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Experimental study of water debinding on water soluble PEG behavior for SS 316L parts printed by pellet-based additive manufacturing process

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Abstract - Water debinding for Metal Injection Molding (MIM) process is well studied and research is still ongoing. However, only few articles are found in the literature concerning hot metal extrusion with water debinding in additive manufacturing. Steps for hot metal extrusion process are as follows: first choice of feedstocks, second extrusion of filament or pellets, third printing of the part, fourth debinding and to finish sintering. The goal of this article is to study a binder mixture for MIM technology but using additive manufacturing as pellets technology. The main objective is to see if the same binding system as MIM can be used with hot extrusion process and what would be the results. The binders used are PolyEthylene Glycol (PEG) and PolyMethyl MethAcrylate (PMMA). PEG is the most used binder for water debinding and PMMA is thermally degraded during the sintering step. These two binders are used with 316L stainless steel powder. The prepared feedstock is transformed into pellets using an extrusion machine, then the test specimens are printed using the hot extrusion process. Testing parts are then immersed in water at different temperatures (40°C, 50°C, 60°C, 70°C, 80°C) for 12 hours. At this point, the testing samples are dried and weighed every 2 hours to follow the evolution of PEG mass. Microscopic observations as well as relative density measurements also illustrate the evolution of PEG mass in the testing parts. Finally, experiments have proved that similar results are obtained in additive manufacturing and MIM for the chosen feedstock with PEG binder.

Keywords: SS 316L, Polyethylene Glycol (PEG), PolyMethyl MethAcrylate (PMMA), water debinding, pellet based additive manufacturing, density measurement, Hot Metal Extrusion

I. INTRODUCTION

For printing parts containing metal powder with Fused Filament Fabrication or pellet there are 5 steps to follow which are: choice of feedstocks, extrusion of the filament or pellets, printing of the part, debinding and sintering (Fig. 1). The debinding step is very important because it allows the degradation of the binders used before sintering step, while

maintaining the shape of the part. There are two main methods of debinding: chemical debinding (using solvents) and thermal debinding. This article focuses on chemical debinding with water as solvent. Water debinding is more environmentally friendly and safer for the user compared to chemical solvents which can also be flammable and carcinogenic. The binders used in this contribution are Polymethyl Methacrylate (PMMA) and Polyethylene Glycol (PEG). The primary role of PMMA is to maintain the overall shape of the part after dissolution of the PEG during the debinding step. One of the most used binders in the case of water debinding is Polyethylene Glycol (PEG) [1]. The molar mass of Polyethylene Glycol is very important because it will influence the experimental results. For a solid PEG, the molar mass can vary between 600 and 20,000 g/mol. In this article the chosen PEG has a molar mass of 4000 g/mol.

Water debinding is already used in MIM (Metal Injection Molding) technology [1-14], for materials such as stainless steel [3,6], titanium [1], alumina [4,5], zirconium [13,8] and Inconel 718 [14,11]. In the MIM process, a lot of research is carried out for the development of new binder systems adapted to the various existing materials. This kind of debinding is not yet used in additive manufacturing and no cases have been found in the literature [15]. However, the MIM process is very similar to the Fused Filament Fabrication (FFF) or pellets-based extrusion process, and no contraindications have been found for the use of water debinding with this technology.

The recipe and method used for these experiments is inspired by the work of Manam et al. [3]. The aim is to prove that the materials used in MIM for water debinding can also be used in additive manufacturing with similar results.



Figure 1 : Manufacturing process in Hot Metal Extrusion or pellets extrusion process

II. METHODOLOGY

The powder used in this research is a commercial SS 316L gaz atomized powder (Oerlikon metco). The particle size is on average 31.59 microns (Table 1) and the shape of the particles is round (Fig. 3). PMMA was supplied by Polymix and PEG 4000 by Zundel. The pellets are loaded with 80 wt.% metal. The binder composition used was 60 wt. % of PMMA and 40 wt.% of PEG 4000. The melting temperature is determined by DSC analysis (Fig. 4 and Fig. 5).

TABLE 1 : 316L STAINLESS STEEL POWDER PARTICLES SIZE DISTRIBUTION

D10 (µm)	D50 (µm)	D90 (µm)
19	32	52

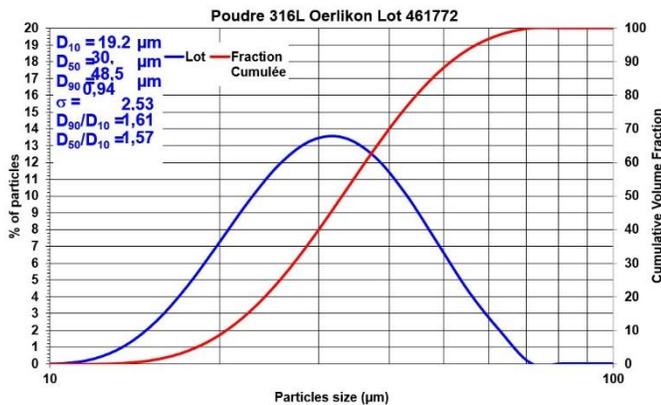


Figure 2 : 316L Stainless Steel particles size distribution

TABLE 2 : CHEMICAL COMPOSITION OF 316L STAINLESS STEEL POWDER

Elements	Mass (wt.%)
Cr	17.09
Mo	2.39
Si	0.55
Mn	0.85
Ni	10.58
P	0.010
C	0.007
S	0.005
O	0.057

TABLE 3 : BINDERS USED AND THEIR PARAMETERS.

Binder	Melting temperature (°C)	Density (g/cm ³)
Polymethyl Methacrylate (PMMA)	93.32	1.18
Polyethylene Glycol 4000 (PEG)	65.40	1.2

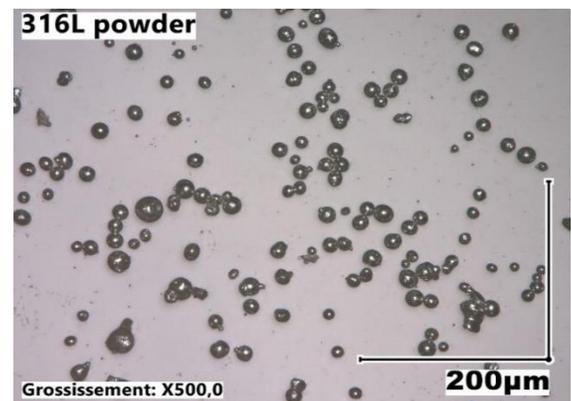


Figure 3 : Photo of the 316L stainless steel powder used

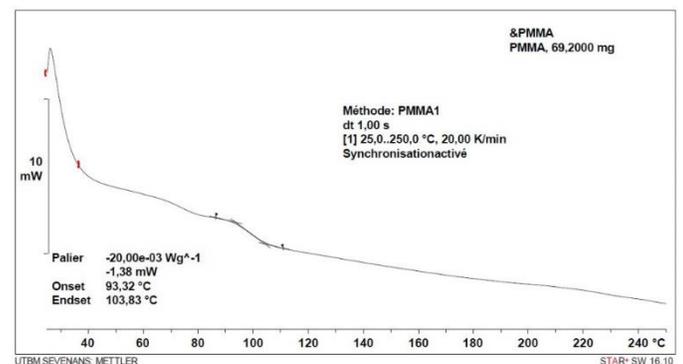


Figure 4 : DSC analysis of PMMA

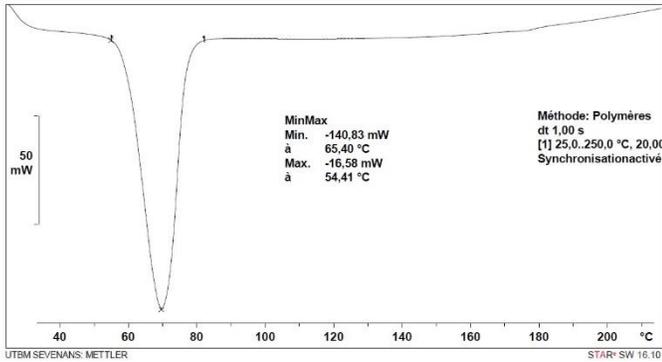


Figure 5 : DSC analysis of PEG

Before extruding the pellets, the mixture of PMMA and PEG 4000 binder is placed in an oven at 75°C for 40 min. The mixture is regularly stirred by hand to ensure homogeneity. After cooling the mixture at room temperature, the extrusion of the pellets is carried out. The extruder used is a Thermo Fisher twin-screw extruder (Process 11). As the melting temperatures of each binder are below 100°C, the extrusion temperature does not exceed 100°C to avoid damaging the binders. In addition, when the temperature is too high, the binder mixture is too liquid, and manufacturing pellets is impossible. The pellets are extruded at a speed of 30 rpm. The extrusion rate is set at 0.4 kg/h for the metal powder and 0.1 kg/h for the binder mixture. The subsequent pellets are then used in a 3D pellet printer (Fig. 6). The printing parameters used are given in Table 4. The printed parts are then immersed in distilled water for 12h at various temperatures (40°C, 50°C, 60°C, 70°C, 80°C). The printed parts are then dried and weighed every 2h to measure PEG 4000 mass loss over time. To dry the parts, they are left to air dry for a minimum of 12 hours.

TABLE 4 : PRINTING PARAMETERS

Nozzle size (mm)	1.2
Printing temperature (°C)	230
Building platform temperature (°C)	60
Infill (%)	100
Layer height	0.4
Infill pattern	Gyroid
Speed (mm/s)	5

III. RESULTS AND DISCUSSION

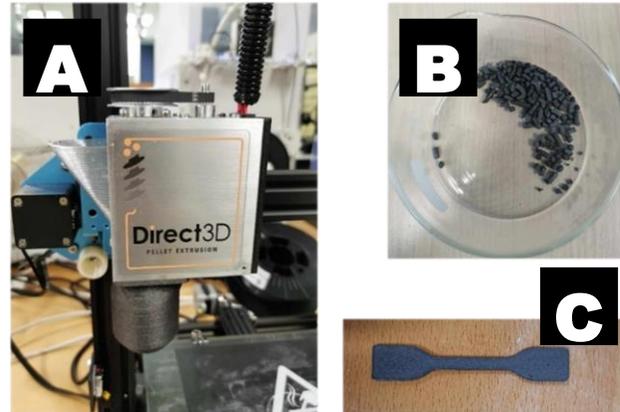


Figure 6 : (A) 3D pellets printers, (B) Feedstock for 3D printing and (C) the specimen printed by pellets additive manufacturing process

Fig. 6 shows the feedstock used for printing and the final results of the printed part. The water gradually diffuses into the binder (PEG), reacts with it and dissolves it, creating interconnected pore channels (Fig. 7) that facilitate evaporation of the remaining binder during the sintering stage. As time goes on, the pore network tends to extend deeper and deeper into the core of the part and the water takes longer and longer to reach the core of the part, so the rate of debinding decreases. 80°C seems to be the best choice of temperature (Fig. 8) of the PEG is then degraded. However, at this temperature, the deformation of the part is observed. Indeed, we observe the curvature of the part and cracks. At 40°C, PEG 4000 degradation is too slow. The higher the temperature, the more defects appear. Furthermore, with a too low temperature, PEG does not dissolve. The best compromise must be found. The percentage of mass loss in PEG after 12 hours is the same for temperatures 50°C, 60°C and 70°C (approximately 80% mass loss in PEG). It is therefore best to choose a temperature of 50°C or 60°C in order to have optimal debinding.

The formula used to calculate the percentage of PEG mass loss is as follows:

$$\%m_{PEG\ loss} = 100 - \left(\frac{m_{PEG\ after} \times 100}{m_{PEG\ initial}} \right) \quad (1)$$

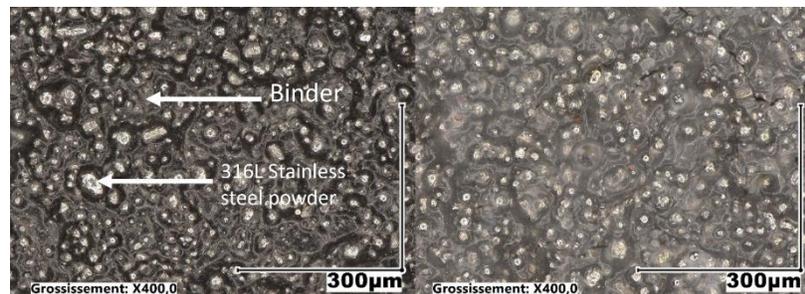


Figure 7 : Optical microscope observation of part surface before and after debinding (magnification x400)

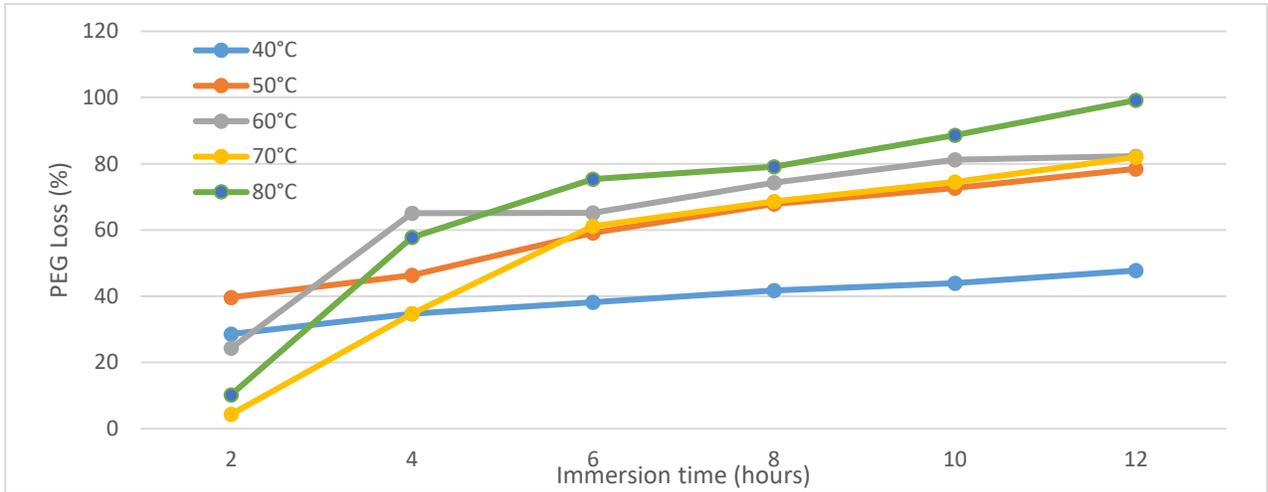


Figure 8: PEG degradation rate as a function of immersion time and temperature

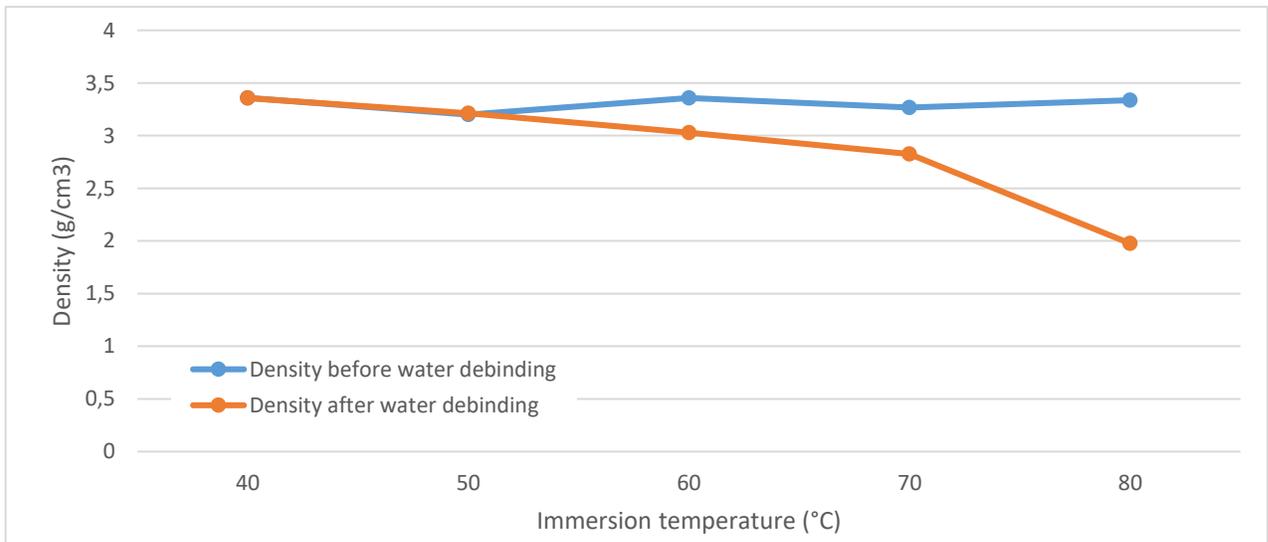


Figure 9: Density of parts before and after water debinding

The relative density of the parts is calculated according to Archimedes' principle which says that any body immersed in a liquid in equilibrium undergoes from this liquid a vertical thrust oriented from bottom to top equal to the weight of the liquid displaced. The relative density is calculated with the following formula:

$$\rho = \frac{A}{A-B} \times \rho_0 \quad (2)$$

with ρ = density of the solid
 A = weight of solid in air
 B = weight of the solid immersed in the liquid

ρ_0 = density of the liquid at the given temperature (0.997 g/cm³ at 25 °C for water)

The variation in part relative density is particularly noticeable at temperatures above 60°C (Fig. 9). The change in relative density is further proof that the PEG has dissolved.

IV. CONCLUSION AND PERSPECTIVES

It has been demonstrated that water debinding is not only compatible for use with MIM technology but also with additive manufacturing. With PEG and PMMA as mixture of binders, the



temperature of the twin screw extruder must not exceed 100°C so as not to degrade the components. Above 100°C the mixture is too liquid to be extruded correctly and the manufacture of pellets is impossible. No problem is encountered when printing the parts. It is not recommended to exceed 70°C during debinding as this could cause deformations and cracks to appear. Consequently, for optimal PEG degradation, a temperature between 50°C and 70°C is recommended. To have more precise and repeatable results, other experiments will be carried out. In particular, the extrudability of the binder mixture during the manufacture of the filament and during printing will be studied by varying the quantity of PEG in the binder mixture.

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