Grain growth and densification behavior of 316L stainless steel metallic components produced via binder jet-powder printing (3-D) system using water atomized powders. Hsiang-Ling Juan¹, Y. Zhou¹, C. Schade², and C.I. Garcia¹ Ferrous Physical Metallurgy Group-Mechanical Engineering and Materials Science Department Swanson School of Engineering, University of Pittsburgh¹ Pittsburgh, PA. 15261 Hoeganaes Corporation²

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The goal of this paper was to study the effect of initial water atomized powder size and sintering processing conditions on the grain growth and densification behavior of metallic components of 316L stainless steel. Of particular interest was to establish the relationship between grain growth and densification. The results showed that prior to grain growth the pores are attached to the austenite grain boundaries and/or to annealing twins, suggesting two mechanisms; 1) the pores at the grain boundaries act as pinning force to prevent grain coarsening, and 2) the mobility of high angle grain boundaries act as compressing force to reduce the pore size. After grain growth, the pores are left behind the grain boundaries. At this condition, the sintering of the metallic component becomes nearly impossible to achieve. The grain growth and sintering behavior were systematically analyzed using advanced electron optic techniques. The results will be presented and discussed.

Keywords: Additive manufacturing, Binder, Densification, Fractal dimension, Grain growth, Sintering.

Introduction

Additive Manufacturing (AM) is a process that translates the 3D model data into real products [1]. Unlike other rapid deposition systems, the binder jetting system will not have distortion by residual stress under heat. Binder jetting comprises ink-jet printing technologies to bond the particles layer by layer [2]. Therefore, it can work with almost any material that is available in water atomized or gas atomized powder form. The limitations or shortcomings of this technology have been discussed extensively in the literature.

As most binder jetting technologies focus on achieving full density parts, controlling the grain size during sintering is also important. However, the control of grain growth and densification in metallic components using the binder jetting processes has not been extensively explored. In this study, the Powder-binder Jetting system called M-flex was used to fabricate metallic components using stainless steel 316L water atomized powder. The important variables that have been investigated included: initial particle size, sintering temperature and heating holding time. The present research focused on the relationship between temperature ratio (T_S/T_M) and the pore-grain boundary interaction mechanism during sintering.

Experimental Procedure

Water-atomized 316L stainless steel powders with different particle size were used in this study.

Table. I shows the chemical composition of the 316L stainless steel. An ExOne M-Flex binder jet-powder 3D printing system was applied for sample fabrication. During printing, powders were spread layer by layer at a certain layer thickness, bonded with binder at 70% saturation to the void volume between particles to form an object. Afterward, curing took place at 195 °C for 8 hours to remove the binder, hence the samples would be ready for sintering.

Sintering was performed under an argon/hydrogen mixture (96% Argon + 4% Hydrogen) atmosphere to prevent samples from oxidation. The samples were sintered at different temperatures from 1300 °C to 1380 °C, and held isothermally from 90 min to 1440 min, as described in Table. II. Heating rate was 5°C/min below 1000 °C and 1 °C /min above 1000 °C, cooling rate was 1 °C/min above 1000 °C and 3 °C/min below 1000 °C. Three intermediate isothermal holds for 120 min at 350 °C and 60 min at 630 °C and 420 °C were applied for equipment protection.

	Chemical Composition (wt.%)									
Elements	Fe	Cr	Ni	Mo	Mn	Si	N	Р	С	S
Standard 316L	Bal.	18	14	3	2	1	1	0.045	0.03	0.03

Table. I. Chemical composition of standard 316L stainless steel.

8	1						
Standard 316L							
Sintering temperature T _S (°C)	T_S/T_M	Sintering holding time (min)					
1300	0.95	90, 360, 1440					
1328	0.97	90, 360, 1440					
1356	0.98	90, 360, 1440					
1380	0.99	90,360					

Table. II. Sintering temperature and time for standard 316L.

Sintered density was determined by the Archimedes method [3], as Eq. (1) shows,

$$\rho = \frac{A \times \rho_W}{B - (C - A + D)} \tag{1}$$

where ρ_W is the density of water[4], A is the mass of the sintered part without glue in air, B is the mass of part with glue in the water, C is the mass of part with glue in air and D is the mass of support part in water.

To evaluate the grain growth, samples were characterized by optical microscope and the micrographs using ImageJ software analysis in accordance with liner intercept method (ASTM E112) [5]. Fractal dimension was applied to describe the stereological shape changes of the pores during sintering. Using this technique, a two-dimensional object can be divided into $N(\varepsilon)$ small squares and each of them is measured by the length ε . Therefore, the fractal dimension D can be calculated as:

$$D = \frac{\ln N(\varepsilon)}{\ln \varepsilon}$$
(2)

In this research, the fractal dimensions were determined with the help of ImageJ using box counting method [6,7].

Results and Discussions

Densification Response

The densification (percentage of the theoretical density of stainless steel 316L) of the sintered samples are listed in Table. III. It was observed that samples with finer water atomized particle size attributed to a higher densification at 1300 °C and 1356 °C. Sintered density of samples with particle size at 24 and 15 microns increased as sintering temperature increased before 1356 °C, but decreased at 1380 °C, which means after 1356 °C increasing the temperature did not improve densification.

Densification		Temperature (°C)					
Particle size (µm)	Green density	1300	1356	1380			
41	40.45%	68.41%	82.00%	84.38%			
24	33.65%	69.13%	82.13%	76.88%			
15	33.70%	73.89%	92.35%	80.00%			

Table. III. 316L stainless steel different particle size densification.

Effect of Sintering Temperature

The microstructure evolution using the particle size of 15 µm is given as an example in Figure 1. From Figure 1. (a), a high volume fraction of large pores are attached to the grain boundaries and triple-point grains edge. When the pores are attached to the grain boundaries, grain boundary diffusion is the main transport mechanism. With increasing heat treatment temperature, there is a small but progressive reduction on porosity due to some pores are still attached on annealing twin boundaries and grain boundaries. Many annealing twins are present at 1328 °C, shown in Figure 1. (b). However, in Figure 1. (c), most of the pores are small and isolated inside grains, indicating pore-boundary separation. The energy of the system is lower when the pores are located at the grain boundaries; when pore and the boundary are separated, the energy of the system increases because of newly created interfacial area[8,9,10].

As the sintering temperature increases, see Figure 1. (d), the pores become larger and appear on the grain boundary again. The number of the pores does not decrease, and the pore size increases. When sintering at higher temperature, densification will be slower at the final stage due to the isolated pores within the grains. When the pores are isolated within the grains, the main diffusion mechanism changes from grain boundary diffusion to volume diffusion, which makes the motion of the pores difficult, hence the densification is limited. In Figure 1. (d), most pores are isolated inside the grains and some are re-attached to the grain boundary. This stage suggests that grain boundary mobility is faster than pore migration.

During sintering, there are three possible interaction stages between pores and grain boundaries: 1) the pore attached on the grain boundary exerting a pinning force on the grain boundary and

hence retards grain growth; 2) the pore is dragged by the moving grain boundary during grain growth; and 3) the grain boundary mobility is faster than pore mobility and the pores are left behind (the grain boundary breaks away from the pores). Figure 2. shows the schematic of the relationship between grain growth, densification and pore migration during sintering process. The first three stages are related to the process of pores/grain boundary interaction. The last and fourth stage shows the swelling behavior of the pores and slower grain growth behavior.



Figure 1. Optical micrographs of the 316L stainless steel (particle size 15 μm) sintered at (a) 1300 °C, (b) 1328 °C, (c) 1356 °C and (d) 1380 °C for 90 min.



Figure 2. Shows the schematic process of grain growth versus densification and pores migration.



Figure 3. Variations of density and pores fractal dimension versus sintering temperature.

Figure 3 shows the changes in the fractal dimension of the pores during sintering. At the start of sintering the pores have an irregular shape (fractal dimension > 1), when sintering progresses the fractal dimension of the pores approaches to a spherical shape (fractal dimension ~ 1.0). The fractal dimension seems to increase at 1380 °C because of the pore coarsening and reattaching to the grain boundary which increase the average dimension of pores [13].

Effect of Sintering Holding Time

Table III and Figure 4 show the relationship of densification and holding time for samples with 15-micron particle size. As expected, densification increased as the holding time increased for a given sintering temperature. The highest density appeared at 1356 °C with a holding time of 360 min, and did not improve at longer holding time. As shown in Figure 4, the densification at 1356 °C was higher than 1300 °C. However, the 1300 °C curve continued arising and the 1356 °C curve remained stable as the holding time increased. At 1380 °C, the density decreased compared to 1356 °C. Thus, there seem to be an optimum sintering temperature no higher than 1300 °C for the system studied in this work. On the other hand, it seems that longer holding times at 1300 °C may increase the densification (%). This will be studied in future work.



Figure 4. Densification versus holding time at different sintering temperature (15µm).

Figure 5. (a)-(f) show the microstructure of the 15µm specimens sintered from 90 min to 24 hours at 1300 °C and 1356 °C. At 1300 °C, most of pores were located at grain boundaries in faceted-shape when holding for 90 min. Increasing the holding time to 360 min, as shown in Figure 5. (e), some pores broke away from the grain boundaries and some are attached to the annealing twin boundaries. Increasing the holding time, as shown in Figure 5. (f), the grain size increased and the amount of pores decreased which contributed to the increased densification. At 1356 °C, most of the pores were isolated in the grains with the holding time for 90 min, as shown in Figure 5. (a). When increasing the holding time to 360 min, the densification slightly increased, and did not improve after a holding time of 24 hours, see Figure 5(c), the figure shows pores coarsening and the amount of pores did not decrease which caused the density decrease. In addition, the grain growth was delayed due to the pores exerting a pinning force to the motion of grain boundaries.

At higher sintering temperature, grain boundary mobility is faster than pore mobility and the pores are left behind the grain boundaries. The specimens which contained isolated pores have shown that pore coarsening occurs by Ostwald ripening and a coalescence mechanism as has

been shown in previous studies[14,15,16]. In addition, isolated pores entrapped with gas will prevent full densification[14,17].



Figure 5. Optical micrographs of particle size 15 μ m samples sintered at 1356 °C for (a) 90, (b) 360 and (c) 1440 min. Sintered at 1300 °C for (d) 90, (e) 360 and (f) 1440 min.

The grain growth kinetics was studied based on Kang's model. For the systems containing mobile pores and in which grain boundary migration controlled by pores, Kang assumed that the volume of material transport from grain boundary to a pore is affected by the surface area of the pore. For lattice diffusion, the densification rate is written as[18,19]:

$$\frac{d\rho}{dt} = \frac{441D_L\gamma_S V_m}{RTG^3} (1-\rho)^{1/3}$$
(3)

Integrating Eq. (3)

$$G^{3} = \frac{k_{3}}{T(1-\rho)^{2/3}}t$$
(4)

where D_L is the lattice diffusion coefficient, γ_S is specific surface energy, V_m is the molar volume, G is grain size, ρ is relative density, t is time, T is the absolute temperature and k_3 is a constant related to the material and grain growth mechanism.

In the case of grain boundary diffusion, the densification rate is expressed as:

$$\frac{d\rho}{dt} = \frac{773D_b\delta_b\gamma_S V_m}{RTG^4} \tag{5}$$

$$G^4 = \frac{k_4}{T\rho}t\tag{6}$$

Integrating Eq. (5)

where D_b is the grain boundary diffusion coefficient, δ_b is the diffusion thickness of grain boundary diffusion and k_4 is a constant related to the material and grain growth mechanism. In the case of surface diffusion, the densification rate is the same as the Coble's model. Fittings of the experimental results plotted according to the Eq. (5) and (6) are shown in Figure 6. The grain growth mechanism was identified by comparing the correlation coefficient \mathbb{R}^2 . A correlation coefficient of 1 would be an ideal fit to the corresponding mechanism. It can be seen that a good linear fit was observed for the lattice diffusion controlled grain growth when sintering for 360 min and grain boundary diffusion controlled grain growth when sintering for 90 min.

Experiments on grain growth and densification kinetic of the microstructure shows that for 316L stainless steel 15 μ m sintering 90 min, the controlling mechanism was surface diffusion, the pores inhibited the grain boundary migration in a similar fashion as solute drag. Grain boundary diffusion controlled the grain growth kinetics. For sintering after 360 min, lattice diffusion is the controlling mechanism and lattice diffusion controlled the kinetics of grain growth.

The experimental results of densification and grain growth, showed a good agreement with the Kang's model.



Figure 6. 316L stainless steel 15 μ m grain growth data of microstructure fitted according to: (a) Kang's model of lattice diffusion controlled densification and (b) Kang's model of grain boundary diffusion controlled densification.

Conclusions

This study investigated three variables (particle size, sintering temperature, and holding time) during the sintering of 3D printed metallic components using water atomized 316L Stainless powder. The conclusions from this study can be summarized as follows:

- 1. The samples fabricated by 15 μ m powders showed the best sintered densification. This effect is strongly related to the larger surface energy due to the finer particles which is released faster during sintering.
- 2. The highest densification achieved was 93.90% when sintering at 1356 °C for 360 min. However, 1356 °C is too high according to the results.
- 3. The optimum sintering temperature seem to be strongly related to the grain coarsening behavior. That is, the sintering temperature should be selected at or below the grain coarsening temperature of the metallic system.
- 4. Grain boundary diffusion plays an important role during the sintering process. If the pore and boundary are separated, the grain boundary mobility is too fast. The separation of pore-boundary will prevent full densification.

References

- 1. I. Gibson, D. Rosen and B. Stucker, "Additive Manufacturing Technologies: 3D Printing," *Rapid Prototyping and Direct Digital Manufacturing* (Spring New York, 2nd edition, 2015).
- 2. Y. Zhou, S.C. Siw, C. Schade, M. Chyu and C.I. Garcia, "Development and Optimization for Metallic Parts/Components Using Powder Bed Additive Manufacturing," *Materials Science & Technology*, (2015), 175-218.
- 3. ASTM Standard B962-15: Standard Test Methods for Density of Compacted or Sintered Powder Metallurgy (PM) Products Using Archimedes' Principle, ASTM International, West Conshohocken, 2015.
- 4. A. B. Spierings, M. Schneider and R. Eggenberger., "Comparison of density measurement techniques for additive manufactured metallic parts," *Rapid Prototyping Journal*, (17) (5) (2011), 380-386.
- 5. ASTM Standard E112-88: Standard Test Method for Determining Average Grain Size, 1995 Annual Book of ASTM Standards, (3.01) (3).
- 6. L.T. Dougan and P.S. Addison, "Estimating the cut-odd in fractal scaling of fractured concrete," *Cement and Concrete Research*, (31) (2001), 1043-1048.
- 7. Y.Shi, X.P. Lou and S.H. Quan, "Fractal dimension computation methods for gas diffusion layer of PEM fuel cells," *Journal of Wuhan University of Technology*, (29) (2005), 79-82.
- 8. R.M. German, Sintering Theory and Practice (John Wiley & Sons, Inc., 1996).
- 9. R.M. German, *Powder Metallurgy Science* (Metal Powder Industries Federation, 1989).
- 10. F.K. Yan et al., "Strength and ductility of 316L austenitic stainless steel strengthened by nano-scale twin bundles," *Acta Materialia*, (60) (2012), 1059-1071.
- 11. J.R. Cahoon, Q.Li and N.L. Richards, "Microstructural and processing factors influencing the formation of annealing twins,"*Materials Science and Engineering:A*,(526)(2009), 56-61.
- 12. K.H. Song, Y.B. Chun and S.K. Hwang, *Materials Science and Engineering: A*, (454-455) (2007), 629-636.
- 13. J. Konget al., "Evolution of fractal features of pores in compacting and sintering process," *Advanced Powder Technology*, (22) (2011), 439-442.
- 14. A. Bose and R.M. German, "Sintering atmosphere effects on tensile properties of heavy alloys," *Metallurgical Transactions A*, (19) (1988), 1467-1476.
- 15. Seong-Jai Cho, Suk-Joong L. and Duk N. Yoon, "Effect of entrapped inert gas on pore filling during liquid sintering," *Metallurgical Transactions A*, (17) (1986), 2175-2182.
- 16. K.S. Churn and D.N. Yoon, "Pore formation and its effect on mechanical properties in W-Ni-Fe heavy alloy," *Powder Metallurgy*, (4) (1979), 75-178.
- 17. G.L. Powell, "Mass spectrometric determination of hydrogen thermally evolved from tungsten-nickel-iron alloys," *Analytical Chemistry*, (44) (1972), 2357-2361.
- L. Liu et al., "Densification and grain growth of stainless steel microsize structure fabricated by μMIM," *Applied Physics A: Materials Science & Processing*, (83) (2006), 31-36.
- 19. S.J.L. Kang and Y.I Jung, "Sintering kinetics at final stage sintering: model calculation and map construction," *Acta Materialia*, (52) (2004), 4573-4578.