NEW APPROACHES TO IMPROVING STRUCTURAL INTEGRITY IN BINDER JETTING PRINTING (BJP) PROCESS AND DEVELOPING ADVANCED APPLICATIONS BY COMBINING BJP AND POWDER METALLURGY TECHNIQUES

By

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ABSTRACT

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Binder jet printing (BJP), one of the early metal 3D printing technologies, has distinct advantages over the other additive manufacturing (AM) processes to directly build 3D parts. Some of the advantages of BJP include printed parts free of residual stresses, a less amount of labor, without the starting build plate, and a higher powder reusability. However, the BJP technology has been adopted only in the very limited applications in prototyping due to its technical difficulty in achieving full-density parts. This work has concentrated in developing a new BJP protocol to attain full-density parts made of Stainless Steel (SS) 420 and 316L. The effect of the average particle size, mixture ratio, and sintering additives on the densities of green and sintered parts is investigated for SS420 and SS 316L powders. Multiple powders distinct in average particle sizes are mixed to improve the packing density. A systematic study of the binder burn-out procedure is conducted using thermogravimetric analysis, leading to a complete removal of binder phase without extensively oxidizing SS420 and SS 316L powder. The optimal sintering condition for promising powder mixtures is determined to maximize the final density with the addition of a small amount of boron compounds as sintering additives. The quality of the fully-sintered SS420 and SS 316L parts is evaluated using the various measurements including density, microstructure, hardness, and surface roughness. Relative densities up to 99.6% are obtained for both SS420 and SS 316L without pronounced structural distortion. After achieving the parts with a full density, we were able to prove the ability of printing a shell of a part instead of the entire solid part. After

sintering, both printed samples have similar quality in term of powder consolidation. The shellprinting using BJP offers expediting the printing time and reducing the amount of binder phase used in printing process. Furthermore, we successfully developed a process to fabricate a completely enclosed serpentine channel with the length of 500mm and the width of 0.5mm in a 20mm x 10mm x 5mm block. This enclosed miniature internal structure fabrication is a unique accomplishment that is not easily achieved by any available AM technique. It offers potential applications such as fabricating columns for separation in gas chromatography and heat exchangers. Lastly, we employ BJP to print stainless steel parts (SS420) and sinter them in a reactive environment (e.g., oxygen), rendering the surfaces of the powder particles to be reacted and converted to electrically non-conducting ceramics (e.g., metal oxides). This metal/metal oxide hybrid structures exhibit several orders of magnitude higher electrical resistivity compared to the unreacted metal part. As a proof-of-the-concept demonstration, we have fabricated pin-fin-based miniature heating elements for rapid and energy-efficient heating and reaction applications. This dissertation is dedicated to my parents, my wife, my son, my daughter, and my siblings, who are all the meanings of my life

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CHAPTER 1

NEW APPROACH TO IMPROVING STRUCTURAL INTEGRITY IN BINDER JETTING PRINTING (BJP) PROCESS FOR STAINLESS STEEL 420

In this chapter, the author proposed some modifications in binder jetting process to achieve fully densified part without losing mechanical properties due to infiltrating low melting material as commercial method. A small amount of additive, boron compound, is added to investigate the enhancement in sintering process. We were able to achieve 99.6% dense of stainless steel 42p printed part by adding 0.5% boron nitride and sintering in vacuum at 1250°C. For a full text of this published work go to:

https://www.sciencedirect.com/science/article/pii/S0890695516304758

CHAPTER 2

ADDITIVELY MANUFACTURED FULL-DENSITY STAINLESS STEEL 316L WITH BINDER JET PRINTING

2.1. INTRODUCTION

Additive Manufacturing (AM) is an umbrella term for a variety of innovative processes characterized by building layer by layer to fabricate three-dimensional objects. While early AM processes were geared towards rapid prototyping of plastics, recent advancements in the field have prompted the production of metal components comparable to those produced by traditional manufacturing methods. In addition, they are able to create complex features difficult or impossible to produce using conventional machining, including hollow cavities, dense net structures, and curved internal channels. The versatility of these systems frees the design process from the constraints of conventional manufacturing techniques, offering exciting new opportunities in lightweight design, design complexity, and topologically optimized structures [1][2][3].

Depending on the method of material deposition, metal AM processes are classified into, most notably, Binding Jet Printing (BJP), Powder-Bed Fusion (PBF), and Direct Energy Deposition (DED) [4]. Both BJP and PBF are powder bed systems that typically provide better printing resolution and are more flexible in terms of material choices (because numerous materials are available in a powder form). In the powder bed system, each layer of powder is distributed uniformly across the build bed surface and consolidated by either a heat source or binding agent to form a 3D part. Selective Laser Sintering (SLS), Selective Laser Melting (SLM), and Electron Beam Melting (EBM) are a few examples of the popular PBF technology and have been extensively investigated as a viable metal 3D printing technique [3][5][6][7][8][9]. In PBF, each powder layer is exposed to a heat source such as laser or electron beam, which not only locally melts the topmost layer but also diffuses to the layer below. Therefore, each segment will experience multiple melting and solidification processes while being affected by the state of neighboring powder and the environment condition of the build chamber. Residual stresses are inevitably generated due to the large thermal gradients induced by localized heating and rapid cooling, causing part distortion and crack formation [10]. In addition, rapid cooling and directional solidification can result in metastable phases and anisotropic, heterogeneous microstructures sacrificing the final structural integrity [11].

On the other hand, BJP builds a part at room temperature, where a polymeric binder temporarily binds the powder in a layer by layer fashion to construct the desired shape. After curing the powder bed with the desired shape, the loose powder in the powder bed is removed. At this point, the as-printed part remains highly porous (about 50% of a theoretical density) and is normally infiltrated with a low melting-point metal such as bronze [12] In other words, the BJP part serves as a scaffold, and the property of the metal that fills the open pores ultimately determines the overall structural integrity. Because a low melting-point metal has a relatively low strength, the final BJP part is used in limited applications where the part's mechanical strength is not critical. A variety of materials have been printed by BJP including stainless steel [13] , titanium[14], graphene oxide [15] copper [16] Inconel [17], lead zirconate titanate [18], calcium polyphosphate [19], etc. These BJP parts have been used in the applications of solid-oxide fuel cell [20] and ceramics scaffolds for bone tissue. [21]

A few methods have been introduced to address the main disadvantages of BJP, that is, a high percentage of porosity of as-printed parts and the low mechanical strength of the common

infiltration metals. First, our group and other have reported an improvement in packing by varying the powder size and mixture ratio [22][23][24][25]. In a similar approach, Moon et al. [26] have modified powder-based BJP to fabricate ceramic parts by using slurry deposition (small size powder added to binder) to achieve a higher packing density (approximately 60%). Second, infiltration materials with a high melting point have been employed with high sintering temperature. For example, alumina powders of various sizes have been added to the powder mix and sintered at 1600°C to achieve densities of 96% [27]. Mostafaei et al. [28] processed Inconel 625 and achieved the density of 99.6% by simply increasing the sintering temperature to 1280°C. Thirdly, the addition of sintering additives can significantly improve the packing density even at lower sintering temperatures. In our previous works [22] [23], we added a small amount of boron compounds to stainless steel (SS) 420 powders of two different average particle sizes and sintered in a vacuum environment at 1250°C to achieve the density of 99.6%. However, the resultant parts made of SS420 were difficult to machine (due to the martensitic phase) and therefore were not suitable for some applications. SS316L was determined to be an effective replacement for SS420, featuring excellent corrosion resistance and much better machinability.

The objective of this paper is to present our recent effort to develop a BJP protocol to attain fully-sintered, high-density parts made of SS316L. We have leveraged our previous experimental findings on SS420 as a starting point and investigate the effect of the average particle size, the mixture ratio, and sintering additives on the densities of the final SS316L parts. Three different sizes of SS316L powder particles as well as a small amount of boron compounds as sintering additives are mixed prior to sintering. The optimal sintering temperature for a given mixture of powders is determined to obtain the maximum density without affecting the part shape. Both binder burnout and sintering processes are monitored by thermogravimetric analysis (measuring a weight change at a given temperature as a function of time). The quality of the fully-sintered SS316L parts is evaluated using the various measurements including density, microstructure, hardness, and surface roughness. A relative density of 99.6% has been obtained for SS316L without structural distortion. This is the first demonstration of such high density for SS 316L using the BJP technology without any infiltration.

2.2. MATERIALS, PROCESS, AND EXPERIMENTS

2.2.1. Materials

Four sizes of stainless steel 316L powders were used to perform experiments. The powders were denoted as S (small), M (medium), D (default size, 30 µm), and L (large) whose average particle sizes are presented Table 2.1. Mixing multiple sized powders is beneficial to achieve a higher packing density as opposed to using only one powder. The resulting packing ratio is directly impacted by the particle arrangement of the powders, their size ratio, and their mass ratio. In order to achieve the maximal packing density for SS316L powders, a number of experiments were performed to find the optimal mixture based on multiple combinations of particle sizes. Powder mixtures of two different particle sizes and three different particle sizes were tested to find the ideal mixture ratio for the best packing.

Small amounts of sintering additives are known to drastically enhance the sintering process in the field of powder metallurgy. In our previous findings [23], a small amount of boron compounds were used to reduce the sintering temperature and enhance the sintering of SS 420 powder. Three boron compounds were used: boron (B), boron nitride (BN), and boron carbide (BC) (see Table 2.1).

2.2.2. Processing

2.2.2.1 Mixing powder

In order to perform the experiment with different particle size combinations, the mass of powder must be measured accurately. Powder masses were measured using a high resolution analytical lab scale, Adventurer AR 2140, manufactured by Ohaus (Parsippany, NJ, USA). Each mixture was prepared using a high speed mixer (DAC 150 supplied by FlackTek, Inc., Landrum, SC, USA). The high speed mixer runs in three cycles with an angular velocity of 2000 rpm and 90 s per cycle. The mixture of powder was then deposited into the powder supply bed in our BJP printer.

			Size	Density
Powders		Provider	(µm)	(g/cm^3)
Main Powder	SS 316L (S)	Epson Atmix Corp.	4	7.93
	SS 316L (<i>M</i>)	Oerlikon Metco (US) Inc.	14	7.93
	SS 316L (D)	Oerlikon Metco (US) Inc	30	7.93
	SS 316L (<i>L</i>)	Oerlikon Metco (US) Inc	82	7.93
Sintering	В	Sigma Aldrich (St. Louis, MO)	1	2.34
Additive	BC	Panadyne (Montgomeryville,PA)	0.6	2.51
	BN	Sigma Aldrich (St. Louis, MO)	1	2.29

Table 2.1: List of SS316L powder and sintering additive materials and their size and density

2.2.2.2. Printing and curing

The experiments are performed with the X1-lab, manufactured by ExOne (Huntington, PA, USA). The process was described thoroughly in our previous work [15]. The system has two beds: one is for building desired parts (namely, a build bed) and the other contains stock powder (namely, a supply bed). In the beginning, the first layer of powder was uniformly spread on the build bed by a raking mechanism. After printing the first layer, a polymer binder is injected from the print

head and the build bed is lowered by the preset increment to accommodate a new powder layer from the supply bed. After completing all the layers, the printed part remains on the build bed with the loose powder. The part is then put into a convection oven (DX302C, Yamato, JAPAN) to cure the binder phase at 195 °C for two hours. The curing process improves the structural integrity of the part before removing the loose powder.

2.2.2.3. Binder burning

The cured binder inside the printed structure needs to be eliminated from the structure before sintering otherwise the binder phase will turn into carbon in the sintering process, which later can easily diffuse inside the part and deteriorate its ductility. Oxygen is required to burn the binder and thus the sample was heated in the air furnace (KSL-1100X, MTI Corp.). Note that SS can be oxidized in the presence of oxygen at high temperatures. For this reason, the binder burn-out temperature needs to be minimized. In our previous work [23], we reported that most of the binder phase was removed within 2 hours at 460°C without much oxidation on the powder surface. The same procedure has been implemented due to the high oxidation resistance of SS316L with higher percentages of Cr and Ni compared to SS420.

2.2.2.4. Sintering

After burning out the binder in the air furnace, the samples were sintered in the high temperature furnace with the environmental control capability (Materials Research Furnaces, Model G- 3000, Allenstown, NH, USA). In general, SS powder after compaction is sintered in the hydrogen, argon or nitrogen environment [19]. In this research, we sintered the samples in vacuum environment since it is believed to eliminate the internal pores before consolidating the powder.

Multiple steps were implemented to attain the high vacuum level in the furnace as described in [23].

2.2.3. Characterizations

2.2.3.1. Relative density

The density is measured at two stages: the packing density of the printed samples and the relative density of the sintered samples. The samples were printed at the size of 8 mm \times 8 mm \times 8 mm in the highest resolution setting (layer thickness of 100 μ m). The packing density was determined by measuring the mass (Adventurer AR 2140 scale) and the volume through the sizes of the cube (Mitutoyo 500 caliper, accuracy 10 μ m). Because some samples lost their original cubic shape during sintering, the Archimedes method was used to accurately measure the part volume.

2.2.3.2. Confocal microscopy

The surface finishes of the printed and sintered samples are measured by the confocal microscope (Olympus Spectra FV1000, Tokyo, Japan). The recorded images are saved as OIB files (which is utilized by Olympus) then converted to Tiff files. Those files containing the height data of the surface topography are processed with the custom MATLAB program to obtain the roughness profiles.

2.2.3.3. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

JEOL 6610LV (JEOL, Japan) was used to observe the powder size, powder packing, and microstructure of the sintered samples. The samples were polished by using different grit sandpapers and a lapping film with diamond paste (1 μ m) as the final step. These polishing and

imaging acquisition procedures were to expose the micro pores inside the sintered samples. The JEOL 6610LV was also used to conduct elemental analysis via EDS to determine how the samples were oxidized after burning the binder and sintering in a vacuum environment.

2.2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (STA 449 F5 Jupiter, Burlington, MA, USA) is performed to measure the weight change of each sample during the binder burning process. This experiment enables us to optimize the burning temperature in order to eliminate the binder content in the printed/cured samples completely. Typically, in the powder processing of metals, oxygen should be avoided. However, oxygen is required to burn the binder and its carbon residue. TGA is used to monitor a weight change of raw SS powder and as-printed parts, so that we can estimate the extent of SS oxidation during the binder burning process.

2.2.3.5. Hardness

To measure the hardness accurately, each sample is first polished to remove the rough outer layer which is a common source of inconsistencies. The samples are hot-mounted in a thermoset resin using a hot mounting press to facilitate the polishing process. Each potting represents one combination of sintering temperature (1200, 1300, 1350°C) and boron compound (B, BN, BC). Each potting contained one sample for each weight percent (0.25, 0.5 and 0.75 wt%) of the respective boron compound and sintering temperature. All samples are mounted in the same orientation as printed. After mounting, the samples are polished using a lapping machine with 60, 120, 240, and 320 CAMI grit sand papers.

2.2.3.6 Tensile tests

To characterize the material strength, tensile bars were produced using 0.75%B and 0.75%BC, both sintered at 1200°C. Due to the printer's limited build platform (60mm x 40mm x 34mm), a standard ASTM tensile bar could not be produced. Instead, a custom tensile bar was designed and tested using ANSYS FEA software, to ensure fracture occurred along the gauge length. To ensure dimensional accuracy and eliminate printed surface effects, the tensile bars were cut from solid blocks of printed materials using Electric Discharge Machining (Brother HS-704, EDGE Machine tools, Illinois, USA). After cutting, tests were performed using an Instron Universal Testing System (3367 UTS, Instron, Northwood, MA, USA). Unfortunately, elastic modulus and yield strength could not be determined as the extensometer was too large for the samples. Instead the extension was measured by the built-in encoder. Four samples were made for each additive to ensure the repeatability of the measurements and uniformity of the printed parts.

2.3. RESULTS AND DISCUSSION

2.3.1. Packing ratio

The BJP equipment used in our research is designed to evenly spread powder layer with the particle size ranging from 30 to 60 μ m. Powder is spread out by a roller without any compaction. With the default single-size powder with narrow size distribution *A1* or *B1*, the packing of the printed part is relatively ineffective, approximately 50% (Fig. 2.1(d) and Fig. 2.1(e)). Because of this low packing density, it is difficult to fully sinter the parts. Furthermore, the samples are also distorted extensively during the consolidation process. Powders of substantially different particular sizes have resulted in poor spreading and inconsistent thickness of the powder layer. Since no compaction or shaking process can be performed in a powder

spreading process, it is reasonable to expect that mixing multi-size powders allows the small particles to occupy the gaps between the larger ones. McGeary [29] has performed a fundamental research of mixing various sizes of uniform spherical powders to find out the relationship among particles size ratios. All of his experiments were conducted by mechanically vibrating the glass particles to achieve the highest possible packing. For single-size spherical particles, the packing density of 62.5% was attained, which was noticeably higher than around 50% accomplished by BJP. For binary packing of a radius ratio of 7:1 and a mixing ratio of 70:30, the highest packing density of 83% was achieved. In this research, we started adding powder of 4 μ m in average diameter(*S*) to 30 μ m (*D*) and investigated the effect of weight percent ratio on the packing densities of the samples in their green state.

A radius ratio of 7.5 (= 30/4) is close to the ideal ratio (~7) reported by McGeary [29]. Different amounts of each powder were mixed and printed to examine the packing density. When using only one powder size (*A1*; 100% *D*), the packing density is only 51.3% of the theoretical density. Adding more *S* powder initially increases the packing density, but beyond *A4*, the density decreased (see *A5*, *A6*, *A7* in Fig. 2.1(d)). This trend agrees with the experimental results reported by McGeary [29]. The highest density was achieved with *A4*. With the binary mixtures, the packing ratio was increased from 51.3% % (*A1*) to 60.3% (*A4*). McGeary also showed that, with the addition of another powder size, the maximum packing density increased from 83% (binary mixture) to 90% (ternary mixture). Thus, we conducted additional experiments on ternary mixtures (*L*, *M*, and *S*). Each powder mixture ratio is denoted as shown in Figure 2.1(e). Sample *B4* (70*L*-25*M*-5*S*) resulted in the highest packing density of 63.87%. The result is far lower than that achieved by McGeary. However, unlike McGeary's experiment, our BJP system does not allow the powder bed to be shaken.

Fig. 2.1(a-c) shows the SEM images of the printed samples with different mixtures (B1, B7 and B4 respectively). We can visually confirm that the ternary mixture provides a better packing density. The smaller particles fill the interstitial gaps among larger ones. Based on this finding, B4 was chosen for the remaining experiments.

2.3.2. Thermos-gravimetric analysis (TGA)

In our previous study, the binder decomposition temperature was found to be 389° C [23][30]. However, because the binder phases are trapped among the powders, higher temperatures are needed to effectively burn out the binder phases. For the densest packed sample (59.4%) in our earlier work, most of the binder phase was burned out in 2 hours at 460°C (with a ramp rate of 5°C/min). Since *B4* of this study has a higher packing density (64%), the TGA experiment was conducted to determine the effectiveness of the binder burning process. The TGA result is shown in Fig. 2.2, Printed sample (blue line). The weight change is drastic when the temperature reached above 300°C. The weight continued to drop until the temperature rose up to 460°C. The weight increase after 110 minutes is speculated to be SS powder oxidizing, but a continual removal of the residual binder phase may influence the weight change.



Figure 2.1: Powder packing of different mixtures. (a) SEM of L printed, (b) SEM of M printed, (c) SEM of mixture B4 printed, (d) density of mixtures of 2 powders, (e) density of mixtures of 3 powder

To isolate the effect of powder oxidation, raw SS 316L powder of the same size without the binder was oxidized using the same temperature profile. The weight change is illustrated in the yellow line labeled as 'Powder' in Fig. 2.2. The overall trend is that the powder weight increases monotonically with increasing temperature, indicating the continual oxidation of the powder. The slopes of two curves, Powder and Printed sample, after 120 mins are similar, suggesting that little to no binder phase is burning out.



Figure 2.2: TGA results showing (a) weight change of powder and printed samples. (b) the difference between weight percentage of powder and printed sample

The percentage of binder weight in the printed part can also be estimated based on the binder saturation rate and porosity of the sample. In our BJP process, we used the default values for the binder saturation rate and packing density, which are 70% and 60%, respectively. This means that the printed part would have 40% of porosity and the binder will occupy 70% of porosity of the sample. Thus, the binder volume is $V_b = 70\% \times 40\% = 28\%$. Since the densities of the binder and SS316L are 1.06 g/cm³ and 7.93 g/cm³, the packing density of **B4** (green state) is 63.87%. The wt% of binder in the printed sample after printing is:

$$wt \% of \ binder = \frac{V_b \rho_b}{(V_b \rho_b + V_s \rho_s)} \times 100\% =$$
$$= \frac{0.28 \times 1.06}{(0.28 \times 1.06 + 0.6387 \times 7.93)} \times 100\% = 5.53\%$$

Our previous work on SS420 showed 10.45% of the binder remaining after curing. Other components in the binder are solvents like isopropanol alcohol and ethylene glycol monobutyl which would quickly evaporate at the temperature much lower than the curing temperature of 195° C. Therefore, the amount of binder in the printed part after curing is $10.45\% \times 5.53\% = 0.578$ wt% of the printed part. In Fig. 2.2, difference in percentage of the Powder and Printed sample

does not vary in the linear regions (120~210 min) and is around 0.517, which is related to binder burn-out. The amount of burned-out binder is 100 x 0.517/0.578 = 89.44%. Thus, it can be concluded that approximately 90% of the binder has burned out from the printed sample *B4* after soaking at 460°C in 2 hours.

To understand the oxidation behavior of SS316L at high temperatures, another TGA experiment was conducted for B4 with the same ramp rate (5°C/minute) up to 900°C. Figure 2.3 shows the temperature profile as well as the corresponding weight change of sample B4. A significant oxidation started to occur only when the temperature increases beyond 700°C (i.e., less than 0.5% weight gain up to 700°C with the ramp rate of 5°C/min). This is expected because SS316L contains a sizable amount of Cr and Ni (16~18% each) showing a high resistance to oxidation. However, when the temperature goes above 800°C, SS316L becomes substantially oxidized, necessitating the inert or vacuum environments for high-temperature sintering.

The EDS analysis was conducted on *B4-0.5B* (*B4* plus 0.5% boron additive) sintered at 1300°C under vacuum. Note that the sample underwent the binder burning process at 460°C for 2 hours before sintering. The sample surface was directly imaged and analyzed without any post-processing to evaluate the extent of oxidation. As shown in Fig. 2.4, many locations on the sample surface were scanned, and no oxygen peak was found in any of spectra. Considering the volume of primary excitation due to an electron beam in EDS, the characteristic x-ray signals come from $1\sim3 \mu m$ below the surface. While the EDS spectra are not sensitive within the few hundred nanometers from the surface, it can be concluded that the BJP samples subject to the binder burnout and vacuum sintering are essentially free of significant oxidation.



Figure 2.3: TGA result of B4 after oxidation in air with the ramp rate of 5° C/min and soaking at 900° C

2.3.3. Density

Samples with the highest green packing density (i.e., B4) were combinatorically mixed with 0.25, 0.5, 0.75 wt% of B, BC, and BN. All the samples with and without additives were printed and sintered in vacuum at 1200°C, 1300°C, and 1350°C for 6 hours. Three cubes of 8 mm

x 8 mm x 8 mm were printed for each sample. The reported density of each sample was averaged from those 3 samples (Table 2.3). Figure 2.5 shows the photographs of the as-sintered samples and the plots of their relative densities. The samples without additives have 71.6%, 72.7% and 72.9% densities for the sintering temperatures of 1200°C, 1300°C, 1350°C, respectively. These samples have relatively low densities even sintered at the temperature close to the melting point of SS316L (~ 1400°C). By adding a small amount of additive, the densities have significantly increased (see Fig. 2.5). From the images, the samples with boron additives reached to the liquid-phase sintering earliest and generally have higher the final relative densities in comparison to the samples with boron nitride and boron carbide additives. The samples with 0.75%B and 0.75%BC sintered at 1300°C and 1350°C exhibit extensive distortion. Our goal is to select the sample with the highest density and least distortion. Three samples meet our selection criteria: 0.75%B, 0.75%BC sintered at 1200°C, and 0.5%B sintered at 1300°C with the relative densities of 98.13%, 99.67%, and 98.33%, respectively.

The microstructures of the samples were also investigated using SEM to inspect the presence of porosities. The samples with 0.5%B and 0.75%B and sintered at 1300°C show the dense structures with no apparent large-size pores (see Fig. 2.6(c-d); several pores smaller than 5 μ m can be observed). At the same sintering temperature, the samples without additive and with 0.25%B exhibit large pores over tens of microns in size (Fig. 2.6(a-b)). The samples with 0.75%B and 0.75%BC and sintered at 1200°C also show relatively dense materials but with pores of noticeable sizes (see Fig. 2.6).



Figure 2.4: EDS results on the sample surface (B4-0.5B) after binder burning at 460°C and vacuum sintering at 1300°C.

Table 2.2: EDS results at different locations on the sample surface (**B4-0.5B**) after binder burning at 460° C and vacuum sintering at 1300° C

	Spec.	Spec.	Spec.	Spec.	Spec.
Wt%	6	7	8	9	10
Fe	69.1	37.5	36.2	60.4	51.3
Cr	9.0	39.5	41.3	18.5	16.5
Ni	15.4	0	0	10.6	9.1
Mo	2.1	6.0	4.3	5.3	8.7
С	3.8	4.2	4.6	4.8	6.1
O2	0	0	0	0	0



Figure 2.5: Densities and images of samples with different additives sintered at different temperatures

Table 2.3: Relative densities of samples with different additive and sintered at different temperatures

1200	0%	0.25%	0.50%	0.75%
BN	71.6	73.93	81.25	88.14
В	71.6	86.42	91.07	98.13
BC	71.6	85.17	93.56	99.67
1300	0%	0.25%	0.50%	0.75%
BN	72.7	76.484	87.3	96.06
В	72.7	92.15	98.33	98.36
BC	72.7	90.13	96.59	99.85
1350	0%	0.25%	0.50%	75%
BN	72.9	78.4	89.25	97.06
В	72.9	97.42	99.5	99.07
BC	72.9	93.11	95.59	99.43

2.3.4. Surface finish

One of the main drawbacks in AM technology is rough/poor surface finish. Before being used in real applications, fully-sintered parts normally entail post-processing such as polishing and other surface finishing. The surface roughness of the AM part depends mostly on the printer resolution, layer thickness, and powder size. In case of the BJP procedure, a sample printed with one powder size results in rough surface finish. Mixing multiple powder sizes improves not only the packing ratio but also the surface finish of the samples [31] as smaller powder particles can fill the gaps created among larger powders and improve the surface quality. Here the surface finish was measured using the confocal microscopy for as-printed and as-sintered (1300°C) samples. The samples under testing were B1, B4, and B4-0.5B. The rendered topographies were shown in Figure 2.7 and Figure 2.8. Figure 2.7(a) and 2.7(b) compares the surface roughness for as-printed samples of single powder size (B1) and ternary mixture (B4). It can be observed that the ternary mixture sample (B4, Fig. 2.7(b)) resulted in better surface finish. Also, 2D profiles at three different locations (Y = 100 μ m, 300 μ m, and 500 μ m) of the ternary mixture sample (**B4**; Fig. 2.7(b2), 2.7 (b3), and 2.7 (b4)) show less ups and downs compared to the single powder size sample (B1; Fig. 2.7(a2), 2.7(a3), and 2.7(a4)). The average surface roughness of B1 and B4 is estimated to be 22.7 µm and 17.27 µm, respectively. After sintering, **B4** still has better surface finish (Fig. 2.8(b)) than **B1** (Fig. 2.8(a)).



Figure 2.6: Microstructure of samples sintered at 1300oC (a) no additive, (b) 0.25%B, (c) 0.5%B, (d) 0.75%B and samples sintered at 1200oC (e) 0.75%BC, (f) 0.75%B



Figure 2.7: Topographies of as-printed samples: (a) B1 and (b) B4

The average surface roughness was calculated to be 14.84 μ m and 20.33 μ m, respectively. Adding additives also helped improving surface finish because additives situated along the interstitial spaces of large SS particles promote the liquid-phase sintering at lower temperature. This phenomenon facilitates local reflow of the peaks and valleys and smoothens out the surface. The result of surface finish of *B3-0.5B* sintered at 1300° C in Fig. 2.8(c) proved the abovementioned point. The average surface roughness of this sample is 8.5 µm. Therefore, we can conclude that mixing different size of powders and adding sintering additives help achieving better surface finish



Figure 2.8: Topographies of samples after sintering at 1300oC: (a) Large powder (B1) only, (b) mixture B4, (c) mixture B4 with 0.5B

2.3.5. Hardness

Three Rockwell B hardness (HRB) tests were performed on each sample. The averaged hardness measurements are recorded in Table 2.4. To ensure accurate readings, a standard of hardness 98.5 HRB was tested before, during, and after the experiment. The result for all three of these tests was 99.0 HRB, showing that the machine was consistent in its readings. For comparison, a commercially obtained SS316L bar has the Rockwell B hardness (HRB) of 80 [32]. From Table 2.3, it is clear that there is a positive correlation between percent additives and hardness. Also, in all but one instance, the sample with B additive was harder than those with BN or BC of the same concentration and percent additive. Boron also had the highest overall hardness of 94.17 HRB for both 1350 °C and 1300 °C samples. The inconsistencies in trends between the different temperatures are likely due to porosity.

2.3.6. Tensile strength

The tensile strength of four specimens machined from each printed block were tested. The testing results for ultimate tensile strength (UTS) and strain at failure are presented in Table 2.5. The average UTS of 0.75%B is 404 MPa. The 0.75%BC samples exhibit a higher average UTS of 457 MPa, which is comparable to 515 MPa for the SS316L annealed bar [32]. The result can be explained by the higher density of this 0.75%BC sample in comparison to 0.75%B sample (99.67% and 98.13% respectively, see Table 2.3).

1200 °C	0%	0.25%	0.50%	0.75%
BN	29.5	34	35.17	33.67
В	29.5	44.17	44.17	79.33
BC	29.5	28	59	78.33
1300 °C	0%	0.25%	0.50%	0.75%
BN	30	35.67	36.5	72.17
В	30	62.17	70.83	94.17
BC	30	33.33	70.17	82.17
1350°C	0%	0.25%	0.50%	0.75%
BN	42	47.17	51.67	74
В	42	63.33	84.17	94.17
BC	42	29.83	52.33	75.17

Table 2.4: Hardness data of various samples (HRB)

Table 2.5: UTS and strain at failure for four samples of each additive (0.75%B and 0.75%BC)

			UTS
Addit	ive	Sample	(Mpa)
0.75	wt%	1	382
В		2	387
		3	416
		4	432
		Avg.	404
0.75	wt%	1	465
BC		2	460
		3	450
		4	454
		Avg.	457

In addition, it is well known that adding carbon into steel distorts its crystal lattice and strengthens the steel by reducing the dislocation movement. Averaged strains at failure for the 0.75%B and 0.75%BC samples are 38.9% and 52.7%, respectively, and smaller than 60% of the annealed bar [32]. Therefore, it can be concluded that the BJP parts show higher UTS values but lower strain at failure compared to the traditionally machined parts.
2.4. CONCLUSION

In this chapter, we presented a systematic study to develop a protocol for BJP to attain fully-dense SS316L parts. By mixing three different sizes of powders, the packing density was improved to 63.87% in comparison to 50.77% which is obtained by printing single powder. The binder burn-out procedure was characterized using thermogravimetric analysis to maximally remove the binder phase while minimizing oxidation on the final parts. Instead of infiltrating a low melting-point metal in a typical BJP process, a small amount of boron compound additives was added to enhance consolidation during sintering in a vacuum furnace. We were able to produce SS316L parts with a near full density but without any distortion of the final part shape. In particular, the relative densities of 98.13% were achieved with the addition of 0.5% B after sintering at 1300°C. With higher amounts of sintering additives, the relative densities of 99.67% and 98.33% were attained with the addition of 0.75% BC and 0.75% B after sintering at 1200°C. Across all samples presented in this study, the hardness of each sample is comparable to that of bulk SS316L, which is reported to be 80 HRB. The samples with 0.75wt% B and BC exhibited the hardness values near or exceeding 80 HRB. The highest hardness of 94.17 HRB was obtained with the sample with 0.75wt% B sintered at 1300°C and 1350°C. The surface finish of the printed samples was also studied, revealing that the parts with boron additives displayed significantly improved surface finish of the final parts

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CHAPTER 3

SHELL PRINTING

3.1. INTRODUCTION

Although additive manufacturing possesses many advantages such as freedom in design to create complex structures and fast product life cycles, it also has a number of challenges that need to be addressed. One of the main drawbacks of AM is the extended printing time, which encumbers any practical application in the mass production. For the direct energy deposit process, the electron or laser beam is concentrated to melt the powders in a small spot once at a time. Some SLM machines adopted multiples laser sources to melt many points simultaneously to increase the printing speed. However, it induces the difficulty of control reflective mirror systems and effusive energy intensities to create homogenous parts. One way to reduce the printing time is to reduce the printing area on each layer. For binder jetting system, the printing process is taking place in the similar way as the laser or electron beam melting. Instead of the laser or electron beam, the inkjet head is moving to inject binder on the selected areas. In general, the point printing method is limited in speeding up the printing due to many reasons such as accuracy loss, controllability, and un-melted powders due to the fast scanning rate (In SLM and EBM systems).

Reducing the printed volume is not feasible for the direct energy methods such as EBM or PBF because the powders were melted and solidified throughout the printed area. The BJP may provide one method to print each layer by printing the outline and using the boron based consolidation developed in Chapter 2. Because of the driving forces of the consolidation, the whole part can be sintered in the furnace afterward to from a solid part. This simple idea of 'printing shell' has not been explored or published in literature. Other than accelerating the printing process, printing shell also save the amount of the binder phase consumed in compared to printing the whole body. The amount of binder can be easily estimated by the difference in the total volume of solid part versus the volume of the shell. Another major advantage of printing shell is the amount of the time to burn out binder can be substantially reduced especially as the part size becomes larger. Oxygen is essential to burn the binder phase and, in the shell printing method, the shell sections containing the binder phase are readily exposed to oxygen for the burnout. With the reduced burnout time, the oxidation level of the powders can be substantially diminished, which helps to enhance sintering process as well as mechanical properties. It is well-known that the sintering of oxide phase is much slower than that of metal phase and the presence of oxygen deteriorates many structural mechanical properties. The samples produced with the shell printing method are expected to provide better mechanical quality because a small amount of binder residue can be left inside the structure yielding high carbon content even after the burnout process.

The proposed shell-printing process is showed in Figure 3.1. After finalizing the design, the CAD file is imported into FEM model with an initial thickness. The stress induced by the powder inside the shell is calculated. This stress is compared to the fracture strength will be measured by the maximum hoop stress (see Section 6.3.3). With the set safety factor, the thickness of the shell can be determined. The proper safety factor value would require further statistical experiments which is beyond the scope of this research. The shell thickness can be also varied depending on the stress. The part with the shell thickness large enough to hold the powders with the shell is simulated finally to examine if the maximum stress does not exceed the limit (Fig. 3.1a). In the next step, the CAD file of the shell print design is converted into a STL file to print using the mixture of SS316 with 0.5B (Fig. 3.1b). After curing the printed part and removing the

powder outside the shell (Fig. 3.1c), the part containing the powder inside the shell is put into the air furnace at 460°C for 2 hours and subsequently sintered in the vacuum furnace at 1250°C to achieve a full density part (Fig. 3.1d).



Figure 3.1: a) Design part and run FEM analysis to calculate the stress and estimate the thickness of the shell b) Printing the shell only, c) Cure and remove external loose powder, d) Heat processing (binder burning and sintering)

3.2. MATERIALS AND PROCESSING

3.2.1. Materials

In this research, the spherical stainless steel 316 powder (Oerlikon Metco (US) Inc.) with the average size of 14µm was mixed with 0.5% weight percentage of the boron powder with the average size of 1µm (Sigma Aldrich, St. Louis, MO) (Table 2.1). Boron is known to enhance the sintering process of the ferrous powder as discussed in Chapter 2. Powder weights were measured by using a high resolution analytical lab scale, Adventurer AR 2140, manufactured by Ohaus (Parsippany, NJ, USA) and mixed by a high speed mixer (DAC 150 supplied by FlackTek, Inc., Landrum, SC, USA) in 30 seconds at 2000 rpm. The mixture of SS316 with 0.5% B and the only SS316 powder were both printed and processed to show the effect of boron in helping forming connection between printed and non-printed area when sintering. (See Figure 3.2).

3.2.2. Shell printing

To prove the idea of shell printing instead of printing the whole parts, two cylindrical containers of 30mm in diameter with different wall thickness of 1.5mm and 7.5mm were printed. After curing process, the powders outside the shell were removed while the powders inside the shell were remained. The samples were burned in air at 460°C for 2 hours to burn out the binder phase and then sintered at 1150 °C in argon gas environment for 6 hours. The samples are shown in Figure 3.2

3.2.3. Strength testing

It is obvious that the thinner the shell is the lesser time of printing and amount of using binder. The question is how thin of the shell can we print for a given part. In order to estimate the thickness of the shell for a given design that can sustain the internal pressure created by the total powders inside the shell, the transverse rupture strength test on the bars and the hoop fracture strength test on thin cylinders were conducted.

3.2.3.1. Transverse rupture strength (TRS)

In this test, the bars with 40mm in length, 5mm in width and various thickness of 2mm, 2.5mm and 3mm were printed and then cured at 195 °C in two hours. These bars were tested by using TA Instruments RSA III, USA for determining the TRS of the printed parts. (Figure 3.3a)

3.2.3.2. Thin vessel pressure

Five types of cylinders with different wall thickness 1mm, 1.5m, 2mm, 2.5mm and 3mm were printed for a hoop stress test to estimate the fracture strength of the printed part. (Figure 3.3b) After curing and removing loose powder, the printed cylinders were tested by applying the pressure into a thin rubber balloon. The pressure was increased slowly by controlling the pressure gauge until the cylinder broke. The whole process was videotaped and the highest pressure was extracted from recorded data to determine the fracture strength.

3.3. RESULT AND DISCUSSION

3.3.1. Shell printing results

The samples after sintering are showed in Figure 3.2a and 3.2b. There is no difference between sample from mixture and sample from only SS 316 powder. The darker printed area is distinguishable from the brighter unprinted area without the binder phase. After sintering, the samples printed from SS316 without B are shown in Fig. 3.2a0 and 3.2b0. The separation gap between printed and unprinted areas exists. This can be explained by the difference in content of carbon in those areas causing different densification rate in the samples. Even after the binder burnout, a traceable amount of binder residue can be left in the structure. This minute variation in elemental compounds leads to the difference in the consolidation rates creating the gaps between printed and unprinted areas after sintering.

The sintered samples of the mixture SS316 with 0.5B are shown in Fig. 3.2a1 and 3.2b1. No gap between printed and unprinted areas exists in the samples with the boron additive. Boron significantly improves sintering process, and based on the fact that with approximately 0.04% of Carbon residue left in the printed part, which has less effect on enhancing sintering than 0.5%B. Thus, the enhanced densification with 0.5%B surpassed that of the carbon residue present in the sample. Therefore, the mixture of SS316 with 0.5%B produced better sintered samples. After polishing off the thin layer on the top of the printed parts, the boundaries between two areas are effaced (Fig. 3.2a2 and 3.2b2). The shade difference between two areas, which is visible only on the sample surface, can be explained by small amount of binder residue left in the printed volume even after burning in air at 460°C. The SEM images were taken at 1400X for center (Fig. 3.2a3) and edge area (Fig. 3.2a4) (printed and unprinted areas, respectively). The microstructure of printed and unprinted areas presented the similarity in terms of powder solidification that affirms the ability of fabricating the part based on printing the shell only and subsequent sintering the whole part.



Figure 3.2: Thick and thin wall printed plates after sintering at 1150oC a) 7.5mm wall, b)1.5mm wall, a1) and b1) Polished samples, a2) SEM image of non-printed area, a3) SEM image of printed area



Figure 3.3: Printed samples for a) TRS tests, b) Hoop stress tests

3.3.2. Transverse rupture strength

The TRS tests were performed on the bars (40mm in length x 5mm in width) printed with distinct thickness (2mm, 2.5mm, and 3mm) as showed in Figure 3.3a. Also, the effect of two printing directions, vertically (V) and horizontally (H), was also tested. The cross section on each printed layer of vertical bars is *length* × *thickness* whereas the cross section on each printed layer of horizontal bars is *length* × *width*. Figure 3.4 shows the results of the TRS tests. The samples were labeled as the number presents the thickness and the letter exhibits the printing direction, V or H. For example, the 2V sample has the thickness of 2mm and was printed vertically. Five samples of each category were tested.

From the gathered results, the TRS is not stable on the thin bars (Fig. 3.4). The 2H bars have the highest strength over 4 MPa whereas the 2V bars have the lowest value at 2 MPa, exhibiting the significant instability for the thin structures. The instability could be caused by the variation of powder spreading and binder permeability in neighboring locations. In the larger features, these variations are diminished as more layers are added, resulting in less variations in the properties of the printed parts. The difference in TRS of 3H and 3V samples is less than the difference between 2.5H and 2.5V. In other words, the strength averaged over the samples does stabilize with the increase in the printed thickness. The trend of TRS of the part after printed and cured is getting converged to the value of 3 MPa. (Fig. 3.4).



Figure 3.4: Transverse rupture strength of printed samples



Figure 3.5: Maximum internal pressure applied on the tubes



Figure 3.6: Stress analysis on tubes by FEM Ansys. a) Pressure applied on internal surfaces, b) Imm thick tube, c) 1.5mm thick tube, d) 2mm thick tube, e) 2.5mm thick tube, f) 3mm thick tube

Tube thickness (mm)	Hoop stress (MPa)	FEM/ANSYS (MPa)
 1	0.1359	0.1387
1.5	0.1914	0.1965
2	0.2558	0.2580
2.5	0.2785	0.2811
3	0.3175	0.3204

Table 3.1: Maximum stresses of printed cylinders



Figure 3.7: Fracture strength of tubes with different thickness gathered from a) Thick wall stress formula and b) FEM analysis

3.3.3. Cylinder pressure:

The maximum pressures that the cylinders withstood before breaking apart were showed in Figure 3.4. These pressures were put into Lame's equations for thick-wall cylinder stress model to estimate the fracture stress of the printed parts and they also were plugged in a FEM model to solve by ANSYS.

The Lame's equations under the internal pressure evaluated at the interior surface where the stresses are most critical:

$$\sigma_{\theta} = P_i \left[\frac{r_0^2 + r_i^2}{r_0^2 - r_i^2} \right], \sigma_r = -P_{i,\sigma_z} = \frac{P_i r_i^2}{r_0^2 - r_i^2}$$

where P_i is the pressure, r_0 is the external radius, r_i is the internal radius of the tube.

The equivalent von-Misses stress is:

$$\sigma_{equ}^{von} = \sqrt{\frac{(\sigma_r - \sigma_\theta)^2 + (\sigma_\theta - \sigma_z)^2 + (\sigma_z - \sigma_r)^2}{2}}$$

The analysis results of each cylinder were presented in Figure 3.6 where Figure 3.6a is the model setting with pressure on the internal surface of the cylinder. The model was imported from the CAD file used to print the cylinders. The model was modified by changing the thickness of a cylinder and applied the equivalent breaking pressure measured by testing each cylinder. The maximum stress as a function of the thickness of the cylinder in each model was tabulated in Table 3.1. Both results from Lame's equations and ANSYS are quite similar. The fracture strength was showed in Figure 3.7. It is interesting to note that the thinner the cylinder is, the lower the fracture strength is. This can be explained by the way to print the curved shape in a layer by layer fashion in additive manufacturing (Fig. 3.8). For 1 mm thick tube, the misalignment between 0.1mm thick layers are relatively noticeable to the thickness of printed part. With the thicker tube, the effect of the misalignment is less on the tube. That explains why the tube's fracture strength is higher when it is thicker. Because the size of printed bed of the ExOne Lab machine is limited, any thicker tube could not be printed to reassure the argument made above.



Figure 3.8: Effect of layer printing on the real thickness of the tube. a) Thin tube shows thin section at some locations b) The thicker tube shows more uniformity

3.4. CONCLUSION

In this chapter, we explored the shell printing method that helps to reduce the printing time and the amount of the binder phase consumed. By printing different shell from the mixture of SS316 with 0.5% B then sintering at 1150°C, the printed parts showed no separation on the boundaries and no difference in terms of microstructure between printed and non-printed areas.

The fracture strength was tested on thin bars and cylinders to determine the fracture strength of printed parts. With the thin bars, the fracture strength values are getting more stable with the increase in thickness. The thin cylinder (1mm) shows very low strength and the strength becomes higher with the increase in wall thickness. Based on the maximum stresses in each case, the optimal shell thickness pf a part can be estimated and the CAD file with the shell design is converted to a STL file for printing.

CHAPTER 4

JOINING IN ADDITIVE MANUFACTURING

4.1. INTRODUCTION

Particularly, a powder bed AM system is limited in the size of the printed parts dictated by the size of the build bed. Increasing the size of the build bed involves a lot of difficulties including larger environment controlled chamber, laser or electron beam focus alignment and movement control. The beam focus alignment is the main reason leading to inhomogeneity in the printed parts.

Joining is one method to overcome the size limitation dictated by a particular machine. Also, it can be used to combine multiple materials for a wide variety of applications, e.g. brazing yttria-stabilized-zirconia to stainless steel for the solid oxide fuel cell [1]. There are many joining techniques existing in traditional manufacturing processes such as welding, soldering, and brazing. The joining technique of BJP parts developed in this research is close to the metallurgical joining or diffusion bonding, which has been studied and applied widely [2-7].

However, the AM community has not been paid enough attention in joining because AM allows us to print any design. However, there are some complex thin internal structures that are impossible to fabricate with any AM technique. For example, printing small enclosed channels is challenging for direct energy methods, for instance EBM or PBF, because the loose powder is stuck inside during the printing process. For small cross section and long internal features, it is tedious or even impossible to remove the loose powders.

Vlasea et. al [8] invented a hybrid process based on the BJP system that has an ability to fill a sacrificial photopolymer with the syringe in the channel. That polymer phase was burned

later leaving the internal channel. The limit of this method is the shape controllability of the channel highly deformable polymer used as support structure. Also, the channel shape is limited to a circular shape. A few groups used SLM to print internal channel for micro column in gas chromatography [9] and heat exchanger [10]. However, they have a common difficulty in removing the loose powder in long narrow channels after printing. They had to leave the ventilators connecting the internal channel on the printed parts to pressurize the loose powder out after printing.

In this works, a unique method is proposed to make a completely enclosed channel by combining the BJP technique developed in Chapter 2 with diffusion joining method. The combination of these techniques works well because after printing the part with open channels, it is easy to get rid of the loose powder by blowing out with the compressed air even for the narrow and deep channel. Also, the printed part is still in the powder form with large surface area that allows faster diffusivity. The accomplished results are very promising with the completed joining area and the good channel shape. This primary result can be further developed to apply in the gas chromatography, heat exchanger and internal cooling channel and other applications requiring intricate internal structures.

4.2. MATERIALS AND PROCESS

4.2.1. Materials

Stainless steel 316L (average size $14\mu m$) was selected to perform this experiment because of its excellent machinability. To enhance the diffusion process required for joining, 0.5%B 1 μm was also added to SS316 powder (Table 2.1). The mixture was printed as described in Chapter 2.

4.2.2. Bonding strength test

The joining process of two printed parts is possible because they are in powder forms possessing high surface area. The presence of boron, with high diffusivity in iron (diffusion coefficient of Boron in Fe 30%Ni at 1154°C is 1.172x10⁻¹⁰m²/s [11]), is expected to enhance the bonding process at high temperature. The blocks whose size is 15mm x 10mm x 8mm were printed for this test. After printing and curing, each pair of blocks was stacked up and sintered at different temperatures: 1130°C, 1135°C, 1140°C in 6 hours and 1135 °C in 12 hours. All the sintering processes were done in argon environment. The joined blocks were sliced into thin bars with the thickness of 1mm by EDM (Electric Discharge Machining, Brother HS-704, EDGE Machine tools, Illinois, USA). (Figure 4.1). To estimate the bonding strength, the bars were loaded in Instron Universal Testing System (3367 UTS, Instron, Northwood, MA, USA) for tensile test.

4.2.3. Internal channel fabrication

The main objective here is the feasibility test of fabricating an enclosed internal serpentine channel, which has the width of 0.5mm and the total length of 500mm. The design of the core part containing open serpentine channel is showed in Figure 4.2a. The core was printed with the serpentine channels on both top and bottom sides. All the printed parts were set up as in Figure 4.2b for sintering process. Each setup was sintered at different temperatures: 1130°C, 1135°C, 1140°C in 6 hours and 1135 °C in 12 hours to join the core with top and bottom sides. The samples were then cut by diamond saw to examine the channels. (Figure 4.2c).

4.3. RESULTS AND DISCUSSIONS

4.3.1. Samples slicing and pulling:

Two blocks were stacked up and sintered at different temperature and time profiles to bond as showed in Figure 4.1. The sample sintered at 1130° C show the visible separation between 2

blocks. The boundary of 2 blocks on the 1135°C sintered for 6 hours is harder to be recognized. The 5°C difference makes a huge improvement in bonding. Both samples, 1135°C soaked in 12h and 1140°C soaked in 6h, show no visible bonding boundaries. In order to test the bonding strength, the joined samples were cut by EDM to thin strips as in Figure 4.1. There strips of each sample were tested by using tensile method. The samples' fracture strengths are showed in Figure 4.3. The samples sintered at 1130°C has significant lower strength in compare with others. By sintering in 6 hours longer, the bonding strength of sample 1135°C 12h noticeably higher than the one sintered at the same temperature but soaking for only 6 hours (Approximately 40MPa improved). It is important to notice the locations of breaking points of the samples. Strips from two samples 1130°C and 1135°C sintered for 6 hours broke at the bonding areas whereas strips of samples, 1135°C sintered for 12 hours and 1140°C sintered for 6 hours, broke at the grabbing locations with high stress concentration. This at least proves that the secure bonding is successfully accomplished at 1135°C 12h and 1140°C 6h. It also should be noted that from our previous results (Chapter 3), the tensile stress of annealed SS 316 has the tensile strength of 520 MPa. The tensile stress of printed parts sintered in vacuum, which have higher density than these samples sintered in Argon in this test, are around 400 MPa. The average fracture strengths of the samples sintered at 1135°C for 12 hours and at 1140°C for 6 hours are 217 MPa and 227MPa, respectively, which are about a half of the fracture strength of the printed SS 316. The bonding strengths are even higher than the fracture strength because the break points are not at the joining areas.



Figure 4.1: Procedure steps of bonding strength tests of joined blocks sintered at different temperatures



Figure 4.2: Two stages serpentine channel design and fabrication process



Figure 4.3: Fracture strength of the bonded parts sintered at different temperatures and soaking at different time. a) Tensile tests of a single sample in each category, b) The maximum stress at breaking point of three samples in each category

4.3.2. Internal channel sample joining

The samples after joining at different temperatures were cut to expose the internal channel. The images of the samples and their channels showed in Figures 4.4 - 4.8. Figure 4.4 shows the samples sintered (joined?) in 1150°C with the channels where some of them are closed. The sample was cut to expose the cross section of the internal channels, which are distorted and some channels

were melted and merged with others. Based on the condition of the channels, 1150°C is too high to join these samples. The sample joined at 1130°C (Figure 4.5) show the gap in bonding areas, which means that either the temperature or the sintering time is not adequate to join the parts. The investigation is narrowed by finding optimal sintering temperature between 1135°C and 1150°C. The sample sintered at 1140°C (Figure 4.7) has good shape of the rectangular channels. However, the inclined channels suggest that the sintering temperature was too high. To reduce the distortion, the sintering temperature should be lower than 1140°C. The sample sintered at 1135°C in 6 hours (Figure 4.6) shows some small disconnected areas between the wall of the channels and the cover plate. To remove these disconnection, another batch of the samples was sintered the samples at 1135°C and holding for 12 hours to provide more time for diffusion process to take place in order to improve the bonding. Figure 4.8 shows this sample with the clear and aligned channels. The cross section also remained in a rectangular shape and it sizes are quite similar in terms of both height and width. The channel width and height are approximately 0.5mm is 2mm, respectively.

4.3.3. Process optimization

After determining the joining temperature and sintering time, the same design was printed in two third smaller in all dimensions. The designed channel in the scaled printed part is 0.5mm in width and 2mm in depth. After printing and sintering at 1135°C for 12 hours (Figure 4.9), the sample shows some promising results with the sharp corners in the channel cross section without any noticeable distortion and good bonding areas providing a leakage proof part. In order to test the limit of channel width and wall thickness, another design (Figure 4.10) with the channel patterns containing 0.2mm, 0.3mm, 0.4mm, 0.5mm and 0.6mm in width and the wall thickness of 0.3mm, 0.45mm and 0.6mm was fabricated. Figure 4.8 shows the cross section of the sample. Thus, it is possible to print 0.4mm channel with the wall thickness of 0.45mm.



Figure 4.4: Two stages serpentine channel with the width of 0.75mm. Sample was sintered at 1150 °C for 6 hours (Scale bar is 5mm)



Figure 4.5: Two stages serpentine channel with the width of 0.75mm. Sample was sintered at 1130 °C for 6 hours (Scale bar for left figures is 5mm)



Figure 4.6: Two stages serpentine channel with the width of 0.75mm. Sample was sintered at 1135 °C for 6 hours (Scale bar for left figures is 5mm)



Figure 4.7: Two stages serpentine channel with the width of 0.75mm. Sample was sintered at 1140 °C for 6 hours (Scale bar for left figures is 5mm)



Figure 4.8: Two stages serpentine channel with the width of 0.75mm. Sample was sintered at 1135 °C for 12 hours (Scale bar for middle figures is 5mm)



Figure 4.9: Two stages serpentine channel with the width of 0.5mm. Sample was sintered at $1135^{\circ}C$ for 12 hours



Figure 4.10: Testing the minimum channel width and wall thickness fabricated successfully

4.4. CONCLUSION

The diffusion bonding of printed parts at high temperature was explored to create small scale internal features such as serpentine channels. The optimal condition is to join at 1135°C for 12 hours without any visible separation between two joined parts and the breaking point in the joined area. The tensile strength of the joined parts is more than 220MPa, which is comparable to the tensile strength of annealed SS 316 (520 MPa).

This joining technique enabled us to fabricate completely closed serpentine channels on the AM parts. The successful fabricated part contained enclosed 0.5mm wide and 450mm long channel after sintering from the designed channels with 0.75mm wide and 600mm long on the printed part. The cross sections of the consistent channels show the undistorted rectangular shape. To understand how small or the channels and how thick of the wall between channels can be accomplished, the limitation test was conducted based on the design of different values of channel width and wall thickness. It showed that design of 0.4mm channel and 0.45mm wall could be printed and processed successfully resulting in approximately 0.3mm channel with 0.45mm wall on the sintered part. BIBLIOGRAPHY

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CHAPTER 5

ELECTRICAL PROPERTY CONTROL OF 3D PRINTED STAINLESS STEEL 420 STRUCTURES USING CHEMICALLY INDUCED SINTERING

5.1. INTRODUCTION

Additive manufacturing (AM), also known as 3D printing, is an advanced process of producing parts directly by building materials in a layer-by-layer fashion or feeding materials onto the existing parts. It is different from many traditional manufacturing methods based on subtracting or forming materials. AM offers many advantages including design flexibility with externally and internally complicated features, rapid product development, and reduction in materials consumption [1]. However, with limited processing materials and low mechanical properties of printed parts, AM was initially considered only for rapid prototyping (RP) applications. Tremendous research efforts are being, therefore, made to improve the mechanical properties of the AM parts that are on par with [2] or even better [3] than those of the traditionally manufactured counterparts.

Powder-based AM of metal parts have been extensively studied and the resulting parts has been characterized for their mechanical performance. Electrical and/or thermal components for high-temperature heat exchangers or microreactors applications fabricated by any AM technique have been seldom studied. In developing a 3D-printed metal microreactor, a direct Joule heating through the printed structure is desirable due to its high energy efficiency, but most printable metals have a very low electrical resistivity, unsuitable for typical heating applications. For instance, stainless steel (SS) has an electrical resistivity of about 0.7 $\mu\Omega$ ·m, so if one prints a heating element of 0.1 mm in diameter and 2 cm in length, the resistance is on the order of 1 Ω , too small for heating applications. Considering the printing resolution of the metal AM technology and the size of the microreactor, the resistance value would be much smaller. Therefore, the materials, whose electrical resistivity is a few orders of magnitude larger, are needed for such applications. Semiconducting materials like silicon, germanium, and some metal oxides have a suitable range of resistivity ($0.01 \sim 10 \text{ m}\Omega \cdot \text{m}$). Unfortunately, 3D printing technology of these materials is still in its infancy and needs significant development.

Another approach to achieving 3D printing of the materials with the target resistivity is to mix the conducting (i.e., metal) and insulating (i.e., ceramic) powders in the bed. But this type of heterogeneous materials poses significant issues in printing, including the residual stresses and frequent part failure. An alternate approach is needed to alter the electrical resistivity of the printed metal structure.

In this chapter, we introduce the post-processing technique, namely chemically-induced sintering (CIS), to alter the electrical resistivity of as-printed metal structures with interstitial spaces from a binder jet printing (BJP) machine [4]. The CIS process utilizes a reactive gaseous environment during sintering and allows the metal powders to partially be converted into more resistive metal oxides. The resultant structures would be a metal-ceramic hybrid structures, significantly modifying the physical properties, especially electrical resistivity. We study the effect of the part dimension and reaction temperature on the property control. Moreover, an extent of oxidation reaction is characterized using scanning electron microscopy and energy dispersive spectroscopy. Our data show that a small diameter post becomes fully oxidized, thus highly electrically insulating, while the oxidation does not propagate into the core of a larger diameter post, leaving the part to be conducting. Based on these results, self-heating of the 3D printed metal

structure is demonstrated and compared to the external heating of the same structure, proving the efficacy of the Joule heating.



Figure. 5.1. (a), (b) A sample design for an array of cylindrical posts with various diameters (0.5 to 4 mm); (c) a schematic diagram showing chemically sintered sintering of a printed part, producing a metal/ceramic composite.

5.2. EXPERIMENTAL PROCEDURES

5.2.1. Materials and sample design

Stainless steel (SS) 420 powder used in this experiment is provided by Oerlikon Metco (Troy, Michigan, U.S.A). The average powder size is 30 microns. To systemically study the extent of chemically-induced sintering through the 3D printed parts, we design the sample shown in Fig. 5.1(a), (b) with an array of the cylindrical posts with different diameters between two thin plates. Four identical posts of each diameter are included for the statistical purpose. The post diameters are 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 3.5, and 4 mm. The top and bottom plates have a 2-mm thickness.

Figure 5.1(c) shows a conceptual drawing for chemically-induced sintering. The printed parts from the BJP process are porous especially after the binder burn-out, allowing reactants to diffuse into the structures when the part is sintered in a reacting environment. For example, steel powders (black circles in Fig. 5.1(c)) can be oxidized in an oxygen atmosphere to produce iron oxides (green shells also in Fig. 5.1(c)) on the powder surface. The overall process of sample printing and preparation is schematically shown in Fig. 5.2(a) and described below.

5.2.2. Binder jet printing and chemically-induced sintering

The BJP system (ExOne X1-Lab) has two powder beds: one for building a part and the other for supplying the powder. First, the build bed is lowered by one layer to accommodate a new powder layer from the supply bed. Then, a binder phase is injected (or printed) onto the area of the powder layer intended to be consolidated according to the imported 3D CAD design. These two steps are repeated until the part is completed. During printing, the build bed is heated to partially pre-cure the binder phase. The printed part with support powder is therefore put into an oven to completely cure the binder at 195°C in 2 hours. The cured binder within the part is strong enough to hold the structure, allowing us to remove the loose powder (see Fig. 5.2(b)).

Prior to the chemical reaction, the part is heated to 460°C in the atmospheric air of the high temperature furnace and held for 2 hours to burn out the binder phase. To determine the protocols for the CIS process, the part is sintered at five different temperatures, 875, 900, 925, 950, and 975°C for 2 hours at the ramping rate of 10°C/min in the atmospheric air (see Fig. 5.2(c) and Fig. 5.3). During oxidation, the sample is sandwiched between two alumina dishes to reduce oxidation of the plate exterior surfaces. The goal here is to maintain the printed plates at a low oxidation level, so that the resistance across the plate can be minimized. After removed from the oxidation furnace, the sample is potted in epoxy for surface finishing. The potted sample is
polished to expose the posts at one side and remove the oxidized portion of the plate at the other side (see Fig. 5.2(d)).



Figure 5.2: (a) A process flow chart for sample printing and preparation for electrical measurements; photographs of the sample after (b) the BJP process, (c) oxidation, (d) polishing, (e) contact establishment and electrical measurements.



Figure. 5.3: A temperature profile used to burn out the binder phase and carry out chemically-induced sintering.

5.2.3. Electrical and materials characterization

In order to ensure the ohmic contacts for electrical measurements, the plate (bottom) side of the sample is deposited with copper in 5 µm thickness. On the other side, a small piece of a thin deformable indium foil is used to cover the cross section of an individual post. A sample is placed on the Au-coated stage of the probe station and measured for the current-voltage relation (IV) behaviour of each post as shown in Fig 5.2(e). A high-precision source meter unit (Keithley 2602B) is used to scan over a range of voltages. To avoid self-heating, a voltage range is chosen not to draw too much current through the post. A resistivity of the post is calculated based on its dimension and the resistance value obtained from the IV curve. The cross-sectional images of the printed posts are obtained from scanning electron microscopy (SEM; JEOL 6610LV), revealing both degrees of oxidation and sintering. Quantification of the oxidation level through the post structure is determined using energy dispersive spectroscopy (EDS) in the same SEM instrument.

5.2.4. Mass change after sintering

In order to quantify oxidation behaviour of induce sintering SS420 printed parts, the cylinders of 5mm in length x 2mm in diameter were printed and sintered in air furnace at different temperatures: 850°C, 875°C, 900°C, 925°C, 950°C, 975°C, and 1000°C. The tests of sintering temperature at 950°C with different dwelling time of 2 hours to 16 hours were also conducted to estimate level of oxidation. The weights of the samples were measured before and after sintering to extract the weight gains. The KSL-1100X furnace (MTI Corporation, Richmond, CA, USA) was used to run all the oxidation experiments.

5.2.5. Mechanical properties test

In this test, several bars size 40mm x 5mm x 1mm were printed and then cured at 195°C in two hours. These bars were processed differently depending on its groups. Five non–sintered bars were tested directly by using TA Instruments RSA III, USA for determining TRS. Five bars were sintered in vacuum environment at 950°C for 2 hours. These other bars were successively fired at different temperatures (900°C, 9925°C, 950°C, 975°C). All heating processes followed the temperature profile showed in Fig. 5.3. Thereafter, the fracture strength tests were performed on sintered samples by the same instrument.

5.2.6. Structural heater testing

A separate design, which consists of an array of the cylindrical posts with 1.5 mm in diameter and 12 mm in height sandwiched by the two plates, is used to demonstrate that the metal structure with appropriate electrical resistances can be used as a robust heating element.

The same procedure is employed and optimized to produce a 3D printed SS heater with a resistance of a few hundred ohms. After a thin copper layer is sputter deposited on both top and bottom sides of the polished plates, aluminium foils are pressed against by a custom-built package to supply electrical power to the 3D structure. Multiple layers of a ceramic fiber-based thermal insulation film are placed between the sample and the package to minimize the convective loss. Various voltages are applied across the 3D printed SS heater to induce a Joule heating effect. The temperature of the heated structures is recorded using an IR thermal camera.

5.3. RESULTS AND DISCUSSIONS

The CIS process converts a metal powder particle into a metal-ceramic core-shell structure, significantly altering its physical properties, especially electrical resistivity. The composition of

SS420 raw particles is mostly Fe with about 12 to 14% of Cr, <0.15% of C, <1% of Mn, <1% of Si, and other trace elements. When oxidized, iron oxides (Fe_xO_y) and chromium oxide (Cr_xO_y) will be formed on the particle shell whose electrical resistivities are more than 10 orders of magnitude higher than that of the metallic phase. Therefore, depending on the extent of oxidation, a 3D-printed SS part after the CIS process can possess a wide range of resistivities.

5.3.1. Electrical measurements

Electrical resistivity, ρ , can be estimated from the measured resistance, R_{meas} , of the part using the following relation: $\rho = R_{\text{meas}}*A/L$, where *A* and *L* are the cross-sectional area and the length of the part, respectively. The electrical resistance can be determined from the IV curve, i.e., R = V/I, an inverse of the slope in the IV curve. Figure 5.4 shows some representative IV curves from the various cylindrical (post) samples with different diameters and oxidation temperatures. Interestingly, both linear and nonlinear behaviours have been observed, and the characteristics displayed by each sample seem to depend on the extent of oxidation. The linear IV curve shown in Fig. 5.4c indicates the pure metallic (ohmic) behaviour of the hybrid structure. In this case, the resistance is constant and can be easily estimated. The nonlinear behaviours of Fig. 5.4a, 4b, and 4d can be attributed to a few different reasons. First, it is possible that the semiconducting/metalsemiconductor junctions present in the resulting hybrid structure is responsible for nonlinearity. The metal-semiconductor junctions can produce Schottky barriers in energy potentials, exhibiting a diode-like behaviour.

Another source of nonlinearity is the temperature dependent resistance. For the materials with high temperature coefficients of resistance (TCR), a small change in temperature of the sample can meaningfully change the resistance. A care must be taken when measuring IV characteristics since with a high power deposited to the sample can induce self-heating during the

measurement. This self-heating can change the temperature of the sample, making the IV curve deviate from the linear line. We can estimate the sample temperature during the testing using the first-order approximation (e.g., lumped capacitance model as the Biot number is much smaller than 0.1). For example, if 10 µW, 1 mW, or 100 mW of power is expended in the 1-mm diameter cylindrical post, the post temperature may increase by 0.1, 9, and 72°C, respectively. Therefore, we conclude that the power delivered during the experiment for Fig. 5.4(b) and 5.4(d) is significant enough to alter the resistance of the sample. In case of Fig. 5.4(b), the sample (1-mm post oxidized at 900°C) becomes more resistive with the voltage greater than 2 V. This can be contrasted to the other sample (1-mm post oxidized at 975°C) of Fig. 5.4(d), showing a less resistive behaviour at high voltages. The former sample exhibits a positive TCR while the latter shows a negative TCR. The positive TCR is commonly seen in metals while ceramics possesses the negative TCR. Therefore, depending on the oxidation temperature, the same printed parts can exhibit either metallic or ceramic characteristics for their electrical behaviours.



Figure. 5.4. IV curves obtained from the SS420 structures after oxidation for 2 hours; (a) 0.5mm post oxidized at 900°C, (b) 1-mm post oxidized at 900°C, (c) 0.5-mm post oxidized at 925°C, (d) 1-mm post oxidized at 975°C.

5.3.2. SEM and EDS Results

The previous section suggests that both oxidation conditions (e.g., temperature) and part's geometry (e.g., post diameter) are the significant factors determining the electrical resistivity and IV characteristics. To quantify the extent of oxidation in the structure and its relation to the resulting resistivity, the elemental mapping is conducted across the polished cross-section of the post surface. Figure 5.5 shows the SEM images of the 2-mm dia. post cut and polished to reveal

the oxidized SS420 powder particles at different locations. It is anticipated that the powder particle near the center of the post becomes less oxidized while the particle near the post edge is more reacted with oxygen. The particles near the center of the post remain metallic with no apparent morphological changes (see Fig. 5.5(d)), but the particles near the edge show different phases. The darker colored regions indicate more presence of the ceramic (i.e., metal oxide) phases. The elemental mapping from EDS in Fig. 5.5(e) indeed shows the increase in the oxygen content from the powders closer to the edge of the structure, corroborating the hypothesis that the limitation in the mass transport of oxygen during the CIS process creates a compositional gradient in a hybrid structure. While the complete set of data is not shown here, the resistivities of the various oxidized posts have been measured. For instance, 1-mm dia. posts oxidized at 850, 875, 900, 950, and 1000°C exhibit the resistivities of 20M, 2k, 35, 0.005, and 2 Ω ·m. At low oxidation temperatures, the powders are insufficiently sintered, and the relatively large space among the powders enables a high degree of oxidation resulting in high resistivity. At high oxidation temperatures, the SS particles are oxidized extensively again increasing the resistivities.



Figure 5.5. (a) SEM image of the cut plane of a SS420 column 3D-printed (2-mm diameter) by BJP and processed by CIS; SEM images of the single particle located in the edge (b), middle (c), and center (d) of the column in (b); (e) EDS elemental scan revealing the oxygen/iron ratio of each location, which proves the property control of the structure. Scale bar: (a) = 1 mm, (b)-(d) = 10 μ m.

5.3.3 Sintering weight variation:

The results of weight gain due to oxidation are showed in Fig. 5.6. In the case soaking for 2 hours (Fig. 5.6a), the weight does not change intensively until the sintering temperature reaches 925°C. The value is only 7% at 900°C. From 900°C to 925°C, there is a big jump of weight change. From 925°C to 950°, there is another big jump from 20% to 30%. These results suggest that when

changing the processing temperature in a small window, 50°C, it observes an immense variation in terms of oxidation. That means that the resistivity is expected to change sharply in this temperature range because of the transformation of metal to metal oxide (i.e. ceramics or insulative material). When the temperature reaches 1000°C, there is 40% weight gained showing that the sample was oxidized extensively and the resistivity is out of the conductive and semi-conductive ranges. In the case sintering at 950°C and keeping in different period of times, after sintering for 8 hours and longer, the weight changes are over 37% and have the saturated trend at 40%. Again, these changes create non-conductive phase, which is out of this research's interest.



The time range from 2-6 hours is promising with the weight change is around 30%.

Figure 5.6: Weight gains of printed samples, (a) Samples dwelling time is 2 hours at different temperatures, b) Samples kept at 950°C in different period of time

5.3.4 Transverse rupture strength:

The green samples before sintering have low strength (\approx 3 MPa, Fig. 5.7) because the bonding relies solely on cured polymer (i.e. binder). The bars sintered in vacuum environment at 950°C (the samples were likely not oxidized) have the average TRS of 39MPa. Note that the fully dense sintering temperature is much higher than 950°C. The wrought stainless steel 420 was

reported to have very high strength at approximately 240MPa [5]. Although the TRS of samples sintered at 900°C, 925°C, and 950°C are only around 22 MPa, which is much smaller than the wrought SS420 however, they are much higher than the samples in green state and they are comparable with the sample sintered in vacuum. This proves that oxidizing SS420 at the right condition does not degrade extremely the mechanical properties. However, when raising the sintering temperature to 975°C, we observe a big recessive step in strength. Due to extensive oxidation on the particles hindering the sintering process at 975°C. The sintering temperature of oxide is higher than the sintering temperature of its metal. Based on the TRS results, the processing temperature should fall down the range from 900-950°C to have good mechanical strength.



Figure 5.7: TRS of samples processed by different methods.

5.3.5. Heater Testing

Finally, the model microreactor (shown in the inset of Fig. 5.8) oxidized at 950°C for 2 hours is tested for heating performance. Two different heating arrangements, (a) membrane heating vs. (b) direct structural heating, are compared for the same applied power, as shown in Fig. 5.8, demonstrating a faster heat transfer for the direct heating scenario.



Figure 5.8. IR temperature measurements of two different heating scenarios (same convective condition and applied power, that is, 1.6 W): (a) a membrane heater located at the left side; (b) direct heating through the structure. Inset: SS420 microreactor device under testing.

5.4. CONCLUSIONS

In this chapter, we have reported the reaction-based post-processing method, namely chemically-induced sintering (CIS) to modify the electrical resistance of the 3D printed SS structure in a controllable manner. The porous nature of the binder jet printed structure is utilized to allow reactants to diffuse and react with the metal particles. The resulting metal/metal oxide hybrid structures possess the electrical resistivities orders of magnitude higher than the unreacted

part, conferring a suitable resistance for the heating application. The CIS samples possess decent TRS that can be applied in many applications.

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CHAPTER 6

FULLY-ENCLOSED CERAMIC MICRO-BURNERS USING FUGITIVE PHASE AND POWDER-BASED PROCESSING

6.1. INTRODUCTION

Miniaturization of chemical system has garnered significant attentions in chemistry and biology due to many advantages such as enhancement in heat/mass transfer rates at small scale, reduction in expensive reagents and hazardous wastes, and facilitation of massive parallelization in reaction/catalyst screening and optimization [1][2][3]. The significant technological advancements for micro-chemical systems (µCSs) have been focused on chemical reactions, separation, and sensing in a low-to-medium temperature range (20°C to 600°C). One notable example is a lab-on-a-chip or micro total analytical system, in which the total sequence of laboratory processes is integrated to perform chemical synthesis, transport, and analysis, and it has profound influence in chemistry and biomedical areas [4][5]. In some cases, the microreactors and heat exchangers in μ CS need to be operated at high temperatures (> 600°C) and/or under highly corrosive environments like solid-oxide fuel cells [6][7][8][9], fuel reformers [10][11][12], combustion burners [13][14], and gasifiers [15][16]. However, high-temperature µCSs with sophisticated design and similar level of integration found in low-temperature counterpart have rarely been realized mainly because the conventional µCSs such as silicon, glass, polymers, metals and conventional metal alloys are not stable at these high operating temperatures. Ceramic materials offer excellent high-temperature compatibility and corrosion resistances, but pose significant manufacturing challenges due to their hardness and brittleness.

Several groups have demonstrated the promise of ceramic-based microreactors for medium-to-high temperature reactions such as hydrogen production from continuous reforming of propane [17][18][10], oxidative coupling of methane [19][20], catalytic combustion [21], and nanoparticle synthesis [22]. One of the paramount challenges in fabricating ceramic μ CSs is that the microfabrication techniques borrowed from well-established microelectronics and microelectromechanical system (MEMS), which are very effective for silicon- or polymer-based µCSs, are not compatible with ceramic materials. Instead, the conventional and non-conventional ceramic processing techniques have been utilized to create ceramic microreactors and other components of µCSs. These techniques include rapid prototyping using low-pressure injection molding [19][23], micromachining [20][24], sol-gel/nanoparticle casting [25][26], and tape casting [27][28]. In the rapid prototyping process, a negative silicone mold is first created from the original polymer mold fabricated by micro-steoreolithography, which is used directly for lowpressure injection molding [29][30]. The resolution and surface quality of the ceramic components depend on the stereolithography quality of the original polymer mold [23], and the critical dimension of hundreds of microns (which is a relevant length scale in most μ CSs) can be easily obtained. More recently, the smallest feature size on the order of a few microns in ceramic structures has been fabricated using the soft-lithographic molding technique like micromolding in capillaries combined with sol-gel casting [26][31]. However, these molding/casting-based techniques can create only the open channel or chamber structures due to the demolding requirement. To utilize them in μ CS applications, the fabricated structures need to be bonded with or packaged in another high-temperature material to form sealed microchannels or microreactors. Tape casting with low-temperature co-fired ceramic (LTCC) is perhaps the most widely used technique when it comes to the fabrication of the ceramic microreactors and microchannels

[28][32][33][34][35][36]. While low co-firing/sintering temperature (< 900°C) is beneficial for integrating metal electrodes and other applications, the operation temperature is typically limited due to the presence of the glass phase. Unlike the various molding techniques, tape casting is capable of producing suspended structures, enclosed cavity or microchannels for μ CSs. However, the suspended structures tend to deform and sag due to high lamination pressures and the softening of the glass component in the ceramic composite during sintering [35]. Multilayer lamination with fugitive materials such as waxes, polymeric materials, and carbon materials was used to support the embedded structures during lamination and sintering [37]. Wax- and polymer-based fugitive materials, however, were completely burnt out even before the sintering of LTCC, and therefore sagging of the suspended region cannot be prevented during sintering [38]. Moreover, in tape casting, each machined layer needs to be aligned to the previous layers before lamination, entailing some special equipment for alignment and lamination.

Here we propose a simple, inexpensive, reliable, and reproducible ceramic manufacturing technology for high-temperature μ CSs and microdevice application. The proposed technique employs the cold compaction of metal-oxide powders with a graphite fugitive phase for the embedded features. Without a binder phase in the powder mix, the final chemistry and dimension of the sintered ceramic structures can be more precisely tuned. The advantages of the proposed powder-based technique include (1) a one-pot, cost-effective process to create either open or fully-enclosed ceramic microreactors and microchannels, (2) near-full density ceramic structures without any other phases (e.g. organic or glass materials) in the final devices, (3) partially-sintered ceramic structures facilitating machining, and (4) abilities to control the surface finish of the internal cavity walls and easily incorporate additional features on the cavity surface. The key process steps such as powder compaction, graphite burn-out during partial sintering, machining of

partially sintered ceramics, and final densification will be investigated to optimize the process. As a proof-of-the-concept demonstration, a fully-enclosed ceramic structure with sub-millimeter internal cavities is used for micro-burner and micro flame ionization detector (μ FID) applications.

6.2. MATERIALS AND METHODS

6.2.1 Fabrication Procedure:

The overall fabrication protocols for these two configurations are depicted in Figure 6.1. The open-channel configuration is denoted as '1' (e.g., b1, c1, ...) while the fully-enclosed configuration as '2' (e.g. b2, c2, ...). The fabrication of the first configuration (open-channel configuration) is only slightly different from the 2nd one (fully-enclosed configuration). Thus, the fabrication protocol for the fully-enclosed micro-burner configuration is described in more details.

Alpha-phase alumina (AKP-50, Sumitomo in Japan) powder with the purity higher than 99.99% and the particle size between 0.1 and 0.3 micrometer was purchased for fabricating the proposed micro-burners. The common first step, as denoted in Figure 6.2a, is to cut the 0.9 mm thick graphite sheet (EDM-3, Saturn Industries) in a CNC machine into the integrated shape of the combustion chamber and the internal channels. This graphite piece served as a fugitive phase that would later burn out during partial sintering and leave the cavities for the combustion chamber and the internal channels. This graphite piece served as a fugitive phase that would later burn out during partial sintering and leave the cavities for the combustion chamber and the internal channels. Once the graphite fugitive phase was machined, a half of alumina powder (about 2 grams) was poured into the die. Prior to depositing the alumina powder, the interior of the die, whose inner diameter is 22.2 mm, was lubricated by zinc stearate ($C_{36}H_{70}O_4Zn$) with 12.5-14% of ZnO (Alfa Aesar). This solid lubricant mixture facilitates the release of the powder compact. In addition, it also helps to reduce the frictional force that may be exerted to the powder compact with the graphite fugitive phase. After the first half of the alumina powder was deposited, the die stage was shaken with mild vibration and the punch gently pressed the powder with its own

weight (~ 200 grams) to flatten the powder surface. Subsequently, the machined graphite was placed onto the powder surface (see Figure 6.1b). The placement and orientation of the graphite piece with respect to the die reference point is crucial because it is difficult to identify the location of the cavity once the fully-enclosed cavity is formed. The other half of alumina powder was poured into the die, followed by the full compaction of the powder and the embedded graphite using MTS Insight 300 (MTS Systems Corp.) with the compaction pressure of 50MPa at a speed of 1 mm·min⁻¹ (see Figure 6.1c and 6.1d). The powder compact was then partially sintered in the furnace (Carbolite-HTF1700, UK) at 800°C for 2 hours to burn out the graphite fugitive phase (Figure 6.1e). The graphite reacts with oxygen in the furnace and becomes CO_2 gas which escapes through the partially-sintered alumina compact (Figure 6.1f). This partially-sintered sample with the formed cavity was drilled to make the connecting channels for fuel and oxidant sources for the micro-burner applications (Figure 6.1g). The portion corresponding to the burner exhaust was milled to reveal the embedded channel. The detailed account of the machinability of the partiallysintered alumina compact will be given in a later discussion. Finally, the partially-sintered sample was fully sintered at 1350°C to provide the mechanical integrity of the micro-burner (Figure 6.1h and 6.1i).



Figure 6.1: Sequence of the proposed powder processing: a. powder placement; b. placement of a fugitive phase (for b1 and b2) and the remaining powder (for b2); c-d. powder compaction; e-f. partially sintering and removal of fugitive phase; g. drilling and other machining, h-i. full sintering.

6.2.2 Material Characterization:

In order to determine an appropriate partial-sintering temperature and graphite burn-out behavior, a thermogravimetric analysis (TGA Q500, TA Instruments, USA) was conducted at a constant ramping rate $(15^{\circ}C \cdot min^{-1})$, which is the same as the temperature ramping rate used in the proposed process. TGA measures a change in weight of the sample as a function of temperature, revealing the kinetics of graphite vaporization. During the TGA experiments, air was constantly flowing at 60 mL·min⁻¹ to ensure complete oxidation of graphite. The densification process of alumina powder compact during sintering was investigated using a thermomechanical analyzer

(TMA, Setaram 95, France). TMA results present the correlation between sintering temperature and sample densification kinetics in real time. A flat compacted sample was placed in between an alumina plate as a base and an alumina probe. The probe was then adjusted to zero. A change in dimension of the sample was measured by recording the movement of the alumina probe. Scanning electron microscopy (SEM) was used to evaluate the microstructures of the partially-sintered alumina samples that were sintered at different temperatures. The presence of the cavity and channels embedded in the fully-enclosed alumina sample was visualized by a computerized tomography (CT) scan (GE eXplore Locus RS micro CT) that has the highest resolution up to $27 \,\mu\text{m}$.

6.2.3 Micro-burner Testing Setup:

Both configurations of the micro-burners (as schematically shown in Figure 6.1) were prepared for the flame testing. A micro-burner with a transparent window was used to characterize the flame shape and optimize the flow rates of fuel and oxidant streams. A quartz disc (25-mm in diameter, Quartz Scientific Inc.) was bonded to the open channel device of the sintered alumina using a medium-temperature adhesive (1531 DURASELTM, maximum service temperature of 343°C). Through the quartz window attached on the channel side, an oxy-hydrogen flame can be visually observed to determine the presence and location of the flame within the chamber. The holes on the surface of the alumina micro-burner was made to insert the stainless steel (SS) tubing (0.46 mm I.D., 0.90 mm O.D.) for the fluidic connections and fixed with RESBONDTM 907GF, which can endure up to 1260°C. Once the adhesives to bond the quartz window and the SS tubing were cured at room temperature for 24 hours, the micro-burner was completed for testing. Hydrogen and oxygen were created using a commercial electrolyzer (E-65 from h-tec) coupled to the custom-made flow manifold to control the flow rates of each stream. Because the electrolyzer

produces hydrogen and oxygen at a fixed stoichiometric ratio ($H_2:O_2 = 2:1$), a miniature pump was added to deliver air to the oxygen line to independently control the fuel-to-oxidant ratio. A flame image was taken using a Nikon camera (D50, shutter speed: 30 second, ISO 2.8) in a dark room. Under the normal circumstances, an oxy-hydrogen flame is not visible to bare eyes or regular cameras, and therefore the special UV intensifier would be required to image the flame. We introduced a trace amount of organic contaminants (diffusion oil) to visualize the flame.

6.3. RESULTS AND DISCUSSIONS

To demonstrate the feasibility of the proposed powder processing, we consider a microburner whose critical dimension is below 1 mm. The micro-burner design employed in this study was previously reported [39] and adopted without major modifications. Unlike most ceramic processing techniques that start with ceramic powders or sols mixed with polymeric binder phases, our approach exploits cold compaction of raw powders while utilizing a graphite fugitive phase to create internal cavities and channels. The proposed fabrication scheme allows the fabrication of open and fully-enclosed cavities/microchannels, and both configurations will be considered here (see Materials and Methods for the detailed process). A prototype micro-burner device with an open ceramic structure covered with a transparent quartz top will be employed to visualize and optimize the flame in the micro-burner before the fabrication of the micro-burner with the fullyenclosed combustion chamber. We will base our initial development on a flat circular disc with a small thickness-to-diameter ratio (~ 0.1) because the thin circular disc is one of the simplest shapes known to successfully compact the powder in a uniform density under a uniaxial load.

6.3.1 Fabrication Results

We have successfully fabricated the alumina micro-burners in both open-channel and embedded-channel configurations. Figure 6.2 shows the photograph images of the micro-burner samples in each process stage. It is shown that a 0.9-mm-thick graphite layer was CNC-machined (Figure 6.2a) and sandwiched/cold-pressed into the alumina powder without damage (Figure 6.2b). The fabrication result for the open-channel micro-burner with the quartz top is shown in the top row in Figure 6.2 (Figure 6.2c1-e1) while the fully-embedded micro-burner in the bottom row (Figure 6.2c2-e2). For the fully-embedded sample, the other half of the alumina powder was deposited and compacted to what is shown on Figure 6.2b. Figure 6.2c1 indicates that the graphite layer was completely burn out during the partial sintering at 800°C as the decomposition temperature of the graphite phase is lower than 800°C. In case of the fully-enclosed sample, whether or not the graphite layer was completely removed was not clear by the visual inspection. We will address this issue in more details with the sintering characterization results in the following section. The partially-sintered state of the alumina allows us to use the conventional machining (e.g. milling, drilling, etc.) for further modification. The holes were drilled in the partially-sintered alumina burner for fluidic connection (see Figure 6.2d). The mediumtemperature epoxy (red color on Figure 6.2e1) was used to seal the open-channel micro-burner (between the 25-mm dia. quartz disc and the 22-mm dia. alumina disc). Stainless Steel (SS) tubing fixed with the high-temperature epoxy provides gas-tight delivery of fuel (e.g. hydrogen) and oxidant (e.g. oxygen and/or air) to the burner cavity.



Figure 6.2: Photographs of a. a 0.9-mm-thick CNC-machined graphite layer; b. the graphite layer inserted into an Al2O3 powder bed; c. the rest of the powder being applied (only for c2), compacted, and the partially sintered, removing the graphite fugitive phase; d. holes drilled on the partially-sintered alumina devices; e. fluidic tubing connected for micro-burner testing. Scale bar in all images is 1 cm.

Figure 6.3 shows the cross-section views of the fully-sintered micro-burner with the embedded channel configuration. We used x-ray micro-computed tomography (micro-CT) technology to noninvasively image the internal channels (see Figure 6.3a). This technique can be particularly useful to orient and position the internal cavity and channels of the fully-enclosed structure for drilling or other machining process of external features. It is shown that the internal features took the exact shape of the graphite phase and the machined holes were well aligned to the internal channels. The photograph of the crosscut sample reveals that no noticeable cracks or defects were found (see Figure 6.3b). Performing the micro-CT scan each time to locate the internal feature can be costly. Alternatively, we modified the design by extending the exhaust part of the graphite and exposing it to the exterior surface, which allowed us to find the internal channels for machining. Another unique aspect of this technique is an ability to incorporate additional structures on the channel wall without adding a process step. For example, Figure 6.3c shows two protruded lines of the trapezoidal cross-section at the bottom of the submillimeter channel embedded in the alumina device. This was done by simply making two grooves in the

graphite fugitive phase before compaction. This type of the structure would be difficult to be fabricated within the cavity walls using any other ceramic processing technique discussed in Introduction. Moreover, the surface finish quality of internal cavities can be tuned as it is directly related to the surface finish of the fugitive phase.



Figure 6.2: Images of the internal cavity and channels: (a) X-ray micro-computed tomography (micro-CT) for the fabricated alumina micro-burner with various cross-sectional views; photographs of the cross-sectional views for (b) the same micro-burner and (c) the submillimeter internal channel with the additional features on the wall. Scale bar for (b) and (c) is 5 mm.

6.3.2 Processing Characterization

We utilized the *fully-enclosed* design of the alumina micro-burner for the process characterization including powder compaction, optimization of the sintering temperature profile, and thermogravimetric analysis (TGA) experiments for graphite burn-out. One of the most critical steps in the proposed fabrication scheme is compaction. The presence of the stiff graphite of a complex shape impedes the powder flow, frequently causing non-uniform stress distribution and resulting in cracks in the final component. One simple remedy is to remove sharp edges and geometric complexities in the machined graphite layer. The rounded edges and corners facilitate the powder to flow around them, preventing undesirable cracks due to the non-uniform density distribution. The edges of the graphite after cut in a CNC machine were smoothened by manual grinding. In addition, the sharp protrusion or the feature of graphite with a high aspect ratio makes the resulting powder structure susceptible to crack formation during fully sintering because of the non-uniform density distribution. For example, the region (circled in Figure 6.2d1) intersecting two gas channels to the combustion chamber was found to be prone to the crack formation. Moreover, if the size of the graphite fugitive phase is too large in comparison to the overall ceramic sample, the ceramic sample may become collapsed or fractured. Since the powder holds its shape after compaction with the friction among the powder, the sufficient powder area is needed in terms of both thickness and planform area.

In a typical LTCC process, the burning of fugitive materials requires large openings because ceramic tapes consisting of the ceramic matrix infiltrated with polymeric or glassy phases are non-porous, leaving little room for gas diffusion. Because we compact pure alumina powder without any binder phase, the powder compact is still substantially porous, allowing gases (e.g. O_2 and CO/CO₂) to diffuse in and out. Among many materials serving as fugitive phases [37], we chose graphite for two reasons. First, graphite has a very low coefficient of the thermal expansion (2–6 μ m·m⁻¹·K⁻¹), which minimizes the stress exerted onto the powder compact during partial sintering. This is important because the ceramic powders are in an extremely fragile state when the graphite is burnt out. Also the dimension of the integrated cavity can be predicted with better accuracy compared to other polymer-based fugitive phases. Secondly, the graphite burns out before the alumina powder starts to consolidate. Adequate interstitial spaces are provided for the byproducts of graphite oxidation, mainly CO and CO₂, to escape. However, each graphite grade is slightly different in its oxidation temperature and a care must be taken in determining an appropriate temperature ramp rate and a soaking temperature and duration if necessary. Figure 6.4

shows the two different sintering temperature profiles (oven temperature vs. time) and the resulting alumina micro-burners. When a full sintering temperature was reached at a constant ramp rate $(15^{\circ}\text{C}\cdot\text{min}^{-1})$ without any soaking step, a crack was observed at the side or corner of the final structure (see Figure 6.4a). A similar crack was observed even at lower ramp rates. We performed thorough visual inspection of the compacted green ceramics using a microscope and removed the ones with observable cracks due to the improper die pressing.

Of course, there is still a possibility that cracks formed inside are not observable with visual inspection. In fact, the initial crack formation probably occurs at the edge or corner of the graphite during compaction. These preformed internal cracks can propagate to the exterior surface during the sintering process. We hypothesized that the crack propagation and structural integrity of the sintered ceramic structure would be significantly affected by the sintering temperature profile for the following reasons. On one hand, a higher ramp rate would induce a higher temperature gradient within the structure and in turn cause internal stresses to be developed, leading to crack propagation. On the other hand, an insufficient amount of time for graphite to completely burn out would generate a pressure build-up in the internal cavity as the consolidation of alumina powders progresses. We believe the former factor is less important since no crack was observed in the open-channel configuration regardless of the ramp rate. In the open-channel sample, the graphite phase is fully exposed to outer environment, and therefore there is no restriction for CO/CO_2 to be released. Conversely, a competition between graphite volatilization and powder consolidation exists in the fully-enclosed sample. If the alumina powders become consolidated before all graphite phases are burnt out, CO/CO₂ has little interstitial space to escape and the pressure will build up until the structure bursts open. This net increase in pressure within the cavity can be attributed to the different gas permeabilities of O₂ and CO₂ in porous metal oxide

structures (see Supplementary Information). To facilitate graphite volatilization, we added a soaking step at 800° C – the temperature high enough for graphite to burn out while low enough for alumina powders *not* to sinter (or consolidate) significantly. The modified sintering cycle allowed us to obtain the crack-free ceramic structures with the internal cavities (see Figure 6.4b).



Figure 6.3: Sintering temperature profile affecting the micro-burner structure with the internal cavity: (a) a single ramp-up in temperature bursting out the structure (see text); (b) adding a 2-hour-long soaking step at 800°C, allowing graphite fugitive phase to get oxidized before powder consolidation. Scale bar is 1 cm in both images.

To understand the kinetics of the graphite burn-out with and without the presence of alumina powders, we conducted thermogravimetric analysis (TGA) on a small piece of graphite and a graphite piece embedded in the alumina powder compact. First, a pure graphite sample was tested to determine the onset temperature of decomposition (or oxidation) for the graphite materials used in this study. Figure 6.5a shows a percent weight change as a function of temperature for the pure graphite sample (~10 mg). The temperature was increased from room temperature to 850°C

at a constant ramp rate of 10° C·min⁻¹ with air flowing through the sample chamber. The weight loss started to take place at around 650°C. The onset temperature (T_d) of intense thermal decomposition can be determined by the intersection point of tangents to two branches of the TGA curve and be estimated to be approximately 760°C (see Figure 6.5a). This observation served as a basis for determining the soaking temperature of 800°C in Figure 6.5.

Next, the TGA experiment for the graphite piece embedded in the alumina powder compact was performed to model the graphite decomposition process in the fabrication of the micro-burner. A small (~7 mm in dia.) alumina compact encapsulating a graphite piece was fabricated in the same way that the micro-burner was made. The size of the graphite piece was scaled proportional to the alumina structure such that the mass and volume ratio of graphite to alumina remained the same as the original burner structure. The temperature profile used in the experiment was similar to the partial sintering step of the alumina micro-burner and consisted of (i) temperature rise from room temperature to 800°C at the ramp rate of 15°C min⁻¹, (ii) soaking at 800°C for 2 hours, and (iii) ramping again to 900°C at the ramp rate of 15°C·min⁻¹. The weight loss as a function of temperature is shown for the "graphite with alumina" sample in Figure 6.5b. As expected, a noticeable decrease in weight was observed around 760°C, corresponding to the onset temperature of the graphite decomposition. In the final ramping step (from 800°C to 900°C), no apparent weight loss was witnessed, suggesting that the entire graphite phase was completely burnt out during the 2-hour soaking step at 800°C. After cooling down, the graphite/alumina sample was retrieved and inspected under the optical microscope. No crack was visible in the sample. Therefore, we conclude that the modified sintering schedule was capable to completely remove the graphite phase without damaging the ceramic structure. On a separate note, we unexpectedly observed a minute yet reckonable ($\sim 0.5\%$) decline in weight in the initial ramping step (from room

temperature to 650°C). Since no weight loss was seen in the pure graphite sample up to 650°C, the alumina powder should be responsible for this initial weight loss. To understand this trend, we ran another testing only with the alumina powder of the same mass with the same operating condition and noticed the similar initial decrease in weight (see the red dotted curve in Figure 6.5b). We exclude the possibility of the impurity inclusion as the alumina powder purchased has purity higher than 99.99% and was used in the as-received condition. Instead, we attribute this behavior to the hygroscopic nature of alumina powder – consisting of high-surface-area sub-micron-particles that absorbed moisture from ambient. Upon heating, these bounded water molecules were desorbed, leading to the initial weight loss [41].



Figure 6.4: Thermogravimetric analysis (TGA) results: (a) a pure graphite sample; (b) a graphite piece embedded by and compacted with the alumina powder.

The linear shrinkage of alumina in air was measured by thermomechanical analysis (TMA) and is shown as a function of time and temperature in Figure 6.6a and 6.6b, respectively. The sintering temperature profile used in the TMA experiment was the same as the micro-burner sintering process. After an initial deep (which is related to the translation deformation induced by the load), there is a constant increase in displacement up to 800°C, representing the thermal

expansion of alumina powders. Because sintering had not occurred significantly below 800°C, thermal expansion dominates over particle consolidation. In the 2-hour soaking period at 800°C, the dimension of the sample did not change – the isothermal condition causing neither thermal expansion nor particle consolidation. Lack of shrinkage in the alumina sample at that temperature also indicates that the pores in the sample were still interconnected, allowing CO/CO₂ emitted from graphite oxidation to escape without much barrier. The densification rate, a time derivative of displacement, is also plotted with temperature in Figure 6.6b, showing that the temperatures for the onset of densification and the maximum densification essentially stopped at the temperature above 1350°C. Finally, during the cool-down process, the sample was shrunk due to thermal contraction.



Figure 6.5: Thermomechanical analysis (TMA) results for compacted, pure alumina sample (3.8 mm in thickness): (a) linear shrinkage (blue) and temperature profile (red) plotted with time; (b) linear shrinkage (blue) and densification rate (green) plotted with temperature

The TMA results were compared to the dimensional change of the micro-burner measured from the cross-sectional image (see Figure 6.3). Table 6.1 shows the overall size and internal channel dimension of the alumina micro-burner at each process stage (see Supplementary Information). The green state (after compaction) of the sample had the diameter of 22.2 mm and the thickness of 4.98 mm. Just as the TMA shrinkage indicated, the sample size barely changed after the partial sintering at 800°C. However, dimensional changes over 18% were made at the end

of the full sintering process around 1,350°C. The similar dimensional reduction was observed for the internal channel. We can also infer the dimensional shrinkage from the density (or volume) ratio of the green and sintered sample. In our process, the relative densities of the green and sintered ceramics were estimated about 52% and 96%, respectively. The volume ratio is then: $V_{sintered}/V_{green} = (1-S)(1-S)(1-S) = 52/96 = 54\%$, where *S* is a dimensionless shrinkage (assumed to be the same in all three directions). This leads to $S \approx 18.6\%$, which is consistent with the TMA results (maximum shrinkage rate of 18.3%) and the other reported values [42][43][44]. The volume ratio of 54% also suggests that the green-state ceramics (after compaction) are 40 ~ 50% porous. Since the TMA result indicates no significant shrinkage up to 1000°C, the partially sintered alumina possesses the same level of high porosity, providing sufficient gas permeability for the graphite removal through the fully-enclosed structure and corroborating our earlier argument.

6.3.3 Machining of Partially Sintered Ceramic (PSC):

It has been widely known that fully sintered ceramics including alumina in this study have poor machinability due to its stiffness and brittleness [45]. Machining green or white ceramic compacts [46][47][48] would be easier if the final tolerance is not strict. Green machining is referred to as the machining of a ceramic in the unfired state, i.e., a powder compact before exposing to high temperature. In green machining, the powder is usually mixed with a binder phase (typically organic polymer or wax) to achieve the sufficient strength for machining. In this study, pure alumina powder was utilized without any binder phase. Therefore, the compacted powder was too difficult to handle and prone to fragment during machining, preventing us from performing green machining. On the other hand, white machining is an approach to machining on partially sintered ceramics (PSC) [48]. The powder compacts can be partially sintered by firing at a temperature substantially below their typical sintering temperature. The formation of necks among the individual powder particles during partial sintering provides PSCs with the strength to withstand during machining. Here we chose white machining to create fluidic connections to the enclosed channels in the micro-burner.

The extent of neck formation in PSCs, which determines the strength of the powder compact, highly depends on partial sintering temperature [49]. For this reason, the partial sintering condition such as pre-sintering temperature and its duration has been shown to significantly affect the quality of the machined features [45]. To understand the effect of partial sintering temperature on the machined features on PSCs, we prepared four alumina samples that were partially sintered at four different temperatures (600°C, 800°C, 1000°C, and 1200°C). The conventional machining processes such as drilling and milling were performed on these PSC samples using a small benchtop CNC machine. The quality of the machined features was correlated to the amount of chips and cracks generated around holes during machining. The optimal machining parameters (feed rate of 1 mm·min⁻¹ and cutting speed of 1500 rpm) for PSCs were determined based on the past work [45] and used throughout the study.



Figure 6.6: Effect of the partial sintering temperature (four different temperatures - 600, 800, 1000, 1200°C) on the machined features of alumina PSCs: optical microscope images of (a-d) 1 mm diameter drilled holes and (e-h) 1 mm wide milled grooves; (i-l) SEM images of the corresponding microstructures. Scale bars are 0.5 mm for (a-h) and 200 nm for (i-l).

Figure 6.7 shows the effect of the partial sintering temperature on the machined features of alumina PSCs. The alumina sample partially sintered at 800°C exhibited no pronounced surface chipping or cracks around the edges of the holes and grooves (see Figure 6.7b and 6.7f). Minor cracks and chips were observed in the sample partially sintered at 600°C (Figure 6.7a and 6.7e) while more noticeable defects were seen for the 1000°C sample (Figure 6.7c and 6.7g). The sample partially sintered at 1200°C exhibited the extensive chipping damages around the edges of the machined features (Figure 6.7d and 6.7h). X-ray diffraction (XRD) analysis on the green (unfired) ceramic and these four PSCs suggests that the starting alumina powder is in the α -phase and there is no phase change during partial or full sintering. Therefore, the marked differences in the machined features of the alumina PSCs partially sintered at the different temperatures are not
likely coming from the phase change of alumina. Unlike metals whose major removal mechanism is a local shear deformation, the underlying mechanism of machining PSCs is related to the breakage of necks between particles. When the partial sintering temperature increased from 600 to 800°C (i.e., initial stage of partial sintering), more neck formation occurred, providing stronger connections among individual particles and more resistance to chipping or cracks. However, once the partial sintering temperature increased to 1000°C or above, the consolidation taking place beyond the neck formation were too extensive such that brittle fracture became a dominant material removal mechanism. The high-resolution scanning electron microscopy (SEM) images in Figure 6.7(i-l) show the extent of the neck formation and particle consolidation (or lack of porosity) for these four samples, corroborating our mechanistic explanations. Extensive neck formation on the powder compact can be clearly observed for the samples with higher partial sintering temperatures. To further characterize the mechanical properties of the PSCs sintered at different temperatures and correlate them to the observed machining behaviors, we conducted a 3-point bending test to measure the flexural strength of the PSCs. Combined with the results shown in Figure 6.6, we can conclude that the PSC sample partially sintered at 600°C was too fragile to machine while the sample partially sintered at 1200°C was strong but too brittle to machine.

6.3.4 Micro-burner Testing:

The fully-sintered alumina sample fabricated in this study was tested for micro-burner applications. Both open-channel and embedded-channel configurations were experimented for visualization and proof-of-the-concept purposes, respectively. Figure 6.8a shows how the fuel (H₂) and oxidant (O_2 or air) streams are connected to the micro-burner as well as the location of the exhaust. In essence, hydrogen generated by the electrolyzer [40] and air from a miniature gas pump were fed to the open-channel micro-burner (bonded with a quartz window, see Figure 6.2e). Under

the laminar flow condition, these two streams create a stable hydrodynamic boundary layer in the flame region where a folded diffusion flame would be formed [39]. When the H₂ flow rate was high (~ 100 sccm), the flame was ignited at the outside of the exhaust channel (see Figure 6.8b). As the H₂ flow rate (controlled by the electrical power applied to the electrolyzer) was reduced to $30\sim50$ sccm, the flame started to move into the exhaust channel and eventually became anchored in the cavity. In order to reduce the amount of air that needed to be pumped, we added an O₂ flow co-generated by the electrolyzer to the oxidant stream. The oxidant flow rate (O₂ plus air) was determined to keep the fuel-to-oxidant ratio stoichiometrically correct or under lean-burn condition. A stable folded flame was observed for the range of the hydrogen flow rates (40~55 sccm) and oxidant flow rates (20~27 sccm for oxygen and 20~80 sccm for air).

After we identified the H_2 and air flow rates that anchored the flame inside the combustion chamber, we tested the enclosed micro-burner with the similar flow conditions. The flame generated within the enclosed micro-burner cannot be observed due to the opaque nature of the alumina walls. Therefore, we indirectly verified the presence and approximate location of the flame by recording the outer wall temperature of the micro-burner. Figure 6.8c depicts the temperature distribution of the burner's exterior surface measured by the thermocouple from 7 by 7 points (49 total measurements with each point 1.5 mm apart). The region of the highest temperature indicates the location of the flame, which resembles the flame location of the quartz/alumina micro-burner. The maximum steady-state temperature of the alumina outer surface was measured to be around 170°C (for flow rate conditions: H_2 35 sccm and O_2 17.5 sccm/air 20 scccm). This temperature is much lower than the adiabatic flame temperature of the oxyhydrogen flame, which is between 2210 and 3200°C depending on the fuel-to-oxidant ratio and oxygen-to-air ratio in the oxidant stream. The low thermal conductivity of alumina (12~38 W·m⁻ 1 ·K⁻¹) therefore provided reasonable thermal isolation compared to the other common microburner materials like metals or silicon. The enclosed micro-burner was continuously operated for more than 6 hours with the stable flame throughout. More than 10 micro-burners have been tested over the 10-month period, and no structural damage has been observed due to the high operation temperature or repeated heating/cooling (i.e. thermal stresses) from each run.



Figure 6.7: Micro-burner testing: (a) a photograph of the open-channel alumina micro-burner (18 mm in diameter); (b) flame characterization - reduction in a H2 flow rate anchoring a flame in the micro-burner; (c) temperature distribution of the embedded micro-burner, indirectly representing the flame location; (d) signal collected upon natural gas injection after the micro-burner configured as a micro flame ionization detector (red arrows indicating the injection events).

Finally, the alumina micro-burner was tested as a micro flame ionization detector (μ FID). Two tungsten wires (0.5 mm diameter) were inserted into the exhaust to serve as electrodes. A flame was ignited and anchored into the micro-burner cavity with the flow rate conditions of H₂ 45 sccm and O₂ 22.5 sccm/air 20 scccm. This oxy-hydrogen flame ionizes hydrocarbon molecules, and the produced ions are driven by the applied electric field and collected by the electrodes. Without further optimization, we injected a train of 0.1 mL of natural gas through the analyte port using a gas-tight syringe (red arrows in Figure 6.8d). With the applied voltage of 160 V between the electrodes, a generated current was converted to an amplified voltage via a transimpedance amplifier (gain = 10^5). Each peak in Figure 6.8d corresponds to each event of natural gas injection. Due to large dead volumes associated with the injection port and the manual syringe injection setup, the obtained signals were short and broad. The electrode design and operation conditions were far from being optimal, and therefore the further characterization of the µFID would significantly improve the device performance. Though the performance of the µFID does not quite match that of the state-of-the-art system, this testing demonstrates a practical use of the micro-burner created by the proposed ceramic processing.

6.4. SUPPLEMENTARY INFORMATION

6.4.1. Surface Finish:

Ceramic processing techniques that can create embedded sub-millimeter channels or cavities (e.g. LTCC or 3D printing) in general have difficulties in controlling the surface finish of the internal features. In our proposed process, the surface finish of the inner walls is directly related to that of the graphitic fugitive phase, which is controllable through machining and other traditional processes. Figure 6.9 shows how two different surface finishes of the graphite (Figure 6.9a and 6.9c) can be translated into the surface finishes of the alumina walls (Figure 6.9b and 6.9d).



Figure 6.9. Profilometric scans of the graphite surfaces with two different surface finishes (a) and (c) and their corresponding alumina surface finishes (b) and (d), respectively.

6.4.2. Crack Monitoring:

Improper die pressing would be one of the main reasons for having cracks in the sample. In fact, the initial crack formation probably occurs at the edge or corner of the graphite during compaction regardless of the subsequent processes. For some cases, these cracks propagate to the surface of the green ceramic during compaction and can be easily spotted by bare-eye or microscope inspection (see Figure 6.10a). This frequently happens when the shape of the fugitive phase is distorted from what we considered to be axisymmetric. Therefore, we had to change the shape of our micro-burner design a few times to minimize macroscopic crack formation during compaction. As shown in Figure 6.10, we performed visual inspection at each process stage and removed the sample with the visible cracks. When the powder compact having the cracks prevalent on the exterior surface was further sintered using the optimized process (sintering temperature profile given in Figure 6.4b), no apparent change was seen (see Figure 6.10b1). Of course, there is still a possibility that cracks formed inside are not observable with visual inspection. These preformed internal cracks can propagate to the exterior surface during the sintering process. A macroscopic crack seen in Figure 6.3a was therefore not directly caused by the poor powder compaction, but rather by the stress developed during sintering. A slower ramp rate and the addition of the soaking step to sintering alleviate the internal stress development responsible for crack propagation, leading to the crack-free sintered structure (see Figure 6.4b). As discussed, the crack propagation was mainly caused by the net increase in pressure within the cavity. To further explain the mechanism of how the gaseous byproducts can be accumulated within the internal cavity during partial sintering, we provide more supporting arguments to the proposed working principle. We attribute the net increase in pressure within the cavity to the different gas permeabilities of O₂ and CO₂ in porous metal oxide structures. Generally speaking,

 O_2 is lighter than CO_2 and therefore exhibits a higher diffusion coefficient (*D*) than that of CO_2 under the same condition (for example, $D_{CO2, air} = 0.17 \text{ cm}^2 \cdot \text{s}^{-1}$ and $D_{O2, air} = 0.215 \text{ cm}^2 \cdot \text{s}^{-1}$ at 1atm and 300 K) [50]. More importantly, at elevated temperatures, it has been known that metal oxides are exceptionally more permeable to O_2 than other heavier gases [51]. Therefore, for a given partial sintering condition, a higher permeability of O_2 in the alumina structure provides sufficient O_2 for oxidizing a graphite fugitive phase while the byproduct CO_2 cannot easily escape from where it is produced. This issue of excessive byproduct build-up may become more severe with the decreasing pore size as the alumina structure gets consolidated further.



Figure 6.10: Photographs of the fully-enclosed alumina micro-burners at different process stages and with different sintering recipes. (a-c) green ceramics, i.e., as-pressed alumina structures; (a) the sample with the macroscopic cracks are not processed further, (b) the sample with a small, hair-like crack has been sintered using Recipe B (a slow ramp rate plus a soaking step) but the same crack has remained (b1), (c) the sample with no observable crack has been sintered using Recipe A (a fast ramp rate without a soaking step), which generates a large size crack (c1). If the sample (c) has been sintered using Recipe B, a crack-free ceramic structure can be obtained (c2). (c1') The sample (c1) has been cut in the middle to show the cross-section but shattered due to the brittleness of the fully-sintered sample. (c2') The sample (c2) has been drilled for fluidic inlets in its partially-sintered state. All scale bars are 1 cm.

6.4.3. Recording Dimensional Change

Alumina Sample Dimension	Green state	800°C	1350°C (% Shrinkage)
(all units in mm)	(after compaction)	(partial sintering)	(full sintering)
Overall Diameter	22.22	22.14	18.11 (18.5%)
Overall Thickness	4.98	4.90	4.02 (19.2%)
Channel Height	0.9	0.89	0.74 (17.7%)
Channel Width	2.19	2.15	1.79 (18.2%)

Table 6.1. Change in the overall size and internal channel dimensions of the alumina microburner at each process stage

6.4.4. XRD Analysis

The XRD (Bruker AXS D8) was carried out on the unfired, partially sintered at 600°C, 800° C, 1000° C and 1200° C samples (see Figure 6.11). Based on the similar peak locations of all samples, we can conclude that there is no phase change during partial or full sintering. This is expected because the starting alumina powder (without firing) is in the *alpha* phase which is stable throughout our processing route. The crystallite size (*L*) can be calculated from the XRD peaks using the Scherrer Equation or Modified Scherrer Equation [R4]:

$$L = \frac{K\lambda}{\beta\cos\theta}$$

where λ is the X-ray wavelength in nanometer (= 0.154 nm for Cu K-alpha), β is the peak width of the diffraction peak profile at half maximum height in radians, *K* is a shape factor for nonspherical crystallites (typically regarded as 0.9), and θ is the Bragg angle in radians. This equation is valid for the crystallite size smaller than 100 nm. Since the size distribution of alumina powder is from 100 to 300 nm, we can assume that the crystallites would be smaller than 100 nm and it is valid to use the Scherrer Equation. After plugging the relevant data into the equation, we obtain 8.59 nm for the average crystallite size. Since the peak widths of the diffraction signals are essentially unchanged, we can conclude that the crystallite size did not change over the samples we prepared.



Figure 6.11: XRD reflection peaks from the green (unfired) ceramic and the alumina PSCs partially sintered at four different temperatures (600, 800, 1000, and 1200°C)

6.4.5. Flexural Strength

We carried out a 3-point bending test to measure the flexural strength of our alumina samples. Each compacted sample was partially sintered at 600, 800, 1000 or 1200° C and then cut into a rectangular bar with the dimension of $0.5 \times 1.5 \times 18 \text{ mm}^3$. The four sides of each specimen were slightly polished by a 600-grit sandpaper to eliminate edge flaws for the testing. For each sample, the flexural strength was measured with a span length of 10 mm and a crosshead speed of $0.01 \text{ mm} \cdot \text{sec}^{-1}$ (TA Instruments RSA III, USA). The results are shown in Figure 6.12 and explains the trend we observed in machining PSCs. The sample partially sintered at 600°C was too fragile

to machine while the sample partially sintered at 1200°C is strong but too brittle to machine. This result of the flexural strength is well correlated to the extent of neck formation observed in PSCs (see Figure 6.7).



Figure 6.12: Plots from the 3-point bending test for PSCs with four different sintering temperatures (600, 800, 1000, and 1200°C). (Left) flexural strength vs. displacement and (Right) flexural strength vs. sintering temperature.

6.4.6. Micro-burner Testing



Figure 6.13: (a) A photograph of the 7 by 7 locations where the alumina micro-burner wall temperature was measured (burner size is 18 mm in diameter and 4.2 mm in thickness);
Temperature distribution at different flow rate conditions of (b) 40 sccm of H₂, 20 sccm of O₂ + 60 sccm of air; (c) 45 sccm of H₂, 22.5 sccm of O₂ + 35 sccm of air; (d) 50 sccm of H₂, 25 sccm of O₂ + 10 sccm of air.

6.5. CONCLUSIONS

In this part, we presented a unique ceramic powder processing method to fabricate the ceramic structures with internal cavities and channels for microchemical system applications. High-purity, binder-free alumina micron-powder was compacted with the graphite fugitive phase embedded in the powder bed. The graphite was later burnt out during partial sintering, leaving the cavity and channels. The sintering schedule used in partial (and full) sintering critically influenced the structural integrity of the final alumina structure. Instead of the continuous temperature ramping to the full sintering temperature, the compacted alumina was partially sintered at 800°C for two hours, which not only facilitated the removal of the graphite fugitive phase but also promoted the optimal neck formation for the subsequent machining processes. The TGA and TMA results showing graphite oxidation and alumina densification kinetics supported the competing nature of graphite burn-out and powder consolidation. The quality of the machined features on the partially sintered alumina was investigated using various imaging techniques, revealing that the partial sintering temperature is an important parameter for machining. Finally, the fabricated openchannel and fully-enclosed alumina micro-burners were tested in various flow rate conditions of hydrogen and oxygen/air, demonstrating that the fully-enclosed device functioned as designed without failing over long-term and cyclic operations.

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