

Effects of nitriding on salt spray corrosion resistance of additively manufactured 17-4 PH steels

J.R. Jessy Michla ^a, Nagarajan Rajini ^{a,*}, Sikiru Oluwarotimi Ismail ^b, T. Ram Prabhu ^c
Faruq Mohammad ^d, Suchart Siengchin ^e, M.P. Indira devi ^f

^aDepartment of Mechanical Engineering, Kalasalingam Academy of Research and
Education, Krishnankoil 626126, Tamil Nadu, India

^bDepartment of Engineering, Centre for Engineering Research, University of
Hertfordshire, Hatfield AL10 9AB, United Kingdom

^cCEMILAC, Defence R&D Organization, Bangalore 93, India

^dDepartment of Chemistry, College of Science, King Saud University, P.O.Box 2455,
Riyadh, Saudi Arabia 11451

^eDepartment of Materials and Production Engineering, King Mongkut's University of
Technology North Bangkok, Bangkok 10800, Thailand

^fDepartment of Science and Humanities, AAA college of Engineering and Technology,
Amathur-626005, Sivakasi, Tamilnadu

**Corresponding author: N. Rajini; rajiniklu@gmail.com; +919942139392*

Abstract

This work addresses the effects of varying nitriding temperatures of 530, 560 and 580 °C for 2 hours on corrosion resistance of additively manufactured (AM) 17-4 PH steels, using neutral salt spray (NSS) method for 104 hours. The morphological analysis indicated the presence of columnar grains along the built direction of additive manufacturing process. The refined grain size and the amount of the precipitates increased with an increasing nitriding temperature. The results of the analysis showed

that a minimum weight loss was observed at 580 °C, due to the formation of passive oxide layer and nitrogen rich precipitates on the surface. The X-ray diffraction (XRD) showed the presence of these compounds: Cr₂N, (Fe, Cr)₄N, (Fe, Cr)₂₋₃N, Fe₂O₃, FeOOH, and Cr₂O₃ on the nitrided sample after the salt spray test.

Keywords: Additive manufacturing; Corrosion; Grain boundaries; Microstructure; Nitriding.

1. Introduction

Precipitation hardened (PH) stainless steels are commonly used because of their excellent strength, wear resistance and toughness, which can be obtained through additive manufacturing. With solving geometric complexity, additive manufacturing is an advanced process towards industrialisation, as applicable to the manufacturing of metal alloys [1]. Among various AM processes, direct metal laser sintering is a revolutionary type that solves industrial challenges economically and environmentally [2]. Hence, this work reported additively manufactured (AM) 17-4 PH steels that are widely used in the fabrication of components, including storage tanks, hydrometallurgical pump impellers, shafts, gears, among others [3,4]. Though, these steels have outstanding mechanical performances, but their life expectancies are reduced due to their poor corrosion resistances [5,6].

Nitriding enhances the corrosion and wear resistances of metals by hardening their surfaces [7,8]. Liquid (salt-bath), plasma and gas nitriding are the commonly used nitriding techniques for stainless steels. However, salt-bath nitriding is more effective for low-carbon steels for better surface protection [9], economic effectiveness, eco-friendliness and shorter processing time than nitro-carburizing, anodizing and plating [10,11]. Wang et al. [8,12] studied the effect of nitriding on wrought 17-4PH steel by

varying the time and temperature. The results showed that higher nitriding temperature above 650 °C reduced the hardness and wear resistance than lower nitriding temperature. Importantly, there are no reports on understanding the effects of salt-bath nitriding on corrosion properties of AM 17-4PH stainless steels. Therefore, this study focused on effects of nitriding temperatures on AM 17-4 PH steel, aiming at improving corrosion resistance using neutral salt spray (NSS) test.

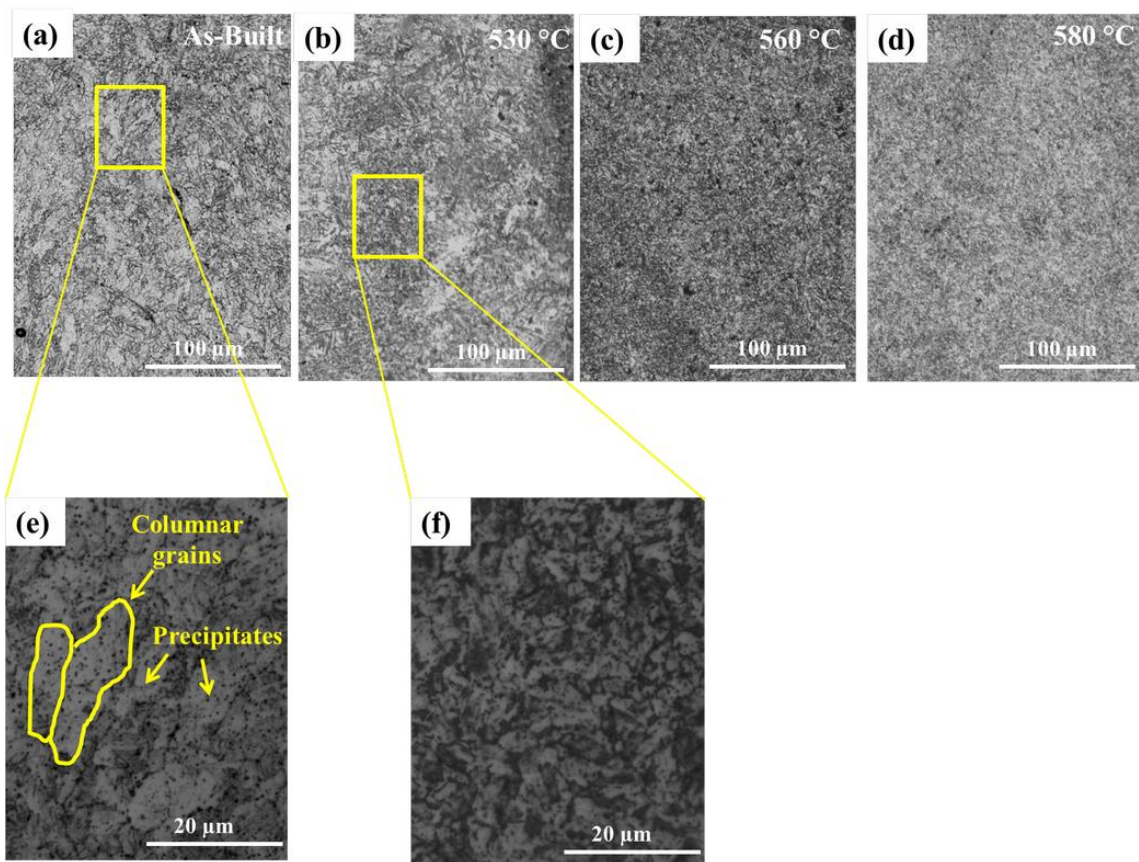
2. Experimental procedures

The 15 x 5 mm AM 17-4 PH steel sample was subjected to salt-bath nitriding at three different temperatures of 530, 560 and 580 °C for 2 hours. NSS is one of the universally accepted accelerated testing methods conducted in accordance with ASTM B117 standard. The salt spray set-up contained 5 wt.% of NaCl solution and the test was performed by maintaining the chamber temperature at 35 ± 2 °C for 104 hours. The weight of the individual sample was recorded every 8 hours interval and the average weight loss was measured. Detailed procedures are available in the previous study [14].

3. Results and discussion

Optical images of as-built and nitrided 17-4PH steel samples were observed along their cross-sectional areas, just below the nitride layer. Fig. 1(a) and its magnified image (Fig. 1e) show the presence of columnar grains throughout the sample cross-section along AM-built direction. As-built steel has expanded columnar grains, which enhanced corrosion, owing to minimal grain boundary volume and less thick passive layer on corrosion. However, the grain size of nitrided samples decreased from 70.2 ± 39.8 μm (as-built) to 67.37 ± 36.6 μm (530 °C), 66.42 ± 34.1 μm (560 °C), and 65.79 ± 41.9 μm (580 °C). Increasing nitriding temperature reduced nearby grains (Figs 1b-d). The thickness of a nitride layer on stainless steel improved corrosion resistance [13]. AM 17-4 PH

steel nitride layer thickness values were 12.01 ± 2.80 , 24.55 ± 1.40 and 25.79 ± 0.16 μm at 530, 560, and 580 $^{\circ}\text{C}$, respectively. The cross-sectional SEM image (Fig. 1g) shows the 580 $^{\circ}\text{C}$ nitrided sample, nitride layer, diffusion layer and substrate. Cu and Ni rich precipitates increased with nitriding temperature, improving corrosion resistance [14]. A sudden increase in layer thickness was observed by 69% when the temperature was increased from 530 to 560 $^{\circ}\text{C}$, due to the diffusion process that speeded up the nitrogen to rapidly diffuse with the substrate [10].



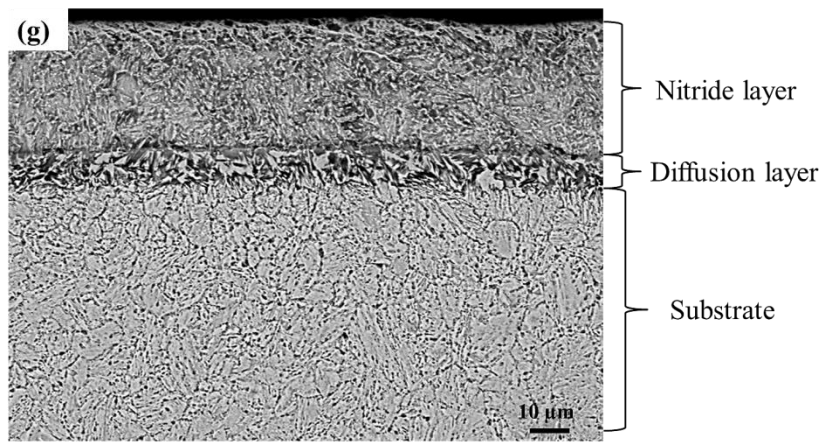


Fig. 1. Optical images of: (a) as-built, nitrided 17-4 PH steel at (b) 530, (c) 560, (d) 580 °C, (e) and (f) magnified images of (a) and (b), (g) SEM image of nitrided 17-4 PH steel at 580 °C.

On the contrary, percentage of increase in layer thickness reduced to 5%, while maintaining the temperature from 560 to 580 °C. Photographic views on surface morphologies of as-built and nitrided samples before and after corrosion (104 hours) test are shown in Fig. 2.

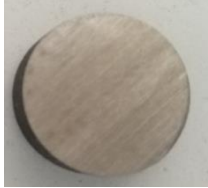
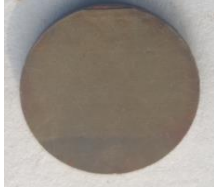
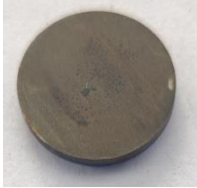





Time (hours)	17-4 PH steel			
	As-built	Nitriding temperature (°C)		
		530	560	580
Before corrosion				
After 104 hours				

Fig. 2. Surface morphologies of 15 x 5 mm as-built and nitrided 17-4 PH steel samples under salt spray corrosion for 104 hours.

During oxidation, atmospheric oxygen reacted with surface components to form metal oxides. The metal oxides formed can dissolve after a period or certain time. Therefore, there is a possibility of weight gain or loss, due to the increased amount of metal oxides or dissolution of oxides [15]. As-built sample corroded severely, due to fast oxide layer development at 24 hours. Rust formed after 56 hours for nitrided samples at 530 and 560 °C, while only minor rust formed after 96 hours at 580 °C. The weights measured before and after corrosion are presented in Table 1. The weights loss after 104 hours were observed as 5.1×10^{-6} , 1.7×10^{-6} , 1.5×10^{-6} and 7×10^{-7} grams for as-built and nitrided samples at 530, 560 and 580 °C, respectively. Continuous spraying of salt solution over sample surface caused oxide layer disintegration and deterioration. Active chloride ions from alkaline salt spray attacked weak zones, causing localized pitting corrosion [16]. On the other hand, the nitrided steel exhibited minimum weight loss at 580 °C.

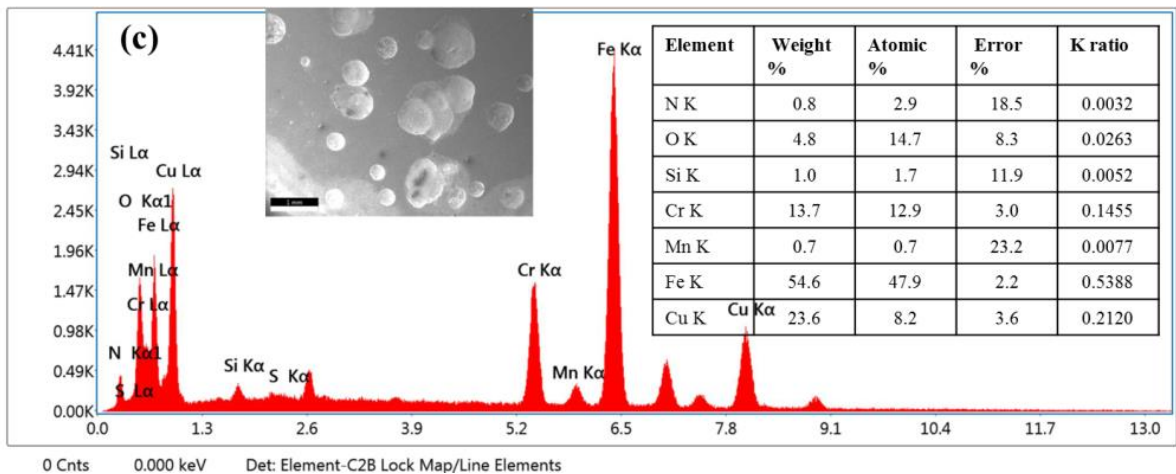
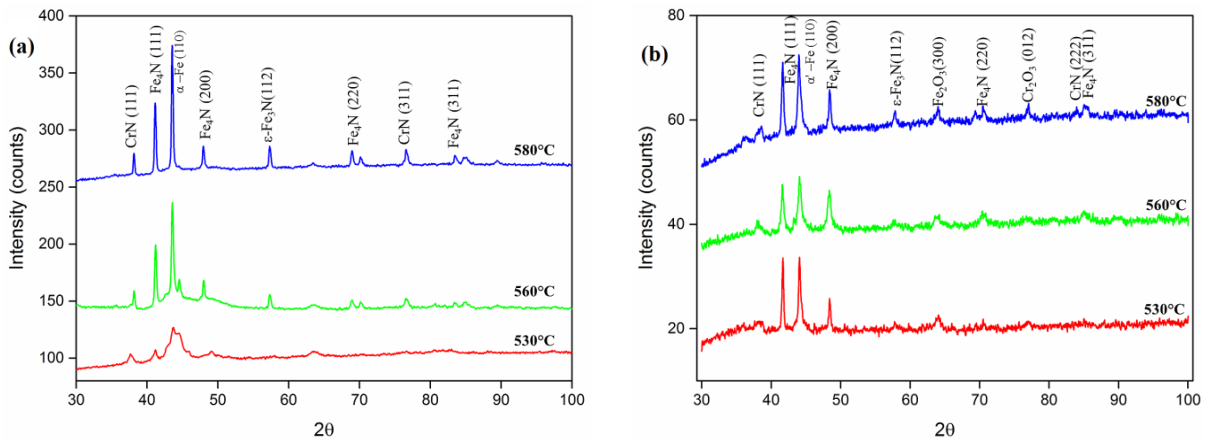
Table 1 Weights measured before and after corrosion after 104 hours.

Time (hours)	Sample weights (in grams)			
	As-built	Nitriding temperatures (°C)		
		530	560	580
Before corrosion	2.7567	2.6789	2.7083	2.6557
8	2.7565	2.6788	2.7083	2.6557
16	2.7562	2.6787	2.7084	2.6556
24	2.756	2.6786	2.7081	2.6555
32	2.7559	2.6785	2.7083	2.6556
40	2.7552	2.6785	2.7081	2.6554
48	2.7547	2.6781	2.7079	2.6554
56	2.7543	2.6779	2.7078	2.6553
64	2.7539	2.6779	2.7078	2.6552
72	2.7532	2.6777	2.7076	2.6552
80	2.7528	2.6776	2.7071	2.6551
88	2.7526	2.6772	2.7070	2.6551
96	2.752	2.6771	2.7071	2.6551
104	2.7516	2.6772	2.7068	2.6550

Eq. (1) was used to determine the corrosion rate based on weight loss of the steel,

$$\text{Corrosion rate (mpy)} = \frac{\text{Weight loss(g)} \times 534}{\text{Density of the steel (g/cm}^3) \times \text{Area(sq. in)} \times \text{Time(hours)}} \quad (1)$$

Using Eq. (1), the corrosion rates for as-built and nitrided steels at 530, 560 and 580 °C were 4.423, 1.474, 1.299 and 0.606 mpy, respectively. The presence of nitrogen on the surface led to the formation of surface passive layer and produced least corrosion rate for nitrided sample at 580 °C. Through X-ray diffraction (XRD) analysis, the formation of γ -Fe₄N, ϵ -Fe₃N, CrN, and Ni₃N compounds were observed in nitrided AM 17-4 PH steel when compared with as-built counterpart with untreated condition (Fig. 3a).



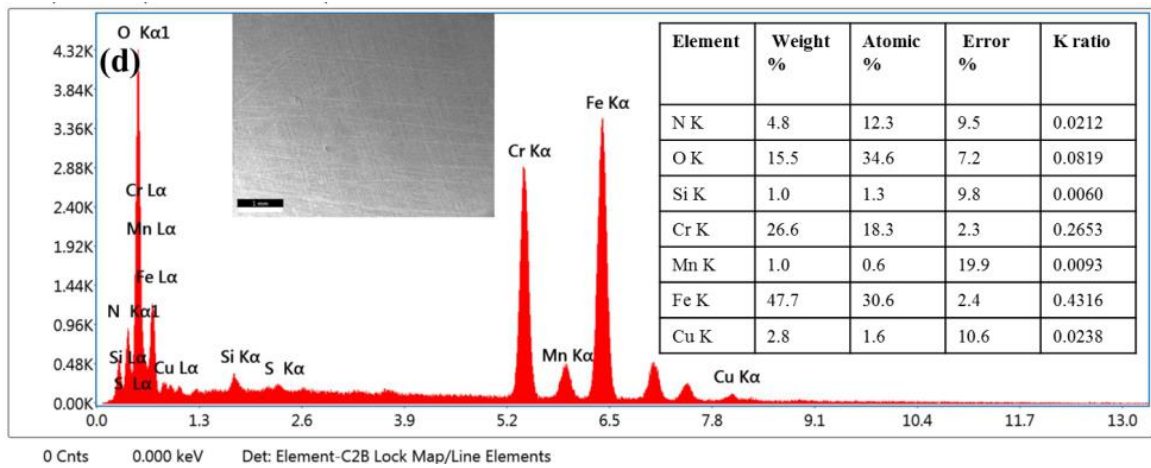


Fig. 3. XRD analysis of nitrated 17-4 PH steel, (a) before, (b) after salt spray test, (c) and (d) energy dispersive spectroscopy (EDS) line mapping of as-built and nitrated 17-4 PH steel at 580 °C.

The compounds formed after subjecting the nitrated samples to salt spray test for 104 hours are shown in Fig. 3(b). In addition, EDS line mapping confirmed the presence of the aforementioned compounds in as-built and nitrated 17-4PH samples (Figs 3c and d). On corrosion test, the salt spray acted as an electrolyte wherein it allowed the metal (iron) to lose its electrons more easily and formed oxides: Fe_2O_3 , FeOOH and Cr_2O_3 [17]. The formed chromium oxides were more stable than iron oxides that formed a protective film and reduced the rate of corrosion. Similarly, chromium present in 17-4 PH steel combined with nitrogen to form chromium nitrides along with iron nitrides [18]. Both chromium nitrides and iron nitrides acted as a barrier and formed a passive protective film that prevented the surface from corrosion. With increasing nitrating temperature, the formation of nitrides increased, which reduced the formation of oxides. The grain refinement after nitrating also supported the corrosion resistance by accumulating chromium along the grain boundaries, which formed strong bond with nitrogen and prevented corrosion. Therefore, the nitrated sample at 580 °C showed excellent resistance to corrosion.

4. Conclusion

The following inferences can be drawn from the investigation:

- The as-built steel showed more rust formation on its surface than the nitrided sample, whereas nitrided sample exhibited a better corrosion resistance at 580 °C.
- The corrosion rate of 4.423 mpy in as-built sample reduced to 0.606 mpy in nitrided sample at 580 °C. Chromium and iron nitrides acted as a barrier by forming a passive protective film that prevented the surface from corrosion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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