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Valente, Emilie Hørdum; Nadimpalli, Venkata Karthik; Andersen, Sebastian Aagaard; Pedersen, David Bue; Christiansen, Thomas L.; Somers, Marcel A. J.

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Influence of atmosphere on microstructure and nitrogen content in AISI 316L fabricated by laser-based powder bed fusion

Emilie Hørdum Valente1, Venkata Karthik Nadimpalli1, Sebastian Aagaard Andersen1, David Bue Pedersen1, Thomas L. Christiansen1, Marcel A. J. Somers1

1 Technical University of Denmark, Department of Mechanical Engineering, 2800 Kgs. Lyngby, Denmark
emhval@mek.dtu.dk

Abstract
The present work focuses on the influence of the composition of the protective gas (argon or nitrogen) used in laser-based powder bed fusion (L-PBF) on the nitrogen content, microstructure and hardness of AISI 316L austenitic stainless steel. L-PBF of AISI 316L powder using Ar gas resulted in loss of nitrogen in the final part. On the other hand, L-PBF using N2 gas resulted in an increase in nitrogen content in the final part, showing that nitrogen is absorbed during L-PBF manufacturing in N2 gas. The nitrogen absorption implies that the build part is actually AISI 316LN rather than AISI 316L.

The microstructures of 316L specimens manufactured in both atmospheres exhibited highly elongated γ-austenite grains, with a cellular structure. The hardness of the part manufactured in N2 gas was systematically higher than the part manufactured in Ar. For the part manufactured in Ar, a clear gradual decrease in hardness was observed with increasing distance from the build plate, while for the N2 manufactured part this hardness decrease is first observed at some distance from the build plate.

For the part manufactured in Ar, a larger variation in the measured nitrogen content was observed. Moreover, a systematically lower and position dependent micro-hardness and inhomogeneous etching response of this specimen indicate an inhomogeneous microstructure in the build.

The results demonstrate that the nitrogen content of L-PBF manufactured AISI 316L depends on the composition of the gas atmosphere used in the chamber. It is discussed qualitatively how desorption and absorption of nitrogen from the applied atmosphere play a role on the resulting composition and microstructure of the build part.

1. Introduction
Laser Powder Bed Fusion (L-PBF) is a popular Metal Additive Manufacturing (AM) process which requires the use of an inert atmosphere for safe laser melting of metal powders. For stainless steel, this is usually realised by flushing with argon or nitrogen until the chamber reaches a sufficiently low oxygen level (typically less than 0.1 %), followed by a continuous flow of the selected gas.

Argon is an inert gas but depending on the grade of the industrial gas quality used it will contain impurities such as oxygen. In addition to this, the build chambers in most L-PBF setups are not fully gas-tight, which means that oxidation will occur during the printing process; this implies enhanced oxygen levels in the finished parts. Besides the abovementioned oxygen contamination, nitrogen is not inert at elevated temperatures, and an appreciable amount of nitrogen can be dissolved in stainless steel.

Nitrogen “pick-up” is in particular relevant for austenitic stainless steels above, say, 900 °C, where there is an appreciable capacity for nitrogen in the solid state (in the austenite and by formation of Cr-nitrides). At these temperatures molecular nitrogen gas can dissociate and can easily result in nitrogen contents of more than 1 wt % (at equilibrium) depending on temperature. Uptake of nitrogen during processing can actually result in higher strength without loss of ductility and improved corrosion resistance provided it resides in solid solution in the austenite. However, at too high nitrogen concentrations the material can suffer from formation of hard chromium nitrides and local sensitization at elevated temperatures, thereby – negatively – changing the mechanical and anti-corrosion properties of the steel. [1, 2]

In an investigation of shielding gas in laser welding, Elmer et al. hypothesised that the reactivity and solubility of nitrogen, in comparison to argon, would reduce the amount of keyhole porosity in stainless steel; their calculations showed that a 6 vol.% N2 gas dissolved in AISI 304L leads to a mere 0.001 wt.% increase [3].

Zhang et al. compared ten combinations of argon, nitrogen, helium (protective gases) and hydrogen (as a deoxidizer) with regards to their influence on porosity. They concluded that argon and nitrogen, pure and with 10 and 30 vol.% hydrogen all resulted in dense parts [4]. Unfortunately, the evaluation did not include chemical or microstructural investigations.

Several publications addressed the influence of the gas flow on part quality. Ladewig et al. focused on the flow uniformity and the responding removal of by-products [5].

So far, limited work has been published on the influence of the atmosphere on the microstructure and chemical composition. Lou et al. reported a small increase in oxygen and carbon content and a decrease in nitrogen content after processing in nitrogen-gas atomized 316L powder by L-PBF in an argon atmosphere [6].

In the present work the influence of the gas atmosphere on the quality of L-PBF parts is addressed. To this end two batches were made: one batch was manufactured in Ar gas; a second batch in N2 gas. The microstructure, microhardness and nitrogen contents of the powder and the L-PBF parts are investigated.
2. Experimental Procedure

2.1. Materials and L-PBF fabrication

AISI 316L stainless steel powder from LPW technology was used with a particle size of (53 ± 15) μm and a certified composition (in wt%): Fe = Bal., C = 0.020, Si = 0.70, Mn = 0.76, P = 0.008, S = 0.004, Cr = 17.7, Ni = 12.6, Mo = 2.32, Cu = 0.02, N = 0.09, O = 0.02. For each build fresh powder was used. The powder was processed in the Aurora Labs S-titanium Pro laser powder bed fusion (L-PBF) system, which is a low-cost metal 3D printer utilizing two 150 W CO₂ lasers as the energy source. When powered simultaneously, the two beams pass through a set of optics before entering into the build chamber. A schematic of the build chamber is shown in Fig. 1.

Figure 1. Schematics of the build chamber in the used PBF system from Aurora Labs. Placement of the three specimens is shown approximately.

The two beams are focused onto a single spot, using a focus lens in the scan head that is mounted on a XY-stage equipped with stepper motors. A shielding gas was used to protect the focus lens during operation. The spot size of the focussed laser beams was about 150 μm in diameter. In comparison to other L-PBF processes, the Aurora Labs system is unique in its powder delivery as it uses a set of three hoppers located above the build chamber. These hoppers are connected to the inert gas and protective gas moves with the scan head, while a stationary fan is placed above the XY-stage at the right side of the build chamber, providing circulation of the chamber atmosphere.

Two different builds were made: L-PBF-Ar using 99.998 % argon gas, and L-PBF-N₂ using 99.999 % nitrogen gas. The chamber was purged such that the O₂ level in the chamber remained below 0.2 % throughout the build as measured on top of the build chamber. The build plate was expected to experience a lower concentration of O₂. After purging, the base plate was heated to 90° C and the powder hoppers to 50° C. Then the L-PBF process was initiated with powder delivery, followed by a sweeping action to deposit a thin powder layer. The focus lens mounted on the XY axes traverses across the powder bed melting regions of interest, similar to an extrusion-based 3D printing system.

In this study, 40 mm/s build speed, 120 μm hatch spacing, 30 μm layer thickness and 100 % laser power (averaging 255 W measured by Gentec-EO 300 W powder meter) were utilized to build three cuboids with dimensions 10 mm x 10 mm x 7 mm. A 90° rotation was used between layers such that the scan tracks do not remelt the same path in each layer. The volumetric energy density [7, 8] is calculated as 1770 J/mm³. The typical energy density range using fiber or Nd-YAG lasers in L-PBF is reported to be between 40-90 J/mm³. Even though the energy density is an order of magnitude higher, the CO₂ laser power absorbed by the powders is much lower. CO₂ lasers are inefficient at transferring energy to a powder bed, however, they offer a low-cost alternative to the more expensive fiber and Nd-YAG lasers.

2.2. Characterisation

The nitrogen content of as-received powder and L-PBF manufactured AISI 316L was measured by instrumental gas analysis (IGA), using a LECO TN500. The setup employs combustion by a high-frequency induction furnace, to release the nitrogen from the samples, and inert gas fusion-thermal conductivity (IGF-TC) to measure the nitrogen content. Four independent measurements were done for each batch.

The crystalline phases of the L-PBF manufactured AISI 316L were identified by X-ray diffraction (XRD) analysis. A Bruker D8 Discovery equipped with CuKα radiation was used to record the X-ray diffractograms, employing parallel beam geometry and symmetrical 9-2θ scanning, using a stepsize of 0.04° 2θ and a measurement time of 4 s per step. XRD was done on both yx and zx cross sections that were cut, ground and polished (final step was 3 μm diamond polishing).

For hardness measurement and microstructure investigations, a specimen from each build was cut along the build direction (in the zx-cross section) at the centre of the sample. The hardness of the as-built L-PBF AISI 316L was determined by Vickers microhardness indentations on embedded, ground and polished samples, using a Struers DuroScan 70-G5 microhardness tester. A load of 100 g was used with a dwell time of 10 s, measuring five profiles on each specimen, along the build direction (z).

For microstructural investigations, the embedded samples were etched in a solution of 4% HNO₃ and 1% HF for 16 minutes. A Zeiss Axio A1 light optical microscope was used to capture the micrographs of the etched L-PBF samples.

3. Results and discussion

3.1 Nitrogen content of L-PBF parts built in Ar and N₂

The nitrogen content in the powder was measured to (0.093 ± 0.002) wt %, confirming the 0.09 wt % certified by the supplier. The nitrogen content of the specimen built in argon was reduced to (0.086 ± 0.007) wt %, indicating desorption of nitrogen from the molten powder during the L-PBF-Ar process. Additionally, desorption from the solid state at elevated temperatures could also contribute to the loss of nitrogen.

Figure 2. Nitrogen content of AISI 316L powder, L-PBF build in argon and L-PBF build in nitrogen. Dotted line marks the min. nitrogen content for AISI 316N(9) and the max. nitrogen content for the powder as specified by the supplier, LPW technologies.

The specimen built in a nitrogen atmosphere had a nitrogen content of (0.105 ± 0.002) wt %, confirming that nitrogen was picked up in the material during the L-PBF-N procedure. The standard deviations in nitrogen content for the powder and the N₂ build are the same, suggesting that the nitrogen is more evenly distributed in the specimen build in N₂, than in the specimen built in Ar. The nitrogen content of the specimen built
in the nitrogen atmosphere meets the AISI 316N specification, as illustrated in Fig. 2, and hence essentially changed the alloy from 316L to 316LN. As the oxygen and carbon contents of the as-built parts were not measured, it is unknown whether the compositions are still in the AISI 316L range. Following Lou et al. [6], the carbon and oxygen contents are not expected to increase significantly, even though the L-PBF system used in the present work deviates from that in [1].

3.2 **Microstructure of L-PBF parts built in Ar and N2**

Cross sections of the built parts are shown in figure 3, where the etching revealed both layering and long columnar grains.

The microstructure is shown in greater detail in figure 4. Clearly, both processes resulted in elongated austenite grains, (Fig. 4 a and d), containing a fine cellular structure, shown in Fig. c and f. In both specimens the cellular structure is interrupted at the fusion-boundaries and can continue or change its growth direction beyond the fusion boundary, depending on the local cooling conditions. It is worth noting that the cellular growth mainly continues across the fusion boundaries, indicating an epitaxial nucleation and growth from the previous parent microstructure (black circle).

The melt pool shapes and the 90° rotation between consecutive layers are visible in fig. 4 b and e. The melt pools are bowl shaped with a fairly regular geometry, indicating that no key-holing occurred. This is consistent with only few irregularly shaped porosities at fusion boundaries.

Fig. 4 a shows two different areas of L-PBF AISI 316L, because the etching response of the argon built sample was not as homogeneous as for the nitrogen built sample (also clearly observed in Fig. 3). The darker areas at higher magnification (Fig. 4 a and d) are caused by various effects. The variations in the cross-sectioned cell size were demonstrated to have different chemical compositions and dislocation densities in cell interior and cell wall thus lead to changes in etching response [10]. The crystallographic direction of the austenite phase also influences the etch rate. Furthermore, inhomogeneity in chemical composition and dislocation density, caused by the selective melting, remelting and cyclic re-heating can have an influence. It is noted that in particular nitrogen has an important influence on the passivity of stainless steel [11]. An inhomogeneous nitrogen distribution, as for the Ar build, will be accompanied by inhomogeneous etching response.

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**Figure 3.** Macrograph made by stitched micrographs of L-PBF 316L build in Ar gas (a) and in N₂ gas (b). Etched in 4% HNO₃ 1% HF sol. for 16 min.

**Figure 4.** Light optical micrographs of L-PBF 316L built in argon (a-c) and in nitrogen (d-f). Etched in 4% HNO₃ and 1% HF solution for 16 min.

**Figure 5.** X-ray diffractograms of L-PBF 316L samples fabricated in either argon or nitrogen, measured on both yx and zx cross sections.
X-ray diffraction analysis results in Fig. 5 confirmed that both the argon and the nitrogen built specimens are fully austenitic. There is no evidence for the presence of α- or δ-ferrite. The γ peak intensity and shape in the diffractograms of the 316L-Ar and 316L-N₂ samples were similar. However, large intensity differences between the 111γ, 200γ, peaks and the 220γ, peaks are observed for the yx and the zx cross sections. This indicates that both the argon and the nitrogen builds resulted in similar and strongly textured specimens.

### 3.3 Microhardness of L-PBF parts built in Ar and N₂

The average hardness from the microhardness profiles of the L-PBF 316L built in argon was (257 ± 17) HV₀.₁, while the parts built in nitrogen had an average hardness of (267 ± 10) HV₀.₁, i.e. no significant difference in hardness.

Nevertheless, the hardness profiles in figure 6 show that the hardness values for the N₂ build are systematically higher than for the Ar build. Furthermore, while the hardness for the Ar build decreases gradually with distance to the build plate, it remains largely constant for the N₂ build.

![Figure 6. Vickers microhardness profiles for 316L L-PBF fabricated in argon and nitrogen. Measured on polished zx cross-section. Each data point is an average of 5 independent measurements, the profiles were calculated by polynomial fitting, and the total average for each specimen is given with the standard deviation in top right corner.](image)

The observed decrease in hardness of the Ar built sample could be due to two factors. Firstly, the increase in temperature of the part during L-PBF processing leads to lower cooling rates as the build height increases. This can lead to an increase in the cell size and the associated decrease in hardness [12].

Secondly, it is suggested that the differences are related to the nitrogen contents in the builds. A higher nitrogen content corresponds to a higher hardness [13], consistent with the systematically higher hardness for the 316L-N₂ build. Then, the gradual decrease in hardness for the 316L-Ar build can be understood as follows. The solubility of nitrogen in AISI 316L depends strongly on the combination of temperature, nitrogen pressure and state (solid or liquid). Thermodynamic calculations for AISI 316L [13] show that the solubility of N in the liquid state in equilibrium with 1 bar N₂ is approximately twice as high as in the powder used in this investigation, while, obviously, the solubility is nil in equilibrium with 1 bar Ar. During solidification the equilibrium solubility first reduces in the ferrite phase, which exists for a narrow temperature interval, and thereafter increases in the austenite phase, which has a higher solubility for nitrogen than the liquid phase [13]. With increasing thickness of the build, i.e. increasing distance to the build plate, the cooling rate is likely to decrease. Accordingly, this provides more time for nitrogen to dissolve into or evaporate from the liquid phase in N₂ and Ar atmosphere, respectively. The exchange (absorption or desorption) of nitrogen with the gas during cooling can continue until a temperature of, say, 900 °C is reached, where the alloy is austenitic.

The net effect of larger cells and nitrogen exchange with the gas leads to a decrease in hardness in the Ar build, while the hardness is maintained in the N₂ build, indicating that the hardness reduction by larger cells is counteracted by more nitrogen uptake.

The nitrogen content in austenitic stainless steel is determined by the partial pressure of nitrogen in the gas mixture, i.e. there is an equilibrium between the imposed partial pressure of nitrogen and nitrogen in the solid state. Hence, the amount of nitrogen “pick-up” or the amount “lost” during metal AM depends strongly on the applied nitrogen partial pressure in the gas atmosphere. Since the nitrogen content in the 316L-N₂ build is beyond the maximum value allowed for 316L, the application of Ar-N₂ gas mixtures, for controlling the nitrogen contents in the printed parts, should be investigated.

### 4. Conclusion

Two different L-PBF builds were successfully performed; one in Ar gas, and one in N₂ gas.

L-PBF manufacturing of 316L in argon leads to nitrogen loss, as the nitrogen content of the AISI 316L specimen manufactured in Ar was reduced by 0.007 wt %, compared to the AISI 316L powder. In contrast, L-PBF of 316L in N₂ gas leads to nitrogen increase, as the specimen manufactured in N₂ gas had a significant increase of 0.012 wt %, compared to the AISI 316L powder. Similarly, the hardness of the specimen manufactured in N₂ gas was 10 HV₀.₁ higher than the specimen manufactured in Ar gas, due to the increased nitrogen content.

The microstructure of both L-PBF 316L specimens was fully austenitic, with a cellular structure. The specimen manufactured in Ar had a more heterogeneous structure, possibly associated with an increased heterogeneous nitrogen distribution.

The results showed the influence of gas chemistry used in L-PBF on the nitrogen content on the final parts and possibly on the homogeneity of microstructure and hardness. Nitrogen has a paramount importance in the alloying of stainless steel, as even minor changes will have a major impact on the mechanical and electrochemical properties. Future works will therefore focus on the influence of powder reuse with regard to nitrogen content and establishing a method for choosing the atmosphere chemistry in which the nitrogen content in the printed part is controlled.

### References