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Improving Kinetics of MIM Process by Applying New Methods of Debinding and Sintering

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Abstract

The processing of MIM Inconel 718 components is investigated in order to reduce the time and energy consumption. The two alternatives investigated are polymer extraction by a supercritical fluid and the Field Assisted Sintering. If a default is produced during a step of the MIM process, it will be near impossible to compensate it during the next one, which is why it is important to understand the impact of each new methods on the component. The first part of this study introduces the optimization of the two alternative methods followed by the characterization of the final MIM components. The impact on the phases obtained after sintering is observed via SEM and TEM observations. The surface quality of the components is characterized via a roughness analysis. Finally, the mechanical performances of the material are obtained by tensile strength tests and nano-indentation tests.

Introduction

Nickel Chrome super alloys exhibit good mechanical strength and high resistance to creep at high temperatures in addition to corrosion resistance [1]. Thus, they can be operated in combined conditions of strength and temperature under the influence of a corrosive media. The problem of this kind of material is the difficulty to machine a mechanical part due to its ductility, imposing dimensional limits and strong loss of material in order to obtain the desired component [2]. Metal Injection Molding (MIM) relies on shaping metal particles, and then sintering them. This method combines the advantages of PM and the flexibility of the thermoplastic molding process. The final product achieves nearly full density with mechanical characteristics close to the machined product [3]. The high production quantities of complex shaped components coupled with low loss of material makes this method competitive with the other methods [4]. There are three steps in the MIM process: the formulation of a feedstock by mixing of a metallic powder with a polymeric binder, the molding of that feedstock by injection into tooling with a determined pressure, and finally the solvent and thermal processing of the shaped sample. In the case of Inconel 718, the sintering is followed by an aging treatment in order to obtain the best performance of the alloy [5]. This method consumes a lot of time and power. In order to improve these parameters, new ways of sintering have been investigated.

This study is based on the optimization of the two processes. The first step is to optimize the debinding and sintering parameters of these two methods by finding the best density while keeping the advantages of the MIM process with complex geometry. The microstructures in function of the sintering temperature will allow comparing the behavior of the material. The effect of this parameter directly impacts the grain size and so the mechanical properties, so the hardness of the samples is compared.

1. Materials and methods

1.1 Powder and binder

The Inconel 718 powder is provided by Sandvik Osprey Ltd and its chemical composition is presented in Table 1. The grain size distribution has been measured (fig. 1) and the diameter values corresponding to cumulative volume fractions D_{10}, D_{50} and D_{90} are 3.53 µm, 6.24 µm and 10.97 µm respectively. The standard deviation is 0.86 µm. According to the literature [6], the microstructure of the Inconel 718 after sintering is composed of a γ matrix reinforced by a γ' phase Ni_3 (Al, Ti) and a γ'' phase Ni_3 (Nb, Ti). These two

intermetallic phases are responsible for a rise of the hardness and the good performance of the alloy at high temperature. The carbon content must be limited as much as possible in order to avoid the formation of Niobium and Titanium carbides, as there is a fear of lowering the mechanical performances of the component by reducing the volume fraction of the strengthening elements in the matrix.

Table 1 Chemical composition in mass percentage of the Inconel 718 powder provided by Sandvik Osprey

Ni	Fe	Cr	Mo	Al	Ti	Nb	C
52.5	19.0	19.0	3.0	0.5	0.9	5.3	0.0

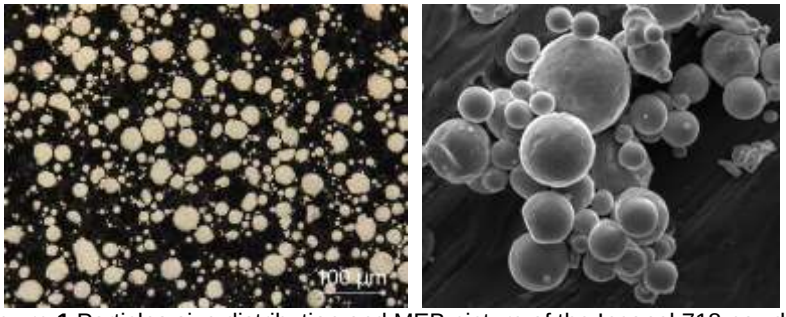

Figure 1 Particles size distribution and MEB picture of the Inconel 718 powder

The selected binder is composed of Polypropylene (PP), Polyethylene Glycol (PEG 20K) and Stearic Acid (SA). The compatibility of this binder with fine grain size powder is also helping during the injection. PEG is used to improve the flow of the mix and make the injection easier. PP's purpose is to rigidify the green part structure and allowing manipulation after debinding. SA is a long chain polymer which is going to assure homogeneity inside the feedstock. The composition of the binder is given in table 2. The mixing of the binder with the metallic powder was performed of a twin screw mixer Brabender Plastograph EC. The feedstock was then milled in order to make easier the next manipulations. The feedstock is injected into green parts in the form of cylinders by using an injection press Arburg 220S.

1.2 MIM samples treatments

The optimized process of the MIM samples composed of Inconel is composed of 4 different steps. The green parts first undergo a solvent debinding step. They are introduced into distilled water at around 35 °C temperature for 48 hours in order to remove the PEG. They are then dried in an oven at 75 °C for 2 hours. The PP is eliminated by thermal debinding at 500 °C for 2 hours under Argon atmosphere. A heating temperature rate of 2 K/ min is applied during all the cycle in order to avoid overpressure inside the sample during the degradation of the polymer. Once the thermal debinding is over, the sample is sintered at a temperature of 1290 °C during at least 3 hours at a heating rate of 5 K/min. The cooling is done naturally at a rate of 10 K/min. In order to improve the mechanical characteristics of the material a thermal treatment is applied by using annealing at 980 °C during 1 hour and age treatment successively at 720 °C and 620 °C during 8 hours. This treatment will allow the diffusion of the hardening phases γ'' as found in the literature [5, 7].

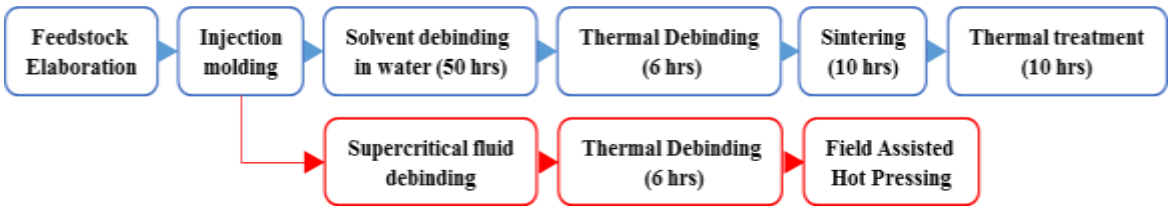

Figure 2 MIM Processing scheme using conventional methods (blue) and substitute road (red)

All these steps are taking around 80 hours in order to obtain a sample. The solvent debinding is the step that is taking most of the time due to the time the water needs to extract the PEG. In order to reduce the

time needed for that step, supercritical fluid is going to be used. The extraction by supercritical fluids of MIM binder components has already been studied with paraffin wax as one of the component [8]. The FAHP is a sintering method known for the fast heating rates and the possibility of improving the mechanical characteristics of the material sintered. This method could then be used to replace both the sintering and the thermal treatment [9].

2. Experimental Procedures

2.1 Supercritical debinding

The supercritical state of a fluid can be reached at a certain temperature and pressure, called triple point. The conditions for the CO_2 is at 304.1 K and 73.8 bar. The equipment is a supercritical extractor from Separex. The system is designed to introduce supercritical fluid inside an autoclave at the temperature and pressure desired. The programmed cycles consist of 5 steps. First, the CO_2 is cooled down around 0 °C in order to be liquid. The pressure is going to be raised via a pump and then the fluid is passing inside a thermal exchanger. The CO_2 is then introduced inside the reaction chamber in presence of the samples. It will react with the polymers inside the binder and smoothly start the extraction process. The fluid mixed with the residues of the polymer is then going through a separator in order to allow the CO_2 to follow a recycling line for a new cycle. Once the cycle is finished, the used CO_2 is purged of the system and the samples taken out of the equipment.

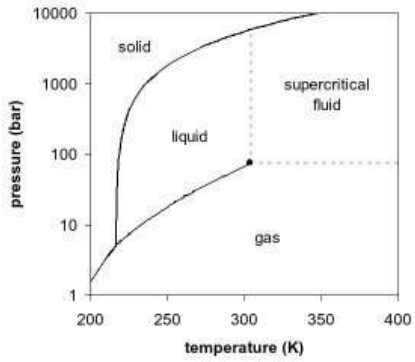

Figure 3 Phase diagram of the carbon dioxide[8]

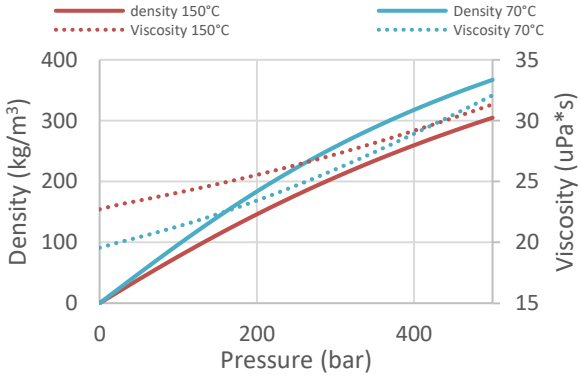

Figure 4 Evolution of Carbon dioxide properties in function of the pressure [10]

The performance of the extraction of the sample is going to be determined by mass difference and TGA. The parameters of the cycle that can be controlled are the temperature and the pressure of the fluid, the time of reaction, and the rates of increase and decrease of the pressure. In order to keep the shape of the MIM sample, the pressure is raised at the desired pressure at 10 bar/min and decreased in two times, from the dwelling pressure at 20 bar/min then from to 90 bar to ambient pressure at a lower speed of 3 bars/min. This is due to the phase diagram of the CO_2 (Fig. 3), going back from supercritical to gas phase. During this transition, there is a probability of overpressure inside the samples that needs to be avoided. The temperature and the pressure applied are changing the properties of the fluid, such as the density (Fig. 4). The optimisation of these parameters is going to impact on the kinetics of the test.

2.2 Field Assisted Hot Pressing

In the case of the FAHP (Fig. 5), the Inconel 718 powder is directly introduced into a graphite die. The graphite die is composed of main cylinder pierced with an intern diameter of 20 mm and of two punches of the same diameter. In order to protect the equipment and to improve the electric contacts between the different parts of the system, a foil is placed between the powder and the die. The foil is composed of pure tungsten, which will block the carbon diffusion inside the Inconel 718. If the powder is in contact with carbon during the test, an important diffusion of the carbon could weaken the characteristics of the sample [11].

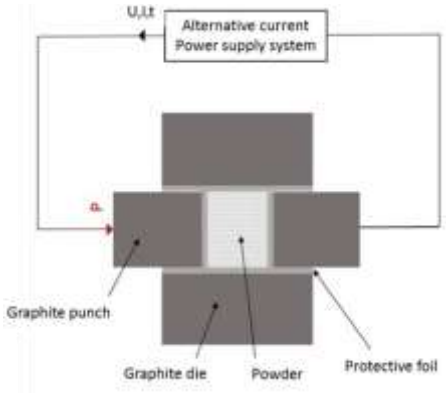

Figure 5 FAHP system

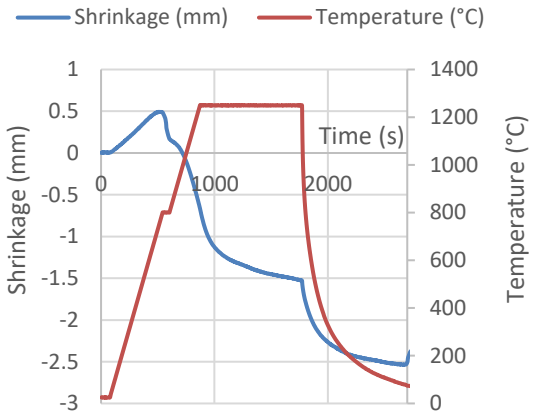

Figure 6 FAHP of Inconel 718 MIM sample at 1250°C during 15 min and under 10 MPa pressure

The samples have been consolidated in a Gleeble 3800 equipment by the application of a strong electric current going through the punches under vacuum. The temperature of the samples is measured via two thermocouples. One is at the center of one of the punches and the second one close to the powder inside the graphite die. The shrinkage of the sample is measured via the displacement of the punches (Fig 6.). The heating rate of the sample is fixed at 100 K/min until reaching the desired temperature. A dwelling time is applied at 800 °C during the application of a pressure of 10 MPa and it is maintained until the cooling is done.

3. Results

3.1 Supercritical debinding

The temperature and pressure conditions in order to obtain the complete extraction of the PEG inside the binder have been found to be 400 bars and 150°C. With these parameters, no external damages have been observed. The next steps in order to check the effects of the debinding were to complete the MIM process with thermal debinding and sintering. The same was done for a sample debinded inside of water. The microstructure obtained with supercritical debinding is close to the one obtained via conventional one. The main difference that can be observed on the images (Fig. 7) is on the border of the samples. The supercritical debinded sample is showing a nice cylindrical shape while the water debinded looks less regular.

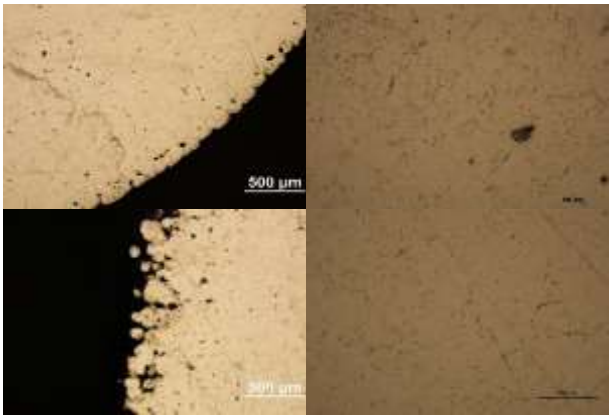

Figure 7 Optical microscopy of samples sintered after supercritical debinding (above) and water debinding (below)

In order to determine the effect on the surface of the samples, roughness analysis have been performed via optical analysis of the samples on 3D modelling of the samples (Fig. 8). It was made for two samples

that have been analysed after each step of the MIM process. In case of water debinding, the roughness has been doubled after the sintering treatment and reached a Rp of 9.27 µm and a Ra of 3.77 µm. On the other hand, in the case of supercritical debinding, the roughness has been limited to a Rp of 6.03 µm and Ra of 2.21 µm. The strong increase of roughness in the case of the water debinding can be explained by a much longer time immerged into the solvent, leading to a modification of the rigidity of the component. The result is a surface more damaged by the debinding process, which is amplified after the thermal treatments. As the fluid in supercritical state is diffusing inside the MIM sample more like a gas, the sample is less damaged, giving a better final surface.

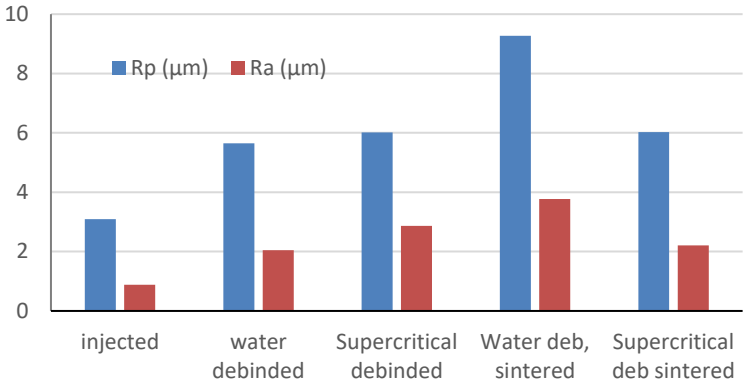

Figure 8 Roughness results after each treatments on the MIM samples

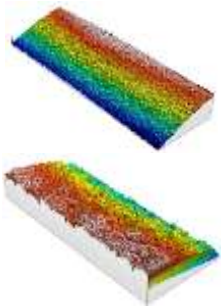

Figure 9 3D Roughness profile of sintered samples debinded by supercritical CO_2 (above) and in water (below)

3.2 Field Assisted Hot Pressing

After the debinding step, the MIM sample is only composed of powder and a little bit of polymer barely holding the particles. Because of that, they are extremely brittle and have to be carefully manipulated. In order to be able to use them in the Gleeble equipment, the samples are sintered at low pressure10 MPa) for that kind of process. A density of 98.8 % was obtained at a temperature of 1250 °C maintained during 15 minutes. The cooling was naturally done in around 20 minutes. The hardness of samples is 253±11 HV. A fine microstructure was obtained with a mean grain size of 6.2 µm. It was obtained after grinding the sample and electro polishing during 10 s at 2 V with an electrolyte of 8 mL of sulfuric acid and 100 mL of water. This treatment was carried out in order to reveal the presence of the Niobium phases.

Element %	Zone 1	Zone 2	Zone 3	Zone 4
C K	0.2	0.15	-	3.2
O K	0.5	4	0.2	3.11
AlK	0.08	-	1.69	0.47
NbL	7.52	36.52	4.6	5.46
TiK	1.52	4.72	-	1.53
CrK	18.22	12.86	17.76	17.29
FeK	18.66	11.25	20.43	16.81
NiK	53.3	30.5	55.32	52.13

Figure 10 SEM observation and EDX analysis of the MIM sample sintered with a heating rate of 100°C/min 1250°C during 15 min and under 10 MPa pressureThe EDX analysis (Fig. 10) is bringing different information on the phases present inside the material. The zone 1 has a composition close to the initial composition of the powder, corresponding to the matrix of the material. The electro polishing revealed white grains at the surface of the material present inside the grains and the borders. They are mainly composed of Niobium and Nickel. From the literature, there are two phases that could match. The first one is a δ phase that is appearing at temperatures higher than 1100 °C. The second one is the γ'' and γ' phases (tetragonal) that are expected after a thermal treatment between 900 and 750 °C. There is a strong possibility of these grains to be in δ phase, as the hardness of the sample is close to the one after sintering in a furnace. There was also a presence of some black phases inside the grains and they contain a lot of aluminum. They are more

probably γ phases. Finally, a strong presence of Carbone was found at the grain boundaries, meaning carbides are present inside the samples. It was already observed in other cases of MIM sample sintering with nickel super alloys [5]. The Carbon content has been increased during the thermal debinding step and residues have been left before sintering, helping the formation of metal carbides. They could impact the mechanical properties by lowering the tensile strength.

Conclusions

The objective of this work was to investigate new methods in order to improve the time of treatment of a MIM sample. The debinding by CO_2 in a supercritical state showed interesting results as it is taking only 6 hours instead of 50 hours for the solvent debinding and is even improving the final aspect of the surface of the samples, reducing the probability of post treatment of the samples. About the FAHP sintering, the sintering can be completed in 40 minutes. Thanks to a fast heating rate and a low dwelling time, the microstructure was impacted with a much lower grain size, explaining an improvement of the mechanical properties. In conclusion, the use of these two methods could lead to an improvement of the kinetics of the MIM treatment while improving the quality of the samples produced.

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