DEVELOPMENT OF MASTER ALLOY POWDERS, INCLUDING NICKEL-BASED SUPERALLOYS, FOR METAL INJECTION MOLDING (MIM).

P. A. Davies[1], G. R. Dunstan [1], A. C. Hayward [2] and R.I.L. Howells [1]

[1] Osprey Metals Ltd. Red Jacket Works, Millands Road,
Neath, SA11 1NJ, U.K.

[2] Metal Injection Mouldings Ltd. Davenport Lane,
Altrincham, Cheshire,
WA14 5DS U.K.

ABSTRACT

The range of gas atomised master alloy powders has increased in response to a demand for components manufactured by Metal Injection Molding (MIM) for a diverse range of applications, some of which demand high temperature mechanical properties and corrosion/oxidation resistance. The development of master alloys produced by gas atomisation with highly alloyed contents of up to 3 times that of the standard pre-alloyed material, for subsequent blending with carbonyl iron and in some cases carbonyl nickel, is described. Master alloys utilise the inherent physical properties of carbonyl iron and nickel, specifically high purity and fine particle size distributions, which can enhance sintering and maximise the density of the final component and provide increased resistance to distortion during and prior to debinding. The development of novel master alloys for nickel-based super-alloys is discussed. Preliminary mechanical properties and scanning electron microscopy, including energy dispersive x-ray microanalysis, are presented.

KEYWORDS

Powder Injection Molding, Metal Injection Molding, Master Alloy & Superalloy

INTRODUCTION.

The development of master alloys dates back to the origins of powder metallurgy, where powders of different elemental compositions were blended together and sintered to form an alloy with a homogenous composition. The major advantages of a Powder Metallurgy (PM) route are the reduced probability of segregation, often present in cast ingots, and the fine microstructures of the sintered parts. Blends of carbonyl Fe and carbonyl Ni provided the very first types of feedstock for MIM and still form the backbone of the MIM industry. However, the problems associated with heterogeneous microstructures, specifically nickel rich areas that can produce drill breakages due to localised toughness, is well known. Pre-alloyed gas atomised powders provide an alternative to the basic Fe-Ni alloys because the range of materials include stainless steels, tool steels, Co based and Cu based alloys and also Ni based super-alloys. The use of pre-alloyed powders offers the ability to manufacture MIM parts with equivalent compositions to the alloys used in conventionally cast, forged and machined parts.

Gas atomised master alloy powders can combine the benefits of gas atomised pre-alloyed powders with the cost benefits of carbonyl powders. They are blended with the appropriate proportion of carbonyl Fe and in some case's carbonyl Ni and binder in order to formulate a MIM feedstock. Master alloys for common stainless steels, which are principally blended with carbonyl Fe, have been available for several years and include 2:1 17-4PH, 2:1 316L and 3:1 420 master alloys. Demand is expected to increase dramatically in 2003 with an estimated production of at least 60 tonnes, equivalent to approximately 180 tonnes of pre-alloyed stainless steel MIM parts.

The sintering process is activated by the diffusion of the alloying elements created by the compositional gradients between the master alloy and the carbonyl particles in addition to the capillary forces, due to interfacial and surface tensions, which are directly related to the particle size distribution. This phenomenon has a beneficial effect on the stability of the as-molded part during debinding and on the density of the sintered part, which is produced as a homogenous microstructure with the desired composition.

Metal injection moulding of pre-alloyed Alloy 718 has been shown [1] to provide a cost effective alternative to wrought components, principally manufactured by machining, for high-performance turbine engines. Alloy 718, a precipitation-hardened material, is extensively used for aerospace applications due to its combination of strength at high temperatures (>500°C) and oxidation resistance. Hardening precipitates include Ti, Al and Nb. The material exhibits a delayed response to precipitation hardening temperatures and has a significantly better weldability than most precipitation hardened materials because the heat of the weld does not induce hardening and consequent post weld cracking.

The aim of this investigation was to formulate a master alloy for Alloy 718 designed to be blended with the appropriate proportions of carbonyl Fe and carbonyl Ni and to determine whether a homogeneous structure was formed after sintering of the MIM part. The master alloy route is thought to benefit from improved green and brown part strength, enhanced sintering performance and reduced overall MIM feedstock cost. Tensile test specimens were injection molded, de-binded and sintered for mechanical testing and microscopy. Scanning electron microscope based Energy Dispersive X ray (EDX) analysis was used to investigate the distribution of alloying elements in the sintered material.

EXPERIMENTAL PROCEDURE

The chemical composition for pre-alloyed Alloy 718 is shown in Table 1. The Alloy 718 master alloy was designed to include additions of both carbonyl Fe and carbonyl Ni. However, the contribution of the carbonyl Fe is limited because Nb has a melting point of 2468°C and therefore has to be added as ferro-niobium, which is a standard superalloy hardener and has a lower melting point. As a general rule, increasing the proportion of alloying elements, such as Nb and Mo increases the melting point of the alloy and difficulties in dissolving the elements can arise. Therefore, a 4:1:1 ratio (Master Alloy: Fe: Ni) material was formulated, also shown in Table 1.

The alloy was melted in an induction furnace within an argon atmosphere and atomised with high-pressure argon, using proprietary atomiser design technology, in order to produce fine powder suitable for MIM. The as-atomised powder was air classified to comply with the specific particle size 90% -22µm. The particle size distribution for the classified powder, which was measured by laser diffraction, is shown in figure 1. The yield of in-size powder was high (>70%) compared to the yields produced from standard close-coupled atomisers, which typically produce about 20-30 % yield of powder in this size range. This improved yield of fine powder is due to improvements in atomiser design and performance, developed in the mid 1990's [2].

Table 1. Alloy Compositions

	Alloy 718 Pre-Alloyed			**Alloy 718 Master Alloy**		
	Nominal (% wt.)	**Maximum (% wt.)**	**Minimum (% wt.)**	**Nominal (% wt.)**	**Maximum (% wt.)**	**Minimum (% wt.)**
Ni	54.500	55.000	50.000	52.000	53.000	50.000
Cr	19.000	21.000	17.000	28.500	29.000	25.500
Fe	16.611			4.350		
Nb	5.100	5.500	4.700	7.500	8.250	7.050
Mo	3.100	3.300	2.800	4.650	4.950	4.200
Ti	0.950	1.150	0.650	1.425	1.725	0.975
Al	0.500	0.800	0.200	0.750	1.200	0.300
Cu	0.200	0.300		0.300	0.450	0.000
C	0.035	0.070	0.030	0.080	0.120	0.045
B	0.004	0.006	0.002	0.006	0.009	0.003
Si		0.220		0.300	0.330	
Mn		0.120		0.140	0.180	

The blended powders were mixed with a proprietary binder system, and pelletised for injection molding. The form of the tensile test specimen is important because the MIM tensile specimen must be compared directly with the standards for wrought and sheet material. Tensile test bars, as shown in fig. 2, were produced by injection molding in a single cavity mold designed to comply with European Powder Metallurgy Association (EPMA) guidelines. The basic sinter cycle involved a pre-sinter stage at 600°C in hydrogen followed by a dwell for at temperature for 120 minutes and a second ramped stage up to the final sintering temperature in vacuum. The samples were then furnace cooled and back-filled with nitrogen when the temperature dropped below 600°C.

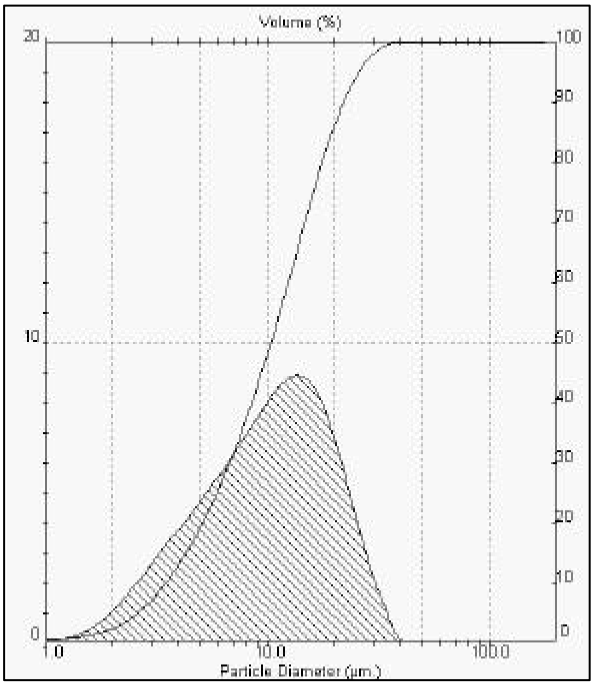

Figure 1. Particle size distribution for the classified 90% -22 micron, (D10=3.5µm, D50=10.4µm, D90=22.0µm), Alloy 718 master alloy powder.

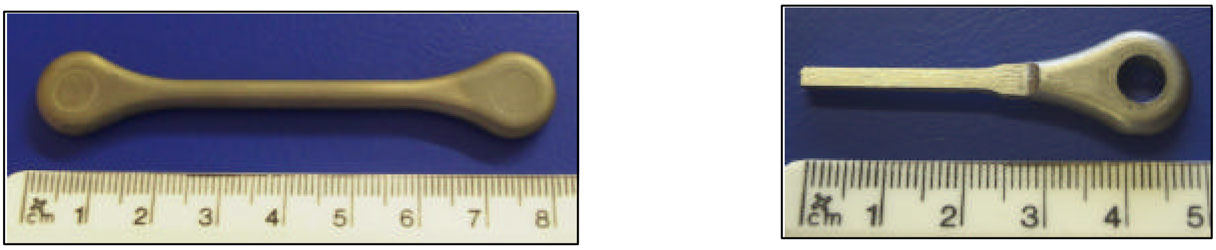

Figure 2. (a) MIM tensile test bar. (b) One half of an as tested machined MIM tensile test bar.

The tensile test bar was machined, in order to remove the thermally etched surface texture and produce a square profile, which complied with Standard EN 10002-1. The mechanical properties were evaluated by tensile testing. Specimens were prepared by standard metallographic techniques. The polished surfaces were electrolytic etched (4.5 volts for 10-20 seconds) in a 5% aqueous sulphuric acid solution, which preferentially etches the precipitates.

RESULTS AND DISCUSSION

The optical micrographs of a polished and etched section of an Alloy 718 as-sintered tensile specimen (fig. 3) clearly show precipitates, which are characteristic of Alloy 718. The precipitates are generally too coarse to provide significant increase in strength. The Back-Scatter Electron (BSE) micrograph, shown in fig. 4, highlights the difference in chemical composition between the different types of precipitates because the levels in the greyscale image are directly related to the atomic weight of the elements present in the material. The images feature at least two types of precipitates including large randomly distributed precipitates, probably TiN and intergranular and transgranular precipitates. The transgranular precipitates are situated within grains, in high densities, and are often surrounded by intergranular precipitates. Other regions are virtually free of precipitates.

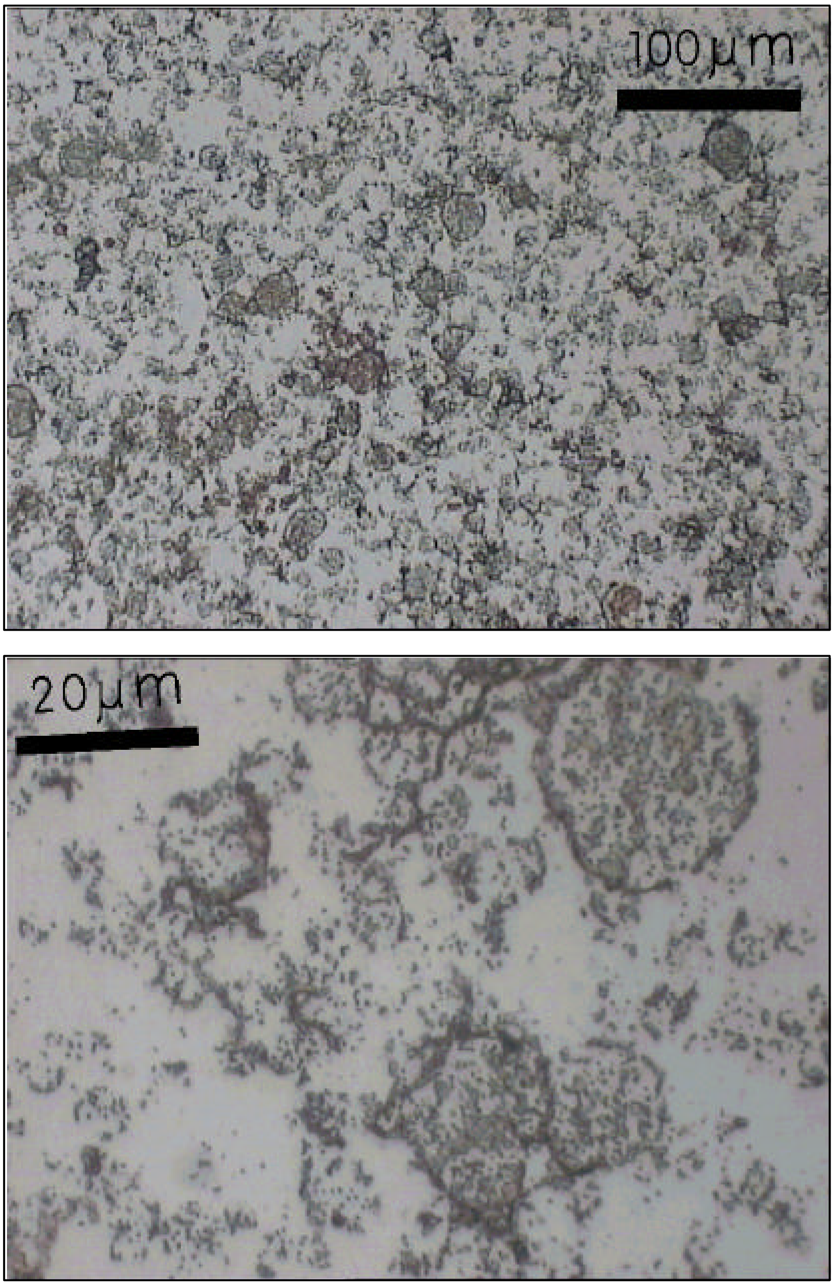

Figure 3. (a) Optical micrograph (mag. ×200) features both intergranular and transgranular precipitates as well as regions where no precipitates evident. (b) Optical micrograph (mag. ×1000) which shows the precipitates in detail.

The fracture surface of a broken tensile test specimen was investigated by electron microscopy. The BSE image, shown in fig. 5, features both intergranular and ductile fracture identified by the smooth curved surfaces and dimpled features, respectively. The precipitates are also clearly visible. EDX analysis results are shown for a fixed area (×100 magnification), for the primary alloying elements in fig. 6. The results, quantified in Table 2, indicate that the chemical composition matches the defined specification for alloy 718, as shown in Table 1. An EDX map, shown in fig. 7, highlights the distribution of Ti, Al and Nb around the grains and, significantly, shows that the carbonyl Fe and Ni have been diffused into the matrix producing a homogenous microstructure.

The X-ray spectra, shown in figure 8, acquired from points within the precipitates positively identify the precipitates present throughout the microstructure including the intergranular precipitates. Sintering in hydrogen is known [2] to produce a continuous second phase surrounding the individual particles, which is composed of a niobium rich Laves phase (44Ni-12.5Nb-16.4Cr-16Fe-3.2Mo-1.4Si). Low temperature sintering is known to result in excessive coarsening of the second phase particles resulting in lower temperature phase or Laves-types phase at the grain boundaries.

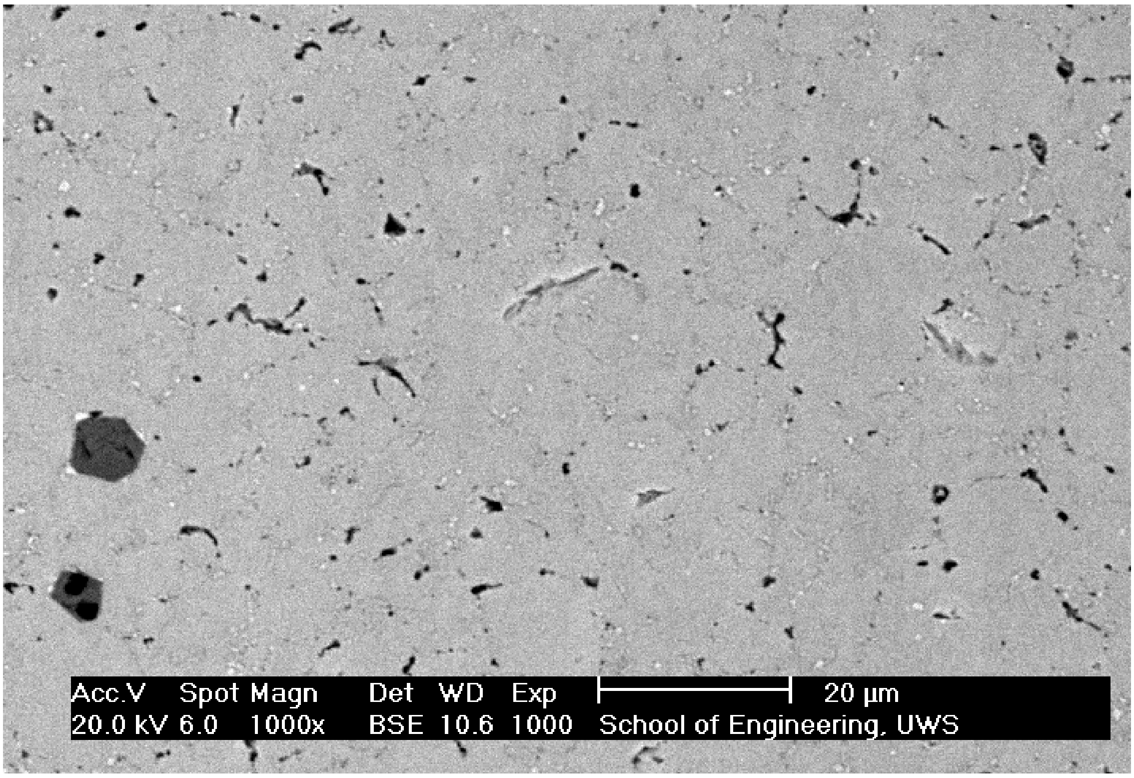

Figure 4. Back-Scattered Electron micrograph of a polished and etched section of an Alloy 718 as-sintered tensile test specimen.

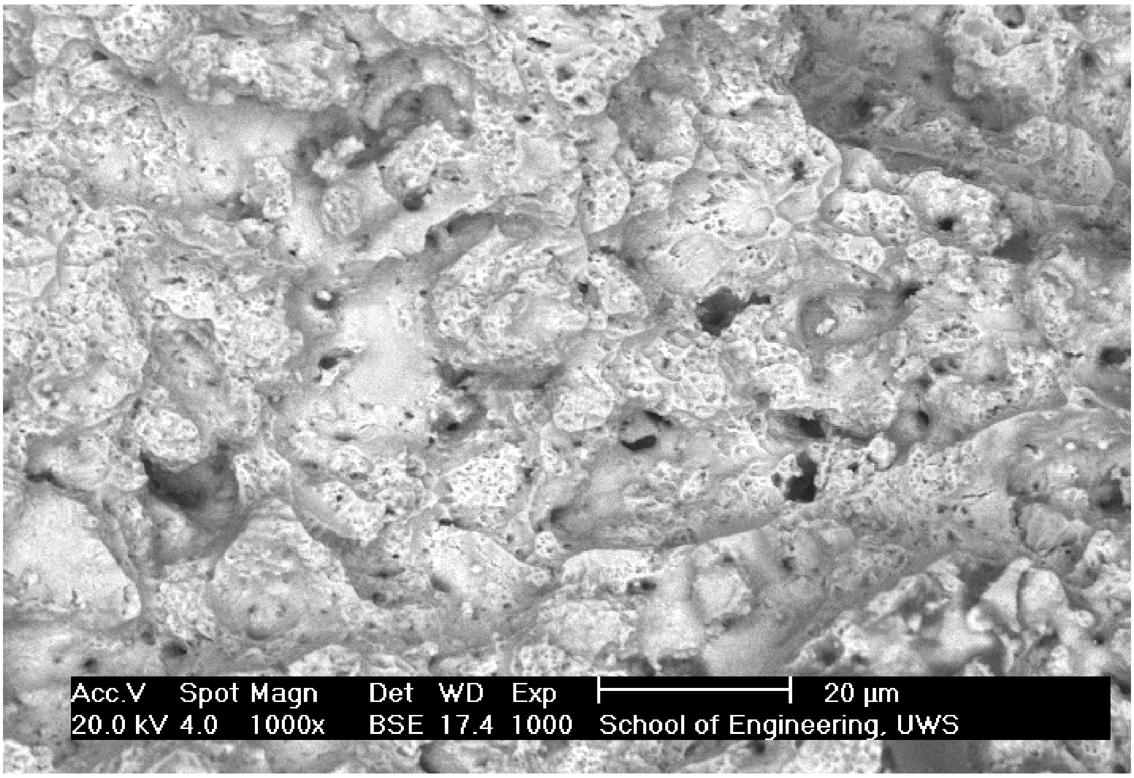

Figure 5. BSE micrograph of the fracture surface of an Alloy 718 as-sintered tensile test specimen.

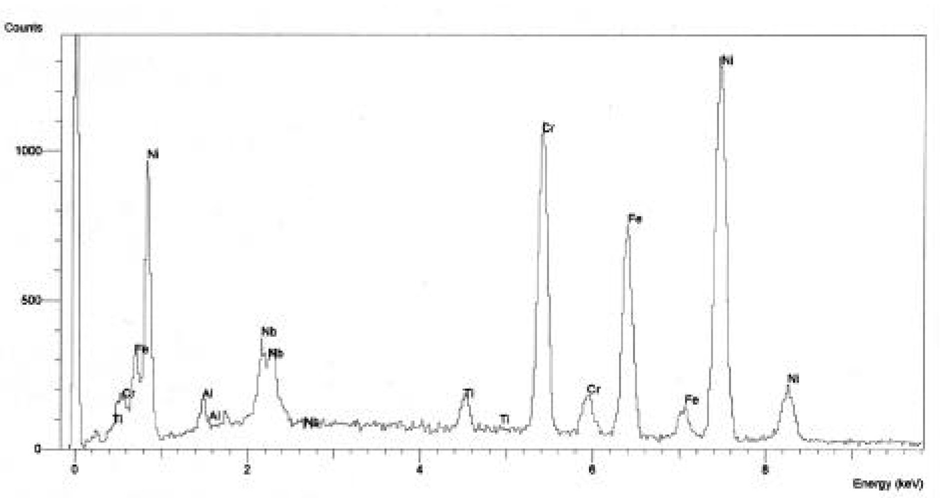

Figure 6. EDX analysis spectra acquired from a sectional area (×100 magnification) for the sintered alloy 718, which highlights the proportions of alloying elements throughout the matrix.

Table 2. Quantitative EXD analysis Results.

EDX Analysis (% wt.)	
Ni	54.6
Cr	18.7
Fe	18.2
Nb	4.7
Ti	1.3
Al	1.0
Si	0.3

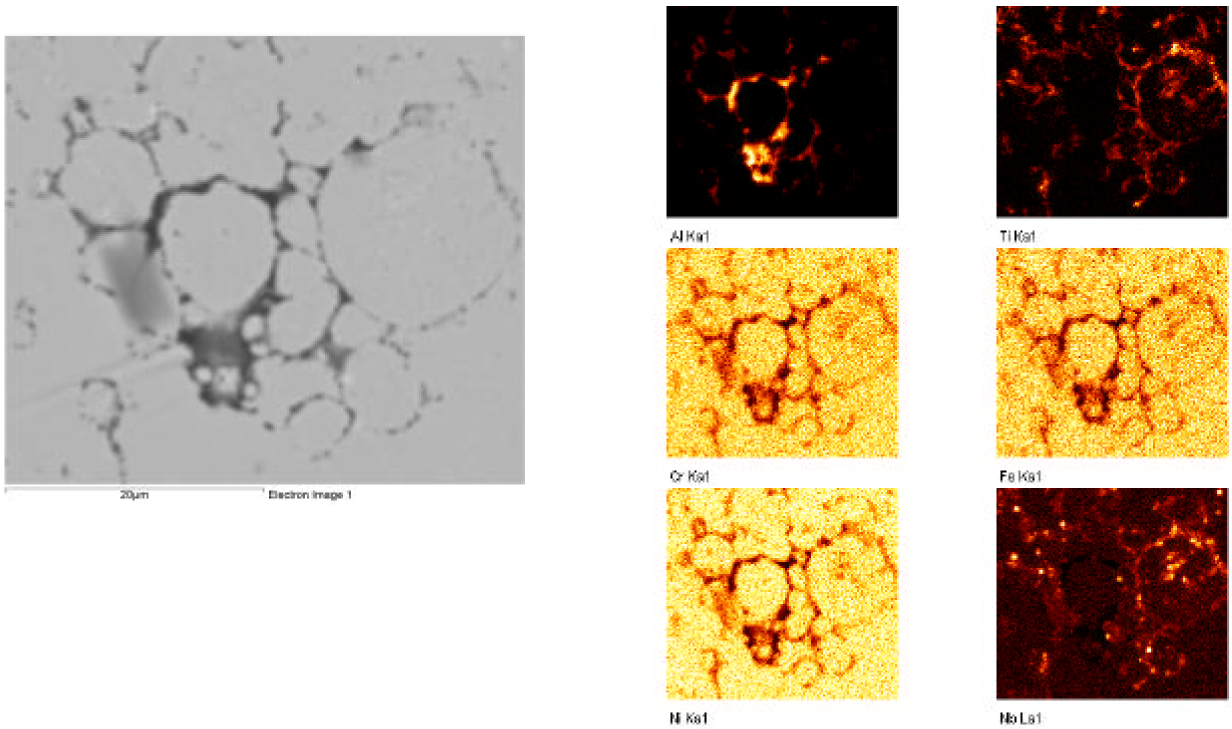

Figure 7. Electron micrograph and EDX map of a section through the sintered master alloy 718 tensile test bar, which highlights the distribution of the precipitates (Courtesy of Mark Peers, Oxford Instruments Analytical, High Wycombe, U.K.).

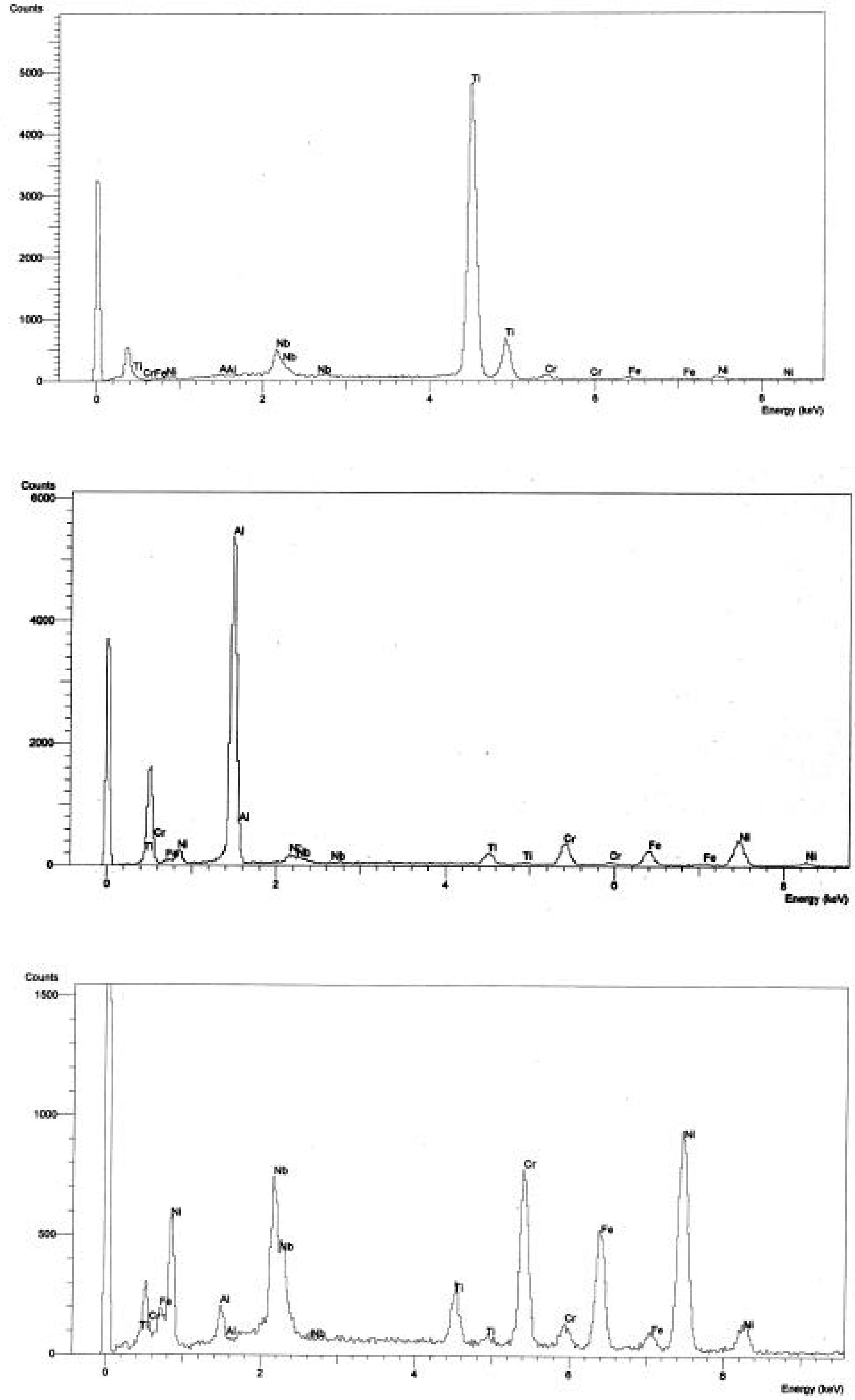

Figure 8. The precipitates present in the microstructure of the sintered alloy 718 are characterised by EDX analysis and feature (a) Ti rich precipitates, (b), Al rich precipitates and a Laves phase which is rich in niobium.

The results of the tensile tests, conducted at room temperature (20°C), are summarised in Table 3, for different sintering conditions. The table also includes typical values for cast, annealed and heat-treated wrought Alloy 718. The results indicate that the mechanical properties of the as-sintered MIM Alloy 718 are comparable with cast and annealed material but as expected fall short of the ASM minimum requirements for wrought and heat-treated material. This is probably due to the fact that the MIM material has not been solution and precipitation heat-treated and the precipitates are not producing any beneficial increases in strength. The Laves phase may also reduce the strength of the material and may be the cause of the intergranular fracture, shown in fig. 5.

Table 3. Tensile Test Results.

Alloy 718 Sample	**Sintering Conditions**	**0.2% Proof Stress (Mpa)**	**Ultimate Tensile Strength (Mpa)**	**Elongation (%)**
C1026-1	1285°C 40 minutes		913	20.5
C1026-2	1285°C 40 minutes		915	20.0
C1064-A	1285°C 40 minutes	449	932	17
C1064-B	Pre-sintered at 1090°C in H_2 1285°C 40 minutes	458	891	15
C1068-A	1287°C 60 minutes	574	931	19
C1068-B	Pre-sintered at 1090°C in H_2 1287°C 60 minutes	526	844	13
C1069	1287°C 60 minutes Held at 620°C for 240 minutes	661	980	11
C1071	1285°C 60 minutes	497	933	19
C1073	1285°C 60 minutes	509	939	21
Alloy 718	*Cast*	*414*	*862*	*51*
Alloy 718	*Cast and Annealed*	*462*	*935*	*41*
Alloy 718 Wrought Bar [a.]	*Heat Treated Condition* [b.]	*1185*	*1435*	*21.0*

a. ASM International Handbook Vol. 1.
b. ASM 5663 specification (solution heat treatment 1 hour in Ar at 950°C then air cooled, followed by precipitation heat treatment at 718°C for 8 hours, furnace cooled at 38°C/min. to 620°C held for 8 hours and finally air cooled.)

Previous investigation [3] of the sintering conditions determined that to prevent the formation of Laves phase the optimum conditions were a heating rate of 15°C/min and a sintering temperature of 1260°C for 6 hours in vacuum. However, the results of this investigation indicate that a shorter dwell time (less than 1-hour) at the maximum sintering temperature (1287°C) produced the best as-sintered mechanical properties. Optimisation of the mechanical properties was achieved by heat treatment as defined by the ASM 5663 specification, consisting of a solution treatment followed by one or more precipitation treatments.

The mechanical properties of metal injection molded 718 were previously investigated [4] in order to demonstrate that components produced by this route can meet the rigorous demands of aerospace material specifications. The results of the tensile tests for pre-alloyed MIM alloy 718, summarised in table 4, confirm that the properties compare favourably with the minimum requirements specified in ASM 5596. Similarly the results of the creep tests meet the ASM 5596 criteria but the stress rupture values fell below the minimum requirements. However, specimen distortion and thermal etching at the surface of the specimens was thought to have influenced the results. Polished specimens and specimens machine from MIM blanks showed improved results. Also an additional heat treatment, developed to increase the amount of δ phase, improved the stress rupture elongation to exceed the minimum values required by the ASM 5596 specification. However, increased amounts of δ phase are thought to increase the sensitivity too hydrogen embrittlement, where micro-cracks form at the δ phase/matrix interface.

Table 4. Tensile Test Data for Pre-Alloyed Alloy 718.

Sintered and Heat Treated ASM 5663 and tested at 20 °C [4].			
Heating Ramp Rate (°C)	Yield Strength (Mpa)	Ultimate Tensile Strength (Mpa)	Elongation (%)
1	1088	1297	13.3
10	1063	1206	9.4
15	1061	1237	11.4
ASM 5662G/5596	1034	1241	12.0

CONCLUSION

The preliminary results indicate that master alloys can be used in the MIM fabrication of nickel based super alloys to produce high-density sintered parts. The microstructures are comparable to those obtained by MIM using pre-alloyed powder and cast materials, prior to final heat treatment. The results of the EDX analysis suggest that the carbonyl Fe and carbonyl Ni powder has been successfully diffused into the matrix during sintering, producing a homogenous microstructure. The tensile properties of the sintered material are comparable with both cast, and annealed Alloy 718. However, as expected they do not match the properties of heat-treated wrought Alloy 718. Similarly, they can not be compared with the previous reported data for heat-treated MIM alloy 718, which exceeded the defined limits in specification ASM 5596. Solution heat treatment followed by precipitation heat treatment is required to improve the mechanical properties of the material with the aim of exceeding the ASM 5596 specification. Such heat treatments on MIM master alloy 718 specimens are currently being undertaken.

REFERENCES

1. Bose, A., Valencia, J.J., Spirko, J. and Schmees, R.M. "Powder injection molding of inconel 718 aerospace components." *Advances in Powder Metallurgy & Particulate Materials,* Part 18, 1997, Pg 99-112.

2. Dunstan, G.R., Howells, R.I.L., and Pratt, R.C., "Osprey improves atomiser for MIM powder production", *Metal Powder Report*, March 1994.

3. Valencia, J.J., Spirko, J. and Schmees, R. M., "Sintering Effect on the Microstructure and Mechanical Properties of Alloy 718 Processed by Powder Injection Molding." *TMS 4th International Symposium on superalloys 718, 625, 706 and various derivatives,* Edited by E. A. Loria, The Minerals, Metals and Materials Society, 1997, pg. 753-762.

4. Schmees, R.M., and Valencia, J.J., "Mechanical Properties of Powder Injection Molded Inconel 718" *Advances in Powder Metallurgy & Particulate Materials* Part 5, 1998, Pg 107-118.