XPS, XRD, and SEM characterization of the virgin and recycled metallic powders for 3D printing applications

N E Gorji, R O’Connor and D Brabazon
Dublin City University, I-Form Advanced Manufacturing Research Centre, Dublin 9, Ireland
E-mail: nima.gorji@i-form.ie

Abstract. We characterized the surface and microstructure of both feedstock (virgin) and recycled Stainless Steel 316L powders used for selective laser melting process. Reusing the recycled powders can significantly reduce the powder consumption, production cost and time. We have performed X-ray photoemission spectroscopy (XPS), Scanning electron microscopy (SEM), X-ray Diffraction (XRD) and rheology analysis on steel powders both on the virgin powder and the powders not adhered to the printed parts but recycled in the powder bed. The results confirm that the oxygen level on the surface of the recycled powder is increasing and the metallic oxides diffuse out to the surface of the powder particles during the manufacturing process. Nevertheless, the changes are not significant which promise the reusability of the recycled powders for several cycles. We observed no change on the phase of the recycled powder. Further characterizations are ongoing to measure the chemical composition and morphology of both virgin and recycled powders to correlate them with the mechanical properties of the printed parts. These characterizations allow extending the powder reuse for a number of reusing cycles and reducing the manufacturing time and cost without reducing the mechanical properties of the final parts.

1. Introduction
Advanced manufacturing (AM) and 3D printing of metallic parts has attracted much attention of many industries ranging from biomedical to aviation. Reducing the manufacturing time, promoting the mechanical strength of the 3D printed parts and reducing the materials waste from AM process is now the critical aspects of the R&D sector of these industries [1]. Selective laser melting of the powder to the substrate and solidification process leaves a significant portion of the powder unused. There is a debate in literature that the recycled powder (non-solidified powder) can be reused for other layers build-up if there is no significant change on its surface composition, bulk and microstructure. Reusing the non-solidified powder could potentially contribute to process sustainability and manufacturing cost-cut [2]. However, risk-intolerant industries such as aviation and some biomedical applications do not consider reusing the recycled powder due to quality concerns. Nevertheless, as long as the mechanical properties of the final printed parts made of recycled powders (or a mix of virgin and recycled powders) are not significantly different than the ones made of solely virgin powders, we can consider the reusing the non-solidified powders in 3D printing process [3]. Characterization techniques are vital to ensure the particle size distribution, oxidization and surface/bulk composition of the recycled powders for a certain powder alloy in order to confirm its degree of change and degradation through the process. Very recently, articles are published on characterization of recycled powders and number of cycles being used for various applications [4, 5].
Galicki et al have characterized the microstructure and rheology of both virgin and reused 316 stainless steel and reported that the recycled powder (including spatter) have a significantly higher oxygen pick up [6]. Similarly, Heiden et al reported a slightly increase in oxygen content on the reused powders but minor changes to its size distribution, bulk composition, and hardness [7]. Nevertheless, several research groups have reported that there is no significant change on oxidation level of reused powder and even that small increase might be due to turbulence in oxygen level in the manufacturing chamber during the deposition process [8, 9]. XPS analysis show that the oxide sensitive elements such as Cr, Mn, and Fe tend to diffuse out to the particle surface in reused powders [9]. The size of the reused powders changes slightly for a certain build cycles. However, the powder particles see more satellites and porosity on the surface of recycled powders. They reported no consistent trend in the mechanical strength and ductility relative to powder reuse for up to twelve cycles of reuse [10]. The National Institute of Standards and Technology (NIST) has also reported that the recycled powder reveals no significant changes in its tensile, mechanical, materials properties, particle size distribution (PSD), and particle shape but apparent density and the martensitic-ferritic phase in the predominately austenitic S17-4 PH powder increases during 11 times reuse [11].

Here we present our surface and microstructure characterizations on Stainless Steel 316L powder of both virgin and recycled states which has been used for selective laser melting of several parts. Comparing the surface composition and microstructure variation of the virgin powder during the additive manufacturing elucidates if the recycled powder can be reused for printing the parts and if that will still ensure the desired mechanical properties of the printed parts. This would also provide a guide if we should add virgin powders to the recycled powder before we reuse it as the mechanical strength of the printed part remains in an acceptable level then.

2. Materials and methods
The Steel powder was purchased from commercial producers EOS and Castolin Ltd. and the powder average particle size are 60 μm. The particle size was analysed by Malvern Mastersize. The surface composition were characterized by our VG Microtech electron spectrometer, at base pressure of 1×10⁻⁹ mbar, and a conventional Mg Kα (hν= 1253.6 eV) X-ray source. The XPS curves were fitted using CASAxsps software. The analysis was calibrated to carbon peak. No chemical treatments were conducted on the particles prior to XPS scans in order to reduce the surface contamination. The acquisition conditions were 20 eV pass energy, at 0.1 eV step 0.1 eV and 30° take-off angle. We also performed microstructure analysis using EVO-LS15 Scanning Electron Microscope (SEM). For these measurements we dipped the carbon pad onto the powder kit and mounted that into the characterization chambers. Degassing of the powder particles delayed bringing down the vacuum inside the characterization chambers. The recycled powders were sieved for particles bigger than 80 μm before characterization, however, some spatters were still present in sieved. The apparent density of the virgin powder is 4.11 g/cm³. X-ray diffraction (XRD) has been performed on both virgin and reused powders using a Bruker Bede D1 X-ray Diffractometer with a scan speed of 2.0°/min for the 2θ range from 40°-100° to evaluate the phase and plane orientation of the austenitic Steel powders before and after SLM process. The X-ray source is Cu Kα and powder was filled in a cavity mount. The EOSINT M280 SLM 3D machine has been used to print several tensile cube parts and also to get powder samples from every reused cycle. The correlation of the mechanical properties with the XRD, XPS, and SEM characterization will be presented elsewhere.

3. Results and discussions
The SEM, XPS, and XRD characterization results are presented in figures 1-4, respectively. We performed characterization on both virgin and recycled powder regularly just to ensure the results are reproducible. The SEM images (figure 1) show a slight difference in the size of the powder particles after SLM process. Note that particles with diameter over 80 μm including overexposed condensate particles were sieved from the recycled powder. The recycled powder shows more satellite on surface and more contamination is present. However, the contamination is also observed on the virgin powder
probably from environment and during handling the powder. Also bonded particles are present in the recycled powder and some particles show deformed shape from spherical. Some spatter is also present in the recycled powder indicating that some of the melted particles solidify during the flight and before adhering to the part or before impinging on powder bed [1, 2]. These are in agreement with the SEM results presented by Terrassa et al. on virgin and recycled Steel 316L powders [12]. Figure 2 was taken in closer zoom to probe the shape and irregularity of the particles. Several features are observed in the recycled powders such as elongated particles, satellites on surface, spatter, bonded particles and particles with irregular shapes. Overall, the morphology of the recycled powder shows insignificant changes. However, XPS characterization can better reveal the presence of various elements on the surface of the powders especially on the recycled powder.

Figure 1. SEM images taken from both virgin (left) and recycled (right) powders.

Figure 2. SEM images from the recycled powder (in 20 µm and 10 µm zoom) indicating the elongated particles, satellites on surface, spatter, bonded particles and particles with irregular shapes.

The XPS measurements presented in figure 3 for both virgin and recycled powders. The Oxygen level on the powder surface has increased from 27.04% to 34.19%. The increased oxygen level may be from the chamber environment [12]. The oxygen uptake also depends on how the powder was produced. In our case, this change is only 7% which is not dramatic. Jelis et al have reported that a high oxygen level on powder surface can promote the porosity and accelerate the degradation of the part’s mechanical properties [2]. We also see that the carbon level reduced from 56% to 45.55% which could be because the other elements such as metallic oxides have now dominated the surface. For
example, Mn and Fe show slight increase from 2.02% and 1.04% on virgin powder to 2.27% and 2.70% on recycled powder. However, these are still small changes. It is believed that some metallic powders with more electronegativity to oxygen may diffuse out to the outer-surface of the powder to absorb Oxygen during the SLM process. The presence of heavy metals on the surface such as Ge (5.22%) and Sb (2.86%) is also surprising and is under further examinations. The Si peak is almost constant or decreasing negligibly from 10.83% on virgin powder to 10.07% on recycled powder. This is in agreement with the oxygen rise on the surface (< 10 nm) since the growth of Si oxide layer on the surface impedes the oxygen diffusion into the bulk of the powder. If Oxygen diffuses into bulk, the Mn or Fe oxides would form quite thicker than the virgin powder. This is in agreement with XPS analysis reported by Simonelli et al. on virgin and recycled Steel 316L powders [1]. Also the Mn value obtained here is in the same range reported by Yakout et al. [13].

In his PhD thesis, Barnhart presented his XPS analysis on virgin and recycled powders and reported the Cr, Mn, Fe oxide are dominant on recycled powder and the peak is slightly broader [14]. Depend on the number of reusing cycles, the oxide thickness of surface chemistry would be different and, generally, finally after 10 cycles, the powder starts to show different microstructure. It is also recommended that the virgin powder must be mixed with the reused powder literally after 5 cycles in order to retain the mechanical strength of the printed ports [2, 14]. Further XPS analysis are ongoing to understand concentration of every metal oxide formed on the surface of recycled powder. We run XPS for narrower range of binding energies, for example, for Si, Mn, Fe peak detections.

![Figure 3](image_url). The XPS measurements on both virgin (top) and recycled (bottom) powders.
To confirm the phase and crystallinity of the powders we ran XRD analysis on both virgin and recycled powders. As shown in figure 4, there is no change in phase of the recycled powders and all the XRD peaks are overlapping with the ones of virgin powder. We see all the XRD peaks (111), (200), (220), (311), (222) of an austenitic stainless steel. All the peaks present an austenitic stainless steel with FCC structure. Dissimilar to XRD results presented by Heiden et al [7], we detected no additional peaks at 43° and 65° indicating an insignificant contamination through SLM process and no change on the phase. Note that Heiden et al have reused the powder for 30 cycles and they could detect some ferritic BCC phase after. Our XRD results are in agreement with the one reported by Terressa et al as they have also reported no significant change on the phase of the recycled powders (9 cycles) [12]. There might be a slight change in plane orientation as we recorded higher intensity from the recycled powder. However, it is reported in literature that reusing for over 10 times normally can influence on the phase of the powder and for few repeated reuse times, the phase will not change under normal SLM printing conditions [7, 11]. Also the powder will not see much difference on the porosity before it is recycled over 10 times. However, it was reported in most literature that the density of the powder will increase by progressive reuse times and the contamination on surface will increase as well [12].

![Figure 4. XRD analysis of virgin and recycled powders.](image)

### 4. Future research vision

Further investigations or ongoing on characterizing the recycled powders for reuse in SLM process. We are conducting further SEM analysis to reveal the porosity induced on the recycled powder and the degree of porosity variation by the number of reusing cycles. We also conduct rheology analysis to trace the change on particle size distribution and density. To characterize surface composition, we use XPS measurements in specific ranges where the metal oxide formation is more probable. We’re also running synchrotron analysis to get information on bulk composition. Finally, we are running nano-indentation to trace the hardness change of the powders and the final parts by the number of reuse cycles. The printed parts are also characterized for tensile and strength and these data are correlated with the surface and microstructure of the reused powders to optimize the number of reusing cycles.

### 5. Conclusions

We presented our surface and microstructure characterizations on virgin and recycled stainless steel 316L powders. The recycled powder was collected from SLM process and particle size, shape, surface composition and phase was compared to its virgin powder. There was insignificant change on size of
the powder, however, there is a mix of irregular shape, bonded particles and spatter particles present in the recycled powder even after sieving the oversized particles with diameter >80 μm. The SEM images show more satellites on recycled powders and XPS measurements show that the metal oxides are slightly increasing on its surface as well. Oxygen is showing the most increment on surface increasing from 27.04% to 34.19%. The XRD result show no change on the phase of the recycled austenitic stainless steel compared to virgin powder. There is no additional ferritic BCC peaks on recycled powder indicating a low contamination and phase change after SLM process.

6. References
[1] Simonelli M, Tuck C et al. 2015 Metal. Mat. Transac. A 46(A) 3842
[2] Jelis E, Clemente M, Kerwien S, Ravindra N and Hespos M 2015 JOM 67(3) 582
[3] Yakout M, Elbestawi M and Veldhuis S 2018 Int. J. Adv. Manuf. Technol. 95 1953
[4] Hann A B 2016 SAE International 01 2071 209
[5] Sartin, B, Pond T, et al. 2017 Solid Freeform Fabrication, Proceed. 28th Ann. Int. 351
[6] Galicki D, List F, et al. 2019 Metall. Mater. Transac. A 1582
[7] Heiden M, Tung D, et al. 2019 Additive Manufacturing 25 84
[8] Mellin P, Shvab R, et al. 2017 Powder Metallurgy 1
[9] Lutter‑Günther M, Gebbe C, Kamps T, Seide C and Reinhart G 2018 Production Engineering 12 377
[10] Nezhadfar P, et al. 2018 Solid Freeform Fab. Proceed. 29th Ann. International 1292
[11] Jacob G, Brown C, Donmez A, Watson S and Slotwinski J 2016 NIST Adv. Manufac. Series 100-6
[12] Terrassa K, Haley J, MacDonald B and Schoenung J 2018 Powder Technology 338 819
[13] Yakout M, Elbestawi M and Veldhuis S 2018 Int. J. Adv. Manuf. Technol. 95 1953
[14] Bradley K B 2017 Characterization of powder and the effects of powder reuse in selective laser melting PhD thesis - Case Western Reserve University