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Enhanced corrosion resistance of additively manufactured stainless steel by modification of feedstock

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Additive manufacturing (AM) is an emerging technology to produce engineering components. However, the major challenge in the practical application of AM is the inconsistent properties of additively manufactured components. This research presents a strategy of feedstock modification to improve the corrosion performance of selective laser melted (SLM) 316L stainless steel (SS). Modified feedstock powders were produced by ball-milling of commercial-316LSS powder with 1wt.% chromium nitride (CrN). The SLM coupons produced from modified feedstock powders (SLM-316L/CrN) exhibited significantly improved corrosion performance, as evident from the high pitting and repassivation potentials and absence of metastable pitting. The microstructural characterization revealed fine oxide-inclusions comprising Si, Mn, and S in SLM-316L and only Si and Mn in SLM-316L/CrN. The absence of sulfur-containing oxide-inclusions in SLM-316L/CrN and refined cellular structure, and the change in chemical composition were attributed to corrosion resistance enhancement due to the CrN addition.

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INTRODUCTION

Austenitic 316L stainless (316L) has a wide range of industrial applications ranging from kitchenware to nuclear, and aerospace industries¹. However, the production of complex structures of 316L by conventional manufacturing technologies entails high production time and cost and deteriorates the durability in many instances². Additive manufacturing techniques like selective laser melting (SLM) are suitable for producing complex structures and can revolutionize the manufacturing and application of materials. SLM is a powder bed fusion AM technique and has earned massive research attention owing to its ability to manufacture complex structures in a single-step operation employing computer-aided design. Nominally, SLM involves selective melting of powders using a high-energy laser beam followed by fusing metallic powder at a solidification rate of $\sim(10^4\text{--}10^7)$ K/s³.

Successful production of 316L components manufactured by SLM has been reported extensively. Superior and reproducible corrosion properties of SLM printed components are crucial to extend their engineering applications. However, the corrosion behavior of SLM-316L SS reported in the literature is inconsistent. Some studies^{4–6} showed superior corrosion resistance of the SLM-316L than wrought-316L, whereas others^{7–10} showed inferior properties. The inconsistency in the corrosion performance has been attributed to the manufacturing defects (like porosity) and microstructural heterogeneities^{6,11,12}. Post-processing is performed on the SLM-316L components to eliminate the manufacturing defects and obtain improved and consistent properties. However, the post-processing is time-consuming, expensive, causes material wastage, and sometimes does not result in the expected outcomes⁵. Deterioration in corrosion performance of SLM-316L has been reported after post-processing using hot-isostatic pressing (HIP) and heat treatments at elevated temperatures (900–1200 °C)^{5,13–15}. One of the approaches to overcome the issues could be improving the corrosion resistance of the as-printed components. The strategy of feedstock modification can enhance the corrosion resistance, compensating the deleterious

influence of the processing defects and microstructural heterogeneities, and the need for post-processing could be circumvented^{10,16–20}. These modified composite feedstocks can be produced by (1) mechanical alloying of a suitable additive and feedstock powder^{17,20–23}, (2) deposition/coating of additive on the surface of the feedstock powder^{24,25}, and (3) simple mixing of additive and feedstock powder²⁶. The research on AM from the modified feedstock material has been focused on investigating the microstructure and improving mechanical properties^{18–20}. Studying the corrosion behavior of additively manufactured stainless steel from the modified feedstock has attracted only limited attention^{10,17,27}. None of the studies reported improved corrosion performance of SLM-316L produced using modified feedstock. Additives used in feedstock modification, mostly ceramics, are envisaged to introduce electrochemical heterogeneities and therefore deteriorate the corrosion performance. On the contrary, an appropriate choice of additives that can refine the microstructure and/or suppress the formation of deleterious inclusions can be hypothesized to enhance corrosion resistance. This signifies a research gap in developing corrosion-resistant SLM-316L components.

Corrosion in stainless steel is attributed to the presence of inclusions such as manganese sulfide (MnS)³. The size and chemical composition of inclusions have been reported to control the corrosion of stainless steel^{28,29}. Moreover, high nitrogen-containing stainless steels amassed researchers' attention for decades for their high corrosion resistance due to nitrogen^{30–32}. Therefore, stainless steels with the absence of inclusions, homogenous microstructure, and high nitrogen content are anticipated to provide high corrosion resistance. The authors hypothesize that SLM can produce highly corrosion-resistant stainless steels if the feedstock is modified using additives that suppress the formation of deleterious inclusions, homogenize microstructure, and introduce nitrogen. Therefore, chromium nitride (CrN) was selected as an additive in this research. The melting point of chromium nitride (1770 °C) is less than the SLM

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processing temperature, and therefore CrN should melt and be part of the matrix.

A comparison among the corrosion performance and microstructure of wrought 316L (W-316L), SLM coupons produced using commercial 316L feedstock (SLM-316L), and modified feedstock (SLM-316L/CrN) has been presented herein. The commercial-316L powders were modified by ball milling of commercial feedstock with CrN. Test coupons produced from the modified feedstock (SLM-316L/CrN) showed high corrosion performance, as evident from high pitting and repassivation potentials. Furthermore, the post-corrosion investigation revealed no metastable and stable pits in SLM-316L/CrN. Thus, this work shows a method of improving corrosion performance of additively manufactured alloys and merit in modifying the feedstock for improving properties and exploring more additives that can improve the lifespan of the AM components.

RESULTS

Microstructural characterization

Scanning electron microscopy (SEM) of the modified feedstock (ball-milled 316LSS + 1 wt. % CrN) showed no significant change in the powder particle size and shape due to the milling process (Supplementary Fig. 1). The energy-dispersive X-ray spectroscopy (EDS) area maps showed that the CrN additive was distributed on the surface of the modified feedstock powder particles, Supplementary Fig. 1b. The density of Wrought-316L, SLM-316L, and SLM-316L/CrN using Archimedes principle were similar and calculated as 7.9 ± 0.01 , 7.9 ± 0.01 , and 7.89 ± 0.01 g/cm³, respectively. The X-ray diffraction analysis of SLM-316L and SLM-316L/CrN revealed the presence of only austenite phase, whereas W-316L showed austenite and along with a peak corresponding to either martensite or ferrite-phases, Supplementary Fig. 2. Literature shows possibility of martensite^{12,33,34} or alpha-ferrite^{18,35} or delta-ferrite^{36–38} in 316L stainless steel.

The backscattered electron images of SLM-316L and SLM-316L/CrN are depicted in Fig. 1. The melt pools generated from laser scanning of the individual specimen are shown in Fig. 1a, b. The melt pool's width and depth are influenced by the SLM processing parameters, selected additive and its quantity to the feedstock^{19,39}. On the contrary, SLM-316L and SLM-316L/CrN have similar melt pool widths and depths, which indicates that the CrN additive did not influence the melt pool dimensions.

The intragranular dislocation network, which also consists of elemental cellular segregation, in short, called the cellular structure, was observed in both SLM-316L and SLM-316L/CrN. The shape of the cellular structure can be viewed as equiaxed cellular structure (ECS) and columnar cellular structure (CCS), as depicted in Fig. 1c, d. The cellular structure comprises cells (also called sub-grains) and cell boundaries (also called cell-wall/sub-grain boundaries). The near polygon-shaped cells, shown in Fig. 1e, f, are referred to as ECS³⁹, whereas elongated cells as the CCS, as depicted in Fig. 1g, h. The width of the cell boundaries, in both ECS and CCS, were significantly higher in SLM-316L (Fig. 1e–h). A sub-cellular structure was identified inside each cell of ECS and CCS. Figure 1e–h depicts the sub-cells within each cell of ECS and CCS. The sub-cellular structure is not reported in the literature, which could be because this feature does not appear at high accelerating voltage (Supplementary Fig. 3), and the use of high accelerating voltage (20–30 kV) is a common practice. Figure 1i, j indicates the histogram representing the sub-cells area in SLM-316L and SLM-316L/CrN. The maximum number of sub-cells has an area between 0.05 and 0.15 μm^2 in SLM-316L, whereas, in SLM-316L/CrN the maximum number of cells has <0.005 μm^2 area. The refined sub-cell area of SLM-316L/CrN was caused by CrN addition and can be attributed to the role of CrN in providing heterogeneous nucleation sites or changing the thermal history

during solidification of the melt pool^{40,41}. Understanding the precise mechanism of sub-cell refinement due to CrN addition warrants dedicated future work.

Bright-field (BF) scanning transmission electron microscopy (STEM) image presented in Fig. 2 reveals the region of CCS of SLM-316L containing the columnar cells, cell boundaries, and sub-cellular structure. The cells were surrounded by dense entangled dislocations called cellular boundaries, whereas sub-cells were fenced by thin dislocations (interior of the cells) called sub-cellular boundaries, which can be correlated with SEM images, Fig. 1. The dislocations at the cellular boundaries and the interior of the cells have been widely reported in literature⁴². A series of spherical nanosized oxide-inclusions was observed at the cell boundaries and at the junction of sub-cell boundaries Fig. 2b. In addition, a tiger stripe-like pattern (termed as B-stripes) was observed in some of the cell interiors, as shown in Fig. 2c. Interestingly, no sub-cell or dislocations were noticed within B-stripe regions, whereas high dislocation densities were seen adjacent to the B-stripe pattern.

Figure 3 represents the STEM micrographs of CCS of SLM-316L/CrN where the columnar cells and cell boundaries are observed. A refined sub-cell size/area of SLM-316L/CrN than SLM-316L was noticed, which compliments the histograms from SEM analysis, Fig. 1e–h. Figure 3b reveals the oxide-inclusions present at the columnar cellular boundaries and the sub-cellular region.

The STEM-EDS of SLM-316L and SLM-316L/CrN are presented in Fig. 4a, b. In both the specimens, the columnar cellular boundaries showed segregation of Cr, Ni, Mo, and S and depletion of Fe. The presence of Cr, Ni, Mo, Mn, Fe, and Si have been reported in the cellular structure of SLM-316L^{11,43}. However, the EDS map of sulfur has not been reported in the literature. The chemical composition of nanosized oxides-inclusions in SLM-316L (30 ± 15 nm) comprises of Si, Mn, O, and S, Fig. 4a, whereas the oxide-inclusions in SLM-316L/CrN (53 ± 14 nm size) have Si, Mn, and O (Fig. 4b). Some oxide particles also contained Cr, Fig. 4b. It is worth noting that the oxide-inclusions were enriched with sulfur in SLM-316L but not in SLM-316L/CrN. The STEM analysis could not identify any nitrogen segregation in both specimens. However, the LECO ONH836 nitrogen analyzer detected 0.0820 and 0.165 wt.% nitrogen in SLM-316L and SLM-316L/CrN, respectively.

Corrosion resistance

The representative cyclic potentiodynamic polarization (CPP) curves of W-316L, SLM-316L, and SLM-316L/CrN in 3.5 wt% NaCl are presented in Fig. 5a–c. The breakdown potential (E_b), repassivation potential (E_{rep}), and maximum current density (i_{max}) were determined from the CPP curves and presented in Fig. 5d. The forward scan of W-316L depicted in Fig. 5a shows metastable pitting initiated at ~ 150 mV_{SCE} and gradually increased with potential, eventually reaching a breakdown potential (E_b) of 546 ± 20 mV_{SCE}. The reverse scan was commenced after reaching the set current density limit of 100 $\mu\text{A}/\text{cm}^2$. During the reverse scan, maximum current density (i_{max}) of 1510 ± 62 $\mu\text{A}/\text{cm}^2$ and the repassivation tendency as measured by repassivation potential (E_{rep}) as 129 ± 13 mV_{SCE} were obtained for W-316L. Similarly, the forward scan of SLM-316L represents the metastable pitting initiation at ~ 250 mV_{SCE} and E_b at 795 ± 63 mV_{SCE}, Fig. 5b. During the reverse scan, i_{max} of 2276 ± 97 $\mu\text{A}/\text{cm}^2$ and E_{rep} of -113 ± 30 mV_{SCE} were determined in SLM-316L. The forward scan of SLM-316L/CrN CPP curve, Fig. 5c, revealed no metastable pitting and higher breakdown potential ($E_b = 1018 \pm 38$ mV_{SCE}). The reverse scan for the SLM-316L/CrN showed significantly lower i_{max} (104 ± 20 $\mu\text{A}/\text{cm}^2$) and higher E_{rep} (994 ± 69 mV_{SCE}).

SLM-316L/CrN achieved significantly higher E_b , i.e., ~ 220 mV_{SCE} (20%) higher than SLM-316L and ~ 470 mV_{SCE} (45%) higher than W-316L. The i_{max} of SLM-316L/CrN is minimal compared to SLM-316L and W-316L. The repassivation behavior measured by E_{rep} of

Fig. 1 SEM-BSE images at different magnifications showing the microstructure of etched SLM-316L and SLM-316L/CrN. **a, b** Cross-sectional view; **c, d** CCS – Columnar cellular structure and ECS – Equiaxed cellular structure; **e–h** ECS and CCS revealing the cells, cell boundaries, sub-cells, and sub-cell boundaries; **i, j** Histogram representing the area distribution of sub-cells.

Fig. 2 STEM micrographs of SLM-316L. **a** BF image depicting the columnar cellular structure with cells and cell boundaries. **b** HAADF image showing the nanosized oxide-inclusions and sub-cells. **c** HAADF image of the B-stripe pattern.

Fig. 3 STEM micrographs of SLM-316L/CrN. **a** BF image revealing the columnar cellular structure with cells and cell boundaries. **b** HAADF image showing the nanosized oxide-inclusions and sub-cells.

SLM-316L/CrN drastically improved and faster than SLM-316L and W-316L. Unlike wrought and SLM-316L, no metastable pits were identified in SLM-316L/CrN. The metastable pits developed in W-316L and SLM-316L are attributed to cause the pitting corrosion, which is evident from the lower breakdown and the repassivation potentials. The addition of CrN resulted in superior corrosion resistance noted by the absence of metastable pits, higher breakdown, and repassivation potentials, and lower current density during repassivation.

Post-corrosion surface morphology

Figure 6a–d illustrates the surface morphology after potentiodynamic polarization (PDP) of SLM-316L and SLM-316L/CrN. Figure

6a, b depicts the pit, after PDP of SLM-316L, having corroded cells and intact cell boundaries^{5,11}. Unlike SLM-316L, SLM-316L/CrN exhibited different corroded cellular structure, Fig. 6c, d. Firstly, no pit was identified for the specimen. Secondly, the cell boundaries were corroded, and cells remained intact, Fig. 6d. This intracellular corrosion behavior could be crevice corrosion as it was only observed at the periphery of the exposed area to the electrolyte.

The potentiostatic polarization (PSP) tests were conducted for 90 min at ~ 100 mV_{SCE} below E_b , i.e., applied potential (E_{applied}) of 700 and 900 mV_{SCE} for SLM-316L and SLM-316L/CrN, respectively. The current density was plotted against time, as depicted in Fig. 6e. The PSP plot of SLM-316L exhibited metastable pitting with peak current densities between ~ 60 –700 $\mu\text{A}/\text{cm}^2$. Stable pitting

Fig. 4 STEM-EDS micrographs (HAADF). **a** SLM-316L, **b** SLM-316L/CrN.

occurred after metastable pits, and an example of current transients is displayed in Fig. 6e, where eight current transients are visible. SEM characterization following PSP reveals six pits with 15–30 μm diameter, resulting in low peak current densities (60–600 $\mu\text{A}/\text{cm}^2$). The two higher intensity peaks of (600–700 $\mu\text{A}/\text{cm}^2$) are attributed to large pits ($\sim 200 \mu\text{m}$ diameter) shown at the right end images (orange arrows) of Fig. 6f. The PSP plot of SLM-316L/CrN did not show any metastable pitting throughout the testing period, Fig. 6e, and the SEM examination of the specimen following PSP did not reveal any noticeable corrosion. The metastable pit frequency, λ ($\text{cm}^{-2}\cdot\text{s}^{-1}$), can be determined by normalizing the number of metastable pitting events to the product of surface area and exposure time^{6,44}. The λ value of SLM-316L and SLM-316L/CrN are 0.063 and 0 $\text{cm}^{-2}\cdot\text{s}^{-1}$, respectively

Passive film characterization

The passive films of SLM-316L and SLM-316L/CrN were characterized after 24 h of immersion in 3.5 wt.% NaCl using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). The XPS peak fitting parameters, which include the binding energies and full width at half maxima (FWHM) of respective elements, are presented in Table 1.

After subtracting the Shirley baseline, high-resolution detailed XPS spectra of $\text{Fe}2p_{3/2}$, $\text{Cr}2p_{3/2}$, $\text{Ni}2p_{3/2}$, and $\text{Mo}(3d_{3/2}, 3d_{5/2})$ were deconvoluted, Fig. 7. The survey scans of SLM-316L and SLM-316L/CrN are presented in Fig. 7a. The $\text{O}1s$ spectra depicted in Fig. 7b is

a combination of two peaks; peak-A contributions are from FeOOH , $\text{Cr}(\text{OH})_3$, MoO_3 , and H_2O , whereas peak-B from Cr_2O_3 , CrO_3 , Fe_3O_4 , NiO , and MoO_2 . Figure 7c represents the $\text{Fe}2p_{3/2}$ spectra as a combination of four constituent peaks, i.e., Fe^0 , FeOOH , Fe_2O_3 , and Fe_3O_4 . The $\text{Cr}2p_{3/2}$ spectra presented in Fig. 7d comprises four peaks, i.e., Cr^0 , $\text{Cr}(\text{OH})_3$, CrO_3 , and Cr_2O_3 . Researchers reported that the outer layer of the passive film mainly consists of $\text{Cr}(\text{OH})_3$, while the inner layer will be of Cr_2O_3 ⁴⁵. However, the co-existence of CrO_3 and Cr_2O_3 , due to similar standard free enthalpies, was evidenced by Olsson et al.⁴⁶ and Clayton et al.⁴⁷. Figure 7e presents the $\text{Ni}2p_{3/2}$ spectra deconvoluted into two peaks, i.e., Ni^0 and NiO . The $\text{Mo}(3d_{3/2}, 3d_{5/2})$ spectra depicted in Fig. 7f consists of six constitute peaks i.e., Mo^0 ($3d_{3/2}, 3d_{5/2}$), Mo^{+4} ($3d_{3/2}, 3d_{5/2}$) and Mo^{+6} ($3d_{3/2}, 3d_{5/2}$). The Mo^{+4} and Mo^{+6} were found to be the primary oxidation states of Mo. The existence of Mo^{+6} as MoO_4^{2-} , inhibits Cl^- absorption on the sample surface and can promote the formation of Cr_2O_3 and CrO_3 ^{48,49}.

The oxide/hydroxide ratios were calculated using the intensity (%) given in Table 1. The ratio of the oxides and hydroxides of Cr and Fe (given as $\text{Cr}^{\text{ox}+\text{hy}}/\text{Fe}^{\text{ox}+\text{hy}}$) for SLM-316L and SLM-316L/CrN is 2.66 and 2.85, respectively. Cr-oxides are Cr_2O_3 and CrO_3 , Cr-hydroxide is $\text{Cr}(\text{OH})_3$, Fe-oxides are Fe_2O_3 and Fe_3O_4 , and Fe-hydroxide is FeOOH . Also, the total oxide (Cr_2O_3 , CrO_3 , Fe_2O_3 , Fe_3O_4 , NiO) to hydroxides ($\text{Cr}(\text{OH})_3$ and FeOOH) ratio given as $\text{Total}^{\text{ox}}/\text{Total}^{\text{hy}}$ of SLM-316L and SLM-316L/CrN are 3.58 and 3.03, respectively. These ratios indicate the higher participation of chromium oxide in the passive film.

Fig. 5 Representative cyclic potentiodynamic polarization (CPP) curves. **a** W-316L, **b** SLM-316L, and **c** SLM-316L/CrN tested in 3.5 wt% NaCl. The inserted graphs depict the metastable pitting of the individual specimen.

Fig. 6 Post-corrosion characterization after corrosion testing in 3.5 wt% NaCl. BSE micrographs of (a, b) SLM-316L and (c, d) SLM-316L/CrN after potentiodynamic polarization. (e) Potentiostatic polarization curves of SLM-316L and SLM-316L/CrN conducted at applied potential (E_{applied}) of 700 mV_{SCE} and 900 mV_{SCE}, respectively. f BSE micrographs of metastable pits after potentiostatic polarization of SLM-316L.

Figure 8 presents the ToF-SIMS negative ion depth profiles of SLM-316L and SLM-316L/CrN. The intensities of secondary ion characteristics of the passive film ($^{18}\text{O}^-$, OH^- , FeO_2^- , CrO_2^- , NiO^- and MoO_2^- shown in Fig. 8a, c) and substrate (Fe_2^- , Cr^- and Ni^- shown in Fig. 8b, d) are plotted in logarithmic scale for individual specimens. Similar depth profiles of oxide and metallic ions are observed in both specimens. The interface, represented by bold dotted line, was determined at a particular sputter time where a significant change in slope of metallic peaks was observed^{50,51}. A gray dotted line (~25 s) was drawn where the hydroxide and oxide zones can be bifurcated. The hydroxide and oxide zones can be represented in zone-1 and zone-2, respectively. The oxygen characteristic of the oxide scale is explained by $^{18}\text{O}^-$ as $^{16}\text{O}^-$ saturates the detector. High-intensity peaks of OH^- , FeO_2^- , MoO_2^- were found in zone-1, whereas NiO^- are found in zone-2, Fig. 8a, c. The high-intensity peaks of OH^- and FeO_2^- indicate a high probability of Fe-hydroxide (FeOOH) formation in zone-1, i.e., the outermost region of passive layer^{48,52}. The high-intensity peak of MoO_2^- profile found in zone-1 may indicate that oxides of Mo are enhancing the stability of the passive film^{49,50,53}. The CrO_2^- profile intensity is uniform almost throughout the passive layer, Fig. 8a, c, which agrees with XPS results that chromium has higher participation in the passive film, Fig. 8d. The enrichment of Ni^- metallic ions at the interface between passive layer and metallic substrate was observed^{51,53}, Fig. 8b, d.

As evidenced from XPS and ToF-SIMS, both the SLM-316L and SLM-316L/CrN exhibited similar passive film compositions. Therefore, the possible role of change in passive film composition in improving corrosion resistance can be overruled.

DISCUSSION

The pitting corrosion resistance (Fig. 5) was in the order of SLM-316L/CrN > SLM-316L > W-316L. The higher corrosion resistance of SLM-316L in comparison to W-316L can be attributed to the absence of MnS. It is well known that the manganese sulfide (MnS) inclusions are the common impurities found in wrought and are the reason for pitting corrosion⁴. The nucleation frequency and metastable pitting have been reported to depend on the size and distribution of MnS particles^{54,55}. A critical MnS particle size of ~0.7 μm is required for stable pit formation^{28,29}. The rapid solidification rate during the SLM does not provide enough time for the elements to diffuse and form MnS inclusions⁶. Therefore, the absence of MnS inclusions in SLM-316L, confirmed by the SEM and STEM analysis, is attributed to higher E_b than wrought-316L, which is in agreement with the literature⁶. However, other sulfur-rich inclusions can act like MnS inclusions causing corrosion. Ke et al.²⁹ had reported three types of inclusions in austenitic stainless steel: MnS, the existence of multielement (Al, Mn, Cr) oxides, and a mixture of sulfides and oxides inclusions. It was stated that the multielement oxides and combination of sulfide and oxide inclusion could initiate corrosion^{29,54}. Although MnS inclusions were absent in SLM-316L, the next possible sulfur-rich inclusions (Si-Mn-S-O), as evident from STEM (Fig. 4a), is attributed to act as potential cathodic site and initiate pitting corrosion. The chemical inhomogeneity in the cellular structure favored transforming the metastable pitting into a stable pit. The cells having depletion of solute were preferentially targeted, causing superior corrosion within cells than cell boundaries, Fig. 6a, b. The absence of sulfur-rich inclusions in SLM-316L/CrN was attributed to the elimination of metastable pitting followed by stable pitting

Table 1. XPS parameters of SLM-316L and SLM-316L/CrN.

Elements	Compound	SLM-316L			SLM-316L/CrN		
		BE (±0.1 eV)	FWHM (±0.1 eV)	Intensity (%)	BE (±0.1 eV)	FWHM (±0.1 eV)	Intensity (%)
Fe	Fe2p _{3/2}	706.9	1.3	13	706.9	1.3	11.5
	FeOOH	711.3	2.0	3.6	711.4	1.9	3.3
	Fe ₂ O ₃	709.8	2.0	6.6	709.7	1.9	6.1
	Fe ₃ O ₄	708.2	2.0	7.7	708.0	1.9	7.5
Cr	Cr2p _{3/2}	574.0	1.6	6.6	574.0	1.6	7.6
	Cr(OH) ₃	577.8	2.1	10.9	577.9	2.3	13.3
	CrO ₃	579.6	1.8	2.8	579.5	1.2	0.9
	Cr ₂ O ₃	576.5	2.7	33.9	576.5	2.7	34.3
Ni	Ni2p	852.6	1.3	8.1	852.6	1.3	6.8
	NiO	853.6	2.0	1.0	853.6	2.0	1.6
Mo	Mo3d _{3/2}	230.6	1.3	1.1	230.6	1.2	0.8
	Mo3d _{5/2}	227.6	1.3	1.1	227.6	0.9	0.9
	Mo ⁺⁴ 3d _{3/2}	231.4	1.5	0.6	231.4	1.8	1.1
	Mo ⁺⁴ 3d _{5/2}	228.8	1.5	0.7	228.6	1.8	1.1
	Mo ⁺⁶ 3d _{3/2}	235.2	3.3	1.1	234.9	4.0	1.5
	Mo ⁺⁶ 3d _{5/2}	232.3	1.3	1.1	232.1	2.5	1.5

Binding energy (BE), Full width at half maximum (FWHM), and Intensity (%) values of XPS spectra of SLM specimens following 24 h of immersion in 3.5 wt% NaCl.

corrosion, Fig. 6e. This eventually favored higher E_p , and the inability to cause pitting corrosion might have supported the faster repassivation ability.

The improvement in corrosion performance of SLM-316L/CrN can also be attributed to increased nitrogen%. The nitrogen% of SLM-316L and SLM-316L/CrN is determined to be 0.0820 and 0.165 wt%, respectively. Many researchers reported enhanced pitting resistance, repassivation ability, and reduced metastable pitting of high nitrogen induced 316L in chloride solution³², sodium sulfate solution⁵⁶, and thiosulfate-chloride solution³¹. Several mechanisms were suggested to explain the phenomena: 1. Nitrogen in solid solution promotes NH_4^+ formation, which can reduce oxidation inside the pit³¹. 2. Improving the passive film stability by nitrogen enrichment and preventing the attack of Cl^- ions⁵⁷. 3. Producing nitrate ions which can improve the pitting corrosion resistance⁵⁸. 4. Nitrogen alloying enriched the chromium% within the passive film³². The presence of NH_4^+ commonly found in the passive layer was evidenced to improve the corrosion behavior^{30,31,56,59}. Lee et al.³² studied the effect of nitrogen% on metastable pitting susceptibility of 316LSS using PSP experiments. The authors reported the decreased metastable pitting with increased nitrogen%, and no metastable pitting was observed in specimens having nitrogen% ≥ 0.151 wt%. A high acidic environment (low pH) favors faster metal dissolution and initiating metastable pits. Nitrogen in solid solution can combine with H^+ forming NH_3 and NH_4^+ thus, increasing the local pH³¹. Nitrogen-induced 316L having higher local pH promoted higher pitting potential and faster repassivation^{31,32}. A similar interpretation can be obtained for SLM-316L/CrN. From XPS and SIMS analysis, no evidence of nitrogen active compound and ion was detected, respectively, which could be attributed to low nitrogen% in SLM-316L/CrN. Dai et al.³¹ investigated corrosion performance of 316LSS with different nitrogen content and reported that the N1s XPS high-resolution spectra of passive film formed on 316LSS with ≥ 0.2 N% comprised peaks of NH_3 and NH_4^+ .

The chemical composition of specimens determined using inductively coupled plasma optical emission spectrometry, is presented in Table 2. Higher percentage of Mo, Ni, and Cr in SLM-316L/CrN than SLM-316L was observed. The increased Cr content

in SLM-316L/CrN can be expected from CrN addition. Besides, the CrN addition might be effective in restricting the evaporation of Ni and Mo during SLM. The elements like Mo, Ni, and Cr are known for inhibiting pitting corrosion in austenitic stainless steels by favouring a stable passive film formation^{51,60–62}.

In summary, the corrosion performance of SLM of 316L was significantly improved by feedstock modification using the CrN additive due to modification of microstructure and chemical composition. Similarly, several other additives, most importantly nitrogen-containing, have the potential to create a highly corrosion-resistant stainless steel alloy using AM. This work shows merit in exploring more additives and further understanding the role of CrN addition in enhancing corrosion resistance.

METHODS

Feedstock modification and sample manufacturing

The gas-atomized 316L stainless steel powders were procured and termed commercial feedstock herein. The commercial feedstock has particles with maximum $d_{\text{particle}} = 63 \mu\text{m}$, and its chemical composition is provided in Table 2. The wrought 316L (as W-316L) sheets are purchased from McMaster. Chromium nitride (CrN) additive with $d_{\text{particle}} = 1\text{--}3 \mu\text{m}$ was purchased from US Research Nanomaterials. The composite feedstock powders were produced by ball-milling of commercial feedstock along with 1 wt% CrN. The ball-milling was carried out using stainless steel balls and jars at 180 RPM for 5 h with a 1:1 ball-to-powder ratio (BPR) in a planetary ball mill.

The selective laser melting (SLM) was conducted using the Renishaw AM400 laser powder bed fusion system, employed to 400 W ytterbium fiber laser with 70 μm laser diameter. The test specimens of commercial and composite feedstock were printed in an argon atmosphere with an oxygen setpoint <2000 ppm, and the building parameters are given in Supplementary Table 1. The printed specimens are cylinder in shape with 15 mm diameter and 5 mm height. In this research, the SLM printed specimens using commercial and modified feedstock are termed SLM-316L and SLM-316L/CrN, respectively.

Characterization

The chemical composition of SLM specimens was determined using an Agilent inductively coupled plasma optical emission spectrometer (ICP-OES),

Fig. 7 Passive film characterization using XPS. The high-resolution XPS spectra of (a) Survey scan (b) O1s (c) Fe2p_{3/2} (d) Cr2p_{3/2} (e) Ni2p_{3/2} and (f) Mo(3d_{3/2}, 3d_{5/2}) of the passive film formed on SLM-316L and SLM-316L/CrN after immersion in 3.5 wt% NaCl at room temperature.

LECO carbon/sulfur analyzer and LECO ONH836 oxygen/nitrogen/hydrogen analyzer following the AL0025 and ASTM E1019 standard procedure. The density of the specimens was measured following Archimedes' principle. X-ray diffraction (XRD) of SLM specimens was conducted using Rigaku smartlab X-ray diffractometer with graphite monochromatized Cu-K α radiation ($\lambda = 0.154056$ nm).

Scanning electron microscopy (SEM) using FEI Verios 460L field emission electron microscope was performed for microstructural characterization. The SLM specimens were ground to 1200-grid SiC sandpaper and later fine polished till 0.05 μ m. After polishing, the microstructures were observed, followed by electro-etching with 10% oxalic acid at 15 V for 60 s (as per the ASTM A262 practice- A). The sub-cell area was measured using ImageJ software.

Scanning transmission electron microscopy (STEM) was performed using Talos F200X G2 scanning transmission electron microscope operating at 200 kV. The STEM High-angle annular dark-field (HAADF) and bright-field (BF) imaging of SLM-316L and SLM-316L/CrN TEM lamellae were conducted along with SuperX energy-dispersive x-ray spectroscopy (Super-X EDS) recorded. The STEM sample preparation was performed using the Focused Ion Beam (FIB) technique. The electropolished samples were loaded into the Quanta 3D FEG Focused Ion Beam microscope to prepare site-specific TEM lamellae from SLM-316L and SLM-316L/CrN specimens. The Quanta FIB is a dual-beam instrument combining an electron beam and ion beam for simultaneous imaging and milling. The specimens were aligned according to the feature of interest; later, ~ 2 μ m platinum cap was deposited on the surface to protect it from ion beam damage during high-current ion beam milling. After the cross-sections were ~ 2 μ m thick, they were cut and placed on TEM grids using the

Omniprobe micromanipulator, enabling in-situ TEM sample preparation. The thinning down and polishing of the cross-sections were completed using low current and voltage to avoid sample amorphization and damage, and then electron transparent TEM specimens were taken for TEM characterization.

The passive film of SLM-316L and SLM-316L/CrN was developed following immersion in 3.5 wt.% (0.6 M) NaCl for 24 h. The passive film of the immersed specimens was characterized using X-ray photoelectron spectroscopy and secondary ion mass spectroscopy.

The chemical composition of the passive films formed over the SLM specimen's surface was quantitatively investigated using SPECS X-Ray photoelectron spectroscopy (XPS) with 300 W Mg-anode ($h\nu = 1253.6$ eV) X-Ray source. The experiment was performed at a 60° take-off angle using a 2×2 mm² scan area. First, survey spectra were recorded from 0–1100 eV binding energy with a 0.5 eV step size to identify all the elements present on the passive film. Later, the high-resolution regional spectra of O1s, Fe2p, Cr2p, Ni2p, and Mo3d with 0.1 eV step size were recorded to comprehend the passive film behavior and their respective oxidation states. Deconvolution of peaks from XPS spectra was performed using Casa XPS software after Shirley-type background subtraction. The binding energies were calibrated with the adventitious carbon C1s peak position at 285 eV.

Elemental depth profiling on all the SLM passive film developed specimens were carried out using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) operated under 5×10^{-9} mbar pressure. A pulsed 25k eV Bi₃⁺ primary ion source delivering 0.32 pA of target current over 100×100 μ m² area was used for analysis. Depth profiling was performed by interlacing secondary ion analysis with sputtering using a Cs⁺ ion beam with 1 keV giving 7.2 nA target current over 200×200 μ m² area. Edge

Fig. 8 Passive film characterization using ToF-SIMS. ToF-SIMS negative ion depth profiles of (a, b) SLM-316L and (c, d) SLM-316L/CrN after immersion in 3.5 wt% NaCl for 24 h at room temperature.

Table 2. Chemical compositions in wt.% of W-316L, SLM-316L and SLM-316L/CrN.

Title	Fe	Cr	Ni	Mo	Mn	Si	Cu	P	S	C	N
W-316L	Balance	16.55	10.03	2.02	1.18	0.27	0.42	0.034	0.001	0.016	0.062
SLM-316L	Balance	18.02	13.36	2.55	0.56	0.81	0.16	0.020	0.013	0.028	0.0820
SLM-316L/CrN	Balance	20.17	15.00	3.05	1.52	0.24	0.006	0.010	0.010	0.018	0.165

effects were avoided by centering the analysis inside the eroded crater. The profiles were recorded with negative secondary ions due to the high sensitivity to ion yield of the oxide film.

Corrosion tests

Cyclic potentiodynamic polarization (CPP) of the W-316L, SLM-316L, and SLM-316L/CrN was conducted in 3.5 wt% NaCl electrolyte at room temperature on the specimens metallographically prepared to 1200-grit SiC grinding. A three-electrode flat cell having a saturated calomel reference electrode (SCE) and a platinum mesh counter electrode (CE) was used for corrosion testing. The CPP tests were initiated at 0.20 V_{SCE} below open circuit potential (OCP), and a scan rate of 1 mV/s was used. The forward scan was terminated, and a reverse scan was initiated when either the potential reached 1.5 V_{SCE} or a current density reached 100 $\mu A/cm^2$. Before polarization, open circuit potentials were recorded while the specimens were stabilized in test electrolyte for 1 h. The breakdown potential (E_b), repassivation potential (E_{rep}), and maximum current density (i_{max}) were determined from the CPP curves, which were used to compare the corrosion performance of the tested specimens.

Potentiodynamic polarization (PDP) and potentiostatic polarization (PSP) experiments were conducted on SLM-316L and SLM-316L/CrN, and the post-corrosion investigation was performed on the tested specimens. The PDP test was conducted similarly to the CPP test, except the forward scan

was ceased when either the potential reached 1.5 V_{SCE} or a current density reached 1000 $\mu A/cm^2$, and no reverse scan was initiated. The PSP tests of SLM-316L and SLM-316L/CrN were conducted at applied potential ($E_{applied}$) of 700 and 900 mV $_{SCE}$, respectively, to an exposed area of 0.079 cm 2 , for 90 min. Later, the PDP and PSP tested specimens were taken under SEM to observe metastable and stable pit morphologies.

DATA AVAILABILITY

The raw data that support the findings of this research can be shared upon reasonable request.

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AUTHOR CONTRIBUTIONS

V.B.V. performed the experiments, including ball milling, SEM, and electrochemical tests and data analysis, including XRD, TEM, XPS, and SIMS. J.C. conducted the XPS and SIMS experiments and analyzed the resulting data. A.A.D. performed the TEM

experiments and data analysis. Additive manufacturing science, process optimization and SLM sample preparation was provided by S.M.S. The manuscript was drafted by V.B.V. and revised by all the authors. R.K.G. supervised the whole work.

COMPETING INTERESTS

The authors declare no competing interest.

ADDITIONAL INFORMATION

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