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Investigation of the Deposition and Densification Parameters on the Mechanical Properties of Pressurized Spray Deposited (PSD) 3-D Printed Ceramic Components

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Materials Science and Technology Division
Advanced Manufacturing Office

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ABSTRACT

Oak Ridge National Laboratory (ORNL) and HotEnd Works teamed to investigate the use of pressurized spray deposition (PSD) technology for the production of ceramic parts via additive manufacturing. Scanning electron microscopy of sintered parts provided by HotEnd Works revealed voids large enough to compromise the mechanical properties of PSD manufactured parts. Scanning electron microscopy and particle size analysis of the alumina oxide powder feedstocks indicated that the powders contained some large particles and some agglomerations in the powder. Further classification of the powder feedstocks and removal of the agglomerates by sonication in the liquid used for the PSD process are recommended. Analysis of sintered parts indicated that the sonic modulus for the alumina part is consistent with other known values for alumina. The density for this part was determined by standard Archimedes immersion density methods and was found to be > 99.7 % of the theoretical density for pure alumina.

1. INVESTIGATION OF THE DEPOSITION AND DENSIFICATION PARAMETERS ON THE MECHANICAL PROPERTIES OF PRESSURIZED SPRAY DEPOSITED (PSD) 3-D PRINTED CERAMIC COMPONENTS

This phase 1 technical collaboration project (MDF-TC-2015-061) was begun on January 14, 2016 and was completed on July 5, 2016. The collaboration partner HotEnd Works, LLC is a small business. ORNL provided characterization research for the partner's alumina powder and sintered ceramic parts.

1.1 BACKGROUND

This technical collaboration between HotEnd Works and ORNL evaluated a new additive manufacturing (AM) technology, pressurized spray deposition (PSD), which has the potential to generate complex ceramic parts at near full density without the use of costly directed energy sources (e.g. electron beams or lasers), and without the strong thermal gradients associated with those technologies.

While AM presents tantalizing potential for geometrically optimized parts to minimize weight and material use while maximizing function, the utilization of AM for advanced ceramics has languished due to prohibitively low relative densities achievable with current commercial AM technologies. Initial results by HotEnd Works using PSD showed green (as-printed) densities of up to 60% using fine ($<10\mu m$) powders, much higher than the <30% relative density typical of green bodies fabricated via binder jet using flowable, spray-dried powders. The combination of high green densities and small powder size suggest a high likelihood that full density printed parts could be achieved when an appropriate densification protocol is employed.

The PSD process works by applying a heated and pressurized stream of ceramic slurry to a substrate. The material is heated to a level such that the time for the slurry to solidify is a matter of seconds. This provides a sound building block for the remainder of the layers to be applied, while still allowing for slight melting to occur to provide a suitable bond between layers for both the green state and the final sintered state.

After part formation, the binding material that makes up the ceramic slurry as well the support material is removed from the part prior to sintering. This is a thermal debinding process with a typical cycle time of approximately 6 hours. After debinding is complete, the part is sintered using typical firing schedules for the material.

1.2 TECHNICAL RESULTS

The project focused on the characterization of the alumina oxide (Al_20_3) powder used by HotEnd Works. The characterization of HotEnds' alumina powder included SEM and powder particle size measurement. Additional SEM analysis was conducted for sintered parts (made from the same Al_20_3 powders) fabricated by HotEnds' Pressurized Spray Deposition (PSD) 3-D printed technique. Sonic Modulus was measured by ORNL's Non-Destructive characterization facility. Due to large voids and pores found within the furnished PSD part, the mechanical properties were not determined.

1.2.1 Characterization of Aluminum Oxide Powders

ORNL used scanning electron microscopy (SEM) and powder particle size measurement to characterize two different alumina oxide feedstocks provided by HotEnd Works. SEM images of the SG and LS alumina oxide powders are shown in figures 1-8.

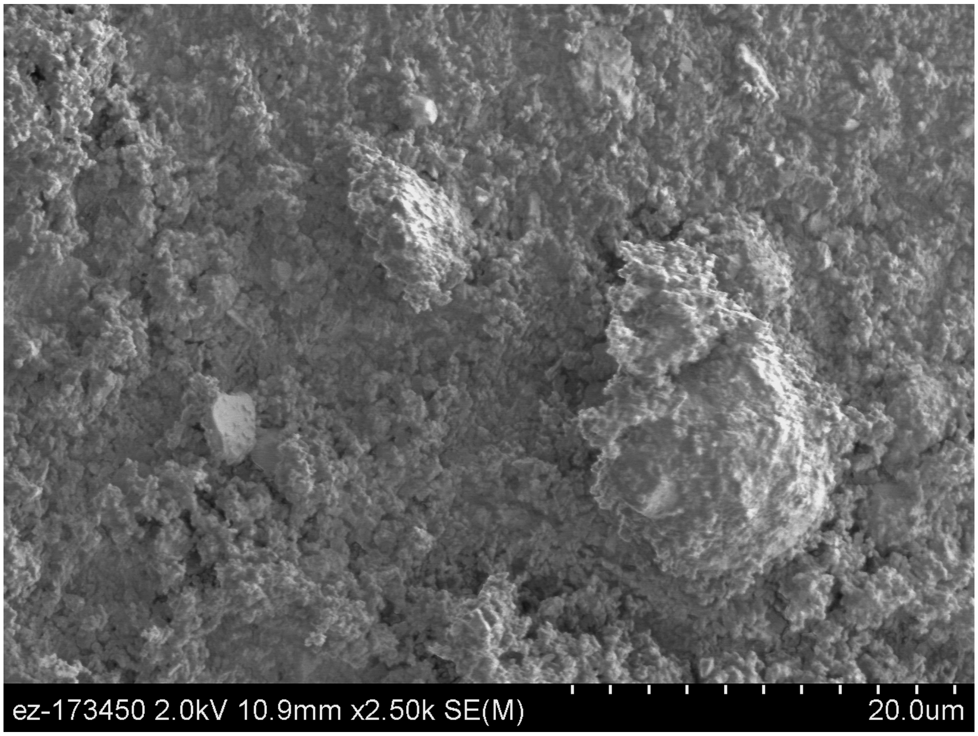


Fig. 1. SEM of "SG" Al_2O_3 powder (agglomerated fine particles).

Figure 1 shows a range of particle sizes (<4 um). Figure 2 below features a ~4um particle. The samples were re-examined after carbon coating. In general, the powder particles appear to be below 5 microns. Since the largest particles become the stress concentrators for parts made from these powders, future improvements could be made by further powder classification to remove the larger particles.

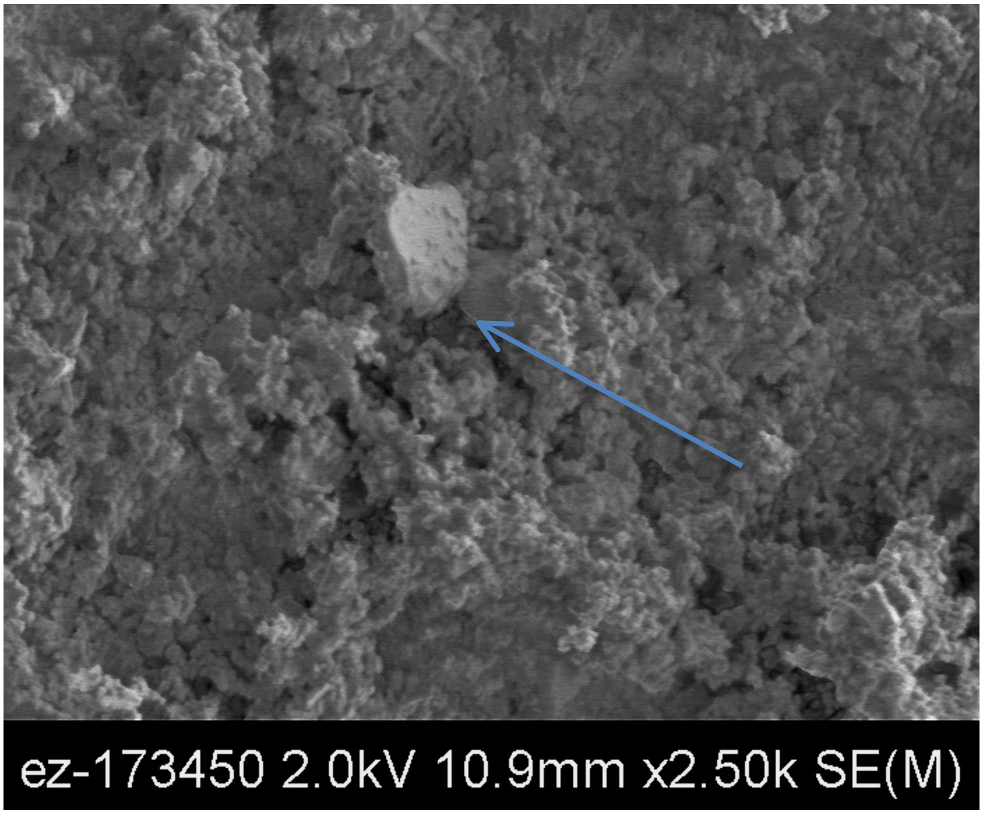


Fig. 2. Enlarged area of “SG” with ~ 4 um Al_2O_3 powder particle.

Additional SEM efforts were conducted this period, in order to capture representative particle populations for review. The powders were first sputter-coated with carbon to improve the electrical conductivity and in order to prevent charging. Below are the images from this session. Although review of the Horiba particle size analysis (included below) indicates that there are larger particles in the 10-30 um range present for both of the “as-received” powders, the “as-sonicated” particle size analysis for both powders falls back to a range of 0.1 – to 2 um, which is an indication that soft agglomerates (which were broken up by sonication) were present in the as-received powders and were the source of the 10-30 um range particles described above.

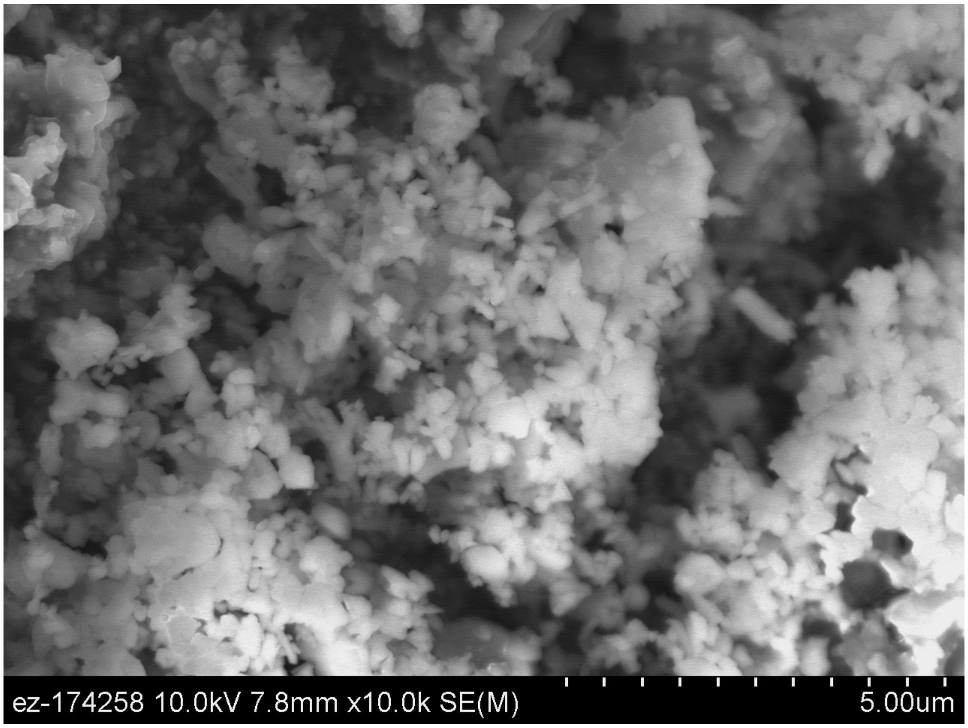


Fig. 3. SEM Image of SG Powder.

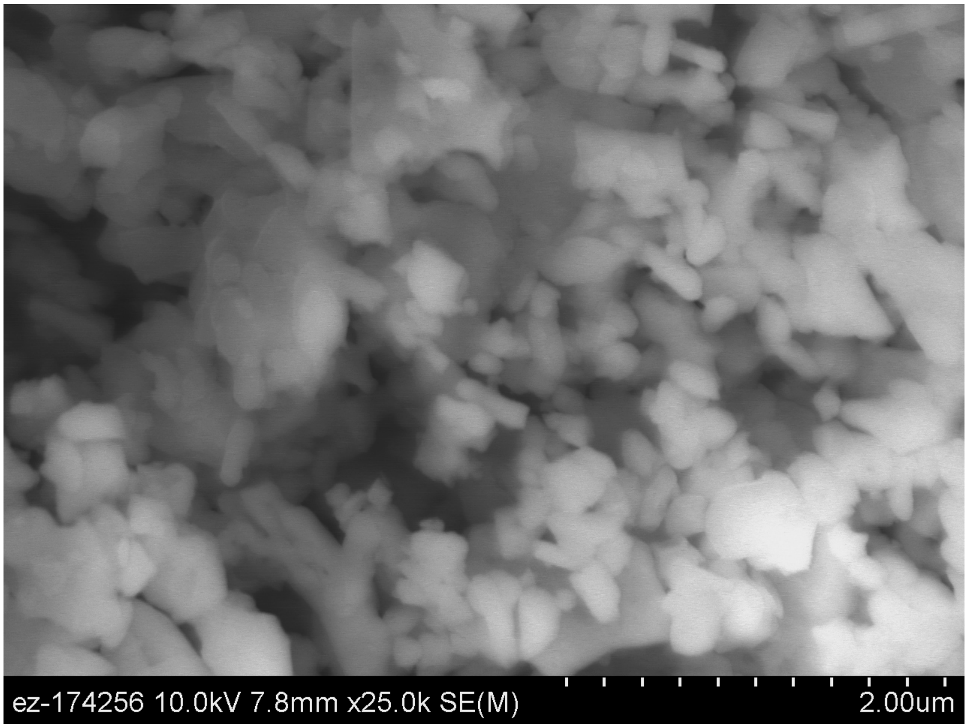


Fig. 4. SEM Image of SG Powder, medium view.

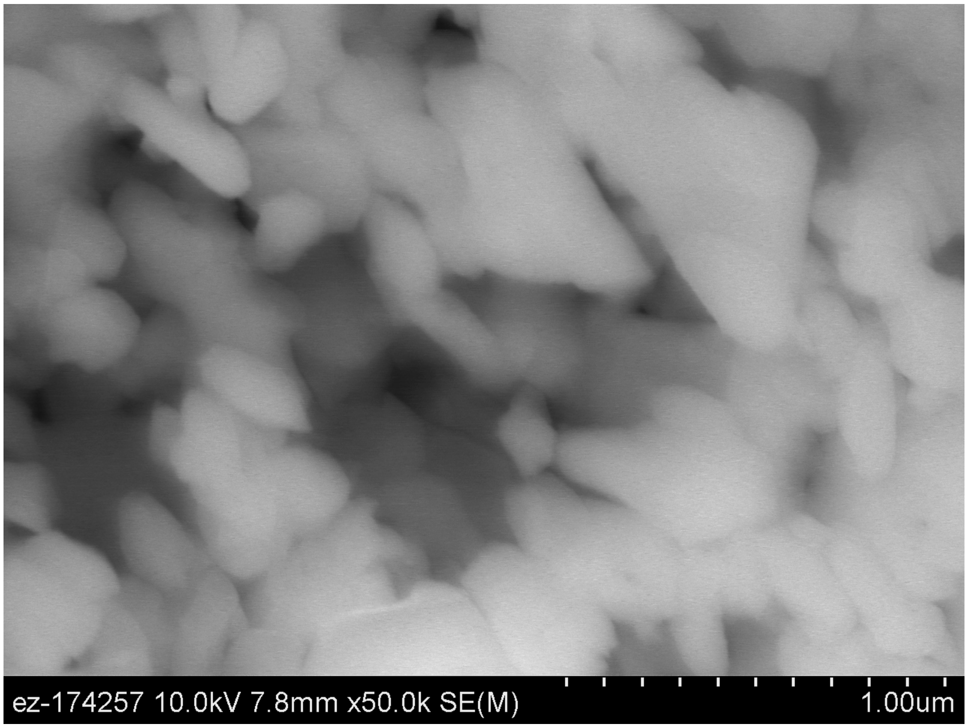


Fig. 5. SEM image of SG Powder, detailed view.

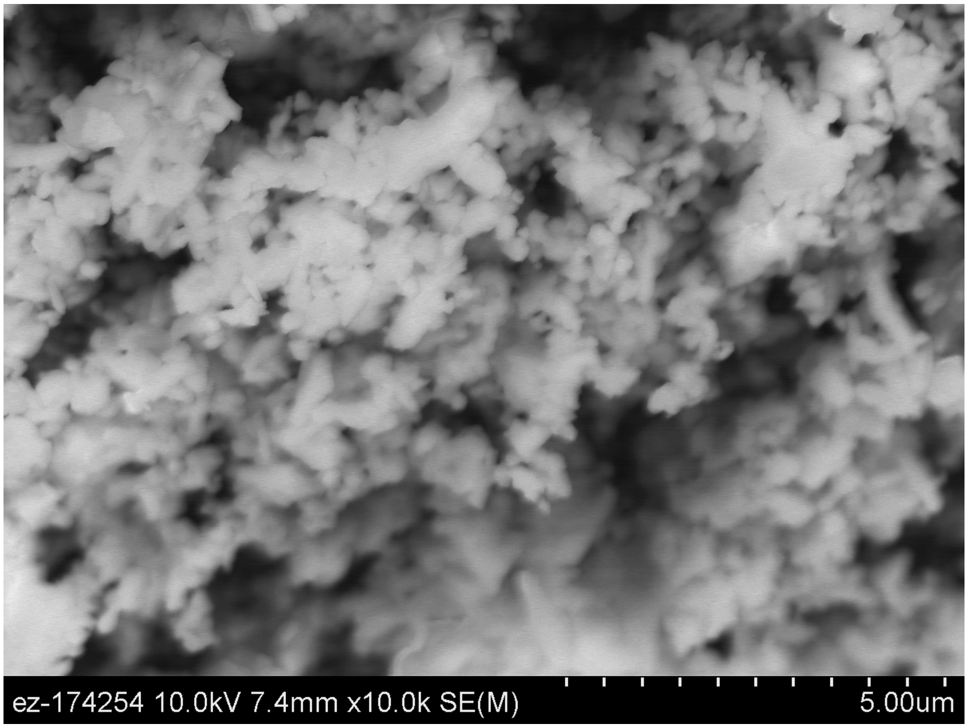


Fig. 6. SEM image of LS Powder.

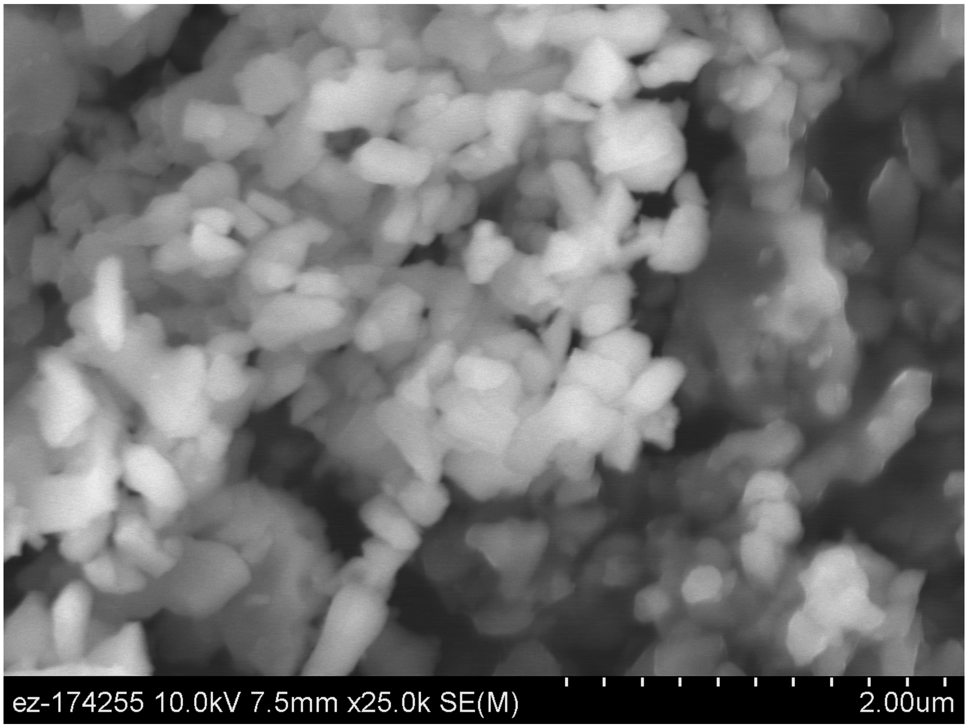


Fig. 7. SEM image of LS Powder, medium view.

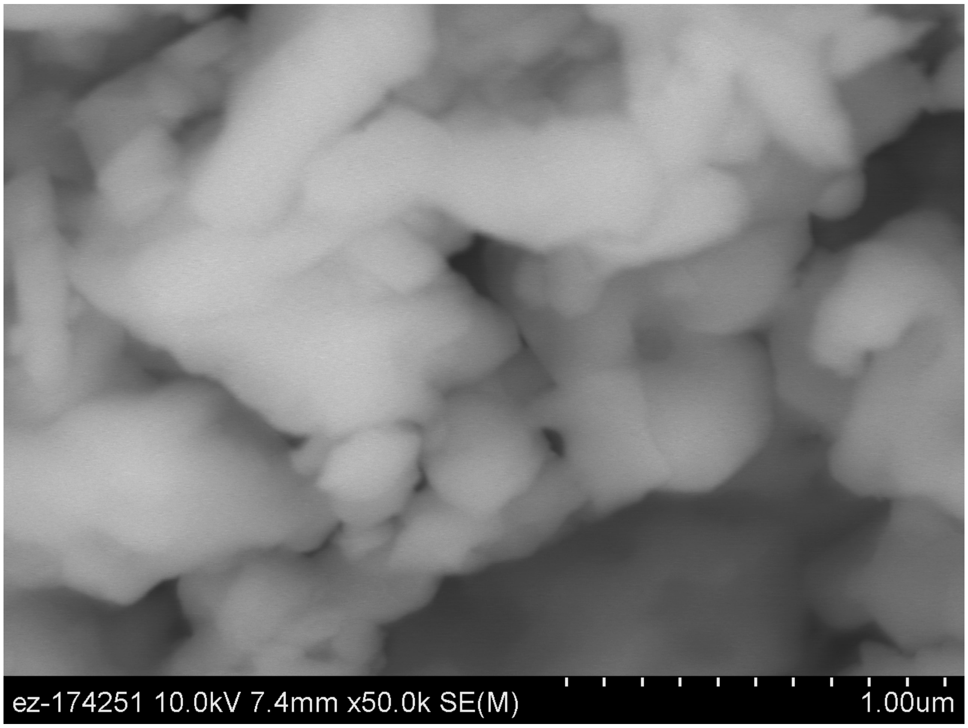
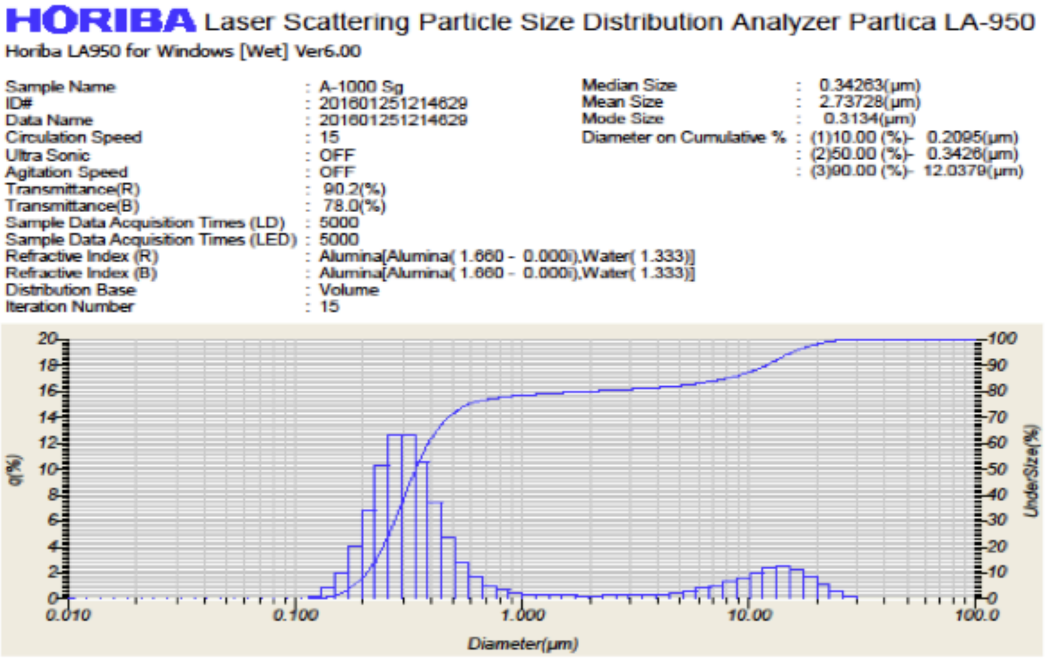


Fig. 8. SEM image of LS Powder, fine view.

For process optimization, sonication in the liquid (used for the PSD process) would be recommended along with an effective dispersant, i.e. Darvan C or 821-A (Vanderbilt Minerals, LLC) in order to prevent re-agglomeration.

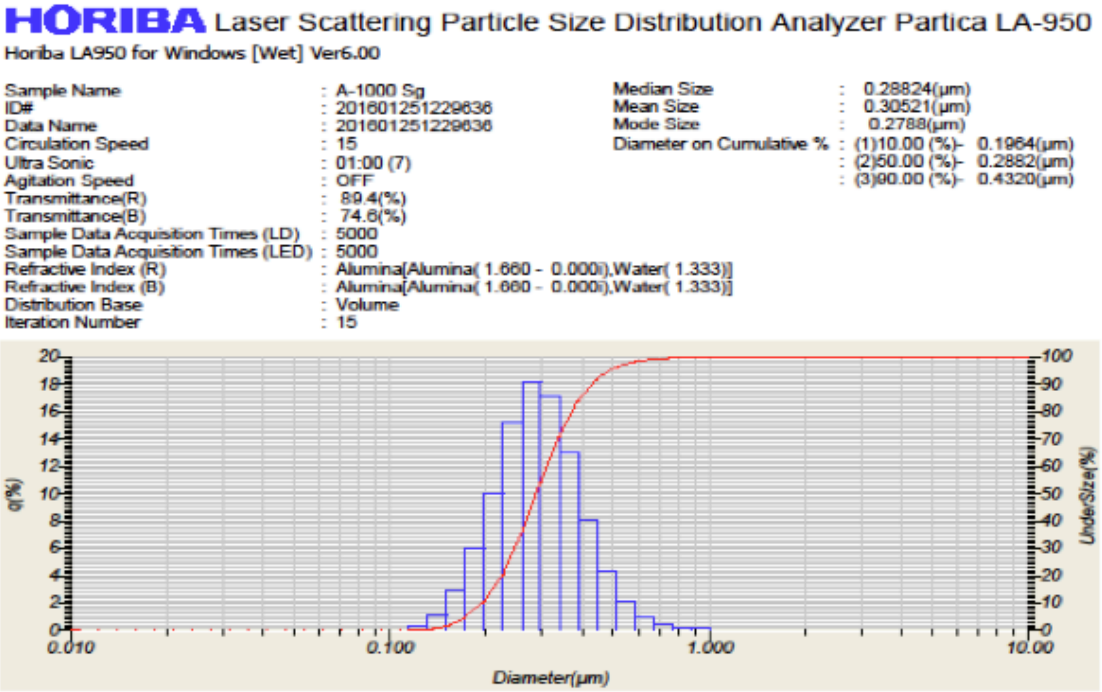
The particle size analysis was conducted with a Horiba Laser Scattering Particle size distribution analyzer (Partica La-950) with yielded the following data for comparison for SG powder before and after sonication (Figures 9-10). Comparison of the two figures indicates that sonication successfully breaks up the 10 um powder agglomerations in the as received powders.



```
HORIBA Laser Scattering Particle Size Distribution Analyzer Partica LA-950
Horiba LA950 for Windows [Wet] Ver6.00

Sample Name                           : A-1000 Sg                       Median Size              :  0.34263(µm)
ID#                                   : 201601251214629                 Mean Size                :  2.73728(µm)
Data Name                             : 201601251214629                 Mode Size                :   0.3134(µm)
Circulation Speed                     : 15                              Diameter on Cumulative % : (1)10.00 (%)-  0.2095(µm)
Ultra Sonic                           : OFF                                                      : (2)50.00 (%)-  0.3426(µm)
Agitation Speed                       : OFF                                                      : (3)90.00 (%)- 12.0379(µm)
Transmittance(R)                      :  90.2(%)
Transmittance(B)                      :  78.0(%)
Sample Data Acquisition Times (LD)    : 5000
Sample Data Acquisition Times (LED)   : 5000
Refractive Index (R)                  : Alumina[Alumina( 1.660 -  0.000i),Water( 1.333)]
Refractive Index (B)                  : Alumina[Alumina( 1.660 -  0.000i),Water( 1.333)]
Distribution Base                     : Volume
Iteration Number                      : 15
```

Fig. 9. Particle size analysis of as received "SG" powder.



```
HORIBA Laser Scattering Particle Size Distribution Analyzer Partica LA-950
Horiba LA950 for Windows [Wet] Ver6.00

Sample Name                           : A-1000 Sg                       Median Size              :  0.28824(µm)
ID#                                   : 201601251229636                 Mean Size                :  0.30521(µm)
Data Name                             : 201601251229636                 Mode Size                :   0.2788(µm)
Circulation Speed                     : 15                              Diameter on Cumulative % : (1)10.00 (%)-  0.1964(µm)
Ultra Sonic                           : 01:00 (7)                                                : (2)50.00 (%)-  0.2882(µm)
Agitation Speed                       : OFF                                                      : (3)90.00 (%)-  0.4320(µm)
Transmittance(R)                      :  89.4(%)
Transmittance(B)                      :  74.6(%)
Sample Data Acquisition Times (LD)    : 5000
Sample Data Acquisition Times (LED)   : 5000
Refractive Index (R)                  : Alumina[Alumina( 1.660 -  0.000i),Water( 1.333)]
Refractive Index (B)                  : Alumina[Alumina( 1.660 -  0.000i),Water( 1.333)]
Distribution Base                     : Volume
Iteration Number                      : 15
```

Fig. 10. Particle size analysis of "SG" powder after sonication.

1.2.2 Characterization of PSD Sintered Parts

ORNL characterized a disc shaped sintered sample provided by HotEnd Works with SEM and measured the modulus and density of the sample.

The modulus was measured for the disc shaped sintered sample provided by the supplier (Table 1). The sonic modulus for the alumina part is consistent with other known values found in open literature for alumina.

Table 1. Modulus

Young's Mod	Shear Mod	Bulk Mod
GPa	**GPa**	**GPa**
378.46	153.88	233.36

The density for the sintered part was determined by standard Archimedes immersion density methods and was found to be close to full density (>99.7 % of theoretical density (T.D.)) (Table 2).

Table 2. Density

SAMPLE DENSITY (g/cm3)	T.D. (g/cm3)	% T.D.	Open porosity, %
3.94	3.95	99.74%	-0.06

SEM images of the cross-sectioned polished surfaces of sintered parts provided by HotEnd Works are shown in figures 11 and 12. Voids were found in both samples large enough to severely limit the mechanical properties of the parts (with some as large as 3.3 mm by 340 um in size).

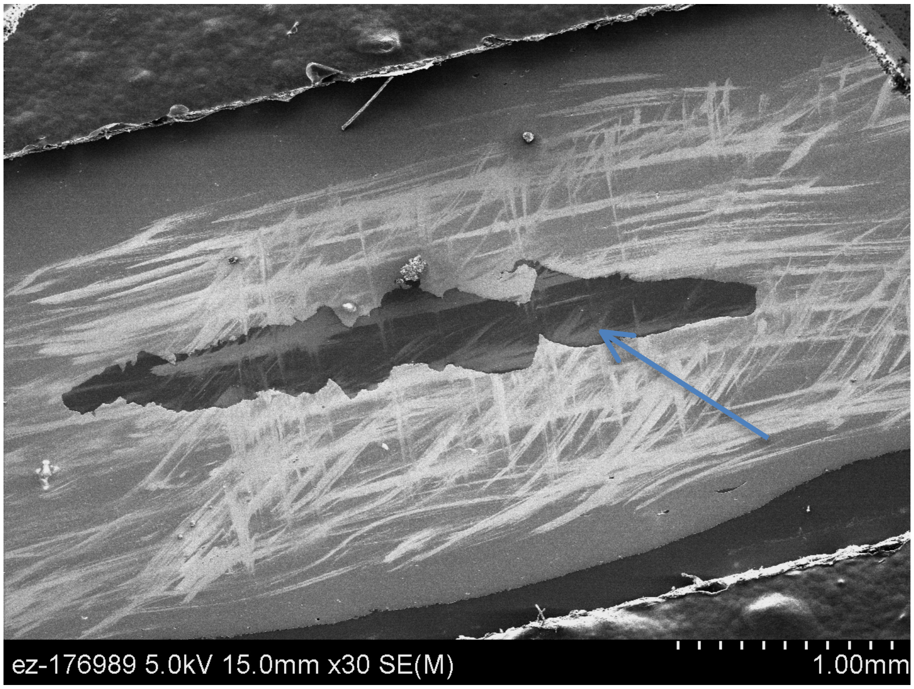


Fig. 6. Large void (flaw) in sintered part.

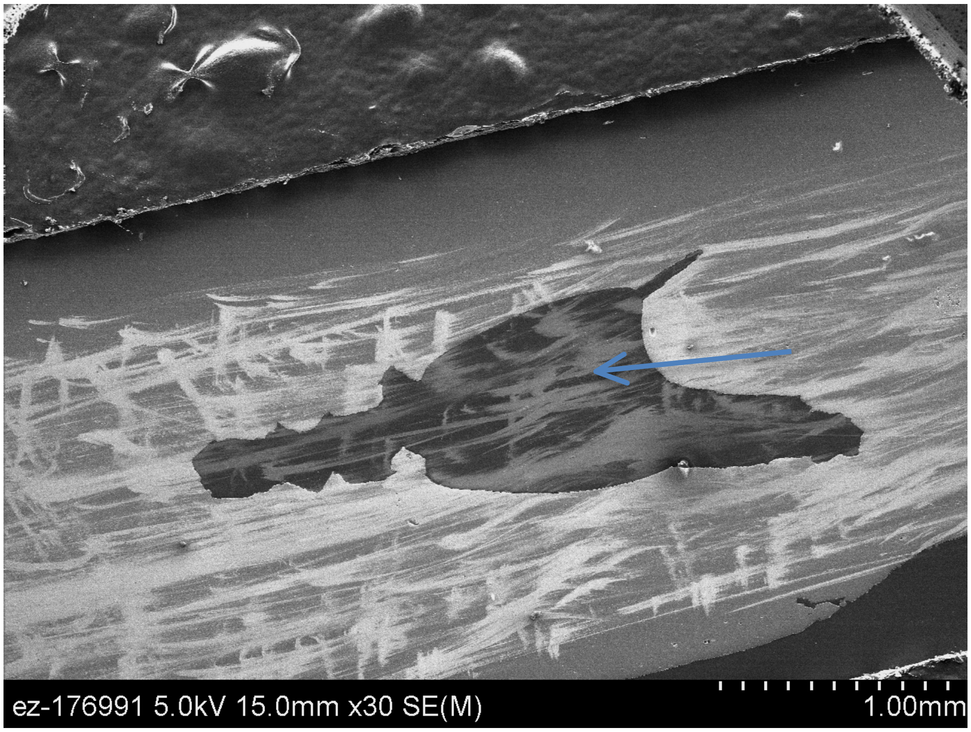


Fig. 7. Large void (flaw) in sintered part.

1.3 IMPACTS

The material processing optimization suggestions based on the material analysis performed will aide in producing higher performance components for current and future users of the PSD technology. The information also provided a deeper understanding for materials developing when moving forward into other areas such as silicon carbides, boron nitrides, etc.

The pressurized spray deposition (PSD process has the potential to generate complex ceramic parts at near full density without the use of costly directed energy sources (e.g. electron beams or lasers), and without the strong thermal gradients associated with those technologies. The utilization of AM for production of parts from advanced ceramics has a number of energy related applications.

The quality related issues discovered in this investigation are largely process related, and with further optimization by the partner, could be reduced, or eliminated. By providing the necessary characterization for the partner, there is now a path forward, which should lead to reduced manufacturing waste, reduced energy consumption, overall improvements in production efficiency, and improvements in the final material properties for HotEnd Works' PSD fabricated parts.

1.4 CONCLUSIONS

The project completed characterization of aluminum oxide powder feedstock used in the PSD process by HotEnd Works and provided limited characterization of sintered parts provided by the company. Several issues were discovered during the project. The alumina powder submitted for characterization was found to have agglomerates and some large particles (Fig 2), which have contributed to the flaw population in the final sintered parts. Large voids were found to exist within the alumina parts produced by HotEnd Works' PSD method (Figs 11-12). Microstructural examination by SEM found large voids (with some as large as 3.3 mm by 340 um in size) (Figs 11-12). Ultimately, flaws of this size are severely deleterious and would be responsible for limiting the mechanical properties and (until these flaws are eliminated by processing improvements), will continue to do so. However, the particle size analysis performed by ORNL indicates larger particles present in the feedstock can be removed by further classification and that the relatively soft agglomerates in the feedstock could be removed by sonication in the liquid used for the PSD process would be recommended along with an effective dispersant, in order to prevent re-agglomeration.

In addition to powder and sintered part microstructural characterization, the sonic modulus for the alumina part was also measured and determined to be consistent with other known values found in open literature for alumina. The density for this part was determined by standard Archimedes immersion density methods and was found to be > 99.7 % of the theoretical density for pure alumina.

By providing the necessary powder and property characterization for the partner, there is now a path forward, which should lead to reduced manufacturing waste, reduced energy consumption, overall improvements in production efficiency, and improvements in the final material properties for HotEnd Works' PSD fabricated parts.

2. PARTNER BACKGROUND

HotEnd Works is an additive manufacturing company that has developed an advanced materials 3D printing system which is capable of printing materials such as technical ceramics and carbides. The company uses a proprietary, highly advanced processing technique that produces parts comparable to traditionally-manufactured advanced material components.