Direct Ink Writing of AISI 316L Dense Parts and Porous Lattices

Lisa Biasetto* and Hamada Elsayed

The focus of the present work is the development of a metallic ink that possesses controlled rheological properties: by keeping printing parameters constant both AISI 316L dense parts and porous scaffolds have been produced. Shrinkage, porosity, and mechanical properties have been studied to evaluate the link between the ink rheological properties and the final part. Depending on binder composition, linear shrinkage ranging from 9% to 22% and porosity from 34 to 7 vol% are measured. Tensile strength for specimens sintered at 1240 °C reach the value of 444 MPa and elongation at a break of 12.3%. These values are still far from additively manufactured AISI 316L parts with powder bed fusion technologies, but represent an improvement compared to previously reported data in the literature for AISI 316L parts 3D printed by DIW. Porous scaffolds with a spanning distance of 1.2 mm are printed and sintered. Porosity of 74 vol% and compression strength of 74 MPa are measured for this set of samples showing how the produced ink represents a valuable alternative to pastes already present in the literature.

1. Introduction

The production of metallic components by additive manufacturing (AM) technologies is today recognized as a standardized method,[1–4] especially when direct energy deposition (DED) and powder bed fusion (PBF) processes are employed. For instance, AM parts are currently produced by PBF and commercialized by GE Aviation,[5] by 2027 52% revenues of AM are expected to be covered by the aerospace, automotive, and energy sectors.[6] The difference between DED and PBF lies in the powder delivery mechanisms: in DED, the powder can be delivered as is or as a filament and melted on flight by a heat source, in PBF technologies a powder bed is selectively sintered (SLS) or melted (SLM) by a laser or electron beam (EBM).[6]

The common points of PBF technologies are the use of micron-size gas-atomized powders and the direct melting or sintering of the powders. If this represents an advantage in terms of printable geometries and production time, in contrast, the methods hide several side back effects: the need for a protective atmosphere to avoid oxidation, not all metals or alloy can be melted or sintered by the laser or electron beam power source, during printing high-temperature cooling rates (10¹⁰–10¹⁹ K s⁻¹) are responsible for the formation of metastable microstructures with consequences on the mechanical properties (anisotropy). The powders delivery mechanism does not allow the production of closed hollow shapes, so the laser path is responsible for poor control of surface roughness.

In addition, PBF processes are not suitable for multi-material 3D printing, being this the next challenge for AM technologies.[7] For instance, powders delivery systems need to be redesigned to grant for proper multi-material combination.

Another class of emerging technologies to 3D print metallic components are those classified as extrusion-based, where a metallic-based filament or paste is extruded through a nozzle at mild or room temperature. In both cases, gas-atomized metallic powders are mixed with a polymeric binder to obtain an extrudable filament or paste. In the first case, the technology is called fused deposition modeling (FDM, used for rapid prototyping) or fused filament fabrication (FFF), while in the second case it is called direct ink writing (DIW).

FFF and DIW show the advantage of printing at mild or room temperature and the versatility to use more filaments or pastes, for instance, to 3D print multi-material components; the printed part must undergo a de-binding and sintering treatment to remove the polymeric binder and to densify the metallic powders into the final part. The preparation of a homogeneous and printable filament or paste remains one of the key points of these techniques, so de-binding and sintering must grant for the absence of organic binder residues. Sintering at high
temperatures must avoid oxidation, precipitates formation, and residual porosity. This is most critical when highly reactive metals or alloys are used, such as Ti-based alloys.\cite{8,9}

It should be noted that FFF filaments are extruded through a heated nozzle on a heated plate in the air. The filaments are composed of a mixture of commercially available gas atomized powders and thermoplastic and elastomeric polymers. Consequently, most of the works reported in the literature are focused on the printing strategy, de-binding, and sintering optimization.\cite{10–13} Some companies (e.g., Markforged, Desktop Metal, and Nanoe) already commercialize the filaments, the printing units, and the de-binding and sintering setup for FFF.

In the DIW process, gas atomized metallic powders and a polymeric binder are extruded through a nozzle at mild or room temperature depending on the composition of the polymeric binder: in Ref. \cite{14} a thermoplastic binder was formulated to 3D print copper parts that were extruded by pressure in a heated syringe. The French company Pollen and the German AIM3D commercialize 3D printers that make use of injection molding pellets to 3D print at mild temperature (up to 450 °C), plastic, metallic, or ceramic components. In other studies,\cite{8,9,15–17} a fluid binder was used showing a shear thinning behavior at room temperature: room temperature shear thinning inks are not yet commercially available and research is focused on how to optimize their composition, so as on the printing strategy to produce metallic parts with proper design constraints and tolerances. In Figure 1a, a schematic overview of available DIW techniques is reported.

The main challenges for DIW ink formulation are: 1) Ink’s stability, meaning avoiding phase separation and clogging (upon storage and printing). 2) Ink’s viscoelastic properties, meaning a shear thinning behavior at room temperature capable to grant a constant flow through the nozzle, and a continuous filament. 3) Ink’s thixotropic properties, meaning the capability of the ink to recover its elastic properties at rest, this being extremely important for porous or complex structures or even to grant for adequate tolerances.

![Figure 1. Schematic overview of the different setups of direct ink writing (DIW) 3D printing technology and main process parameters.](https://www.advancedsciencenews.com)

Powder size, powder size distribution, powder aspect ratio, particles over binder volume ratio, and binder composition represent the parameters most affecting the ink’s properties and the quality of the final 3D-printed part.\cite{18–20}

The effect of powder size, shape, and distribution on the ink’s rheological behavior has been systematically studied for micronized powders.\cite{21–23} More recently in Ref. \cite{24}, the authors developed ceramic inks using two yttria-stabilized zirconia spherical particles possessing different Y2O3 molar percentages and size distribution. Their results showed that with decreasing particles size, the filler/binder volume ratio should be correspondingly decreased to get the best mechanical performance of 3D-printed scaffolds.

Inks for DIW have been widely studied for polymers and ceramics\cite{25,26} while the literature is more recent for metals.\cite{8,9,12,15,27–29}

In DIW printing, the main tricky points are: 1) The quality of the printed part in terms of geometrical constraints, for instance, a poor control of the DIW process may leave behind residual porosity due to incomplete filling or discrepancies with the design geometry. 2) The control of de-binding and sintering process should be capable to avoid unwanted by-products and residual porosity.

Both these types of defects affect the final component’s structural (mechanical strength and ductility) and functional (i.e., corrosion resistance) properties.

To satisfy the above-listed requirements, a highly loaded ink must be developed (particle in the range of 60 vol%). This drives into the field of wet-granular materials characterized by a low amount of binder that does not fully penetrate the empty spaces among particles. Interparticle interactions and binder–particle interactions create a material with a complex, non-Newtonian response to deformation, characterized by high viscosities at rest and a yield stress. To control the printability of such inks, a minimum pressure and a constant flow can be tuned by mean of the following equations\cite{30}:

| Direct Ink Writing-DIW |
|------------------------|
| **Material Source**     | In-lab developed ink |
| **Printing Principle**  | Extrusion of highly loaded pseudoplastic paste |
| **Temperature**         | Room Temperature |
| **Environment**         | Air |
| **Process parameters**  | Ø Nozzle diameter  
|                        | Ø Flow rate  
|                        | Ø Head speed  
|                        | Ø Extrusion Pressure  
|                        | Ø Layer height  
|                        | Ø Fill pattern |
| **Thermal De-binding**  | Ø Time and T  
| **Sintering**           | Ø Time and T  
|                        | Ø Atmosphere  
|                        | Ø Pressure |
where $P_{\text{min}}$ is the minimum driving pressure, $L$ is the length of the extrusion nozzle, $D$ is the diameter of the nozzle, and $\tau_{\text{yield}}$ is the material yield stress. High-stress yield requires high pressure to be constantly applied. After yield, the driving pressure to grant for a constant flow will depend on power law fluid by

$$\eta = k\gamma^{n-1}$$

where $\eta$ is the viscosity at a particular shear rate $\gamma$, $k$ is the consistency index, and $n$ is the power law exponent that determines the degree of shear thinning or thickening. For $n < 1$, the material is shear thinning for $n = 1$ Newtonian, for $n > 1$ shear thickening, with $n$ values approaching 0 being representative of very shear thinning materials.

Using the power law model, the flow can be related to the rheological behavior of the material by:

$$Q = \frac{\pi R^4}{8} \left( \frac{\Delta P}{T} \right)^{\frac{1}{n}}$$

In Equation (3), $Q$ is the volumetric flow rate, $R$ is tube radius, $\Delta P$ is pressure drop, and $L$ is tube length. As can be seen, lower consistency indices ($k$) will result in a lower pressure requirement for higher flow rates, and smaller $n$ will create materials that are easier to flow as applied pressure increases.

The main objective of this work is the development of a simple water-based ink (made of a few components) to produce AISI 316L parts by means of a commercially available DIW printer. Two different binder systems are developed to produce dense parts and porous scaffolds: the focus is on the control of ink properties over the printed part and the analysis of microstructural defects to achieve final parts with improved mechanical properties. The de-binding and sintering steps are only partially investigated and will be the object of further studies.

### 2. Experimental Section

#### 2.1. Inks Preparation

The inks prepared for this work were constituted of a physical gel binder composed of polyvinyl alcohol (PVA, Sigma Aldrich $M_w = 9000–10,000$ g mol$^{-1}$, 80% hydrolyzed) and polyethyleneglycol (PEG, Sigma Aldrich $M_w = 950–1000$ g mol$^{-1}$) solved in distilled water and gas atomized AISI 316L micro-sized powders ($d_{50} < 10 \mu m$, TLS Technik Spezialpulver GmbH, Germany). The powder’s composition is reported in Table 1, as from the manufacturer datasheet. Particle size was selected following previous work reported in Ref. [8,17].

The two binders’ compositions were prepared using the following weight ratios: 1) Binder 1, B1 in the following: PVA: PEG:H$_2$O = 17:11:72; 2) Binder 1, B2 in the following: PVA: PEG:H$_2$O = 18.75:16.25:65.

PVA and PEG were solved into the water at 80 °C for 2 h under magnetic stirring and then left gently cooling overnight.

The powder over binder weight ratio was kept constant at 90.9/9.1.

A Thinky centrifugal mixer was used to mix the powders with the binder using the following cycle under air: 2 min at 400 rpm, 2 min at 1000 rpm, and 2 min at 1200 rpm followed by defoaming at 400 rpm for 2 min. The ink was kept inside a cooled container to prevent overheating and solvent evaporation upon mixing.

#### 2.2. Rheological Characterizations

To fulfill the printability properties highlighted in the introduction, inks underwent a rheological characterization using a plate-plate rheometer ($d = 40$ mm) (Netzsch, Kinexus) with a solvent trap under water. The following measurements were performed: 1) Large amplitude oscillatory shear stress (LAOSstress) measurements$^{[90]}$ were performed at controlled shear stress in the range 1–3500 and 1–1000 Pa at 0.5 Hz with a 0.4 mm gap, for AISI316LB1 and AISI316LB2 respectively. Non-Newtonian fluids are characterized by a complex modulus $G = G' + iG''$, where $G'$ is defined as the storage or elastic modulus while $G''$ is the viscous or loss modulus. The shear thinning behavior is represented by the decrease of viscosity at increasing shear stress or shear rate as expressed by Equation (3). By mean of linear fitting of viscosity versus shear rate plot in the transitory region $k$ and $n$ were determined with an $R^2 > 0.999$. By mean of storage modulus $G'$ and loss modulus $G''$ versus shear stress log-log plots the following parameters were determined$^{[31,32]}$ the storage modulus in the linear viscoelastic region LVR, $G'_1$ (Pa), the stress at the crossover point $\gamma_f$ where $G' = G''$, and the flow transition index FTI (dimensionless) defined as the ratio between the stress at the crossover point $\gamma_f$ and the stress at the yield point $\gamma_y$ ($G' = 0.95 G'_1$). The stress at the yield point is the point where the gel-like structure is partially destroyed by the acting shear stress. The crossover point defines the step over which the viscous behavior overcomes the elastic behavior, meaning that the ink’s structure (bonds between binder and metallic particles) is heavily destroyed by the acting shear stress. The thixotropic properties of the inks were measured by means of a three steps recovery test at controlled shear stress: a stress, of 0.1 and 100 Pa, was applied for 30 s, and finally, the viscosity recovery was monitored with a stress of 0.1 Pa for 600 s.

| Table 1. Composition of the metallic powders used to 3D print AISI 316L samples. |
|---------------------------------|-----|
| Chromium                        | 16.9|
| Nickel                          | 11.8|
| Copper                          | –   |
| Silicon                         | –   |
| Molybdenum                      | 2.3 |
| Manganese                       | 1.1 |
| Niobium                         | –   |
| Carbon                          | 0.02|
| Phosphorous                     | –   |
| Sulfur                          | –   |
| Iron                            | Balance |

© 2022 The Authors. Advanced Engineering Materials published by Wiley-VCH GmbH
2.3. Printing by DIW

T-bone samples for tensile tests following standard ASTM E8-04 were 3D printed by DIW (Figure 2). Samples were oriented parallel to the plate and the filling of the samples was run at + and −45° for each layer. Three concentric shells (in red in Figure 2) were printed before filling the volume with 45° orientation. The printed dimensions were exceeding 10% of the design dimensions to take into account shrinkage due to the sintering process.

The inks were printed using a WASP 2040 Clay 3D printer (WASP, Massa Lombarda-Ravenna, Italy). The ink was loaded into a 50 mL syringe with a polyethylene piston and an 840 μm conical nozzle tip. The ink was extruded by compressed air at 3.5 × 10^5 Pa, with the printing head moving at 20 mm s⁻¹. The layer height was kept at 0.9% of the nozzle tip to grant for a complete filling of the printed geometry. The CAD design was sliced using the software Slicer, Repetier software was used to convert the sliced design into a Gcode.

The porous lattices were printed through a conical nozzle with 410 μm (Nordson, Italia S.p.a., Milano, Italy). Therefore, tetragonal lattices with 12 orthogonal layers of parallel struts of 400 μm and a layer height (in the Z direction) of 320 μm, to guarantee an interference between the printed layers, fabricating lattices with good integrity. The spanning line (distance in X-Y directions) between the filaments was set at 1200 μm.

2.4. De-Binding and Sintering

To define the target temperature for binder decomposition, thermal gravimetric analysis (TGA) was performed on the binders’ components (PVA and PEG), B2, and AISI316LB2 ink using a TGA-differential scanning calorimetry 3° star System, Mettler Toledo from RT to 700 °C under Argon flow with a heating rate of 5 °C min⁻¹. Before sintering, printed samples were left gently drying at RT overnight; this step was necessary to grant sufficient strength to the printed part, to resist handling operations. Sintering of T-bone samples was run in a tubular furnace under Argon flow using the following cycle:

0.5 °C min⁻¹ up to 500 °C, dwelling time 2 h, 2 °C min up to 1200 and 1240 °C, dwelling time 4 h.

The porous lattices were sintered at 1200 °C, where they were fired, up to 500 °C for 3 h with a heating rate of 0.5 °C min⁻¹, and a heating rate of 2 °C min⁻¹ up to 1200 °C. Then, the cooling rate was 5 °C min⁻¹ to room temperature.

2.5. Samples Characterization

Linear shrinkage before and after sintering was measured by a digital caliper, and the total porosity was calculated by

\[ P_{\text{tot}} = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{th}}} \]  
\[ P_{\text{closed}} = 1 - \frac{\rho_{\text{app}}}{\rho_{\text{th}}} \]  
\[ P_{\text{tot}} = P_{\text{open}} + P_{\text{closed}} \]

where the \( \rho_{\text{th}} \) was 7.8 g cm⁻³ for AISI 316L powders, as measured by He-Pycnometry (AntonPaar Ultrapyc 3000). The bulk densities of the printed and sintered samples (\( \rho_{\text{bulk}} \)) were also measured by He-Pycnometry on rectangular pieces of bulk samples, that were previously cut by a circular saw.

Optical analyses (Leica DMLA) were performed on embedded sections of the sintered samples that were grinded up to a 1200SiC grit and polished using a 40 wt% colloidal SiO₂ suspension (particles size from 20 to 24 nm) to reveal the microstructure. Electrochemical etching with 20% NaOH solution with a 9 V DC supply was performed on the surface of the samples to identify secondary phases.

Scanning electron microscopy analysis was performed on the as received AISI316L powders, on the printed part, on the polished sections of the sintered specimens, and on fracture surfaces of the specimens after tensile tests, using an SEM-FEG (Quant-LEI Eindhoven, Netherland) at 20 kV and 10 mm working distance. Electron dispersive spectroscopy (EDS) analysis was performed using an EDS probe (ThermoScientific, Ultradry).

Figure 2. Specimen target dimensions as for: a) ASTM E8-04, b) printing strategy, c) specimen target dimensions and d) printed part.
Vickers microhardness was measured on an AISI316LB1-1200 polished section using 0.005 Kgf and 15 s holding time.

Tensile mechanical properties were measured using an MTS809 tensile machine with a max load of 10 kN, at a constant elongation rate of 3 mm min\(^{-1}\), equipped with an extensometer, following ASTM08-04 standard. Compression tests were performed using a universal compression testing machine (25 kN) on the scaffolds, following ISO 13 314:2011 standard.

3. Results and Discussion

3.1. Ink Development

In Figure 3, SEM (secondary electrons) images of AISI 316L powders (Figure 3a,b) and dried ink after printing (Figure 3c,d) are reported. They show the typical spherical shape of gas atomized powders with a size congruent to the one declared by the manufacturer (\(d_{90} < 10\) μm). The AISI316LB2 printed ink is reported as an example of how the metallic powders are well dispersed through the polymeric binder, keeping their shape unaltered with a uniform distribution. The two inks developed in this work are characterized by the same binder over powders ratio, with binders differing in the amount of water and on PVA-PEG weight ratio. We want here to quantify the effect of binder composition on the inks’ rheological behavior.

As can be seen in Figure 4, the used inks exhibit a shear thinning behavior, where complex viscosity can be represented by a Newtonian behavior at a low shear rate and a power law behavior for a shear rate higher than 0.14 s\(^{-1}\) for AISI316LB1 and 0.05 s\(^{-1}\) for AISI316LB2. Both inks show high values of zero shear rate viscosity with AISI316LB1 higher than AISI316LB2, this confirms how the decrease in the amount of water in B2 and the different PVA-PEG ratios weaken the material structure.

![Figure 4. Viscosity versus shear rate plot for AISI316LB1 and AISI316LB2 inks.](image)

Figure 3. a,b) AISI 316L as received powders and c,d) AISI316LB2 dried ink after printing. Arrows highlight the presence of the binder on the surface of the particles and between adjacent particles.
In AISI316LB1, the transition from the zero-shear rate plateau to the infinite viscosity plateau has a similar slope to AISI316LB2, even if at a high shear rate the curve diverges from linearity for AISI316LB1. The values of consistency index k and of the exponent n for the two inks are reported in Table 2.

 Compared to data from Ref. [20], k values are very high and n values tend to be zero. High values of k and low values of n imply a high ΔP to be applied in order to control the flow.

The measurement of the complex moduli $G'$ (Figure 5) shows that: 1) For both inks $G' > G''$ at low shear stress, thus confirming that at low shear stress the elastic component of the ink is stable so as its gel-like structure. 2) The cross-over points for both inks are well defined, this can be related to the homogeneity of the bonds’ energy between particles and binder. 3) After the crossover point, $G''$ is kept higher than $G'$, this confirms that the bonds between binder and particles are not reformed at higher shear stress. 4) AISI316LB1 possesses higher values of $G'_{LVR}$ than AISI316LB2 so as its crossover point $\tau_f$. The FTI values for the two inks are similar, showing a proportionality between $\tau_r$ and $\tau_f$, with higher FTI for AISI316LB2.

In Ref. [33] where AISI 316L scaffolds were printed by DIW using a carrageenan-based ink, the shear stress at yield showed a value of 4000 Pa. This value is in good agreement with the value measured for our ink (Table 2) formulated with B1, confirming this composition is well suited for porous structures.

In Table 2, an overview of rheological parameters is reported. It should be noted that the shear yield value for AISI316LB2 is close to the lower limit of recommended values found in the literature for graphene oxide filled polymeric inks to grant for a self-supportive ink (500–2500 Pa), while AISI316LB1 is exceeding the upper limit.

Table 2. Overview of the rheological properties for the two inks.

|                | AISI316LB1 | AISI316LB2 |
|----------------|------------|------------|
| $n_0$ [Pa s]   | 321 899    | 124 000    |
| $K$ [Pa s$^2$]| 23 955     | 4314       |
| $n$            | 0.004      | 0.078      |
| $G'_{LVR}$ [Pa]| $1.03 \times 10^4$ | $3.9 \times 10^3$ |
| $\tau_f$ [Pa]  | 764        | 127        |
| $\tau_r$ [Pa]  | 3820       | 762        |
| FTI            | 5          | 6          |
| $t_f$ [s]      | 125        | 365        |

Figure 5. Storage and loss modulus plot versus shear stress for AISI316LB1 and AISI316LB2.
3.3. Production of Tensile Specimens and Scaffolds

In Figure 9, the T-bone specimens after printing and sintering with the two inks are reported. Samples didn’t show bending after printing and sintering.

It can be seen in Figure 8-left how printing lines oriented at 45° are still present on the sample structure produced using AISI316LB1, while in AISI316LB2 the printing path is almost completely lost due to the sticking of consecutive lines. This behavior can be related to a higher recovery time for viscosity in AISI316LB2, as highlighted with the thixotropy test, so as to the corresponding higher flow of material for AISI316LB2, at constant printing parameters. In Figure 10, scaffolds after sintering are reported.

In Table 3, the average bulk density, the calculated total porosity, and the linear and volumetric shrinkage after sintering for the sets of tensile samples are reported.

Shrinkage increases from AISI316LB1 to AISI316LB2, with a further increase at increasing sintering temperature. For sintering temperature of 1200 °C, shrinkage is isotropic in the x, y, and z directions, while for samples sintered at 1240 °C shrinkage becomes anisotropic in the z direction. This behavior is not yet understood. The shrinkage is reduced compared to Ti64 scaffolds produced with similar technique and ink.[8,9] Total porosity is higher for samples prepared using B1 and sintered at 1200 °C, so as the open porosity that can mainly be attributed to defects occurred during printing operations: as predicted from rheological parameters and from Equation (1), the minimum pressure to activate flow in AISI316LB1 should be equal to \( P_{\text{min}} = 3.3 \times 10^5 \text{ Pa} \), whilst for AISI316LB2 \( P_{\text{min}} = 0.6 \times 10^5 \text{ Pa} \). It should be noted that Equation (1) is valid for the circular tubes, here we used a conical nozzle and for this reason, we calculated the \( P_{\text{min}} \) using the average diameter \( D_{\text{max}} = 4.2 \text{ mm} \) and \( D_{\text{min}} = 0.840 \text{ mm} \). The pressure used during the printing process \( (P = 3.3 \times 10^5 \text{ Pa}) \) stays on the upper limit of the values calculated here. For this reason, the exceeding pressure used for AISI316LB2 caused an overflow that was associated with the higher recovery time, resulting in a complete filling of the printing path.

Since the scope of the present work is to determine the effect of ink properties on the quality of the printed part, the printing conditions in terms of applied pressure and printing speed are not optimal for the ink prepared using B1. As can be seen in Figure 10a), the cross-section of AISI316LB1 sintered at 1200 °C shows the presence of large pores of irregular shape due to insufficient ink flow. For samples prepared with B2, these macro-defects are almost completely absent showing that the ink flow during printing is big enough to fill all volume. For AISI316LB2 samples sintered at 1200 and 1240 °C the values of total porosity and closed porosity are very close showing that porosity can be mainly attributed to defects occurring during the sintering process. In AISI316LB2-1200 (Figure 10c), irregular shape and circular shape black spots are visible, while for AISI316LB2-1240 (Figure 10e) the black spots show higher density and more regular shape. These black spots can be attributed to both the presence of pores and oxides. Irregular shape porosity originated from poor control of the printing process and circular porosity originated from the gas deriving from binder decomposition that is entrapped within the structure upon sintering.

![Figure 6](https://www.aem-journal.com/doi/figure/10.1002/aem.2101729)

**Figure 6.** Viscosity versus time plot from thixotropy test at controlled shear stress \((\tau = 0.1 \text{ Pa})\).

![Figure 7](https://www.aem-journal.com/doi/figure/10.1002/aem.2101729)

**Figure 7.** Midspan deflection over time for the two inks, calculated by Equation (8) and (9).

### 3.2. De-Binding and Sintering

TGA analysis of PVA and PEG polymers and of B2 are reported in Figure 8a). Polyvinyl alcohol TGA curve shows three weight loss regions, as reported in previous studies.\[36\] The region between 50 and 200 °C can be attributed to the loss of absorbed water molecules, and the second one between 200 and 340 °C is related to the loss of water bound to the matrix. The third region between 340 and 450 °C is associated with the decomposition of the polymer (Figure 8b). PVA leaves behind a 3 wt% residue at a temperature even higher than 450 °C. PEG loses weight in one step between 350 and 400 °C.\[37\] The binder shows a decomposition compatible with the two polymers and a similar residue as measured for PVA. The measured weight loss of the ink is equal to 6.2 wt%: the weight loss is less than the amount of binder introduced, however, it should be noted that before sintering samples underwent drying in air. Before drying, samples could not be handled.
Figure 8. a) Thermal gravimetric analysis (TGA) analysis under argon atmosphere of PVA, PEG, and B2, b) derivative curve over temperature.

Figure 9. AISI316LB1 and AISI316LB2 printed and sintered samples at 1200 °C.

Figure 10. AISI316LB1 scaffold after sintering: top view, cross-section, at low and high magnification, and EDS scan of the matrix.
Oxides can be better observed, in Figure 11b,d,f, where optical microscopy images of polished sections of the samples are reported. In the case of 11b and 11d, sections were electrochemically etched to better reveal the structure. The use of B1 has the main effect of producing a high number of pores due to process defects, but a lower amount of oxides compared to AISI316LB2-1200, where grain boundaries are less defined and oxides are more abundant both at the grain boundaries and within the grain. In AISI316LB2-1240, oxides show a larger size compared to AISI316LB2-1200. The lower amount of oxides for the sample prepared using B1 can be attributed to the binder composition. This is also confirmed by the EDS maps shown in Figure 12 and 13. At grain boundaries, a Cr-rich phase precipitates, while the black spots show the presence of Mo and O compatible with oxide formations already found in the literature. The Cr precipitation at the grain boundaries will affect the corrosion resistance of the AISI316L triggering localized corrosion. The presence of Cr and Mn together with O confirms the presence of oxides formation upon sintering. Together with oxygen and porosity, the presence of residual carbon may negatively affect the mechanical properties of the final part, being responsible for δ-ferrite formation.

It should be noted that literature reports on the presence of oxides on the surface of atomized AISI316L powders: in particular, in inert gas atomized powders (as is the case of this work) Fe₂O₃, Cr, Mn, Si oxides are formed. Oxides should be removed to activate the sintering process, diffusivity being higher for oxides than for pure metals. The sintering process here was run under argon atmosphere: the binder was first decomposed, and we suppose the carbon residue reacted with oxygen resulting in CO gaseous byproducts. At higher temperature, oxide particles were generated by reoxidation between metallic particles and CO gas confined in pores that are closed during the sintering process. This mechanism can be seen in Figure 14, where

| Sample name | ρ_{app} [g cm⁻³] | ρ_{bulk} [g cm⁻³] | P_{closed} [%] | P_{tot} [%] | ΔWt. [%] | ΔL [ %] | Δb [%] | Δa [%] |
|-------------|----------------|----------------|---------------|-------------|---------|---------|--------|-------|
| AISI316LB1-1200 | 6.41 ± 0.02 | 5.1 ± 0.1 | 18.1 ± 1.2 | 34.4 ± 0.8 | 2.8 ± 0.3 | 9.0 ± 0.7 | 9.9 ± 1.2 | 8.6 ± 1.3 |
| AISI316LB2-1200 | 6.94 ± 0.01 | 6.6 ± 0.1 | 11.2 ± 0.6 | 15.1 ± 0.4 | 3.3 ± 0.3 | 11.4 ± 0.2 | 12.3 ± 1.2 | 12.6 ± 0.6 |
| AISI316LB2-1240 | 7.23 ± 0.01 | 7.2 ± 0.1 | 7.5 ± 0.5 | 7.6 ± 0.5 | 3.2 ± 0.1 | 13 ± 0.2 | 15.5 ± 0.8 | 22.2 ± 0.4 |

Table 3. Overview of density (ρ), weight loss (Wt.), porosity (P), calculated from Equation (4)–(6), and linear shrinkage for AISI316L samples after sintering at 1200 and 1240 °C. Shrinkage values refer to the nomenclature given in Figure 2.

Figure 11. a) Cross-section of sintered samples AISI316LB1-1200, c) AISI316LB2-1200, e–f) AISI316LB2-1240 and the same section after electrochemical etching: b) AISI316LB1-1200, d) AISI316LB2-1200.
the spherical oxides mixture can be clearly identified in the section of AISI316LB2-1240 samples. The use of a binder, with a higher water amount (B1), drives to the presence of porosity generated during the printing process and not removable by sintering, and a lower number of oxides than the sample prepared using B2 and sintered at 1200 °C.

Figure 10 shows the porous lattices prepared using AISI316LB1. It can be clearly observed the high strength of AISI316LB1 ink is well matching with the design constraints of a porous scaffold. In addition, the large span of 1200 μm doesn’t affect the integrity of the printed line. The higher values of viscosity at rest, of LVR, and the very short recovery make this specific ink suitable for porous structures.

3.4. Mechanical Properties
The stress–strain curves of tensile tests are shown in Figure 15 for sintered samples. Samples sintered at 1200 °C, both
AISI316LB1 and AISI316LB2 show high $E$ and low $\sigma_y$, $\sigma_b$, and $\epsilon_b$ (Table 4). AISI316LB1 shows a more brittle structure compared to AISI316LB2. AISI316LB2 sintered at 1240 °C shows lower values of $E$ and higher values of $\sigma_y$, $\sigma_b$, and $\epsilon_b$. These data drive to the conclusion that the presence of porosity generated upon the printing process has a major impact on the structural properties than oxides formation. In AISI316LB2 sintered at 1240 °C, the reduced amount of porosity and the corresponding presence of oxides of average larger dimensions improve the tensile properties of the produced samples, which however still lay behind the tensile properties of AISI316L samples produced with alternative technologies such as FFF or metal injection molding (MIM). However, samples produced in this work show higher values of $E$ and $\sigma_b$ compared to tensile samples produced by DIW.\[15\]

The surface fracture of samples after tensile tests are shown in Figure 16. 316L steel samples show a multiple layer fracture surface and the presence of macro pores deriving from the printing process for AISI316LB1 (Figure 16a) and closed pores for AISI316LB2 sintered at 1200 °C (Figure 16b) and 1240 °C (Figure 16c). At higher magnifications (Figure 16d–f), dimples are clearly visible confirming a ductile fracture mode.\[41\]

The analysis of literature data is summarized in Table 4, where tensile properties of both 3D printed and metal injection molded AISI316L are reported.

DIW still lies behind the values of parts produced by the FFF, PBF, and MIM process. The presence of porosity and oxides represent the main issues to be solved. However, the samples prepared in this work show remarkably higher values of tensile properties than DIW printed AISI316L T-bone samples found in the literature.\[15\] In contrast, the compression strength of scaffolds, showing a total porosity of $\approx 74\%$, is equal to 73.7 ± 5.5 MPa. Previous work reported in the literature, where 316L scaffolds were produced by DIW showed a $\sigma_y = 31.7$ MPa, for a total porosity of 52.4%.\[42\] The higher compression strength of our scaffolds can be correlated to the higher density of the

![Figure 14. Cross-section of AISI316LB2-1240 sample with circular agglomerates of oxides highlighted.](image)

![Figure 15. Stress–strain curves for AISI316LB1 and AISI316LB2 specimens and comparison with literature data.](image)

| Table 4. Overview of tensile properties of AISI316L parts produced by AM process and standard MIM. |
|--------------------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Extrusion Based | FFF | DIW | MIM | SLM | EBM |
| AISI316L | \[43\] | \[44\] | \[45\] | This work | \[15\] | \[46\] | \[47\] | \[48\] |
| $\sigma_y$ [MPa] | 167 | 148 | 251 | 141 ± 7.5 | 175 ± 20 | 211 ± 6 | 140 | 345 | 253 |
| $E$ [GPa] | 152 | 157 | – | 211 ± 8 | 192 ± 8 | 174 ± 9 | 0.053 | – | 187 | – |
| $\sigma_b$ [MPa] | 465 | 444 | 561 | 212 ± 18 | 304 ± 60 | 444 ± 4 | $\approx$200 | 450 | 563 | 509 |
| $\epsilon_b$ [%] | – | 44.3 | 53 | 3.6 ± 0.6 | 6.3 ± 3.3 | 12.3 ± 4 | $\approx$4 | 40 | 30 | 59 |

---

www.advancedsciencenews.com | www.aem-journal.com

Adv. Eng. Mater. 2022, 24, 2101729 | 2101729 (11 of 13) © 2022 The Authors. Advanced Engineering Materials published by Wiley-VCH GmbH
struts, as shown in Figure 10. Indeed, the scaffolds produced in previous work[42] showed a bimodal porosity, where struts are porous due to partial sintering.

Microhardness tests performed on the AISI316L-B1 section showed an average value of 177 ± 15 HV, in good agreement with literature data of DIW-printed AISI 316L specimens.[33] Further studies are forecast to define the amount of carbon content after sintering and its effect on the mechanical performance of the sintered components.

4. Conclusions

The main objective of this work was the development of a highly loaded ink for 3D printing by DIW AISI316L parts.

The ink was developed considering the following constraints: 1) Use of few components, use of water as the solvent, with a high load of powders. 2) Control of rheological properties to produce both dense and porous parts.

Two binders were developed (B1 and B2), changing the water amount and the relative weight ratio of the two polymeric components (PVA and PEG); consequently, two inks (AISI316LB1 and AISI316LB2) were prepared using the two binders and keeping the powder over binder weight ratio constant.

The rheological characterization of the two inks showed how both inks were suitable for DIW printing, with AISI316LB1 showing higher values of zero-shear rate viscosity, LVR, stress at the yield and crossover points, and shorter recovery time than AISI316LB2. Binder, with a higher water amount and a higher PVA over PEG ratio, is responsible for this behavior. Our tests showed how the presence of a higher amount of water affects the particle-binder interaction. Focused studies are needed to comprehend in-depth the behavior of this system. The 3D printing of tensile specimens was performed using fixed parameters to enhance the effect of the rheological properties of the ink on the quality of the printed structure.

Samples printed using AISI316LB1 showed the presence of macro-defects deriving from the printing procedure, whilst AISI316LB2 showed a uniform surface and section. After sintering at 1200 °C, porosity was 34% for AISI316LB1 and 15% for AISI316LB2 decreasing to 7% for AISI316LB2 sintered at 1240 °C and consequent higher shrinkage.

In contrast, samples produced using B1 showed a lower amount of oxides compared to samples produced using B2: the higher amount of polymers used to produce B2 released a higher amount of gaseous by-products that eventually reacted with metals present in the alloy such as Cr and Mo.

The effect of such defects on the mechanical response was clearly visible: the ductile behavior was inhibited by the presence of macro-defects in AISI316LB1. Closed pores and oxides agglomerates in AISI316LB2-1240 still affected the ductile response of the steel, which however showed higher values than DIW printed samples reported in the literature.

In addition, AISI316LB1 was used to produce porous scaffolds, with a span of 1.2 mm and the results show how the rheological characteristics of this ink were more suitable to produce self-supportive parts.

Figure 16. a–d) SEM micrographs of fracture surfaces of AISI316LB1, b–e) AISI316LB2-1200, c–f) AISI316LB2-1240.
To move a step forward DIW printing of metals, a deeper knowledge of ink rheological properties combined with a fine-tuning of printing parameters is necessary. In addition, a more detailed study of de-binding and sintering conditions will help to improve the mechanical properties of the printed parts.

Acknowledgements

The authors are thankful to Gloria Rigon (a former student of the University of Padova), Alberto Fabrizi (Department of Management and Engineering) for helpful discussion on the microstructural characterization, Gian Paolo Savio and Giacomo Mazzacavallo for assistance with mechanical tests. L.B. is grateful to the CeramGlass research group managed by Prof. Paolo Colombo, Department of Industrial Engineering, University of Padova for hosting part of the experimental activity.

Open Access Funding provided by Universita degli Studi di Padova within the CRUI-CARE Agreement.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

AISI 316L, direct ink writing, porous lattices, water-based ink, wet granular materials

Received: December 14, 2021
Revised: September 16, 2022
Published online: October 11, 2022

[1] ASTM F2792, Standard Terminology for Additive Manufacturing Technologies.
[2] ISO/ASTM 52900, Additive Manufacturing — General Principles — Terminology.
[3] ISO/ASTM 52901, Additive Manufacturing — General Principles — Requirements for Purchased AM Parts.
[4] ISO/ASTM 52910: Standard Practices-Guidelines for Design for Additive Manufacturing.
[5] G. Warwick, Aviat. Week Space Technol. 2014, 176, 43.
[6] D. Svetlizky, M. Das, B. Zheng, A. L. Vyatskikh, S. Bose, A. Bandyopadhyay, J. M. Schoenung, E. J. Lavernia, N. Eliaz, Mater. Today 2021, 29, 271.
[7] HORIZON-CL4-2022-RESILIENCE-01, A digitised, Resource-Efficient and Resilient Industry 2022 (Single-Stage).
[8] H. Elsayed, N. Novak, M. Vesenjak, F. Yanini, S. Carmignato, L. Biasetto, Mater. Sci. Eng. A. 2020, 787, 139484.
[9] M. Coffigniez, L. Grenmiller, S. Balvay, J. Lachambre, J. Adrien, X. Boulant, Addit. Manuf. 2021, 39, 108159.
[10] T. Kurose, Y. Abe, M. V. A. Santos, Y. Kanaya, A. Ishigami, S. Tanaka, H. Ito, Materials 2020, 13, 2493.
[11] H. Gong, D. Smelling, K. Kardel, A. Carrano, JOM 2019, 71, 3.
[12] M. Galati, P. Minetola, Materials 2019, 12, 4122.
[13] D. Godec, S. Cano, C. Holzer, J. Gonzalez-Gutierrez, Materials 2020, 13, 774.
[14] L. Ren, X. Zhou, Z. Song, C. Zhao, Q. Liu, J. Xue, X. Li, Materials 2017, 10, 305.
[15] T. J. C. Nocheseda, F. P. Liza, A. K. M. Collera, E. B. Caldana, R. C. Advincula, Addit. Manuf. 2021, 48, 102380.
[16] M. Y. N’Jock, E. Camposi, L. Gremillard, E. Maire, D. Frabegue, D. Chicot, K. Tabaleiev, J. Adrien, Mater. Des. 2017, 121, 345.
[17] H. Elsayed, P. Rebesan, G. Giacomello, M. Pasetto, C. Gardin, L. Ferroni, B. Zavan, L. Biasetto, Mater. Sci. Eng. C. 2019, 103, 109794.
[18] J. Lewis, Curr. Opin. Solid State Mater. Sci. 2002, 6, 245.
[19] R. Kramb, C. F. Zukoski, J. Rheol. 2011, 55, 1069.
[20] M. Sweeney, L. L. Campbell, J. Hanson, M. L. Pantoya, G. F. Christoph, J. Mater. Sci. 2017, 52, 13040.
[21] J. F. Morris, Rheol. Acta. 2009, 48, 909.
[22] J. C. van der Wef, C. G. de Kruijf, J. Rheol. 1989, 33, 421.
[23] P. Mills, P. G. Rognon, F. Chevoir, EPL 2008, 81, 64005.
[24] M. Yarahamadi, P. Barcelona, G. Fargus, E. Xuriguera, J. R. Roa, Ceram. Int. 2022, 48, 4775.
[25] J. Yan, S. Huang, Y. V. Lim, T. Xu, D. Kong, X. Li, H. Y. Yang, Y. Wang, Mater. Today 2022, 54, 110.
[26] M. A. S. R. Saadi, A. Maguire, N. T. Pottackal, M. S. H. Thankur, M. M. Ikram, A. J. Hart, P. M. Ajayan, M. M. Rahman, Adv. Mater. 2022, 34, 2108855.
[27] H. Park, H. Choe, D. C. Dunand, Mater. Sci. Eng. A. 2021, 815, 141262.
[28] C. Kenel, N. R. Geisendorfer, R. N. Shah, D. C. Dunand, Addit. Manuf. 2021, 37, 101637.
[29] C. Xu, B. Quinn, L. L. Label, D. Thiriault, G. L’Esperance, ACS Appl. Mater. Interfaces. 2019, 11, 8499.
[30] M. Pospischil, J. Specht, M. Kornig, M. Horteis, F. Clement, D. Biro, IEEE J. Photovoltaics 2014, 4, 498.
[31] C. J. Dimitriou, R. H. Ewoldt, G. H. McKinley, J. Rheol. 2013, 57, 27.
[32] V. G. Rocha, E. Saiz, I. S. Tirichenko, E. Garcia Tunon, J. Mater. Chem. A 2020, 8, 15646.
[33] R. C. Pack, B. G. Compton, Adv. Eng. Mater. 2021, 23, 2000880.
[34] J. E. Smay, J. Casarano, J. A. Lewis, Langmuir. 2002, 18, 5429.
[35] T. Scholdt, F. Keppenner, N. Travitzky, P. Greil, J. Ceram. Sci. Technol. 2012, 3, 676.
[36] J. M. Yang, C. Y. Chiang, H. Z. Wang, C. C. Yang, J. Membr. Sci. 2009, 341, 186.
[37] S. Han, C. Kim, D. Kwon, Polym. Degrad. Stab. 1995, 47, 203.
[38] Y. Zhang, E. Feng, W. Mo, Y. Lv, R. Ma, S. Ye, X. Wang, P. Yu, Metals 2018, 8, 893.
[39] D. Riabov, E. Hryha, M. Rashidi, S. Bengtsson, L. Nyborg, Surf. Interface Anal. 2020, 52, 694.
[40] H.-J. Sung, T. K. Ha, S. Ahn, Y. W. Chang, J. Mater. Process. Technol. 2002, 130–131, 321.
[41] J. Gonzalez-Gutierrez, F. Arbeiter, T. Schlauf, C. Kukla, C. Holzer, Mater. Lett. 2019, 248, 165.
[42] M. Kachit, A. Kopp, J. Adrien, E. Maire, X. Boulant, J. Mater. Res. Technol. 2022, 20, 1341.
[43] T. M. Mower, M. J. Long, Mater. Sci. Eng. A. 2016, 65, 198.
[44] C. Tosto, J. Tirillò, F. Sarasini, G. Cicala, Appl. Sci. 2021, 11, 1444.
[45] BASF ultrafuse 316L datasheet, https://forward-am.com/material-portfolio/ultrafuse-316l/ (accessed: November 2021).
[46] ASTM B883, Standard Specification for Metal Injection Molded (MIM) Materials: 2019 Edition.
[47] G. Singh, J. M. Missiaen, D. Bouvard, J. M. Chaix, Addit. Manuf. 2021, 47, 102287.
[48] Y. Zhong, L. E. Roannar, L. Liu, A. Koptuyg, S. Wikman, J. Olsen, D. Cui, Z. Shen, J. Nucl. Mater. 2017, 486, 234.