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Corrosion Behavior of Fe-35Ni-22Cr and Fe-17Ni-17Cr Alloys in Acid Pickling Solutions

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Abstract

This work aims to study the corrosion behavior of two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr in acid pickling solutions. The corrosion behavior of two alloys in HCl and H_2SO_4 was studied using the weight-loss method and potentiodynamic polarization, at a different time at 30 °C, 40 °C and 60 °C. The morphology of two alloys was analyzed by scanning electron microscope (SEM) and energy dispersive X-ray (EDS) analysis. The effect of temperature at constant acid concentration solutions has a strong influence on the corrosion rate of two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr. The activation energy (Ea), enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) were calculated and discussed. Results obtained from weight loss and potentiodynamic measurements were in good agreement and confirmed that Fe-35Ni-22Cr alloy is a higher corrosion resistance than Fe-17Ni-17Cr alloy in HCl and H_2SO_4 acid solutions.

Keywords: Fe-Ni-Cr alloys; Corrosion rate; Thermodynamic parameters, Kinetic parameters; Acid pickling solutions

1. Introduction

Corrosion is the deterioration of a material due to the reaction with its environment which results from loss and damages of many materials and life. Exposing of metals to different aggressive environments as the acidic and alkaline media uses for pickling, industrial acid cleaning of metal, chemical, and electrochemical etching, cleaning of oil refinery equipment, oil well acidizing and acid descaling, lead to metal loss because of the corrosion [1]. The problem of metallic corrosion has reached significant concerns. The good properties of Fe-Ni alloys thus they are usually used in the industry as distinctive magnetic properties, good mechanical properties, and low thermal expansion coefficient at smaller temperatures [2]. The high corrosion and heat resistance of the alloys which have 36:46%Ni used as superalloys with a large wide of applications [3, 4]. Increasing the Ni content leads to increase the corrosion resistance in the Fe-Ni alloys. The corrosion protection of Fe-Ni alloys in different strong media has investigated by several authors [5-7]. The industrial process like pickling, etching, acid cleaning, acid de-scaling, iron is dealing with aggressive solutions as acidic (HCl, and H_2SO_4) which lead to corrosion attack. The metal corrosion magnitude depends on the acid concentration, operating temperature and contact period. The surfaces of the Fe-Ni alloys of these media were discussed by several authors [8]. These work asses to study the corrosion behavior of two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr in different acidic media (1M HCl, and1M H_2SO_4). The corroded surfaces of the two investigated alloys when being immersed in 1M HCl solutions for 96 hr. were studied using a scanning electron microscope (SEM) and energy-dispersive x-ray analysis (EDAX) and comparing corrosion behavior, kinetics and activating parameters of the two alloys.

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2. Material and Methods

Sample Preparation

The two alloys, with the chemical composition (wt. %) as presented in Table 1, are named as Fe-35%Ni-22%Cr (Alloy 1) and Fe-17%Ni-17.7%Cr alloys (Alloy 2). These alloys have a cylindrical coupon shape with the specimen of 2 cm x 2 cm were prepared for weight loss measurements. The coupons were ground with emery paper grades 320, 400, 800, 1000 and 1200 then polished with a plunge into 1:1 HCl acid solution for 15 min. They were washed with

tap water then double distilled water, dried in air then washed with acetone. All specimens dried in hot air and weighed on an analytical balance to accuracy. The specimen weights were noted and then plunge into test solution of acids at different temperatures 30, 40 and 60 °C. At regular time intervals up to 30 min, the specimen was removed from the test solution and washed with the tap, double distilled water, dried in the air, washed with acetone and again dried in hot air. Finally, the weights recorded after 200 min. The differences in weights at each interval were noted and the corrosion rates and specific reaction rates were calculated.

TABLE 1. Chemical composition in wt.% for two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr

Alloys	Ni	Cr	Mo	Fe	Si	Mn	Al	Ti	Nb
Alloy 1	35.2	21.9	<0.0050	40.7	0.584	0.938	0.127	0.320	0.048
Alloy 2	17.0	17.7	1.26	60.9	0.349	1.45	0.015	0.004	0.748

Corrosive Media Preparation

A stock solution of analytical grade HCl acid (37 %, 1.18g/L) and H_2SO_4 acid (98%, 1.84 g/L) were prepared by using double distilled water. The acid solutions of required concentrations of 1M were prepared by appropriate dilutions. All the chemicals utilized in this investigation, for the solution preparation were of analytical grade.

Weight loss Measurement

During the weight loss experiments, Fe-Ni-Cr alloys a cylindrical shape coupon were weight (w_1) and suspended completely in 1 M solutions of different acids in 100 ml beaker respectively. The solution volume was kept at 50 ml. The coupons were retrieved after 30, 60, 90, 120, 150 and 200 min, washed with distilled water, dried with acetone and reweighed (w_2). The immersion time with relatively higher weight loss was adopted as optimum immersion time. From the weight loss data, the corrosion rate in Fe-Ni-Cr alloys $cm^{-2}.hr^{-1}$ was calculated using Eqs. 1and 2 [9]:

$$\Delta W = W_1 - W_2 \qquad (1)$$

$$C.R. \ (mg/cm2h) = \frac{Weight \ loss}{Area \ x \ Time} \qquad (2)$$

Where w_1 and w_2 are the coupons weight before and after immersion in the corroding medium respectively.

Effect of Temperature

To study the temperature effect, the prepared weighted Fe-Ni-Cr alloys coupon was immersed in 1M corroding concentration at 30, 40 and 60 °C for 3hr. The final weight was taken; the weight loss and corrosion rate were calculated.

Potentiodynamic polarization

Potentiodynamic polarization studies were carried out with the test specimens in the range from -0.4 V to +0.4 V using a scan rate of 5 mV/sec. The cell consisted of test specimens as a working electrode, the auxiliary electrode was a platinum sheet and SCE (Hg/Hg_2Cl_2-Sat. KCl) as a reference electrode connected to a conventional electrolytic cell of capacity 25 ml. The corrosion rate, C.R., can be computed using Faraday's Law as follows [10]:

$$C.R. \ (\mu m/year) = 3.3 \, I_{corr} \frac{M}{zd} \qquad (3)$$

Where; z = ionic charge, M = atomic weight of Fe alloy, d = density of Fe alloy, and I_{corr} = corrosion current density, $\mu A/cm^2$.

Spectroscopic analysis

The two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr surfaces were ground and polished before being immersed in the electrolytic solutions and performing the weight loss measurements. Scanning electron microscopy (SEM) micrographs and energy-dispersive x-ray analysis (EDAX) profiles were obtained for the surface of the alloys after 96 hr of immersion in 1M HCl solutions. For this purpose, we used a scanning electron microscope with an attached energy dispersive spectroscopy (JEOL).

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3. Results and Discussion

The Effect of Immersion Time

Weight loss measurement has been recorded as ideally good as other techniques for alloy corrosion evaluation in an immersion test **[11].** In this investigation, the gravimetric weight loss method was used to assess the corrosion of Fe-Ni-Cr alloys in the HCl and H_2SO_4 medium. The weight of each of the samples was measured before immersion and then measured after 3 hr of total immersion in the medium at a different temperature to obtain the weight loss. The difference in initial and final weights was used to measure the weight loss during the interval period. The weight loss measurements were analyzed at the intervals of 3 hr for the complete period of immersion and the results were presented in the forms of cumulative weight loss and total weight loss. The cumulative weight loss per area centimeter square of corrosion of two alloys exposed to acids solutions at different immersion time is presented in Fig. 1.
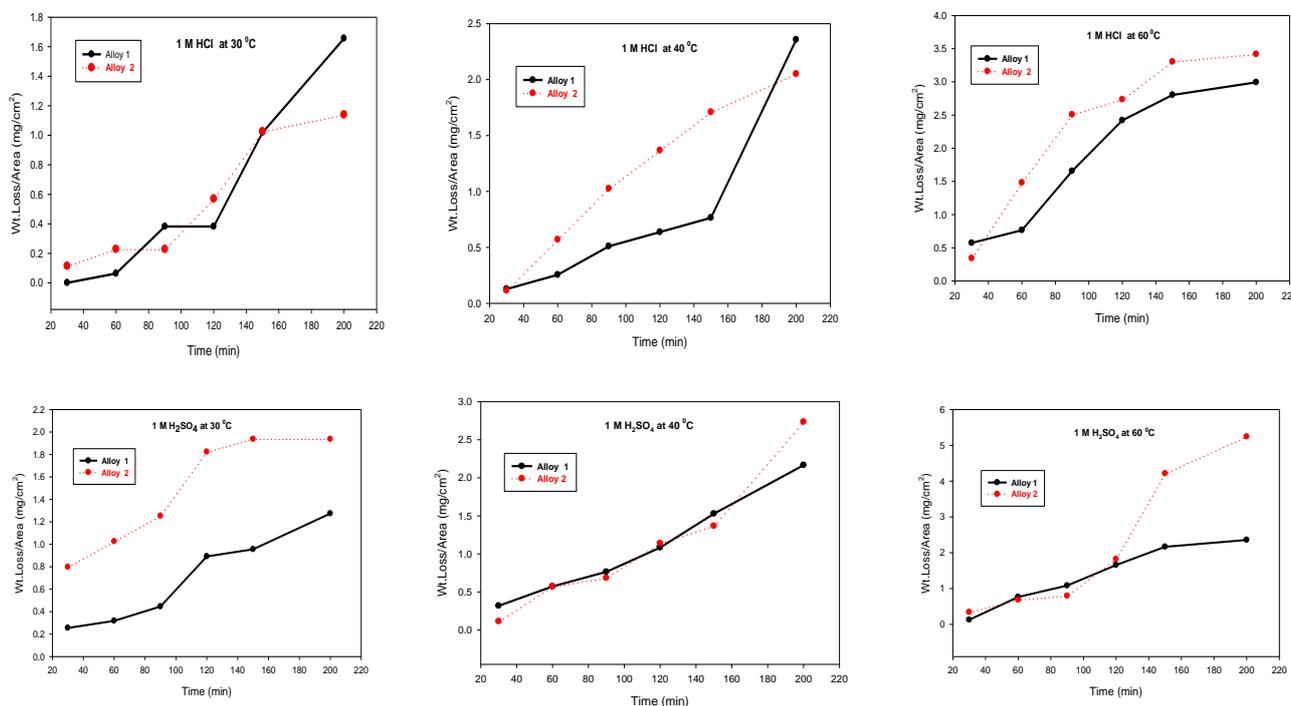

Fig. 1. Cumulative weight loss for Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions at different immersion time

From Fig. 1, it can be observed that the Alloy 1 which contains Fe-35%Ni-22%Cr has the highest corrosion resistance than Alloy 2 which contains Fe-17%Ni-17.7%Cr in all used media since the lowest weight was lost during the exposure period. The evident increase in both weight loss and progression pathway of cumulative weight losses for alloys with an increase in exposure time was observed. The constant difference in cumulative weight loss from the start until the end could be a result of the composition and structure difference generated by the different addition amounts of Ni and Cr. The role of Ni and Cr is the same; it enhances the formation of passive surface films, in the existence of oxygen. These passive films decrease the corrosion rate process by the formation of protective oxides [12].

Hydrochloric acid is very corrosive, and its aggressiveness can change drastically depending on the acid concentration, temperature, and contamination of the acid (e.g. ferric ions). Table 2 illustrate the effect of temperature on the corrosion rate of Fe-Ni-Cr alloys in different aggressive acid media. The corrosion rate gradually increases with an increase in temperature. For two alloys, a threshold temperature is reached, below which the corrosion rate is negligible due to the alloy passivation; Above the threshold temperature, the corrosion rate increases rapidly as the temperature increases.

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Sulfuric acid is the most widely used acid in all branches of industry. It is a smaller amount corrosive than acid, and its aggressiveness is extremely hooked into acid concentration, temperature, and also the presence of impurities.

Table 2 illustrate the weight loss data for Fe-Ni-Cr alloys corrosion in the acid medium increased with an increase in immersion time. At least temperature of 30 ^{0}C, the weight loss of Fe-Ni-Cr alloys in HCl and H$_2$SO$_4$ are 0.0.026 and 0.020 g for Alloy 1, and 0.01, 0.017 g for Alloy 2, while at highest temperature of 60 ^{0}C of 3 hr the weight loss increased to 0.047, 0.037 g for Alloy 1, and 0.0.030, 0.046 g for Alloy 2. The rate weight loss of the alloys increase in the given acids indicates the instability of protective film for the longer contact period. Increased weight loss with immersion time is due to the interaction that occurs between the acid and the metal surface in solution, which tends to destroy the metal surface gradually with time thereby increasing the metal weight loss. Weight loss in constant concentration of the corroding increased with an increase in immersion time. The cathodic reaction in the concentrated acid solution for metals and alloys is the hydrogen evolution reaction as known, so the cathodic reaction for the Fe-Ni-Cr alloys in 1M HCl can be expressed by the following reaction [2]:
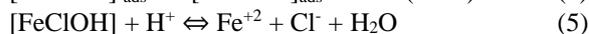
$$2H^+ + 2e^- = H_2 \qquad (1)$$

While the anodic reaction at this conditions the Fe dissolution from the alloy surface as in Eq. 2 [13];

$$Fe = Fe^{2+} + 2e^- \qquad (2)$$

This dissolution reaction appears the abrupt increase of current with increasing the applied potential in the anodic branch. The first increasing in the corrosion rate values was due to the Fe dissolution [14]:

$$Fe + H_2O + Cl^- \Leftrightarrow [FeClOH]^-_{ads} + H^+ + e^- \qquad (3)$$

$$[FeClOH]^-_{ads} \Leftrightarrow [FeClOH]_{ads} + e^- \quad (r.d.s.) \qquad (4)$$

$$[FeClOH] + H^+ \Leftrightarrow Fe^{+2} + Cl^- + H_2O \qquad (5)$$

Where [FeClOH]$_{ads}$ and [FeClOH]$^-_{ads}$ are the adsorbed intermediates which each of them is involved in the rate determining step.

The corrosion rate of Fe-Ni-Cr alloys exposed to acids solutions for 3 hr has been determined by the weight loss method at 30 °C to 60 °C are existed in Table 3 and Fig. 2. It is observed that Fe-Ni-Cr alloys corrode in concentrated 1M HCl and 1M H$_2$SO$_4$ because there is a considerable decrease in the original weight of the specimen. The corrosion is because of water, air and hydrogen ion, which increase the corrosion process. The corrosion happens at the Fe surface, which is a reaction site. Fig. 2 illustrates the increase of corrosion rate with an increase in temperature of acid and time. Initially, there is a ferric hydroxide layer formation and increases the concentration lead to the content of a protective layer of ferric hydroxide on the iron specimen surface, which decreases the weight loss [15]. The higher the Ni and Cr contents in the alloy, the lower the corrosion rate. The corrosion resistance of alloy which contains 35 % Ni and 22 % Cr is a consequence of the formation of insoluble metal hydroxides and salts, which slow down the dissolution rate of the alloy.
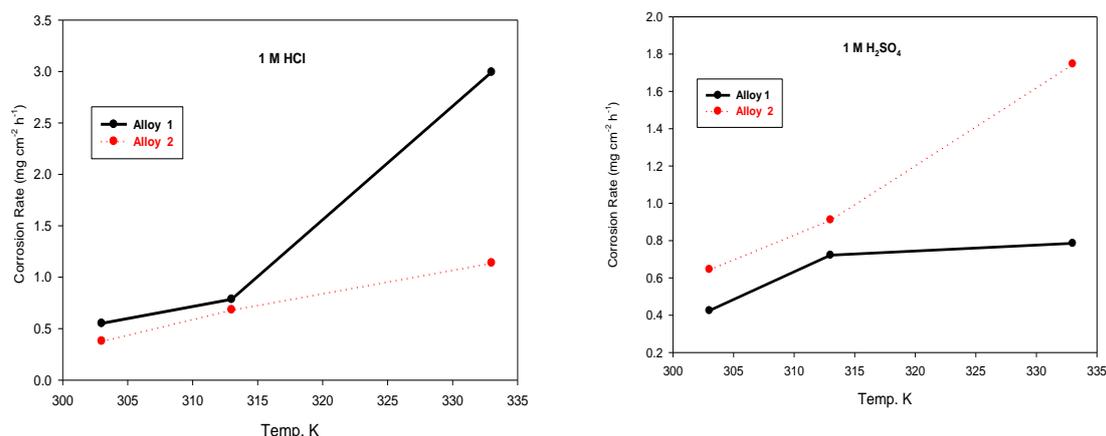

Fig. 2. The corrosion rate of Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions

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TABLE 2. Weight loss data for corrosion of two alloys exposed to different aggressive media at different immersion time and temperature.

Temp.	Time (min)	Alloy 1		Alloy 2	
		1 M HCl	1 M H$_2$SO$_4$	1 M HCl	1 M H$_2$SO$_4$
		Weight loss (g)	Weight loss (g)	Weight loss (g)	Weight loss (g)
30	30	0.00	0.004	0.001	0.007
	60	0.001	0.005	0.002	0.009
	90	0.006	0.007	0.002	0.011
	120	0.006	0.014	0.005	0.016
	150	0.016	0.015	0.009	0.017
	200	0.026	0.020	0.01	0.017
40	30	0.002	0.005	0.001	0.001
	60	0.004	0.009	0.005	0.005
	90	0.008	0.012	0.009	0.006
	120	0.01	0.017	0.012	0.01
	150	0.012	0.024	0.015	0.012
	200	0.037	0.034	0.018	0.024
60	30	0.009	0.002	0.003	0.003
	60	0.012	0.012	0.013	0.006
	90	0.026	0.017	0.022	0.007
	120	0.038	0.026	0.024	0.016
	150	0.044	0.034	0.029	0.037
	200	0.047	0.037	0.030	0.046

TABLE 3. The comparative corrosion rate of two alloys exposed to acids solutions for 3 hr at different temperature in terms of weight loss (mg) parameter

Media	Temp. °C	Alloy 1			Alloy 2		
		Weight loss (g)	Weight loss (mg)	CR, (mg.cm^{-2}.hr^{-1})	Weight loss (g)	Weight loss (mg)	CR, (mg.cm^{-2}.hr^{-1})
1 M HCl	30	0.026	26	0.55201	0.01	10	0.37982
	40	0.037	37	0.78556	0.018	18	0.68368
	60	0.047	47	0.99363	0.030	30	1.13947
1 M H$_2$SO$_4$	30	0.020	20	0.42462	0.017	17	0.645700
	40	0.034	34	0.721868	0.024	24	0.911577
	60	0.037	37	0.785562	0.046	46	1.747189

The Effect of Temperature

Table 3 provides the increase of corrosion rate with an increase in temperature. High temperature produces more severe corrosion condition. At the lowest temperature (30 °C) used, the weight loss and corrosion rate of Fe-Ni-Cr-alloys in HCl and H$_2$SO$_4$ are (0.026, 0.020 g) and (0.5520, 0.4246 mg.cm^{-2}.hr^{-1}) for Alloy 1 and for Alloy 2 (0.01, 0.017 g) and (0.379, 0.6457 mg.cm^{-2}.hr^{-1}). With increasing the temperature to 60 °C the weight loss and corrosion rate increased to (0.047, 0.037 g) and (0.9936, 0.78556 mg.cm^{-2}.hr^{-1})

for Alloy 1 and for Alloy 2 (0.030, 0.046 g) and (1.139, 1.747 and 0.1899 mg.cm^{-2}.hr^{-1}). An increase in temperature leas to increases the solubility of the protective films by an increase in the average kinetic energy of the constituent particles. As the average kinetic energy increases the velocity of the particles and collides more frequently which increases the reaction rate [16, 17]. In all the three given parameters above HCl, indicates the high reactivity over H$_2$SO$_4$. In the effect of concentration, the corrosion rate at 1M solution of HCl and H$_2$SO$_4$ are 0.55201 and 0.4246

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mg.cm^{-2}.hr^{-1}. In the effect of temperature, the corrosion rates of HCl and H$_2$SO$_4$ at 60 °C are 0.9936 and 0.78556 (mg.cm^{-2}·hr^{-1}). The highest reactivity of HCl is due to do the fact that HCl is a typical reducing acid across its entire concentration range. Its strongly acidic character and the harmful effect of the chloride ion combine to make it a very severe corrosive **[1].**

Fig. 2 clears that there is a large increase in weight loss and corrosion rate as the temperature increased from 30 °C to 60 °C. This indicates that the corrosion of Fe-Ni-Cr alloy in acid media increases at a higher temperature, which is according to the principles of chemical kinetics. The weight loss increase might also be due to diffusion and ionization of reactants or because of the solubility increase of the protective layer, which makes the surface susceptible to corrosion.

Thermodynamic and Kinetic Parameters

Temperature investigations are important in corrosion studies because they make it possible to determine the activation energy (E$_a$) and calculated the dissolution process [18]. The apparent activation energies (E$_a$) were calculated from Arrhenius Eq. 4 [19] and the results are presented in Table 4.

$$\ln C.R. = \ln A - \frac{E_a}{RT} \qquad (4)$$

Where A is a constant, R is the universal gas constant 8.314 J/mol.K, and T is the absolute temperature (K). The plot of ln (C.R.) Vs reciprocal of absolute temperature (1/T) presented in Fig. 3 gives a straight line with slope = − E$_a$/R, from which the activation energy values for the corrosion process were calculated. The Thermodynamic parameters enthalpy and entropy of activation were calculated using the transition state Eq. 5 [1, 20].

$$\ln\left(\frac{C.R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \qquad (5)$$

Where his Plank's constant and N is Avogadro's number. A plot of ln (CR/T) vs. 1/T which shown in Fig. 4 provides a straight show with slope = −ΔH$_{ands}$/R and intercept = ln(R/Nh) + ΔS$_{ads}$/R. The calculated values of enthalpy and entropy from the plots were presented in Table 4.
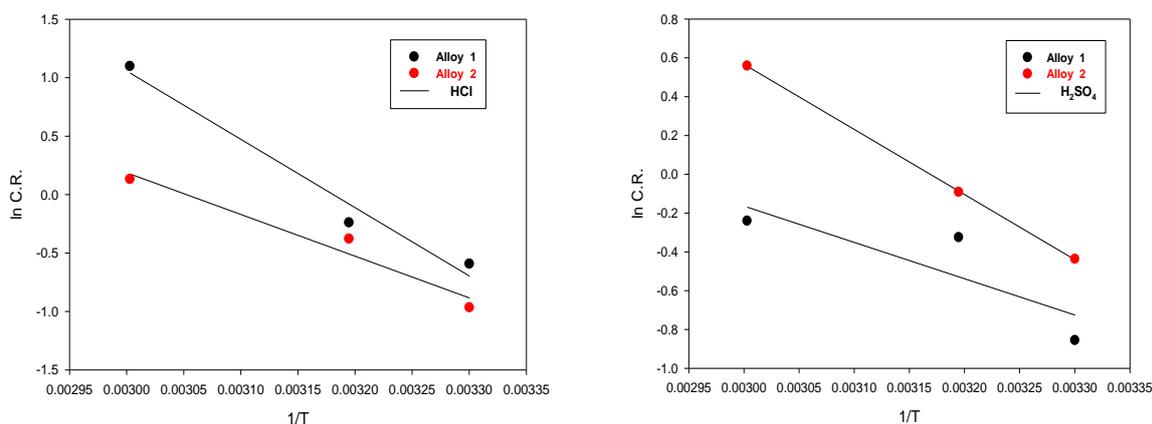

Fig. 3. Arrhenius plots of ln C.R. vs. 1/T for Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions at optimum concentration 1 M
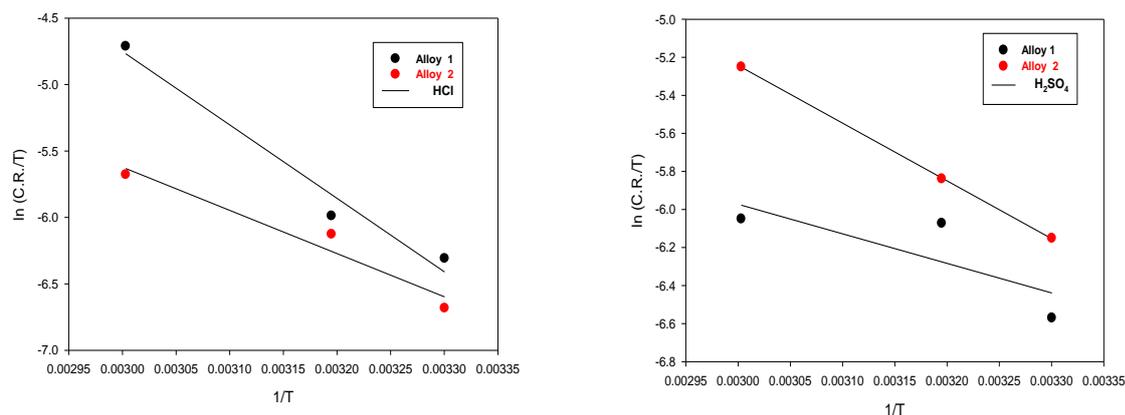
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Fig. 4. A plot of ln C.R./ T versus 1/T for Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions at optimum concentration 1 M

TABLE 4. The values of activation parameters two alloys exposed to acids solutions from corrosion rate values

Alloy	HCl			H_2SO_4		
	E_a kJmole^{-1}	ΔH kJmole^{-1}	ΔS Jmole^{-1}K^{-1}	E_a kJmole^{-1}	ΔH kJmole^{-1}	ΔS Jmole^{-1}K^{-1}
Alloy 1	48.580	45.935	-99.240	15.558	12.915	-208.45
Alloy 2	29.679	27.033	-163.18	27.880	25.234	-165.42

Table 4 lists the activation energy values for Fe-Ni-Cr alloys corrosion in HCl and H_2SO_4 are 48.58, 15.55 kJ mol^{-1} for Alloy 1and 29.67, 27.88 kJ mol^{-1} for Alloy 2. The E_a values of all the acid are greater than 20 kJ mol^{-1}; this suggested that the whole process is controlled by surface reaction [18]. The values of the entropy change (ΔS) for the corrosion of Fe-Ni-Cr alloys in HCl and H_2SO_4 are -99.24, -208.45 Jmol^{-1}K^{-1} for Alloy 1and -163.18, -165.42 Jmol^{-1}K^{-1} for Alloy 2. The ΔS values are large and negative that indicates the activated complex in the rate-determining step represents association rather than dissociation implies that a decrease in disorder takes place. The values of enthalpy change (ΔH) for the corrosion of Fe-Ni-Cr alloys in HCl and H_2SO_4 are 45.935 and 12.91 kJ mol^{-1} for Alloy 1and 27.03, 25.23 kJ mol^{-1} for Alloy 2. The positive signs of ΔH reflect that transition state (the activated complex) is an endothermic process.

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Kinetic study

The initial weight of Fe-Ni-Cr specimen and change in weight of specimen at the various instant of time in acid media were calculated. From these values, the specific reaction rate values were calculated using first-order rate expression Eq. 6 **[21],** when a plot of log initial wt of specimen/wt at the time (t) vs. time as shown in Fig. 5,

$$k = \frac{2.303}{t} \log \left(\frac{\text{Initial wt. of specimen}}{\text{wt. at time } t}\right) \quad (6)$$

The half - lifetime values were calculated by formula

$$t_{1/2} = \frac{0.693}{k} \quad (7)$$ It was observed that specific

reaction rate, k increases with an increase in temperature from 30 °C to 60 °C and the corresponding decrease in half - lifetime takes place as existed in Table 5 and Fig. 5. It confirms the first-order kinetics for the corrosion of Fe-Ni-Cr alloys in 1 M HCl solution. Similar specific reaction rate, k and half – lifetime values were estimated for the corrosion of Fe-Ni-Cr alloy in H_2SO_4 acid solution. In both alloys, the corrosion indicates first-order kinetics as given in Table 5. The energy of activation, E_a^*, for the corrosion of Fe-Ni-Cr alloy in HCl and H_2SO_4 was evaluated by determining specific reaction rates at temperatures range 30 °C to 60 °C.

TABLE 5. Effect of temperature on the corrosion rate of two alloys exposed to acids solutions

Alloy	Temp.	HCl			H_2SO_4		
		Specific reaction rate, k x 10 min^{-1}	Half-life $t_{1/2}$ x 10^{-2} min	The energy of activation E_a^* kJmole^{-1}	Specific reaction rate, k x 10 min^{-1}	Half-life $t_{1/2}$ x 10^{-2} min	The energy of activation E_a^* kJmole^{-1}
Alloy 1	30	2.0486	3.338	18.469	1.0282	6.74	11.2378
	40	1.5827	4.37		1.1053	6.27	
	60	1.0539	6.57		1.5178	4.57	
Alloy 2	30	1.4422	4.81	6.6005	0.5635	12.29	27.4401
	40	1.5131	4.58		1.6304	4.25	
	60	1.1659	5.94		1.7056	4.06	

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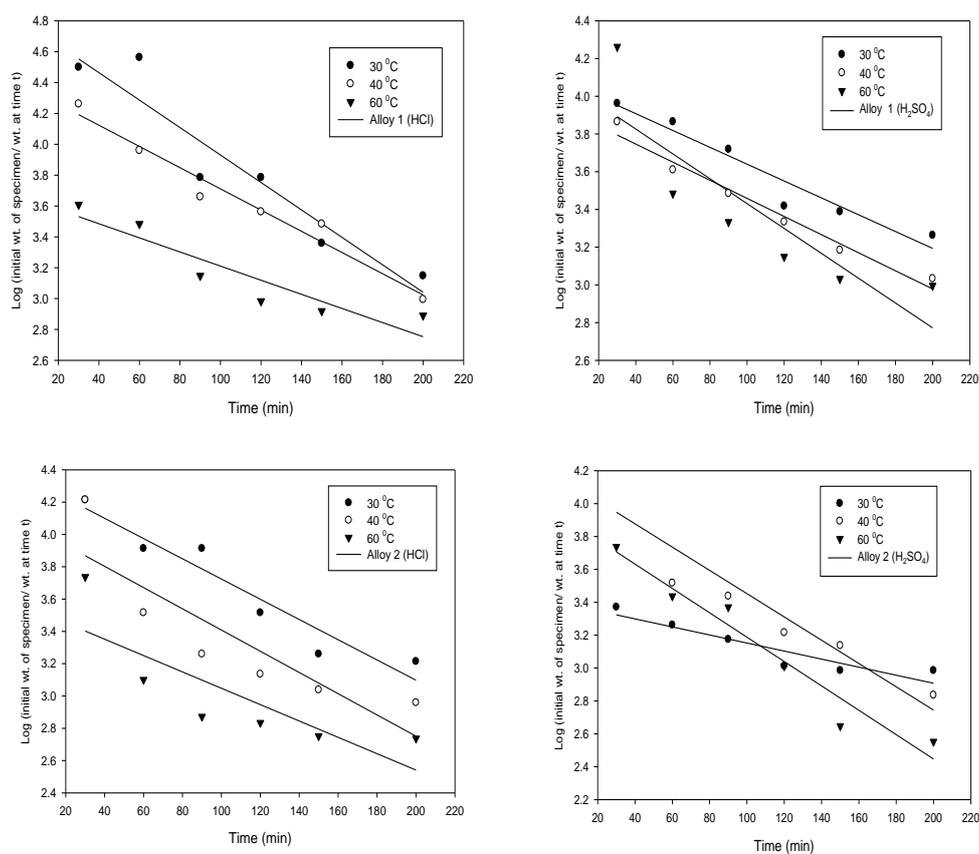
Fig. 5. A plot of log ([Initial wt. of specimen]/[wt. at time, t]) versus time for Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions to calculate Specific reaction rate, Half-life

The Arrhenius equation $k = A\,e^{-E_a/RT}$ (8) was used to evaluate the energy of activation values. The plot of ln K Vs reciprocal of absolute temperature (1/T) shown in Fig. 6. gave a straight line with slope = $-E_a/R$, from which the activation energy values for the corrosion process were calculated and listed in Table 6. The entropy of activation, ΔS^* and enthalpy of activation, ΔH^* were calculated using transition state Eq.9 [15] as shown in Fig. 7 and tabulated in Table 6.

$$K = \frac{RT}{Nh}\,.\,e^{\Delta S^*/R}\,.\,e^{-\Delta H^*/RT} \quad (9)$$

$$\ln\left(\frac{K}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

TABLE 6. Kinetics of corrosion of two alloys: activation parameters

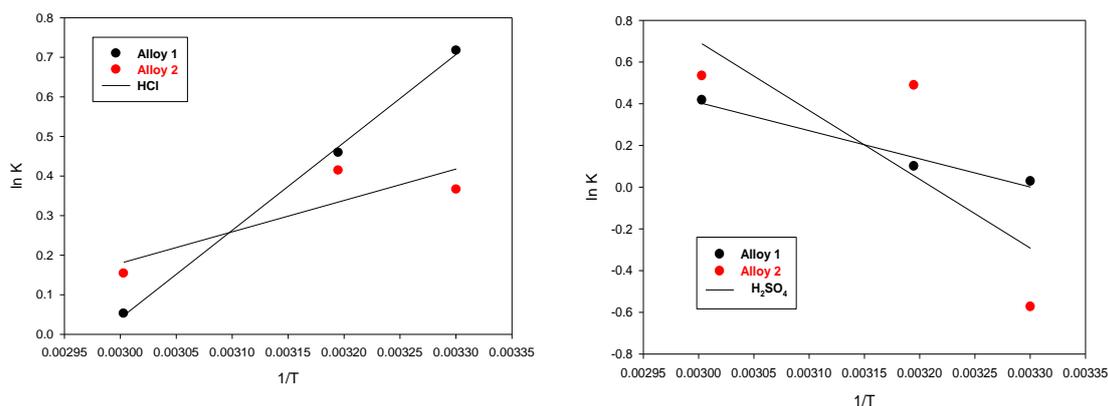| Alloy	HCl			H$_2$SO$_4$		
	E_a^* kJmole^{-1}	ΔH^* kJmole^{-1}	ΔS^* Jmole^{-1}K^{-1}	E_a^* kJmole^{-1}	ΔH^* kJmole^{-1}	ΔS^* Jmole^{-1}K^{-1}
Alloy 1	18.469	20.969	-289.3	11.2378	8.5924	-165.5
Alloy 2	6.6005	9.2436	-252.9	27.4401	24.794	-146.5

Fig. 6. A plot of ln K versus 1/T for Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys exposed to acids solutions to calculate activation energy from kinetic study measurements
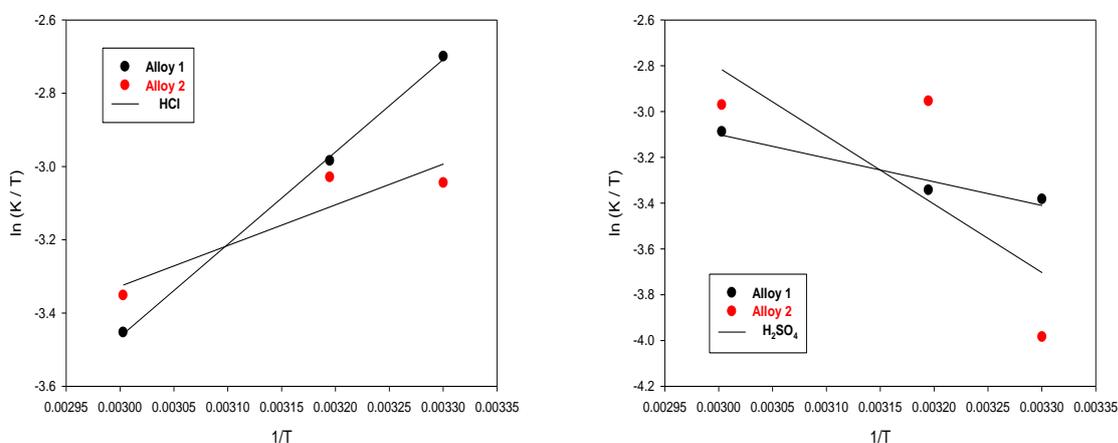

Fig. 7. A plot of ln (K / T) versus 1/T for Fe-35Ni-22Cr and Fe-17Ni-17Cr Alloys exposed to acids solutions at optimum concentration 1 M.

Potentiodynamic Polarization Measurement

The potentiodynamic polarization curve of two alloys Fe-35Ni-22Cr and Fe-17Ni-17Cr in different acidic media (1M HCl and 1M H_2SO_4) at different temperatures are shown in Fig. 8. These reveal that the cathodic current density which corresponds to hydrogen evolution decreases gradually reaching a definite value at the steady-state corrosion potential, which depends on the type of the electrode as well as on the acid concentration. The hydrogen evolution and mass loss are produced by the same reaction from adding Eqs 1 and 2 as the following reaction:

$$Fe \text{ (solid)} + 2 H^+ = Fe^{2+} + H_2 \text{ (gas)} \qquad (6)$$
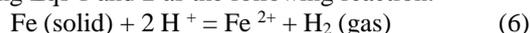
On the other hand, the anodic curves in the potential range examined. The current, I would change with the applied potential, E, according to Tafel Eq. 10 [22].

$$E = a - b\log I \qquad (10)$$

Where a and b are constant. The polarization curves show that both the anodic and cathodic polarization curves were shifted to higher current densities and the

corrosion potential ($E_{corr.}$) of the working electrode is shifted into the noble (positive) direction with increasing temperature. As shown, both anodic and cathodic Tafel slopes are not changed by increasing temperature, which indicates that the mechanism of alloys dissolution does not change with increasing temperature. $E_{corr.}$ Value is shifted to more positive potentials with increasing temperature, indicating that the polarization occurs mostly at the anode, hence the corrosion rate is said to be anodically controlled [23]. The electrochemical parameters such as corrosion potential, E_{corr}, corrosion current density, I_{corr}, and corrosion rate, C.R., are tabulated in Table 7. It was found that increasing the temperature from 30 to 60 °C leads to increasing the corrosion current density, $I_{corr.}$, corrosion rate, C.R., accompanied by an almost change in the corrosion potential, $E_{corr.}$, of the two alloys. The shift of potential in the less negative direction came from the thin layer formation of corrosion products that partially decreases the

attack on the alloy surface by an obstruction in a number of its exposed areas. The positive potential difference between the two alloys is probably due to the higher ability of Fe-35%Ni-22%Cr (Alloy 1) in developing a thicker layer of corrosion products, which retains a higher corrosion resistance for the Fe-35%Ni-22%Cr (Alloy 1) compared to Fe-17%Ni-17.7%Cr alloys (Alloy 2). The electrochemical theory shows that the reciprocal of the polarization resistance, $1/R_p$, is directly proportional to the corrosion rate [19]. This means that the polarization resistance decreases with increasing

temperature which is listed in Table 7. The polarization resistance (R_p) values were determined using Stern–Geary Eq. 11 [24]:

$$R_P = \frac{\beta a \cdot \beta c}{2.303\ I_{corr}\ (\beta a + \beta c)} \qquad (11)$$

The decreases in R_p values with an increase in the temperature of two acids solution suggest an increase in the rate of corrosion of Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys.

TABLE 7. Electrochemical parameters of Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys in different acidic media at different temperature

Alloys	Temp.	1 M HCl			
		E_{corr} V	I_{corr} µA/cm^2	C.R. µm/y	R_p Ωcm^{-2}
Alloy 1	30	-0.260	0.794	6.201	0.17007
	40	-0.180	1.000	7.806	0.06176
	60	-0.110	1.258	9.820	0.02714
Alloy 2	30	-0.150	0.398	3.107	0.21806
	40	-0.204	0.501	3.911	0.11516
	60	-0.147	2.512	19.608	0.02305
Alloys	Temp.	1 M H$_2$SO$_4$			
		E_{corr} V	I_{corr} µA/cm^2	C.R. µm/y	R_p Ωcm^{-2}
Alloy 1	30	-0.202	0.631	4.924	0.14786
	40	-0.150	0.794	6.198	0.06810
	60	-0.205	1.995	15.573	0.03591
Alloy 2	30	-0.204	1.202	9.385	0.04013
	40	-0.140	1.259	9.827	0.04309
	60	-0.154	2.238	17.470	0.01210

SEM/EDAX Investigations

To visualize the morphology of the surface as well as the elemental analysis for the parts on the surface of the alloys once its exposure for long immersion time within the acid test solution, SEM/EDAX investigations were carried out.

Fig. 9 displays SEM micrograph for the surface of the Fe-Ni-Cr alloy after its immersion in 1M HCl solutions for 96 hr and the corresponding EDAX profile analysis shown in the SEM image. It

is seen from Fig. 8 (Alloy 2) that the surface looks smooth and homogeneous with a thin layer of corrosion products with some deposits. This indicates that the alloy suffers moderate uniform corrosion thanks to the corrosiveness attack of the acid solution towards the surface with no indications on the localized corrosion prevalence.
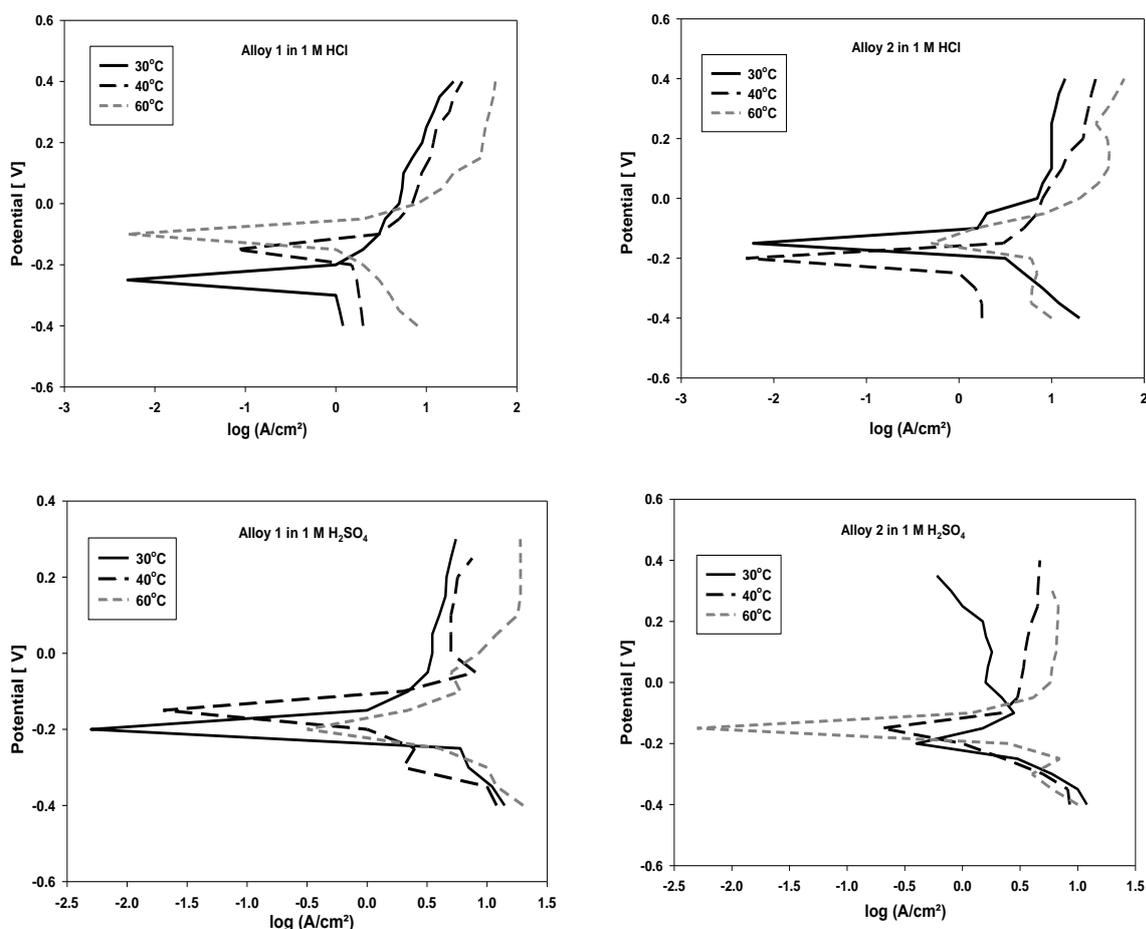
Fig. 8. Potentiodynamic polarization curve of Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys in different acidic media (1M HCl and 1M H₂SO₄) at different temperatures

The weight percentages (wt.%) of the elements found on the surface were as follows: 31 wt.% Fe, 6 wt.%Ni, 40.3 wt.%O, and 8 wt.% Cr. The low Fe% and the high Ni% compared to its original percentages in the alloy indicate that the alloy dissolution took place via the Fe dissolution as mentioned before in Table 1. Oxygen presence also indicates that the corrosion product layer may contain some oxides such as FeO and Fe₂O₃, which may give some protection to the alloy surface. Fig. 9 (Alloy 1) shows that the SEM image for Fe-35% Ni-22%Cr alloy surface exhibits thicker corrosion product layer compared to the corrosion products as illustrated in Fig. 9 (Alloy 2) for Fe-17% Ni-17.7%Cr alloy. This explains the reason why the potential of Fe-35% Ni-22%Cr alloy shifts towards a positive direction and shows less negative values than those obtained for Fe-17% Ni-17.7%Cr alloy. Fig. 9 illustrates the elements found on the alloy surface and represented by the EDAX pattern depicted in the same figure recorded 26.6wt.% Fe, 13 wt.%Ni, 35.5 wt.%O, and 12 wt.%Cr. Here, the

very low percentages of Fe and Ni compared to their values in the alloy before their acid solution exposure is due to the thick layer formation of corrosion products. This layer covers the alloy surface resulting in its protection and concealment of the first surface of the alloy beneath the corrosion products. The high percentages of the detected oxygen confirm that the formed layer on the alloy surface has some oxide films. These oxides' presence will increase the alloy passivity still as its corrosion resistance against the tough result of the acid solution towards the alloy surface [2]. Therefore, the formed layer of corrosion products might be covers the whole alloy surface and decreases the aggressiveness attack of the acid molecules on it and ensures the data obtained by weight-loss method and potentiodynamic measurements that Fe-35%Ni-22%Cr alloy has more corrosion resistance compared to the alloy with lower Ni, Fe-17%Ni-17.7%Cr alloy. This implies that the Fe-Ni-Cr alloys under

investigations suffer pitting corrosion and the pitting intensity is lower for Fe-35% Ni-22%Cr alloy. The measured results along with the calculated data thus suggested that the alloy with higher Ni content, Fe-35% Ni-22%Cr, has higher resistance against uniform as well as pitting corrosion than the alloy with low Ni content, Fe-

17% Ni-17.7%Cr, in 1M HCl solutions at the same conditions. It has been reported that the iron compound film formation offers the surface some protection against corrosion.
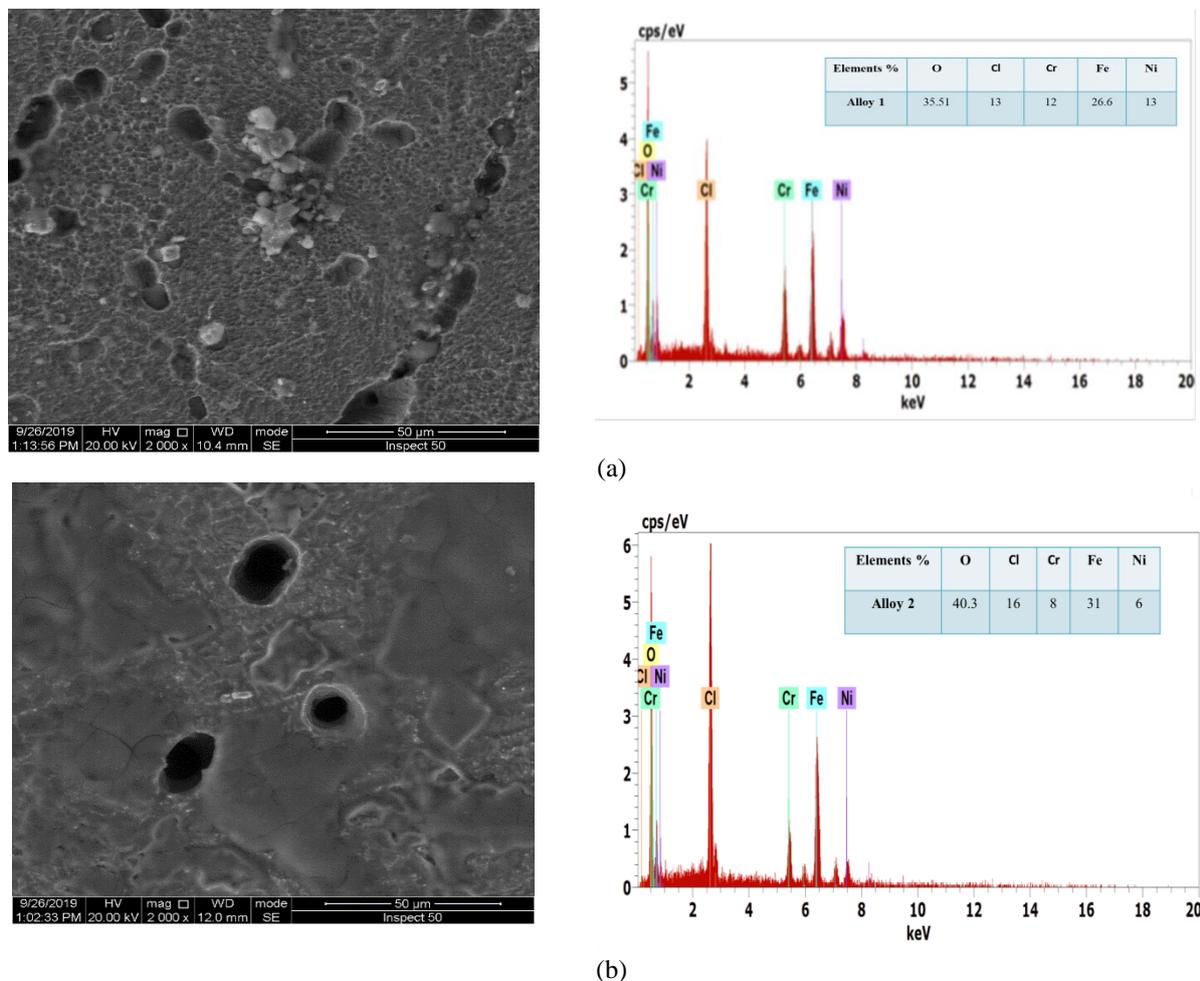

(a)

(b)

Fig. 9. SEM micrographs for the surface of the Fe-35Ni-22Cr and Fe-17Ni-17Cr alloys after its immersion in 1M HCl solutions for 96 hr and the corresponding EDAX profile analysis shown in the SEM image (a) Alloy 1 and (b) Alloy 2

The Fe-Ni-Cr alloys that should be considered for service in pure HCl acid are shown a nine segment chart organized by concentration and temperature. It indicates that, of the Fe-17%Ni-17.7%Cr alloys, only those from the Ni-Mo group are suitable at high concentrations and temperatures. Mo is the most important alloying element for the good performance of Fe-Ni-Cr alloys in pure HCl acid. The oxidizing ferric ions promote the passivation by the Cr rich oxide film formation that reduces the uniform dissolution rate.

4. Conclusion

The corrosion resistance for Fe-35%Ni-22%Cr alloy (Alloy 1) and Fe-17%Ni-17.7%Cr alloy (Alloy 2) in HCl and H_2SO_4 acids was investigated using the weight-loss method, potentiodynamic polarization, and spectroscopic techniques. Weight loss increases with the immersion time increase in acids environment. The corrosion rate increases with an increase in temperature. SEM/EDAX

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investigations after 96 hr in the acid test solution presented the surface of Fe-35%Ni-22%Cr alloy (Alloy 1) developed a thicker corrosion product layer. Results were in good agreement with others and confirmed clearly that the corrosion resistance for Fe-35%Ni-22%Cr alloy (Alloy 1) showed much better corrosion resistance than that obtained for Fe-17% Ni-17.7%Cr alloy (Alloy 2).

5. Conflicts of interest

"There are no conflicts to declare".

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