

Corrosion behaviours of additively manufactured nitrided 17-4 PH steels in different environments

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Abstract

The destructive effects of corrosion on structural materials can never underestimated. These challenges depend on the constituents of engineering materials, their manufacturing techniques and working environments. Application, functionality and durability/life span of materials can be reduced, due to the attack of corrosion on them. In an attempt to further understand and reduce this problem, the corrosion behaviours of additively manufactured nitrided 17-4 PH steels in different environments were experimentally investigated. The influence of nitriding on corrosion resistance of 3.5 wt.% of sodium chloride (NaCl) and 0.5 M of sodium sulphate (Na₂SO₄) environments was investigated. The salt bath nitriding process was carried out on the 17-4 PH steels at three different temperatures of 530, 560 and 580 °C for 2 hours, separately. The corrosion test was conducted using electrochemical test. From the results obtained, it was evident that the as-built specimens exhibited corrosion in form of pits in both environments. From energy dispersive X-ray spectroscopy (EDS) analysis, the pit region showed the presence of manganese (Mn), sulphur (S), copper (Cu) and oxygen (O). The nitrided 17-4 PH at 580 °C produced the best/optimum corrosion resistance property when compared with as-built and other nitrided steels in both environmental conditions. The improved corrosion resistance can be attributed to the presence of homogeneous distribution of chromium (Cr) and nitrogen (N) on the surface along with other compounds. Summarily, these information or results can help to guide the choice of these engineering materials especially in thermal applications, harsh conditions and chemical/nuclear sector.

Keywords: Nitrided 17-4 PH steel; Additive manufacturing; Corrosion behaviour; Temperature; Environment.

1. Introduction

Additive manufacturing allows complex geometry parts to be made in a short time. It has become one of the most creative methods for building metallic components. Additively manufactured 17-4 PH is a precipitation hardened stainless steel that contains nearly 4 and 17

wt.% of nickel (Ni) and chromium (Cr), respectively. Due to the combination of desirable mechanical properties and quite good corrosion resistance, these steels are widely used in many industrial applications, such as nuclear power plants, aircraft parts [ref], marine applications [1], biomedical equipment [2], chemical and nuclear industries [3]. Generally, high strength and toughness are achieved through annealing and heat treatment process of 17-4 PH steels [4,5]. Though, the heat treatments improve the mechanical properties of PH steel, there is a need for further improvement of properties, including hardness, wear and corrosion properties.

Besides, corrosion is the deterioration of a substance, caused by electrochemical attack. Pitting has been identified as the main corrosion mechanism of the martensitic stainless steels [6]. The corrosion failure of metal components has been a serious concern by researchers and users of these materials for a long time. The metal corrosion could destroy the strength of the metallic parts and lead to the loss of reliability, causing great economic loss and even disastrous accidents. Several studies on the corrosion resistance of steels had been conducted, including general corrosion, pitting, hydrogen embrittlement and stress corrosion cracking [2,7].

Also, nitriding, a surface treatment process comes into consideration for the surface hardening of 17-4 PH steel without disturbing the interior properties. Salt bath nitriding is an environment friendly process, which gives good fatigue strength, excellent wear and corrosion resistance. Research studies indicate that surface corrosion resistance offered by complex salt bath heat-treatment is superior to hard chrome plating or other galvanic layers. It is found to be an efficient and a low-cost method with a number of benefits, including low treatment temperature, quick treatment time, repeatability, high shape and dimensional stability. The complex salt bath process is a viable engineering technology for improving corrosion properties. When dipped in an oxidising salt melt, a corrosion-resistant compound layer is found to be improved. However, most of the existing studies focused on the corrosion resistance of plasma nitrided and nitrocarburised 17-4 PH steels [8–12], with little or no report on additively manufactured nitrided 17-4 PH steels.

Therefore, this present paper investigated into the effects of corrosion on additively manufactured nitride 17-4 PH steels. Precisely, the effects of nitriding process on additively manufactured 17-4 PH steel through corrosion performance of two different solutions were investigated in this experimental study. Electrochemical test was carried out on as-built and nitrided 17-4 PH steels at three different temperatures of 530, 560 and 580 °C, respectively. Based on the results obtained, their corrosion rates and pitting behaviours were identified accordingly and subsequently elucidated.

2. Material and methods

2.1. Material and treatment

The chemical compositions of the as-built 17-4 PH steel used in this study are presented in Table 1. Direct metal laser sintering (DMLS) was used to fabricate 17-4 PH steels with a diameter and a length of 15 and 100 mm round bars. The bars were cut into specimens with thickness of 5 mm and subjected to salt bath nitriding. The surfaces of the specimens were

polished with silicon carbide (SiC) of 1200 grade before nitriding. The nitriding process was carried out at three different temperatures of 530, 560 and 580 °C for 2 hours, respectively. After nitriding process, the specimens were immediately quenched in water. Then, they were treated with ethanol and acetone before electrochemical corrosion test was conducted.

Table 1 - Chemical compositions of additively manufactured 17-4 PH steel.

Element	Cr	Ni	Cu	Si	Mn	P	S	C	Nb+Ta
Wt.%	15-17.5	3-5	3-5	1	1	0.04	0.03	0.07	0.15-0.45

2.2. Electrochemical test

The corrosion behaviours of as-built and nitrided 17-4 PH steel were evaluated by Potentiodynamic polarisation test in accordance with the ASTM G3-89 standard. The experiment was carried out in different environments. For different environments, the electrolyte solutions used were 3.5 wt.% of sodium chloride (NaCl) and 0.5 M of sodium sulphate (Na₂SO₄). The electrochemical test was conducted in a three-electrode cell system. The reference electrode employed was silver/silver chloride (Ag/AgCl), while platinum foil was employed as a counter electrode. All tests were conducted at a room temperature with the constant scan rate of 1.0 mV/s. For anodic curves, a potential corresponding to current density value of 100 µA/cm² when its surface exposed to the electrolyte was 1.0 cm². To achieve a steady state condition, the open circuit potential (OCP) of the working electrode was measured before 60 minutes of potentiodynamic polarisation test.

2.3. Microstructural studies

Microstructural characterisation was carried out through scanning electron microscope (SEM), equipped with energy dispersive X-ray spectroscopy (EDS) to identify morphologies of pits and identify presence of elements after corrosion.

3. Results and discussion

3.1. Corrosion behaviour of nitrided 17-4 PH steel

The electrochemical responses of 17-4 PH steel on the as-built and nitrided surfaces were studied by potentiodynamic polarisation tests and the results obtained are subsequently discussed. The specimens were immersed to reach the steady state corrosion potential [8,13]. Generally, after the passivation film breakdown; there was an increase in potential, which led to the formation of corrosion attack [8]. Considering both Figs (1) and (2), it was observed from as-built 17-4 PH steel specimen that there was no evidence of passive film. The absence of passive film led to the corrosion of metal, as the corrosion current increased. A highest current density of 6.68 mA/cm² is obtained for as-built steel on 3.5 wt.% of NaCl. An ionised sodium ions (Na⁺) produced by the applied potential acted as a strong depolariser that easily

took away electrons from the metal and promoted the dissolution reaction of the steel anode to cause metal corrosion [14]. Also, the chloride ions (Cl^-) reacted with the metal surface led to an increase in corrosion current density (I_{corr}) [15]. From NaCl electrochemical test, the active chloride ions that were strongly negative charged in nature attacked the passive film and affected the defective areas, leading to the formation of localised pitting corrosion [ref]. Pitting is an autocatalytic process that has enough chlorides in pit, preventing re-passivation. It provides oxidising agent, which keeps the surrounding surface to be passivated and allows the pit to grow [ref].

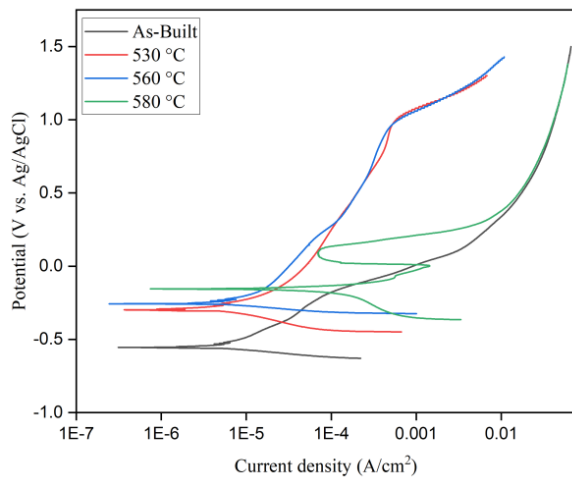


Fig. 1 - Potentiodynamic polarisation curves for 17-4 PH steel nitrided at different temperatures in 3.5 wt.% of NaCl solution.

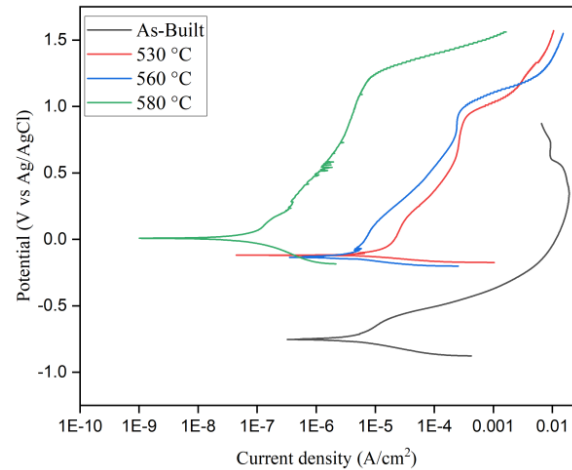


Fig. 2 - Potentiodynamic polarisation curves for 17-4 PH steel nitrided at different temperatures in 0.5 M of Na_2SO_4 solution.

Furthermore, the nitrided 17-4 PH steels at 530, 560 and 580 °C showed better corrosion resistance than the as-built steel. Some studies reported that certain compounds formed during electrochemical test had no protective effect on the substrate and some led to corrosion [14,16]. However, nitride layer formed during nitriding reduced the formation of corrosion compounds, which prevented corrosion. Also, large amount of active nitrogen atoms present on the surface prevented further corrosion. Observing the results of nitrided steel at 530 and 560 °C, corrosion potentials (E_{corr}) of -298 and -257 mV were obtained in NaCl environment behaviour with a sudden rise in current t, respectively. It also showed a passive region during the electrochemical test. The corrosion resistance was achieved by the formation of oxide layer on the surface of stainless steel. The protective layer was formed by chromium rich oxide and iron rich hydroxide layers [17,18]. On increasing the anodic current, the passive region showed a complete breakdown of passive film, leading to uniform corrosion.

The active nitrogen accelerated the formation of passive film. Hydrogen ions (H^+) reacted with nitrogen atoms and form ammonium ion, as expressed in Eq. (1).



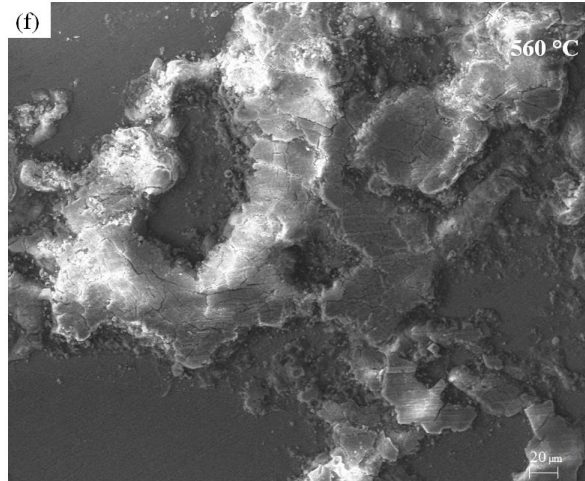
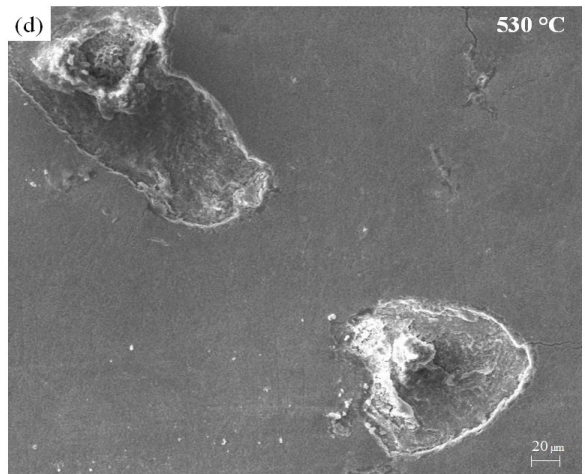
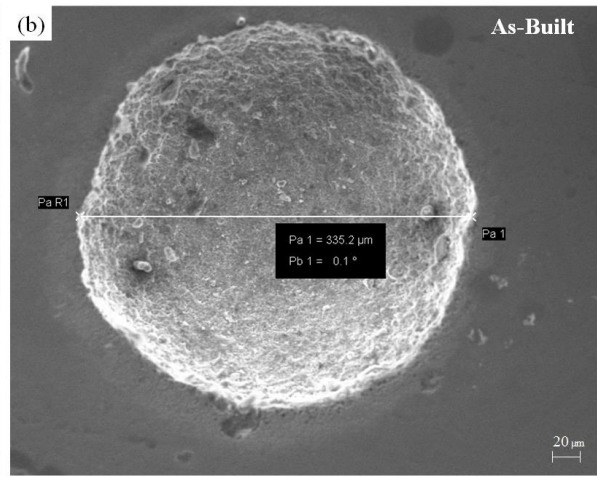
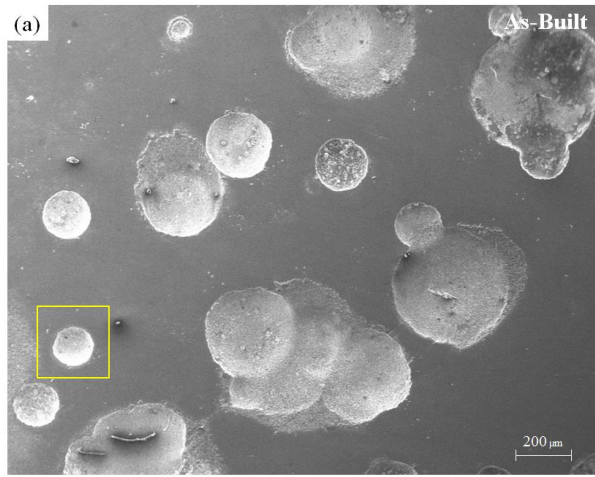
The H^+ ions in the solution prevented the pH value from decreasing. 17-4 PH steel nitrided at 580 °C showed passivation behaviour with a sudden rise in current density and also exhibited re-passivation behaviour. Therefore, the highest corrosion potential of -155 mV with low corrosion current density (I_{corr}) of $1.14E^{-8}$ mA/cm² was achieved.

Similarly, the potentiodynamic polarisation curve of 0.5 M of Na₂SO₄ solution is previously shown in Fig. 2. The as-built 17-4 PH steel showed the lowest corrosion potential. A similar observation to that of NaCl condition was obtained, where there was no passivation film formed on as-built 17-4 PH steel in Na₂SO₄ environment. As the corrosion current density was directly proportional to the corrosion rate, the as-built steel showed the corrosion potential of -753 mV and has the high corrosion rate, whereas the nitrided 17-4 PH steels at 530 and 560 °C showed the potentials of -134 and -119 mV, respectively. Also, surface conditions of materials determine their corrosion resistances. The polished surface recorded a better corrosion resistance than the rough surface [19]. The surface roughness of nitrided 17-4 PH steel was comparatively less than that of as-built specimen. It was therefore evident from Fig. 2 that at 580 °C, a corrosion potential of 8.11 mV and a low I_{corr} value of $1.14E^{-8}$ mA/cm² were obtained. As the pitting potential was towards positive, it showed more resistance to breakdown of passivation film. The presence of nitrogen in the nitrided steel led to re-passivation, which suppressed the formation of pit [20]. Besides, high level of chromium and nickel in the matrix provided a better corrosion resistance. From the results, it was significant that nitrided 17-4 PH steel at 580 °C exhibited a better resistance to corrosion.

3.2. Surface characterisation through SEM-EDS

3.2.1 SEM-EDS analysis after corrosion test in 3.5 wt.% of NaCl solution

SEM images of as-built 17-4 PH steel after electrochemical testing with 3.5 wt.% of NaCl are shown in Fig. 3. Generally, pitting corrosion initiated at the zones of microstructural defects and or discontinuities [21]. The cracks caused by corrosion grew along the grain boundaries [22]. From Fig. 3(a), the pits were apparently visible and more in number. The average diameter of pit formed on the surface of 17-4 PH steel for as-built condition was 330 µm. Fig. 3(b) depicts the magnified image of the pit. For as-built specimen, the iron concentration significantly declined on the surface, which means the destruction of passive film risked the corrosion resistance of the untreated specimen, leading to the appearance of large number of corrosion pits on the surface [14].



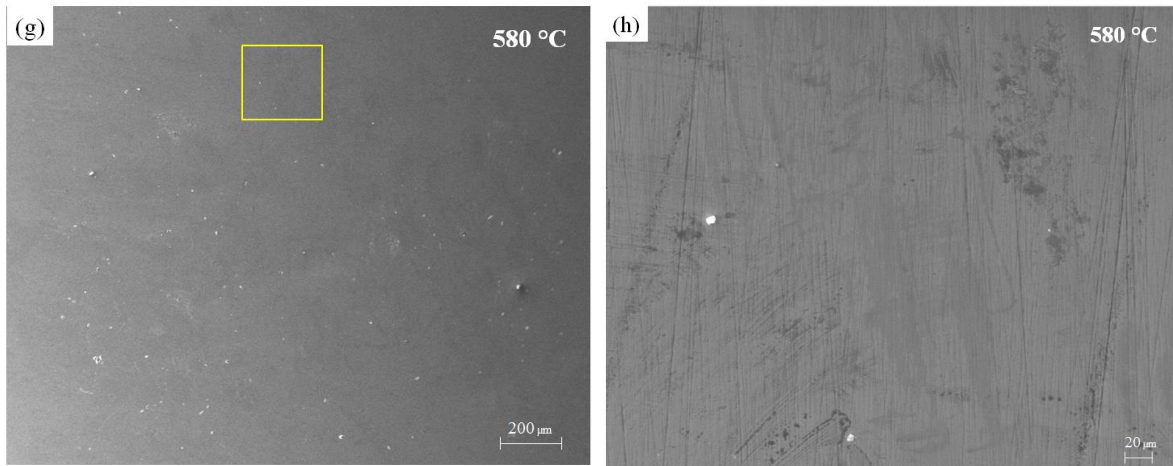


Fig. 3 - SEM images of 17-4 PH steel after corrosion test in 3.5 wt.% of NaCl for: (a) as-built (c) 530, (e) 560 and (g) 580 °C nitrated, showing (b, d, f and h) the magnified images of the yellow marked portions of (a, c, e and g), respectively.

During anodic polarisation, iron (Fe) and chromium (Cr) present in the active region oxidised to form their ions (Fe^{2+} , Fe^{3+} , Cr^{2+} and Cr^{3+}) and formed an oxide layer. Further increase of the polarisation current during anodisation produced defective oxide films.

The corrosion compounds formed on untreated and nitrated steels were almost the same. The untreated and nitrated martensitic stainless steels mainly formed oxides and sulphides. Oxides and sulphides were formed on the outer layer and inner surface, respectively. Table 2 presents the compounds formed during electrochemical reaction on martensitic steels when exposed to NaCl and Na_2SO_4 solutions [14,21,23].

Table 2 - Compounds formed on martensitic stainless steels during electrochemical test on NaCl and Na_2SO_4 solutions.

Elements	Corrosion compounds
O	Cr_2O_3 , FeOOH
S	FeS_2 , SO_4^{2-}
Cr	Cr_2O_3 , $\text{Cr}(\text{OH})_3$
Fe	Fe_2O_3 , FeOOH
N	CrN , Cr_2N , $(\text{Fe}, \text{Cr})_4\text{N}$, $(\text{Fe}, \text{Cr})_{2-3}\text{N}$

The nitride layer exposed to corrosive NaCl environment produced compounds, such as CrN , Cr_2N , $(\text{Fe}, \text{Cr})_4\text{N}$, $(\text{Fe}, \text{Cr})_{2-3}\text{N}$, Fe_2O_3 , FeOOH , Cr_2O_3 and $\text{Cr}(\text{OH})_3$ [24–26]. The nitrated steel at 530 °C showed some visible pits (Fig. 3c), but with smaller size when compared with the as-built condition. The growth of the pits formed was controlled by the formation of iron oxide compound layer on the surface. [Li & Bell 2006, 2007]. The nitrated steel at 560 °C also

showed a possible form of corrosion (Fig. 3f). But, the corrosion rate decreased on the surface of nitrated steels. The increase in thickness of passive layer exhibited a high corrosion rate [Friedrich & Schlett, 1994]. On the contrary, there was no trace of corrosion attack on the surface at 580 °C (Fig. 3g). The nitrated layer consisted of ϵ -nitride, a thinnest passive layer with less oxygen content (Fig. 4), which possessed a high corrosion potential and a low corrosion rate [24]. There were other oxide and nitride elements formed during corrosion test on the surface of 17-4 PH steel, in addition to iron oxides. They are subsequently discussed.

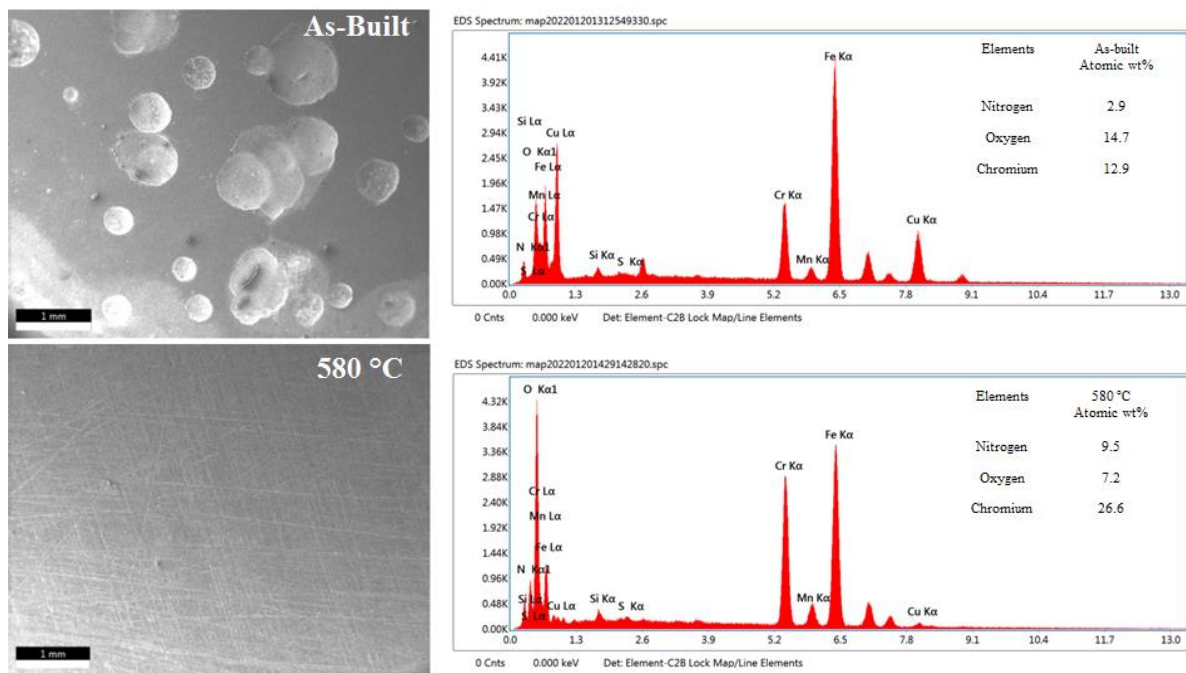


Fig. 4 - EDS spectrum analysis of (a) as-built and (b) nitrated 17-4 PH steel at 580 °C after corrosion test in 3.5 wt.% of NaCl solution with EDS mapping.

Moving forward, the chromium ions hydrolysed to form chromium hydroxides that might restrict further dissolution of the surface. Chromium hydroxides, $\text{Cr}(\text{OH})_3$ with cation selective permeability made the film more stable. It effectively prevented the anion from penetrating the protective film and reduced the rate of corrosion. Chromium oxides were more stable than iron oxides. Also, chromium rich sulphides were more resistance to pit nucleation than manganese sulphide (MnS) [s11661.9]. Iron readily dissolute and formed oxides and nitrides to produce a passive layer. As reported by Basso et al. [25], the formation of ϵ - Fe_{2-3}N and γ' - Fe_4N with addition to the chromium nitride (CrN) precipitate offered good corrosion resistance on nitriding at 520 °C.

Grain refinement also plays a vital role in corrosion analysis. The grain boundary corrosion occurred by chromium depletion on the near grain boundary zones. Strongly depleted layer did not passivate. To avoid chromium depletion, nitriding was carried out at optimum time and temperature [24]. Besides, the PH value was maintained above 6 for perfect passivation. The influence of grain size on the corrosion resistance altered the surface reactivity. The grain refinement improved the formation of passive layer, due to an increase in grain boundary density and therefore improved the corrosion resistance [15,26].

As reported by Ke and Alkire [27], Cu acted as a stabilising agent that suppressed the active dissolution in chloride solution and thus suppressed pit formation. Copper has better corrosion resistance properties. The EDS mapping showed the presence of various elements after the exposure of as-built and nitrided 17-4 PH steels to NaCl solution at 580 °C. The reduction in percentage of oxygen implied that the oxide layer formed was very thin and negligible [24].

3.2.1. EDS analysis after corrosion test in 0.5 M of Na₂SO₄ solution

The EDS analysis of the pit formed on as-built 17-4 PH steel is showed in Fig. 5. The microstructural characterisation of as-built and nitrided 17-4 PH steels with respect to their corrosion behaviours in 0.5 M of Na₂SO₄ is later shown in Fig. 6. For as-built steel, the pits were visible and their magnified view is clearly shown in Fig. 6(b). The average diameter of the pit for this case was 271 μm.

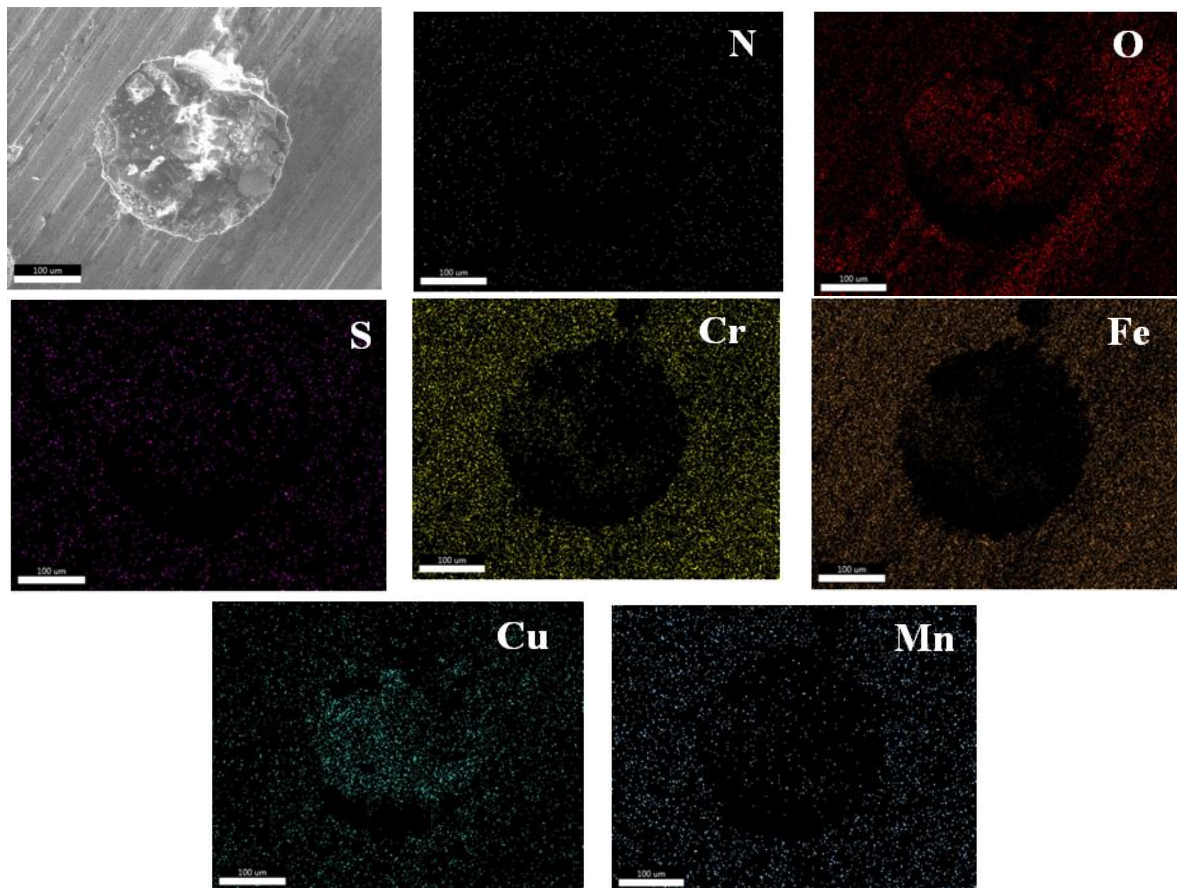
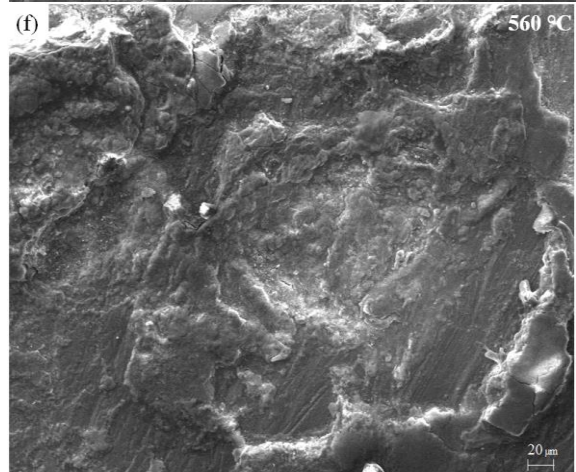
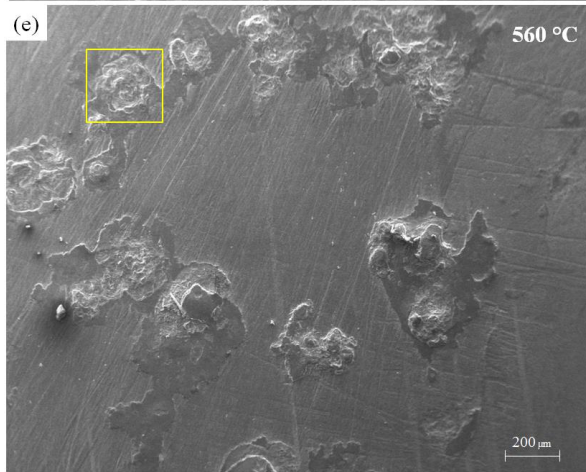
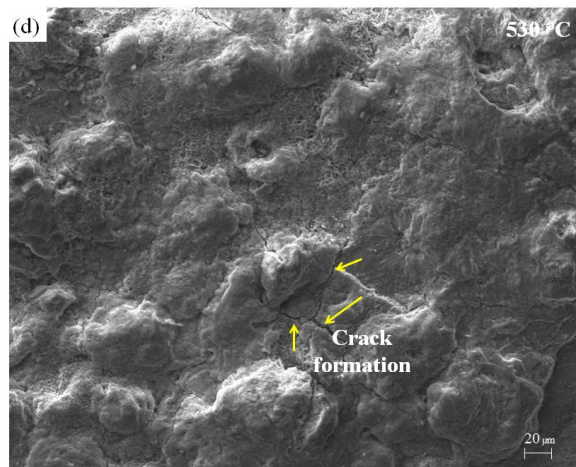
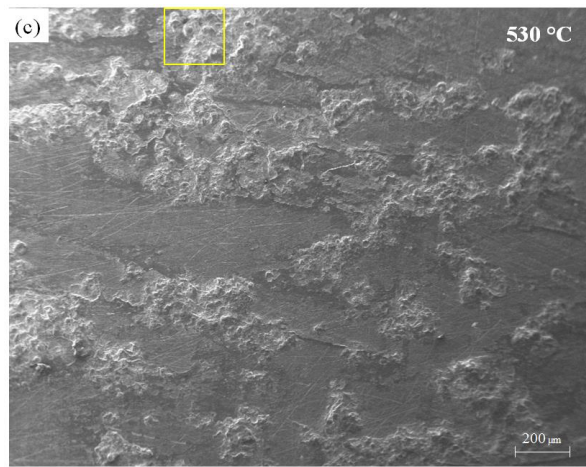
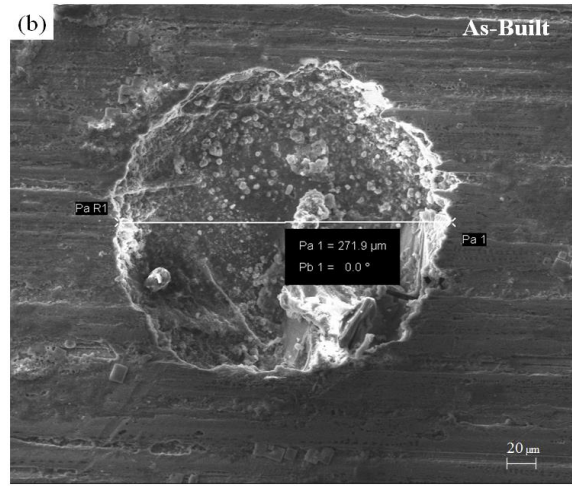
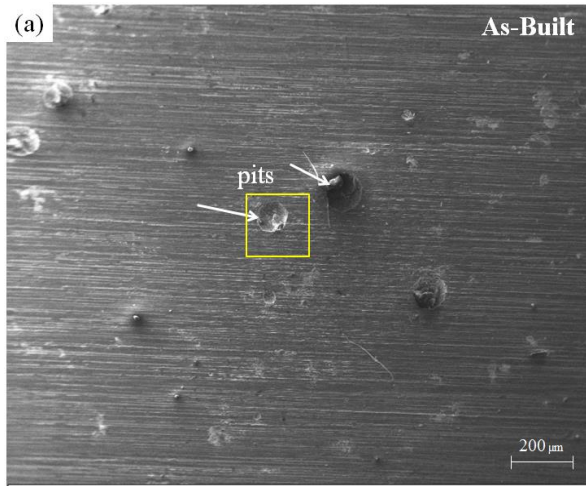


Fig. 5 - SEM- EDS mapping of the pit formed on as-built 17-4 PH steel through 0.5 M of Na₂SO₄ solution.



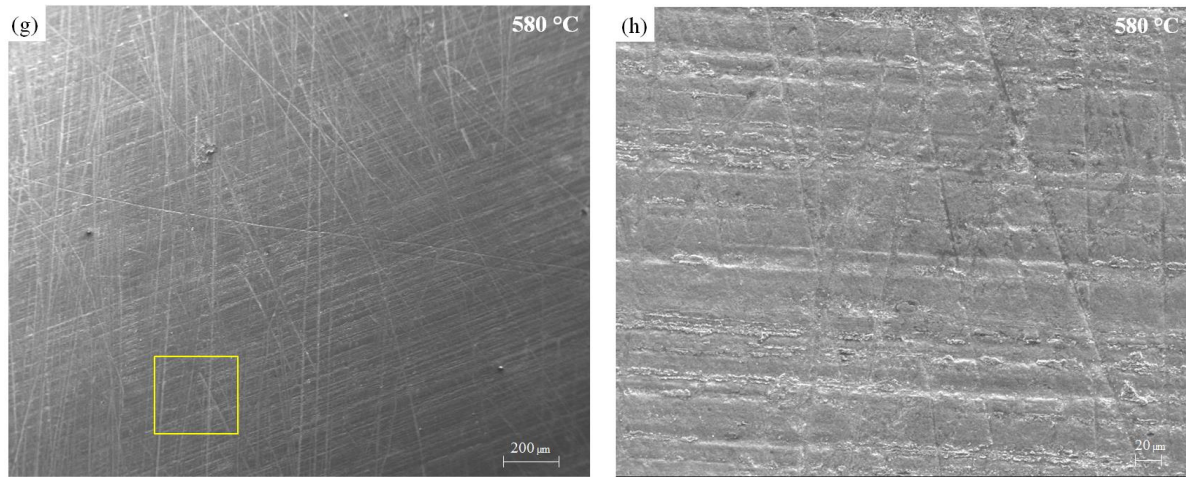


Fig. 6 - SEM images of nitrated 17-4 PH steel after corrosion test in 0.5 M of Na₂SO₄ for: (a) as-built, (c) 530, (e) 560 and (g) 580 °C, showing (b, d, f and h) the magnified images of the yellow marked portions of (a, c, e and g), respectively.

Through EDS analysis, more inclusion of manganese (Mn) and sulphur (S) in the pit region was observed, which indicated that pit initiation was due to the addition of Mn and S. This was in agreement with other similar studies [18,19]. The pits were deep with some form of precipitates and they were analysed through EDS mapping, Mn, S and oxygen (O) are shown in Fig. 5. 316L stainless steel exhibited higher corrosion rate, due to the presence of MnS and associated Cr depletion [26]. Iron sulphide (FeS₂) and sulphate ions (SO₄²⁻) were formed mainly during corrosion in Na₂SO₄ environment. Sulphides formed on the surface were poorly protective and promoted corrosion. Cr was not observed on the pit region and the Cr-depleted region suffered from inter-granular attack [28-30]. A high concentration of hydrogen ions built up the pit. Hydrogen ions promoted the dissolution of most elements present in steel and accelerated the pitting process. The solubility of oxygen in the pit was very limited, therefore cathodic reaction occurred on the metal surface around the pit, protecting the surface cathodically and ensuring that the pit remained anodic [31]. There was more trace of Cu on the pit region, which implied that copper oxide/copper sulphide was formed on the pit zone and it provided protection on further dissolution.

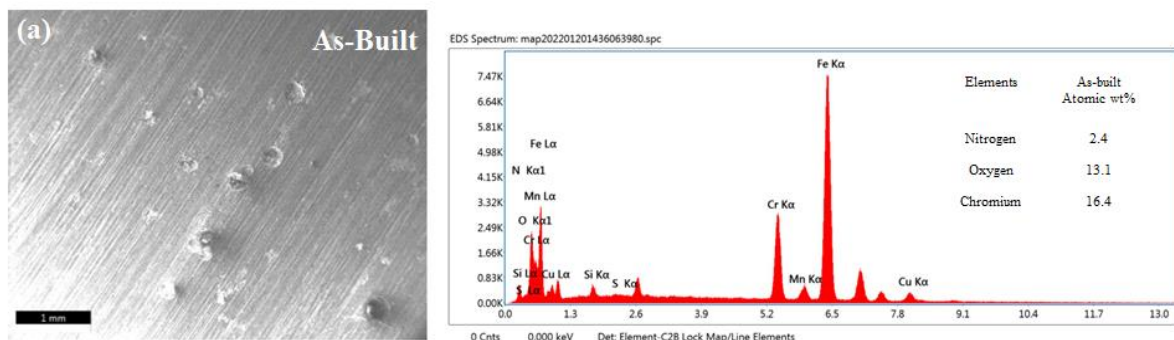
Moreover, the surfaces of the nitrated specimens at 530 and 560 °C were corroded in an irregular pattern, as shown in Figs 6(c) and 6(e), respectively. Oxide layer effectively prevented the corrosion of Na₂SO₄ solution to a certain extent. An increase in the potential destroyed the inherent protective film, causing the corrosion compounds to enter into the interior and generated corrosion. The Na₂SO₄ induced-corrosion occurred with the formation of cracks. The cracks formed during the corrosion attack became the active region for the nucleation of corrosion, which protruded to the next layer of the surface [23].

Nitrated 17-4 PH steel at 580 °C recorded no trace of corrosion. The nitride layer which contained chromium nitride acted as a protective passivation film and protected the surface from corrosive outbreak [22]. The nitride layer partially reduced the formation of corrosion compounds and partially prevented hydrogen atoms to enter into the substrate and hence it prevented corrosion. The presence of nitrogen acted as an inhibitor and therefore prevented

pitting corrosion [22]. Nitrogen formed ammonium ions, which increased the pH value of the solution and passivated the attack of anions, such as chlorides and sulphates. Nitrogen also expanded the passive region by shifting the potential in the positive direction [14]. Therefore, 580 °C showed a better corrosion resistance even in Na₂SO₄ environment, due to the enrichment of Cr and nitrogen, as they formed a passive film and protected the surface from corrosion [32].

In addition, manganese aided the solubility of nitrogen. This would be another beneficial to the development of passivity in Na₂SO₄ solution. On the other hand, manganese has negative effect on weakening the passive film of stainless steels, because of the formation of magnesium sulphide which was detrimental to the pitting resistance [33]. Manganese recorded a little effect on the surface of the nitrated 17-4 PH steel specimen. An increase in nickel content of 17-4 PH steel caused a decrease in its corrosion rate. The presence of nickel increased the corrosion resistance of stainless steel by weakening the oxidising sulphate and chloride solutions. This shifted the corrosion potential to the positive value by expanding the passive region [34].

EDS analysis for as-built and nitrated at 580 °C after corrosion test in 0.5 M of Na₂SO₄ solution is shown in Figs 7(a) and 7(b), respectively. The oxygen concentration decreased significantly at 580 °C in the nitrated layer. The concentration of nitrogen seemed to be increased during nitrating, which improved the corrosion resistance. Nitrogen solubility increased the corrosion resistance. The presence of nitrogen on the surface of the molybdenum free steels showed a better development of passivation in Na₂SO₄ environment, especially with H₂SO₄ and Na₂SO₄ solutions. Nitrogen in solid solution dissolved to form ammonium (NH₄) ions, which consumed the protons during corrosion attack. This passivated the layer and became stable. Ammonium ions also combined with active oxidants, which were less aggressive to the metals. Improvement in grain boundary corrosion resistance can be attributed to nitrogen addition, because the nitrogen diffused faster than carbon to the grain boundaries for the formation of dichromium nitride (Cr₂N).



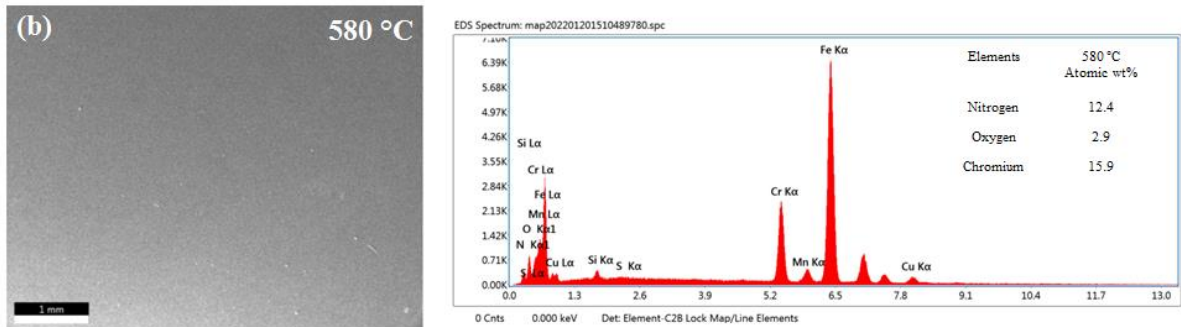


Fig. 7 - EDS spectrum analysis of (a) as-built and (b) nitrided 17-4 PH steel at 580 °C and after corrosion test in 0.5 M of Na₂SO₄ solution with EDS mapping.

4. Conclusions

The influence of nitriding on corrosion resistance of additively manufactured 17-4 PH steels in different environments of 3.5 wt.% of NaCl and 0.5 M of Na₂SO₄ has been investigated at three different temperatures of 530, 560 and 580 °C for 2 hours, separately. The following concluding remarks can be drawn from the experimental results obtained.

- The 17-4 PH steel nitrided at 530 and 560 °C recorded corrosion potentials (E_{corr}) of -298 and -257 mV in NaCl solution, respectively. Significantly, 17-4 PH steel nitrided at 580 °C showed passivation behaviour with a sudden rise in current density. It exhibited re-passivation behaviour with the highest corrosion potential of -155 mV and low corrosion current density (I_{corr}) of 1.14E^{-8} mA/cm².
- The as-built steel showed the corrosion potential of -753 mV and has the high corrosion rate, whereas the nitrided 17-4 PH steels at 530 and 560 °C recorded potentials of -134 and -119 mV in Na₂SO₄ environment, respectively.
- The polished surface recorded a better corrosion resistance than the rough surface, as the surface roughness of nitrided 17-4 PH steel was comparatively less than that of as-built specimen. Therefore, it was evident that at 580 °C, a corrosion potential of 8.11 mV and a low I_{corr} value of 1.14E^{-8} mA/cm² were obtained from the nitrided 17-4 PH steel.
- The as-built specimens showed corrosion in form of pits in both environments. Based on EDS analysis, the pit region showed the presence of Mn, S, Cu and O. Significantly, the nitrided 17-4 PH steel specimen the maximum corrosion resistance property at 580 °C when compared with as-built and other nitrided steels in both environmental conditions. The improved corrosion resistance was due to the presence of homogeneous distribution of Cr and N on the surface along with other compounds.

Finally, additively manufactured nitrided 17-4 PH steels can be potential promising engineering materials for industrial (marine, chemical, medical, aerospace and nuclear) applications, including power plants, aircraft parts and biomedical equipment, to mention but a few.

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