Mechanical properties of metal injection moulded 316l stainless steel using both prealloy and master alloy techniques

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Stainless steel 316L MIM components can be made from either prealloyed powders or from master alloys blended with carbonyl iron powder. In this study these two techniques were compared using prealloyed and master alloyed gas atomised powders of -16 µm and -22 µm sizes. Four different compounds were prepared, characterised and injection moulded into tensile bars. The bars were compared for green strength, green defects, sintered strength and microstructure. The green components are stronger when carbonyl iron powder is used with the gas atomised master alloy. This material also seems to be less susceptible to moulding defects. The sintering strength of the material produced using the prealloyed powder was higher than the master alloyed prepared material. Little difference in mechanical properties existed between the materials fabricated from gas atomised prealloyed -16 µm and the -22 µm powders. Also, the viscosity of the mixtures was higher for the -16 µm material and the master alloy mixtures than for the -22 µm gas atomised prealloyed powders.   PM/1120

INTRODUCTION

Stainless steel 316L is one of the most commonly metal injection moulded alloys. Its popularity results from its sinterability to high densities and its corrosion resistance. Typical applications consist of consumer products such as eyeglasses, watchcases and medical devices.

Since this alloy is accepted for metal injection moulding, much study of the properties as a function of process parameters and raw materials has been performed. Gas atomised, water atomised, prealloyed, master alloyed and powder size are some of the powder characteristics that have been evaluated. The prealloy technique utilises atomised powders that are of exactly the same chemistry as the final component. The master alloy technique utilises alloyed enriched atomised powders that are mixed with elemental powder to achieve final chemistry. An example is to use 33% master alloy and 67% iron powder for 316L powders. Different powder sizes are typically designated by the D_{90} size, where the subscript 90 is the percentage of particles smaller that the measured value. Typically, for injection moulding, -16 µm and -22 µm are the standard sizes; however, -31 µm has also been used.

Whychell examined particle size, master alloy versus prealloyed, gas flowrate effects and setter material effects on the formation of defects.[1] Although powder sizes of -22 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 findings were that a high gas flowrate and a porous setter material are required to eliminate defects. Ji et al. have used a Taguchi method to optimise the sintering process of a MIM grade water atomised powder.[2] In their study, they determined that all sintering process parameters including sintering temperature, sintering time, heating rate and atmosphere significantly influence the density of the component. A peak density of only 96% was obtainable using this water atomised powder. Bakan et al. were able to use a gas atomised powder that had a D_{90} of 125 µm for injection moulding with a water soluble binder system. However, this was only possible by mixing this powder with an irregularly shaped water atomised powder to give the moulded component strength during debinding and also by the addition of boron sintering aids to obtain high density.[3] Anwar et al. evaluated another water soluble binder system for spherical -22 µm gas atomised 316L powder.[4] In their study, a best density of 97% theoretical was achieved at a sintering temperature of 1350°C for 90 min. Tingskog et al. investigated the particle size effect and also the use of prealloyed versus master alloyed technique.[5] 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 -31 µm powder was more susceptible to defect formation during debinding and sintering. Defects were reduced by increasing heating rates and by increasing gas flowrate. 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 examined. Also, no information with regards to the strength of the green components was reported.

In this study, green strength and sintered properties were compared for two different powder sizes, specifically -16 µm and -22 µm, while using a prealloyed and a master alloy technique. The purpose was to compare the properties of these materials in order to determine the benefit of the different techniques in forming quality MIM components.

EXPERIMENTAL PROCEDURE
Powder characterisation
The objective of this study was to compare master alloyed powder (mixture of 33·3 wt-% 55Cr38Ni7Mo and 66·7 wt-% Carbonyl) with prealloyed powder for the forming of 316L stainless steel metal injection moulded components for two different powder sizes. Powders were analysed for tap density, pycnometer density and particle size distribution. The powder characteristics are shown in Tables 1 and 2.

Notice that the gas atomised powders have carbon contents that are less than or equal to 0·03 wt-% carbon and that the carbonyl powder has a carbon content of 0·79 wt-%. This carbon needs to be eliminated during thermal processing. This is accomplished by using hydrogen gas and having a decarborisation hold above 1000°C.[6] This temperature is high enough to permit high diffusivity of carbon and high reaction kinetics of the carbon with the hydrogen to form hydrocarbon gases, eliminating the carbon in the samples. Early experiments with the master alloy mixes, that did not incorporate the decarborisation hold, resulted in the formation of a low temperature eutectic liquid and subsequent distortion. Carbon measurements on these samples made without decarborisation hold showed carbon levels in the 0·3 wt-% range. Note that ASM specification for 316 is 0·08 wt-%C and 0·03 wt-%C for 316L.[7]

The above powder characteristics show that the carbonyl powder has the smallest particle size and that there are only slight differences in the particle size distributions between the −16 μm and the −22 μm powder. Typically, as the powder size decreases, the solid state sintering activity increases. The data also shows that the pycnometry 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 cm⁻³) since it has high oxygen and carbon contents, which reduce the density. The oxygen and carbon content of this carbonyl iron are reduced during thermal processing, thus, this content and ratio need to be controlled to control not only chemistry but also dimensional stability. The master alloy powder has a lower density since it has a different composition and most likely a different crystal structure than the prealloyed powders have. This is apparent since one would expect the master

alloy to have a density that is greater than 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.

Feedstock and moulding
Prealloyed and master alloyed blends were compounded into four different feedstocks. The powder was loaded at 65 vol.-% into the polymer according to the description in Table 3. The preparation consisted of dry blending of the powders with the binders, followed by twin cam co-rotational mixing at 170°C. This was performed twice with granulation between each mixing to ensure homogenisation of the mixture. The feedstock was then characterised using capillary rheometry and pycnometer density. The apparent viscosity of all feedstocks was measured at a constant ram rate of 5·08 cm min⁻¹, a temperature of 170°C and a die diameter of .1996 cm and length of 3 cm. After compounding, the feedstocks were injection moulded into tensile test specimens at a melt temperature of 170°C, a mould temperature of 20°C, an injection speed of 15 cm³ s⁻¹ and a pack pressure of 500 bar.

Solvent and thermal debinding
Samples were placed on stainless steel trays and debound in heptane at 60°C for 4 h. After solvent debinding, the parts were dried at room temperature overnight. Thermal

Table 3   Feedstock composition

	Fractional wt-%	
	Master Alloy	Prealloyed
Powder		
BASF carbonyl iron powder	0·667	0
Osprey master alloy	0·333	0
Osprey prealloyed	0	1
Binder system		
Paraffin wax	0·5	0·5
Polypropylene	0·4	0·4
Linear low density PP	0·1	0·1

Table 1   As received powder chemistry

Element	BASF carbonyl iron powder lot: 73491324U0	Osprey 55Cr38Ni7Mo −16 μm lot 025578-583	Osprey 55Cr38Ni7Mo −22 μm lot 025578-583	Osprey 316L SS 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	Bal.	Bal.
O	0·280	0·13	0·13	…	…
C	0·790	0·03	0·03	·022	·022

Table 2   Powder characteristics

Powder type	D_{10}, μm	D_{50}, μm	D_{90}, μm	Pycnometry density, g cm⁻³	Tap density, g cm⁻³
BASF carbonyl iron	1·8	3·8	7·7	7·68	3·96
Osprey 55Cr38Ni7Mo −16 μm	3·4	8·0	15·5	7·76	4·6
Osprey 55Cr38Ni7Mo −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

debinding was conducted in a Lindberg furnace with an Inconel retort at temperatures between 200 and 500°C and presintered to 1000°C. Tensile bars were randomised on 99% alumina sheets. Randomisation consisted of randomising the parts throughout the plates and furnace to prevent any experimental artefacts due to sample locations in the furnaces. The randomisation was also used for the high temperature sintering.

Furnace atmosphere consisted of dry flowing hydrogen at 1·5 L min^{-1}, which was equivalent to 10 furnace changeovers per hour. Gas flowrate is very important to ensure that the binder is swept away to prevent defects.[1] When the gas flowrate is not high enough, the carbon will become solid black soot on the part surface and potentially cause unexpected melting at high temperature sintering. Also, the components are more susceptible to defects such as cracking and blistering if the gas flowrate is too low. A setpoint of 1000°C was used to impart handling strength. One interesting observation is that the samples that contained carbonyl iron powder presintered to much higher densities than the prealloyed powders did. The carbonyl iron shows a strong solid state sintering response at temperatures below 900°C.[8] 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

Sintering was performed in a CM box furnace in dry hydrogen at 1340°C and 1360°C. The parts were placed on alumina trays and stacked in the furnace. The furnace parameters are outlined in Table 4.

Material evaluation

The different compositions were evaluated in the green state for defects and transverse rupture strength. The transverse rupture strength was measured using an MTS mechanical tester utilising a 4448 N load cell, a 0·254 cm min^{-1} rate and a 2·54 cm spacing according to MPIF Standard 15.[9] These bars were also evaluated in the as sintered condition for density, carbon level, hardness, tensile strength and elongation. Density measurements were taken using an Accupyc model 1330 machine and represent an average of five measurements for each sample. Carbon content was measured using a Horiba EMIA8200 carbon–sulphur analyser. A 1 g sample of each condition was prepared by slicing 1mm thick sections from the gage section of the tensile bars using a Struers Accutom precision saw. The pieces were ultrasonically cleaned in acetone and dried prior to testing. Mechanical testing was conducted with an MTS Sintec mechanical tensile test machine utilising an 89 kN load cell and carbide friction grips. Crosshead speed was set to 0·254 cm min^{-1}. Per cent elongation was calculated by measuring the change in gage length, with a 2·8 cm initial length. A minimum of five tests were run per

Table 4 Furnace conditions for sintering 316L SS MIM tensile bars

Furnace condition	Set point
Ramp 1	10 K min^{-1}
Set point 1	1100°C
Dwell 1	1 h
Ramp 2	5 K min^{-1}
Set point 2	1340°C or 1360°C
Dwell 2	1 h
Ramp 3	10 K min^{-1}
Set point 3	20°C
Furnace atmosphere	H$_2$ 50 SCFH
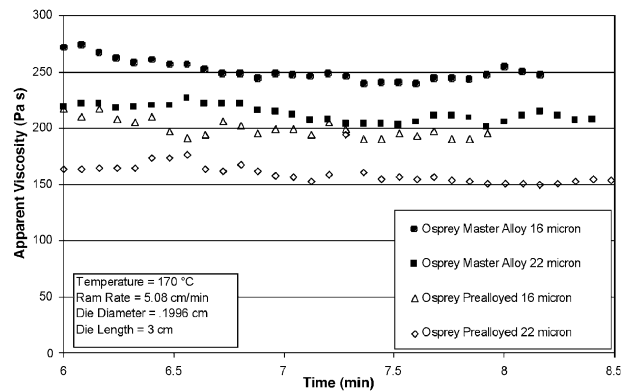
1 Apparent viscosity of different powder types in same binder system

condition and the results averaged. All results were included, except in cases where an internal (moulding) flaw was noted at the fracture surface. Hardness testing was also conducted, using a Leco semiautomatic tester and Rockwell B indenter. Indents were taken in the grip portion of the tensile bars. The results are an average of six tests per condition. One sample of each condition was also mounted and polished for metallographic examination of grain size. Samples were polished to a 0·05 μm finish and etched in Frys reagent (40 mL HCl, 5 g CuCl$_2$, 30 mL H$_2$O, 25 mL ethanol).

RESULTS

Feedstock characterisation

The four feedstocks were characterised for pycnometer density and apparent viscosity. Table 5 and Figure 1 show these results. The pycnometer density for the prealloyed material was higher than the master alloy, which signifies that the powders were of different chemistries. The reason for this behaviour was discussed in the experimental section of this paper.

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 behaviour results from the higher surface area of the finer powders, which produce higher viscosity due the increase in friction surface for the same amount of binder.

Moulding observations and green strength

In general, both feedstocks moulded well. There was a higher tendency for powder/binder separation near the gate for the gas atomised powders, while the carbonyl powder didn't show this effect. The master alloy blend that utilises the carbonyl powder showed higher transverse rupture green strength than the prealloyed powders. This is shown in Fig. 2.

Sintering results

All powders sinter densified at typical temperatures for 316L, which is approximately 1350°C. Sinter density results are located in Table 6. Master alloyed −16 μm had a

Table 5 Feedstock characteristics

| Feedstock	Pycnometry density, g cm^{-3}	Average viscosity, Pa s
Osprey master alloy −16 μm	5·11	251·0
Osprey master alloy −22 μm	5·09	212·9
Osprey prealloyed −16 μm	5·33	200·2
Osprey prealloyed −22 μm	5·31	175·5
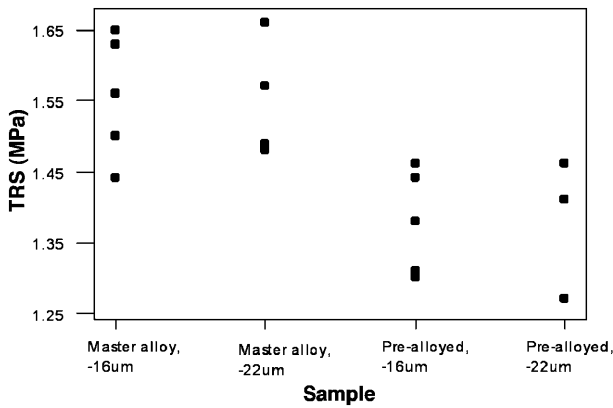
2   Transverse rupture strength of green injection moulded components
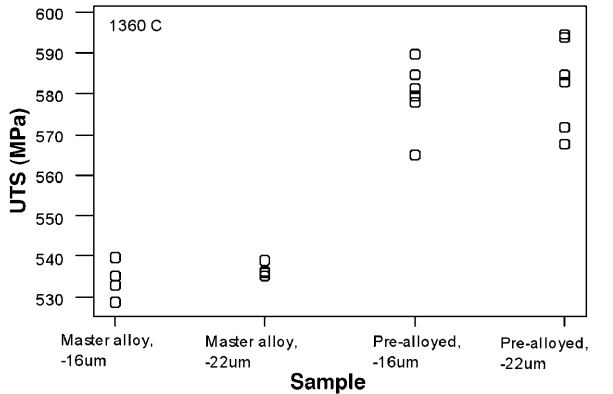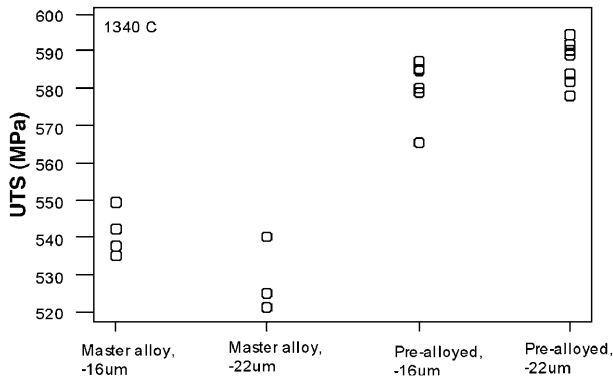
3   Ultimate tensile strength for four different materials at two different sintering temperatures

carbon level of 0·028% and the carbon level of the −22 μm master alloyed product had a carbon level of 0·030%. Prealloyed −16 μm had a carbon level of 0·028% and the carbon level of the −22 μm prealloyed powder was 0·014%. All values are lower than the ASTM 316L stainless steel carbon specification.[7]
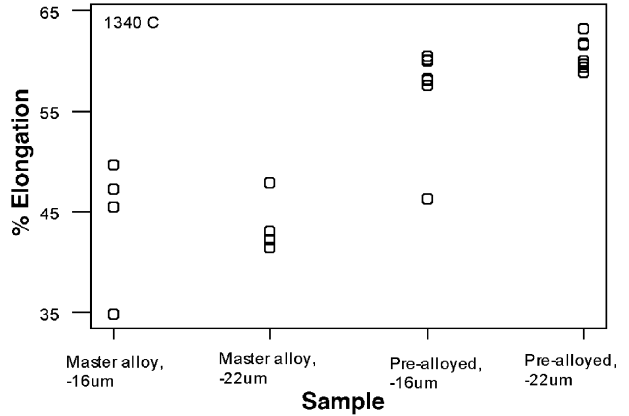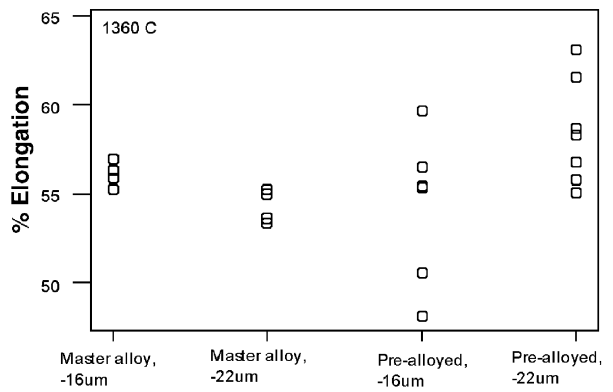
4   Elongation to fracture for four different materials at two different sintering temperatures

Mechanical testing

Table 6 and Figs. 3 and 4 show the tensile and elongation results. The general trend is that the prealloyed materials produce better strength and elongation results than the master alloyed materials did. No significant difference in mechanical properties is observed between the −16 μm and −22 μm powders. All results are comparable to MPIF Standard 35 for MIM 316L stainless steel.[10] Standard 35 states that the minimum UTS and per cent elongation are 450 MPa and 40% elongation. Typical values are 520 MPa for UTS, 50% elongation and an HRB of 67.

Metallography

Samples of each condition were mounted, polished and photographed, both as polished and etched. The pictures are arranged so that the upper left and right pictures are as polished and the lower left and right are etched samples at the same sintering temperature. The samples are illustrated in Figs 5–8.

The metallographic samples were also utilised to calculate percent porosity and ASTM grain size for the different sintering temperatures. Results are as expected, with higher sintering temperature showing an increase in

Table 6   Density, hardness, tensile and elongation results for 316L SS powders sintered at 1340 and 1360°C

| Condition	Sintering temperature	Average density, g cm⁻³	Average hardness, HRB	Average tensile strength, MPa	Average elongation, %
Osprey master alloy −16 μm	1340°C	7·86	68·1	541·0	44·2
Osprey master alloy −22 μm	1340°C	7·88	68·1	527·7	43·6
Osprey prealloyed −16 μm	1340°C	7·84	67·9	581·1	57·2
Osprey prealloyed −22 μm	1340°C	7·90	67·6	587·0	60·6
Osprey master alloy −16 μm	1360°C	7·88	65·9	534·2	56·1
Osprey master alloy −22 μm	1360°C	7·89	68·1	536·5	54·3
Osprey prealloyed −16 μm	1360°C	7·92	67·4	581·3	56·3
Osprey prealloyed −22 μm	1360°C	7·81	68·7	582·5	60·2
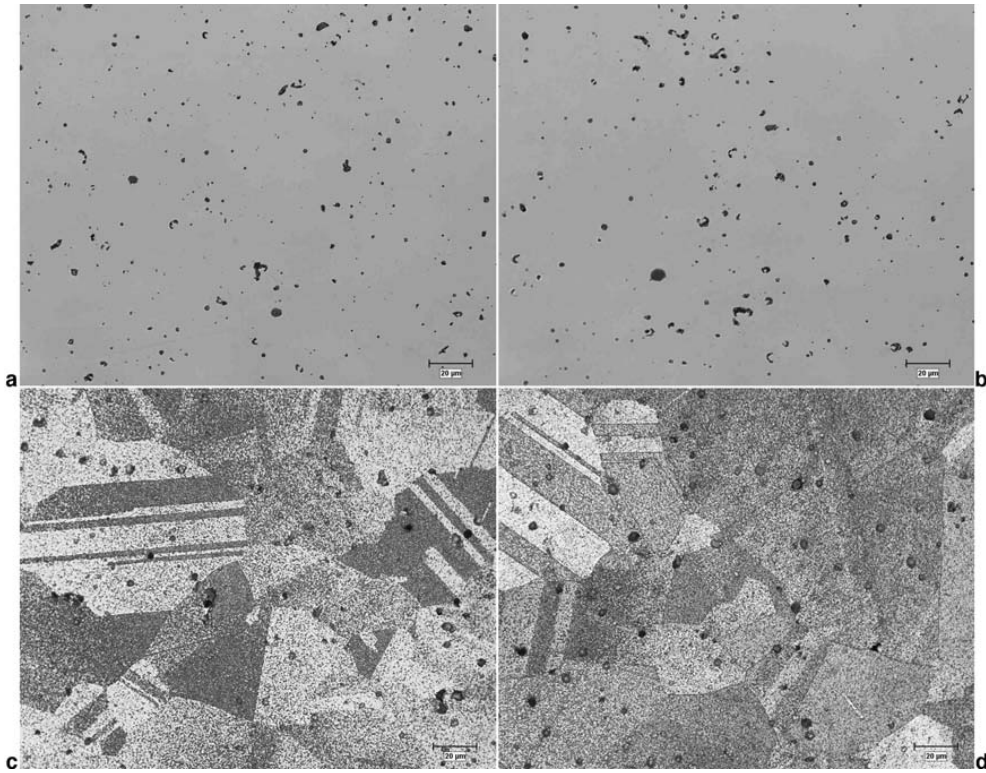
5 Osprey 316 master alloy, −16 μm, sintered at 1340°C (*a* and *c*) and 1360°C (*b* and *d*)

grain size (smaller ASTM grain size number) and a decrease in per cent porosity. Table 7 shows these results.

CONCLUSIONS

Both prealloyed and master alloy mixes of 316L powder can be used to produce material that match or exceeds the MPIF Standard 35. The prealloyed powders produced marginally better mechanical properties. The master alloy material requires a decarborisation hold to eliminate the carbon that is left from the carbonyl iron powder manufacturing technique. In general, all materials densified to better than 98% density and had elongations in the 40% range. The master alloy blended with the carbonyl iron powder shows better green strength and less tendency for powder–binder separation near the gate. One would expect
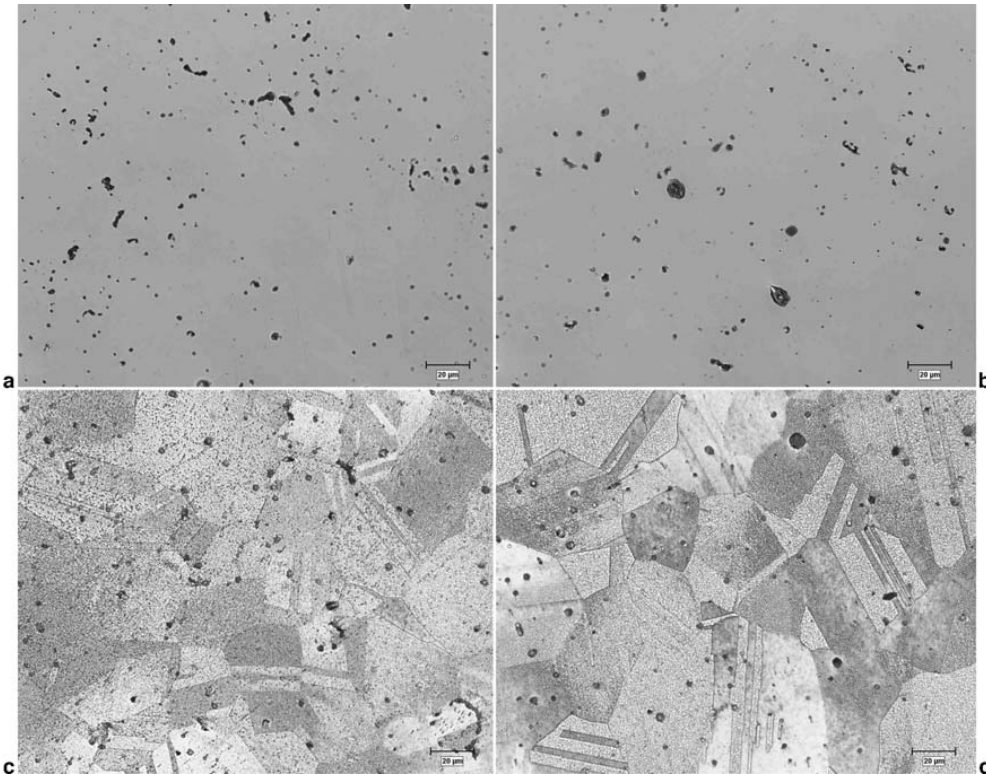
6 Osprey 316 master alloy, −22 μm, sintered at 1340°C (*a* and *c*) and 1360°C (*b* and *d*)
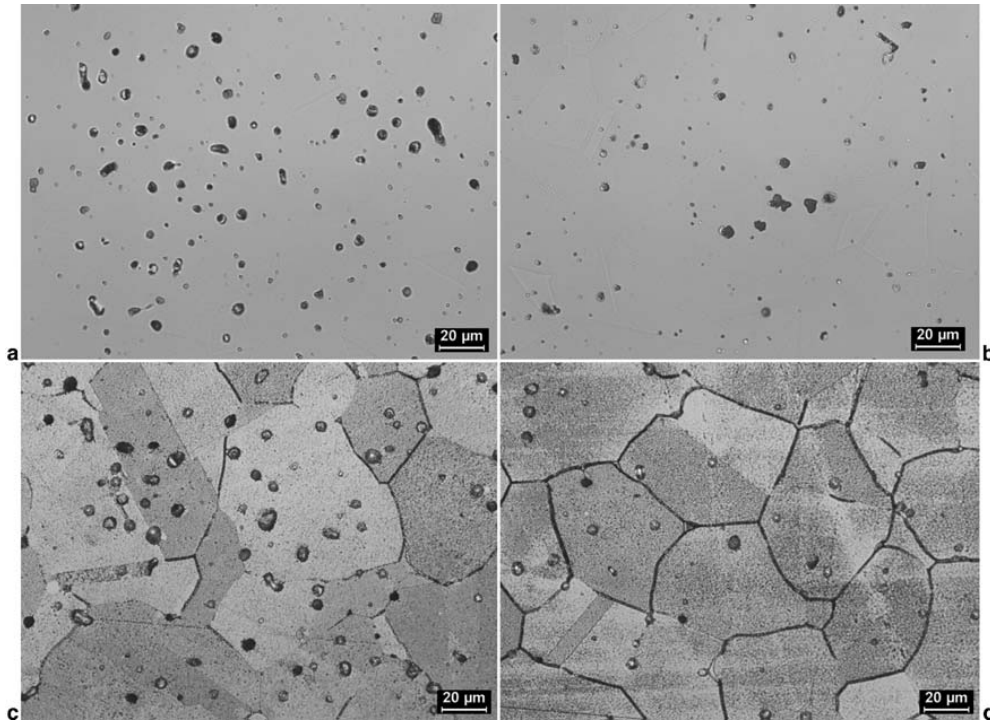
7   Osprey 316 prealloy −16 μm, sintered at 1340°C (*a* and *c*) and 1360°C (*b* and *d*)
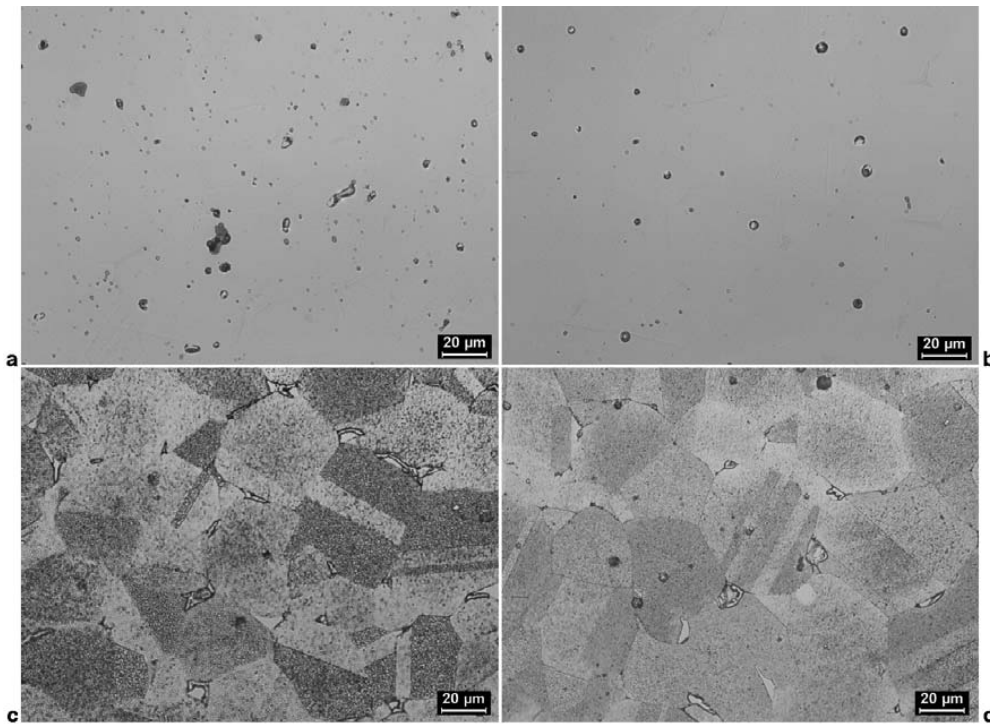
8   Osprey 316 prealloy −22 μm, sintered at 1340°C (*a* and *c*) and 1360°C (*b* and *d*)

Table 7   Grain size and per cent porosity data for varying sintering temperatures

Condition	Sintering temperature, °C	Porosity, %	ASTM grain size, μm	Average grain size, μm
Osprey master alloy −16 μm	1340	1·65	6·3	39·5
Osprey master alloy −22 μm	1340	2·28	6·3	39·5
Osprey prealloyed −16 μm	1340	4·55	5·2	61·5
Osprey prealloyed −22 μm	1340	2·20	5·6	52·2
Osprey master alloy −16 μm	1360	1·80	5·7	51·0
Osprey master alloy −22 μm	1360	2·30	5·5	53·4
Osprey prealloyed −16 μm	1360	2·10	4·9	66·0
Osprey prealloyed −22 μm	1360	0·90	4·5	76·0

that this mix would also have less distortion during debinding as a result of the greater green strength.

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