

CORROSION EXPERIMENT ON NON STANDARD AUSTENITIC STEEL A1, IN REACTOR COOLANT WATER

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ABSTRACT

CORROSION EXPERIMENT ON NON STANDARD AUSTENITIC STEEL A1, IN REACTOR COOLANT WATER. Experimental corrosion studies on non standar austenitic SS, A1, have been carried out. The samples were immersed in reactor coolant water medium with pH variation of 5.95, 6.0, 6.15, and 6.31. 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 products. For further verification x-ray diffraction method was also used to detect any possible emerging corrosion products type on the samples' surfaces. Experimental results confirm that non standar austenitic SS immersed in reactor coolant water 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 reactor coolant water corrosion medium. 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 chrome oxides and iron oxides.

Keywords: Corrosion, non standard austenitic stainless steel, reactor coolant water

ABSTRAK

EKSPERIMEN KOROSI PADA BAJA AUSTENIT NON STANDAR A1, DALAM AIR PENDINGIN REAKTOR. Telah dilakukan percobaan korosi dari bahan austenitic baru yang non standar, A1, dalam medium air pendingin reaktor, dengan variasi pH, yaitu 5,95, 6,00, 6,15, dan 6,31. Eksperimen dilakukan dengan alat uji potensiostat-galvanometer tipe M-273 EG & G. Dilanjutkan dengan karakterisasi pada sampel yang telah dikorosikan, yaitu pemeriksaan struktur mikro yang dilakukan dengan SEM dilengkapi EDS (energy dispersive spectroscopy) untuk mendeteksi adanya produk korosi yang mungkin ada pada permukaan sampel. Juga dilakukan percobaan difraksi sinar-X untuk konfirmasi hasil produk korosi tersebut. Hasil eksperimen menunjukkan bahwa baja austenite non standar yang dibuat ini sangat tahan korosi terhadap air pendingin reaktor, dan hanya terjadi sedikit korosi sehingga menurut kriteria Fontana, baja austenit non standar A1 ini memiliki ketahanan korosi yang sangat baik dalam medium air pendingin reaktor. Hasil pemeriksaan dengan EDS dan difraksi sinar-X juga menunjukkan bahwa produk korosi yang paling mungkin ada adalah oksida besi dan oksida chrom.

Kata kunci: Korosi, baja tahan karat austenite non standar, air pendingin reaktor

INTRODUCTION

One of the requirements for reactor structural materials, particularly vessel and heat exchanger is, that the material must be resistant to corrosion caused by the environment, which among others in this case is the water-cooled reactor. While the other requirement is that a structural material must withstand the mechanical loads, be temperature resistant, and also resistant to neutron radiation.

The main reason behind the synthesis of corrosion-resistant stainless-steel alloys is the fact that the alloy is resistant to a corrosive environment. As a rule, a stainless-steel alloy would contain the one basic alloying element, namely a minimum of 11% chromium^[1]. Besides its role as a stabilizer of the ferrite phase in the alloy, chromium also acts as a good anti-corrosion alloying element. Non standard austenite A1 Stainless Steel alloy is a new austenite type contains several alloying elements, such as nickel, chrome, manganese, silicon, carbon and titanium, and the composition is listed in Table 1 below. Based upon the composition of alloying elements which constitute the austenitic steel, it could be conjectured that this type of steel posses a relatively good anti-corrosion property.

In this work the non standard austenite stainless steel with the name code of A1 made from the granular ferro-scrap, nickel, ferro-chrome, ferro-manganese, and ferro-silicon with small added of titanium by foundry method^[2] Now, this austenitic material has been independently fabricated in the authors' own laboratory. However, it has never been tested before with respect to the strength of corrosion, which is why this material has been chosen as an object of investigation.

The major objective of this work is to gather a complete set of data on this alloy's behavior in a reactor coolant water

environment with a pH variation, supplemented by several minor objectives, among which is to gather information on the various types of byproducts brought about by the corrosion process when the test-samples are immersed in a reactor coolant water medium.

Table1.Elements composition in non standard austenite stainless steel A1^[2,3].

Element	W, %
Ni	18.320
Cr	21.460
C	0.080
Mn	0.075
Si	2.550
P	0.002
S	0.006
Ti	0.003

THEORETICAL REVIEW

Corrosion reaction could be viewed upon a thermodynamic system surrounded by an environment forming an imaginary wall^[5]. 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^[4,5]. Corrosive reaction is a transitional condition, and is often labeled as a transition-reaction.

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 [4,5]. 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^[3,4]. 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 yield 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 available in many technical papers.

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 surface.

The potention-dynamic technique is utilized to determine the active and passive region of the measured alloy system. The overall form of the curve is an indication of the corrosion behavior of the samples immersed in the test-solution. This technique is capable of producing reliable data if be 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 chlorine 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.

MATERIALS AND METHODS

Materials

In this work, the non standard austenite stainless steel plate samples, A1, with a thickness of 5 mm and 15 mm diameter are used as test-materials. The solution media used are reactor coolant demineralization water with varying pH values, namely 5.95, 6.0, 6.15, and 6.31 respectively. How to reach a certain pH variation in this mixture without adding a substance which is either acid or base, is by exposing the reactor coolant demineralization water to the open (ambient) atmosphere, starting first from the unexposed condition, and then successively exposing the substance with a variation in time: 1 month, 2 months and 3 months, and so on.

Instrumentation

The preparation instrumentations used are Buehler abrasive cutter, Karl Kolb double polishing machine, Long-neck measurement flask, vial test-tubes and drop-pipettes for solution preparation. Corrosion test instrument utilized in this work is the M273 EG&G potentiostat/galvanometer (Princeton Applied Research Corp.); the analysis apparatus used are, among other things, is X-ray diffraction machine Shimadzu XD-610 (Japan) to inspect the diffraction pattern after corrosion test. The microstructure is inspected by SEM equipped with EDS that has been utilized to detect any possible by-products of the corrosion process.

METHODS

The austenitic steel produced by foundry method [1] are machined to form rod with 15 mm diameter, and then sliced-up into several pieces each in 5 mm thick. Sample preparation is carried out in compliance with the standard procedure^[5]. Surfaces of the samples were polished in a polishing-machine until a relatively uniform and surface's smoothness and flatness 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 water coolant reactor with different pH as well as mentioned above, 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. 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. Potentio-resistance measurements will yield the free-potential ($E(I=0)$), corrosion resistance (R_p) and also the Tafel-anodic (β_a) and cathodic (β_c) parameters printed automatically by the instrument. From these parameters the corrosion-current, corrosion rate and the correlation factor are derived and are automatically displayed by the test-instruments.

To determine their corrosion products, the corrosion-test samples are observed by an EDS equipped electron microscope (SEM). In order to complete the classification of the resulting types of corrosion-product, each of the samples are examined using an X-ray diffraction

RESULTS AND DISCUSSION

In this work the corrosion experiments have been carried out. The media involved are reactor coolant water with pH values varying from 5.95, 6.0, 6.15, and 6.31 respectively. From potentio-dynamic measurements the free corrosion-potential parameter is obtained. This parameter indicates the situation when the particle is in a free corrosion state which in turn is equivalent to a virtual equilibrium state, meaning that the potentiostat is being turned off with the passive and active potential region.

The results of the corrosion experiments on non standard austenite-SS samples using the polarization resistance and

the potentiodynamic methods in a reactor coolant water medium ($5.95 < \text{pH} < 6.31$) are shown in the following figures: the polarization-resistance pattern of corrosion-potential versus corrosion current curves are shown in Fig. 1a, 1b, 1c and 1d, respectively. The measurement results on non standard

austenite-SS samples using the polarization resistance techniques immersed in reactor coolant water medium with pH variation using the polarization resistance technique yield the following parameters presented in Table 2.

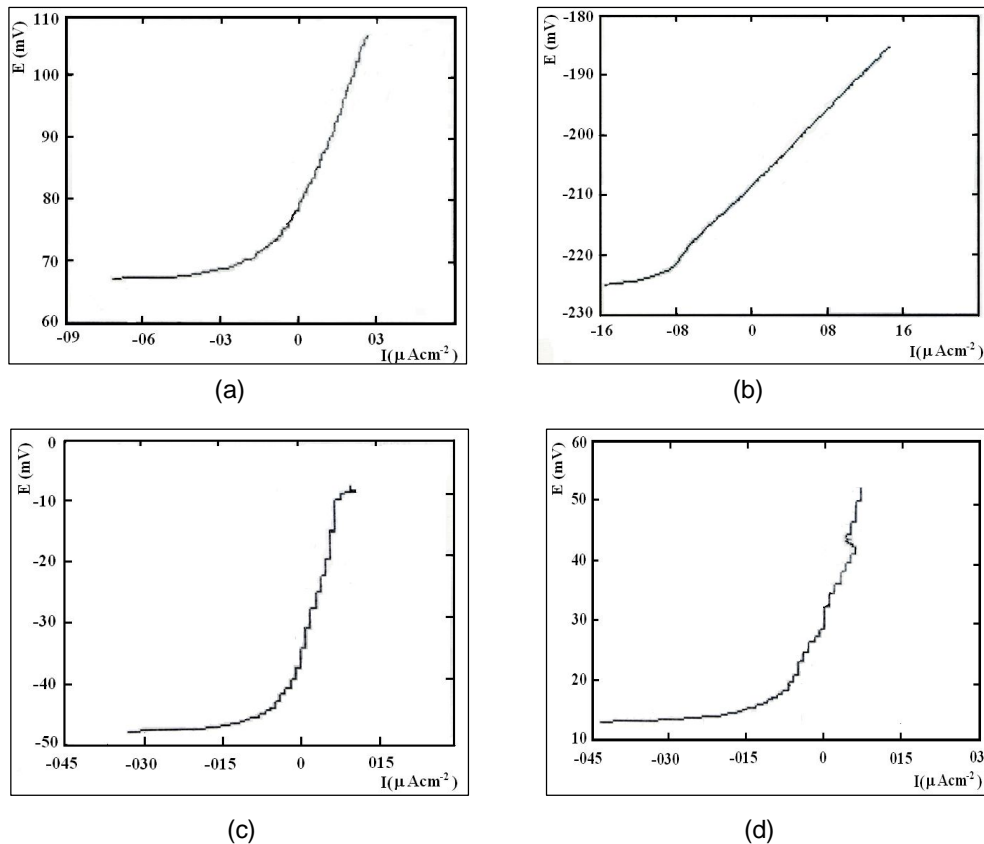


Fig.1 Corrosion-potential of polarization-resistance pattern versus corrosion current curves of non standard austenite-SS sample immersed in reactor coolant water medium with pH variation of : a. 0.4M. b. 6.0 c. 6.15. d. 6.31.

Table 2. Measurement results of non standard austenite-SS samples corroded in reactor coolant water medium with pH variations using the polarization resistance techniques

Measurement/Experimental Parameters	pH			
	5.95	6.0	6.15	6.31
$E(I=0)$ (mV)	79.98	-208.35	-35.97	31.36
R_p ($k\Omega \text{ cm}^{-2}$)	484	154	767	1852
I_{corr} (μAcm^{-2})	0.04	0.014	0.03	0.01
Corrosion Rate (mpy)	0.015	0.047	0.01	0.004
Correlation	1.0	1.0	1.0	1.0
Range of Experimental Potential (mV), $E(I=0) \pm \Delta$ mV	79.98 ± 40	-208.35 ± 40	-35.97 ± 40	31.36 ± 40

The corrosion rate tends to increase with respect to pH value from 5.95 to 6.0 and then decrease from 6.0 to 6.31. In the reactor coolant water medium, the corrosion rate reaches its peak value of about 0.047 mpy, for a pH value of 6.0. For the upper pH values, the corrosion rate will decrease; the main origin of this phenomenon is that with the increasing pH values, the medium is moving toward a condition of diminishing acidity, which means leaning more toward the base condition, because in general steels are more corrosion-resistant in an alkaline medium than in an acid medium. This is because the energy of oxidation in the acid is lower than that of oxidation in alkali^[7, 8]. The data distribution pattern for corrosion rate versus pH values is shown in Fig.- 2.

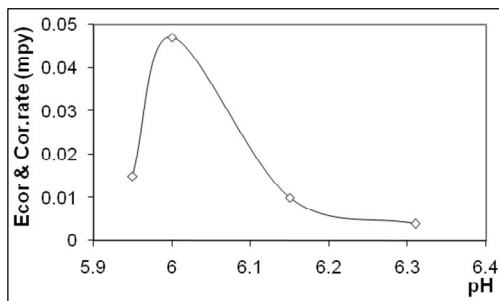


Fig. 2. Plot of Corrosion Rate versus reactor coolant water pH values

The potentiodynamic technique test will cover a wider potential range, especially compared to the polarization resistance technique, causing damages to the samples. The graphs in Figures 3a, 3b, 3c, and 3d, respectively show the potentiodynamic pattern of corrosion-potential versus corrosion current curves in reactor coolant water medium with pH variation as above mentioned. Potentiodynamic method is then employed to study the active-passive behavior of the test-samples. The following general pattern is shown by the potentiodynamic curves: In the beginning, the samples inhibit cathodic properties and with

increasing working potential, the current will be reduced until the free-corrosion potential is reached (E_{cor}), which is a potential level indicating the state of virtual equilibrium; in this state a metal will encounter corrosion without any external potential input. The free-corrosion potential is an experimental parameter, which is a measure of a sample's inclination toward corrosion (corrosiveness or causticity of the sample) in a certain type of solution. The higher the value of this parameter, the more difficult it is for the electrode sample to undergo corrosion. Based upon the experimental results it is evident that non standard austenite-SS samples in reactor coolant water with pH value of 5.95 to 6.31 reach their minimum corrosion potential of -254 mV at a pH value of 6.0. Further, if the external working potential is raised, an increase in corrosion-current will follow and samples will exhibit anodic-type behavior. Samples will start to undergo corrosion and at this point, the potential is starting to reverse, that is to be at a particular level where the passivation process is starting to set in; in this condition, if the working potential is continued to increase, the current is starting to decrease. This situation is made possible through the metal partial protection, for example, corrosion by-products sticking to the samples' surface therefore reducing further contacts between the medium and the metal surfaces. The corrosion measurement results on non standard austenite-SS sample immersed in reactor coolant water medium with pH variation using the potentiodynamic techniques yield the following parameters presented in Table 3. The data distribution pattern for corrosion-, passivation- and transpassive potentials versus pH value is shown in Fig.- 4. It is clearly visible that corrosion-, passivation-, and also transpassive potential tends to increase from pH value of 6.0 to 6.31.

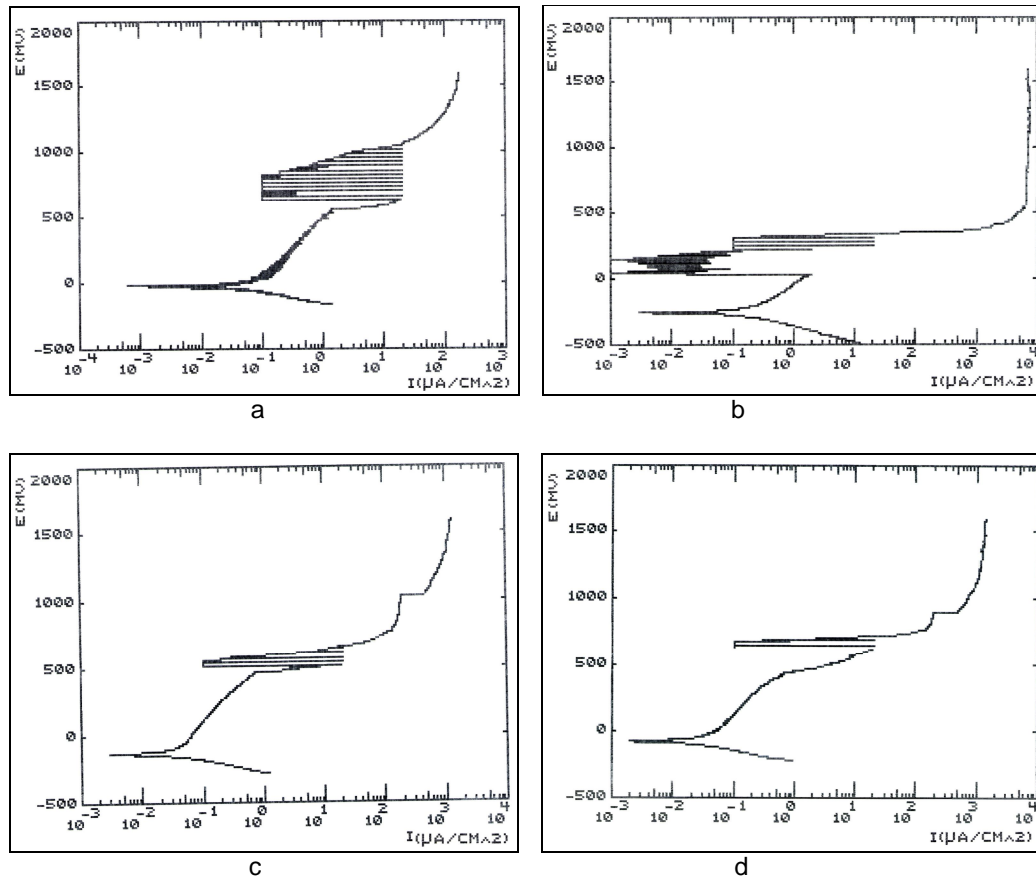


Fig. 3. Potentiodynamic potential versus current curve pattern obtained from new non standard austenite sample immersed in a reactor coolant water medium with pH variation of : a. 0.4M. b. 6.0 c. 6.15. d. 6.31.

Table 3. Experimental results of non standard austenite-SS sample immersed in reactor coolant water medium with pH variation using potentiodynamic method.

pH	Free Corrosion pot (mV)	Passivation Potential (mV)	Transpassive Potential (mV)
5.95	-21.54	610	1100
6.00	-254.35	40	510
6.15	-126.2	500	700
6.31	-73.0	650	900

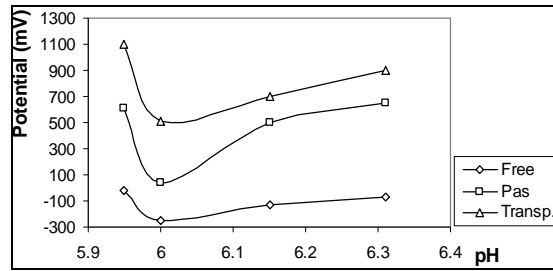
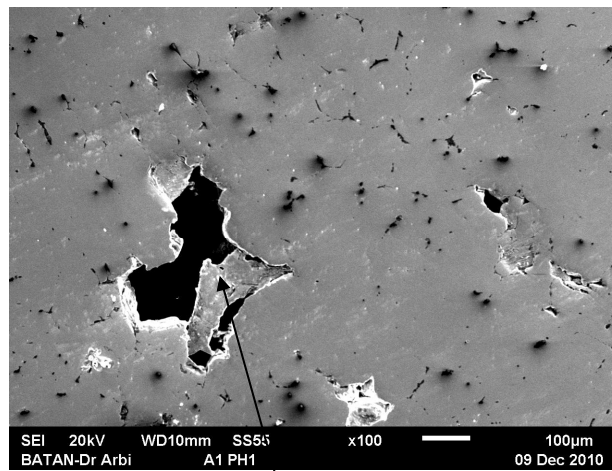
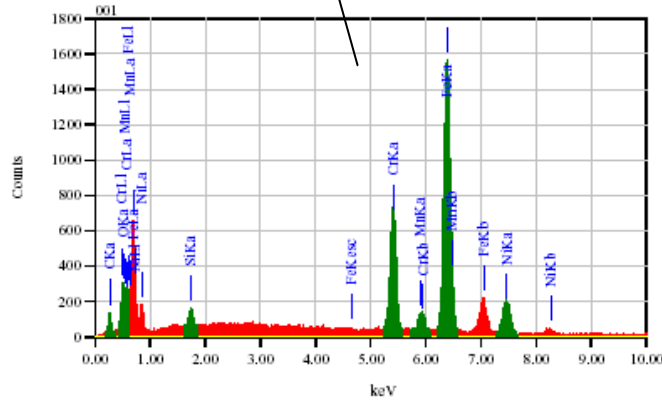


Fig. 4. Data plots for free corrosion -, passivation -, and transpassivation potentials versus reactor coolant water pH values



(a)



(b)

Fig.-5. (a). SEM Micrographs of the microstructure of a corrosion non standard austenite-SS sample immersed in reactor coolant water medium. The micrograph gives a clear indication of the sample surface after corrosion experiment by reactor coolant water medium. The figure was taken in damaged surface part (b). EDS result of sample bulk of grey area dominated by Cr – and Fe element beside oxygen, showing the possibility of chrome-oxide forming there is a possibility that chrome oxide or iron oxide are present on the spot

The results of microstructure investigation on a sample corroded in reactor coolant water medium is shown in Fig. 5. The micrograph was taken with SEM. Here it is obvious that there is sample's surface area part that has been eroded by the corrosion medium, consequently showing corrosion erosion. EDS pattern (Fig. 5.b) on a selected bulk spot in this very small surface area part reveals the possibility of iron oxide (Fe_2O_3) and/or chrome oxide (Cr_2O_3) being present in the sample. Based on the microstructure investigation supplemented by EDS data it

could be claimed that in reactor coolant water medium, pitting/erosion corrosion have certainly occur. This is brought about by reactor coolant water assault on the sample's bulk that is able to penetrate and enter the bulk, and forming porosity, which later on will be filled with corrosion medium causing abrasion in the sample's bulk. The ensuing corrosion byproducts in non standard austenite-SS are chrome oxide, iron oxide. This finding has been confirmed by x-ray diffraction data below.

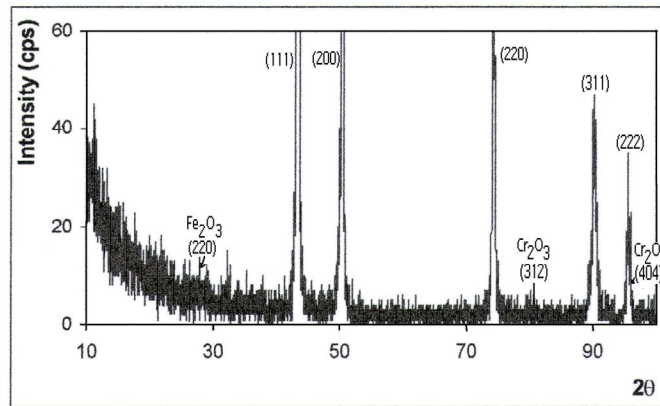


Fig-6. X-Ray diffraction intensity pattern of non standard austenite-SS sample after corrosion in reactor coolant water medium

X-ray diffraction pattern in one corrosion 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 products such as a minor amount of iron oxide ($\beta\text{-Fe}_2\text{O}_3$, Fe_2O_3), and chrome oxide (Cr_2O_3). This result is in line with the EDS results which reveal the existence of a minor amount of chrome oxide (Cr_2O_3) and iron oxide (Fe_2O_3 , $\beta\text{-Fe}_2\text{O}_3$),

so that the solid corrosion products is in correlation one each other.

CONCLUSION

Concluding from the above discussion and analysis, it could be argued that for non standard austenite-SS alloys undergoing corrosion in reactor coolant water medium with pH variation of 5.95, 6.0, 6.15, and 6.31 the corrosion effect with measured corrosion values of only 0.015, 0.047, 0.01, and 0.004 mpy respectively, is so small and practically have not affected 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 reactor coolant water medium. The ensuing type of corrosion is erosion corrosion preceded by pitting corrosion. Corrosion rate will continue to decrease with respect to medium pH values, except from 5.95 to 6.0, where the corrosion rate is increase. The corrosion- passivation -, and the transpassive potential tends to increase, except from 5.95 to 6.0 where the value tends to decrease. Both EDS and x-ray diffraction results reveal that the corrosion products are possibly chrome - and iron oxide.

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