COMPARISON OF MASTER ALLOY AND PRE-ALLOYED 316L STAINLESS STEEL POWDERS FOR METAL INJECTION MOLDING (MIM).

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ABSTRACT

Metal injection molded stainless steel components can be made from either pre-alloyed or master alloys powders blended with the appropriate proportion of carbonyl iron powder. The master alloy route provides significant cost benefits when very fine particle sizes (typically -16μm) are required. In this study these two techniques were compared using pre-alloyed and master alloyed 316L gas atomized powder each with two particle size distributions. Feedstocks from the four different materials were prepared, characterized, and injection molded into tensile bars. The mechanical properties of the tensile bars were compared in the green state and after sintering at different temperatures. The general findings indicate that the product of both the master alloy and pre-alloyed powders exceed the MPIF Standard 35 minimum requirements for sintered density, tensile strength and elongation. Transverse rupture tests of the green parts indicated that the master alloy route improved green strength. There is no significant difference in properties for parts produced from the two different particle size distributions.

INTRODUCTION

The stainless steel grade 316L is one of the most common metal injection molded alloys due to its excellent corrosion resistance and good mechanical properties. Typical applications consist of consumer products such as eyeglasses, watchcases and medical devices. The raw material processing parameters of both water and gas atomized pre-alloyed 316L powders are well known and widely published. The prealloy technique utilizes atomized powders that are of the exact chemistry as the final component. Alternatively, a master alloy technique utilizes alloy enriched atomized powders that are mixed with carbonyl iron powder to achieve 316L composition after sintering.

The processing parameters for master alloy blends, composed of 33% master alloy and 67% carbonyl iron powder for 316L powders are less well known. Particle size distributions are typically designated by the D90 size, where –16 μm and –22 μm are the standard sizes. However, coarser powders including -31 μm have also been used.

Whychell examined the effect of master alloy versus prealloyed feedstock, particle size and sintering furnace gas-flow rate on the formation of defects [1]. Although powder sizes of –22 μm and –31 μm were examined in both the prealloyed and master alloyed methods, no significant results on the effect of particle size or alloying technique were found. The most significant finding was that a high gas flow rate was required to eliminate defects.

Tingskog et al. investigated the particle size effect and also the use of prealloyed versus masteralloyed technique [2]. Their findings were that in the prealloyed state, -16 μm, -22 μm, and –31 μm powders can produce 99.2% density or better. However, the –31μm powder was more susceptible to defect formation during debinding and sintering. Defects were reduced by increasing heating rates and by increasing gas flow rate. Master alloy mixes were also examined for master alloy powders of –22 μm and –31 μm; however, densities of only 98.5 were achievable. Although many studies have been performed to evaluate these different alloying techniques and powder sizes, no mechanical properties other than density were measured. Also, no information with regards to the strength of the green components was reported.

The sintering and distortion characteristics of a master alloy for 17-4PH were previously explored with the aim of investigating the diffusion of the alloying elements in the sintered test bars [3]. The tap density of the blended master alloy and carbonyl Fe powder was higher than that of each component. This is due to the fact that the particle size of the carbonyl Fe powder, typically –5 μm was significantly finer than the gas-atomised master alloy powder. The carbonyl Fe particles fill the voids between the master alloy powder efficiently, which resulted in an increased tap density and ultimately should improve the density of the sintered material. Energy Dispersion X-ray (EDX) analysis for the 17-4PH master alloy was also used to map the distribution of the principle alloying elements Cr, Ni and Cu as well as the base element Fe. The EDX maps clearly showed that for pre-sintered microstructures the alloying elements are concentrated in the master alloy and the carbonyl Fe powder is easily distinguishable from the master alloy. Sintering occurred in the master alloy bars at a significantly lower temperature range (800°C to 1075°C) than the pre-alloyed bars. The range also corresponds to the initiation of alloy diffusion, which is virtually completed by 1000°C. The EDX maps showed visually that the Fe is distributed homogeneously in the sintered parts. Sintering produced a homogenous microstructure with a chemical composition within the standard limits for 17-4PH, indicating that alloy diffusion was completed after sintering. The master alloy bars sinter to near full density with a similar microstructure to the pre-alloyed material.

A series of sag tests were evaluated, throughout the sintering phase of the combined debinding and sintering thermal treatment, for gas atomised pre-alloyed and master alloy powders molded into flat test bars. The results of the study indicated that the master alloy produced increased densification and hardness compared with pre-alloyed 17-4PH during sintering. The master alloy test bars also exhibited significantly less distortion during sintering in part due to the recovery of the test bars, which occurred within the active sintering temperature range. After sintering was completed the final density and hardness of the master alloy was similar to the pre-alloyed material. Additional studies of the distortion recovery of both 1.5× 17-4PH and 316L master alloys found that the phenomenon was repeatable and not a result of the processing regime [4]. The resistance to sagging was improved by decreasing the particle size distribution of the powder, which is an inherent property of a blended master alloy carbonyl Fe powder. Sag recovery was associated with the shrinkage of the carbonyl Fe prior to diffusion into the master alloy and the volumetric expansion after significant diffusion.

The dimensional variability of metal injection molded components is thought, by Heaney and Zauner, to be affected by the variability of certain powder characteristics [5]. Key powder characteristics found to correlate with the final sintered component dimensional variability include the particle size distribution, as defined specifically by the D10 value (10% of the powder by volume, less than particle size diameter in μm) and the pycnometric density. The feedstock pycnometric density is commonly used in powder injection moulding as a characterization tool and qualitative predictor of shrinkage behavior [6].

EXPERIMENTAL PROCEDURE AND RESULTS

The objective of the present study was to compare the green strength and sintered properties of 316L MIM components produced from powders with two different particle size distributions –16 μm and –22 μm, using a prealloyed and a master alloy techniques.

The particle size distribution for a typical as-atomised 316L master alloy powder measured by laser diffraction is represented as a distribution curve in figure 1a. The particle size distribution curves for the classified powder, which were first sieved at –38 μm before air classifying to 90% -22 μm and 90% -16 μm are shown in figure 1b and 1c, respectively. Sieving is an important stage in the classification process because the probability of residual large particles remaining in the product is significantly reduced than by simply air classification alone.
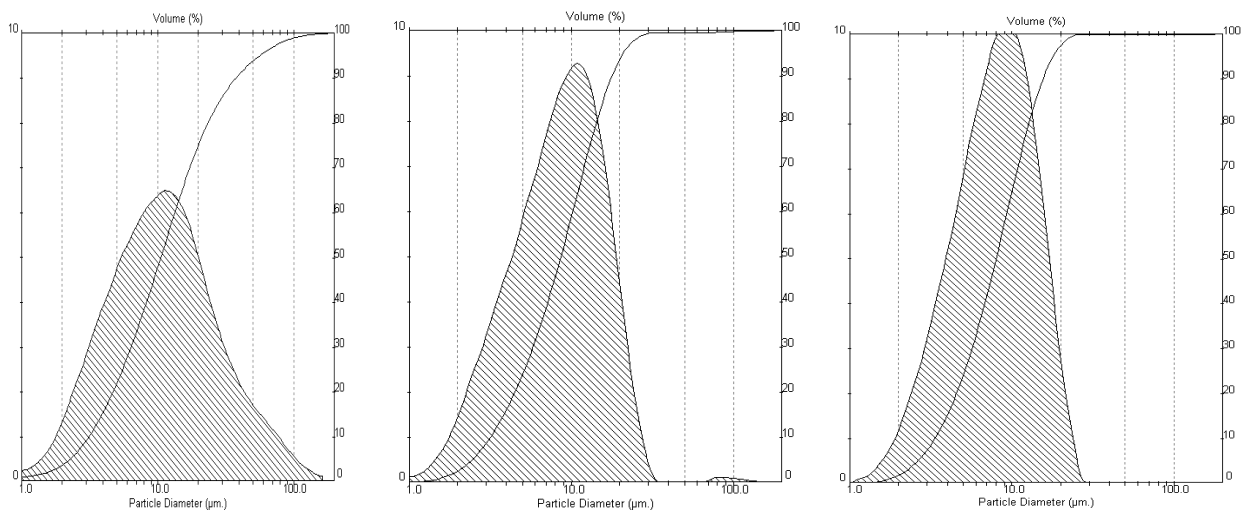
(a) As-atomised powder   (b) 90% -22 μm   (c) 90% -16 μm
Figure 1 : Particle size distribution of as-atomised powder and the sieved and classified powder.

A summary of the particle size distribution analysis of 592 individual batches of as-atomised 316L master alloy powder is shown in Table 1. The data indicates that the average D10 for the as atomised powder is 3.2 μm with a standard deviation of 0.32, which is significantly lower than the standard deviation for the D50 and D90 values. Variability is reduced after classification to a particle size distribution of 90% -22 μm, with the D10 value hardly changing at 3.1 but the standard deviation for D10 and especially the D50 and D90 values is significantly reduced. The data clearly shows that powder production with a reproducible particle size distribution is achievable for the 316L master alloy, within the 3 sigma limits, which in turn should produce sintered components with consistent dimensions, density and properties with low variability. The characteristics, including tap density, pycnometric density, and particle size distribution for all types of powders used are presented in Table 2.

Table 1: Particle Size Distribution of as-atomised and classified 316L master alloy powder.

	D10	D50	D90
As-Atomised powder (average)	3.2	11.0	42.1
Standard deviation	0.32	1.60	15.30
Classified powder to 90% -22 µm (average)	3.1	8.6	19.2
Standard deviation	0.11	0.53	1.47

Table 2: Powder Characteristics

Powder Type	D10 (µm)	D50 (µm)	D90 (µm)	Pycnometry Density (g/cm^3)	Tap Density (g/cm^3)
BASF Carbonyl Iron Grade OM	1.8	3.8	7.7	7.68	3.96
Osprey 316L Master Alloy −16 µm	3.4	8.0	15.5	7.76	4.6
Osprey 316L Master Alloy − 22 µm	3.2	8.6	17.9	7.76	5.2
Osprey 316L -16 µm	3.8	8.9	15.9	7.94	4.6
Osprey 316L -22 µm	4.1	10.5	21.9	7.93	4.8

Pre-alloyed gas atomised powders for MIM are supplied with a defined specification, which includes the chemical composition, particle size distribution and other powder characteristics such as tap density. However, customer specifications for chemical composition often deviate from the recognized international standards, especially for carbon levels. A tailored chemistry is often required to achieve the required final composition of the sintered component. Other cases include pre-alloyed 316L, which has a relatively broad Ni range, from 10% to 14%, where low nickel levels within the range are preferred for achieving high sintered densities by increased liquid phase sintering or in some cases high nickel levels for reduced magnetic susceptibility. The chemical compositions of the powders used in this study are listed in Table 3.

In order to comply with ASM specifications the maximum carbon content is 0.08 wt % C for 316 and 0.03 wt % C for 316L [7]. This tolerance is observed with respect to the 316L master alloy powder alone but the carbonyl powder has a typical carbon content of 0.79 wt %. Producing a carbon level of approximately 0.6% in the blend without even considering contributions from the binder system. Therefore, in order to reduce the carbon in the sintered component a decarburization hold at 1000˚C in hydrogen is necessary [8]. Thermal processing without the decarburization hold typically results in the formation of a low temperature eutectic liquid phase and subsequent distortion and slumping at carbon levels about 0.3 wt %.

The above powder characteristics show that the carbonyl iron powder has the smallest particle size and the differences in the particle size distributions between the −16 µm and the −22 µm atomised powders are relatively small in comparison. Typically, as the powder size decreases, the solid state sintering activity increases. The data also shows that the pycnometric density, which approximates the actual

density of the material, is highest for the prealloyed material and smaller for the carbonyl iron and master alloy powders. The carbonyl powder has density that is less than that expected for pure iron (7.86 g/cc) since it has a high oxygen and carbon content which reduce the density. The oxygen and carbon content of this carbonyl iron are reduced during thermal processing, thus, this content and ratio needs to be controlled not only to control chemistry but also dimensional stability. The master alloy would have been expected to have a greater density than that of the prealloyed powder as a result of the composition and the rule of mixtures, but the density is actually less. The other significant observation is that the tap density of the –22 μm powders is higher than the tap density of the –16 μm powders. This is most likely due to the finer powder having greater interparticle friction, which prevents it from packing to higher densities.

Table 3: As-received Powder Chemistry

Element	BASF Carbonyl Iron Powder Lot: 73491324U0	Osprey 316L Master Alloy -16 μm Lot 025578-583	Osprey 316L Master Alloy -22 μm Lot 025578-583	Osprey 316L Powder -16 μm Lot 03D0237	Osprey 316L Powder -22 μm Lot 03D0240
Cr	-	52.7	52.7	17.6	17.6
Ni	<0.1	38.1	38.1	10.4	10.4
Mo	<0.0	7.1	7.1	2.6	2.6
Si	<0.1	0.91	0.91	.36	.36
N	0.66	0.58	0.58	-	-
Mn	-	0.39	0.39	1.1	1.1
Fe	98.20	0.17	0.17	Balance	Balance
O	0.280	0.13	0.13	-	-
C	0.790	0.03	0.03	.022	.022

In preparation for molding the prealloyed and master alloy/carbonyl Fe blends were compounded into four different feedstocks with a powder loading at 65 volume % into the binder which consisted of 50% Paraffin Wax, 40% Polypropylene and 10% Linear Low Density PP. The feedstock was then characterized using capillary rheometry and pycnometer density with the results listed in Table 4. The apparent viscosity of all feedstocks was measured at a constant ram rate of 5.08 cm/min, a temperature of 170 °C, and a die diameter of 0.1996 cm and length of 3 cm. After compounding, the feedstocks were injection molded into tensile test specimens.

Table 4: Feedstock Characteristics

Feedstock	Particle Size	Pycnometry Density (g/cm^3)	Average Viscosity (Pa-s)
Master Alloy (-16 μm) + Fe & Binder	-16μm	5.11	251.0
Master Alloy (-22 μm) + Fe & Binder	-22μm	5.09	212.9
Prealloyed (-16 μm) & Binder	-16μm	5.33	200.2
Prealloyed (-22 μm) & Binder	-22μm	5.31	175.5

Samples were solvent debound in heptane at 60°C for 4 hours and then dried before thermal debinding at temperatures between 200˚C and 500˚C randomized in the furnace to prevent any experimental artifacts due to sample locations in the furnaces. The randomization was also used for the high temperature sintering. The furnace atmosphere consisted of dry flowing hydrogen with a gas flow rate that ensures that the binder is swept away to prevent defects [1]. A set point of 1000°C was used to impart handling strength. One interesting observation is that the samples that contained carbonyl iron powder presintered too much higher densities than did the prealloyed powders. The carbonyl iron shows a strong solid state sintering response at temperatures less than 900˚C [9]. Therefore, a presinter temperature of 700 to 800˚C would be sufficient for these samples to obtain handling strength. The high temperature of 1000˚C was used on all samples to maintain a consistent experimental procedure. Sintering was performed on alumina trays in a CM box furnace in dry hydrogen at 1340˚C and 1360˚C. The furnace parameters are outlined in Table 5.

Table 5: Furnace conditions for sintering 316L SS MIM tensile bars.

Furnace condition	Set point
Ramp 1	10°C/min
Set Point 1	1000°C
Dwell 1	1 hr
Ramp 2	5°C/min
Set Point 2	1340°C or 1360°C
Dwell 2	1 hr
Ramp 3	10 °C/min
Set Point 3	20 °C
Furnace Atmosphere	H_2 50 SCFH

The different compositions were evaluated in the green state for defects and transverse rupture strength, measured according to MPIF Standard 15 [10]. The tensile bars were then evaluated in the as sintered condition for density, carbon level, hardness, tensile strength, and elongation with five measurements for each condition. Hardness testing was conducted at the grip portion of the tensile bars with an average of six tests per condition. One sample of each condition was also mounted and polished for metallographic examination.

The apparent viscosity was highest for the master alloys, which were mixed with carbonyl iron powder, and also for the −16 μm prealloyed powder. This behavior results from the higher surface area of the finer powders, which produce higher viscosity due to their having less binder available for lubrication. In general, both prealloyed and master alloy + Fe feedstocks molded well. However, there was a higher tendency for powder/binder separation near the gate for the pre-alloyed powders, while the master alloy feedstock did not show this effect. The master alloy feedstock exhibited higher transverse rupture green strength, as compared to the prealloyed powders, as shown in Figure 2. All powders achieved final densities greater than 97% of wrought 316L, at typical sinter temperatures for 316L of approximately 1350°C. The level of carbon in the sintered component for both the pre-alloyed and master alloy + Fe feedstock, in both size ranges are within the ASTM 316L stainless steel maximum carbon specification of 0.03% [7].

The results of the mechanical testing are presented in Table 6. Figures 3 and 4 show the tensile and elongation results. The general trend is that the prealloyed materials produce marginally better strength and elongation results than the master alloy + Fe materials. No significant difference in mechanical properties is observed between the −16 μm and −22 μm powders. However, all results exceed the MPIF Standard 35 for MIM 316L stainless steel [11].
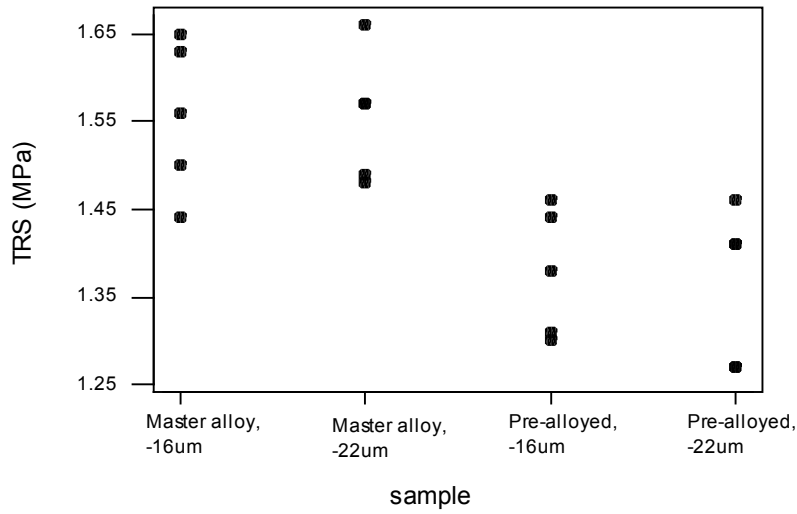
Figure 2: Transverse rupture strength of green injection molded components.
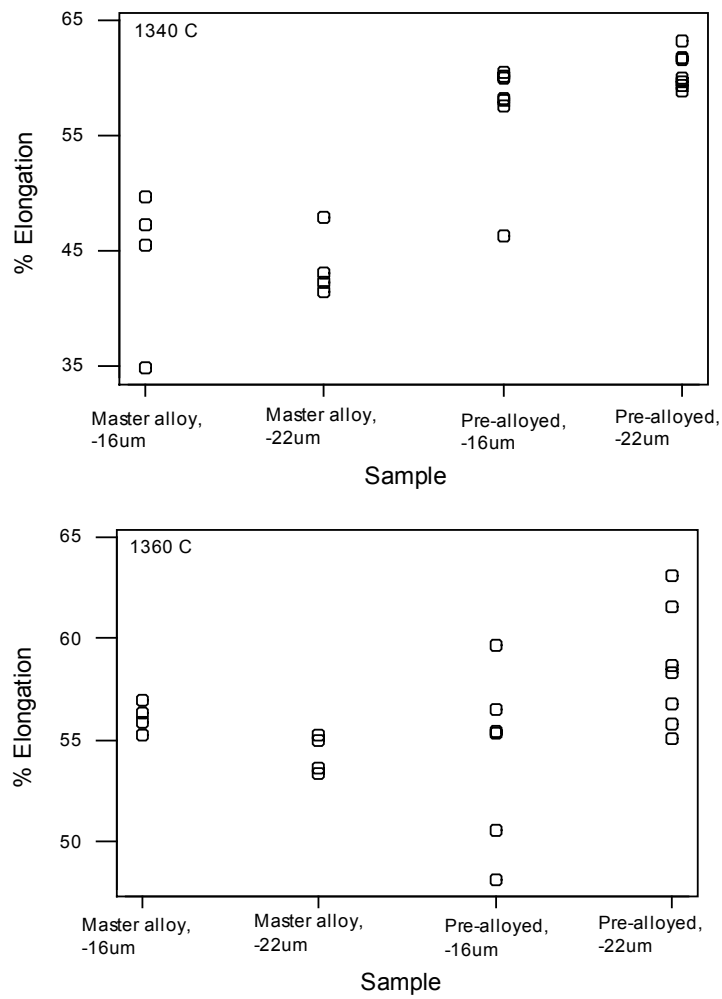

Figure 4: Elongation to fracture for the 4 different materials at the two different sintering temperatures.
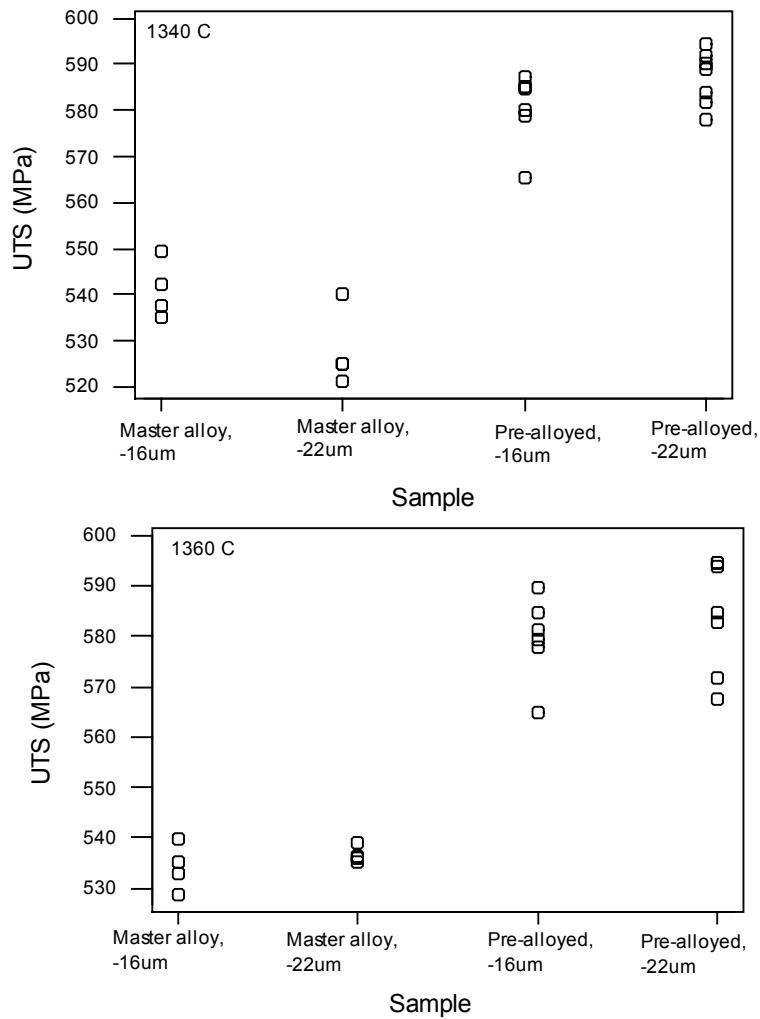
Figure 5: Ultimate Tensile Strength for the 4 different materials at the two different sintering temperatures.

Table 6: Density, hardness, tensile and elongation results for 316L stainless steel powders sintered at 1340 and 1360°C.

Condition	Sinter Temperature (°C)	Average Density (g/cm³)	Average Hardness (Rb)	Average Tensile Strength (MPa)	Average Elongation (%)
Master Alloy (-16 μm) + Fe	1340	7.86	68.1	541.0	44.2
Master Alloy (-22 μm) + Fe	1340	7.88	68.1	527.7	43.6
Prealloyed -16 μm	1340	7.84	67.9	581.1	57.2
Prealloyed -22 μm	1340	7.90	67.6	587.0	60.6
Master Alloy (-16 μm) + Fe	1360	7.88	65.9	534.2	56.1
Master Alloy (-22 μm) + Fe	1360	7.89	68.1	536.5	54.3
Prealloyed -16 μm	1360	7.92	67.4	581.3	56.3
Prealloyed -22 μm	1360	7.81	68.7	582.5	60.2
MPIF Standard 35 for MIM 316L stainless steel		7.6 [a]	67 [a]	448 [b]	40.0 [b]

a. Typical values.   b. Minimum values

Optical micrographs of samples produced from each route are shown as examples of the microstructure, in both polished and etched conditions, in figures 5 and 6. The metallographic samples were also used to calculate the porosity and ASTM grain size for the different sintering temperatures. The results, highlighted in Table 7, indicate that higher sintering temperatures result in increased grain size with a decrease in porosity. The master alloy material has a finer grain size than the pre-alloyed material with less porosity at the lower sintering temperature and powder size.
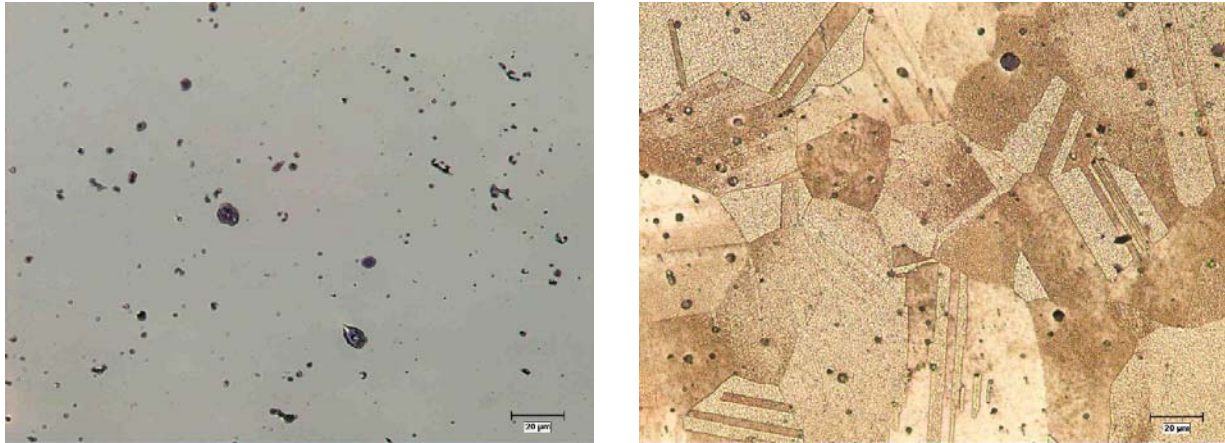

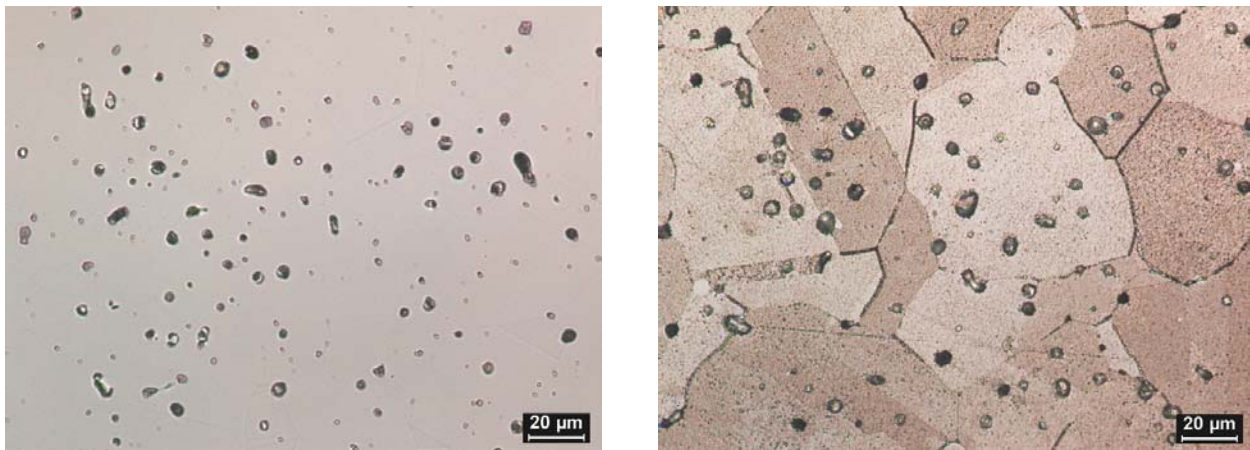Figure 5: Osprey 316L master alloy, -22µm. Sintered at 1360°C, magnification 500X.

Figure 6: Osprey 316L pre-alloy –16µm powder sintered at 1340°C, magnification 500X.

Table 7: Grain size and percent porosity data for varying sintering temperatures.

Condition	Sintering Temperature	Porosity (%)	ASTM Grain Size	Average Grain Size (µm)
Master Alloy (-16 µm) + Fe	1340°C	1.65	6.3	39.5
Master Alloy (-22 µm) + Fe	1340°C	2.28	6.3	39.5
Prealloyed -16 µm	1340°C	4.55	5.2	61.5
Prealloyed -22 µm	1340°C	2.20	5.6	52.2
Master Alloy (-16 µm) + Fe	1360°C	1.80	5.7	51.0
Master Alloy (-22 µm) + Fe	1360°C	2.30	5.5	53.4
Prealloyed -16 µm	1360°C	2.10	4.9	66.0
Prealloyed -22 µm	1360°C	0.90	4.5	76.0

CONCLUSIONS

The prealloyed and master alloy routes were both shown to produce sintered 316L components, by metal injection moulding, that exceeds the MPIF 35 Standard. The 316L master alloy/carbonyl Fe material pre-sinters at a lower temperature and requires a decarburization hold to eliminate the carbon that is left from the carbonyl iron. In general, all materials densified to better than 98% density and had ultimate tensile strengths greater than 555 MPa and elongations in the 40% range. The prealloyed powders produced marginally better mechanical properties. The master alloy feedstock shows better green strength and fewer tendencies for powder binder separation near the gate and less distortion during debinding.

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