Effects of Particle Size and Alloy Chemistry on Processing and Properties of MIM Powders

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ABSTRACT

The continuing growth in the MIM market is testament to a number of factors including growing diversity in applications, the increasing ingenuity shown by designers, the flexibility and cost effectiveness of the technology and growing capacity in the MIM supply chain. In selecting a particular powder for a given application, MIM designers consider processing performance, finished properties and total unit cost of the component including starting powder and processing route. In this paper, we reflect on some of the differences in behaviour of gas and water atomised powders and on gas atomised powders with different particle size distributions. Data are presented to illustrate effects of particle size on processing aspects and properties of precipitation hardened stainless steel parts. It is proposed that the lower oxygen levels and spheroidal shape of gas atomised powders provide benefits which are apparent throughout processing and offer opportunities for lower processing costs, improved quality and higher value addition in finished products.

INTRODUCTION

Despite the steep decline in the world economy in the last 12 months, sectors of the MIM industry appear to be holding up quite well in NAFTA – particularly medical and gun parts. Fortunes have varied around the world and those regions which specalise in automotive (Europe) and 3C (Asia) have fared less well [1]. Nevertheless the advantages of net shape forming have sustained growth in the adoption of MIM. Underlying average annual growth rates are ~10-12% and it is believed that the tonnage of powders sold to the MIM market today is approximately 6000MT pa [2]. Stainless steels remain the dominant alloy family with around 50% of the market with low alloy steels accounting for ~ 25% of volume. Of the remaining minority materials, there has been growth in tool steels and Ni based alloys as a proportion of the total supply of MIM alloys as applications deversify into more wear resistant and high temperature parts.

It is Sandvik Osprey's experience that there is growing polarisation in sales of relatively coarse MIM powders (e.g. -32µm, 80%-22µm) and of finer grades e.g. 90%-16µm and finer. The drives for finer sizes includes demand

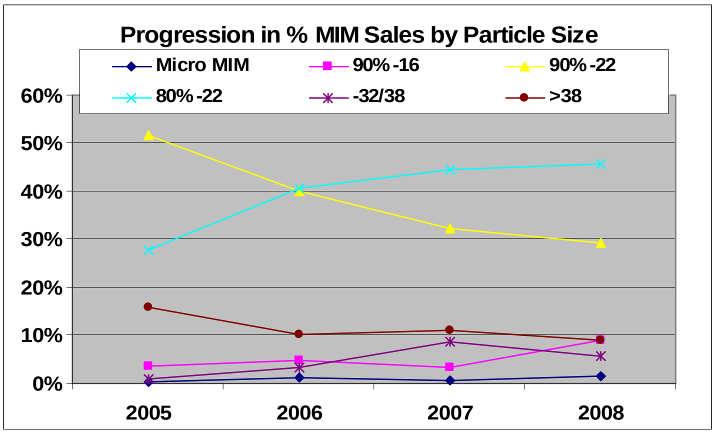


Figure 1. Development in popularity of different MIM powder size grades

for miniaturisation, improved part precision and surface finish. In the former context, medical and special automotive applications require tolerances even better than the 0.3-0.5% typically quoted for MIM and in the latter case, improved surface finish can add value and/or reduce finishing costs in 3C applications.

The most popular stainless steel grades in MIM remain 17-4PH and 316L austenitic stainless steel. The precipitation hardening grades offer high strength and good corrosion resistance at modest cost and show good sintering characteristics. They are sintered typically between 1250-1390 °C [3] and often require no post-sintering heat treatment but, owing to their high hardness, they can be difficult to finish to final dimensions if distortion occurs during furnacing. Post-sinter heat treatments, if employed, are in the range 900 – 1100°C (H900 or H1100) and result in a significant boost in hardness and tensile strength, particularly after low temperature ageing.

The primary strengthening mechanism in PH steels is precipitation of coherent Cu particles and therefore the wide specification range of 3.0-5.0%Cu (in 17-4PH, 2.5-4.5%Cu in 15-5PH) may be the source of some of the wide variation in mechanical properties reported in the literature. This can potentially be exacerbated by added variation in %Cu if evaporation occurs during high temperature sintering. A further variable which has recently been highlighted as influential on tensile properties is carbon content. Muterlle et al. [4] show that %C is inversely related to the quantity of δ-ferrite in the microstructure, which, while encouraging densification, causes a reduction in tensile strength. Increasing C level is therefore advantageous for hardenability.

In this paper we review the effects of these variables in light of a study on the effect of particle size on processing and properties of a 15-5PH steel. 15-5PH has a lower Cu level than its better-known relation, but is capable of achieving similar hardness to 17-4PH alloy. Wrought properties typically quoted for 15-5PH are 1070MPa tensile strength and 39HRC in the H1025 heat treated state.

EXPERIMENTAL

The 15-5PH powder used in this study was manufactured using proprietary gas atomisation technology. A single batch of powder was produced by induction melting the raw materials in an inert atmosphere and atomising using nitrogen gas. The chemistry of the powder batch is shown in Table 1 and conforms to UNS S15500. From the as-atomised powder, three different fractions were extracted by air classification and sieving: -38μm, -32μm and 90% -22μm. Table 2 shows the particle size distribution characteristics D10, D50 and D90 of these powders.

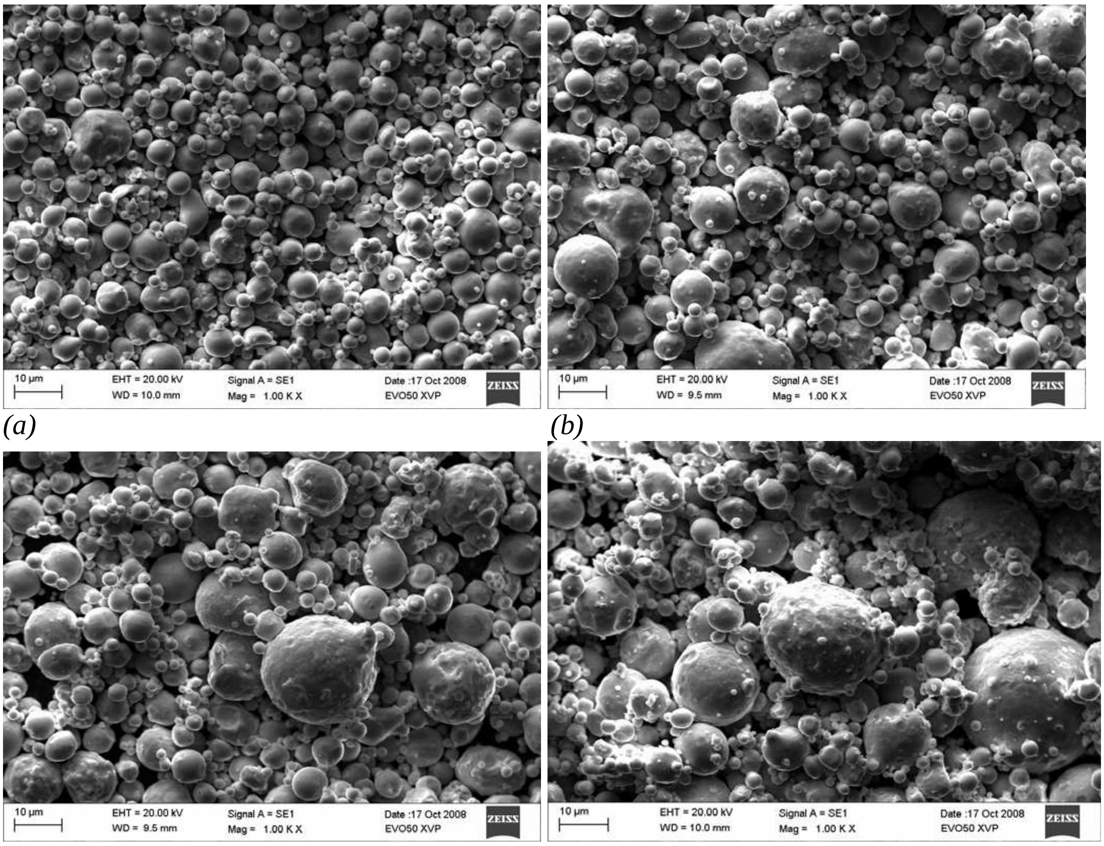
Element	Specification	Analysis	Element	Specification	Analysis
Fe	Balance	Balance	Mn	1.00 max.	0.61
Cr	14.0 - 15.5	15.30	Si	1.00 max.	0.65
Ni	3.5 - 5.5	4.49	C	0.07 max.	0.04
Cu	2.5 - 4.5	3.64	P	0.04 max.	0.02
Nb	0.15 - 0.45	0.38	S	0.03 max.	<0.01

Table 1. 15-5PH chemical specification and powder analysis.

Powder Size	D10 µm	D50 µm	D90 µm	T. D. gcm^{-3}	A. D. gcm^{-3}	%O*	%N*	BET m^{2}g^{-1}*
90% < 22 µm	3.6	10.2	21.9	4.80	3.70	0.068	0.107	0.18
< 32 µm	3.8	11.7	26.0	4.86	4.05	0.065	0.080	0.17
< 38 µm	3.8	11.8	27.7	4.93	4.10	0.060	0.080	0.17

Table 2. Particle size distribution (Malvern Mastersizer 2000) and physical properties. *Typical values

SEM images of powders with different size ranges are shown in Fig. 2 and an extended family of particle size distribution curves is shown in Fig.3. Finer size distributions will be the subject of future studies.



(a) *(b)* *(c)* *(d)*

Figure 2. 17-4PH powder (a) 90%-10µm, (b) 90%-16µm, (c) 90%-22µm and (d) -38µm

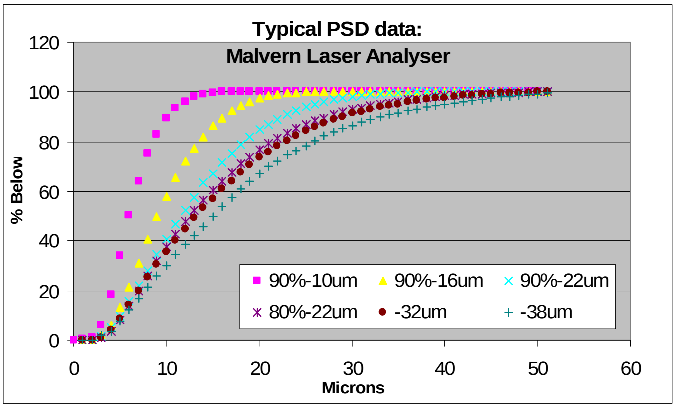


Figure 3. Cumulative particle size distributions of MIM PH steel powders

Feedstock & Parts Manufacture

Three feedstock batches were compounded from the different powders using a proprietary multicomponent binder system in a double-sigma compounder under inert atmosphere. A constant powder loading of 60vol% was achieved. The feedstocks were injection moulded using a Battenfeld HM 400 injection moulding machine to produce the tensile test specimens shown in Figure 4.

Sintering of the green parts took place in a Thermal Technology vacuum furnace at temperatures between 1320 °C and 1380°C in hydrogen. The holding time at temperature was 3 hrs followed by cooling at 10 °C/min. Blaine et al [3] have determined that sintering of precipitation hardening stainless steels is enhanced in pure hydrogen compared with nitrogen/hydrogen atmospheres. They related this to the stabilisation of austenite by nitrogen which retards diffusion and densification compared with the δ-ferrite phase which otherwise forms. As sintered samples were kept for multiple testing and further samples were heat treated (HT) under vacuum for 1 hr at 1050^{o}C followed by quenching with nitrogen gas. Tensile testing was carried out using an AGC SLOW tensile test machine equipped with a Sandner 25 extensometer.

Figure 4. Tensile test specimens before and after sintering.

RESULTS

From each set of conditions which are listed in Tables 3 and 4, a number of the tensile bars were heat treated. The remaining samples were left in the non-heat treated condition after sintering. The ductility results are not presented but were low for all samples at <3% albeit better at higher sintering temperature. The tensile strength of the as sintered samples increases when the sintering temperature rises from 1320^{o}C to 1350^{o}C but no further benefit is seen at 1380^{o}C. There is little evidence of any effect of particle size on tensile strength except at the lowest sintering temperature where the -38μm product shows lowest strength.

Sintering temp. / particle size	90.1% -22 μm	99.9% -32 μm	99.9% -38 μm
1320^{o}C	841	823	797
1350^{o}C	910	893	927
1380^{o}C	906	892	890

Table 3. Ultimate Tensile Strength [MPa] before heat treatment

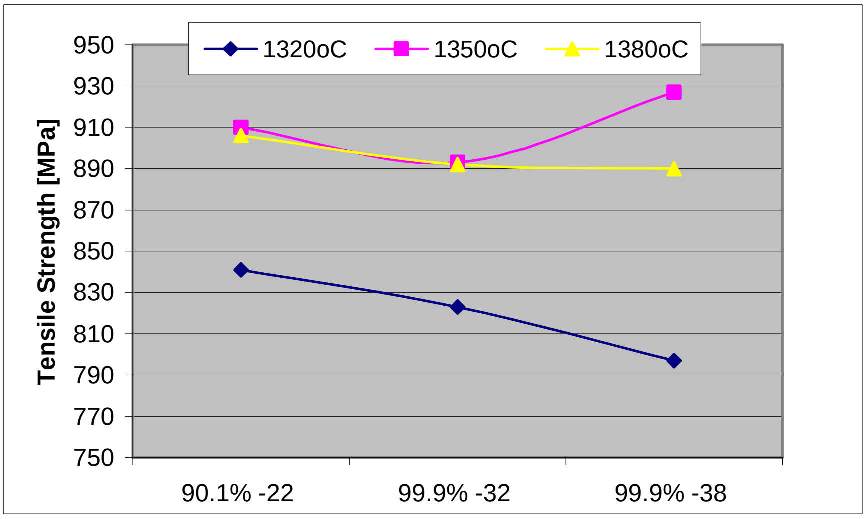


Figure 5. Tensile Strength of as sintered 15-5PH steel vs sintering temperature and powder size.

After heat treatment, there is a dramatic increase in tensile strength of ~300MPa on average for each powder size/sintering temperature combination. Highest strength values are obtained at the highest sintering temperatures and again there appears to be an effect of particle size only for the coarsest powder at the lower sintering temperatures (1320°C and 1350°C).

Sintering temp. / particle size	90.1% -22µm	99.9% -32µm	99.9% -38µm
1320°C	1198	1120	1107
1350°C	1178	1182	1115
1380°C	1229	1186	1217

Table 4 Ultimate Tensile Strength [MPa] after heat treatment

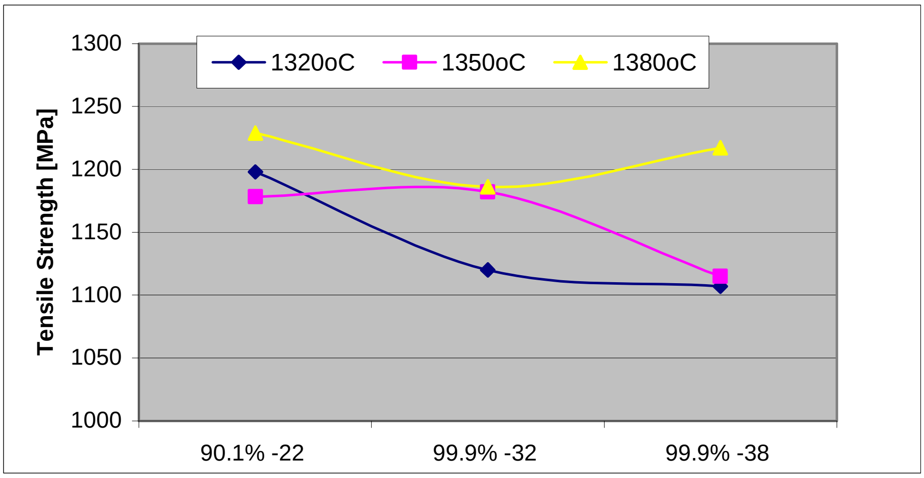


Figure 5. Tensile Strength of heat-treated 15-5PH steel vs sintering temperature and powder size.

Sintered samples were subjected to chemical analysis to determine whether there had been any significant loss of Cu by evaporation. The results shown in Table 5 indicate that there is little difference among the samples although the trend is in the expected direction.

Sintering Temperature, °C	%Cu
1320	3.80
1350	3.77
1380	3.67

Table 5. Cu content in sintered samples as a function of sintering temperature (average of 3 results)

DISCUSSION

The size distributions chosen for this study are representative of the most popular size ranges chosen for the PH family of stainless steels. Finer powder fractions are used for special applications requiring e.g. precise dimensions, thin-walled components and/or excellent surface finish where superior moulding characteristics are essential. The coarser sizes examined here are relatively low cost alternatives and it is therefore worthy of investigation whether acceptable properties can be achieved in order to extend the range of applications where MIM'ed 17-4PH can offer a cost effective solution.

The powder size distributions listed in Table 2 have quite similar median sizes despite widely different top cut off values: the range in D50 is only 1.5µm but the range in D90 is 5.8µm. There is a clear relationship between both apparent and tap density and the powder size distribution: finer powders show lower density due to increased inter-particle friction and inferior particle packing.

It is notable that the measured UTS values in all cases compare well with the wrought 15-5PH properties quoted in the introduction. The results show that for all powder sizes, a sintering temperature of at least 1350°C is required to achieve best UTS and higher temperature also gives best ductility. This is believed to point to improved densification at higher temperature in spite of increasing proportion of δ-ferrite that is known to occur with increasing temperature above 1275°C [5]. It is reassuring that even at 1380°C, there is no significant Cu loss by evaporation (Table 5) so that tensile properties are not compromised at highest sintering temperatures.

It is interesting to compare results obtained in this paper with values in other studies on 17-4PH. It is notable that the %C in 15-5PH at 0.04% is quite typical of PH steels which have a specification of 0.07%max. and is close to the level used in ref. 5, which compares results for gas and water atomised powders. Gas atomised powders are characterised by spherical morphology, high packing density and low oxygen content which are beneficial characteristics in terms of sinterability. Gulsoy et al. [5] conclude that tensile properties (H1050) of specimens made from gas atomised powders are typically 10% higher than those made with water atomised powders across a range of sintering temperatures (see Fig. 6 below). The gas atomised powder used in their study has a D50 similar to that of the 90%-22 µm powder in the present work, and is ~2 µm coarser than the water atomised powder used in their study. In light of the present findings, this means that the superior properties of the gas atomised powder are related to the intrinsic properties of gas atomised powder (low oxygen, high packing density) rather than particle size which would have led to the expectation of worse results for gas atomised powders.

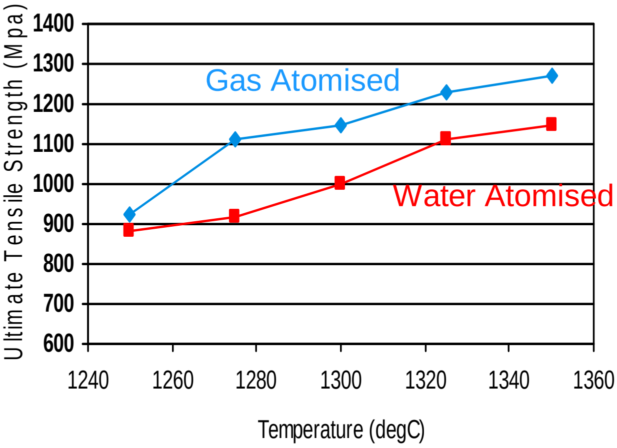


Figure 6. Tensile Strength of 17-4PH (H1050) made from Gas and Water Atomised Powders (after ref. 5).

The low and consistent oxygen levels in gas atomised powders (typically 700ppm +/-150ppm for 17-4PH vs a mean of several ‘000ppm for water atomised powders is also expected to result in more consistent control of final

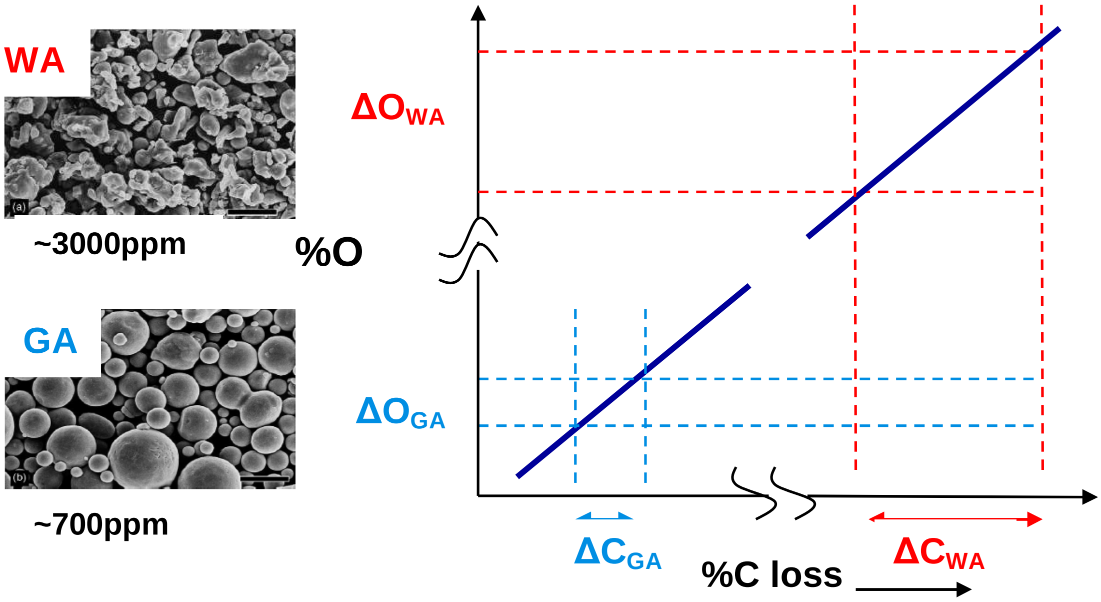


Figure 7. Schematic of variability in O level and therefore C loss from Gas & Water Atomised powders

carbon level in sintered parts, which in turn will influence strength levels [4]. Fig 7 shows the schematic relationship between variability in oxygen level and the corresponding variability in carbon level. Carbon levels are actively controlled by MIM parts makers to achieve desired final levels, but any additional source of variability will make this task more difficult. As Muterlle et al. [4] show, a rise in C level helps stabilise austenite in PH steels and reduce the amount of δ-ferrite. While δ-ferrite promotes more complete sintering, it has a deleterious effect on tensile properties so that higher C generally leads to higher strength.

Regarding the impact of particle size distribution, then it appears that there is little to choose among the finest to the coarsest products in terms of mechanical properties albeit the highest sintering temperature is needed for the -38 µm powder in order to achieve best strength levels. Therefore, for applications where mechanical properties and cost are key drivers, then coarser powders may provide a real advantage provided that the part can be moulded with sufficient precision and surface finish.

A further option in relation to making MIM parts in 17-4PH is to consider using a master alloy (MA) approach. 1.5x and 3x concentration MAs are available and have been shown to offer equivalent mechanical properties to prealloy routes [6,7]. However, MAs have the advantage of enabling a lowering of the sintering temperature since fine carbonyl Fe (median typically 4 µm) gives an overall finer average particle size. The finer overall particle size also offers other advantages in terms of reduced part distortion. A further benefit of the MA approach is a narrowing of the %Cu range from +/-1.0% according to prealloy specification, to +/-0.12% via the 3x MA (12.0-12.7%Cu). This should improve consistency in final mechanical properties.

In a study of the effects of powder type, Stucky et al. [8] found that for 316L and 17-4PH, lowest distortion could be obtained using a gas atomised master alloy plus prealloy gas atomised mix. This could be significant in the drive towards larger MIM parts and/or those which have high aspect ratio or significant bending moment which are most prone to slumping and setter drag. It is not uncommon now for parts producers to seek an optimum blend of gas and water atomised powders to give the best balance of flow, distortion, shrinkage and cost. Future studies will examine finer powder sizes 90%-16µm and 90%-10µm.

SUMMARY & CONCLUSIONS

Gas atomised 15-5PH powders at three different sizes produced by air classification and sieving have been moulded to examine effects on tensile properties. Absolute sintered strength levels are in line with expectation but tensile elongation is lower than expected. In the as sintered state, there appears to be little effect of particle size distribution on tensile strength except for lowest temperature sintering and coarsest powder where significantly lower strength is achieved. The same trend is seen in the heat treated state (H1050) where tensile strength is approximately 300MPa higher. Therefore, equivalent strength level can be achieved with coarser powders provided the sintering temperature is raised sufficiently. It is shown that Cu loss is not significant even at highest sintering temperature of 1380°C. Therefore in applications where cost is critical and mechanical properties dictate material selection, there is scope to evaluate sieved gas atomised powders for MIM which might previously have been thought too coarse to consider. Note that the same may not apply to water atomised powders whose intrinsic characteristics of higher oxygen levels and irregular shape lead to poorer sintering and lower tensile properties. The low and consistent oxygen levels in gas atomised powders should also lead to more consistent C level, delta ferrite content and tensile properties.

As an option to combine best mechanical properties with lowest distortion, a master alloy approach may be considered. This has the added advantage that a narrower range of final chemistry can be achieved leading to improved consistency. Control of % Cu and %C in particular are considered important in relation to densification and tensile properties.

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