Advanced Ceramic Materials and Processes for Three-Dimensional Printing (3DP)

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Abstract: The University of Washington and ExOne, Inc. are collaborating in the development of advanced ceramic materials and processes for three-dimensional printing (3DP). The focus of the research to be presented is work funded by the National Science Foundation to develop a biocompatible alumina-based system for medical and dental applications. Materials design, characterization, and processing considerations will be discussed.

I. SUMMARY OF THE RESEARCH CONDUCTED

This research focused on the development of a novel class of versatile, high-yield nanoparticle ceramic systems. In particular, these systems are intended to be compatible with the Three-Dimensional Printing (3DP^{TM}) process for fabrication of dental restorations. In addition to this specific application, the research was broadly targeted to impact other structural ceramic applications through 3DP, and to provide a vehicle for the training of graduate students in this interdisciplinary area of significant commercial interest.

I.1 Motivation for the Research, Objectives and Specific Tasks

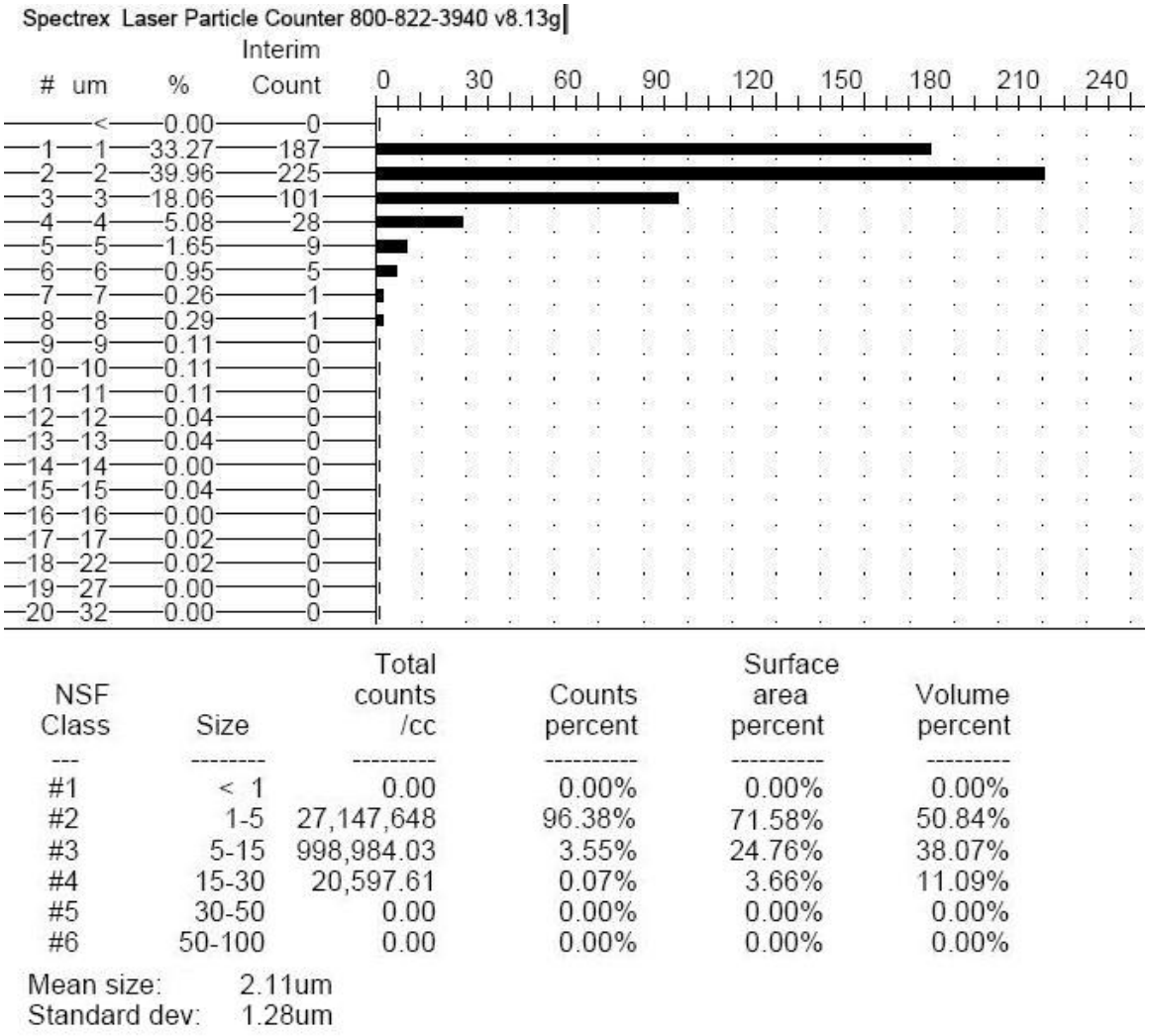
The present research is motivated by a growing market opportunity for ceramic dental restorations via 3DP, on the heels of the current successful commercialization of 3DP application to metal-based dental restorations. Primary research objectives, then, were to determine the feasibility of producing structurally sound ceramic composites by introducing suitable pre-ceramic polymers into the material through the printhead nozzles and/or the print bed in the 3DP process. To meet these objectives, the research tasks included: (i) identification and characterization of potentially suitable print bed ceramics, pre-ceramic polymer binders, and nanoparticle additions; (ii) evaluation of binder compatibility with 3DP printheads; (iii) evaluation of print bed ceramics containing nanoparticles; (iv) thermal processing of fabricated ceramic parts. In all cases, the evaluations were carried out within the constraints imposed by the 3DP process; specifically, these constraints involve limits on physical properties of the binder (viscosity, density, surface tension) and the print bed ceramic powders (flowability).

I.2 Results

Materials Characterization

After screening various candidates, initial characterization focused on Acetate Alumoxane (AA) in both liquid and dry form as a key source of nano particles to be evaluated for this research. A solution of AA was provided as a 10% volume solution in H_2O by Oxane Materials, Houston, TX for its evaluation as a potential 3DP ceramic material. As received, the AA solution was a thick gel with high turbidity. Surface tension was measured at 62.5 dynes/cm (± 20%) and viscosity at 17.64 cPs (± 2.5%).

For compatibility with the R-1 3DPrinter printhead, surface tension of the fluid must be in the range of 25 to 50 dynes/cm and viscosity between 1.5 and 20 cPs. While viscosity of the AA gel is on the upper end of printability, surface tension is out of range. Particle size analysis performed by Spectrex (Figure 1) shows an average suspended particle size of 2.11 μm with a standard deviation of 1.28 μm. Such particle size is too large to be jetted through the drop-on-demand printhead of the R-1 3DPrinter. Nevertheless, while this source of AA is not suitable for printing, it may provide a source of near nano-sized particles in an additive to printed ceramic materials for enhanced green strength or accelerated sintering.



NSF Class	Size	Total counts /cc	Counts percent	Surface area percent	Volume percent
#1	< 1	0.00	0.00%	0.00%	0.00%
#2	1-5	27,147,648	96.38%	71.58%	50.84%
#3	5-15	998,984.03	3.55%	24.76%	38.07%
#4	15-30	20,597.61	0.07%	3.66%	11.09%
#5	30-50	0.00	0.00%	0.00%	0.00%
#6	50-100	0.00	0.00%	0.00%	0.00%

Mean size: 2.11um
Standard dev: 1.28um

Figure 1: Results of AA particle size analysis performed by Spectrex

Similarly, screening of various ceramic powders for the print bed in 3DP led to selection of Sumitomo AA-18 alumina. (In this designation, AA identifies the manufacturer's particular grade of alumina, and is not to be confused with the AA acronym for Acetate Alumoxane.) Due to the requirements of powder spreadability for successful 3DPrinting, it was necessary to find an alumina powder that flows well without agglomerating. To satisfy these parameters the particles should, ideally, be spherical and have relatively large particle sizes on the order of 15 – 30 μm. The Sumitomo AA-18 powder, Figure 2, is of high quality, has a particle size range of 18 – 26 μm, and is made up of faceted, equiangular particles. Particle size analysis is shown in Figure 3. The mean particle size of the powder is 20.93 μm (SD 1.298) and the median particle size is 20.95 μm. Ninety percent of the powder is between 11.5 μm and 31.4 μm (5^{th} – 95^{th} percentile). Visual examination of the bulk powder and spreading trials showed that the powder flowed well and created a smooth, even powder layer in the print bed of the R-1 3DPrinter. Bed packing density ranges from 50 – 55% depending on the spreading parameters and the layer thickness.

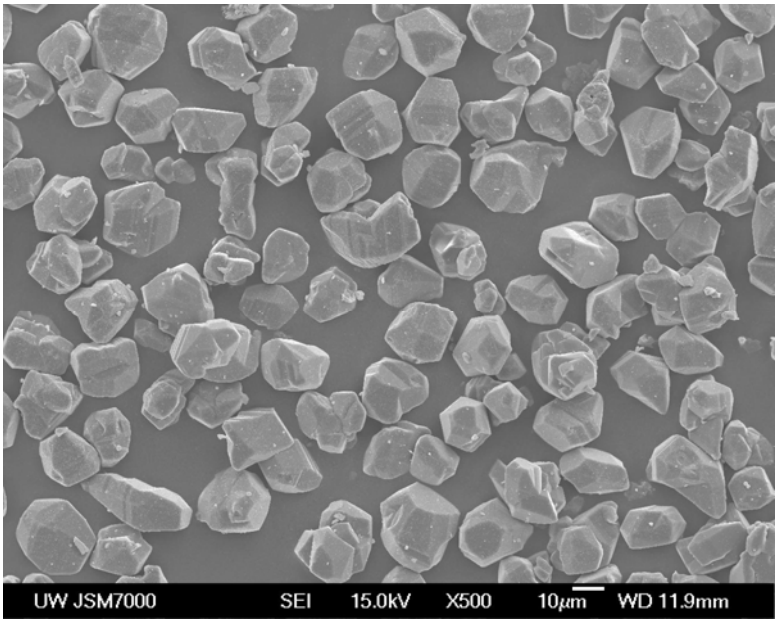


Figure 2: SEM image of Sumitomo AA-18 alumina powder, 500x magnification

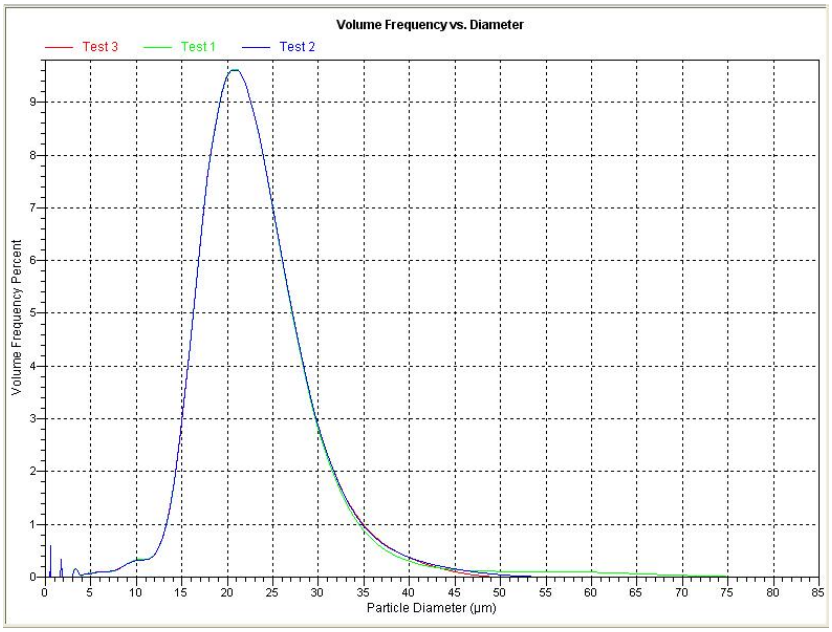


Figure 3: Particle size analysis of Sumitomo AA-18 alumina performed using a Micromeritics Saturn DigiSizer 5200

AA solution as a liquid binder

One use of the AA is as an addition to ceramic print bed powders, injected via the 3DP printhead. The role of the AA in this case would be to increase green strength and increase the ceramic yield in the fired material. Suitable mixtures of alumina powder and

AA solution were identified for two ranges of particle sizes potentially suitable for 3DP: 1) Sumitomo alumina powder, particle size range 18 – 26 μm with a mean particle size of 21 μm; 2) Aldrich alumina powder with particle size <10 μm.

Cast bars (5 x 10 x 25 mm) using AA solution as the binder in combination with the Sumitomo alumina powder were prepared, using a ratio of 7 parts ceramic powder to 1 part AA by weight. The green cast specimens were relatively durable and could be handled without breaking. The castings break cleanly as opposed to crumbling, which is a good indicator of cohesive green strength.

These results indicate that green parts with acceptable green strengths are possible using the selected materials. However, due to the large particle size of the Sumitomo alumina, these samples did not sinter to the desired density, even with the most aggressive sintering run – 6 hours at 1650 ˚C.

AA solid as a liquid activated binder

Another use of AA is as an additive in solid particle form to the print bed ceramic powders. In the solid state, AA is a fine white powder with particle sizes dependent on the liquid processing parameters. On wetting and subsequent drying the powder is observed to clump and bind together. This observation led to the idea of using dry AA as a liquid activated in-bed binder.

Dry AA was provided as a large grain crystalline powder with some particles as large as 5 mm in diameter. This powder was ball milled in grinding media for 24+ hours until it reached the form of a fine powder, shown in Figure 4. Particle size range of this powder was measured to be 1 – 40 μm, which is acceptable for spreading by the 3DPrinter. While a powder bed of pure AA powder could likely be printed successfully, the ceramic yield of any such printing would be around 60% and significant shrinkage would be observed.

Instead, a mixture of AA powder and alumina powder would be desirable as it provides a liquid activated binder in the powder bed, but retains the high yield of a nearly pure ceramic powder bed. Powdered AA in the bed also allows a variety of choices for the activating liquid. This approach has excellent flexibility and the potential to tailor the properties of the raw materials, green part, and ceramic product. Both distilled water and a mixture of water and isopropanol have been found to work as activating liquids. Isopropanol does not activate the alumoxane effectively, but does act to lower the surface tension. Using the AA as an in-bed binder minimizes many of the binder issues such as printhead clogging, waste disposal, cost, and environmental considerations associated with transmission of AA through the printhead.

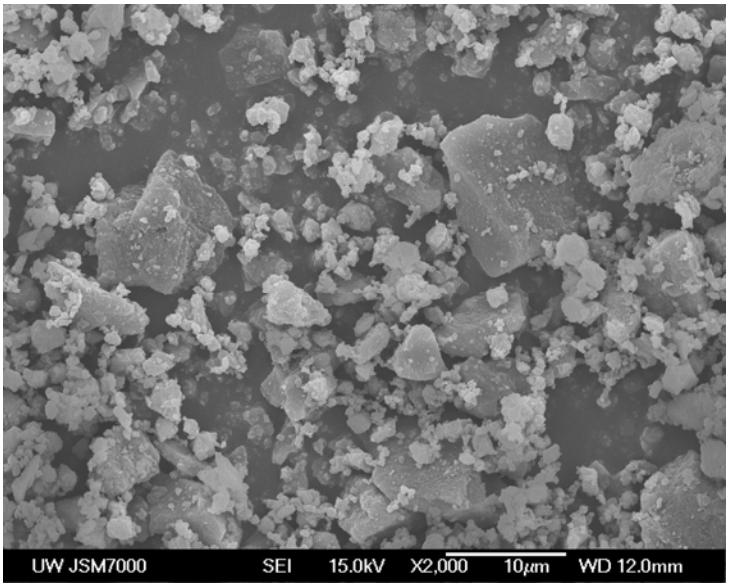


Figure 4: SEM image of powdered alumoxane, 2000x magnification

Tests using powdered alumoxane as the in-bed binder indicated only a very small decrease in the bed's ceramic yield after firing. TGA and binder elimination studies showed the powdered alumoxane has a 60% ceramic yield by weight (Figure 5).

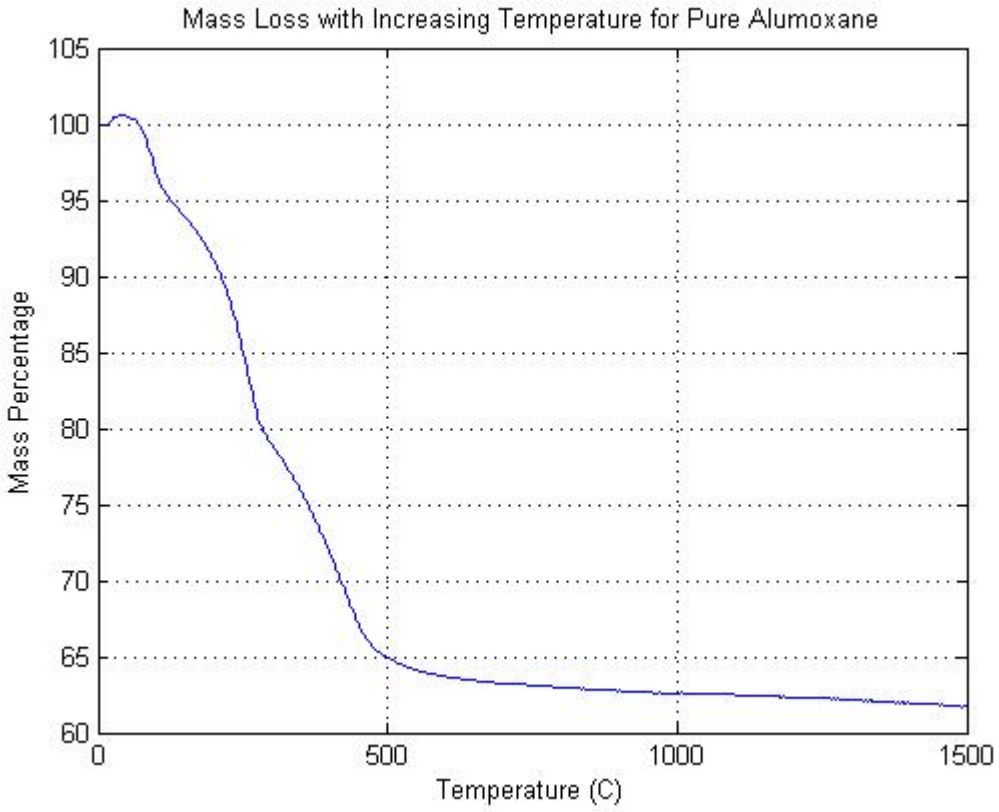


Figure 5: TGA results of pure alumoxane

As described in the previous section, only a small amount of AA gel (one part in 7, by weight) is necessary to create suitable green parts. Experimental studies were performed to evaluate the binding ability of 2.5%, 5%, 7.5%, 10%, and 15% weight mixtures of dry AA with Sumitomo AA-18 alumina. The optimum weight AA mixture with Sumitomo alumina and water binder was determined to be 5%. This mixture resulted in a ceramic yield of ~98.5%, based on TGA analysis (Figure 6). Bars cast with more than 5% alumoxane were slightly better in strength, but resulted in lower ceramic content; bars with less that 5% did not have sufficient green strength. Taking this as the optimum balance between green strength and ceramic yield, a batch of 5% alumoxane/95% Sumitomo ceramic powder was prepared for printing tests.

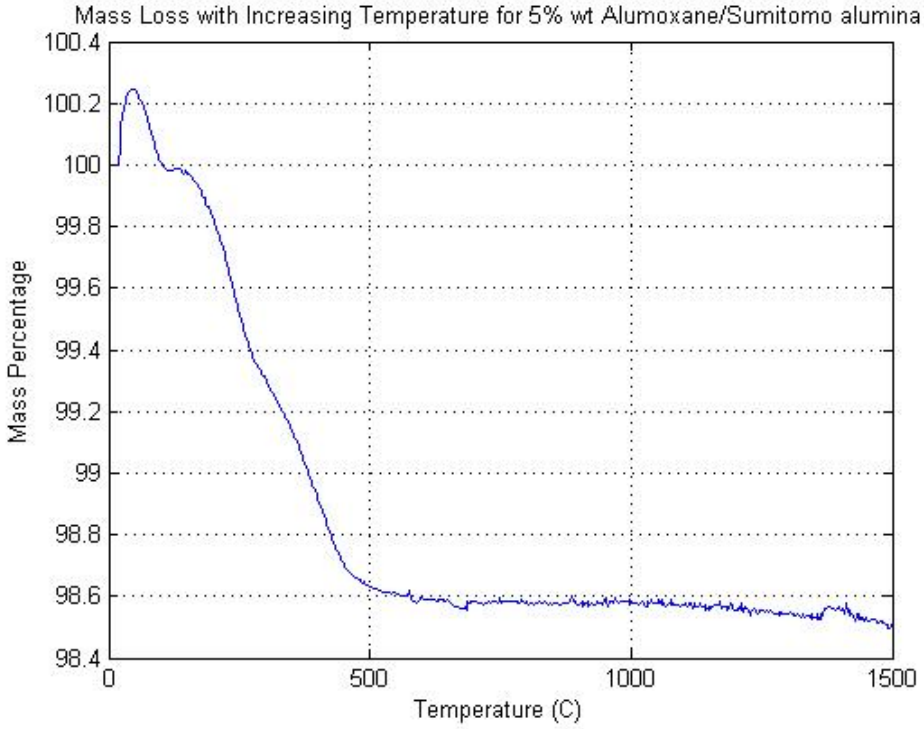


Figure 6: TGA of sample from 5% alumoxane/95% Sumitomo powder mixture

Sintering studies

In order to determine the sinterability of various biocompatible ceramics, a range of alumina powders and their mixtures with zirconia were cast together with the powdered alumoxane as the binder. As a baseline, commercial dental ceramic (InCeram Alumina) was also considered. The compositions of the cast bars are presented in Table 1.

Table 1: Sintering Test Mixtures (STM) Identification

				Weight Percentages		
STM #	**Bulk Powder**	**Additive Powder**	**Binder**	**Bulk**	**Additive**	**Binder**
1	Sumitomo Al2O3, 18-26 micron	Aldrich Al2O3, <10 micron	Powdered AA	84.2%	8.3%	7.6%
2	Sumitomo Al2O3, 18-26 micron	Aldrich Al2O3, <10 micron	Powdered AA	76.8%	15.2%	7.9%
3	Sumitomo Al2O3, 18-26 micron	Aldrich Al2O3, <10 micron	Powdered AA	70.6%	22.0%	7.3%
4	Sumitomo Al2O3, 18-26 micron	InCeram Al2O3	Powdered AA	83.4%	8.2%	8.3%
5	Sumitomo Al2O3, 18-26 micron	InCeram Al2O3	Powdered AA	77.0%	15.5%	7.5%
6	Sumitomo Al2O3, 18-26 micron	InCeram Al2O3	Powdered AA	71.1%	21.4%	7.5%
7	Sumitomo Al2O3, 18-26 micron	Aldrich Zirconia, <5 micron	Powdered AA	84.1%	8.3%	7.6%
8	Sumitomo Al2O3, 18-26 micron	Aldrich Zirconia, <5 micron	Powdered AA	76.3%	16.1%	7.6%
9	Sumitomo Al2O3, 18-26 micron	Aldrich Zirconia, <5 micron	Powdered AA	70.9%	21.6%	7.5%
10	Sumitomo Al2O3, 18-26 micron	K.C.Abrasives, -400 mesh Al2O3	Powdered AA	73.9%	18.4%	7.7%
11	Sumitomo Al2O3, 18-26 micron	K.C.Abrasives, 12 micron Al2O3	Powdered AA	74.0%	18.5%	7.5%
12	Sumitomo Al2O3, 18-26 micron	K.C.Abrasives, 20 micron Al2O3	Powdered AA	73.7%	18.6%	7.6%
13	K.C.Abrasives, 12 micron Al2O3	none	Powdered AA	92.5%		7.5%
14	K.C.Abrasives, 20 micron Al2O3	none	Powdered AA	92.5%		7.5%
15	K.C.Abrasives, -400 mesh Al2O3	none	Powdered AA	92.2%		7.8%

In order to characterize the sintering process the cast pieces were sintered at 1570 ˚C and 1675 ˚C (1 hour hold). Green and sintered densities, as measured by the Archimedes technique, are shown in Table 2. As expected, finer particles do improve the sintered densities and it is possible to obtain relatively high sintered density of approximately 75%, even with the large alumina particles that are required for spreading in the 3DPrinter.

Table 2: Measured densities of Sintering Test Mixtures

	Density (% theoretical)		
STM #	**Green**	**Fired 1570 C (1 hr)**	**Fired 1675 C (1 hr)**
1	63.71%	67.54%	66.86%
2	63.79%	68.35%	66.25%
3	63.37%	*	69.08%
4	60.42%	63.23%	63.39%
5	61.68%	65.44%	68.04%
6	66.68%	71.36%	70.90%
7	63.46%	70.62%	66.44%
8	66.30%	77.64%	72.45%
9	67.55%	73.23%	74.61%
10	59.36%	*	61.62%
11	61.22%	65.24%	64.50%
12	59.54%	65.10%	61.45%
13	52.39%	57.69%	62.97%
14	46.02%	53.25%	54.49%
15	45.69%	52.71%	53.16%

*Wax coating infiltrated porous sample and produced unreliable data

SEM images of STM samples #3, #6, and #9 fired at 1675 ˚C are shown in Figures 7 – 9, respectively. The large particles are the Sumitomo ceramic powder while the smaller particles are a combination of the additive powder and the AA powder. As seen in the higher magnification images, a limited amount of sintering occurs between the larger alumina particles. It is clear that the finer ceramic particles act as binder with some sintering between the larger particles.

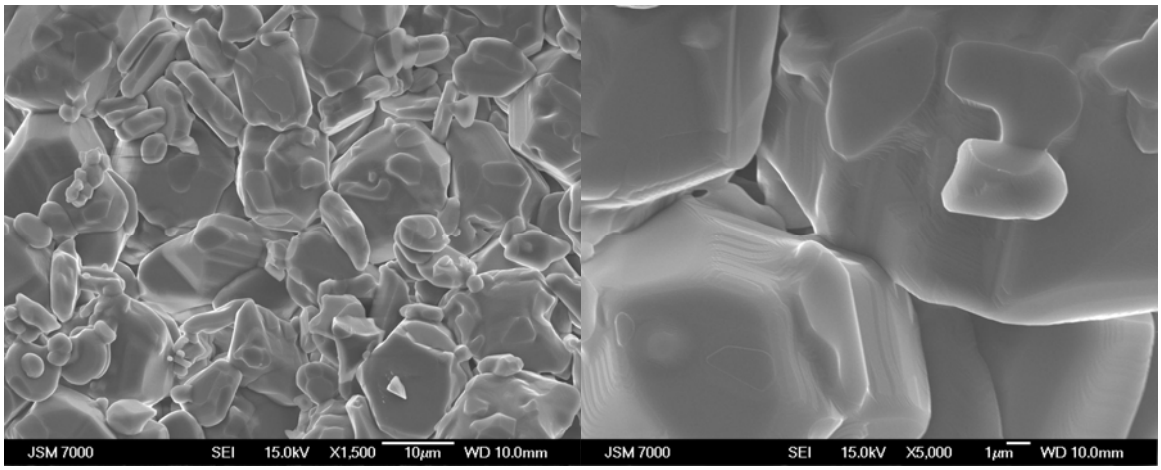


Figure 7: SEM images of bulk Sumitomo AA-18 alumina with 22.0% <10 micron Aldrich alumina (STM #3)

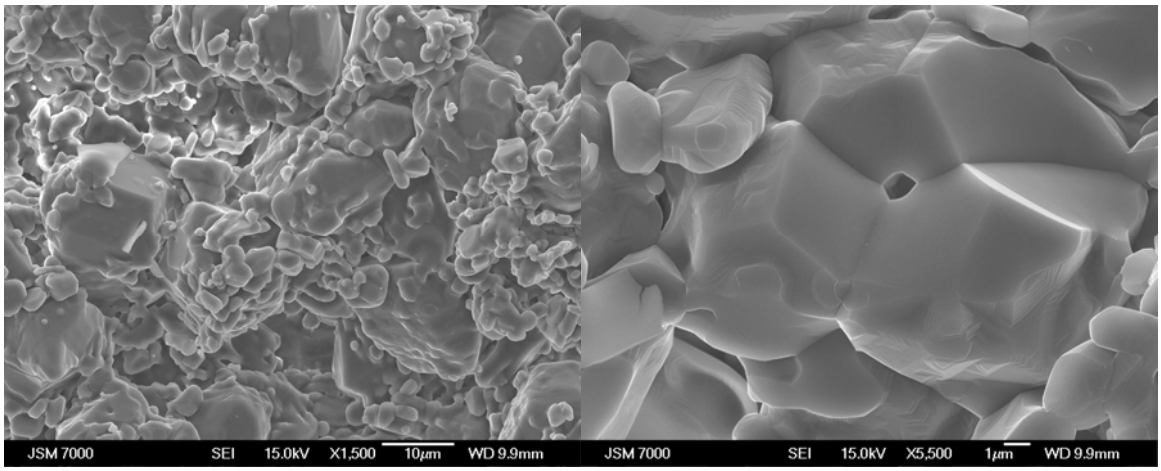


Figure 8: 1500x and 5000x magnification SEM images of bulk Sumitomo AA-18 alumina with 21.4% InCeram alumina (STM #6)

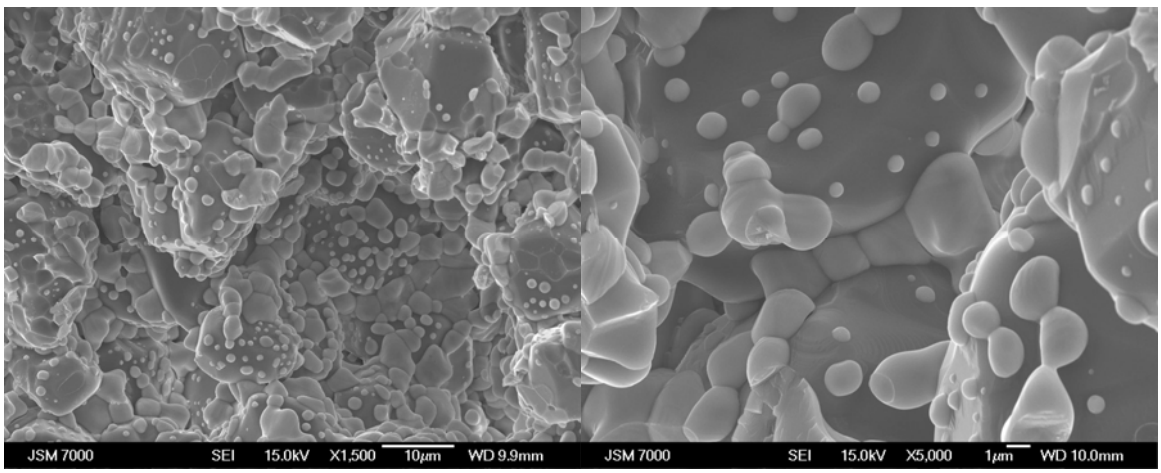


Figure 9: SEM images of bulk Sumitomo AA-18 alumina with 21.6% <5 micron Aldrich zirconia (STM #9)

3Dprinting of Ceramics

Two different 3DPrinting methodologies were tested. The more novel system involved the use of powdered AA as an in-bed binder combined with a wetting agent distributed through the printhead. The traditional method used of the ProMetal S-4 binder (developed for stainless steel printing) with a print bed containing a pure ceramic powder. Both methods proved viable.

While the results of the sintering tests showed that additive powders are beneficial in increasing the fired density of the ceramic, the small particle additives or 'fines' can adversely affect powder spreading. Each of the STM powders that resulted in the highest density samples have more than 20% additive fine powders, which do not spread well. Pits and cracks are formed in the bed as each new layer is spread, and no combinations of layer thickness, roller speed, or carriage traverse speed were found to avoid these issues. A combination similar to STM #5 containing 18.5% InCeram alumina, 78.6% Sumitomo alumina, and 2.8% alumoxane was found spreadable, but there were limitations on the spreading parameters that would result in an acceptable layer spread. Other attempts at spreading Sumitomo alumina powder with 10-20% fines were performed, but all required spreading optimization. Given that a mixture of 95% Sumitomo alumina and 5% AA powder proves spreadable with almost any parameters, this mixture was used for the bulk of the printing tests. Use of this mixture also reduces the powder bed from a three-part to a two-part mixture and helps to reduce the number of variables that could affect the 3DP parts. Table 3 provides initial 3DP parameters that were used to help guide materials and binder development and selection.

Table 3: 3DP parameter identifications for successful printing and spreading

Binder Formulation					
	Viscosity (cps)	Surface Tension (dynes/cm2)	Density (g/cm3)		
Print head specs	5 - 15	28 - 35	none		
Extreme range	1.5 - 20	25 - 50	none		
ProMetal target	7.5	30 - 32	0.9 - 1.35		
Powder Formulation					
	Particle Range μm	Shape	Density	Bimodal	Lubricating powder
Typical powder	10 - 80	Spherical		No	0.25% SiO2
S4D, high dens	10 - 80, sm. 5 - 10	Spherical		Yes	
Suggested ideal	15 - 20	Spherical		No, small dist.	0.25% SiO2

Since the selected powder mixture could be activated with water it was decided that initial testing be done with distilled water. A trial-and-error approach allowed the creation of a repeatable droplet mass by weighing the drops created by different piezoelectric waveforms. After optimization of the saturation levels it was possible to successfully print parts with reasonable surface feature definition. While the distilled water proved to be a workable system, it was decided to develop a new binder with surface tension closer to the ranged targeted for the ProMetal printhead of 28 – 35 dynes/cm^2 in hopes of easing the optimization of the printing process. A mixture of 80% H_2O/20% Isopropyl alcohol, having a surface tension of roughly 35 dynes/cm^2, met this objective. This new binder also has a viscosity of 1.81 cPs as opposed to 0.99 cPs for

distilled H_2O. While this viscosity is still lower than the printhead specifications, the alcohol/ H_2O mixture appeared to be a more reliable binder solution.

Demonstration parts using AA in the powder bed are shown in Figure 10. Considerable definition is observed in the letters, but the block corners are typically smoothed during manual handling.

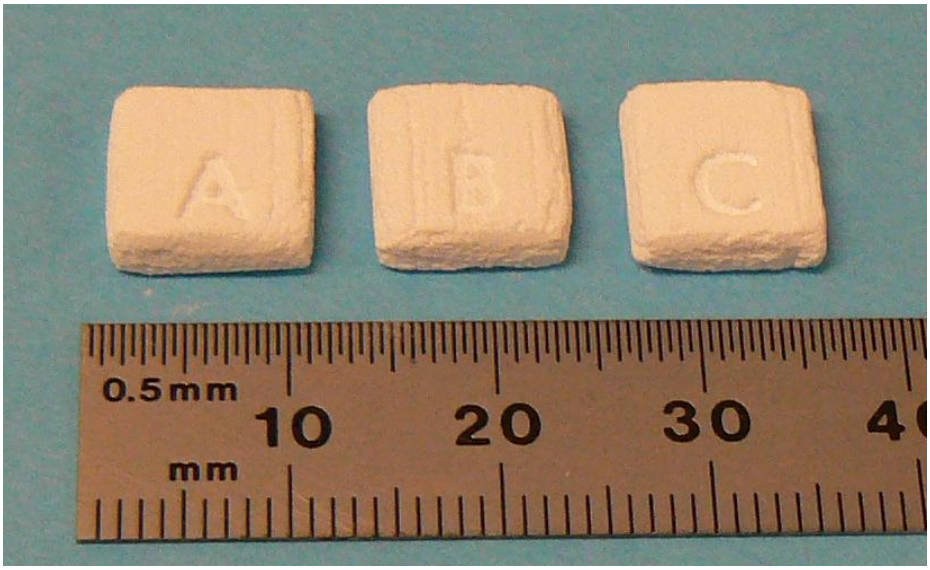


Figure 10: 3DP blocks printed using H20/Isopropal binder with alumoxane/alumina powder bed

The results of printing the ProMetal binder into the Sumitomo alumina are extremely impressive. Figure 11 shows a test array of 25 x 25 x 6 mm block with 3 mm walls and posts. These two blocks were printed at right angles to each other so one was built with the walls in line with the path of the printhead, and the other with the walls perpendicular to it. The orientation causes significant differences in the parts. The parallel array prints the slots better, but the perpendicular array prints a very thin post successfully.

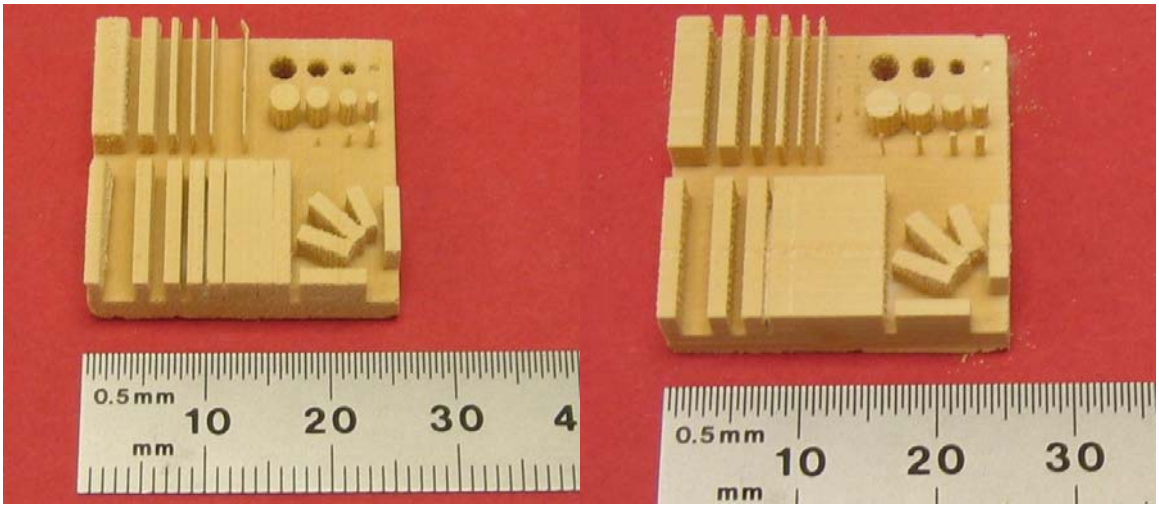


Figure 11: Test arrays printed with ProMetal binder and Sumitomo AA-18 powder, parts parallel and perpendicular to the print direction, respectively

Additional parts were printed using the ProMetal binder and alumina powder to demonstrate the feasibility of producing dental copings and crowns, one direct intended application of this research. Copings are shown in Figure 12 and full crowns in Figure 13.

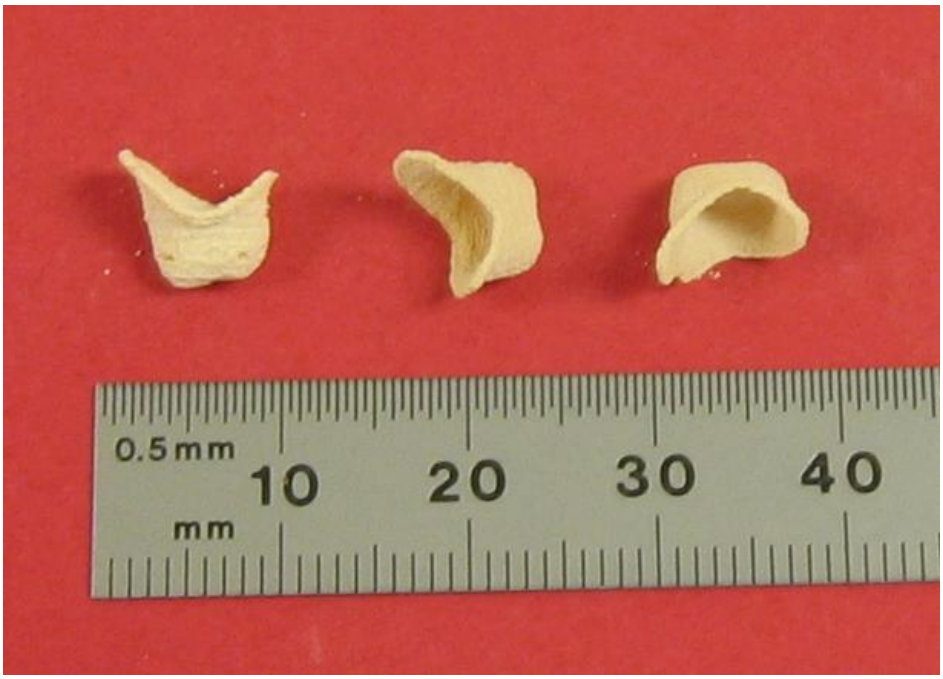


Figure 12: Green copings printed with ProMetal binder and Sumitomo AA-18 alumina

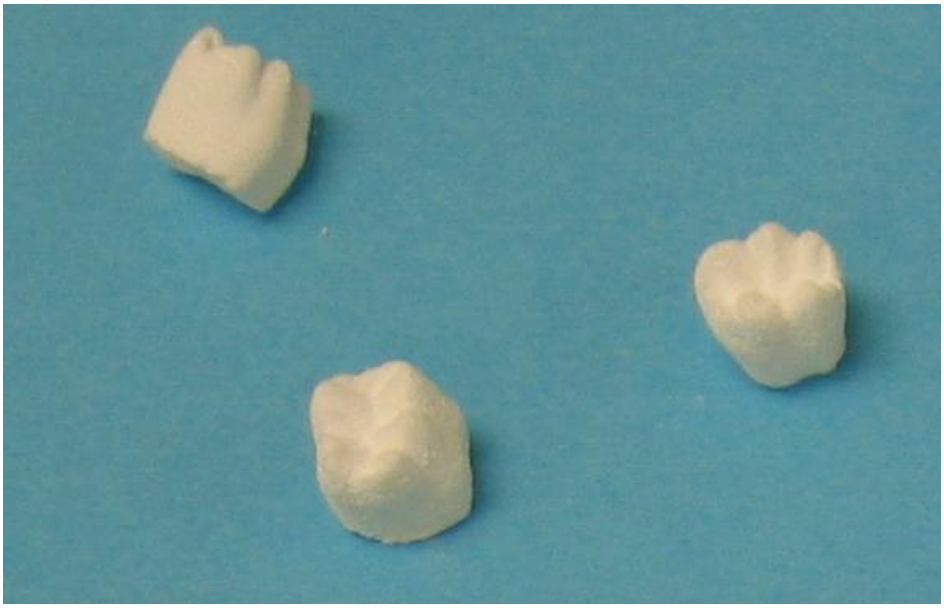


Figure 13: Fired molars (1575 C) printed using ProMetal binder and Sumitomo AA-18 powder. Approximate dimensions are 8 x 8 x 8 mm.

Given the low sintered densities of the various ceramic powder mixtures, infiltration of the printed parts with glass. Preliminary experiments were performed using In-Ceram Z21 Zirconia Glass Powder and the Sumitomo AA-18 alumina molars shown in Figure 13. Using the procedure recommended by In-Ceram, a slurry of water and the glass powder infiltrant was mixed and brushed onto the sample. As the water dried the infiltrant adhered to the sample. The coated part were then fired to 1150 ˚C, which led to successful infiltration of the exterior of the part. The maximum penetration of the glass was about 1.5 mm on a molar with an eight-millimeter diameter. Figure 14 shows a SEM of a cross section of the infiltrated molar. The top of the image shows the infiltrated region. Although the infiltrant only entered to a depth of 1.5 mm, this is sufficient for full penetration in the thin-walled copings shown in Figure 13.

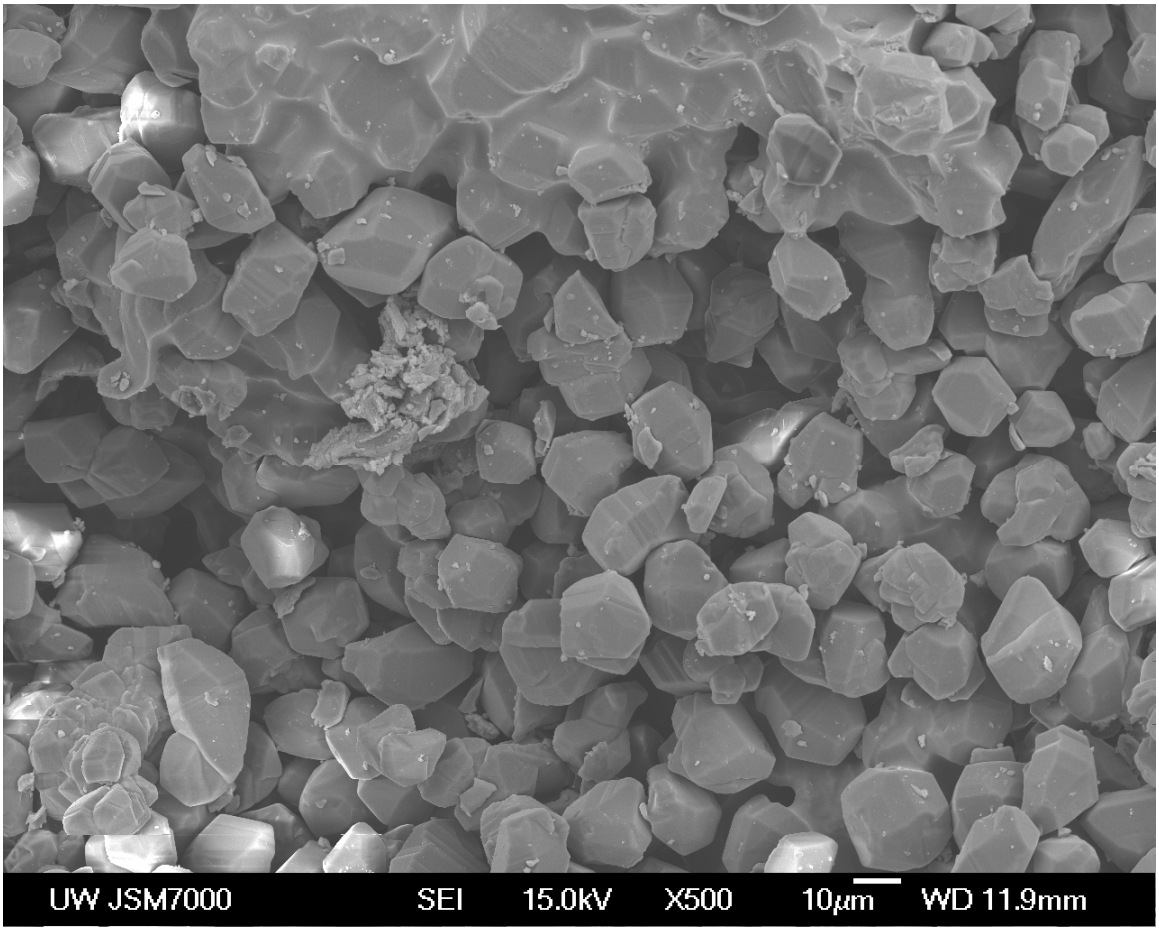


Figure 7: SEM image of infiltrated tooth cross section, upper section infiltrated with glass, lower section uninfiltrated, 500x magnification

While only in the proof of concept stages, the test infiltration of ceramic printed parts shows great promise for the production of fully dense ceramic-matrix materials of customizable properties.

IV. Conclusions

This research was successful in developing a biocompatible ceramic composite with commercialization potential for rapid manufacturing by 3DP. The principles learned about processing parameters, thermal conversion, and final properties of the simple printed shapes are essential for the robust and reproducible processing of complex ceramic parts by solid freeform fabrication methods, and will be applied to geometrically intricate parts in a planned future effort. Overall, the results of our research into ceramic materials compatible with the 3DP process will accelerate the evolution of 3DP methods from prototyping to manufacturing as well as enhance our opportunity for timely entry into the commercial marketplace.

In addition to the significant impact on broader inkjet and 3D printing research and commercial opportunity, this project involved the academic and career preparation of students at many levels. Graduate students and post-doctoral researchers worked closely with the academic and industrial team in aspects of materials synthesis, processing and characterization, and had the opportunity to conduct a portion of their research onsite with ExOne scientists and engineers. Furthermore, plans are underway to expand research programs in 3DP with a broader range of biocompatible materials as well as to incorporate these areas into three multidisciplinary courses currently offered at the University of Washington, across multiple departments. Research in this way will continue to offer a broad, real-world educational opportunity in cutting-edge technology development for students as well as academic and industrial researchers.

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