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Corrosion of some stainless and duplex stainless steel alloys in phosphoric acid plants

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ABSTRACT

Corrosion behavior of austenitic 316L, 904L alloys and a new type of super duplex stainless steel alloy, namely, Ferralium 255 SD50 was studied in aqueous phosphoric acid solution and its mixtures with sulfuric acid and chlorides at different concentrations and temperatures using electrochemical techniques and surface morphology technique, namely, scanning electron microscopy (SEM). Results showed that the corrosion rate of these alloys increases with the increase of temperature, Ferralium alloy which contains chromium, molybdenum and nitrogen in sufficient quantities exhibited lower corrosion rates than the other alloys at higher temperatures, whereas 904L loses its stability at higher temperature. The alloy 316L had the lowest corrosion resistance at all temperatures and concentrations. In addition, phosphoric acid showed lower corrosive action than sulfuric acid at all studied temperatures. Mixing sulfuric acid with phosphoric acid induced an acceleration of corrosion reaction of 316L. On the other hand this addition decreased the corrosion rates of 904L and Ferralium alloys at all tested temperatures and formed a stable passive layer of corrosion product. Pitting tests in the presence of chlorides confirmed that Ferralium alloy had the best performance with highest pitting potential, highest stable passivity, and highest repassivation ability followed by 904L and 316L. In erosion-corrosion tests, experimental set up allowed to follow the electrochemical behavior of tested samples. Under simulated conditions as in Abo-Zabaal plant for phosphate fertilizers, also Ferralium was superior to the others alloys. Surface morphology tests confirmed the results obtained by electrochemical methods.

KEYWORDS

Phosphoric;
Ferralium;
Duplex stainless steel;
Corrosion;
Erosio.

1. INTRODUCTION

Phosphoric acid prepared by dihydrate wet processes generate severe corrosion problems in containers, pumps and agitators caused by the presence of impurities such as chlorides and fluorides in the hot phosphoric acid and by erosion phenomena[1,2] . Super duplex stainless steels (SDSS) have been widely used as structural materials for chemical plants in phosphoric acid production due to their excellent corrosion resistance in chloride environments, compared with other commercial types of ferritic and austenitic stainless steels. These alloys also possess superior weldability and better mechanical properties than austenitic stainless steels. Corrosion problems occurring in wet phosphoric acid (WPA) plants have been investigated in many studies[3,4,5] to examine the behavior of stainless steels and duplex stainless steels under aggressive conditions of dihydrate process at elevated temperatures but the behavior of the new type of super duplex stainless steel, namely, Ferralium 225 SD50[6] alloy has not been studied before. This alloy is characterized with its superior mechanical properties which are 5% higher than any other super duplex currently commercially produced, and its resistance to erosion, abrasion and cavitation-erosion is extremely good and is superior to high alloy austenitic alloys and other duplex stainless steels alloys [7,8]. In the present study, the corrosion behavior of three types of stainless steel alloys, namely, austenitic 316L, super austenitic 904L and super duplex Ferralium), were studied in different concentration of pure phosphoric acid or mixture with sulfuric or hydrofluoric acids and chlorides using two different electrochemical techniques, namely, the open-circuit potential decay and the potentiocyclic polarization. Finally, morphological study of the surface using Scanning Electron Microscopy (SEM) was performed.

2. EXPERIMENTAL

2.1. Steel specimens

TABLE 1, represents the chemical composition of the tested alloys. The specimens were cut from stainless steels rods then formed in the shape of circular disc and connected to the electrode by specific chemical resistant epoxy resin (araldite). Specimen holder, which was personally modified, consisted of a glass tube (with suitable diameter) in which the specimen inserted and fixed with araldite. Then, the face of each specimen was progressively polished with finer grades of wet SiC paper No. 600 and then No.1200, rinsed with de-ionized water, degreased with acetone and finally dried at room temperature.

2.2 Solutions

The aggressive solutions used were made with AR grade 85% H_3PO_4- phosphoric acid and 98% H_2SO_4-sulfuric acid. Appropriate concentrations of acid were prepared using de-ionized water, the solutions were as follows:

1. Mixed acid solution containing 40%phosphoric acidand3%sulforic acid.
2. Different concentration of phosphoric acid 27, 40 and 53%.
3. Mixed acid solutions containing 40% phosphoric acid and 1200 and 2000ppm-part per million Cl^--chlorides.
4. To simulate Abo-Zaabal plant for the production of phosphoric acid by wet di-hydrate process, tests were done on phosphate ore under the following conditions:

Weight of phosphate rock sample was 100gm-grams, Volume of 98% H_2SO_4=55 ml-milliliter, Volume of 25% H_3PO_4=275 ml, Temperature=85ºC-Celsius, Mixing speed=600 rpm-revolution per minute

2.3 Electrochemical measurements

A jacketed glass corrosion cell was used with a capacity of 300ml fitted with 5 necks to accommodate the electrodes, temperature measuring and salt bridge. Schutzart Model Din 40050-ip20 temperature controller was used to maintain acid temperature within ±1-2°C. A stainless steel mixer head with mixer controller type SERVODYNE with a rotation speed of 150-6000 rpm were used. Economical Potentiostat radiometer/ Analytical/SAC Voltamaster 4 Model Voltalab PGP 201 with serial No 642R056 N006 France run on computer system. Potentiocyclic polarizations were done to determine cathodic and anodic behavior and their characteristics and the actual corrosion rates. The working electrode was left at open circuit until a steady potential was attained and corrosion potential was measured (E_{corr}), after which the electrode was first anodically polarized and anodic curve recorded. Then, chathodic potential was subsequently imposed on the electrode and cathodic curves recorded. Corrosion current densities were determined by extrapolation of anodic and cathodic Tafel lines to give corrosion rates and the corresponding corrosion potential-$E_{i=0.}$ Each experiment was repeated using a freshly prepared stainless steel specimen and a freshly prepared solution.

2.4. Morphological studies

For morphological studies, surface features of the

TABLE 1: Chemical composition of tested alloys

Alloy	Cr	Ni	Mo	Cu	N	Si	Mn	P	S	C
Austenite 316L	17	12	2.33	-	-	0.75	0.14	0.0006	0.004	0.011
Austenite 904L	20	25	4.3-5	1.5-1.8	-	0.4	2	0.02	0.005	0.02
Super duplex Ferralium	26.5	6.5	3.6	1.9	0.25	0.7	1.2	0.04	0.02	0.03

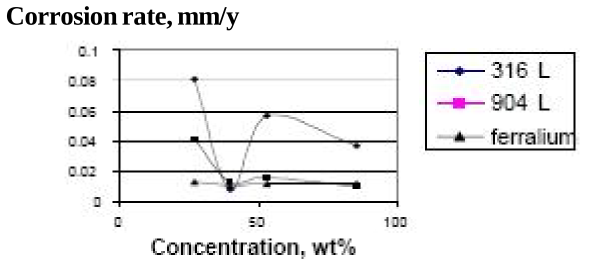

Figure 1: Effect of phosphoric acid concentration on the corrosion rate of 316L, 904L and Ferralium alloys at 25°C

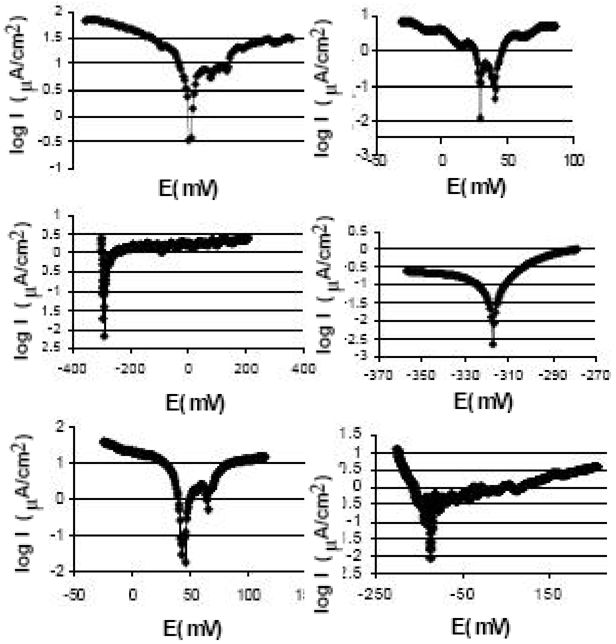

Figure 2: Polarization curves in 3% H_2SO_4 and 40% H_3PO_4 for a1, a2: 316L, b1, b2: 904L and c1, c2: Ferralium at 25 and 85ºC respectively

specimens were examined after exposed to a mixture of 3% H_2SO_4 and 40%H_3PO_4 for 50 days. Scanning was performed under magnifications from 750 × to 3500 and 2000x. Measurements were performed by using Microscope JSM-S410.

3. RESULTS AND DISCUSSION

3.1 Effect phosphoric acid concentration

Open circuit potential and potenticyclic polarization tests were performed for the austenitic 316L, 904L and the super duplex Ferralium stainless steels in different concentration of 27%, 40%, 53% and 85% H_3PO_4 at 25°C as indicated in figure 1 and TABLE 2. Polarization curves for the stainless steels indicated that increasing of phosphoric acid concentration from 27to 40% shifts the corrosion potentials to more positive values and lower corrosion current densities. So, produces passive behavior rather than active due to the higher oxidizing power of phosphoric acid which induce the alloys to passivate. Further more, the strong protective layer which formed and consists mainly from Cr-chromium, Mn-manganese, Mo-molybdenum phosphates. This layer covers the iron surface with phosphate resulting in a decrease of corrosion rate with time. After that, the increase of phosphoric acid concentration dose not affect on the alloys corrosion behavior especially super austenitic 904L and duplex stainless steel. Corrosion rate became almost constant and cathodic or anodic reactions were not significantly decreased which reflects the higher thickness of the protective layer formed, so lower corrosion rates. That effect is less pronounced with the austenitic 316L alloy. At 27% 316L alloy was spontaneously passivtated until a breakage in the passive layer occurred. But for 904L, it kept in the active state with lower corrosion rate until the end of the test. At 40%, all tested alloys exhibited specific lower rates than at lower concentration. All alloy passed from an active region to the passive state. Only Ferralium alloy was spontaneously passivated with out any breakage of the passive layer. At 85% phosphoric acid, only Ferralium alloy which passed from an active state to the passive for long time at current density $i=9.754$ μA-microampere/cm^2. The presence of 27% Cr in super duplex Ferralium alloy accompanied with molybdenum content expands the protection layer at higher potential and gives the alloy the ability to repassivate the broken layer and increases its resistance to general corrosion. Under all conditions the corrosion layer consists of a mixture of $CrPO_4$ and Fe_2O_3 and $FePO_4$. It is suggested that the variation of corrosion rate with acid concentration is associated with the amount of $FePO_4$ in the corrosion products.

TABLE 2: Comparative OCP and potentiocyclic polarization for 316L, 904L and Ferralium alloys in 27, 40, 53 and 85% H_3PO_4 at 25°C

Acid concentration	316L		904L		Ferralium	
	OCP, mV	Corr. Rate, mm/y	OCP, mV	Corr. Rate, mm/y	OCP mV,	Corr. Rate, mm/y
27%	-194.6	0.081	108	0.04086	-117.3	0.01281
40%	85.1	0.00803	292	0.01266	187.8	0.01029
53%	-256	0.05701	127.7	0.01573	-82.66	0.0112
85%	-132.9	0.03665	133.3	0.009283	-175	0.01128

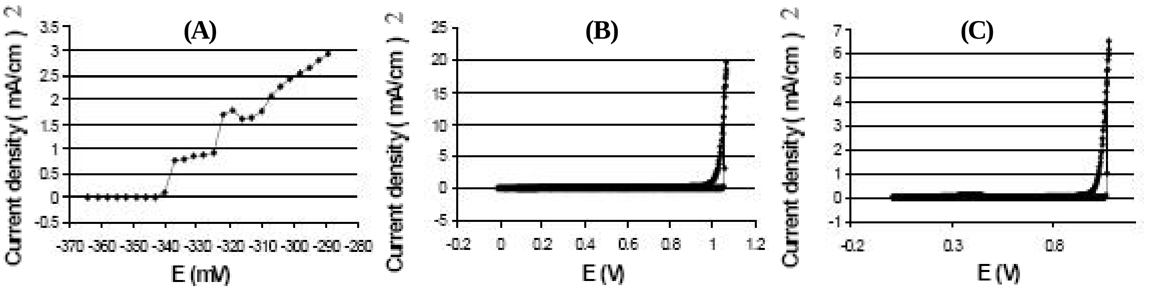

Figure 3: Polarization curve for A: 316L, B: 904L and C: Ferralium alloy in 40 % H_3PO_4 and1200 ppm Cl^- at 85ºC

TABLE 3: Comparative OCP and potentiocyclic polarization for 316L, 904L and Ferralium alloys in 3% H_2SO_4 and 40% H_3PO_4 at 25, 85°C

Alloy	316L		904L		Ferralium	
Temperature	OCP, mV	Corr. rate, mm/y	OCP, mV	Corr. rate, mm/y	OCP mV,	Corr. rate, mm/y
25°C	-267.1	0.246	206	0.01149	2.781	0.01806×10^{-3}
85°C	-313.8	2.380	74.9	0.0654	-16	3.603×10^{-3}

3.2 Effect of temperature

Open-circuit decay-OCPwas monitored during 20 minutes until the steady state attained to measure the corrosion potential(E_{corr}) for 316L, 904L and Ferralium alloys in a mixture of 3% H_2SO_4 and 40%H_3PO_4 at 25 and 85°C as shown in TABLE 3.

TABLE 3 shows that increasing temperature from 25 to 85°C shifts corrosion potential E_{corr} for all alloys to more negative position as an indication of increased acid activities so, faster kinetics generating higher current passed. This is presented by the decrease of areas under curve reflecting the activity of the alloy-acid system to be high at low temperatures. For Ferralium alloy, the decay was very slow and slower than the other alloys, also, it was clear from any oscillations indicating the stable passive layer formed in contrary to the behavior of other alloys.

Potentiocyclic polarization curves (figure 3) for 316L, indicated that the alloy was in the active state during the tests. At 25ºC, there was an appearance of an active peak which formed at high current density i=0.426.5 mA-milliampere/cm^2 and at low potential E=-216 mV-milliVolt. At higher temperature it exhibited higher current density i=1.253 μA/cm^2-microampere per centimeter square. The increase of temperature decreases the βc-cathodic Tafel slope, so, it modifies the mechanism of the hydrogen reduction. However, 316L exhibited the highest corrosion rate and an obvious black surface which can be seen immediately after immersion in the solution. Its corrosion rate was increased from 0.2462 to 2.38 mm/y at 25 to 85°C showing the activity of the alloy with temperature rise. Tests confirmed that 316L and 904L are not recommended at higher temperatures. For 904L, it was active during the whole tests with higher corrosion rate at higher temperature with no passivity, in most cases, increasing of temperature affects the rate of hydrogen evolution. The corrosion rate of 904L alloy was increased from 0.01149 to 0.0654 mm/y-millimeter per year. But for the super duplex Ferralium alloy, results showed that it had the lowest corrosion rates and a stable passive layer, increasing of temperature had very low effect and it corrosion rate was slightly increased. This is due to the ability of Ferralium alloy to repassivate its self and formation of insoluble phosphate layer which increase the stability of the protective layer. Its corrosion rates are also lower than other duplexes in same conditions[5].

Addition of Molybdenum to duplex alloys decreasing the alloy dissolution rate. Combination of the three majoring elements N-nitrogen, Cr, Mo in Ferralium alloy in high amounts gave this alloy a degree of resistance to uniform and localized corrosion. Mo content in super duplex alloy reach to 3.6% is more than twice the level usually found in the 316L and it gave the alloy higher corrosion resistance by extending its passive layer to higher potential. Also the addition of copper to Ferralium The presence of copper in Ferralium alloy has been shown to impart corrosion resistance improvements, as the copper is chemically able to stifle incipient pit growth alloy so, provides added resistance to reducing media such as phosphoric and sulfuric acids.

3.3 Pitting test in 40%H_3PO_4 and 1200ppm Cl^-

To measure the resistance of the austenitic 316L,

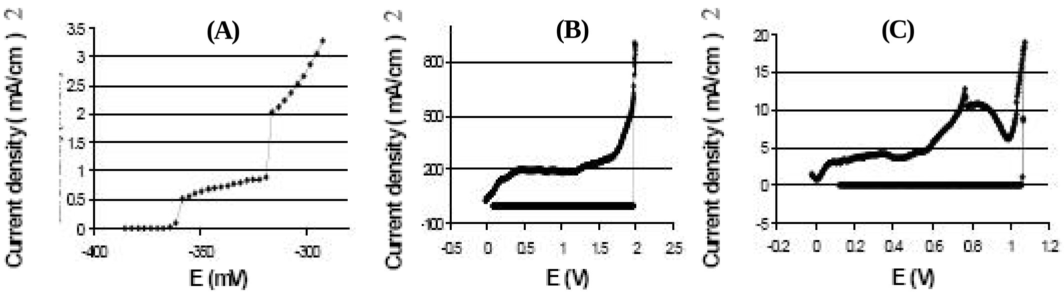

Figure 4: Polarization curve for A: 316L, B: 904L and C: Ferralium alloy in 40 % H_3PO_4and2000 ppm Cl^- at 85ºC

904L and the super duplex Ferralium alloys to pitting caused by chlorides ions, addition of 1200 ppm Cl^- was made to the 40 %H_3PO_4 solution to simulate the slurry of dihydrate phosphoric acid process at 85ºC. From figure 3 and TABLE 3, addition of chloride ions decreased pitting potential of 316L to a very low value from 0.9816 in 40% H_3PO_4 to -0.3423 V-Volt in the mixture, so, pitting occurred rapidly. No repassivation occurred for this alloy after pitting indicating the instability of the alloy in the presence of chlorides. The same behavior was observed with 904L, addition of chlorides decreased pitting potential from 3.087to1.05V with higher pitting corrosion resistance and re-passivation ability than 316L. For super duplex Ferralium alloy, it exhibited the highest pitting resistance; addition of chloride did not affect its pitting potential. Comparing with its value in 40% $H_3PO_{4,}$ pitting potential decreased from 1.064 to 1.054 V, indicating the stability of the alloy to pitting by chloride ions. Also, it did not affect the repassivation potential; however it was increased which confirms its higher re-passivation ability. The duplex microstructure of Ferralium alloy improves stress corrosion cracking resistance. Copper addition to the super duplex alloy increases the stability of the passive layer formed on the surface. Copper is dissolved from the alloy and re-deposit on active corrosion sites, stifling pit growth. Also combination of Chromium and Molybdenum produces an improved level of resistance to chlorides ions preventing pitting corrosion.

3.4 Pitting test in 40% $H_3PO_4$and 2000 ppm Cl^-

From figure 4, increasing the concentration of chlorides from 1200 ppm to 2000 ppm lowered the pitting potential of 316 L alloy to very low potential with the same behavior as at 1200 ppm with no repassivity. This behavior indicates the instability of this alloy in chloride and rapid corrosion takes place. It was revealed that Cu-copper had a detrimental effect on stress corrosion cracking; hence the non copper 316L alloy decreases the re-passivity (pitting protection) potential. For Austenitic 904L alloy the increase of chloride ions to 2000 ppm, induced pitting potential to more values but with a very lower re-passivity potential, the current decrease was slow in the reverse direction indicating the lower corrosion resistance against pitting caused by high chlorides concentration. But higher concentration of chlorides did not affect on the behavior of the super duplex alloy, it had almost the same pitting potential (1.054-1.06)V with lower re-passivation ability than at lower concentrations.

This result confirms the effectiveness of super duplex alloys against pitting with chlorides. The super duplex alloy comes in the first order according to higher content of molybdenum and chromium content which increase the PREN-pitting index over 40 accompanied with the presence of copper more than 2% which stifles incipient pit growth. The presence of nitrogen has a synergistic effect with Cr and Mo to improve pitting resistance and alloy strength. Also, duplex structure gave the Ferralium alloy an excellent performance and resistance to chlorides. Nitrogen has participated to build up passive film. The dissolution of nitrogen combined with the hydrogen ions in solution to form ammonium ions, resulting in increasing solution pH. The alloy could then easily repassivate, hence the corrosion potential and pitting potential would increase. Also, the presence of 1.2% Mn in Ferralium alloy, which stabilized ferrite in the matrix and eventually the tensile and corrosion behaviors, had a detrimental effect to both pitting corrosion and stress corrosion cracking properties due to the significant increase in contact area between the less-noble ferritic and noble austenitic phases. Addition of

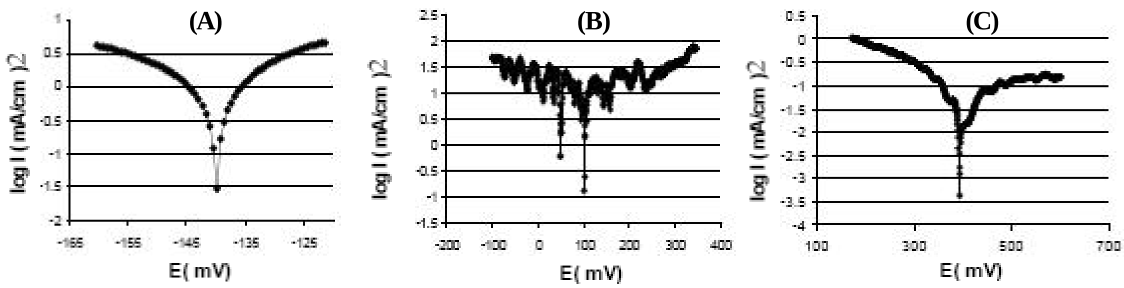

Figure 5: Polarization curve for A: 316l, b: 904L and C: Ferralium alloys in simulated slurry at 85ºC and 600 rpm

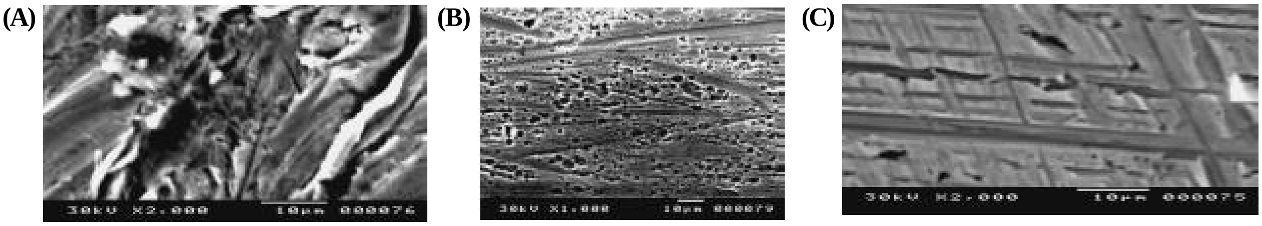

Figure 6 : Micrograph showing the three tested alloys in mixed 3% H_2SO_4and40%H_3PO_4 A: 904L X2000, B: 316L X1000 and C: Ferralium X2000

TABLE 4: Typical mechanical properties of Ferralium alloy[7]

Grade	Ultimate tensile strength N/mm^2- neuten per millimeter square	Elongation hardness %	Impact at 20 °C, J-joule	0.2% proof stress N/mm^2
Ferralium 255-SD50	840	36	250	630

6.2% nickel to the super duplex alloy raises its ability to withstand corrosion fatigue and stop the propagation of cracks. Also addition of high chromium content to the super duplex alloy is most effective and leads to spontaneous passivation in the chloride solution with immunity to pitting corrosion.

The addition of molybdenum or tungsten lowers the corrosion rates.

3.5 Erosion-corrosion study

Erosion- corrosion study was made by simulating the wet dihydrate process for the production of phosphoric acid, the presence of both phosphate ore and mixing increased the corrosion rate of all studied alloys. OCP results showed that increasing mixing rate from 200 rpm to 600 rpm induces a shift of corrosion potential (E_{corr}) to less values, for 316L alloy (from-124.2 to-200 mV), for the austenitic 904L from 207.9 to 189 mV, and for the super duplex Ferralium alloy from 400 to 359.8 mV. The decay for the austenitic alloys was very fast indicating the instability of these alloys; otherwise, for Ferralium alloy it was very slow with some fluctuations due to instability of the passive layer. All alloys were shifted into more active region with a reduction in the number of fluctuations and a decrease in the area under curves. Transforming the flow from laminar into turbulent, increased the erosive action of the phosphate ore. These results are in good agreement with that has been reported by other authors [9]. From figure 5, Potentiocyclic polarization results showed that Ferralium alloy had a corrosion rate of 1.172 mmy at mixing rate of 600rpm which was lower than that for the other alloys (9.152, 12.27 mm/y for 904L, 316L respectively). The super duplex Ferralium alloy only had a stability of its passive layer at very lower current density because of its higher chromium and molybdenum content. The corrosion resistance of high Ni-nickel containing austenitic stainless such as 316L is less effective against erosion-corrosion, corresponding to the active state. Also, the effect of erosion is much less pronounced with Ferralium alloy due to the effective mechanical properties (TABLE 4) and higher hardness of the alloy in addition to the presence of 0.6 % silicon which increases its erosion resistance.

3.6 Morphological study

Figure 6 shows the effect of mixing 3% H_2SO_4 with 40%H_3PO_4 on the austenitic 316L, 904L, and super duplex Ferralium alloy. There was an increase in the destruction of the protective layer and also an increase in the number of pits formed than in plain acid which made a dramatic effect on these alloys. There was some destruction of film formed on 904L alloy and formation of some pits. From the figure, it is obvious that mixing sulfuric acid with phosphoric acid did not affect on the continuous bands of Ferralium alloy with no formation of globules or any pits which confirms the electrochemical test results.

4. CONCLUSIONS

1. Industrial phosphoric acid solutions are more aggressive than plain acid due to impurities coming from the digestion of phosphate ore with sulfuric acid. Sulfuric and hydrofluoric acids lead to corrosion process which activates the ordinary 316L alloy and depassivate the austenitic 904L and duplex stainless steel alloy. Also, the presence of solid particles of silica and gypsum accompanied with fluorides and chlorides lead to erosion-corrosion processes which destroy the stainless steel equipments especially agitators and pumps.
2. Ferralium alloy exhibited the best behavior and lowest corrosion rates in all tested acid concentrations and temperatures followed by the austenitic 904L and at last 316L which had the worst behavior.
3. Higher amounts of copper and chromium in Ferralium alloys expand its passive layers into higher potentials, so, increasing the stability of the passive layer formed on the surface.
4. At higher temperatures 904L loses its stability which reflects the superiority of the Ferralium alloy in serve conditions such as high temperatures and lower acid concentrations. Ferralium alloys at all tested temperatures can form a stable passive layer which acted as a protective surface which lowers its corrosion rate in serve conditions.
5. Ferralium alloy can resist the effect of pitting corrosion caused by chlorides ions; it had the lowest corrosion rate with a stable value and stable passive state which induces the stability of the duplex alloy in aggressive chloride environment. Its addition of 1.2%Mn stabilizes ferrite in the matrix, increasing its pitting and stress corrosion resistance, also, its duplex structure increases its hardness so higher mechanical properties against erosion effect at high temperatures.

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