

Microstructural and Corrosion studies of Super-duplex Stainless steels produced via Additive Manufacturing

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ABSTRACT

This work focuses on the influence of post-processing on microstructure and corrosion properties of additive manufactured (AM) super-duplex stainless steels (SDSS) 2507 consolidated via laser-powder bed fusion (L-PBF). Conventional heat treatment or hot isostatic press (HIP) with different cooling rates; 200 °C/min or 5 °C/min were carried out. The corrosion resistance was analyzed by critical pitting temperature (CPT) using ASTM G150 and immersion testing. Scanning Kelvin Probe Microscopy (SKPFM) was used to evaluate the electrochemical response.

The results suggest that different thermal cycles led to variation in the microstructure and corrosion properties. HIP with a fast cooling rate is recommended to ensure good corrosion resistance of L-PBF 2507. Use of a slow cooling rate after HIP processing can lead to appreciably lower corrosion resistance compared to conventional manufactured 2507 due to the presence of detrimental phases. A conventional heat treatment of the AM components can also give acceptable corrosion resistance. The conclusion is that with the right post-processing, the L-PBF material had similar or even higher corrosion resistance than conventional material and thus a high potential to be used in off-shore applications or other corrosive environments.

Key words: duplex stainless steel, SDSS, additive manufactured, AM, L-PBF, corrosion, SKPFM, pitting, CPT

INTRODUCTION

Powder-based additive manufacturing (AM) of stainless steels has experienced a strong development in recent years to produce complex shaped components with improved properties compared to conventional methods involving casting, working and fabrication.¹⁻³ This has led to an exponential growth of the research field. The AM process generates unique and distinctive microstructures unlike those of any other manufacturing method.³⁻⁵ There are multiple parameters and conditions that can be used during additive manufacturing such as input energy density, laser spot size, powder type, powder size and travel speed. Small variations in these parameters can lead into large modifications of the microstructure, porosity, dislocation networks, heterogenous structure, intermetallic phases, segregation of elements and other factors that can affect the final corrosion and mechanical properties.⁶⁻¹¹

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Post-processing is crucial for super duplex stainless steels and AM manufactured materials are no exception. The choice of post-processing parameters, such as annealing temperature and cooling rate, has a strong influence on the final microstructure, corrosion and mechanical properties.⁹ Hot isostatic pressing (HIP) is well-known for densification of sintered parts and is a common post-process method. The parts are placed in an inert gas in a chamber at elevated temperature and pressure, which isostatically densifies the component. The process affects the microstructure of the component by increasing the density, closing internal pores and consolidating unmelted powder particles in the matrix.⁹ More homogenous microstructures over the build height with reduced porosity are obtained after HIP as shown by Iams *et.al.*¹² in an investigation on AM DSS or by Peter *et.al.*⁸ on Ti-6Al-4V and Inconel 718. For DSS an increased austenite fraction is seen after HIP heat treatment process.^{12,13}

To date the major focus of most investigations concerning AM steels have been on microstructure and mechanical properties, however, more and more attention is being paid to their corrosion properties in order to facilitate use in critical applications. Several variables can affect the corrosion resistance of AM metals such as surface roughness, porosity, solute segregation, inclusions and oxides, grain directionality, refined microstructure and residual stresses.^{3,6,11} Surface roughness can reduce localized corrosion resistance of stainless steels by promoting initiation of crevice corrosion at cracks and concave zones from printing.^{3,11} A similar effect is reported in studies of the effect of porosity on corrosion properties of AM metals. Pores, with a concave and closed geometry, can promote electrolyte stagnation leading to pit initiation and challenging pit re-passivation.^{3,14,15} Solute segregation in AM metals can cause large variations of elemental concentrations between the solute-rich areas and surrounding depleted areas. This can create micro-galvanic couplings that result in local and heterogeneous corrosion at a micro scale level. An influence of Mo and Cr segregation on pitting initiation in laser engineered net shaping (LENS) 316L has been reported.¹⁶ Oxides such as Mn-Si oxides have been shown to modify the corrosion resistance of selective laser melting (SLM) 316L.³ Another factor affecting corrosion of AM stainless is the grain directionality. Previous works showed higher susceptibility to stress corrosion cracking (SCC) for SLM 316 with elongated grains parallel to the build direction.^{17,18} The refined grain size commonly obtained after SLM process has been reported to have a positive effect on corrosion fatigue of SLM 316L.³ However, residual stresses has been found to decrease localized corrosion resistance of SLM 316L.^{3,19}

Numerous studies have focused on the corrosion resistance of AM 316L^{9,14,18–20} however very few publications are found on the corrosion resistance of the newly developed AM SDSS 2507.^{21,22} SDSS has an as-printed non-equilibrium microstructure with a ferritic matrix and small traces of austenite.^{23–25} This ferritic microstructure is more prone to corrosion than austenite²⁶ and combined with the presence of residual stresses decreases the corrosion resistance of the printed SDSS.²⁷ To ensure a high corrosion resistance of the AM SDSS a duplex microstructure of ferrite and austenite must be restored by post-processing heat treatment.^{21,25,28} A higher corrosion resistance after heat treatment has been reported for L-PBF 2507.²¹ Adequate heat treatments are crucial in order to avoid the precipitation of detrimental phases and precipitates such as chi, sigma phase or nitrides that are known to decrease the corrosion resistance of DSS²⁹. In this study, the influence of post-processing on microstructure and corrosion properties of L-PBF of SDSS 2507 is investigated.

EXPERIMENTAL

Materials and manufacturing

In this work additive manufactured SDSS 2507, UNS 32750, was produced from powder Sandvik Osprey® 2507 VIGA* by the printing process Laser powder bed fusion (L-PBF). The nominal composition of the powder was 25Cr, 7Ni, 1.2Mn, 4Mo, 0.8Si, 0.3N, 0.03C. Columns of size 125*30*30 mm were printed on a base plate followed by three different post-processing routes. The first type of post process was to solution anneal and rapidly cool the as-built material to avoid formation of sigma phase, referred in this work as AB+HT. This type

of heat treatment is similar to that used for conventionally produced super-duplex stainless steels. The second treatment involved hot isostatic pressing and heat treatment at 150 MPa and 1075 °C for 2 hours with Uniform Rapid Cooling (URC)[®]* fast cooling (max 200 °C/min) and is referred in this work as HPHT. This is a common post-process for additive manufactured DSS. Finally, the third type of post-processing involved the same HIP cycle but with slow cooling at 5 °C/min and referred in this work as HPHT_SC. This is not a common process, but it is included in this work to investigate the effect of a slow cooling on the microstructure and corrosion properties of AM 2507. Two reference samples of cast and cold rolled 2507, REF and REF_CR respectively, were also included in this work for comparison. The cast reference material, REF (UNS J93404) was purchased in solution annealed and water quenched condition according to ASTM A890/890M. The composition of the alloys investigated and the Pitting Resistance Equivalent Number (PREN) of AM 2507, cast (REF), and cold rolled (REF_CR) are given in Table 1. Optical Emission Spectroscopy analysis (OES) was used for measuring the composition of all the elements except for nitrogen and oxygen content that was determined using LECO. The PREN is often used as an indication of the pitting corrosion resistance of stainless steels; a high PREN corresponds to a high resistance to pitting and a low PREN to a low pitting resistance.

Table 1
Chemical compositions [wt.%] and PREN number (PREN = %Cr + 3.3x %Mo + 16x %N).

	C	Si	Mn	Cr	Ni	Mo	N	O	Fe	PREN
AB+HT	0.020	0.33	0.43	25.28	6.55	3.85	0.300	0.035	Bal.	42.8
HPHT	0.021	0.33	0.43	25.34	6.51	3.85	0.300	0.027	Bal.	42.8
HPHT_SC	0.021	0.33	0.43	25.30	6.51	3.87	0.298	0.025	Bal.	42.8
REF	0.023	0.78	0.54	25.06	6.68	4.29	0.266	0.025	Bal.	43.5
REF_CR	0.020	0.31	0.77	25.07	6.96	3.79	0.303	0.006	Bal.	42.4

Microstructure characterization

A Zeiss Gemini 450 equipped with Back-scattered Electron Detector (BSE) and Energy-dispersive detector (EDS) was used for characterising the microstructure and EBSD analysis. The samples were cut from vertical and horizontal cross-sections of the columns. Prior to examination, the samples were ground from P80 to P4000 followed by polishing using diamond paste 1 µm and 0.25 µm and a final step of oxide polishing with OP-A suspension for 20 minutes.

Grain size measurements were conducted on 3 random areas of size 450x500 µm² on the vertical section of each sample using EBSD. Similar areas were considered for quantifying phase balance in the microstructures as well. Vertical sections cut from the printed and post processed bars were taken and mounted. Polishing steps were performed starting from grinding with P120 paper to finish polishing with a 0.05 µm oxide medium. A Zeiss optical microscope was used to capture images at 50x of the area around 2.5x1.5 cm². Images were then analyzed using in-built pore analysis program, by thresholding the image to report relative densities of various post processed samples.

Corrosion testing

Pitting resistance of the AM and reference 2507 was evaluated using ASTM G150³⁰ standard. Samples sized 5x30x30 mm were cut from cross-sections of the printed columns at different heights parallel to the printing direction. Prior to testing surfaces were ground to P600. Measurements were carried out in a flushed-port cell, in 1 M NaCl at 700 mV SCE (Saturated Calomel Electrode). During testing, the temperature was increased by 1 °C/minute. A modified, more aggressive, version of ASTM G150 in 3 M MgCl₂ was also used to differentiate better the critical pitting temperature (CPT) between the different samples.

Immersion testing was conducted in 10 wt.% H₂SO₄ and 50 wt.% NaOH, following the procedure of ISO 18069.³¹ The purpose of these type of tests was to evaluate the corrosion rate in aggressive media relevant to various service environments and compare to reference

material. Triplicate samples of each material were exposed at three different temperatures. For materials exhibiting corrosion rates <0.1 mm/year the second temperature was increased by 10°C , and for those exceeding 0.1 mm/year the second temperature was lowered by 10°C . The third temperature was selected based on the same corrosion rate limits, though, the temperature change was only up/down 5°C . Prior to testing, the samples were wet ground to a P120 finish on all sides. For each temperature, the samples surface was cleaned in first tap water with a soft brush, then degreased in acetone followed by ethanol, and dried in pressurised air. Two samples were exposed for 24 h (Period I) + 72 h (Period II) + 72 h (Period III). Weighing was performed before and after each period. The solution was changed if the corrosion rate had exceeded 0.1 mm/year after period 1 (24 h), then after period 2 in all cases. Activation of the samples by contact with a piece of zinc was performed before Period III.

Scanning Kelvin Probe Force Microscopy (SKPFM) was used to evaluate the electrochemical response on the microstructure of the investigated materials by measuring the Volta potential difference of the metal with respect to the probe tip over the materials surface.

The Volta potential depends on several factors such as composition of the phases in the alloy, crystallographic structure and interatomic distance.^{29,33} The presence of the passive film can also affect the Volta potential, thus passive film properties such as thickness, compositions or defects are relevant³⁴. External loads or residual stresses that affect the passive film can also lead to variations of the Volta potential.^{34–36} The variations of Volta potential difference over the microstructure can be used as a corrosion resistance indicator where a higher Volta potential difference indicates a nobler phase and thus a phase less prone to corrosion attack compared to a phase with lower Volta potential difference.^{29,36–39} A single publication has been found on the use of SKPFM for investigating corrosion of additive manufactured metal.⁴⁰

The Volta potential analyses in this work were conducted with a Dimension Icon atomic force microscope (AFM) from Bruker using the frequency modulation mode (FM-KPFM). The probe used was a SCM-PIT (PtIr-coated Si) 200–250 μm long with a resonance frequency of 60–100 kHz and a nominal constant spring of 1–5 N/m. Prior to testing the specimens were cut from horizontal cross-sections of the printed columns and ground from P80 to P4000, gradually polished to $0.25\ \mu\text{m}$ diamond paste and a final step of oxide polishing with OP-A suspension for 20 minutes. The test was performed at least 24 hours after the last polishing steps to ensure the repassivation of the oxide film. All the measurements were done in air at room temperature, $\sim 21^{\circ}\text{C}$. The bias was applied on the specimen and no flattening was performed on the Volta potential maps. 1st order flattening was performed on the topography maps. All potential and topography maps were normalized. The scanned area varied between $10 \times 10\ \mu\text{m}$ and $20 \times 20\ \mu\text{m}$, and the duration for each map scan was ~ 15 min. Several scans were repeated at different locations over the specimen surface to confirm average constant levels of Volta potential difference over the surface. The results were analysed using the software NanoScope Analysis V1.9.

RESULTS

Microstructure evaluation of AM 2507 and the effect of post-processing

Microstructural analyses with SEM-BSE and SEM-EBSD of AM 2507 after post-processing AB+HT, HPHT and HPHT_SC are given in Figure 1 and Figure 2. As-built and heat treated (AB+HT) material and hot isostatic pressed material, HPHT, have a duplex structure with no sigma phase. Slow cooling after the HIP process, as for the HPHT_SC material, on the other hand caused formation of sigma phase at the interface between ferrite and austenite, seen as bright zones in the SEM-BSE images in

Figure 1 and in yellow in the SEM-EBSD images in Figure 2. Other factors influenced by the HIP process are the ferrite grain size, which was larger after HPHT compared to the AB+HT material, and the decrease in porosity. No significant differences in the microstructure were

observed for vertical and horizontal cross-sections. In Table 2 the fraction and grain size of ferrite and austenite and the porosity percent for the different materials are given. The ferrite fraction decreased after HIP, both for HPHT and HPHT_SC, but to a greater extent for HPHT_SC due to the formation of sigma phase. Porosity decreased after HIP as seen for HPHT and HPHT_SC in Table 2 with average pores size under 50 μm .

Table 2

Phase fraction and grain size measured on horizontal cross-section of AM 2507 after AB+HT, HPHT, HPHT_SC obtained after SEM-EBSD analysis.

Condition	Phase Fraction		Grain Size		Density [%]
	Ferrite (vol. %)	Austenite (vol. %)	Ferrite (μm)	Austenite (μm)	
AB + HT	49.00	51.01	21	5	99.89
HPHT	45.88	54.12	26	9	99.99
HPHT_SC*	32.81*	62.40*	17	11	99.99
REF	64.08	35.92	320	59	99.73

*HPHT_SC contains sigma fraction – 4.79%

