The influence of concentration and pH on corrosion rate in stainless steels – 316 solution HNO$_3$ medium

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Abstract. The Influence of concentration and pH on corrosion rate on commercial stainless steels-316 materials have been carried out. The experiments were carried out in HNO$_3$ medium with a concentration variation of 0.1 mol, 0.2 mol, 0.3 mol and 0.4 mol corresponding to pH values of 1.0, 0.7, 0.523, and 0.4 respectively. The experiments were carried out using a type M-273 EG&G galvanometer test instrument. The post-corrosion samples’ microstructure has analyzed with the aid of energy dispersive spectroscopy (EDS) equipped SEM instrument to detect the presence of any viable corrosion by products. Experimental results confirm that stainless steels-316 commercial alloys immersed in a nitric acid corrosion medium with a variation of concentration experience very little or almost no corrosion and that according to the so-called Fontana’s criteria these test-materials turn out to have an excellent resistance toward nitric acid corrosion. This is also evidenced by the very low corrosion rate value measured in this study. SEM-EDS study, Its indicate that the possible ensuing corrosion by products are iron oxides, and chrome oxides.

1. Introduction

One of the motivate behind the fabrication of stainless steels are their excellent resistance to corrosion facilitated by the presence of chromium. One of the commercially available stainless steel is the stainless steels-316 which is an austenite-type low-carbon steel. Stainless steels-316 contains chromium as the main alloying element in iron and steel for inhibiting corrosion combines with other alloying elements such as nickel, silicon, titanium, and carbon with a composition listed [1]. Kyung Seon Min et al. have discussed in details all aspects covering the influence of carbide grain boundary density on SS-321 alloy [2], and carbide grain boundary feature correlation with respect to its creep and fatigue properties [3]. Corrosion measurements on SS-321 samples coated with ion implantation and ceramic film have been carried out by F. Noli et al. [4], where H$_2$SO$_4$ solution was used as the corrosion medium. High temperature corrosion measurements on SS-321 in atmospheric environment have been carried out by Nurdin Effendi et al. [5,6].

This experiment would be supplemental to the similar corrosion experiments carried out earlier in an atmospheric medium. In stainless steels-316 alloys nickel acts both as an austenite phase forming agent as well as an anti-corrosion agent [10,11]. Chrome is also known as an excellent alloying element because of its anti-corrosion property. Silicon is used as a nucleation agent because of its high melting and freezing points, as well as its anti-corrosion property [10]. Manganese has an excellent anti-corrosion property and acts as a phase-stabilizer for the austenite phase[10,11], carbon is an excellent hardness-increasing element, and finally titanium functions as a sensitizing element in the alloy [10,11]. The
The purpose of this experiment is to investigate corrosion behavior of stainless steels-316 alloys in nitric-acid solution medium, and the damage of the sample due to the penetration of nitric element.

2. Theory

Corrosion reaction could be viewed upon a thermodynamic system surrounded by an environment forming an imaginary wall [7]. Corrosive reaction in a certain type of environment occurs rather spontaneously by releasing free-energy from the system into the environment. Normally, a system is endowed with a certain amount of internal-energy, and most of this energy could be transformed into another form of energy, called the free energy [7, 8]. Corrosive reaction is a transitional condition, and is often labeled as a transition reaction. According to a theory first formulated by Arrhenius, corrosion rate is determined by two main parameters, free activation energy and temperature. Both parameters form a formula expressing the reaction constant, $k_{corr}$, otherwise known as Arrhenius constant [7]. Activation free-energy is a barrier-energy between the alloy and its corrosion product. For this reason it becomes clear that the condition where the alloy is at a higher energy level compared to its surrounding element is undesirable. In this system, corrosion occurs whenever free-energy is available as the potential to generate the flow of electric current (electrons) between anode and cathode in the sample. In this case the test sample should have more anodicity than the reference potential, to enable the cathode to collect the electron flow generated by the test sample [7, 8]. This electronic current or flow is the main cause of corrosion in the test sample. The resistance to corrosion is measured using the resistance polarization to produce the polarization resistance parameter ($R_p$). Polarization resistance is a measure of the specimen resistance toward corrosion of the specimen while connected to an external potential source. The main function of $R_p$ is to calculate the corrosion current $i_{corr}$, otherwise known as Arrhenius constant [7]. Activation free-energy is a barrier-energy between the alloy and its corrosion product. For this reason it becomes clear that the condition where the alloy is at a higher energy level compared to its surrounding element is undesirable. In this system, corrosion occurs whenever free-energy is available as the potential to generate the flow of electric current (electrons) between anode and cathode in the sample. In this case the test sample should have more anodicity than the reference potential, to enable the cathode to collect the electron flow generated by the test sample [7, 8]. This electronic current or flow is the main cause of corrosion in the test sample. The resistance to corrosion is measured using the resistance polarization to produce the polarization resistance parameter ($R_p$). Polarization resistance is a measure of the specimen resistance toward corrosion of the specimen while connected to an external potential source. The main function of $R_p$ is to calculate the corrosion current $i_{corr}$, which is to be determined prior to calculating the corrosion rate. The following expression elucidate the relation between $R_p$, Tafel constants, and corrosion current $i_{corr}$.

$$\frac{\Delta E}{\Delta I_{spt}} = R_p = \beta_a\beta_c/2.3 \ (i_{corr}) \ (\beta_a + \beta_c)$$

After $i_{corr}$ is calculated, the corrosion rate could be determined as follows:

Corrosion rate (mpy) = $0.13 \times i_{corr} \times E_W/A.d$

$$\text{with:} \frac{\Delta E}{\Delta I_{spt}} = R_p = \text{polarization curve slope}$$

$$\beta_a = \text{polarization tafel constant}$$

$$\beta_c = \text{cathodic tafel constant}$$

$$i_{corr} = \text{corrosion current}$$

Therefore according to equation 2, corrosion current determines the corrosion rate. In this work the polarization resistance / polarization linear technique is carried out first to obtain the polarization resistance ($R_p$). The polarization technique is superior with respect to other techniques because it is faster and it uses a relatively smaller potential scanning which causes insignificant changes or damages to the samples surface.

The potentiodynamic technique is utilized to determine the active and passive region of the measured alloy system. The overall form of the curve (Figure 2) is an indication of the
corrosion behavior of the samples immersed in the test-solution. This technique is capable of producing reliable data if carried out at a relatively low scanning rate. Passivation is defined as the loss of chemical reactivity in materials while subjected to certain environment or conditions. Passivation generally occurs because of the formation of a protective layer in the alloy-electrolyte interface therefore preventing a direct contact between the alloy’s surface and the electrolyte.

The measurement of an alloy tendency toward passivation when it is immersed inside a certain type of environment is very important in order to obtain information on the corrosion behavior or characteristics of that particular alloy. The measurement is accomplished by drawing the characteristic anodic polarization curve of the sample. The halogenic ions, especially the chloride ion could destroy the passivation in the spots or local points on the sample which is passive with respect to the air environment. (e.g. Cr, stainless steels). The local spot of the active alloy acts as an anode whereas the cathode forms the wider region of the passive alloy.

In a potentio dynamic-test measurement, the assigned potential values cover a far broader range compared to the potential values used in a polarization resistance measurement. with the consequent that samples usually experience some damages after a potentio dynamic experiment. The corroding medium concentration also influences the corrosion rate because the concentration will modify the pH value.

3. Experimental Method

3.1 Materials
The test samples used in this work are plates of Stainless Steels-316 alloys with a thickness of 5 mm. The applied solution used as the corrosion-medium is chloric-acid solution with a concentration-variation of 0.1 moles to 0.4 moles with a steady increment in step of 0.1 moles. The choice of this variation is strongly delimited by the instrumental precision limit, i.e. above 0.4 moles the corrosion rate increases steeply outside the range of the detection limits of the instrument.

3.2 Equipment
This experimental work uses a Buehler cutting machine with a Buehler-type disc blade, a double polishing machine fabricated by Karl Kolb (Denmark); sand papers of various grades for polishing. The corrosion-testing machine used is the potensiostat M273 assembled by EG & G Princeton Applied Research Corporation. Equipment with test-beakers, vials and pipe test tube. The supporting analysis instruments for the corrosion-samples are SEM-EDXS (for surface microstructure observations) equipped.

3.3. Methods
Sample preparation is carried out in compliance with the standard procedure [9]. Samples are cut into equal sized and shaped into round-forms by polishing, to a final size of 15 - 16 mm diameters. Afterwards the surfaces of the samples were polished in a polishing machine until a relatively uniform and surface’s smoothness and evenness is achieved. The main objective is to get rid of the oxide-layer in the surface. The first experimental-test performed is the polarization technique experiment. The experimental procedure is outlined as follows: First, the sample is immersed into the three-electrode corrosion-test instrument, which has been filled with a 600 ml of corrosion-fluid, and standard saturated calomel is used as the reference electrode, two carbon-bars are used as supporting electrodes. The sample functions as the working electrode. To start the experimental measurement, the corrosion cell is connected to
the potentiostat by applying a potential 20mV below the corrosion potential and 20 mV above the corrosion potential, and the scanning rate is set at 0.1 mVs-1; from this measurement both $R_p$ values and anodic-cathodic Tafel constants will automatically be obtained. Potentiodynamic technique is carried out next. The primary aim of this measurement is to map the active as well as passive characteristic areas of the specimen-solution system by applying a working potential in the range of 500mV below and 1600mV above the corrosion potential with a scanning rate of 0.5 mVs-1. Finally, these experimental curves are analyzed. To analyze the sample's surface and to determine its corrosion products, the corrosion-test samples are observed under an EDS equipped Scanning Electronic Microscope (SEM). In order to complete the classification of the resulting types of corrosion-product.

4. Result and Discussion
4.1. Analysis of polarization and potentiodynamic.
The curves obtained from the corrosion-test measurements on stainless steels-316 samples using the polarization resistance technique in an HNO$_3$ medium for each pH or concentration value should generate the curves presented in figures 1-a through 1-d and the experimentally measured parameters available in Table 1. The experimental results clearly show that for a stainless steels-316 sample immersed in an HNO$_3$ solution with 0.1-0.4 molar concentration (equivalent to a 1.0 – 4.0 pH value) the lowest corrosion potential of -344.47 mV has been recorded for the pH value of 0.4. The corrosion rate in the sample tends to peak at this pH value, which is around 2.5 mpy (Table-3). According to the rule established by Fontana [7, 8], this particular corrosion rate value should rank stainless steels-316 in a class of materials with excellent corrosion-resistance with respect to nitric acid solution corroding medium. Figures 2-a to 2-d show several potentiodynamic curves of a stainless steels-316 sample in a nitric acid medium with a variation of pH, the concurrently generated experimental parameters are presented in Table 2. In a measurement procedure of potentiodynamic technique, the assigned potential range is far broader than the range used in a polarization-technique experiment, and this would ultimately lead to the sample(s) being damaged or ruined in the process.
Figure 1. Polarization-resistance potential versus current curve pattern obtained from stainless steels-316 sample immersed in a nitric-acid medium: (a) pH = 0.4 (b) pH = 0.522 (c) pH = 0.7 (d) pH = 1.0

The potentiodynamic curves would display the following general pattern: initially the samples are cathodic, because of cathodic protection process initiated by the anticorrosion elements, and in this potential range and up to its free corrosion potential ($E_{corr}$), the current will concurrently decrease. The free corrosion potential is the scale which eventually determines the virtual equilibrium condition; now for this particular condition the alloy would experience deliberate corrosion without any external interference in the form of additional input of potential. After the free-corrosion potential has been reached, then to generate the corrosion process in the sample, the overall potential must be steadily increased, which in turn causes the corrosion current to increase to generate corrosion in the sample. The free corrosion-potential is an indicator whether a sample immersed in a corrosion-medium is easy or difficult to corrode; the higher the free corrosion potential, the more difficult it is for a sample to experience corrosion.
Figure 2. Potentiodynamic potential versus current curve pattern obtained from stainless steels-316 sample immersed in a chloride-acid medium: (a) pH = 0.4, (b) pH = 0.522, (c) pH = 0.7, (d) pH = 1.0.

Experimental results of potentiodynamic technique measurements show that the lowest corrosion potential at pH equals to 0.522, which is equivalent to a 0.3 mol concentration chloride acid solution has been recorded to be -465.69 mV. It is clear that for pH values equal to 0.522 and 0.4 the passivation potential is of the same magnitude which is about -400 mV; on the other hand for pH values equal to 0.522 and 0.4 the transpassive potential is measured to be +175 mV and +125 mV respectively. At pH equals to 0.4 the free corrosion-potential increases from -465.69 mV at pH 0.522 to a value of around -445mV; the reason behind this is an increase of cathodic protection and also because of a stronger acid medium, the exchange current generation becomes more significant forming more abundant hydrogen bubbles which tend to block the corrosion current increases [8].

Table 1. Experimental results of a stainless steels-316 sample immersed in an HNO₃ solution medium Environment with a variation of molar concentration or pH using inside the brackets are pH values.

| Experimental Parameters | Molar Concentration (pH) |
|-------------------------|--------------------------|
|                         | 0.1 (1.0)                |
|                         | 0.2 (0.7)                |
|                         | 0.3 (0.523)              |
|                         | 0.4 (0.4)                |
| E(I=0) (mV)             | -153.06                  |
|                         | -141.9                   |
|                         | -327.96                  |
|                         | -344.47                  |
| Rp (k cm⁻²)             | 83.8                     |
|                         | 44.12                    |
|                         | 0.4549                   |
|                         | 0.2158                   |
| I_corr (Acm⁻²)          | 0.12                     |
|                         | 0.35                     |
|                         | 7.16                     |
|                         | 9.68                     |
| Corr.Rate (mpy)         | 0.0312                   |
|                         | 0.0907                   |
|                         | 1.85                     |
|                         | 2.5                      |
| Correlation             | 1.0                      |
|                         | 1.0                      |
|                         | 1.0                      |
|                         | 1.0                      |
| Range of Exp. Pot. E(I=0) mV | 10                  |
|                         | 10                       |
|                         | 10                       |
|                         | 10                       |
Table 2. Experimental results of a stainless steels-316 sample immersed in an HNO₃ solution medium environment with a variation of molar concentration or pH using the potentiodynamic method.

| Molar Concentration | pH   | Free corrosion potensial (mV) | Passivation Potensial(mV) | Transpassive Potential(mV) |
|---------------------|------|-------------------------------|---------------------------|-----------------------------|
| 0.1                 | 1.0  | -198.26                       | +70                       | +300                        |
| 0.2                 | 0.7  | -211.74                       | +100                      | +310                        |
| 0.3                 | 0.522| -465.469                      | -400                      | +175                        |
| 0.4                 | 0.4  | -455.15                       | -400                      | +125                        |

The corrosion rate tends to decrease with respect to pH; this means that corrosion rate is proportional to the solution’s acid concentration. The higher the concentration of nitric acid applied in the corrosion solution, the higher the corrosion rate is obtained.

4.2. Analysis of microstructure

Results of microstructure measurements on a corrosion sample in chloride acid medium with pH equal to 0.4 is shown in Figure 5: micrograms taken with SEM.
Figure 3. SEM-EDX Micrograms of a corrosion sample immersed in a pH = 0.4 HNO₃ medium. The microgram gives a clear indication of surface erosion caused by the corrosion medium.

Here it is obvious that the sample’s surface has been eroded by the corrosion medium consequently showing corrosion erosion. EDS pattern (Figure 3) on a selected spot in the surface reveals The possibility of chrome oxide (Cr₂O₃) or iron oxide (Fe₂O₃) being present in the sample. Finally the same could be concluded for yet another selected spot, namely that chrome oxide, iron oxide, and iron chloride possibly coexist in the sample. Based on both microstructural investigation supplemented by EDS data it could be claimed that in a nitric acid medium, pitting/erosion corrosion have certainly occur.

5. Conclusion
Concluding from the above discussion and analysis, it could be argued that for commercial stainless steels-316 alloys undergoing corrosion in an nitric-acid medium with a pH variation
of 1.0 , 0.7, 0.523 , and 0.4 the corrosion effect with measured corrosion values of only 0.0312, 0.0907, 1.85, and 2.5.
The ensuing type of corrosion is erosion corrosion preceded by pitting corrosion. Corrosion rate will continue to decrease with respect to corrosion medium pH values. On the other hand corrosion potential and passivation potential tend to increase with respect to the corrosion medium H values.
Potentiodynamic measurements yield the following potentials for pH value of 1.0, 0.7, 0.522, and 0.4 are -198, -214, -465, and -445 mV respectively. The passivation potential for pH value of 1.0, 0.7, 0.522, and 0.4 are +70, +100, -400, and -400 mV respectively. EDS results reveal that the corrosion byproducts are possibly chrome oxide, iron oxide, and nickel hydride oxide.

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