Binder jetting 3D printing of 316 stainless steel: influence of process parameters on microstructural and mechanical properties

N. Lecis, R. Beltrami, M. Mariani

Binder Jetting 3D printing (BJ3DP) is one of the emerging additive manufacturing technologies. The process consists in the use of a chemical binder during printing and must necessarily be followed by different types of post-treatments (e.g. sintering). In the present work, the features of components obtained by Binder Jetting 3D printing technique from metallic powder of 316L stainless steel have been characterized and studied. In particular, the microstructure of the stainless steel, surface characteristics (hardness and porosity) and the mechanical properties of the printed sample after sintering were evaluated. The analyses performed have been aimed to analyse the role of the most significant conditions of the thermal processes (de-binding and sintering) in order to determine their influence on the physical and mechanical properties of a component produced by BJ3DP. This feasibility study has shown how this new technology can be effective for the production of metal parts with mechanical properties comparable with products obtained with traditional techniques and with other additive processes (e.g. Selective Laser Melting).

KEYWORDS: ADDITIVE MANUFACTURING; BINDER JETTING 3D PRINTING; AISI 316 STAINLESS STEEL; SINTERING; POWDER METALLURGY

INTRODUCTION
The 3D binder jetting printing technique (BJ3DP) is an Additive Manufacturing powder bed process developed at MIT in the early 1990s [1,2] that is only recently receiving particular interest in the scientific literature especially because it allows to apply the advantages of freedom component design offered by additive manufacturing to a wide class of materials. BJ consist of the deposition of liquid binder droplets to selectively join powder particles layer by layer to enable the creation of near-net shaped parts. After printing, the BJ process involves the following steps:
- curing at low temperature to promote the polymerization of the binder
- de-powdering to extract the green body from the powder bed
- debinding for complete removal of the residual polymer in the solid
- sintering at high temperature to achieve the densification of the component.

Nora Lecis, Ruben Beltrami, Marco Mariani
Department of Mechanical Engineering, Politecnico di Milano, Milan, Italy
In contrast to other powder bed processes that apply laser or electron beam to fuse powder particles, no heat or fusion is involved in the printing process. Due to this, BJ presents remarkable advantages in comparison with other AM processes. Firstly, it is compatible with a wide range of materials, as metals, ceramics, cermets, polymers, sand and glass, since there are no restrictions regarding high melting points, reflectivity, etc [3]. Then, considering that the printing process is performed at room temperature, no consideration of thermal conductivity needs to be taken. Further there is no need for building support structures during printing that it is not affected by distortion due to heat gradient [4,5]. Lastly, powder reusability percentage is much higher [6,7] compared to SLM or EBM.

Even though BJ is the least mature powder bed AM technique (Technology Readiness Level (TRL) between 1 and 2) whereas other techniques have reached a TRL between 6 and 7, it presents the highest Competitive Potential for its orientation to large volume production series [8]. The comparison that arises automatically is that with the other more consolidated additive techniques, but the relevant differences in BJ do not fully come out in this case.

In the literature there are papers that provide evidence of the use of this technique successfully for metal alloys [4,9–11], ceramic materials [12–15], and others [16,17], but stainless steel is the most widely used material [4,10,18]. Moreover, recently, some review articles have also been published summarizing the influence of different printing parameters and post-treatment conditions on the final properties of components [19–22].

**MATERIALS AND METHODS**

**316L Powder**

The powder used in this research study was an AISI 316L stainless steel spherical shape (chemical composition wt.%: 16-18 Cr, 10-14 Ni, max 2 Mn, 2-3 Mo, bulk Fe, 0.003 C; D90 < 22 μm and D50 = 9 μm) produced by Sandvik (Sandviken, Sweden). Particle size distribution was deeply studied performing static image analysis (Morphologi 4, MalvernPanalytical ltd) with 20x and 50x lens (nominal particles size range 0.150 μm - 130 μm, >1.6E106 analysed particles) on dry powder dispersed sample. Furthermore, in order to analyse particles geometry, chemical and phases composition, a SEM microscope ZEISS EVO 50 (Jena, Germany) with energy dispersive X-ray detector (Oxford Inca, UK) and X-ray diffractometer Rigaku Smartlab II (Tokyo, Japan) at scanning rate of 1°/min in the range of 20–100° (step 0.020°; Cu-Kα radiation λ = 1.5406 Å) at 40 kV and 40 mA with Bragg-Brentano geometry have been used.

**Printing**

The BJ3P process was performed by the ExOne Innovent® Plus 3D printer (Huntington, PA, USA) using an aqueous binder BA-005 (1.069 g/cm3) supplied by ExOne with 30 pL droplet size and 50μm of layer thickness. After printing, the build box containing the printed parts was put into a drying
oven (DX412C, Yamato, Tokyo, Japan) to cure the binder phase at 180 °C for 6 hours. This mandatory process strengthens the printed part before removing the powder from the print bed. The geometries printed were cubes 10x10x10 mm and tensile tests specimens (see section 2.4). Finally, printing parameters have been kept constant for each print and are shown in Table 1.

### Tab.1 - Printing process parameters used for 316L binder jetted samples.

<table>
<thead>
<tr>
<th>Drying time</th>
<th>Target bed T&lt;sub&gt;b&lt;/sub&gt;</th>
<th>Reccoat speed</th>
<th>Roller speed</th>
<th>Roller speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>(°C)</td>
<td>(mm/s)</td>
<td>(rpm)</td>
<td>(rpm)</td>
</tr>
<tr>
<td>12.0</td>
<td>55.0</td>
<td>90.0</td>
<td>500.0</td>
<td>55.5</td>
</tr>
</tbody>
</table>

- Total amount of time that heater element is moved over the print bed
- Desired temperature of the print bed surface
- Traverse speed of the recoater while it is depositing the powder
- Rotation speed of the roller as it passes over the print bed
- Ratio between the volume of the voids and the jetted polymer

### Debinding and sintering processes

The polymeric residual binder has been removed in a furnace by a thermal debinding. Several different cycles have been tested by varying: temperature (470°C and 600°C), heating rate (2°C/min and 5°C/min) soaking time (2h and 4h) and atmosphere (air and argon). For debinding in air, a CARBOLITE GPC 12/36-3216 (Carbolite ltd, UK) furnace has been used. Cubic samples and tensile test specimens have been placed inside the chamber at room temperature before the cycle was started. Conversely, debinding in argon has been performed in CARBOLITE 12/75/700 tube furnace (Carbolite ltd, UK) adopting a tailored plain carbon steel chamber to guarantee argon saturation inside the furnace (see S1 and Figure S1). Finally, a pressure-less sintering was performed and, according to the sintering atmosphere, two different furnaces have been used. Vacuum sintering (10-1 mBar) has been performed on HTS HT-S1 LPC furnace (Mozzanica, Italy) at 1360°C for 3 hours with a heating rate of 5°C/min and cooling system in nitrogen (N2 at 5 bar). Samples have been placed on alumina holders (Figure 1) and a second alumina bracket have been placed above two tensile tests, to prevent possible arching effects.

**Fig.1** - Example of a load before a sintering campaign in vacuum furnace. Cubic and tensile test samples have been placed on alumina bases and a further alumina bracket has been placed upon samples to avoid possible distortion.
Besides, sintering in argon atmosphere has been performed with Nabertherm LHT02/171B furnace (Lilienthal, Germany) placing the sample inside an alumina crucible (Ø 15mm; h=20mm) connected through alumina tube to the argon supply channel (see SI and Figure S2). In Table 2, all performed debinding and sintering cycles are listed.

**Tab.2** - Debinding and sintering cycles performed on 316L cubes and tensile test samples.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Debinding</th>
<th>Sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atm</td>
<td>T (°C)</td>
</tr>
<tr>
<td>T1</td>
<td>Air</td>
<td>600</td>
</tr>
<tr>
<td>T2</td>
<td>Air</td>
<td>470</td>
</tr>
<tr>
<td>T3</td>
<td>Argon</td>
<td>600</td>
</tr>
<tr>
<td>T4</td>
<td>Argon</td>
<td>470</td>
</tr>
<tr>
<td>T5</td>
<td>Air</td>
<td>470</td>
</tr>
<tr>
<td>T6</td>
<td>Argon</td>
<td>470</td>
</tr>
</tbody>
</table>

**Sample characterisations**

To quantify the effects of the residual binder inside the sample due to different debinding atmosphere, carbon content was measured through C-LECO analyser (UK) according to ASTM E1019. After sintering, every printed cubic sample has been analysed internally (bulk) and mirror-polished using abrasive papers (120, 180, 320, 600, 1200, 2500 and diamond pastes 6, 3 and 1 μm) obtaining final density of the part through Archimedes’ method. Successively, micro-hardness tests were performed using a Future-Tech FM-810 (Kawasaki, Japan) test apparatus with 100 g (0.98N) applied load and 15 s duration. Finally, tensile test on sintered samples (powder metallurgy products ASTM E8, see SI and Figure S3) have been carried out on MTS ALLIANCE RT/100 (Torino, Italy) universal mechanical test machine at 1.30 mm/min as strain rate and then observed the fracture surfaces by SEM ZEISS EVO 50 (Jena, Germany).

Microstructure was studied on chemical etched samples (Sigma-Aldrich 37% HCl: Sigma-Aldrich 65% HNO3: H2O 1:1:1 for 30 seconds) with SEM ZEISS SIGMA 300 (Jena, Germany) equipped with energy dispersive X-ray detector (Oxford Inca, UK). Grain size has been calculated following the general intercept method, according to ASTM E112, using the Nikon Eclipse LV150NL optical microscope (Tokyo, Japan) to acquire the images and analysing them by Image software (National Institute of Health, USA). Lastly, XRD analysis have been performed with Rigaku Smartlab II (Tokyo, Japan) at a scanning rate of 1°/min in the range of 20–100° (step 0.02°), using Cu–Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA with Bragg-Brentano geometry. For this study COD DB card number 9014476, 9013475 and 9012051 have been used for austenite, ferrite and mangano-chromite (Cr2MnO4), respectively. Ferrite phase was calculated through Rietveld refinement method using SmartLab Studio II software (Rigaku, Japan).

**RESULTS AND DISCUSSION**

**Powder characterisation**

The 316L powder (SEM-EDX 18.28% Cr, 2.19% Mn, 10.90% Ni, 2.12 % Mo and 66.51% Fe) is spherical with uniform geometry as shown in Figure 2a. Furthermore, XRD analysis has shown the presence of ferrite phase (see Figure 2b). In particular, the Rietveld analysis revealed an amount of 13.72% of ferrite phase (COD DB #9013475) respect to austenite main phase (COD DB #9014476).
In Table 3, distribution values of 316L powder granulometry analysis are shown. Specifically, the powder size is below 30 μm and roundness is confirmed by circularity (1 corresponds to the perfect circle).

**Tab.4** - Granulometry analysis distributions: diameter, circularity (0-1) and elongation (0-1).

<table>
<thead>
<tr>
<th>316L Powder</th>
<th>D90</th>
<th>D50</th>
<th>D10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (μm)</td>
<td>26.6</td>
<td>11.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Circularity (0-1)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.94</td>
</tr>
<tr>
<td>Elongation (0-1)</td>
<td>0.27</td>
<td>0.04</td>
<td>0.002</td>
</tr>
</tbody>
</table>

**Sintered samples**

Firstly, the residual carbon analysis has been performed, whose conditions are listed in the Table 5. The testing procedure has followed the standard ASTM E1019-18 to evaluate the influence of debinding atmosphere on final trapped carbon content inside the part during the densification.

**Tab.5** - Residual carbon content values at different debinding atmospheres and temperatures in sintered samples.

<table>
<thead>
<tr>
<th>Debinding atmosphere</th>
<th>Temperature (°C)</th>
<th>C (wt.%)</th>
<th>Temperature (°C)</th>
<th>C (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>600 (T1)</td>
<td>0.020</td>
<td>470 (T2)</td>
<td>0.021</td>
</tr>
<tr>
<td>Argon</td>
<td>600 (T3)</td>
<td>0.15</td>
<td>470 (T4)</td>
<td>0.13</td>
</tr>
</tbody>
</table>

A relationship between the debinding atmosphere and the residual carbon amount can be highlighted: the residual carbon content does not change by increasing the debinding temperature. The protective Argon atmosphere has not allowed complete carbon burning. The opposite behaviour can be observed considering the air atmosphere where the residual content is in accordance with the standard AISI 316L composition (max C 0.03 wt.%). It can be stated that samples debinded in air atmosphere were sintered with no trace of polymer binder while argon debinded ones present one order of magnitude more carbon during the sintering process. Argon atmosphere prevents the oxidation of the metal but at the same time does not allow a complete removal of the polymer because a pyrolysis takes place instead combu-
stion. On the other hand, the presence of oxygen accumulated during the debinding phase in the air will be at the origin of the formation of oxides during sintering. Concerning the shape of the components, the geometrical accuracy was not lost in the process. In Figure 3, a tensile test sample after the debinding and sintering process is shown. As a matter of fact, every printed part (cubes and tensile tests) after sintering process has undergone a shrinkage of 15% ± 0.8 in each direction and a volumetric reduction of 38% ± 2, without meaningful dependence on the debinding and sintering atmospheres and no observable parts deformation.

![Fig.3](image-url) - 316L tensile tests printed by BJ3P debinded (above) and subsequently sintered (below).

In Figure 4, XRD analysis of samples sintered with different thermal treatments are shown. As visible, no clear differences are detected in crystalline structure between the samples. Indeed, samples show two main phases austenite and ferrite, respectively. Other phases may be present, but their amount is so low that their effect is not detected.

![Fig.4](image-url) - XRD analysis of 316L sintered samples in different debinding and sintering atmospheres (A = air, AR = Argon, V = vacuum).

The images of the microstructures in Figure 5 reveal the effects of the thermal treatment procedures on the densification of the material and the formation of undesired phases. The comparison between Figure 5A and 5B shows that, as could be easily predicted, a higher dwelling temperature promotes the formation of oxides and inclusions in steel, when the debinding atmosphere is air. The presence of these oxides prior to sintering is detrimental twofold: in addition to influencing the mechanical properties because of their hardness and brittleness, they hinder mass transport phenomena during densification thus inducing the formation of porosity in which they remain enclosed. These closed pores furtherly weaken the material, as explained in the following paragraphs. However, another aspect to notice is that the presence of these inclusions seems to limit the grain growth during sintering: the average grain size was 15.02 μm for sample T1 and 28.48 μm for T2. From Figure 5B and 5C, it is possible to compare the effect of the debinding atmosphere on the final microstructure of the material. The inert atmosphere (Argon) is beneficial to
the achievement of a low percentage of oxides and a higher final relative density (96.30% and 97.45% for T2 and T4, respectively). Moreover, the larger presence of residual binder observed before (Table 5) does not seem to induce the formation of additional carbides with respect to air-debinned samples.

Finally, Figure 5C and 5D show the comparison of samples obtained with the same debinding procedure but different sintering atmospheres (Argon for T4 and low vacuum for T6). In this case, remarkable differences regarding oxides and inclusion are not observed. However, closed porosity is slightly higher in argon-sintered samples. This is likely due to the entrapment of gas during the final stage of sintering, which fails to diffuse to the sample surfaces. Therefore, the achieved relative density is limited: 97.45% for argon sintering and 98.92 for vacuum sintering.

The SEM images in Figure 6 show some of the different types of inclusions that may form during sintering. Indeed, in addition to γ-austenite, δ-ferrite and spherical-shaped pores, it is possible to identify three different oxides, enclosed in irregular porosity (see Figure 6A). EDX analysis, presented in Table 6, determined the composition of these phases. Instead, in Figure 6B it is possible to identify iron carbides segregated at the grain boundaries. All these inclusions are detrimental to the final quality of the printed components, through the cycle T6 we were able to drastically reduce their presence and size without the need of further thermal treatments.
Tab.6 - Elemental analysis obtained by EDX of the phases identified in Figure 6.

<table>
<thead>
<tr>
<th></th>
<th>O (%)</th>
<th>Si (%)</th>
<th>Cr (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
<th>Mo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-austenite</td>
<td>0.43</td>
<td>0.5</td>
<td>15.06</td>
<td>68.09</td>
<td>13.09</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>δ-ferrite</td>
<td>0.62</td>
<td>20.32</td>
<td>67.35</td>
<td>5.68</td>
<td>6.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ox1-Cr/Mn</td>
<td>16.58</td>
<td>1.05</td>
<td>33</td>
<td>29.27</td>
<td>4.93</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>Ox2-Si</td>
<td>53.23</td>
<td>43.06</td>
<td>1.42</td>
<td>1.2</td>
<td>1.09</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ox3-Mn/Si/Cr</td>
<td>23.92</td>
<td>19.54</td>
<td>11.63</td>
<td>29.94</td>
<td>12.76</td>
<td>0.42</td>
<td>1.67</td>
</tr>
<tr>
<td>P-Pore</td>
<td>1.48</td>
<td>0.58</td>
<td>15.91</td>
<td>1.06</td>
<td>65.94</td>
<td>12.42</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The graph in Figure 7 describes the relationship between the type of thermal treatment applied to the samples and the Vickers hardness, the grain size and the final relative density achieved. The improvement in terms of porosity reduction obtained with T6 is not correlated to a similar linear variation of the other properties. Indeed, it can be observed that T4 (i.e. Argon-sintering) features the largest grain growth. The comparison between T2 and T5 likely confirm that the excessive grain size could be related to the sintering procedure, with Argon being detrimental also in this case, although the presence of more oxides limits this phenomenon as stated above. It could be possible that at the end of the sintering dwelling time, the transition to the cooling rate set for both procedures was not as sharp in the Argon-containing oven as in vacuum, thus allowing the grain growth mechanism to proceed further. Moreover, the grain size seems to be the determining factor for the microhardness. In fact, T4 samples are not only those with an average grain size above 40 μm, but also the only components featuring less than 140 HV.

Fig.7 - Vickers hardness, grain size and final relative density behaviour of samples obtained from T2, T5, T4 and T6.

Tensile test
Tensile tests were performed on samples T1, T5 and T6. As can be seen from the graph in Figure 8, the progressive reduction of internal closed porosity and inclusion improves the ductility of the samples, as can be noted from the increase of maximum elongation from 12% to 33% for T1 and T6 (see Table 7), respectively. The transition from a more brittle to a more ductile behaviour of the material can be observed also from the extension of the necking mechanism, which led to a drastic section reduction for T6 (see Figure 9). The presence of oxides and other hard phases accelerates the formation of microvoids, as highlighted in Figure 9, which are responsible for the premature failure of the samples. T6 provides optimal performances, although it must be noted that further improvements are required to obtain mechanical properties comparable to conventional manufacturing steel.
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**Fig. 8** - Examples of σ-ε curves obtained from tensile tests on samples T1, T5 and T6.

**Tab. 7** - Average values of Rp02 [MPa], Rm [MPa] and elongation E [%] for samples T1, T4 and T6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rp02 (MPa)</th>
<th>Rm (MPa)</th>
<th>E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>200 ± 16</td>
<td>364 ± 21</td>
<td>12.1 ± 1.5</td>
</tr>
<tr>
<td>T4</td>
<td>197 ± 4</td>
<td>471 ± 18</td>
<td>23 ± 3.2</td>
</tr>
<tr>
<td>T6</td>
<td>184 ± 4</td>
<td>471 ± 19</td>
<td>33.6 ± 4.3</td>
</tr>
</tbody>
</table>

**Fig. 9** - SEM images of the failure cross sections of tensile specimens T1 (a, d), T4 (b, e) and T6 (c, f).
CONCLUSIONS

At the end of this research work some conclusions can be drawn:

• BJ3DP is an effective and flexible technique comparable to other power-bed based AM ones, able to provide near full-density parts, without using high energy sources and with the possibility of recycling the excess unbound powder.

• The mechanical properties of the final parts can be improved by varying the post printing steps of the process. By using Argon atmosphere during the debinding and Vacuum atmosphere during the sintering an increasing of density up to 6%, of real strain up to 150% and of UTS up to 23% is observed.

There are still some critical aspects of process, mainly related to the presence of oxides in the microstructure and carbides at grain boundary that can reduce the mechanical properties.

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