

3D-printed 316 L stainless steel: optimization of low temperature plasma assisted carburizing

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To improve surface hardness and wear resistance of austenitic stainless steels, conventional treatments, carried out at temperatures above 550°C, are not suitable. Therefore, low-temperature treatments have been developed; among them, one of the most promising is plasma-assisted carburizing. In fact, this treatment leads to relevant improvements in surface hardness in very short time frames (less than 8 hours). Previous studies have proved that low-temperature plasma-assisted carburizing treatments can be successfully employed to improve surface hardness of stainless steels produced with both conventional manufacturing processes and additive manufacturing (AM). Since additive manufacturing leads to higher mechanical properties, further analyses have been carried out on 316 L stainless steel produced by Laser Powder Bed Fusion (L-PBF) in order to define optimal carburizing parameters. First, gas carburizing mixtures with different amounts of CH₄ and H₂ have been tested. After treatments of 7 hours at 475°C, the result is the formation of an expanded austenite layer (~25 μm), responsible for the improvement of surface hardness, covered by a thin (~2 μm) over-layer of diamond-like carbon (DLC), which mainly impacts the friction coefficient and lowers the wear resistance. The atmosphere composition of 2.5% CH₄+97.5%H₂ led to the best results considering surface hardness and wear tests. Therefore, in order to determine the influence of treatment time on surface hardness improvement and DLC over-layer formation, new treatments, carried out in an atmosphere of 2.5% CH₄+97.5%H₂, at 475 °C and for shorter times, were performed. The preliminary results of this work indicate that 1 hour of treatment might be a good trade-off, since it leads to hardness values comparable to those obtained with longer treatments, but prevents the formation of the DLC over-layer.

KEYWORDS: 316 L STEEL, LPBF, PLASMA ASSISTED LOW TEMPERATURE CARBURIZING

INTRODUCTION

Austenitic stainless steels are employed in various fields, from biomedical to energetic, due to their excellent corrosion resistance, weldability, and good mechanical properties. On the other hand, in many cases, thermochemical treatments, such as carburizing are required to improve their hardness and wear resistance. Typically, these treatments are performed at temperatures above 550 °C. In austenitic stainless steels, at those temperatures, precipitation of Cr carbides occurs with a consequent detrimental effect on the corrosion resistance. Therefore, low-temperature thermochemical treatments, such as Kolsterising, have been developed to obtain surface hardness improvements without negative effects on corrosion resistance (1), but they usually involve long treatment times.

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A plasma-assisted carburizing treatment, which reduces treatment times, has been developed on 316 L stainless steel produced through traditional manufacturing processes (2, 3).

Additive Manufacturing (AM) processes, such as Laser Powder Bed Fusion (L-PBF), have been gaining increasing attention in recent years for the production of components used in different fields, from biomedical (4) to aerospace (5, 6). Many studies have been carried out on stainless steels to optimize the printing process (7, 8) and achieve better mechanical properties thanks to the finer microstructure (9-11) compared to traditionally manufactured ones. However, the improvements obtained are still not enough in terms of wear behaviour; therefore, further treatment could be necessary and the investigation of plasma-assisted treatment on the 3D printed material showed promising results (12, 13).

The result of plasma-assisted treatments is the formation of an expanded austenite layer (S-phase) covered by a Diamond-Like Carbon (DLC) over-layer. The treatments have been carried out in gas mixtures containing different amounts of CH₄ and H₂ and, although all plasma

treatments improved hardness and wear resistance, the one performed in an atmosphere consisting of 2.5% (CH₄) + 97.5% (H₂) was the most effective (12, 13). However, the hard and brittle DLC over-layer formed on the surface partially reduced the benefits in wear resistance (13).

Since the growth of the DLC over-layer seems to occur after the formation of the S-phase, new treatments, for shorter times (0.5, 1 and 2 hours), have been performed, in a 2.5% (CH₄) + 97.5% (H₂) mixture, to determine the minimum time interval that guarantees hardness improvements without the formation of the DLC over-layer. The samples were investigated by X-ray diffraction (XRD), Raman spectroscopy, and micro-hardness tests.

MATERIALS AND METHODS

Sample preparation

316L stainless steel (nominal chemical composition reported in Tab. 1) samples were produced using Laser Powder Bed Fusion (L-PBF) technique. The diameter of the spherical particles of the used powder ranged from $d_{10} = 18.17 \mu\text{m}$ to $d_{90} = 45.44 \mu\text{m}$.

Tab.1 - Nominal chemical composition (wt.%) of the 316 L stainless steel powders used to produce the samples to be treated

C	Cr	Mo	N	Mn	Si	Ni	P	S	Fe
0.024	16.87	2.06	0.083	1.35	0.40	10.05	0.031	0.029	to balance

The samples were taken from 3D printed blocks (30.5 x 20.5 x 7 mm³) built on a Concept Laser M2 Cusing machine with the following parameters: laser power P = 180 W, scanning speed $v_s = 600 \text{ mm/s}$, laser spot diameter $d_l = 120 \mu\text{m}$, hatch distance $h_d = 105 \mu\text{m}$, layer thickness $t_l = 25 \mu\text{m}$; each layer was printed in the pattern described in a previous work by the same authors (14). The printer was equipped with a single-mode CW ytterbium-doped fibre laser (emission wavelength is 1070 nm). The process was carried out in an inert atmosphere of Ar. The microstructure of the printed material consisted of austenite and a residual δ -ferrite (~5% maximum content).

The blocks were cut into 7 x 6 x 2 mm³ bricks using a diamond saw. A mirror-like surface was obtained by

mechanical polishing with grinding papers and, last, a suspension of 0.3 μm alumina powder in water; before plasma treatment, each sample was immersed for 10 minutes in a sonication bath. Three samples were prepared for each treatment time.

Plasma treatments

The samples were treated with a 2.5% CH₄ plus H₂ gas mixture for different times: 0.5, 1 and 2 hours. Surface treatments were performed using a microwave plasma-enhanced chemical vapour deposition (CVD) reactor (15). Before each plasma treatment, the samples were bombarded with hydrogen, for 15 minutes, on the surface to be treated to remove the passive oxidation layer.

The chamber pressure and microwave power have been kept at a constant value of approximately 70 mbar and in the range 400 – 500 W, respectively, to obtain a temperature ~ 475 °C. This temperature has been proved

to be a good trade-off to reach good surface hardness improvements and to avoid precipitation of $M_{23}C_6$ carbides and undesirable phases (η , χ and σ) (1, 16).

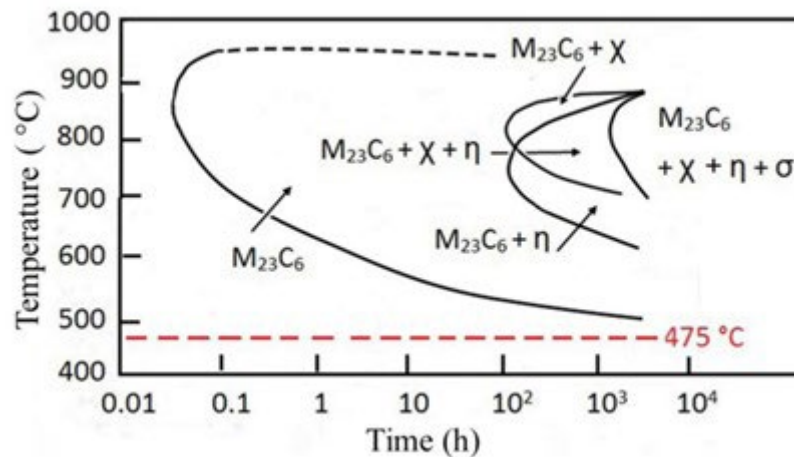


Fig.1 - TTT diagram of austenitic stainless steel.

Sample characterization

To investigate the results of the treatments, Vickers micro-hardness tests (micro-hardness tester Shimadzu Corporation, Kyoto, Japan) have been carried out on the samples using increasing loads (25, 50, 100, 200, 300, 500 and 1000 g) to determine the hardness vs. penetration depth profiles.

Since the improvement in micro-hardness strongly depends on carbon content, XRD measurement was

performed with a PW 1729 diffractometer (Philips, Eindhoven, The Netherlands) using the Mo-K α radiation, with a wavelength $\lambda = 0.07093$ nm, 2θ steps of 0.005° and a counting time of 10 s per step, to record precision peak profiles. The values of C content C_v (wt%) in the S-phase of each treated sample were determined from the lattice parameters of the untreated austenite ($a_{0\gamma}$) and S-phase (a_γ) through the empirical relationship proposed by Ridley et al. (17):

$$a_\gamma = a_{0\gamma} + \alpha C_\gamma \quad (1)$$

being $\alpha = 0.0044$ nm / wt% C, $a_{0\gamma}$ and a_γ have been determined using the $\cos 2\theta$ method (18).

To investigate the formation of the DLC over-layer, Raman Spectroscopy (RS, OPTOSKY, ATR 8300 Series, Xiamen, China) measurements were carried out in the spectral range of 200 - 2000 cm^{-1} , at room temperature and in air by employing a laser wavelength of 785 nm.

RESULTS AND DISCUSSION

Micro-hardness tests on the treated surface

For a homogeneous material, the values of micro-hardness do not depend on the load used in the test. In this case, due to the formation of a hardened C-rich

S-phase layer, micro-hardness changes with increasing applied load: greater loads lead to deeper penetration of the indenting tip, and therefore the S-phase and substrate contribute differently to the results of the test. Moreover, the possible presence of a DLC over-layer can give rise to high Vickers micro-hardness values for low penetration depths.

The measured values are shown in Fig. 2, the Vickers micro-hardness values are plotted vs. penetration depth. The points in each curve correspond to the values measured in tests carried out by using loads of 25, 50, 100, 200, 300, 500 and 1000 g.

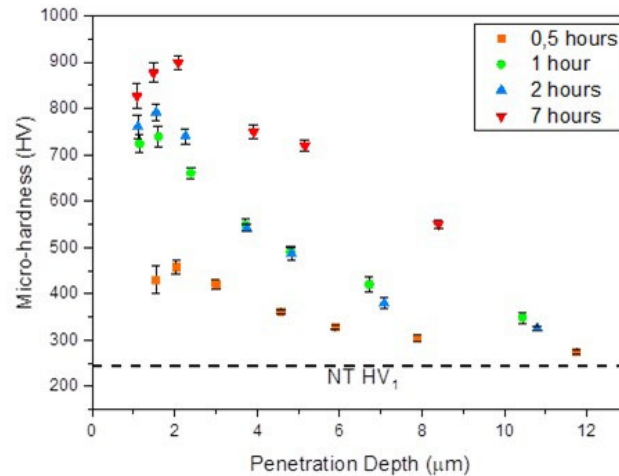


Fig.2 - Micro-hardness vs. penetration depth in samples treated for 0.5, 1 and 2 hours. The Vickers microhardness values of the untreated material (dashed line) and after 7 hours treatment (12) are reported for comparison.

From Fig. 2 it is evident that for all treatment times there is an improvement in surface hardness in comparison with the non-treated material (NT). Longer treatment times lead to higher micro-hardness values, but even after 0.5 hours of treatment, a significant improvement can be achieved.

For all samples, micro-hardness depends on the load used in the test with a significant decrease with increasing load. After 1 and 2 hours of treatment, the trend is similar to what was observed in samples treated for 7 hours, especially for the sample treated for 2 hours, the micro-hardness values for penetration depth lower than 2 μm are comparable to what was obtained after 7 hours, but hardness values decrease more rapidly. These higher values at low penetration depth are in agreement with what has been observed in samples treated for longer times where a DLC over-layer of ~2 μm thickness formed. The tests with higher loads show that the micro-hardness values of samples treated for 1 and 2 hours are comparable, meaning that there is no improvement in the properties of the S-phase. After 0.5 hours of treatment the hardness is significantly lower, but its value is always higher than that of the non-treated samples.

Increasing treatment times from 0.5 to 1 hour gives rise to improved hardness, between 1 hour and 2 hours, the main effect of a prolonged plasma exposure is the growth of an over-layer without any advantages in terms of S-phase

properties. Longer treatment times, for example for 7 hours, can increase surface hardness, but the formation of the DLC over-layer cannot be avoided.

XRD Analysis of the sample after plasma treatment

From XRD analysis, it is possible to observe a shift toward lower angles of the peak positions of all treated samples compared to those of untreated steel (Fig. 3). This lattice expansion evidences the formation of the S-phase, responsible for the observed improvement in hardness. By determining the lattice parameter a_{γ} of each sample, it is possible to calculate the C content using equation (1). For all three samples, the carbon content is around 2.0 wt.%, and the differences between them are within the experimental error (± 0.05 wt.%); this value, which represents the average on a thickness of approximately 50 μm (18), is higher than that of the untreated material.

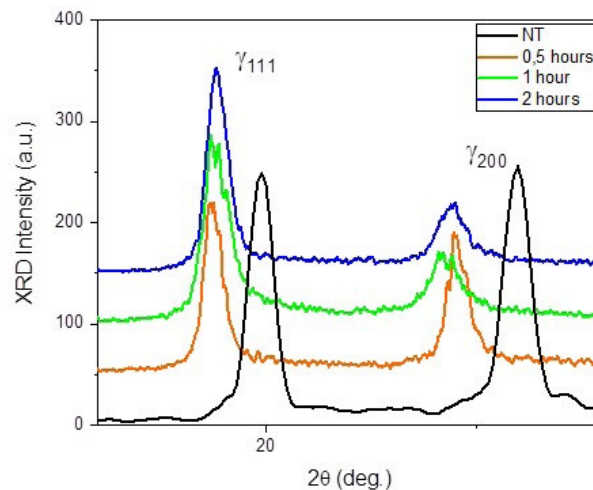


Fig.3 - {111} and {200} XRD reflection of 316 L steel produced by L-PBF in as-built condition (NT) and after plasma treatments carried out for 0,5, 1 and 2 hours.

Raman spectroscopy after plasma treatment

Raman spectra (Fig. 4) were collected to investigate the growth of the DLC over-layer on the S-phase.

Since carbon can exist in electronic hybridisation states sp^3 and sp^2 , the deposition of C atoms on a substrate can give rise to the formation of a great variety of crystalline and disordered structures: there are many different DLC phases of amorphous carbon. These phases are characterized by a specific ratio of sp^2/sp^3 states (19), and their properties strictly depend on this ratio.

In Fig. 4 Raman spectra of non-treated steel and after 0.5, 1 and 2 hours of treatment are reported, as a comparison also the data of the sample after 7 hours of treatment are shown. It is possible to observe that no sample presents the typical diamond peak at 1332 cm^{-1} (20). As discussed

in a previous investigation, after a 7 hours treatment it is possible to observe two distinct peaks: the D and G peaks, related to sp^2 hybridization states which correspond to neighbour atoms moving in opposite directions in the plane of the graphitic sheet (D peak) or perpendicular to this plane (G peak). The presence of those peaks indicates the formation of a DLC over-layer, which was confirmed by other observations. In the new samples, up to 1 hour of treatment no DLC over-layer formed on the surface since the D and G peaks intensities are comparable to the spectrum of non-treated material. After 2 hours of treatment, the peaks are more distinct and their intensity is significantly higher, meaning that a DLC over-layer is present on the treated surface.

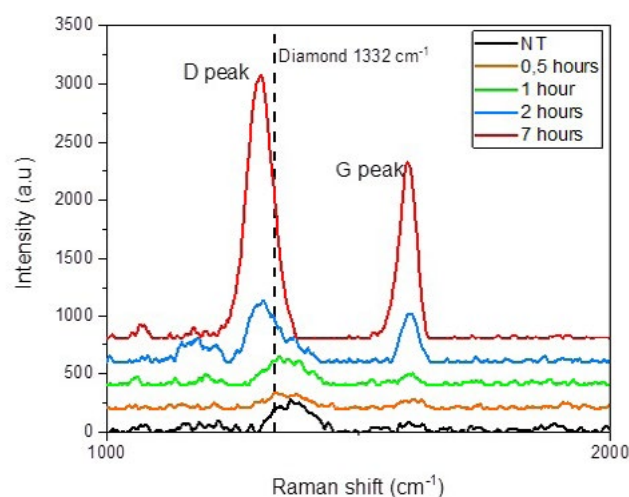


Fig.4 - Raman spectra of 316 L steel produced by L-PBF in as-built condition (NT) and after plasma treatments for 0,5, 1 and 2 hours. Raman spectra of the sample after 7 hours of treatment (12) are reported as a comparison.

CONCLUSIONS

Based on previous investigations, new low-temperature plasma-assisted treatments in 2.5% (CH₄) + 97.5%(H₂) atmosphere have been carried out for shorter treatment times to determine the minimum time interval to obtain the formation of the S-phase and to prevent the growth of a DLC over-layer.

- The S-phase forms even after short treatment times (0.5 hours), but its properties change after 1 hour of treatment.
- No significant improvements in the properties of S-phase can be observed between 1 hour and 2 hours; the only effect of a longer treatment is the formation of the undesired DLC over-layer.

- All the samples present higher values of surface hardness compared to the non-treated material, even if they are lower than the one obtained after 7 hours of treatment.

From these preliminary results, the best trade-off seems to be the treatment carried out for 1 hour since it leads to surface hardness values comparable to the ones obtained after longer treatments but prevents the formation of the DLC over-layer which hinders the wear behaviour. Therefore, longer treatments seem to be disadvantageous. To confirm these results, the wear behaviour of samples treated for 0.5, 1 and 2 hours will be investigated in further research.

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