

Investigation of Pre-thermal treatment and Surface Modification of Fine Metal Powder Feedstock on the Flowability and Agglomeration Behaviors for Binder Jetting Process

Jiemin Huang¹, Su Xia Zhang¹

¹ Singapore Institute of Manufacturing Technology, 73 Nanyang Drive, Singapore 637662
Corresponding Author / Email: huangjm@simtech.a-star.edu.sg

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The use of fine powder materials in powder-based additive manufacturing processes such as binder jet printing and selective laser melting is the most preferred as fine powders can print parts with smoother surface finish with better dimensional accuracy. Furthermore, the strength of green parts printed using fine powder is enhanced as thin powder layers can improve the inter-layer bonding and facilitate binder penetration into powder layers. Fine powder particles also facilitate the sintering process due to their higher driving force for densification. However, fine SS316L powders impose greater challenges as it is more prone to agglomeration issues which affects powder flowability and end properties. Hence, this paper mainly focuses on techniques to improve the flow behavior of pure fine SS316 powders and mixtures of fine SS316L and polymethyl methacrylate (PMMA) polymeric powders for binder jetting process to produce porous metals. Two approaches will be addressed. This includes improving the powder flowability and reducing the agglomeration of fine SS316L powders by modifying the surface with different percentages of polyvinylpyrrolidone 40 (PVP 40) as well as optimizing the processing conditions for mixtures of SS316 and PMMA powders. Firstly, the flowability of pure fine 316L powders can be improved by pre-thermal treatment at 120^o C and 180^o C in vacuum as BFE is reduced from 344mJ to 306mJ and 222mJ respectively. Modification of SS316L fine powder surface by using PVP 40 as surfactant can effectively reduce the agglomeration of fine SS316L powders as BFE values is reduced to 267mJ when 1.5 wt% PVP40 is used in conjunction with pre-thermal treatment at 120^o C. Pre-thermal treatment of as-crushed mixtures at 120^o C significantly reduces BFE value to 142mJ as heating allows polymer to soften and bind towards SS316L powders effectively, leading to better bonding affinity between PMMA and SS316L powders to form small and uniform agglomeration.

1. Introduction

Stainless steel (SS) 316L is the most commonly used austenitic SS and exhibits characteristics such as excellent corrosion resistance due to the formation of adherent chromium oxide layer, resistance to creep at high temperatures and great structural materials with good overall mechanical properties [1]. Hence, SS316L is widely used in industrial production and found in many applications such as aviation, petrochemical, porous materials, precision engineering parts and composite materials. SS316L is suitable for different powder metallurgy processes like powder compaction, metal injection molding and additive manufacturing processes.

Depending on the applications used and the properties to achieve, fine and coarse SS316L powders will be used as starting raw materials. Coarse SS316L powders are generally used due to the greater ease of processing. All powders can be classified under four Geldart Groups namely, A, B, C and D depending on the behavioural characteristics of powders. For fine particles with average particle size of less than 30 μm can be classified under Geldart Group C as it

is the most difficult to fluidise, has large specific surface area with strong interparticle forces and considered to have a high cohesive energy [2]. Particles under this group tend to behave more as particle clusters than single, independent particles [3]. Despite that, Geldart Group C powders have also been widely used due to the improvement in the properties and the special characteristics such as their large surface area to volume ratio. This results in the powder surface to be more active and hence, lowering the sintering temperature to achieve the same properties as compared to using coarse powders [4]. Thereby reduce the sintering energy consumption rate.

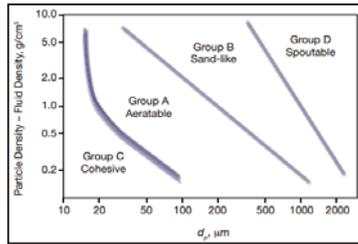


Figure 1: Geldart's classification of powders

However, finer particles impose some challenges as well. The agglomeration behavior of fine powders has always been a major concern and face many challenges in all the above-mentioned powder processing techniques. The degree of agglomeration will affect powder's uniformity, flowability and properties of end product.

Therefore, in order to improve the flowability and dispersibility of fine SS316L and PMMA powders as well as to reduce the agglomeration, various approaches are investigated in this paper, such as optimising the processing conditions and modifying the surface characteristics of fine particle from hydrophilic to hydrophobic using organic or inorganic additives.

2. Experimental Procedure

2.1 Raw materials of fine SS316L and PMMA powders

In this experiment, fine SS316L and PMMA powders from Hoganas and EPRUI Biotech respectively were used in this experiment. Analysis of the powder particle size distribution was conducted using laser scattering (Horiba LA-950 Laser Scattering Particle Size Distribution Analyser) and the average particle sizes of SS316L and PMMA powders used were $4.05\mu\text{m}$ and $4.63\mu\text{m}$ respectively. Table 1 tabulates the SEM images of the as-received SS316L powders under different magnifications. Most of SS316L powders are spherical with clear surface except some are in irregular shapes. Figure 1 shows the SEM images of as-received PMMA fine powders. The untreated powders are regular and spherical in shape.

Table 1: SEM images of as-received pure fine SS 316L powders under 1kx, 5kx and 10kx magnifications

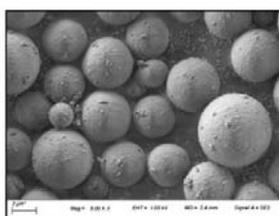
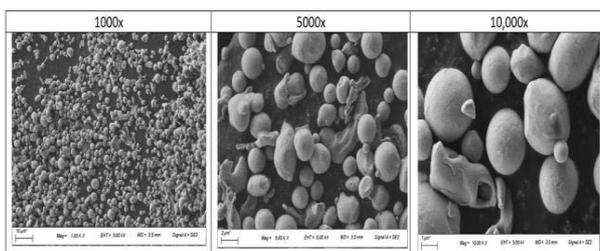


Figure 1: SEM images of as-received PMMA fine powders

2.2 Powder Processing Conditions

There are two approaches applied in this paper to resolve the

agglomeration issue and improve the flowability. The first approach focuses on optimising the processing conditions. In this paper, the feedstock mixture of SS316L and PMMA powders was prepared in three steps. Firstly, prior to using the powders, fine PMMA and SS316L powders were preheated in an oven at 60°C and 100°C respectively to remove the presence of moisture over 24 hours. Secondly, desired amount of fine SS316L and PMMA powders were dried mixed in a tumbler mixing machine with stainless steel grinding balls as medium to break up the agglomerates.

Thirdly, polyvinyl butyral (PVB) was added as binder and dissolved using ethanol with presence of heat in water bath at 70°C . The dissolved PVB was then added into the dry mixed mixtures of fine SS316L and PMMA powders. Tumbler mixed was done for another 24 hours to get a uniform slurry. The slurry was then dried in a heated double planetary mixer to remove the solvents. The dried mixtures of powders were then crushed into finer particle size for further processing steps.

The second approach is the surface modification of fine SS316L powders by using different percentages of PVP 40. In this approach, fine SS316L powders was firstly ball milled in the same tumbler mixing machine with SS balls for 3 hours to break up any presence of agglomerates. The milled powders were then mixed with different amount of PVP 40 (0.5wt%, 1.0wt% and 1.5wt%) to modify surface conditions of fine SS316L powders.

In order to get uniform coating on SS316L powders, PVP 40 was dissolved in ethanol before introducing into the milled SS316L powders. The mixing was then continued in the tumbler mixer for another 3 hours followed by drying in the double planetary mixer. After drying, the mixtures of SS316L powders and PVP 40 were then heated at 120°C in a vacuum oven for 12 hours and sieved afterwards. In order to check on the flowability of powders by using the two approaches mentioned, characterisations will be done.

2.3 Analysis and Characterisations of powders

In this paper, the Basic Flowability Energy (BFE) and Specific Energy (SE) properties of powders were characterised using FT4 Powder Rheometer (Freeman Technology, Gloucestershire, UK).

BFE is used to measure a powder's flow properties when the powder is in a loosely packed state. In this measurement with FT4 Powder Rheometer, a rotating blade will move in a downward direction from the top of the vessel to the bottom across the loosely packed powders transversely in the vessel. For powders with poor flowability, the blade will experience greater resistance to cross the powder and greater amount of work is needed to counter against the resistance, leading to higher BFE value [5].

On the other hand, lower BFE represents powder with good flowability and indicates lower amount of work done and force needed for the blade to overcome the resistance of powders to move in a downward direction. Hence, indicating better flowability of powders. Simultaneously, BFE value of the powders is dependent on some of the particle variables such as the size and distribution, shape, texture, moisture content and surface additives [5].

SE is used to define as the energy needed to break up the interlocking energy within powders. In this measurement, the higher

Table 2: Degree of cohesiveness of powders depending on the range of SE values

SE < 5	Low cohesion
5 < SE < 10	Moderate cohesion
SE > 10	High cohesion

energy is needed to break up the interlocking between particles [5]. SE is also used to relate the cohesiveness of powder and other physical properties such as particle size, shape and texture.

3. Results and Discussion

3.1 Effects of Processing Conditions on Fine pure SS316L Powders Flowability

Figure 2 shows the graph where BFE properties is plotted against the processing conditions for fine pure SS316L powders. Fine pure SS316L with average particle size of 4.05 μm will undergo different processing temperatures to determine which temperature after sieving is able to achieve better flowability. As seen from figure 2, the as-received pure SS316L powders has the highest BFE and SE values of 344mJ and 5.71 mJ/g respectively.

As the powders heated at 120°C with vacuum and after sieving, the BFE values decreased significantly from 344mJ to 306mJ with a lowering in SE value from 5.71mJ/g to 5.2mJ/g. BFE value of 222mJ is the lowest for powders that was being heated at 180°C with vacuum after sieving. The improvement in its flowability is probably due to the removal of moisture as one of the factors affecting the BFE is the presence of moisture in this case. However, pre-thermal treatment of pure SS316L powders is insufficient in preventing moisture, and issues like agglomeration and poor flowability may occur again due to reabsorption of moisture after exposing in air. Hence, alternative approach should be carried out.

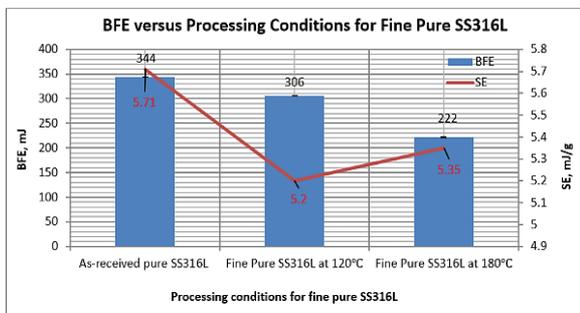


Figure 2: Effects of processing conditions on fine pure SS316L flowability

3.2 Effects of varied percentages of PVP 40 and the effects of with and without heating at 120°C on BFE and SE values

Processing of fine pure SS316L powders has shown to be significantly challenging in terms of powder spreading and recoating in binder jet printing. Finer powder materials often exhibit insufficient flowability due to high inter-particle cohesive forces and absorb moisture very quickly to form agglomerates, which in turn impedes an even and smooth spreading and recoating of the subsequent layers. Hence, this highlights the main objective of this experiment which is to study how the addition of PVP 40 as surfactant helps to reduce the soft agglomerates behavior of SS316L fine powders effectively and efficiently and to determine the optimum amount of PVP 40 that should be added to the mixtures and thereby improving the flowability of fine SS316L powders [6].

Fine SS316L powders did not undergo any heating and vacuum prior to the powder preparation process. This was done to see if the flowability of powders can be improved with the addition of PVP even without heating and vacuuming. By referring to figure 3 below, for powders without prior heating, BFE values for powders with 0.5wt% and 1.0wt% PVP 40 are 451mJ and 454mJ respectively which is so much higher than as-received pure SS316L powder, with BFE value of 344mJ. However, upon adding 1.5wt% PVP 40, the BFE value reduces more significantly to 298mJ. This shows that even if no prior heating was done for SS316L powders, the addition of 1.5wt% PVP40 is enough to lower the BFE value greatly to 298mJ.

Hence, the addition of 1.5wt% PVP 40 is more significant in lowering the BFE and improve the flowability of powders. Simultaneously, BFE value further decreases to 267mJ with additional prior heating at 120°C.

For the as-received powders, even if there is prior heating done to the powders, the change in the BFE value is not as significant due to the absence of PVP 40, as BFE value decreases from 344 mJ to 306mJ. However, large significant change in the decrease in BFE values can be observed for powders with 0.5wt% and 1.0wt% PVP 40 after heating at 120°C.

Therefore, this may indicate that the result shows a more pronounced effect in lowering the BFE value when PVP 40 is used in conjunction with the application of heat at 120°C. While without PVP 40, the change in BFE value is minimal and hence, heating at 120°C is an essential step to achieving better flowability powders along with addition of PVP 40. Therefore, the lowest BFE value achievable is 267mJ when using 1.5 wt% PVP 40 with heating at 120°C.

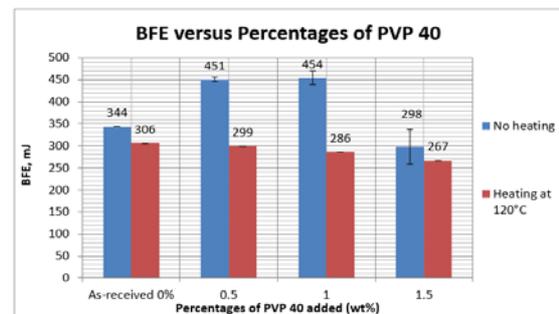
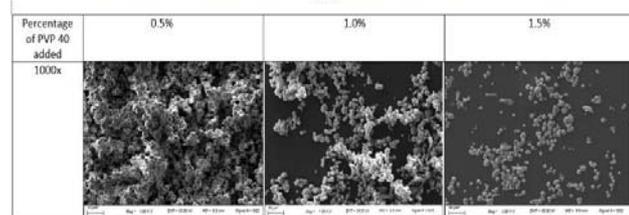


Figure 3: Effects of different percentages of PVP on BFE with and without heating at 120°C

Furthermore, by referring to SEM images from table 3, as percentage of PVP40 increases from 0.5wt% to 1.5wt%, there is an obvious improvement in the degree of agglomeration on fine SS316L powders. Hence, SS316L powders with 1.5wt% of PVP 40 showed that it is able to prevent large clusters formation and powders are more dispersed.

Table 3: SEM images with different percentages of PVP 40 in fine SS316L powders after heating in vacuum oven and sieved



3.3 Effects of processing conditions for fine crushed powders on flowability

Another approach is to study the effects of temperatures on the flowability of SS316L and PMMA crushed powders. Powders are heated at 40°C, 120°C and 180°C for 12 hours and then followed by sieving using 325 mesh. BFE and SE values of treated powders at different temperatures were shown in figure 4. As-received crushed powders with high BFE and SE values of 231mJ and 7.42mJ/g respectively indicate poor flowability.

However, the heating of crushed powders at 40°C further increases the BFE value to 283mJ along with the increase value of SE to 7.71mJ/g, which is unexpectedly higher than the as-crushed powders without heating. For powders heated at 120°C and 180°C, the BFE value dropped significantly to 142mJ and 156mJ respectively along with an obvious lowering in SE values to 4.91mJ/g and 4.85mJ/g respectively.

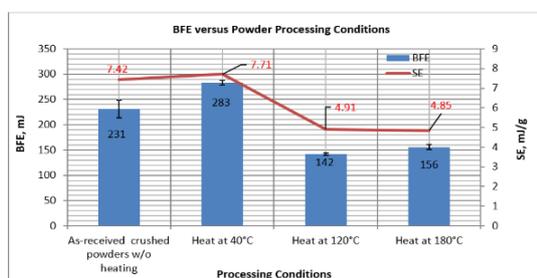


Figure 4: Effects of processing conditions for fine crushed powders on the flowability

From table 4, it was observed that the crushed powders heated at 120°C showed better polymer binding affinity towards SS316L fine powders and powders slightly agglomerated and grew larger in size. As the purpose of heating at 120°C followed by sieving is to allow the polymer within powders to become soften and bind towards the metallic particles. By doing this, it is possible to promote better bonding affinity towards fine SS316L powders and to reduce the overall surface area to volume ratio. Thereby increasing the particle size to prevent the degree of agglomeration between the metallic particles. Hence, achieving the lowest BFE value of 142mJ.

While crushed powders heated at 180°C could be considered as aggregates because they are more dispersed with fragments consisting of small clusters of polymer and SS316L fine powders. Therefore, this shows that the bonding affinity between polymer and metal powders heated at 180°C is weaker and is more loosely compacted together than powders heated at 120°C. Thus, it explains for the poorer flowability properties obtained for powders heated at 180°C.

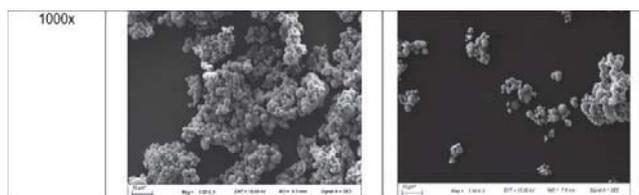


Table 4: Comparing the particle morphology between crushed powders heated at 120°C (left) and 180°C (right) under magnifications of 500x and 1kx respectively

4 Conclusion

In this work, the effects of how powders processing conditions and chemically surface modified powders affecting the flowability of fine SS316L and PMMA powders were addressed. Two different techniques have been considered to reduce the values of BFE and SE and the reduction of the cohesiveness of fine SS316L and PMMA powders: firstly, heating and vacuuming of SS316L and PMMA powders at 120°C instead of 180°C is due to better bonding affinity between PMMA and SS316L powders to form small and uniform agglomeration as shown in SEM images above.

Secondly, prior heating of pure SS316L powders at 180°C to remove as much moisture content as possible before mixing with PMMA and finally, SS316L powders with 1.5wt% PVP 40 used in conjunction with the application of heat at 120°C shows a more pronounced effect in lowering the BFE value greatly. Hence the above methods demonstrated have been proven effective in improving the flowability of fine SS316L and PMMA powders and reduce the degree of agglomeration in fine SS316L powders.

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