Effect of Substituting Ni by N on Corrosion Behavior of Stainless Steel

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Abstract

This article aims at investigating the influence of partial and total replacement of Ni by N in the chemical composition of the exhausted valve steel grade X45CrNiW18-9 on its corrosion behavior. Five experiments were designed. Melting was carried out in an induction furnace with a capacity of 10 Kg under nitrogen pressure. The chemical compositions of produced stainless steels were determined. The produced stainless-steel grades were forged by using free forging. The nitrogen content of each steel grade was determined. Samples of forged stainless-steel grades were subjected to heat treatment at 1050 °C for one hour and then water quenched. Microstructures of heat-treated stainless-steel grades were investigated. The influence of substituting Ni by N on the corrosion behavior of five grades of steel was studied using different concentrations of NaCl-FeCl$_3$ solutions. SEM was used to examine the morphology of the corroded surfaces after the potentiodynamic polarization experiments.

Keywords: Austenitic Stainless Steel; NaCl; FeCl$_3$; Nitrogen; Nickel.

1. Introduction

It was found that the substituting Ni by N has a significant positive influence on mechanical and chemical properties to some extent [1-7]. Also, many authors concluded that alloying stainless steel with N has a positive effect on general corrosion resistance. At the same time, it unambiguously improves the local corrosion resistance (stress corrosion cracking, pitting, intracrystalline corrosion, and crevice corrosion) [8-12]. According to the results obtained by Sakamut et al. [13], increasing the content of N from 0.1 to 0.38 in austenitic stainless steel decreases corrosion rates in boiling 5% H$_2$SO$_4$ solution and in 10% HCl solution at a temperature of 25°C. Truman [14] found that stainless steel grade containing 9%Ni, 22%Cr, 0.4%N, and 2.6%Mo was more corrosion resistant in phosphoric, acetic, and nitric acids compared to the nitrogen-free AISI type 316.

In stainless steel grades containing 17% Cr, 12%Ni and 2.5%Mo, and 0.22% N, the presence of N enhanced the anodic dissolution in 1-2.5 M HCl, while in 4M HCl an opposite effect of N was noticed and in 4.5-5M HCl, the rate of dissolution of N-containing

and N-free steel grades was high [15]. Increasing of N from 0.06% to 0.18% in stainless steel grades - (20% Cr, 25% Ni), and (20% Cr, 25% Ni, 4.5% Mo) decreased the passive current density when tested in HCl and H$_2$SO$_4$ acids [16]. Speidel and others [8-12,17] interpreted the corrosion resistance of stainless-steel grades. They found that N dissolved in corrosion medium to form NH$_3$, which increased pH and hence retarded the electrolyte at less acidic pit sites. This caused an improvement in passivity. Several authors [15, 18-19] referred that N in solid solution dissolves, and NH$_4^+$ cations are liberated, which improves oxidation resistance inside a pit. This leads to retarding Cl$^-$ ions attack and forming a passive layer. Bernard [20] found that the nitride formation in a highly alloyed metal-induced element depletion near nitride.

This article aims at investigating the effect of substitution of Ni by N partially and totally in an austenitic exhausted valve steel grade X45CrNiW18-9 on corrosion resistance in different chloride solutions.

2. Experimental

Five stainless steel grades with different contents of Ni and N were melted in an induction furnace with a capacity of 10 kg under different pressures of nitrogen gas. Reference steel grade was melted in the open air in an induction furnace. Molten stainless-steel grades were cast at about 1600 °C, under pressure. Produced stainless-steel grades were reheated in the heat-treatment furnace. Stainless steel grades were held for about one hour at 1150 °C. The forging started at 1150 °C by use of a one-ton load, free forging. Forging finished at 900 °C. The forged steels were cooled by air. Nitrogen contents in the produced stainless steel were determined by using the Kjeldahl method. The chemical compositions of forged stainless steels were determined using a spectrometer. The stainless-steel samples of five grades were heated up to 1050 °C, held for one hour, and quenched in water. The microstructures of stainless steel grades were then investigated.

Potentiodynamic polarization curves were used to test the corrosion resistance of the stainless-steel grades in chloride solutions at 25 ^{0}C. Autolab potentiostat type PGSTAT30 (computerized) was used to measure the corrosion behavior of the steel grades. 5 mV/S scan rate was used. The current density against the potential was measured. Silver/silver chloride (in saturated potassium chloride solution) was used as a reference electrode. Platinum wire was used as a counter electrode. Stainless steel grades were used as the working electrodes. The morphology of the surfaces of selected stainless-steel grades after Potentiodynamic polarization experiments were investigated using Scanning Electron Microscope (SEM) in different chloride solutions.

3. Results and discussions

Five stainless-steel grades were produced to illustrate the effect of substitution of Ni by N (partially and totally) on corrosion resistance in different chloride solutions. The chloride solutions used in this investigation were; 1 molar NaCl, 0.85 molar NaCl with 0.05 molar Ferric Chloride, and 0.01 molar Sodium Chloride with 0.33 molar Ferric Chloride. Stainless steel samples selected with different chemical compositions based on the different ratios of Ni/N were used for the electrochemical measurements. Table 1 includes the chemical compositions of forged stainless-steel grades.

**Table. 1** Chemical compositions of stainless-steel grades after the forging process.

Element, wt.%	Stainless steel grade 1	Stainless steel grade 2	Stainless steel grade 3	Stainless steel grade 4	Stainless steel grade 5
C	0.42	0.35	0.4	0.41	0.39
Si	3.2	2.74	2.45	2.42	2.77
Mn	1.14	1.27	1.16	1.22	1.16
Cr	18.1	19.39	17.8	20.33	18.6
W	1.2	1.2	1.14	1.22	1.23
Ni	8.56	5.13	0.13	7.06	3.71
N	0.007	0.33	0.501	0.25	0.402
Fe	Bal.	Bal.	Bal.	Bal.	Bal.

The steel samples were heated up to 1050 °C, hold for 1 hour then quenched in water. The microstructures of stainless-steel grades containing nitrogen are austenite as given from experimental results with some carbides and nitrides precipitates as illustrated in Figure 1

4. Corrosion behavior of stainless-steel grades in 1 molar NaCl

Figure 2 shows potentiodynamic polarization curves for different N stainless steel grades in 1 molar NaCl solution at 25 ^{0}C, the potential changed from the cathodic part to the anodic part with a special focus on the anodic polarization. Concerning steel 1 with the highest Ni content, 8.56%, and the absence of nitrogen, from the curve; it is clear that anodic dissolution was carried out; the chloride ions retard the passivation. In other stainless-steel grades (2, 3, 4, and 5) with different percentages of N and Ni. It is noticed that there is a general tendency to form a passive layer. This is in agreement with the literature [20 - 22].

The current for passivation decreases as the N increases and at the same time as the Ni content decreases to a certain extent. This demonstrates that N enhances the formation passive layer for stainless steel. The passivation requires a certain content of Ni to be present confirming previous results published by other authors [18 - 19, 23 - 27].
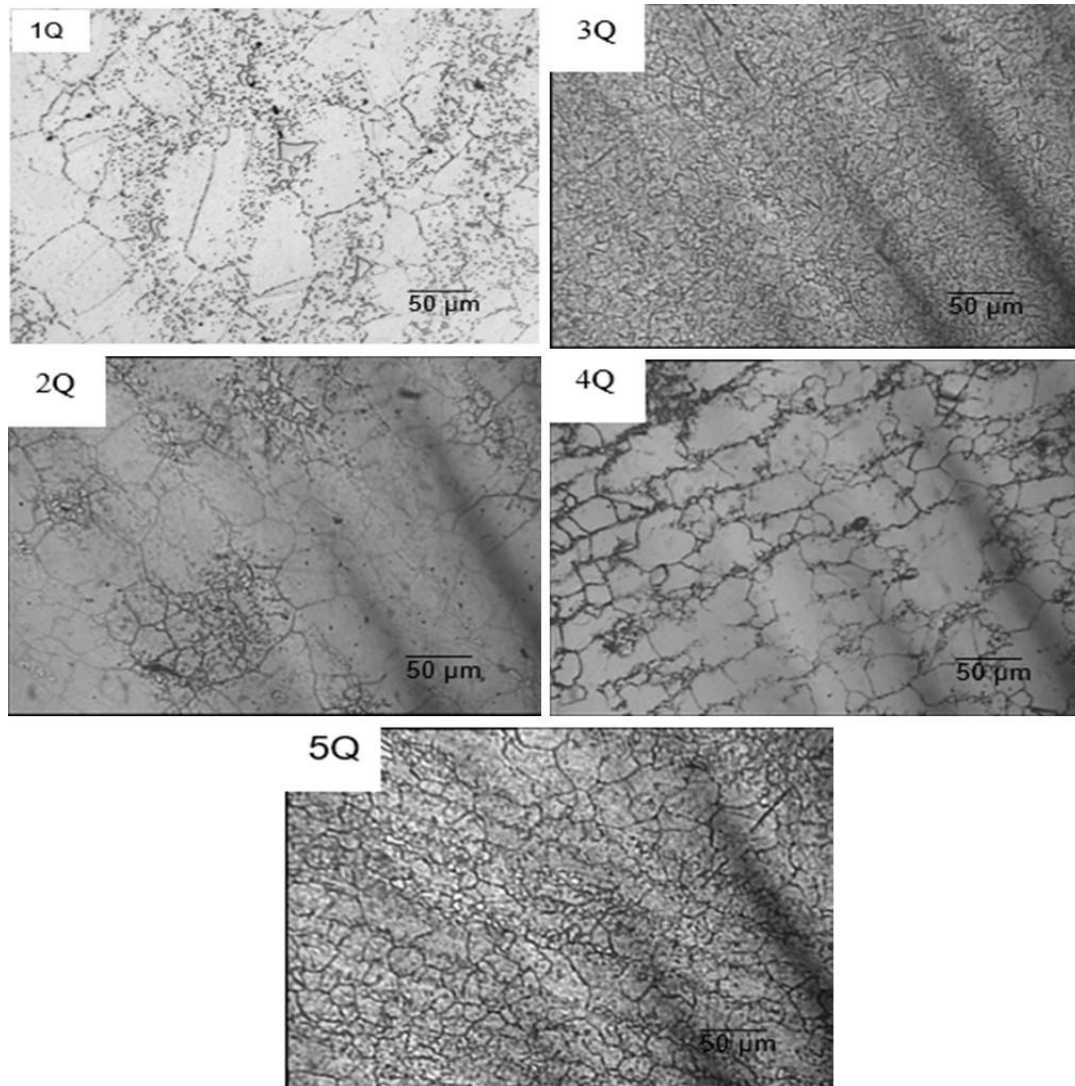
Fig. 1   Microstructures of as-quenched stainless steels.

However, it is noticed that the pit formation and re-passivation refer to the current oscillations (especially in steels 2 and 5).

These experiments explain the role of N for re-passivation. Where N retards pit initiation to great extent and suppresses pit growth by immediate re-passivation. The negatively charged $N^{\delta-}$ is segregated beneath the passive layer. The adsorption mechanism [31] of pit initiation can be used to explain that influence. The adsorbed anion (chloride) causes an acceleration in the dissolution rate for the passive film at the spot of adsorption. In addition, the adsorbed chloride causes thinning of the film and approach of the segregated $N^{\delta-}$. Chloride ions are desorbed as a result of the repulsion interaction between segregated $N^{\delta-}$ and Cl⁻ [31].
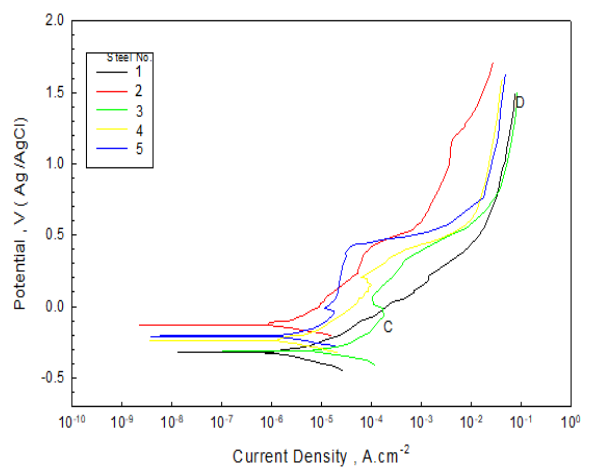
Fig. 2 Potentiodynamic polarization curves of N stainless steel grades in 1 molar NaCl.

Based on the explanation of the results given by authors [32] on one hand and our results, on the other hand, one could propose the following mechanism.

- N in steel alloy dissolved and NH_4^+ ions are produced, causing retardation pit inside oxidation.
- High N concentration in the passive film prevents the attack of Cl^- ions and the surface stabilizes the film.
- Nitrate ions improve the pitting resistance.
- N stabilizes the austenitic phase.
- N causes an increase in electric current for blocks the kink and pit production.

So, it could be concluded that nitrogen shifts pitting potential to the nobler side without effect on the critical current, suggesting that pH buffering is a result of NH_4^+ ion formation within a pit. This is the most probable role of nitrogen. However, there are several other possibilities through which N inhibits pitting corrosion. Enrichment of N may be taking place within or beneath passive films. Another possible explanation for the inhibitive action of N, especially at nobler potentials, is the nitrate ion formation, which is well known as an inhibitor that retards pitting corrosion [32].

## 5. Corrosion behavior of steels in Ferric Chloride solutions

Figures 3 and 4 illustrate curves of potentiodynamic polarization for the stainless-steel grades after corrosion in presence of 0.05 M and 0.33 M Fe^{3+}, respectively. The total Chloride ions contents were adjusted to be 1 molar by the addition of corresponding amounts of Sodium Chloride to the Ferric Chloride solution. Generally, stainless-steel grades (1 and 4) have no passivation. Stainless-steel grades 2, 3, and 5 have passivation as indicated by the breaking current as illustrated in the anodic region. It is clear that the mode of passivation in steel grade 2 (medium N) and Ni is different than that of steel grade 3 (where the N is greatest and Ni free). In steel grade 2, the anodic current is the lowest and the passivation occurred over a wider range of potential (i.e. higher pitting potential). In steel grade 3, the current density decreases with increasing potential but, even to a lower current, the breakdown of passivation occurs immediately. This suggests that the high contents of N strongly lead to passivation, but when there is no Ni the passive film formed is metastable and breaks down immediately due to pitting or crack in the film. This suggestion is in good agreement with the conclusion given by Shahapurkar and Small [53]. They found that

precipitation of nitrides (Cr_2N) as a result of excess N (i.e., more than solubility limit); causes localized depletion for Cr and hence induces localized corrosion around them. Also, Bernard [20] found that the nitride formation in high alloying metal induces element depletion near nitride. Fig. 3 also shows that as the percent of Ni decreases the rate of corrosion at the $E_{Corr.}$ (estimated from the I_{Corr}) increases, regardless of the increasing amount of nitrogen. This means, generally, that nickel has a stronger effect on lowering the corrosion (dissolution) at open circuit potential.
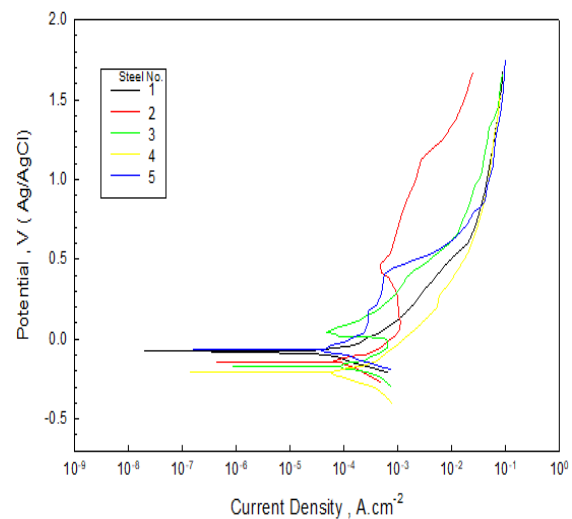

**Fig. 3** Curves of Potentiodynamic polarization stainless-steel grades in (0.05M $FeCl_3$ + 0.85M NaCl).
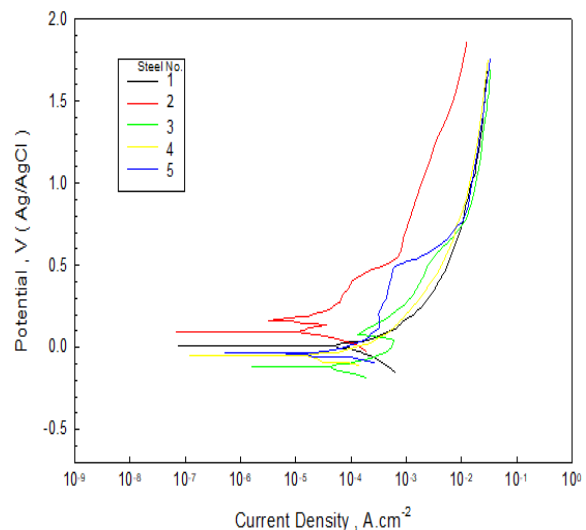
Fig. 4 Curves of Potentiodynamic polarization for stainless-steel grades in (0.33M $FeCl_3$ + 0.01M NaCl).

There are a few authors; who tried to analyze the solutions after the corrosion test of nitrogen steel [34].

Their results showed that the dissolution of the nitrogen steels mainly NH_4^+ is formed. Nitrogen from the stainless-steel surface that is segregated with a negative charge state is directly converted into ammonium ions according to the following chemical reaction:

$$N^{3-} + 4 H^+ \longrightarrow NH_4^+ \tag{1}$$
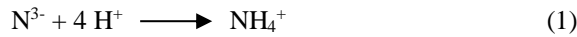
The negative charge of segregated nitrogen on stainless steel was detected by LEED, AES, and XPS [35-36]. Many authors found nitrogen at the top of the passive layer and the oxide/steel interface layer [37 – 38]. There are many parameters affecting the corroding pit; the most affecting parameters are electrolyte composition, drop in pH, and drop in potential. The stability of a corroding pit can be explained by shifts in pH. The hydrolysis of metal ions causes a lowering of pH value according to the following chemical reaction:

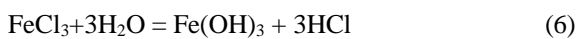$$Me^{z+} + H_2O = MeOH^{(z-1\,)} + H^+ \tag{2}$$
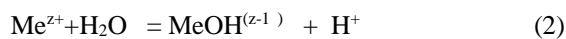
It should avoid precipitation of hydroxide. The pitting potential depends on the pH of the solution according to the following equation;

$$E_p = E_p^0 - 0.059 \; pH \tag{3}$$

for iron $E_p^0 = 0.58$ V

Almost, pitting potential does not shift above the potentiostatically applied value. So, the stainless-steel surface can reach the polarization active range only when the potential is very close to the pitting potential. Nitrogen act as buffers – according to equation 1 – where negative nitrogen ions react with hydronium ion to form ammonium ion (according to equation 2). Also, the presence of nitrogen minimizes the influence of hydrolysis reactions (see equations 4 – 6).

$$Fe \longrightarrow 2e^{-1} + Fe^{2+} \tag{4}$$

$$Fe^{2+} + 2H_2O \longrightarrow FeOOH + 3H^+ + e^{-1} \tag{5}$$

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl \tag{6}$$

With the examination of the obtained results, it can be concluded that:

- Nitrogen retards the pitting attack, where it is able to form a passive layer with increasing N content.
- Nitrogen is absorbed on the metal oxide/ metal interface
- nitrogen act as a buffer; where it reacts with hydronium ion.
- Nitrogen retard the corrosion of the pit and it causes raising in the pitting potential of stainless-steel grades.

Fig.5 illustrates the variation of the breakdown potential as a function of the N/Ni content in the selected investigated steels in different solutions. For the solution I (1 molar NaCl) $E_{crit.}$ increases slightly as N/Ni increases up to a certain maximum then decreases. This means that increasing the nitrogen content decreases the tendency for pitting by increasing the E_{crit}. This result coincides with that given by authors [12,18, 23 – 25] in published literature.

At a high percentage of nitrogen where the percentage of nickel is almost too small, the $E_{crit.}$ decreases indicating that the presence of nickel is necessary for nitrogen to give its protection activity. The presence of 0.05 molar $FeCl_3$ does not dramatically change the feature of the curve. This means that a low concentration of $FeCl_3$ does not affect the values of $E_{crit.}$ For solution III (0.33 molar $FeCl_3$) in total Cl^-, the situation is totally different. As N/Ni increases, the pitting potential (E_{crit}) increases indicating that the presence of nitrogen retards the pitting and delays the breakdown by increasing E_{crit}.
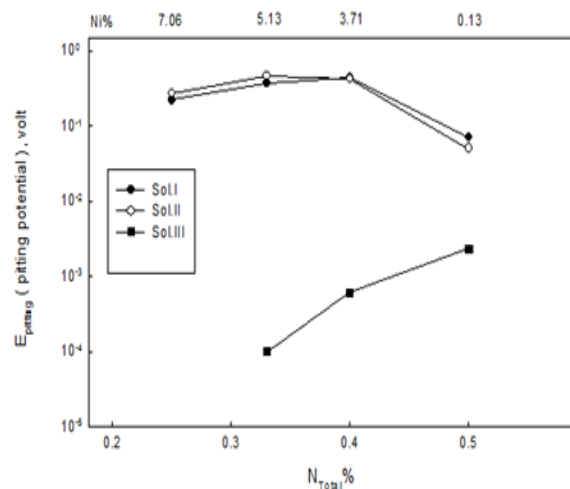
Fig. 5 Variation of pitting potential for the investigated steels as a function of nitrogen and nickel contents in different chloride solutions.

Fig. 6 shows the variation of $I_{crit.}$ with the ratio of N/Ni, the $I_{crit.}$ is defined as the maximum current at the end of the fast dissolution. Beyond the $I_{crit.}$, passivation starts, for solution I (1M NaCl) $I_{crit.}$ decreases to a minimum then increases again. The same trend was observed for solution II (0.05 M $FeCl_3$+ 0.85 M NaCl) but the value of $I_{crit.}$ is comparatively higher. This points to a critical ratio of N/Ni at which the $I_{crit.}$ is minimum.

For solution III, the values of $I_{crit.}$ increase with increasing N/Ni ratio. This means that at a higher N/Ni ratio the tendency for the dissolution is high.
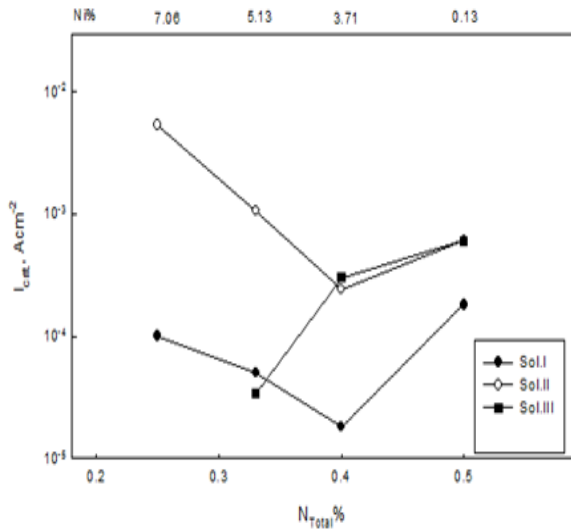
Fig. 6 Variation of critical current density ($I_{crit.}$) for the investigated steels as a function of nitrogen.

To explain pitting morphology, three stainless-steel grades with different Ni and N contents were selected. The highest Ni content and without N addition was represented by stainless-steel grade 1. Stainless steel grade 2 represents steel containing moderate Ni content and high N content while stainless steel grade 3 represents steel with the highest N content and the absence of Ni.

Figure 7 illustrates the effect of the chemical composition of stainless-steel grades on pitting. It is clear that the partial replacement of Ni by N causes increasing the pitting resistance in 1M NaCl solution as shown in photos A and B. This agrees with the authors [15, 19, 39 – 40]. They found that the presence of N in stainless-steel grades causes an increase in pitting resistance. This can be explained as follow: the presence of nitrogen at the metal oxide/metal interface causes a stabilization of the oxide film against chloride, and neutralization of chloride ion with ammonium ion cause inhibition in anodic dissolution inside the pit. Nitrate ion reacts with iron ion and causes inhibition of pitting [40]. Where the complete replacement of Ni by N improves pitting resistance before the breakdown of the passivation layer, while after the breakdown the pitting has turned into a rough deteriorated surface, after the depletion of nitrogen - as shown in photos C and D. This phenomenon may be attributed to the presence of nitrogen ions which carry negative charge in the earlier stage and hence

prevents the chloride ions from the attack by the substrate, at higher voltage nitrogen dissolves in solution and forms ammonium ion according to equation number (7) and decreases hydrogen ions in solution and decrease the pitting

$$NH_3 + H^+ \longrightarrow NH_4^+ \qquad (7)$$

At higher potential, most nitrogen on the surface is exhausted and gross rough pitting starts to be formed as shown in photo D.

As steel sample with moderate nickel content and high nitrogen content has the most pitting resistance in 1M NaCl, further tests were carried out on this steel in different solutions.

Fig. 8 illustrates the effect of solution composition on the pitting tendency of stainless-steel grade 2. This figure clarifies that the addition of $FeCl_3$ in solutions II and III increases the pitting tendency and breaks the passivation. This tendency increases by increasing the concentration of $FeCl_3$, photos B, and C. The morphology of the attack takes the shape of an intergranular attack as clear in photo C. Stainless-steel grade 3 with almost no Ni, although there is a higher percentage of N, the attack is severe such that a deep wide pit is observed over the sample corroded in solution III, as given in Figure 9
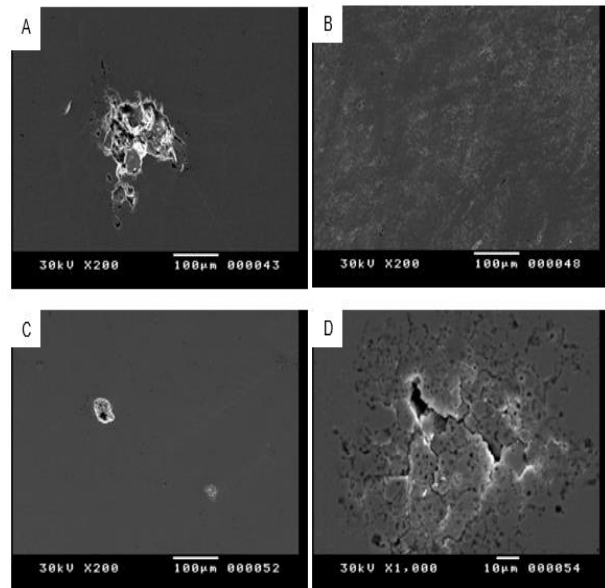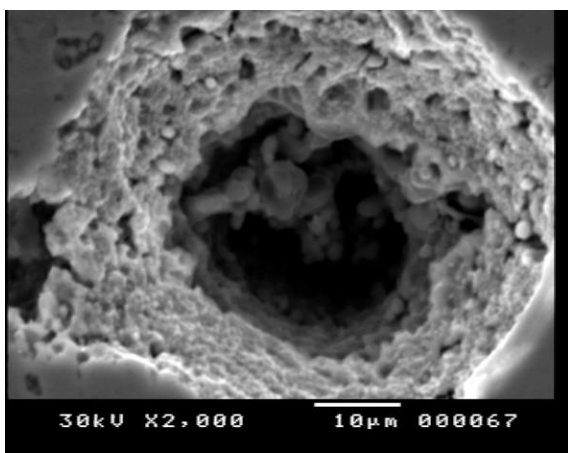

Fig. 7 The effect of nitrogen on pitting in solution I (1M NaCl).
A. Stainless-steel grade 1
B. Stainless-steel grade 2
C. Steel number 3 was taken immediately during the passivation (point C in Fig. 2)
D. Steel number 3 taken at the end of the polarization curve (point D in Fig. 2).
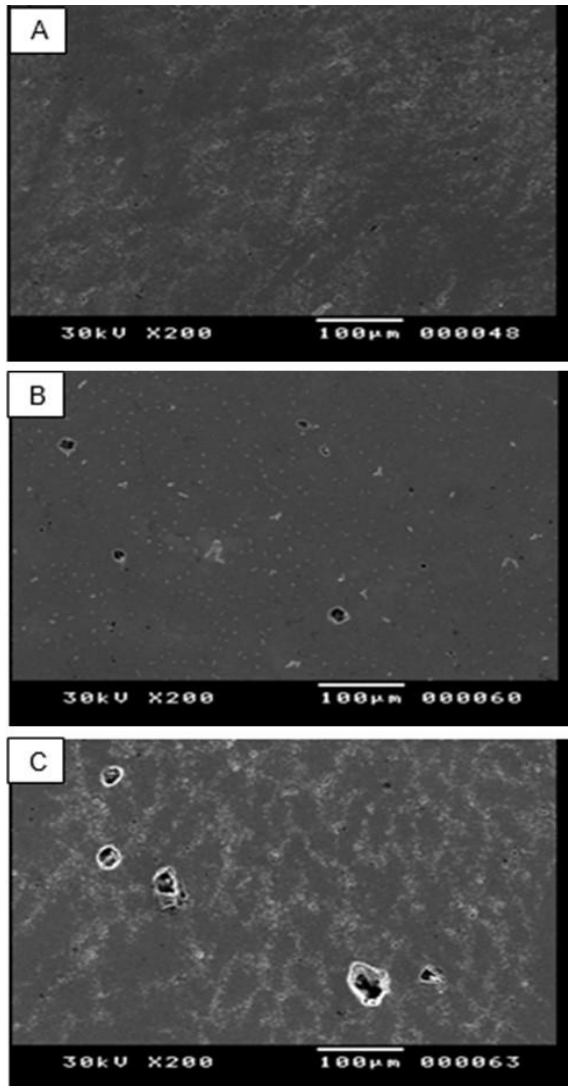
Fig. 8 SEM for pitting of steel grade 2 in solutions. (**A.** 1M NaCl, **B.** 0.05 M FeCl$_3$ + 0.85M NaCl, **C.** 0.33 M FeCl$_3$ + 0.01 M NaCl)

Fig. 9 SEM for pitting of stainless-steel grade 3 in Sol. III (0.33 M FeCl$_3$ + 0.01 M NaCl).

6. Conclusion

From this work, one can conclude that the replacement of Nickel with Nitrogen improves the corrosion behavior. This is attributed to the following:

- Nitrogen is an austenitic stabilizer element; all the produced stainless-steel grades have an austenitic structure.
- Nitrogen shifts pitting potential to the nobler side without any negative significant influence on critical current.
- Nitrogen retards the pitting attack, where it can form a passive layer with increasing N content.
- Nitrogen is adsorbed on the metal oxide/metal interface.
- Nitrogen reacts with hydronium ion in the solution causing a higher pH value and it acts as a buffer ion

Nitrogen retard the corrosion of the pit and it causes raising in the pitting potential of stainless-steel grades.

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