

Corrosion Studies On Ss-321 In Natrium-Hydroxide Solution

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ABSTRACT: *Corrosion Studies On Ss-321 In Natrium-Hydroxide Solution.* Experimental corrosion studies on commercial SS-321 have been carried out. The experiments were carried out in a sodium hydroxide medium with a concentration variation of 0.4 M, 0.5 M, 0.6 M, and 0.7 M corresponding to pH values of 13.6, 13.69, 13.78, and 13.84 respectively. The experiments were carried out using a type of M-273 EG&G potentiostat/galvanometer test instrument. The post-corrosion samples' microstructure were analyzed with the aid of EDS (energy dispersive spectroscopy) equipped SEM instrument to detect the presence of any viable corrosion byproducts. For further verification x-ray diffraction method was also used to detect any possible emerging corrosion byproducts on the samples' surfaces correlated to the SEM-EDS result. Experimental results confirm that AISI-321 commercial alloys immersed in a natrium hydroxide corrosion medium with a variation of concentration experience very little or almost no corrosion, so that according to the so-called Fontana's criteria these test-materials turn out to have an excellent resistance toward natrium hydroxide corrosion. This is also evidenced by the very low corrosion rate value measured in this study. EDS study and X-ray diffraction results indicate that the possible ensuing corrosion byproducts are iron oxides, chrome oxides and silicon oxides.

Keywords: Corrosion, SS-321 material, sodium hydroxide, solution.

INTRODUCTION

SS-321 is one of product classified in the grade class of three (group III) materials [1], and the investigation current status about this steel type among others are as follows: 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 sulphate-acid (H_2SO_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], and the corrosion studies on SS-321 in chloride-acid solution medium have been carried out by Nurdin Effendi *et al.* [7].

SS-321 which is an austenite-type low-carbon steel, contains chromium and nickel as the main alloying element in steel for inhibiting corrosion combines with other alloying elements such as silicon, mangan, titanium, and carbon. Chrome is also known as an important alloying element because of its anti-corrosion property. Nickel acts both as an austenite-phase forming agent as well as an anti-corrosion agent. Silicon is used as a nucleation agent because of its high melting and freezing points, as a phase-stabilizer for high temperature. Manganese has an excellent anti-corrosion

property and acts as a phase-stabilizer for the austenite-phase, carbon is an excellent hardness-increasing element, and finally titanium functions as a sensitizing element in the alloy. If nickel and chrome in question do function as a cathodic shield, it would clearly be distinctively present or observable as the cathodic potential pattern section of the potentiodynamic curves.

Since SS-321 has been selected to be the base material in the fabrication of duct-pipes in the water supply system of a power reactor, it becomes compulsory that corrosion tests should be carried out on the material with respect to any medium, include to Natrium hydroxide, where the pH value is shifted into base region.

So the objective of this work is to study the corrosion behavior and parameters used in the experiment of the steel with respect to a Natrium hydroxide inorganic environment with varying concentration of 0.4M, 0.5M, 0.6M, and 0.7M respectively. Another aim of this study is to gather information on the various types of byproducts brought about by the corrosion process when the test-samples are immersed in a sodium hydroxide medium. This experiment would be supplemental to the high temperature corrosion experiments carried out earlier in an atmospheric medium.

Corrosion reaction could be viewed upon a thermodynamic system surrounded by an environment forming an imaginary wall [8]. 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

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energy, called the free energy [8, 9]. 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 [8]. 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 [8, 9]. 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 relation between R_p , Tafel constants, and corrosion current i_{corr} is expressed in many papers [7].

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 sample's surface.

The potentiodynamic technique is utilized to determine the active and passive region of the measured alloy system. The overall form of the curve (Fig.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 halogen ions, especially the chlor ion could destroy the passivation in the spots or local points on the sample which is passive with respect to the air environment. The local spot of the

active alloy acts as an anode whereas the cathode forms the wider region of the passive alloy.

In a potentiodynamic-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 potentiodynamic experiment.

METHODOLOGY

The test samples used in this work are plates of SS -321 alloys with a thickness of 5 mm; the chemical composition is shown in Table-1. The applied solution used as the corrosion-medium is sodium chloride solution with a concentration-variation of 0.4 M to 0.7 M with a steady increment in step of 0.1 M. The choice of this variation is strongly delimited by the instrumental precision limit, i.e. above 0.7 M the corrosion rate increases steeply outside the range of the detection limits of the instrument.

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 potentiostat / galvanostat M273 assembled by EG & G Princeton Applied Research Corporation, equipped with test-beakers, vials and pipettes test tubes. The supporting analysis instruments for the corrosion-samples are a Shimadzu XD-610 X-ray diffractometer, a Nikon UFX-DX optical microscope (for surface microstructure observations), and an EDS equipped Phillips SEM microscope.

Sample preparation is carried out in compliance with the standard procedure [10]. 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 20 mV 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.

Tabel-1. Alloying elemental composition of SS-321 stainless steel (wt %) [1].

Element	Ni	Cr	C	Si	Mn	Ti	S	P
weight%	9-12	17-19	0.08 (max)	1.0 - 2.0	2.0	min. 5 x %C	0.03 (max)	0.045 (max)

Table 2. Experimental results of a SS-321 sample immersed in an NaOH solution medium with a variation of molar concentration using the potentiostatic method.

Experimental Parameters	Molar Concentration			
	0.4000	0.5000	0.6000	0.7000
$E(I=0)$ (mV)	-415.0600	-443.05	-498.1000	-365.5300
R_p ($k\Omega cm^{-2}$)	223.1000	138.16	107.01	508.2800
I_{corr} ($\mu A cm^{-2}$)	0.0500	0.1000	0.1500	0.0100
Corrosion Rate (mpy)	0.0117	0.0248	0.0394	0.0033
Correlation	1.0000	1.0000	1.0000	1.0000
Range of Experimental Potential. $E(I=0) \pm \Delta mV$	10.0000	10.0000	10.0000	10.0000

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 -1200 mV below and 1800 mV above the corrosion potential with a scanning rate of 0.5 mVs⁻¹. Finally these experimental curves are analyzed.

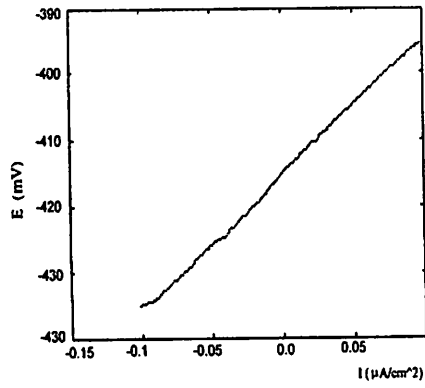
To analyze the sample's surface and to determine its corrosion products, the corrosion-test samples are observed under an EDS equipped electronic microscope (SEM). In order to complete the classification of the resulting types of corrosion-product, the samples are each examined using an X-ray diffractometer. X-ray diffraction analysis is accomplished by consulting the software program available from JCPDS (Joint Committee On Powder Diffraction Standard).

RESULTS AND DISCUSSION

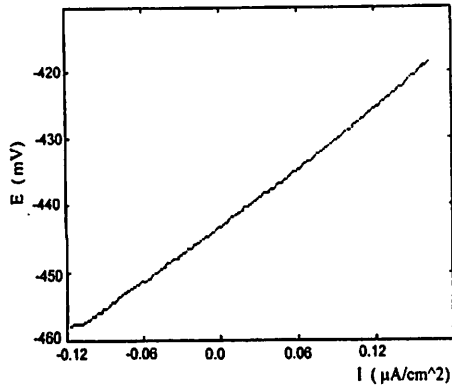
The curves obtained from the corrosion-test measurements on SS-321 samples using the polarization-resistance technique in an NaOH medium for each concentration value should generate the curves presented in figures 1-a through 1-d and the experimentally measured parameters available in Table-2. The experimental results clearly show (in Table-2) that for a SS-321 sample immersed in an NaOH solution with 0.4 - 0.7 M concentration the lowest corrosion potential of -498.1 mV has been recorded for the concentration value of 0.6M. The corrosion rate in the sample tends to peak at this concentration value, which is around 0.0394 mpy (Table-2). According to the rule established by Fontana [7, 8], this particular corrosion rate value should rank SS-321 in a class of materials with excellent corrosion-resistance with respect to sodium hydroxide solution medium.

Figures 2-a up to 2-d show several potentiodynamic curves of a SS-321 sample in a sodium hydroxide

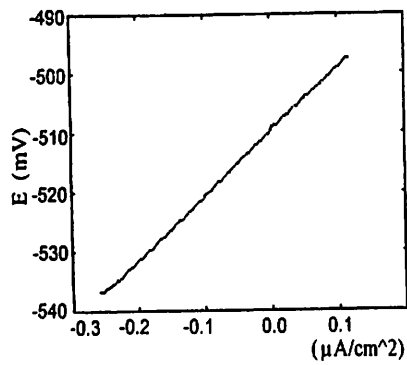
solution medium with a concentration variation, the concurrently generated experimental parameters are presented in Table 3. In a measurement procedure of potentiodynamic technique, the assigned potential range is far broader than the range used in a polarization-technique experiment, and this would ultimately lead to the sample(s) being damaged or ruined in the process. 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. Experimental results of potentiodynamic technique measurements listed in Table-3 show that the lowest corrosion potential lies at concentration value of 0.6M and it has been recorded to be -441.38 mV with first passive potential of -280 mV and without second passive potential. It is clear that for molar values equal to 0.5 and 0.6 the passivation potentials are of the magnitude which is about -200 mV and -280 mV respectively; and for molar values equal to 0.4 the passivation potential is -250 mV.



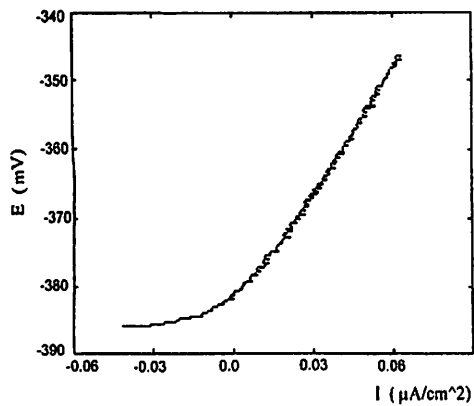
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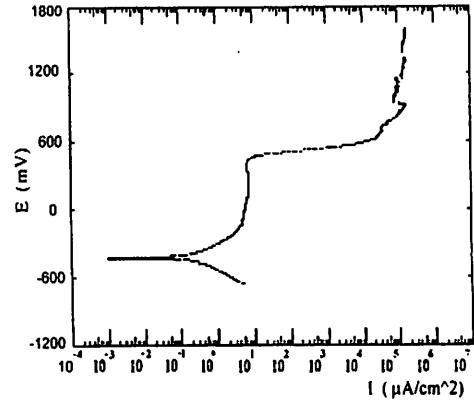
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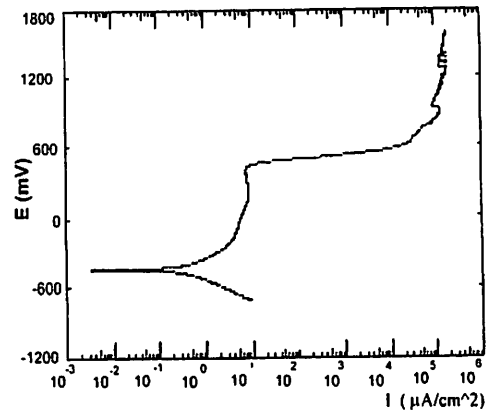
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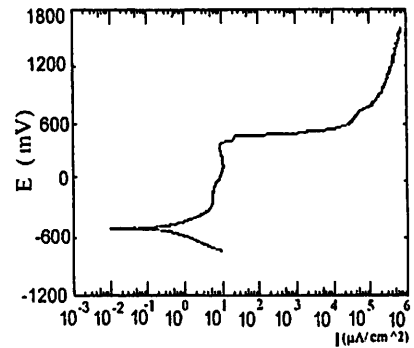
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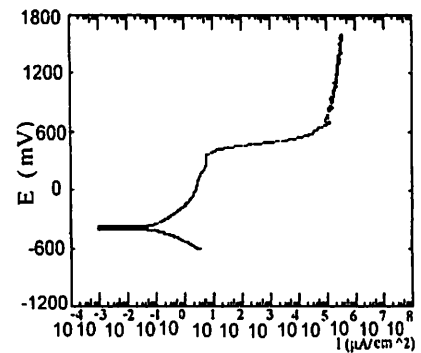
a



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d

Fig.1. Polarization-resistance potential versus current curve pattern obtained from SS-321 sample immersed in a sodium hydroxide solution medium with a concentration of: a. 0.4M. b. 0.5M. c. 0.6M. d. 0.7M.

Fig. 2. Potentiodynamic potential versus current curve pattern obtained from SS-321 sample immersed in a sodium hydroxide solution medium with a concentration of: a. 0.4M. b. 0.5M. c. 0.6M. d. 0.7M.

Table 3. Experimental results of a SS-321 sample immersed in an NaOH solution medium environment with a variation of molar concentration using the potentiodynamic method.

Molar Concentration	Free Corrosion pot (mV)	First Passivation Potential (mV)	Second Passivation Potential (mV)	Transpassive Potential (mV)
0.4	-417.99	-210.00	+820.00	+900.00
0.5	-420.10	-200.00	+800.00	+900.00
0.6	-441.38	-280.00	-	+850.00
0.7	-400.96	0.00	+800.00	+870.00

At molar values of 0.4 to molar values of 0.6 the free corrosion-potential decreases from -417.99 mV to -441.38 mV; but at molar values of 0.6 to 0.7 the free corrosion-potential increases from -441.38mV mV to -400.96 mV; the reason behind this is probably a stronger solution medium. Cathodic protection arises because SS-321 contains anti-corrosion alloying elements as well as nickel and chrome, each with a reduction potential of -0.254 volt and -0.744 volt respectively and comparably more negative with respect to the iron (Fe) reduction potential of -0.037 volt. Before attacking Fe, the corrosion solution must first overcome the negative potentials generated by Ni and Cr. If the external potential increases, energy formed by the external potential will surmount the potential barrier formed by Ni and Cr. Further, increment of the external working potential will induce the corrosion current to increase and the samples will be corroded until the potential reaches the reverse potential. Namely the onset potential where the passivation process starts to occur. At this condition, if the working potential is being steadily incremented. Current would begin to decrease. This is brought about by the alloy partial protection. for example corrosion product adhering to the samples' surface reducing further contact between electrolyte solution and the samples' surface.

The distribution pattern of the variation corrosion rate data versus concentration-solution is shown in Fig-3. The corrosion rate tends to increase with respect to molar from 0.4 to 0.6 and then decrease from 0.6 to 0.7.

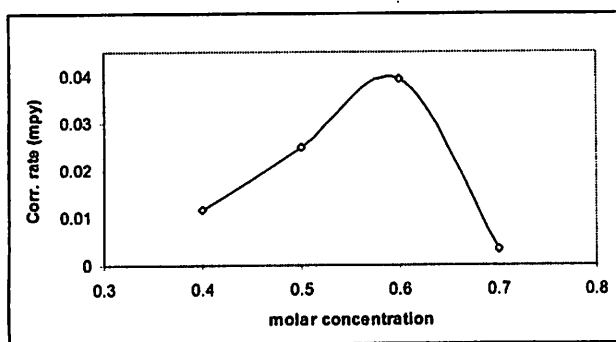


Fig. 3. Plot of Corrosion Rate versus natrium hydroxide solution molar values

The distribution pattern for corrosion potential, passivation - and transpassivation potential versus concentration solution or molar is shown in Fig.- 4. It is

clearly visible that corrosion potential tends to decrease with respect to molar; the passivation potential tends to increase with respect to molar from 0.4 to 0.6 and then decrease from 0.6 to 0.7, as well as corrosion rate pattern in Fig. 3. Meanwhile the transpassivation potential tends to decrease with respect to the molar value.

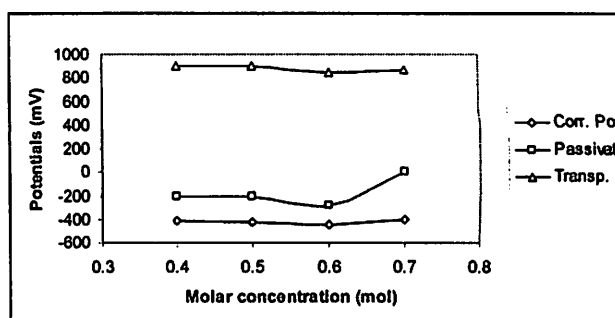


Fig. 4. Data plots for corrosion - , passivation - and transpassivation potentials versus natrium hydroxide solution molar values.

Results of microstructure measurements on a corroded sample in 0.6 M. sodium chloride medium is shown in Fig. 5: micrograms taken with SEM. Here it is obvious that the sample's surface has been eroded by the corrosion medium, consequently showing corrosion erosion. EDS pattern (Fig. 5.b) on a selected spot in the surface reveals the possibility of chrome oxide (Cr_2O_3) or iron oxide (Fe_2O_3) being present in the sample. On another selected spot (Fig. 5.c) EDS pattern reveals the possibility of chrome oxide or iron oxide. EDS pattern on still another surface spot (Fig. 5.d) also reveals the possibility of chrome oxide, iron oxide, and a minor amount of silicon oxide (SiO_2). Another EDS pattern for yet another spot (Fig. 5.e) also strongly indicates the possibility of chrome oxide and iron oxide being present in the sample. Finally the same could be concluded for yet another selected spot (Fig. 5.f), namely that chrome oxide and iron oxide possibly coexist in the sample. Based on both microstructure investigation supplemented by EDS data it could be claimed that in a natrium hydroxide medium, the ensuing corrosion byproducts are chrome oxide, iron oxide, and a minor amount of silicon oxide. This finding has been confirmed by x-ray diffraction data mentioned in below.

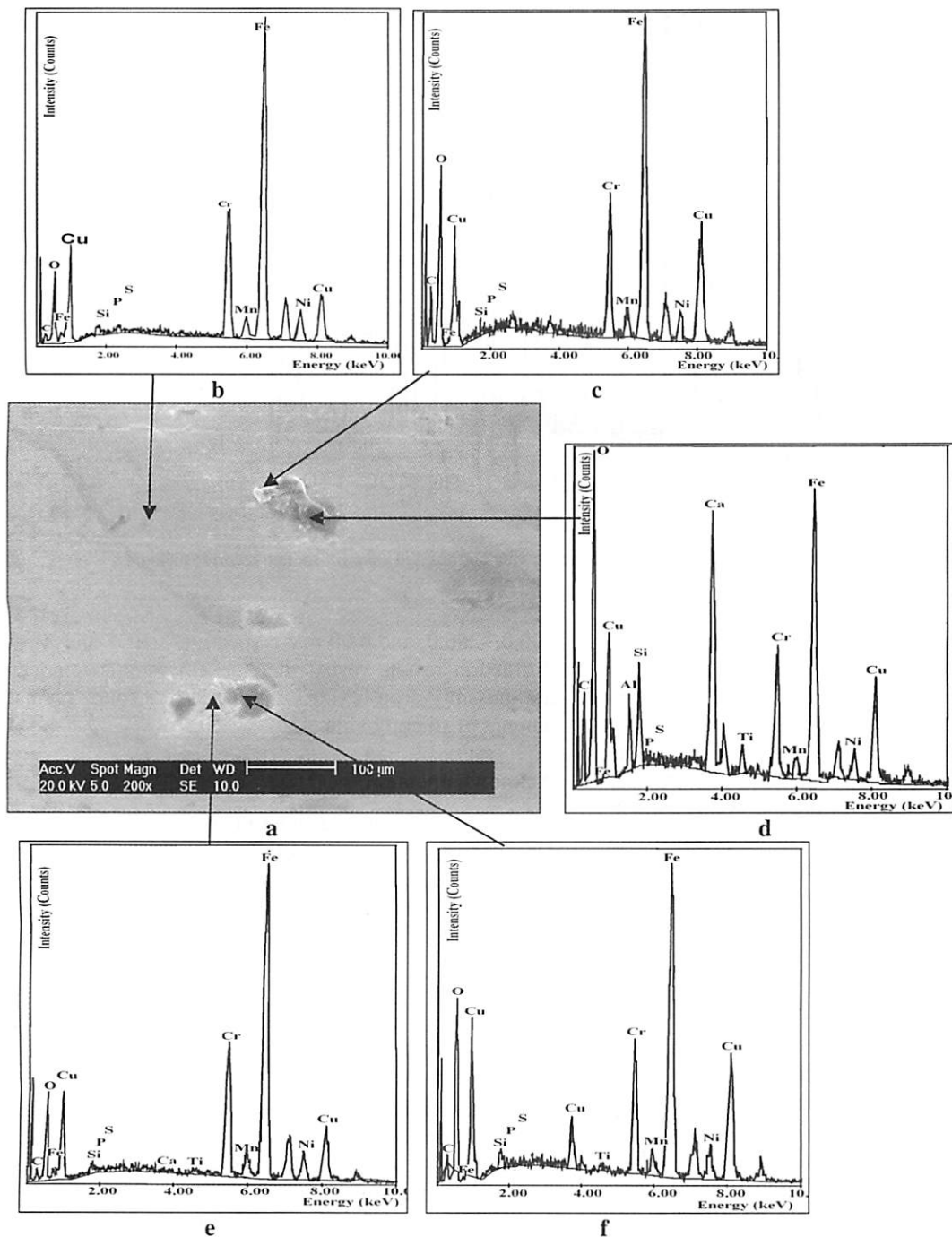


Fig-5. SEM micrograms of a corroded sample immersed in a 0.6 M. sodium hydroxide:

- a. SEM microgram of the microstructure. The microgram gives a clear indication of surface erosion caused by the corrosion medium.
- b. EDS results taken over the sample's bulk surface, shows that the sample's surface still seems to be flat overall; there is a possibility that chrome oxide and iron oxide are present on the spot
- c. This spot reveals the presence of amount of chrome oxide and iron oxide.
- d. EDS pattern showing the possibility of the presence of chrome oxide, iron oxide, a minor amount of silicon oxide.
- e. EDS pattern showing the possibility of the presence of chrome oxide and iron oxide.
- f. EDS pattern showing the possibility of the presence of chrome oxide and iron oxide.

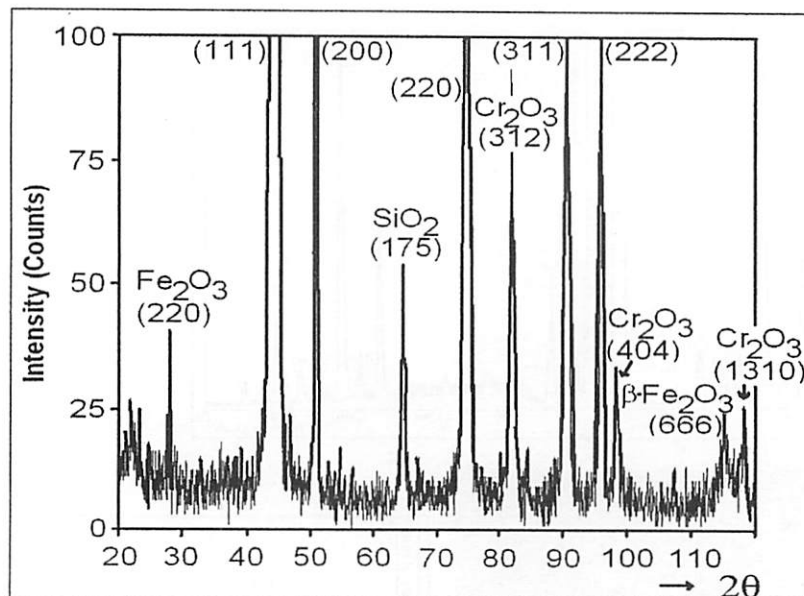


Fig-6. X-Ray diffraction intensity pattern of one corroded sample after corrosion in a 0.6 M. sodium chloride medium

X-ray diffraction pattern in one particular 0.6 M sodium chloride corroded sample is shown in Fig.-6. Diffraction intensity shows the appearance of foreign peaks besides the regular peaks, indicating the presence of corrosion byproducts inside the sample. Analysis using the computer code JCPDS (Joint Committee On Powder Diffraction Standard) available in the CD-ROM format, points to the possible presence of solid corrosion byproducts such as iron oxide (β - Fe_2O_3 , Fe_2O_3), chrome oxide (Cr_2O_3), and a minor amount of silicon oxide (SiO_2).

CONCLUSION

Concluding from the above discussion and analysis, it could be argued that for commercial SS-321 alloys undergoing corrosion in an sodium chloride medium with a molar concentration variation of 0.4, 0.5, 0.6, and 0.7 the corrosion effect with measured corrosion values of only 0.0117, 0.0248, 0.0394, and 0.0033 mpy respectively, is so small and there are no effect to the sample according to Fontana's criteria. Therefore, judging by the Fontana's criteria these test-specimens have been proven to exhibit an excellent resistance toward corrosion when immersed in an sodium chloride solution medium. The ensuing type of corrosion is erosion corrosion preceded by pitting corrosion. Corrosion rate will continue to increase with respect to corrosion medium concentration values, except from 0.6 to 0.7 M, where the corrosion rate decreases. The corrosion potential tend to decrease and the passivation potential tend to increase with respect to the concentration medium values, except from 0.6 to 0.7 M. Potentiodynamic measurements yield the following potentials for molar concentration value of 0.4, 0.5, 0.6, and 0.7 are -417.99, -420.10, -441.38, and -400.96 mV respectively. The passivation potential for molar concentration value of 0.4, 0.5, 0.6, and 0.7 are -210.0, -

200.0, -280.0, and 0.00 mV respectively. EDS and X-ray diffraction results reveal that the corrosion byproducts are possibly iron oxide, chrome oxide, and a small amount of silicon oxide.

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