁴ Another application that requires mesoscale fabrication (i.e., micrometer resolution, but part size between $10\ \mu\text{m}$ and $1\ \text{mm}$) is surgical instruments for the next generation of minimally invasive surgery. Chemical inertness, high elastic modulus, and a reliable failure stress are the important material parameters to consider in the surgical instrument application. Many ceramics are chemically inert and have a high elastic modulus. Zirconia, for example, is approved for use in the body as an implantable material in the load bearing artificial hip application.⁵ A reliable failure stress in a surgical instrument ensures safe

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operation during surgery. A reliable failure stress or high Weibull modulus in ceramics can only be achieved by removing strength-limiting processing defects.⁶ However, processing defects in micro- or mesoscale ceramic parts are typically left uncharacterized when a new fabrication technique is developed even though a micrometer-sized defect represents a relatively large flaw in a mesoscale part.

This study presents a manufacturing method to produce high-aspect-ratio parts and provides three-point bend test data on free-standing mesoscale ceramic bend bars. Data based on mesoscale bend bars rather than macroscale analogues are critical for the design of surgical instruments based on compliant mechanisms rather than conventional rigid-link mechanisms.⁷ The discussion will be limited to the newly developed manufacturing method and the evaluation of three-point bend test bars, whereas details on our surgical instrument design can be found in another report.⁸

The goals of the manufacturing process are the production of high aspect ratio (>50:1), thick (between 10 μm and 100 μm), free-standing parts in large numbers (>100 parts) with an edge resolution below 1 μm . Ceramic mesoscale devices have been fabricated using three basic strategies: direct-writing, self-assembly, and directed assembly via processes such as casting.⁹⁻¹² Direct-writing has the ability to create parts directly from a design, which is an advantage in prototyping but not in manufacturing due to its serial nature and the limited number of parts produced. Self-assembly techniques such as microcontact printing¹³ and microtransfer molding¹⁴ are well suited for patterning layers under 10 μm , but poorly suited for thicker parts such as surgical instruments. Only directed assembly via casting has the advantage of parallel manufacturing to create large arrays of free-standing parts and the ability to create thick parts with fine edge resolution.

A lost-mold approach where the mold is made from patterned photoresist was chosen over a soft molding technique¹² in order to prevent fracture by supporting the green parts while maintaining the as-molded geometry. Mold-forming via photolithography is one of the most cost-effective and widely used strategies in micromanufacturing,¹⁵ but there has been difficulty in adapting ceramic powder processing to a lost-mold process where photoresist is used as the mold. This adaptation means adjusting photolithography to refractory substrates such as α -alumina that can withstand the high temperature required for ceramic particulate sintering. Another difficulty is removing the mold material without distorting or fracturing the unsintered ceramic. Mold removal can be accomplished by several methods including thermal decomposition, chemical dissolution, or reactive ion etching. Chemical dissolution has gained favor over thermal decomposition because the dimensional changes that occur over the thermal cycle can lead to cracking.¹⁶ In contrast, chemical dissolution requires chemically resistant binders in large concentrations, which can potentially incorporate carbon or porosity into the sintered body.^{17,18} Additionally, many soluble photoresists cannot achieve the same high aspect ratio that the epoxy-based photoresists achieve without using an expensive X-ray source for the exposure.^{19,20} Reactive ion etching or dry etching is not common for thick photoresist layers due to the inefficiency of the highly cross-linked epoxy-based photoresists to decompose.²¹ However, progress has been made in this area and it is becoming more practical for layers under 100 μm .²² Thermal mold removal is used to produce the bend test bars described in this paper and the tendency for cracking is discussed.

We show that dense (>99.5% theoretical density) bend test specimens can be fabricated from nanoparticles of tetragonal zirconia polycrystals (TZP) by casting into a photoresist mold that is thermally removed. The improvements that made this process viable occurred over several generations of processing interactions. Generation zero (Gen0) demonstrated that mold fabrication on alumina substrates, casting by rapid infiltration forming (RIF) and thermal mold removal were possible, although part yield and overall quality were low. The Gen0 specimens

could be evaluated by three-point bend strength testing. However, average strength of 670 MPa was considered relatively low.⁸ Generation one (Gen1) solved many engineering challenges that will be discussed in this report and produced mesoscale bend bars with high part yield for which bend strength was measured on 18 specimens. Some of the challenges in the Gen1 materials included nanoparticulate de-aggregation, mold rounding from substrate reflectivity,²³ part adhesion to the substrate,²³ and cracking during mold thermolysis.^{16,23} However, geometric irregularities were noticed during the three-point bend testing of the Gen1 specimens. Therefore, second and third generations (Gen2 and Gen3) are being produced to improve the geometry of the bend bars. In a subsequent report, the geometric improvements from Gen1 to Gen2 and Gen3 will be quantified and evaluated by three-point bend testing, thereby, establishing a link between powder processing and strength in the mesoscale TZP ceramics.

II. Materials and Methods

Figure 1 summarizes the overall fabrication process. A class 10 clean room was used for the mask and mold fabrication, whereas all other processing steps occurred in an open lab. The molds were composed of three layers: an antireflective coating on the substrate, an unpatterned photoresist layer, and a photoresist mold layer. An antireflective coating (Barli-II 90, Clariant Corp., Charlotte, NC) was applied to a polished alumina substrate (courtesy of John Rigby, Kyocera Industrial Ceramics Inc., Somerset, NJ) using the manufacturer's recommendations. The unpatterned layer and mold layer were fabricated by spin coating SU-8-25 photoresist (Microchem Corp., Newton, MA) using the manufacturer's recommended spin coating schedule and developer (SU-8 Developer, Microchem Corp.). The photoresist was exposed for 10 s at an intensity of 12 mW/cm².

The as-received, granulated 3 mol% Y₂O₃ tetragonal zirconia powder (3Y-TZP, Tosoh Corp., Tokyo, Japan) was attrition milled at pH 9, the pH value of minimum yttria solubility²⁴ in the presence of 1.5% by mass ammonium polyacrylate (NH₄-PAA) (Darvan 821A, RT Vanderbilt, Norwalk, CT) on a dry 3Y-TZP powder basis. The attrition mill (HDDM-01, Union Process, Akron, OH) was operated at 1000 rpm for 60 min after a 30-min powder addition period using spherical 1 mm yttria-stabilized zirconia media (High Purity Zirconium Dioxide, Union Process). A 750-mL vessel filled with 1007 g of media was used to mill 200 mL of suspension at 43–45 vol% TZP powder with respect to the aqueous suspension. Primary particle size was calculated as the equivalent spherical diameter by BET surface area measurement (Gemini, Micromeritics, Norcross, GA), while the agglomerate size was measured using dynamic light scattering (DLS) (Nano-S, Malvern Instruments, Southborough, MA). A field-emission scanning electron microscope (FE-SEM) (JSM 6700F, JEOL, Tokyo, Japan) and scanning electron microscope (SEM) (S-3000H, Hitachi, Tokyo, Japan) were used to confirm the particle size and agglomerate size measurements, respectively. All electron microscope samples were sputter coated with Au-Pd to prevent charging. ζ potential was measured using electrophoretic light scattering (ZetaPALS, Brookhaven Instruments, Holtsville, NY). A conductivity meter and probe (Model 3200, YSI Inc., Yellow Springs, OH) calibrated against KCl solutions of known ionic strength was used to measure the ionic strength. The rheology of the suspension was measured using a parallel-plate rheometer (CSL 100, Carri-Med Ltd., Dorking, Surrey, U.K.) with a 2° cone geometry.

Methacrylamide and *N,N'*-methylenebisacrylamide (Sigma-Aldrich, St. Louis, MO) were used in a 6:1 mass ratio as the monomer and cross-linking agents to gelcast the suspension based on Janney *et al.*²⁵ The total monomer content was 5% by mass on a dry 3Y-TZP powder basis. Ammonium peroxydisulfate (Sigma-Aldrich) and *N,N',N',N'*-tetramethylethylenediamine (Sigma-Aldrich) were used in a 10:1 mass ratio to initiate and catalyze the polymerization reaction. The initiator and catalyst were 2.5% by mass of the total monomer content.

The suspension is cast into the molds using RIF in which a squeegee (60 Shore type E, Terra Universal, Fullerton, CA) is moved repeatedly over the mold at an angle of 45° at an approximate speed of 10 cm/s. The suspension infiltrates the mold cavities in a manner similar to that of screen printing except the mold, or screen by analogy, is fixed to the substrate. Once cast, the molds were placed into a container with flowing nitrogen bubbled through water to prevent drying during polymerization of the gelcast agents. Nitrogen was used because oxygen can hinder the polymerization reaction on the part surface resulting in spallation.^{26,27} After an hour, the container was partially opened to decrease the humidity slowly and dry the parts.

Mold removal and sintering were accomplished with a single thermal treatment in air using the following cycle: 1°C/min to 400°C with a 2-h hold, and 10°C/min to 1300°C for 2 h followed by a furnace cool. Hot-stage SEM was performed on a FEI Quanta 200 Environmental SEM (Hillsboro, OR) to evaluate the cracking tendency of the parts during mold thermolysis. Gelcast macroscopic specimens (0.5 cm × 0.5 cm × 2 cm) were sintered at 1200°, 1250°, and 1300°C for 2 h to determine the optimal sintering temperature based on Archimedes density measurements and observation of the grain size.

The flexural strength of the zirconia beams was tested using a three-point bend apparatus with a lower span of 227 μm. The more widely used four-point bend test was not practical due to the small sample size. Forces were applied to the beams using an electrostrictive actuator at a constant voltage rate and average displacement rate of 1.2 μm/s. The bars were placed across the testing span using a tungsten microprobe mounted in a 3-axis manipulation stage, preloaded to approximately 20 μN to ensure placement, and loaded until failure, which occurred when the bars were fully fractured at the centrally located point of loading. The time and applied force were recorded 10 times per second. The mesoscale bend bars were molded with the standard ASTM dimensional ratio of 3:4:50 or nominally 25 μm × 33 μm × 417 μm.²⁸ After testing, it was realized that the bars were not orthogonal, but had a trapezoidal cross section similar to silicon beams in a prior report.²⁹ A nominal sintered thickness of 20 μm was used in calculations of the strength of the specimens, but the short-width and long-width dimensions of the trapezoidal cross-section beams were determined from representative SEM photomicrographs, and averaged values were used to calculate bend strength (22 and 30 μm for the short width and long width, respectively). The short-width side was always the top side as-molded. However, the bend bars were too small to optically determine if the shorter width side or longer width side of the specimen was tested in tension. Therefore, two different fracture stresses were calculated for each specimen.³⁰ The strength data were evaluated using a two-parameter Weibull distribution, which used a maximum likelihood standard regression (calculated using Weibull++7 by ReliaSoft Publishing, Tucson, Arizona).

III. Results and Discussion

(1) Powder Preparation

In addition to forming dense, fine-grained microstructures, dispersion is critical to obtain a fine edge resolution in mesoscale parts. To achieve an edge resolution of 1 μm, the maximum agglomerate size (D) must be < 1 μm to avoid resolution limiting interagglomerate porosity. The resolution limiting number of particles per agglomerate (AAN) can be estimated for a spherical agglomerate and particle using³¹

$$\text{AAN} = \frac{D^3}{d^3} \phi_p \quad (1)$$

where D is agglomerate diameter, d is particle diameter, and ϕ_p is the packing efficiency of the particles within the agglomerate. The specific surface area is used to calculate the particle

diameter (d) because it is assumed the nitrogen adsorbate in the BET measurement has access to the particle surface area within the agglomerates. The AAN calculation compares agglomerate volume to primary particle volume, and so the particle diameter (d) must be based on the volumetric distribution rather than the area distribution, which the BET method measures directly. The analysis by German³¹ that includes the conversion from the area distribution to the volume distribution by Allen³² gives

$$\log(d) = \log\left(\frac{6}{\rho A}\right) + \frac{4.6}{s_w^2} \quad (2)$$

where ρ is the solid density (assumed theoretical density of 3Y-TZP, 6.05 g/cm³), A is the surface area (BET measured 15.4 m²/g), and s_w is the distribution width of the particle size. The distribution width (s_w) is typically 4–5 for a commercial log-normally distributed powder³¹; therefore, a value of $s_w = 4$ is used to estimate the maximum allowable number of particles per agglomerate. The volume based particle diameter of the 3Y-TZP particles from Eq. (2) is 125 nm. The last assumption to calculate AAN is the packing fraction of particles within the agglomerate (ϕ_p), which may be as low as 0.15 for a flocculated suspension,³³ as high as 0.74 for close packed spheres, or more typically 0.6 for loose randomly packed spheres.³¹ Therefore, the maximum number of particles per agglomerate (AAN) to satisfy the 1 μ m resolution target is 314 particles assuming a packing fraction of 0.6. The AAN decreases to 79 for flocculated particles or increases to 388 for close packed spherical particles within the agglomerate. Consequently, the dispersion strategy must at least prevent agglomerates with more than 314 particles from forming.

Chemically aided attrition milling is an efficient method to disperse and concentrate the suspension.³⁴ The combination of impact, abrasion, and shear from the collision, flow, and rotation of media in the attrition mill, and similar interactions among the particles results in aggregate fracture and dispersion in much shorter times compared with ball milling or vibratory milling.³⁵ Commercial 3Y-TZP powder has an initial granule size of 60 μ m (D_{50} by volume) or 36 μ m by number distribution, as shown in Fig. 2. The granules consist of particles with a diameter (d) of 125 nm by volume (46 nm by number using the conversion by Allen³²). Observation of the granules and primary particles in Fig. 2 confirms these size measurements. After attrition milling, the agglomerate size D_{50} is 215 nm by volume or 114 nm by number. Using Eq. (1) with the agglomerate diameter (D) equal to 215 nm, a particle diameter (d) of 125 nm, and a packing fraction of 0.6, the AAN of the milled suspension is three particles per agglomerate. This is much lower than the 314 particles per agglomerate that would limit the resolution of the part due to interagglomerate porosity. Additionally, an average agglomeration number of <10 is generally considered a well-dispersed suspension.³⁶ Both the fine edge resolution of the parts and the dense, fine microstructure described below confirm the well-dispersed state of suspension.

(2) Mold Forming on Ceramic Substrates

Using photolithography as a mold forming process requires modifications to the standard process used to create patterns on silicon wafers. As noted by Schonholzer *et al.*,²³ polycrystalline substrates, such as the α -alumina substrate used here, reflect UV light used to expose the photoresist. This reflection causes the bottom edge of the mold to become rounded. Light that exposes the masked regions on the alumina substrate by reflection is prevented by applying an antireflecting, UV-absorbing coating.³⁷ In addition, the unpatterned, 25 μ m SU-8 layer is applied to prevent the parts from sticking to the substrate during firing. Thicknesses of 5 and 10 μ m were also evaluated, but did not prevent part adhesion. It is hypothesized that the sacrificial SU-8 layer prevents adhesion to the substrate by eliminating intimate contact

between the part and substrate during casting and/or by forming a thin barrier layer of carbon residue between the part and the substrate during firing.

(3) Forming

The viability of the RIF process lies in the pseudoplastic rheological behavior, shown in Fig. 3, of the engineered 43 vol% 3Y-TZP suspension. The Bingham yield point of the suspension (τ_B) is 160 Pa with the suspension relatively Newtonian above a shear rate of 200 s^{-1} . The squeegee speed for the RIF must to exceed 5 mm/s to enter the low-viscosity Newtonian regime assuming simple shear over the typical 25 μm mold thickness. The RIF process typically uses a speed of 10 cm/s, or 20 times the required shear rate to enter the Newtonian regime. In addition to the well-dispersed state of the 3Y-TZP powder, the relatively low $0.65 \text{ Pa} \cdot \text{s}$ (650 cP) viscosity in the Newtonian regime is also a consequence of using low-molecular-weight monomers instead of conventional polymeric binders to form a green part. When the shearing action is stopped, the suspension behaves as an elastic solid permitting the filled mold to be handled.

Because gelcasting is used to form the green body, the wet green density is equal to the solid concentration of the suspension. To improve the dimensional tolerance of the fired part by minimizing shrinkage during sintering, the solid concentration of the suspension must be maximized without compromising the dispersion. Thus, it is critical to control the colloidal interactions among the ceramic particles. In Fig. 4, the theoretical interaction energy as a function of interparticle separation distance is calculated³⁸ for two electrosterically stabilized 3Y-TZP particles with a D_{50} by number of 114 nm, a ζ potential mean of -49 mV, and a 0.1M ionic strength (1:1 electrolyte). The D_{50} by number is used in this calculation because it better describes the size of any given particle—particle interaction rather than the bias toward the higher volume particles in the volume distribution. A polymer layer thickness of 2 nm is used in the calculation based on previous studies with a similar molecular weight $\text{NH}_4\text{-PAA}$ adsorbed onto a zirconia surface at pH 9.^{39,40} The Hamaker constant of $7.2 \times 10^{-20} \text{ J}$ is taken from Bergström with retardation effects included in the calculation.⁴¹ The particles can approach one another to a separation distance of 5.7 nm if 25 kT is taken as the effective barrier energy. The steep energy barrier developed from 8 nm of separation to the 4 nm steric barrier is a result of the high surface charge and high ionic strength (0.1M based on a 1:1 electrolyte calibration), which screens the repulsive potential at long separation distances.

The interaction energy between two electrosterically stabilized particles provides an estimation of the maximum solids loading in a suspension because the electrosteric barrier prevents particles from approaching one another. Although the use of a hard sphere model is generally less accurate for polyelectrolyte dispersed ceramic suspensions at low ionic strength,⁴² the steep energy barrier at high ionic strength shown in Fig. 4 can be thought of as an infinite potential barrier at an interparticle separation distance of 5.7 nm. Assuming the particles are spherical and pack in a loose random manner, the maximum volume fraction (ϕ_m) of the suspension would be approximately 0.6.³¹ However, the electrosteric barrier prevents the particles from touching and decreases the effective volume fraction (ϕ_{eff}) according to the following equation⁴³:

$$\phi_{\text{eff}} = \phi_m \left(1 + \frac{\Delta}{r} \right)^{-3} \quad (3)$$

where Δ is layer thickness and r is the particle radius (57 nm by number from DLS). This equation assumes an incompressible, spherical barrier layer and particle. The maximum volume fraction of zirconia decreases to 0.52 when Δ equals 2.85 nm or half the interparticle

separation distance at an interaction energy of 25 kT. However, the practical solid concentration limit in RIF is lower than 0.52, because drying increases the solid concentration by removing solvent. Thus, a 43–45 vol% solid concentration is used for RIF to buffer against the loss of solvent during casting.

(4) Lost Mold via Thermolysis

Unlike conventional lost mold processing using a wax mold, the thermal removal of the SU-8 mold has the possibility of vastly reducing the yield by distorting and cracking high-aspect-ratio parts. Chemical dissolution is often preferred to thermolysis for this reason, but has other previously mentioned drawbacks. Cracks can form in the parts when the cross-linked SU-8 photoresist is rapidly heated like those shown in Fig. 5 at a 10°C/min heating rate. The longitudinal cracks that appear at 248°C are created by parts sticking to the mold as the mold distorts. The in-plane shrinkage is both a result of a volume decrease as the photoresist further cross-links and the relief of the tensile residual stress in the photoresist. The stress relief occurs above the T_g , which is roughly equal to the hard bake temperature of 180°C for the SU-8 photoresist.⁴⁴ The residual stress is a function of the photoresist exposure dose, the prebake, and the postbake temperatures.⁴⁵ Thus, successful thermal mold removal requires slow heating rates (1°C/min) at temperatures below 400°C.

(5) Sintered Parts

An array of Gen1 mesoscale bend bars is shown in Fig. 6(a) before sintering. There are 12 bend bars per square millimeter, which yields about 80,000 bend bars per 10 cm × 10 cm refractory substrate. This number increases to about 200,000 if closer packing in the array is used. The large number of parts per substrate is the major advantage of directed assembly over direct-writing. Figure 6(b) shows three bend bars after sintering while still on the alumina substrate. These Gen1 mesoscale bend bars were later observed to have a concave top surface, a trapezoidal cross section, and are warped. These issues were discovered during strength testing and the solutions will be addressed in a later report that addresses geometrical tolerances in mesoscale parts. The edge resolution of the mold is defined by the limits of UV-photolithography, but on a straight edge of the mold the corner sharpness approaches the grain size, or about 400 nm as shown in Fig. 6(c). The 1300°C soak temperature was chosen based on the sintered Archimedes density for macroscale analogue specimens. Sintered densities are 96.1%, 98.7%, and 99.8% of the theoretical density as the soak temperature increases from 1200° to 1250° and 1300°C, respectively. The high density and minimal grain growth (300–600 nm grain size) for samples sintered at 1300°C is apparent in Fig. 6(d). The dense, submicrometer microstructure and the fine edge resolution of the parts can be attributed to the effective suspension dispersion and rheological control of the engineered 3Y-TZP suspensions at high solids concentration.

(6) Gen1 Material Strength Testing

Flexural testing is the preferred method to evaluate the strength of brittle materials and is similar to the type of loading the mesoscale surgical instrument will experience. During testing, it was observed that the cross-sectional area of the bend bars was trapezoidal and not rectangular as shown in Fig. 7. A trapezoidal cross-sectional area has also been seen in bend test specimens of silicon, and was attributed to anisotropic etching.²⁹ In the present case, the trapezoidal mold cross section is a result the photoresist exposure, and is reproduced in the specimen also shown in Fig. 7.

Figure 8 shows the probability of failure of the mesoscale beams, and the inset shows an optical image of the test apparatus. The characteristic strength (σ_o) of the beams is between 888 MPa (129 ksi) and 978 MPa (142 ksi) depending on the orientation of the specimen, which was unknown because the trapezoidal cross-section orientation could not be optically observed.

The Weibull modulus (m) is 6.8 and is not dependent on the cross-sectional geometry. The Weibull modulus is lower than desired, but this reflects the geometrical defects in the Gen1 parts for the new manufacturing process. The Gen1 mesoscale zirconia bend bars have strengths comparable to conventionally sized specimens of TZP-zirconia⁴⁶; however, given the geometrical uncertainties (trapezoidal cross section, concave top surface, etc.), it is likely the Weibull modulus will increase with subsequent testing of future generations with fewer geometrical strength limiting flaws. A subsequent report will compare the strength of the Gen1 bend bars, which have a concave top surface, trapezoidal cross section, and were warped to Gen2 bend bars for which these defects are eliminated or significantly minimized.

IV. Summary

A new manufacturing process based on an amalgamation of thick film processing, semiconductor manufacture, and ceramic powder processing produces large numbers of mesoscale ceramic parts with reasonably high strength. A lost mold process using thermal mold removal in combination with RIF and gelcasting produces dense, free-standing, high aspect ratio, ceramic mesoscale parts. Chemically aided attrition milling efficiently disperses and concentrates the suspension allowing a fine edge resolution of 1 μm or less and a dense, fine-grained microstructure. The rheology of the suspension lends itself to RIF, a shear-based casting method that reliably fills the mold cavities. The mold is removed without cracking the parts by adjusting the firing cycle to the thermal properties of the mold. A three-point bend test shows that the parts have strengths similar to macroscopic 3Y-TZP bodies, but the dimensional defects in these Gen1 parts limit the strength and contributed to a low Weibull modulus. Dimensional characterization and additional strength testing of the next generation of specimen will follow in a subsequent report.

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Fig. 1.

The on-substrate, lost-mold fabrication process begins with mask and mold fabrication in a class 10 clean room. Ceramic powder processing begins with chemically aided attrition milling (CAAM) to disperse and concentrate the granulated 3Y-TZP powder. Rapid infiltration forming (RIF) injects the suspension into the mold cavities, while the methacrylamide-based monomers polymerize to form the green body. The mold is then thermally removed during the firing cycle. Once sintered the parts are washed off the substrate to be characterized and strength tested.

Fig. 2.

(a) The individual 3Y-TZP particles after attrition milling appear in white on Au—Pd-coated cleaved-mica in this field-emission scanning electron microscope (FE-SEM) image. (b) The 3Y-TZP powder is granulated and is shown on top of carbon tape in this SEM image. (c) The particle size distributions before and after chemically aided attrition milling (CAAM) are plotted below the SEM images. The particle size of commercial 3Y-TZP powder is reduced from a D_{50} of 60 μm (36 μm by number) to a D_{50} of 215 nm by volume (114 nm by number) during CAAM.

Fig. 3.

The shear stress and viscosity as a function of shear rate shows shear thinning behavior for a 43 vol% solid suspension. The Bingham yield point is 160 Pa and the high shear viscosity (400–500 s⁻¹ average) is 0.65 Pa · s. Each curve represents the line segments connecting 180 data points.

Fig. 4.

The van der Waals attraction, the electrostatic repulsion, and the total interaction energy of two spherical 3Y-TZP particles show a steep repulsive energy that permits the particles to closely approach one another, but not agglomerate. The calculation is based on a particle diameter of 114 nm, a 2 nm layer of ionic polymer, a ζ potential of -49 ± 2 mV, a Hamaker constant of 7.2×10^{-20} J, and a 0.1M 1:1 electrolyte solution.

Fig. 5.

Cracks due to mold thermolysis of the green bend bars in the SU-8 micromolds become visible in the hot-stage scanning electron microscope at 248°C and grow at higher temperatures when heated at a rate of 10°C/min. Slower heating rates are required to minimize this effect.

Fig. 6.

All images were taken of Gen1 specimens using an scanning electron microscope with the exception of image (a), which was taken using an optical microscope in reflection with oblique lighting. (a) An array of green mesoscale bend bars while still in the mold. (b) Three sintered 3Y-TZP mesoscale bend bars sitting on the alumina substrate. (c) The edge sharpness of a sintered bend test bar is approximately that of a single grain (400 nm); however, the overall dimensional tolerance is on the order of a micrometer. (d) The grain size of the sintered zirconia is approximately 300–600 nm.

Fig. 7.

(a) The trapezoidal cross section of a mold cavity is shown in the top layer. The unpatterned photoresist layer and alumina substrate can be seen under the mold layer. (b) The manifestation of the trapezoidal mold cross section is a mesoscale bend bar with a top width of 20 μm and abottom width of 29 μm.

Fig. 8.

A Weibull plot of the failure data for mesoscale beams. The stress at failure was calculated for both possible orientations of the trapezoid-shaped beam cross sections. The inset is an optical picture of the test jig with a three-point bend specimen in place.