Processing of Water-atomised 316L Stainless Steel Powder Using Metal-injection Processes

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Abstract: A water-atomised 316L stainless steel (SS) powder has been evaluated for physical and mechanical properties in a metal-injection moulding (MIM) process using the locally-based binder system palm stearin (PS). The results of the powder characterisation and feedstock preparation assays essentially conform to MIM processing standard requirements. Injection moulding was conducted successfully using a powder loading of 0.62. Solvent extraction and thermal methods were used for binder de-binding. The results show that water-atomised powder could be sintered to 95% of its theoretical density under tested sintering conditions (1360°C, 1 hour). Specimens composed of water-atomised powder exhibited large shrinkage due to the lower green density that is associated with the poor packing properties of the powder. The sintered specimen of water-atomised 316L SS that used the PS-based binder system nearly achieved Metal Powder Industries Federation (MPIF) Standard 35.

Keywords: metal-injection moulding, water-atomised 316L SS, rheological behaviour, debinding, sintering

1. INTRODUCTION

The application of metal-injection moulding (MIM) to stainless steel (SS) samples is of great benefit to the metal industry because of the increased shape complexity compared to the casting process, material utilisation and achievable high final density. The MIM process is composed of four sequential steps: mixing of the powder with an organic binder, injection moulding, de-binding (binder removal) and sintering.1

It has been established that gas-atomised SS powders are suitable for MIM processing because of their high packing densities and associated feedstock rheologies.1–6 However, disadvantages of gas-atomised powders, such as the cost and low interparticle friction, which affects component shape retention, do exist. In contrast, Kipphut and German in 1991 reported that water-atomised powder has improved shape retention because of its lower cost and non-spherical particle shape, which creates higher interparticle friction.7 Even with improved shape
retention, the use of water-atomised powders is challenged by their lower solid-loading potential and lower sintering densities. Additionally, water-atomised powders have specific mechanical and corrosion degradation characteristics, which in turn increase the challenges of using them. Studies reveal that injection-moulded and sintered components that use water-atomised 316L SS powders have similar particle characteristics (residual porosity of 3%-5%) and sintering conditions to those of gas-atomised powders. Most investigations of the water-atomised powders via injection moulding have achieved up to 97% of the theoretical densities with paraffin wax, polypropylene and stearic acid binder systems.1-6

Istikamah7 reported that gas-atomised 316L SS powder homogenously mixed with palm stearin (PS) and polyethylene (PE) can be injection-moulded and that these samples can be successfully sintered without any defects on their component parts. Additionally, all experimental densities approach their full theoretical density. An advantage of this biopolymer binder is that PS is naturally occurring and environmentally friendly. The binder system has also been shown to shorten the overall de-binding process through the use of solvent extraction techniques.8,9

With these characteristics in mind, this study sought to compare potential cost differences in manufacturing by testing water-atomised powders mixed with PS/PE during the mixing, moulding, de-binding and sintering stages.

2. EXPERIMENTAL

The powders used in this study were water-atomised 316L SS powders. The chemical compositions of the powders are shown in Table 1, and all powder characteristics are listed in Table 2. As shown in Figure 1, the powders can be characterised as rounded and irregular in shape. The powder loading levels used were 62 vol%.5 The binder system composition was 70 wt.% PS/30 wt.% PE.7 The powder and binder system mixing processes were carried out using a sigma-blade mixer set at 160°C and with incubation times of 2 hours. Then feedstock was granulated to pellet form to ease feeding into the injection-moulding machine. The feedback viscosity was calculated using a Shimadzu CFT-500D (Japan) capillary rheometer. During the capillary rheometer test, feedstock was forcibly extruded through a small cylindrical orifice of 1.0 mm diameter and 10 mm length (L/D=10). Tests were conducted at 130°C, 150°C and 160°C. Tensile specimens were prepared using a vertical injection-moulding model, MCP HEK-GMBH (Germany). During the moulding stage, temperatures and injection pressures were adjusted until the optimum conditions were obtained. The green
parts present very good homogeneity as deduced from the SEM observation and from green density values.

Table 1: The chemical composition of water-atomised 316L SS powder.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.025</td>
<td>0.81</td>
<td>0.81</td>
<td>0.021</td>
<td>0.011</td>
<td>16.47</td>
<td>12.49</td>
<td>2.09</td>
</tr>
</tbody>
</table>

Table 2: Characteristics of water-atomised 316L SS powder.

<table>
<thead>
<tr>
<th>Item</th>
<th>316L SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vendor</td>
<td>ATMIX</td>
</tr>
<tr>
<td>Shape</td>
<td>rounded and irregular</td>
</tr>
<tr>
<td>Particle size (μm);</td>
<td></td>
</tr>
<tr>
<td>( D_{10} )</td>
<td>3.4</td>
</tr>
<tr>
<td>( D_{50} )</td>
<td>10.79</td>
</tr>
<tr>
<td>( D_{90} )</td>
<td>29.22</td>
</tr>
<tr>
<td>Width of distribution ( S_w )*</td>
<td>2.74</td>
</tr>
<tr>
<td>Specific surface area ( m^2/g )</td>
<td>0.11</td>
</tr>
<tr>
<td>Pycnometer density ( g/cm^3 )</td>
<td>7.9</td>
</tr>
<tr>
<td>Tap density ( g/cm^3 )</td>
<td>4.44</td>
</tr>
</tbody>
</table>

Note: \( S_w = 2.56 \log (D_{90}/D_{10}) \)

Figure 1: SEM micrograph of water-atomised 316L SS powder.

During processing, PS binder was removed by solvent extraction techniques. Here, binder samples were incubated in n-heptane solution (100%) for 5 hours at target temperatures of 40°C, 60°C or 80°C. Binders were then subjected to a thermal de-binding procedure where the organic binder PE was completely removed by heating the binder sample to 450°C at a heating rate of
3°C/min, with a holding time of 2 hours. Sintering was then carried out using a high temperature vacuum furnace where the specimens were sintered at 1360°C at a heating rate of 5°C/min. All sintered samples were then characterised to evaluate the physical and mechanical characteristics of 316L water-atomised powders mixed with a local binder system of PS to evaluate the potential for high packing densities in these samples. Physical measurements were performed on sintered specimens using the tensile test on a Universal Testing Machine (UTM; Instron, USA) machine. Hardness tests (mechanical testing) were carried out using a Vickers (Mitutoyo, Japan) micro-hardness tester with an applied load of 100 gf. Density measurements were then performed on sintered parts applying the Archimedes method, using specific gravity meter. Metallographic observations of sintered specimens were carried out using an optical microscope at a final magnification of 500x. Before samples were observed, thorough sample preparation methods were applied. These included cutting, mounting, grinding, polishing and finally etching the samples.

3. RESULTS AND DISCUSSION

3.1 Rheological Characterisation

In MIM, the rheological properties are important as the sample flow properties affect the flow properties of the feedstock during injection-moulding. Rheological analysis can also be used to quantify the stability of the feedstock during the moulding process.\(^1\)

The viscosity of powder-binder mixtures is very sensitive to temperature and the amount of powder that is loaded into the mixture (powder loading). At low temperatures, mixture viscosities may be too high to allow further processing to the moulding step. At high temperatures, the binder may be too thin, resulting in separation of the powder and binder. For moulded parts, high temperatures also can lead to chemical degradation of the binder polymer and material property changes that could cause physical degradation such as cracking. Therefore, a range of conditions exists over which MIM processing is most viable. Within this range, the mixture exhibits pseudoplastic flow (viscosity decreases with increasing shear rate), and this flow property can help to reduce the required temperature and required pressure for successful moulding.\(^2,3\) It is known that pseudoplastic flow behaviour aids mould filling procedures by minimising jetting and helping to retain the shape of the moulded part.

In the MIM process, the shear rate during moulding usually ranges between 100 and 10000 s\(^{-1}\). Empirical studies have shown that within this shear rate range, maximum viscosities for moulding approach 1000 Pa.s at the
moulding temperature. Capillary rheometers are widely used to characterise the rheological behaviours of MIM feedstocks. The rheological results of the feedstock in this study are shown in Figure 2. We found that sample feedstock viscosities decrease with increasing shear rate. This behaviour is generally called pseudoplastic flow. In our study, the non-spherical morphologies of water-atomised powders gave higher viscosities in all temperatures tested when compared to gas-atomised powders.

Sample viscosity is also temperature sensitive. As temperatures increase, there is a noticeable decrease in the feedstock's viscosity. This phenomenon is mainly due to both a decrease in the powder volume caused by larger heat-induced binder expansion and a disentanglement of the polymer's molecular chain to more random molecular conformations. When the shear rate varied from 100 to 10000 s\(^{-1}\), the viscosity of the feedstock fell below 1000 Pa.s. Thus, the feedstock was considered suitable for injection moulding.

![Figure 2: Viscosity vs. shear rate of MIM feedstock containing water-atomised powder.](image)

### 3.2 Injection Moulding

After several trials, the feedstock was successfully injection moulded, with the nozzle temperature at 210°C and the injection pressures reaching 30 MPa. Overall, the total cycle times for each injection averaged 6 seconds. Figure 3 shows the tensile shape of the injection-moulded parts with a single gate that is located at one end of the part. Our study used a moulding temperature much higher than that used in other reports (100°C to 200°C). Nevertheless during injection, all injection parts remained free from normal defects, such as short shot, flashes at the parting surface and binder separation. To ensure that the
feedstock could flow and be moulded easily, a higher temperature was needed to compensate for the high viscosity of the feedstock.

![Figure 3: Injection-moulded part (green); tensile specimen.](image)

Figure 4 clearly shows the SEM micrograph of green-coloured and successfully processed parts at two different regions: (a) the fracture and (b) the outer surface. In the mixture, binder is seen filling interstitial spaces between powder particles. Spherical and irregular shapes of powders can be seen in fractures of water-atomised green parts. Data from SEM clearly support that the outer surface [Fig. 4 (b)] was filled with more binder than the fracture surface [Fig. 4 (a)]. Many pores can be seen in Figure 4 (a), and the binder flow seems to be non-directional. Further SEM analysis revealed [Fig. 4(b)] that binder flow is clearly more directional compared to other binder. We hypothesised that the presence of pores or voids between the atomised particles was caused by entrapped air and/or binder shrinkage during the cooling process.

At the end of moulding procedure, the binder provides a mechanical interlocking to the particles that gives the compact shape and the necessary handling strength. The SEM micrograph in Figure 4 clearly shows the green specimens at two different regions, at the fracture surface and on the outer surface, for three different particle sizes. The micrograph shows binder filling practically all the interstitial spaces between the powder particles. In addition, the outer surface is filled with more binder than the fracture surface. This is due to a greater feedstock contact with the cavity wall, which is the area where solidification first occurs.

Generally, after the mould is filled, heat is extracted from the feedstock through the die. As illustrated in Figure 5, the heat flow is directed towards the wall. Because the wall is the coolest portion of the sample, heat will flow from the hot zone to the cold zone. The combination of high applied pressure, low viscosity, and rapid die-filling rates led to a trapped air defect in the moulded specimen.
Figure 4: SEM micrograph shows the distribution of the PS/PE binder system on injected parts: (a) fracture site and (b) outer surface.

Figure 5: A schematic of the dissipation of heat through the mould.

The average green density of green parts is 5.01 g/cm³ which is 92.9% of the theoretical maximal density for these mixtures. The less intense green region of the moulded parts is therefore associated with poor packing abilities of the powder. Interestingly though, the moulded parts are free from normal defects.
3.3  De-binding Process

For safe and rapid binder removal and to minimise the possibility of crack and blister formation, solvent de-binding followed by thermal debinding was performed. The chosen binder for our studies, PS, had components that exhibited lower stability and thus were removed in the early stage of de-binding. The removed components, it is believed, generated pore channels inside the material that allowed gas degradation products and allowed remaining binder to harmlessly diffuse out of the structure. The remaining PE binder held particles together during and after extraction to maintain the material's overall shape.

Solvent extraction was performed in n-heptane solvent at different temperatures (Fig. 6). The results indicate that increasing the solvent temperature increases the removal of the end amount of PS product from the green parts. It was observed that leaching at 40°C and 60°C provided better shape retention than leaching at 80°C, which led to slight shape distortion. It was also observed that all samples exhibit good shape retention and better handling for thermal pyrolysis. The data indicate that the best solvent temperature to yield shape retention and handling improvements fell within the range of 50°C to 80°C. High solvent temperatures caused softening effects to the second binder of the materials. This in turn antagonises the function of the second binder and promotes strength in the components after the first stage of de-binding. During solvent extraction, palm stearin and heptane were soluble in each other. Consequently, at higher temperatures, the de-binding rates increased because of higher diffusivity. Figure 6 also shows that at 40°C, approximately 4% to 5% of the PS binder stays in the component, unable to be removed. This clearly supports the requirement for leaching temperature of 60°C.

Because all the PS was removed in the solvent de-binding steps, thermal debinding was performed with a higher speed compared to the usual thermal debinding process. The remaining binder, PE, was removed by thermal pyrolysis (heating rate of 5°C/min to 450°C and held for 1 hour).

3.4  Sintering Process

3.4.1  Physical properties

In this stage, temperatures increase from 30°C to a final sintering temperature of 1360°C at a rate of 5°C/min under vacuum atmosphere. Then the sintering temperature is held for 1 hour. After sintering, our results did not support any signs of defects such as blister and crack in the specimens.
The results show that the average density of the sintered parts was 7.5 g/cm³, approximately 95% of theoretical density. The lower packing density of the water-atomised powder resulted in a lower total material density. Cai and German studied metal injection moulding of water-atomised 316L SS with paraffin wax, polypropylene and stearic acid as a binder system with 62 vol%. They reported a sintered density of 96% after sintering at 1370°C in a hydrogen atmosphere. This density increased to 98% as the sintering temperature increased to 1390°C. Thus to achieve higher densities and better mechanical properties of the sintered parts, processing conditions should be optimised.

Figure 7 shows the tensile fracture surface of the sintered specimen. A few isolated pores (closed pores) can be observed and are indicated by arrows in the figure. The low presence of closed pores suggests that they are a minor contributor to the fracture. The pores are closed, rounded and distributed almost uniformly.

Shrinkages were calculated by comparing the tensile sample dimensions at each stage to that of the die. The dimensions measured were length, which is parallel to the melt flow, and width, which is perpendicular to the melt flow and thickness and parallel to the mould opening direction. Figure 8 compares the shrinkage specimens of our experimental data and data from Cai and German.
Because the water-atomised powder was round and irregular in shape, there is a high probability of anisotropic packing with respect to the flow orientation. The thickness shrinkage in our samples is less than that of green samples, which also differs from Cai and German's observations. The length shrinkage of our experimental samples was higher than of the Cai and German samples, while the thickness shrinkage produced nearly the opposite result. These indicate a larger orientation effect in moulding exists in our experimental samples compared to those of Cai and German. This possibly could be due to the round and irregular particle shapes of our powders compared with the water-atomised particle used by Cai and German, which have a most irregular particle shape. However, as can be seen, shrinkage is almost equal in all three dimensions for our experimental samples, indicating that the feedstock is relatively homogeneous.

### 3.4.2 Mechanical properties

Table 3 shows the comparison of the experimental mechanical properties with MPIF Standard 35. From the results obtained, it can be concluded that the sintered specimen of injection moulding of water atomised 316L using PS based binder system nearly achieved the MPIF Standard 35, but further study considering different temperatures, cycle times and atmospheres is necessary to achieve high mechanical properties of sintered specimen.
Figure 8: The comparison of shrinkage specimen of experimental samples and data from the Cai and German samples.

Figure 9 shows the microstructure of water-atomised powder. The microstructure resembles grain, and the boundary pores remain irregular but rounded. The internal pores, however, are spherical. The micrograph also reveals different stages of pore-grain boundary separation, as indicated by the arrow.

Table 3: Mechanical properties of tensile specimens.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Experimental samples</th>
<th>MPIF standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HV)</td>
<td>222</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>443</td>
<td>≥ 448</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>42</td>
<td>≥ 40</td>
</tr>
</tbody>
</table>

Figure 9: Microstructure of a sintered part, 500x.
4. CONCLUSION

The water-atomised 316L SS powder was successfully injection-moulded using a palm-based binder system with the PE. Sintered specimens achieved a density of 95% of their theoretical maximum values. High powder loading (65 vol%) of water-atomised powder was expected to result in high density. However, high density was not only dependent on high powder loading but also reliant on the packing property of the powder. These results suggest that sintered properties of water-atomised powder can be achieved using high sintering temperatures.

5. ACKNOWLEDGEMENT

The authors wish to thank Ministry of Science, Technology and Innovation (MOSTI) for financial support under Technofun grant no. TF1208D168 and Science Fund grant no. 03-03-02-SF0124, and SIRIM Bhd.

6. REFERENCES

