CHAPTER-V

PASSIVITY BEHAVIOR OFAUSTENITIC STAINLESS STEELS IN DIFFERENT CONCENTRATIONS OF REDUCING ACIDS.

RESULTS AND DISCUSSION:

Austenitic Stainless Steels have substantial usefulness in oxidizing acids like nitric and chromic acids. But they are considered to be poor choice in reducing acids viz. hydrochloric, phosphoric and < 70% sulfuric acids. Presence of chloride ions makes the conditions more aggressive particularly with respect to localized types corrosion. In such conditions addition of molybdenum is effective in conjunction with chromium, as it improves stability of passive film in the sense that it inhibits initiation of pitting when Cl^- ions are present in media (1&2). It is therefore, worth to study the passivation behavior of S.S type 304 and 316 in hydrochloric, dilute sulphuric and phosphoric acid environments, in which they are more active.

Followings are the results obtained, using techniques and procedure described in the preceding chapter on "Experimental Procedure". Results have been plausibly discussed.

5.1 Behavior of S.S. 314 and S.S. 316 in HCl solution:

Generally the hydrochloric acid is more active than other acids, the factors in favor of this fact are; higher mobility of chloride than sulfide/phosphate ions, greater solubility of chlorides and less tendency to form insoluble salts. Almost all metals severely corrode in wide range of concentrations of this acid. In the present work 5% and 10%HCl solutions have been used for evaluating the passivity and corrosion behaviors of S.S. 304 and S.S.316.

5.1.1 Passivity Behavior of S.S. 304 Exposed to HCl Solutoins:

Figure 5-1shows the Nyquist plots for steel type-304 in 5% and 10% HCl solutions. It clearly indicates that in dilute acid SS 304 forms a film which generates semi-circle type of complex plot having almost 6 times larger size than the plot formed by SS-304 in 10% HCl bath, $|Z|_{real}$ and $|Z|_{img}$ values are 410.6 & 134.9Ωin 5% and 47.02 & 22.5Ωin 10% HCl baths respectively. Further the semi-circle fit has diameter 450.8 Ωin dilute acid where as 89.0 Ωin 10% HCl bath, pointing that the level of passivity attained in 5% acid is superior to that of in stronger acid. Also it is

TABLE -5.1: ELECTROCHEMICAL IMPEDANIC DATA FOR STAINLESS STEELS

	304				316			
Bath	**Z_{real} (ohm)**	**Z_{img} (ohm)**	**Z_{ohmic} (ohm)**	**Dia. of Semi-circle fit**	**Z_{real} (ohm)**	**Z_{img} (ohm)**	**Z_{ohmic} (ohm)**	**Dia. of Semi-circle fit**
5%HCl	410.61	134.90	15.27	450.8	375.86	111.6	15.35	468.78
10%Hcl	47.21	22.53	8.15	89.00	82.80	68.75	13.20	377.41
10%SA.	419.80	212.37	4.97	610.5	556.9	241.37	5.52	890.45
20%SA	189.34	66.86	9.82	268.41	382.68	157.34	10.47	532.62
Lab-grade PA	221.54	62.15	20.49	263.1	494.10	158.3	30.71	1.341k
Comm. grade PA	51.33	14.76	16.14	54.90	49.68	11.64	19.34	

Table 5.2 : ELCTROCHEMICAL POLARIZATION DATA FOR STAINLESS STEELS.

MATERIAL	STAINLESS STEEL - 304			STAINLESS STEEL - 316		
Bath	E_{corr} (V)	i_{corr} (A/Cm^2)	C.R. (mpy)	E_{corr} (V)	i_{corr} (A/Cm^2)	C.R. (mpy)
5% HCl	- 0.3624	$42.31 x 10^{-6}$	16.90	- 0.3914	$21.71 x 10^{-6}$	9.76
10% HCL	- 0.4397	$51.45 x 10^{-6}$	21.31	- 0.3472	$31.43 x 10^{-6}$	13.02
10%H_2SO_4	- 0.3844	$0.177 x 10^{-6}$	82.03	- 0.3730	$48.58 x 10^{-6}$	22.44
20%H_2SO_4	- 0.3611	$0.3314 x 10^{-3}$	153.1	- 0.3397	$1.181 x 10^{-3}$	57.98
Comm. Gr. H_3PO_4	- 0.3419	$0.178 x 10^{-3}$	73.75	- 0.2186	$88.51 x 10^{-6}$	36.65
Lab. Gr. H_3PO_4	- 0.2581	$0.8198 x 10^{-6}$	0.4064	- 0.8054	$7186 x 10^{-6}$	0.3320

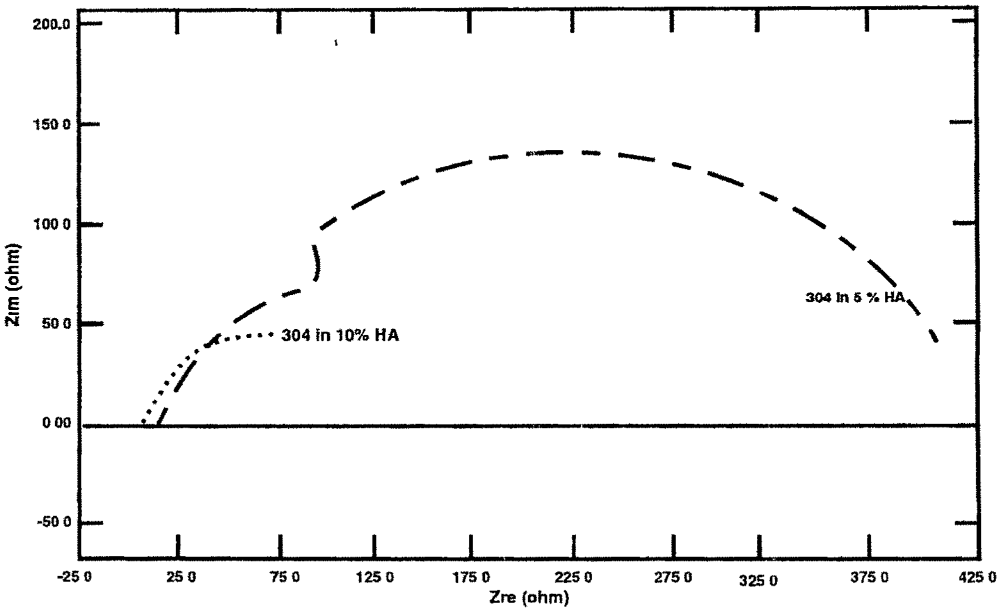

FIGURE 5.1 : NYQUIST PLOTS FOR SS 304 IN 5% & 10% HCl SOLUTIONS

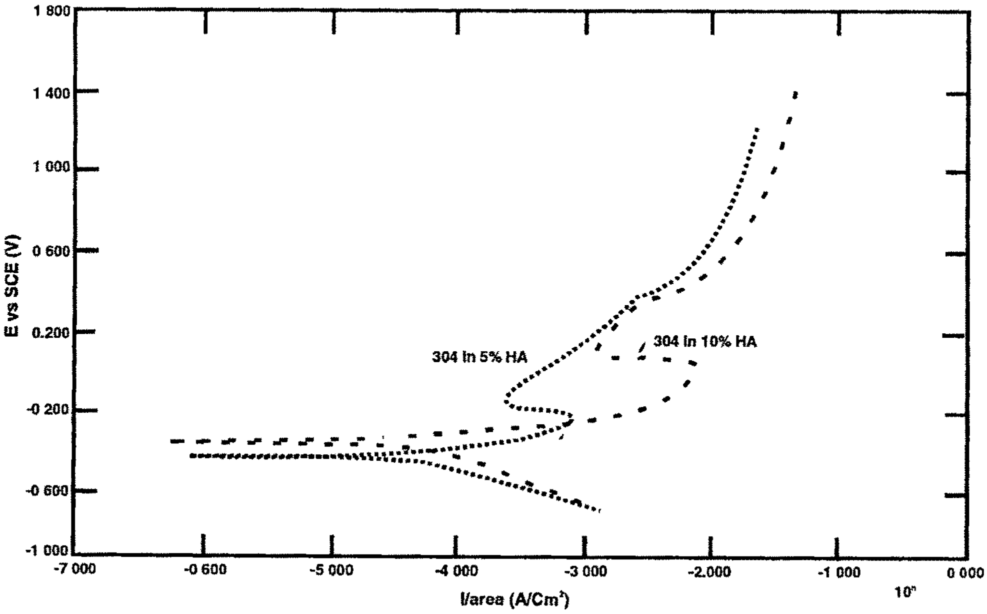

FIGURE 5.2 : POLARISATION CURVES FOR SS 304 IN 5% & 10% HCl SOLUTIONS

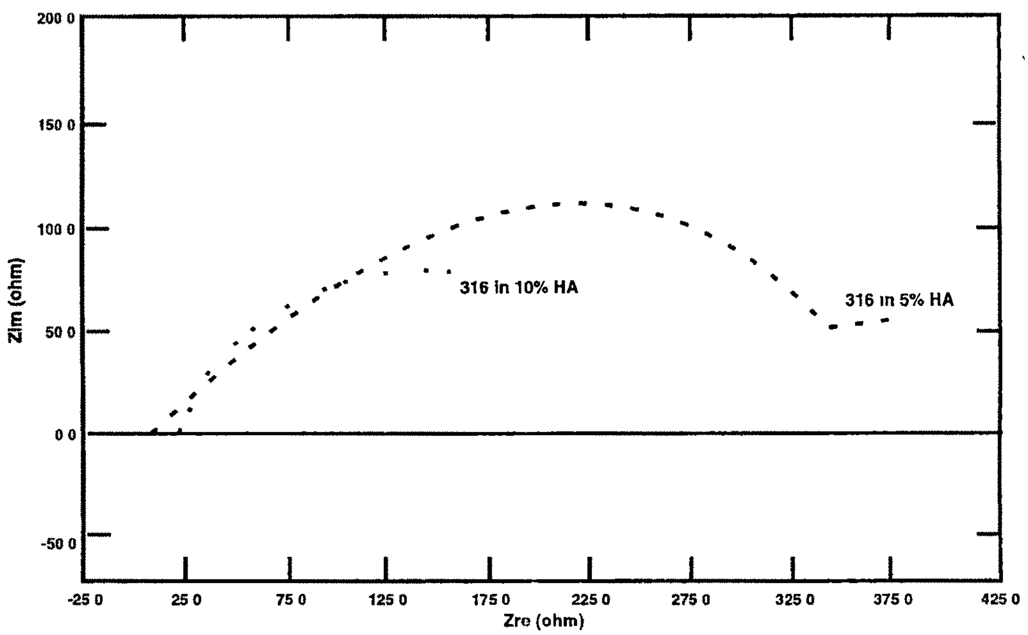

FIGURE 5.3 : NYQUIST PLOTS FOR SS 316 IN 5% & 10% HCl SOLUTIONS

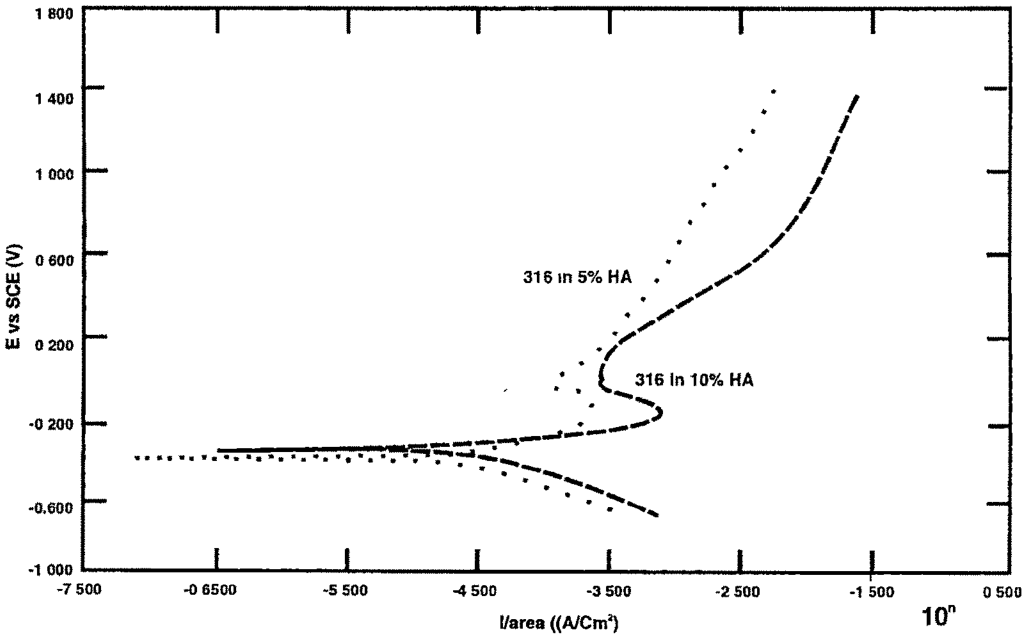

FIGURE 5.4 : POLARISATION CURVES FOR SS 316 IN 5% & 10% HCL SOLUTIONS

polarization resistance and capacitance values are 82.8 & 68.78Ω in 10% HCl solutions. Further the semi-circle fit has diameter 467.8 Ω in dilute acid where as 377.4 Ωin 10% HCl bath. These are much higher than those for SS-304.

Hence, it can be concluded that similar mechanism is operative even in the case of 316-type steel in 5% and 10% HCl solutions as in case of type-304 steel. However now the barrier to charge flow is more at the surface of the alloy. Thus, equivalent electrical circuit is consisting of resistor and capacitance connected in parallel have relatively higher values as compared to those in case of steel type-304. While equivalent electrical circuit for 5% HCl bath involves a W-element corresponds to secondary polarization at the surface of stainless steel-316.

Higher values of impedance components can be ascribed by the presence of Mo in the steel, which stabilizes the passivity in conjunction with Cr. The high resistance of Mo metal to Cl^- ions and reducing acids (3) helps in improving characteristics of the film. This phenomenon is related to electronic configuration and electron exchange among the atoms of metals present in alloy. In S.S. 316 steel, alloys retain large part of the useful corrosion resistance due to molybdenum so long as its d-band energy levels remain unfilled. Here Ni donates electrons up to critical value 85%, as was found in binary alloy Ni-Mo, for its best corrosion behavior. Thus, steel type 316 will act like Mo so far as ratio of Mo/Ni is maintained above 15/ 85, at or above this ratio passivity imparted is primarily by Mo, as its 3-d energy levels remain unfilled.

Figure 5-4 depicts the polarization curves of SS-316 in these concentrations of HCl solutions. Both curves do not exhibit sharp passive range, with higher i_{crt} value in case of 10% HCl higher by about 0.70 order of magnitude. In this steel, rest potentials (E_{corr}) in both the cases remain almost same (-0.3918 & -0.3466 V). Thus the effect of alloying addition (Mo) on passivity behavior of the stainless steel indicating that rate of corrosion increases (from 8.768 to 13.02 mpy) with increment of acid concentration. All these results of polarization study implies the same facts as observed by EIS, i.e. film formed on the surface of SS 316 is superior in case of 5% HCl solution compared to that in 10% HCl.

5.1.3 Comparison of S.S.304 and S.S. 316 in HCl solution:

Nyquist plots of stainless steels 304 and 316 in 5% and 10% HCl solution are shown in figure 5.5. Of all these 4 curves, one for stainless steel type 304 in 5 HCl

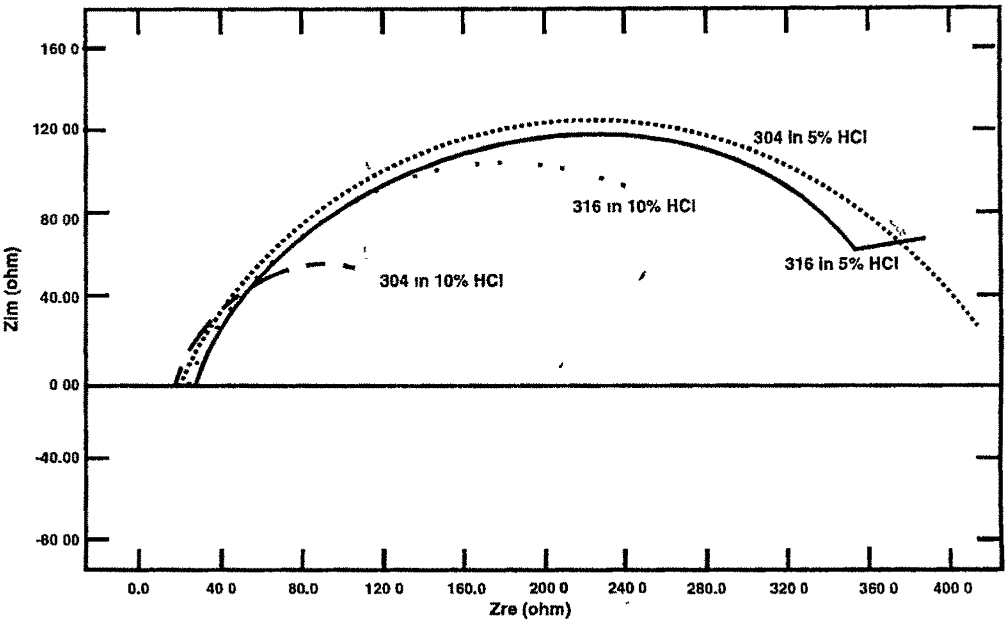

FIGURE 5.5 : NYQUIST PLOTS FOR SS 304 AND 316 IN 5% & 10% HCl SOLUTIONS

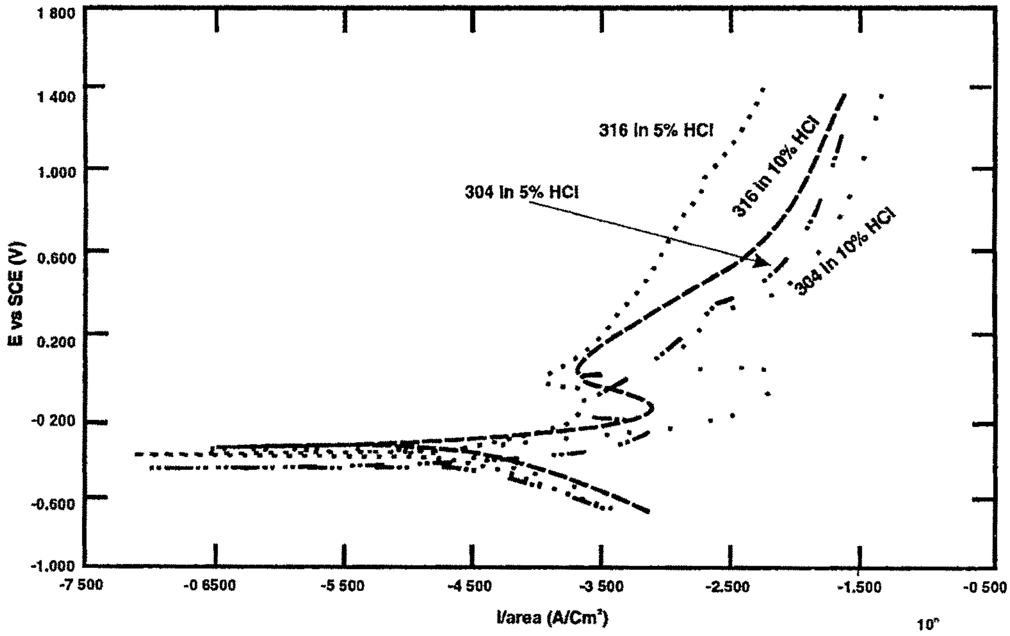

FIGURE 5.6 : POLARIZATION CURVES FOR SS 304 AND 316 IN 5% & 10% HCl SOLUTIONS

solution is seems to be the best amongst all. As can be observed from the table 5.1 that both $|Z|_{real}$ and $|Z|_{img}$ values are competing with these values for stainless steel 316, but presence of Mo induces some polarization resistance as indicated by deviation in Nyquist plot for steel 316 in concentrated acid. Due to this reason, though values of $|Z|_{real}$ and $|Z|_{img}$ in SS 316 are similar to those of stainless steel 304, yet impedance of the film is higher and corresponding flow of corrosion current is less. Note that in either concentrations of HCl acid both the steels, with and without Mo, generate poor passive film, due to feebly available oxygen via natural aeration. Superiority of the film in case of 316 in 5% HCl solution is due to competent values of polarization resistance and capacitance values and presence of W-element in its equivalent circuit, which is absent in other three systems. Alloy addition of Mo is attributed for such a passivity behavior of steel 316 in 5% HCl solution as explained earlier.

Mo-oxide is like Mo has better resistance to dilute HCl acid at room temperature. Also its formation is energy-wise favorable (4) having free energy of formation - 502.4 J/kg mole for MoO_3 and -678.05 J/kg-.mole for MoO_2 at room temperature (298K). These values are comparable to free energy of formation of Cr_2O_3 (-1047.53 J/Kg. mole) at room temperature. Moreover Mo forms chlorides in the solutions containing Cl-ions, which are insoluble and may retain on surface (5, 6), providing some passivity.

In other words, in case of S.S. 316, passive film consist of admixture of oxides and offer more resistance to flow of current through it compare to film consisting of chromium oxide alone as in case of S.S.304. Moreover, this film containing Mo-oxide is cited as self-healing type in literature (7) when the environment is not strongly oxidizing type.

Polarization curves of steels 304 and 316 in two concentrations of HCl baths are depicted in the figure-5.6 and corresponding data in table 5-2.The comparisons clearly reveals that presence of Mo in austenitic stainless steels improves the passivity in HCl solutions, but enhancement in film characteristics is marginal. Passivity breakdown is not seen when Mo is present, this is in agreement with the results cited in literature i.e. Mo prevents initiation of pitting in dilute HCl solutions at ambient temperatures. (8,9,10)

It can be inferred from this discussion that in HCl solutions, though Mo addition to Austenitic Stainless Steel show better corrosion/pitting resistance but the effect is very nominal and in general steels of 300 series should not be considered in material selection procedure when environment is reducing acid containing Cl-ions (11).

5.1.4 Scanning Electron Microscopy of HCl exposed Stainless Steels:

SEM-photomicrographs 5.7 is of stainless steels 304 at magnification (X55), the same specimen exhibits large number of pits on the surface, inferring considerable damage by 10%HCl solution of S.S. 304. As concentration is

In the case stainless steel 316 at X110 magnification (figure-5.8), only few shallow ditches appear in the otherwise intact film. Bright particles are corrosion product attached at the periphery and also fallen in to ditches. This is a similar event as take place in case of hydrogen blistering (13) in the alloy/metals under suitable conditions. This photomicrograph gave visual performance of molybdenum in stainless steel. Even 10% HCl solution is unable to produce much damage to the film in this case, resulting in superior characteristics of film and less attack, as indicated by results of EIS and polarization studies. Higher amount of damage in 304 is also established from the fact that the micrograph 5.7 for S.S. 304 is only at X55, On the other hand magnification of the micrograph 5.8 is double (X110) and yet only 3 ditches are visible with intact film in background

5.1.5: EDAX-Results of Stainless Steels Exposed to HCl solutions:

Energy Dispersion X-ray analysis of stainless steels 304 and 316 are conducted on the complete area of the structure shown in photograph. Results shown in figures-5.9 & 5.10, are average of 3 readings, indicate presence of Cr=18.65% and Ni=8.77% with 2.74% O_2 and 1.63% Mn in steel type-304. In stainless steels type-316, analysis reveals Cr-18.15%, Ni-12.03%, Mo-1.98% and O_2-1.94%.

These results reveal the same facts that in 10% HCl bath, passive film is destroyed but not completely in either steel, as there is an indication of presence of some O_2 in the surface layer in both the cases which may be present in the corrosion product. This confirms that nature of corrosion attack is pitting type rather than uniform.

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EDS TEST REPORT

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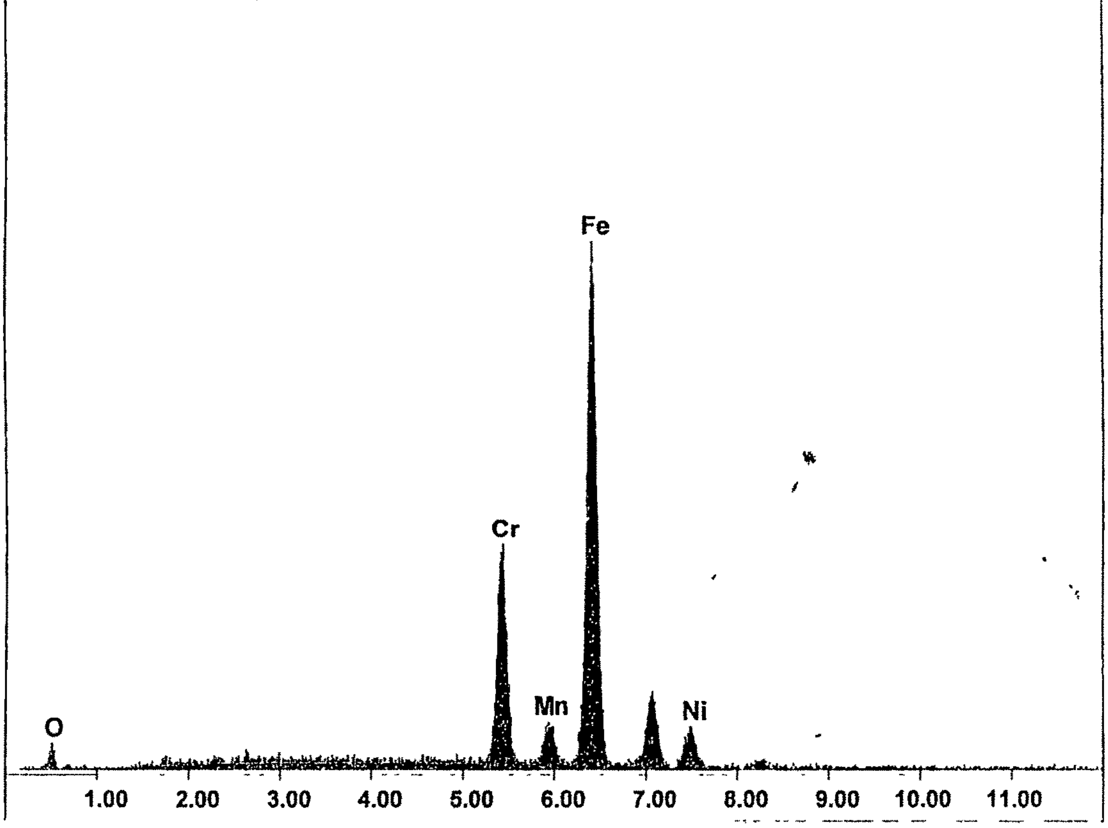
Label:304 in 10%HCl

kV:30.0 Tilt:0.0 Take-off:34.8 Det Type:SUTW+ Res:127 Tc:100

FS : 1349 Lsec : 20 5-Jul- 2 13:22:02



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	2.74	8.87	0.0110	1.1397	0.3514	1.0038
CrK	18.65	18.58	0.2151	0.9903	0.9803	1.1878
MnK	1.63	1.53	0.0159	0.9741	0.9935	1.0106
FeK	68.21	63.27	0.6414	0.9946	0.9330	1.0134
NiK	8.77	7.74	0.0701	1.0147	0.787[illegible]	1.0000
Total	100.00	100.00				

Fig:5.9

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EDS TEST REPORT

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Label:316 in 10% HCl

kV:30.0 Tilt:0.0 Take-off:34.8 Det Type:SUTW+ Res:127 Tc:100

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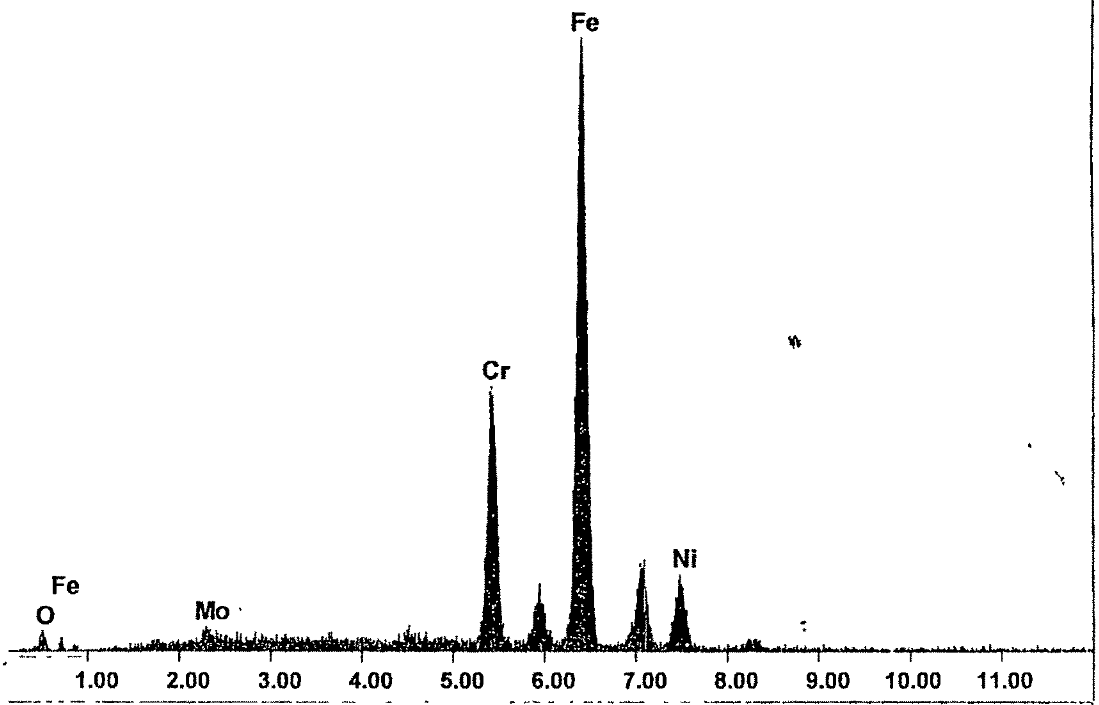

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	1.94	6.48	0.0072	1.1414	0.3244	1.0037
MoL	1.98	1.10	0.0124	0.9288	0.6712	1.0025
CrK	18.15	18.61	0.2063	0.9920	0.9721	1.1788
FeK	65.89	62.89	0.6220	0.9963	0.9301	1.0187
NiK	12.03	10.92	0.0972	1.0165	0.7949	1.0000
Total	100.00	100.00				

Fig:5.10

5.2: Passivity Behavior of S.S. 314 and S.S.316 Exposed to H_2SO_4 Solutions:

Sulfuric acid having concentration more than 68% is oxidizing but act as reducing acid when concentration is less than 68%. It is most aggressive between 50 to 60% concentration, particularly in absence of air and oxidizing agents, for corrosion considerations. Concentrated sulfuric acid is less corrosive, even to the iron and steel at room temperature.

5.2.1 Passivity Behavior of S.S Type 304 in H_2SO_4 Solutions:

This steel is subjected to 10% and 20% H_2SO_4 solutions and the effects are studied. Figure 5.13 depicts the Nyquist plots for S.S.-304 in two concentrations of sulfuric acids solutions. As can be seen from the figure that, passive film formed on the surface, immersed in the 10% H_2SO_4 solution is superior than that formed in 20% H_2SO_4 solution. Here the $|Z|_{real}$ and $|Z|_{img}$ peak-values (representing polarization resistance and capacitance of the passive film respectively) are 419.8Ωand 212.3 Ωin 10% solution, which are almost double than those in the latter case (210.4 & 66.89Ω). Hence passive film formed in dilute acid has a relatively stronger barrier to the flow of charges between metal surface and film- solution interface.

The equivalent electrical circuit, corresponding to complex plot of this nature, definitely includes a Warburg-impedance element. Since both activation and diffusion polarizations seem to exist together. This is due to the facts that, dissolution of metal is nominal in 10%sulfuric acid to combine with available SO_4-ions. Moreover SO_4-ions have tendency to attach with each other, as weak Vander waal's forces exist between them. These factors increases anionic concentration in anodolyte and in turn give rise to activation and diffusion polarizations When the same steel is immersed anodically in 20% H_2SO_4, the scenario changes, as now acid is more aggressive with low pH, this in tern enhances rate of corrosion. Thus, sufficient cations (metallic ions) are available to fix up the anions (SO_4^{-}) and diminish diffusion polarization to a negligible value. Thus, eliminates W- impedance from equivalent circuit, resulting in Nyquist plot having semi-circular shape correspond to a simple circuit consisting of a resistor and a capacitor in parallel. A semi-circular type of plot is seen in the figure 5.11, for Stainless Steel 304 kept in 20% H_2SO_4, having $|Z|_{real}$ and $|Z|_{img}$ values 210.4 & 66.89Ω respectively. Besides these, the semi-circle fit has diameter 610.5Ω for 10% acid solution and 268.4 for 20% acid solution with intercepts at 0.5 & 623.1

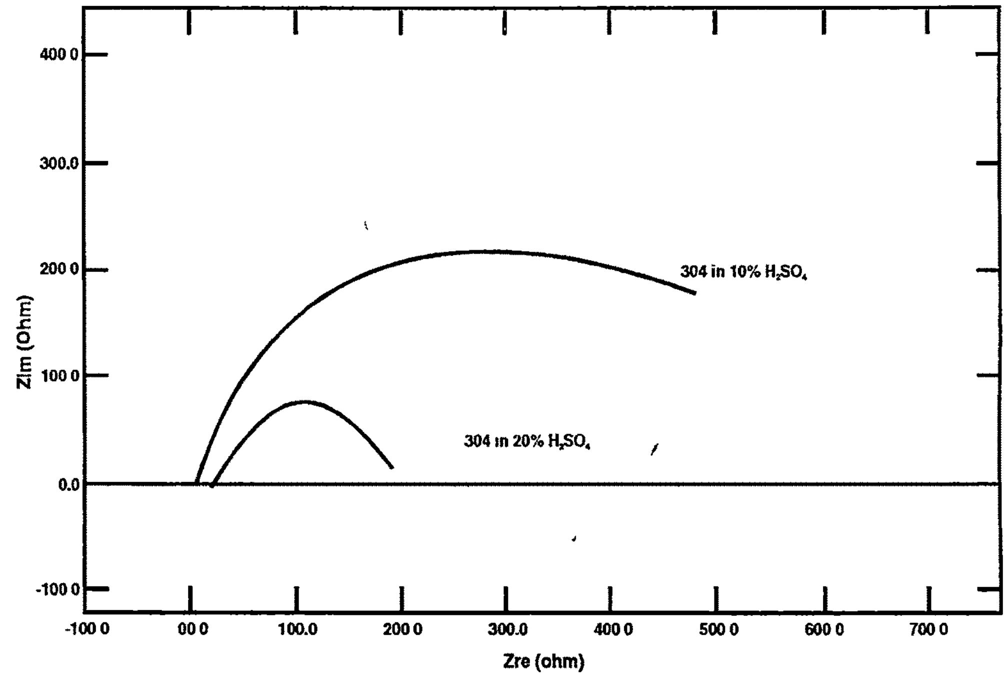

FIGURE 5.11 : NYQUIST PLOTS FOR SS 304 IN 10% & 20% H_2SO_4 SOLUTIONS

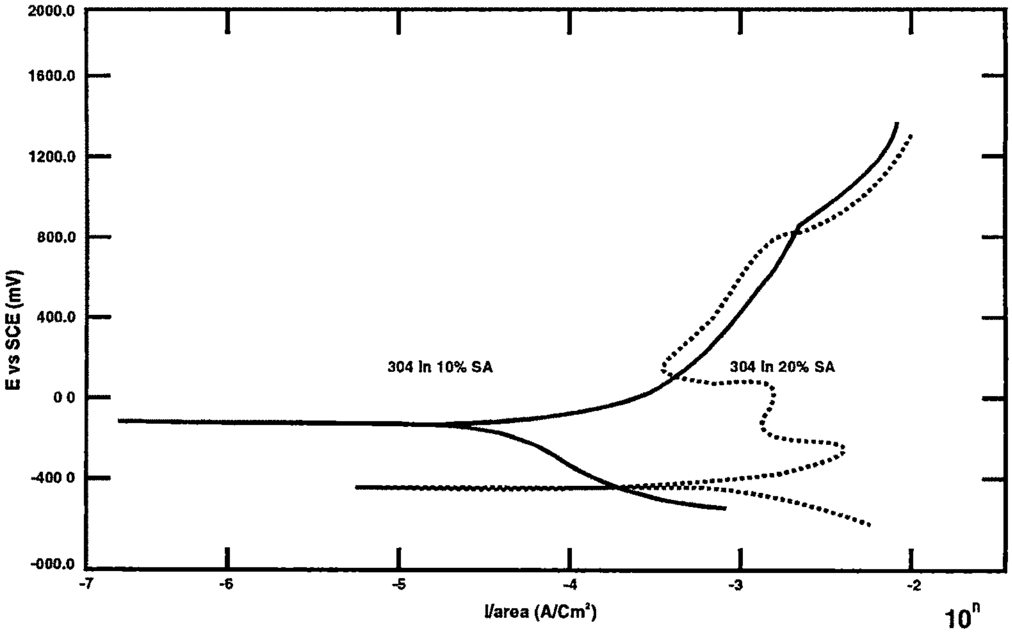

FIGURE 5.12 : POLARIZATION CURVES FOR SS 304 IN 10% & 20% H_2SO_4 SOLUTIONS

for 10% acid solution and 0.8 & 235.7 for 20% acid solution. These readings give actual R_p values in two environments, notice that R_p for this steel in dilute acid bath comes out to be 3 time higher than that for in 20% H_2SO_4. Thus it can be concluded that passive film formed in 10% H_2SO_4 is more stable and resistant than one formed in 20% H_2SO_4

Comparing polarization curves for SS 304 in 10% and 20% H_2SO_4 solutions (Figure-5.14), it can be seen that nature of passive films, which are different in two cases, directly affects the corrosion behavior of metal. In the former case passive film has relatively higher R_p and C_{dl} values, exhibit low corrosion rate (54.49 mpy), with low rate in change of anodic current density between potential values 300 mV to 1100 mV –giving effective passive range. Here, the value for i_{crt} nearly $10^{-3\ 7}$ A/cm^2 with E_{corr} = 88 mV and I_{corr} = $10^{-4\ 3}$ A/cm^2.

On the other hand, when solution has higher concentration (20%), pH falls down and metal ions have plentiful SO_4 ions to combine and form metal sulfate. Passivity is attained in fluctuating manner, from – 45.0 mV to +400 mV, indicating formation of unstable passive film on the surface. This is attributed to the fact that, in reducing environment and at low pH reductive dissolution of passive film occurs. Since chromium at low voltages and in deficiency of oxygen forms Cr^{++}, which is less stable and goes into solution. At intermediate values of voltage, a higher oxidation potential regime, dissolution of film is compensated by formation of stable oxides (Cr^{+++}) in Fe-Cr-Ni alloys (14).

An overall inference can be arrived at that, S.S 304 corrodes more in 20% H_2SO_4 than in 10% H_2SO_4 solution, as passive film in latter case is superior to that in former case.

5.2.2. Passivity Behavior of S.S. 316 in H_2SO_4 solutions:

Figure 5.15 shows the Nyquist plots for SS 316 in 10% and 20% H_2SO_4 environments. In the first case peak-values of $|Z|_{real}$ and $|Z|_{img}$ are 556.9 Ω and 241.21Ω respectively. These are higher than those of when this alloy is immersed in 20% H_2SO_4 solution. The results are given in table 5.1. Further, the nature of plot is again exhibiting a deflection in nearly 45° rather than a regular semi circle type, as in SS 304. Thus film offers total impedance, which can be modeled as an equivalent circuit comprising a resistor in parallel with a capacitor and W-impedance elements.

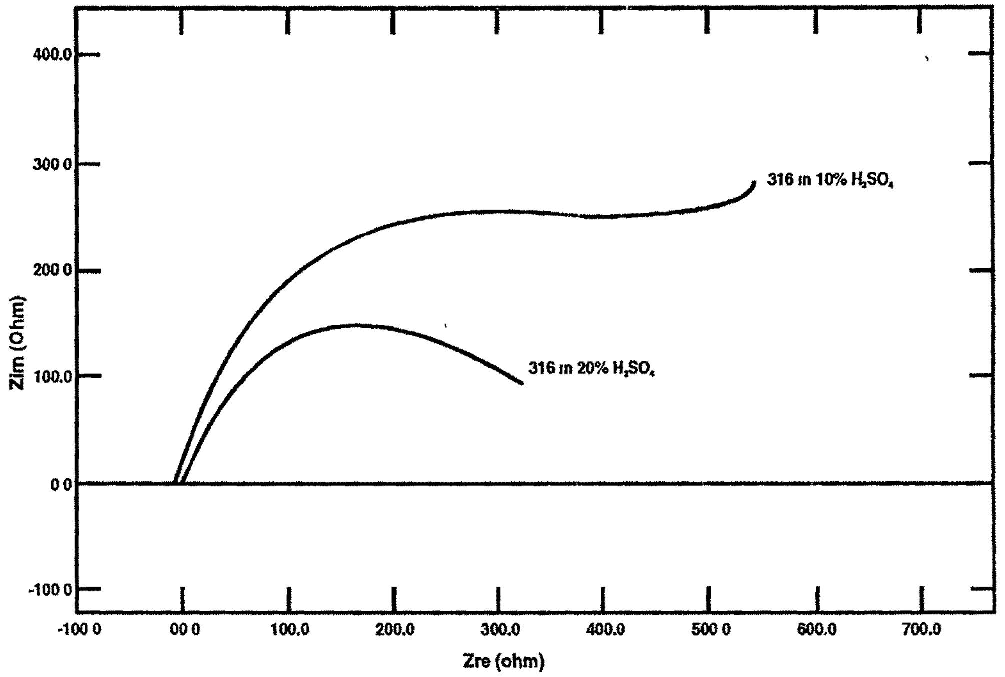

FIGURE 5.13 : NYQUIST PLOTS FOR SS 316 IN 10% & 20% H_2SO_4 SOLUTIONS

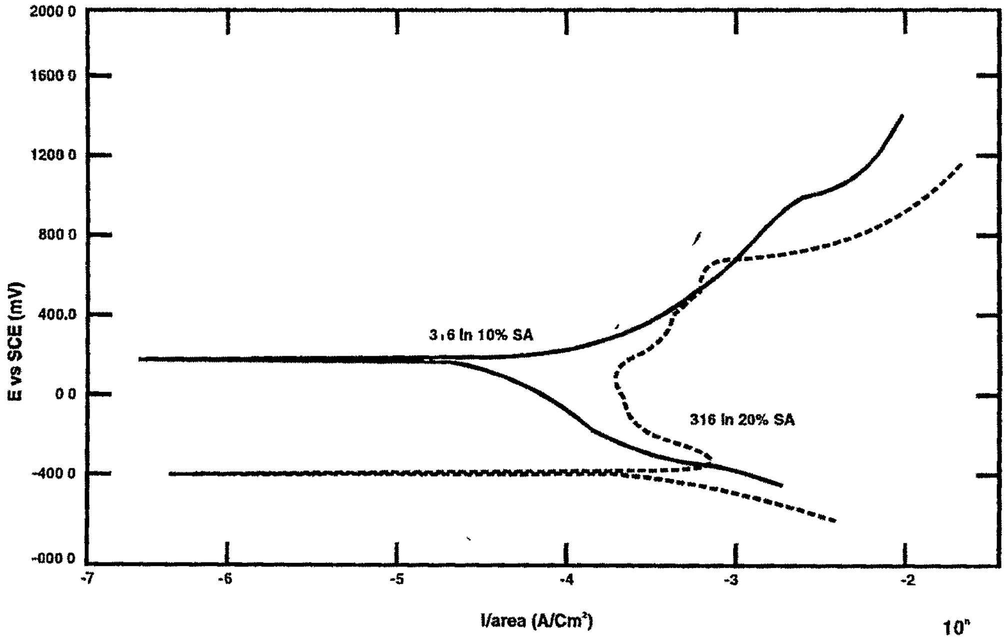

FIGURE 5.14: POLATIZATION CURVES FOR SS 316 IN 10% & 20% H_2SO_4 SOLUTIONS

When this steel is placed in 20% H_2SO_4 environment, its Nyquist plot (figure 5.15) neatly shows a semicircular shape and absence of W-impedance. The maximum $|Z|_{real}$ and $|Z|_{img}$ peak-values are 382.6 Ωand157.3Ω comparatively less than those for the steel 316 – 10% H2SO4 system. The semi-circle fit for 10% sulfuric acid has diameter 890.3Ω, while this values in 20% sulfuric acid depict 532.6Ω diameter. Thus, EIS results indicate that passivity of 316 is poor in 20% H_2SO_4 acid than in 10% H_2SO_4.

Polarization curves, shown in figure 5.16, compare the corrosion behavior of S S 316 in 10% and 20% H_2SO_4 environments. In the case of 10% H_2SO_4 solution steel behaves as a passive metal, since its rest potential is +297.2 mV, while in case of 20% H_2SO_4 acid solution its rest potential is – 380mV, indicating the active state. Also its' passive range is +200 mV to 1100 mV, without exhibiting sharp decrease in current density value (i_{crt}). During this passive range, curve is relatively smooth. When concentration is increased from 10% to 20% the passive range varies from – 300 mV to +1100mV with a sharp reduction in current density (i_{corr}~ $10^{-3}\,{}^{3}$A/Cm^2). But compared to SS 304 the passivity curve is having less zigzag nature. The presence of Mo-0xide in the film makes it more stable than the film formed on SS-314 in the same the environment, as indicated by less waviness in curve. Moreover, in 20% H_2SO_4solution, passive current density is high and so the general corrosion is more than that in 10% H_2SO_4. These results support the EIS results as discussed above, that passive film in 10% H_2SO_4 has higher barrier to flow of charge than the film formed in 20% H_2SO_4 acid solution.

5.2.3 Comparison of Passivity Behavior of S. S. 304 and 316 in H_2SO_4 Solutions:

In H_2SO_4 solutions of different concentrations, on comparing passivity behaviors of S.S. 304 and S.S. 316, effect of Mo addition has spurt out. Figure 5.17 depicts Nyquist plots for S.S 304 and 316 in 10% and 20% H_2SO_4 acid. Amongst these 4 plots one for S.S type-316 in 10% H_2SO_4 turns out to be the most effective. It has maximum values of $|Z|_{real}$ and $|Z|_{img}$ owing to W-impedance in its equivalent circuit. This may be attributed to the fact that in the passive film Mo-oxide is also present along with Cr-oxide. Mo-oxide being acidic in nature (15) does not get effected by reducing acids, as contrast to Cr-oxide, which is basic and get attacked readily in deaerated conditions. Moreover, Mo being nobler metal get exposed and enrich on the

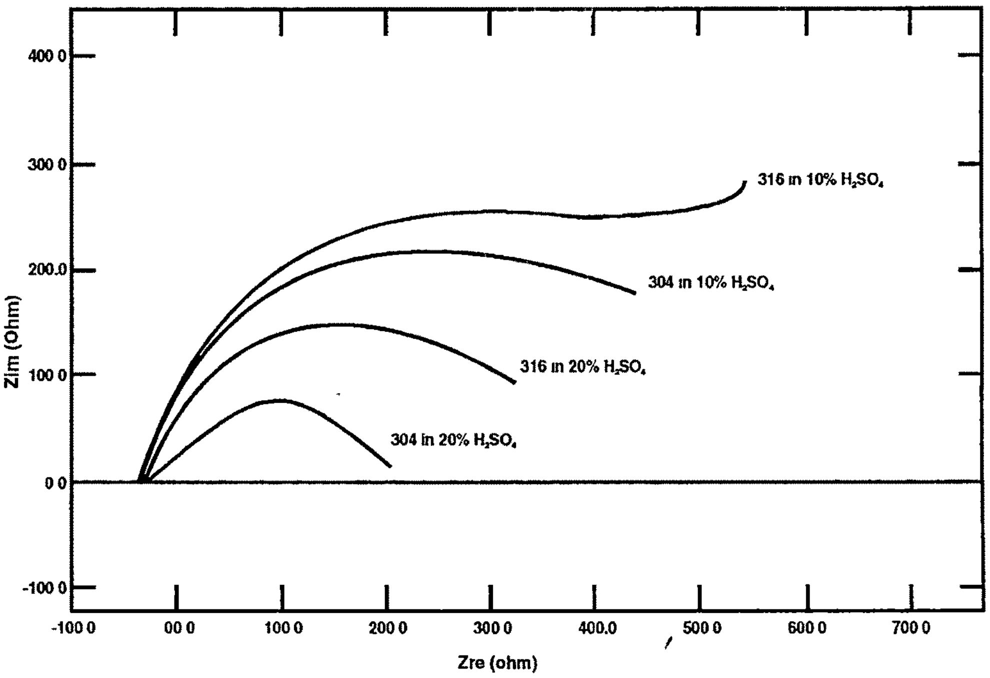

FIGURE 5.15 : NYQUIST PLOTS FOR SS 304 & 316 IN 10% & 20% H_2SO SOLUTIONS

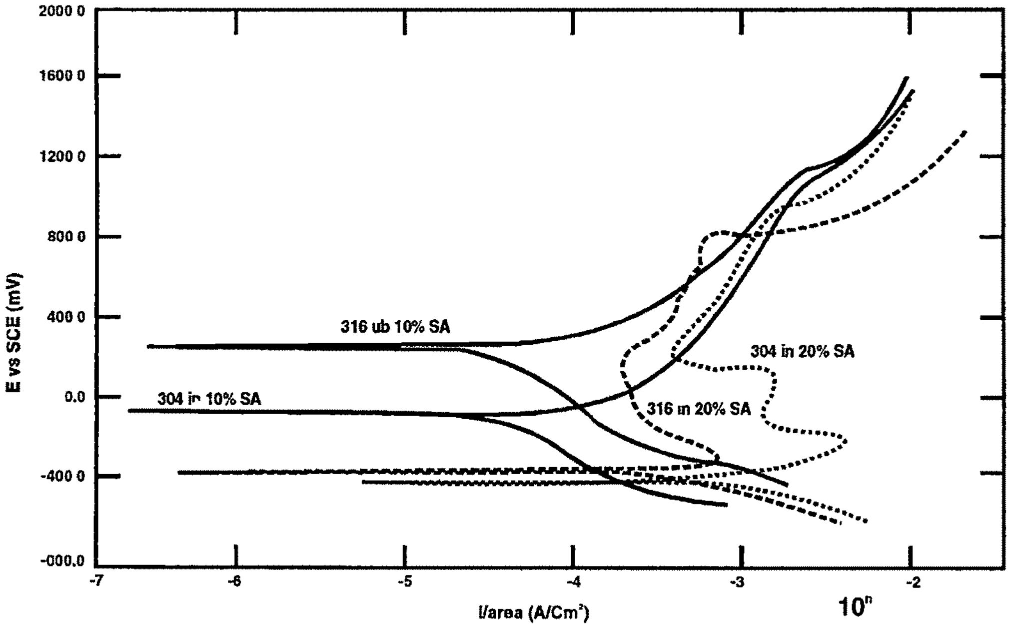

FIGURE 5.16 : POLARIZATION CURVES FOR SS 304 AND 316 IN 10% & 20% H_2SO_4 SOLUTIONS

surface after initial dissolution of alloy, providing cathodic areas and increasing cathodic reaction. Which in tern, provide insitu anodic protection to active-passive metal like S.S., by raising anodic current above critical current required to pass in to passive state. By and large Mo provides an improved self-healing type film, compared to passive film formed on S.S. 304 in this environment.

Similar arguments hold good for S.S. 316 and S.S.304 in 20% H_2SO_4 solution. But now acid is more aggressive and therefore either the film thickness may be much less than the critical (one giving most stable film) or with sufficient amount of Cr availability in the material (~18%), attack by aggressive environment, dissolving more Cr^{3+} ions and may be forming a continuous capillary type paths up to the interior (16). In either case films on both the steels exhibit poor barrier to charge transfer. Yet note that presence of Mo does make a positive difference, and 316 remains superior to 304 even in more concentrated acid solution.

Polarization curves for 304 and 316 in two solutions are shown in figure-5.18. Note that in both the concentrations 316 types S.S appears to be better than type 304 S.S. In 20% H_2SO_4, both 316 & 304 have rest potential – 390, whereas in 10% H_2SO_4 rest potential for 316 is +ve and nobler than type 304 S.S. (See table 5.2) and I_{pp} diminishes. These results of polarization studies implies that Mo addition to austenitic stainless steel improves its corrosion resistance, which support the results of EIS that Mo improves passivity behavior stainless steels.

5.2.4: Scanning Electron Microscopy of H_2SO_4 exposed Stainless Steels:

SEM Photomicrograph 5-17 is of Steel type 304 in 20% H2SO4 solution, at magnification 370X. Deterioration of certain area is clearly visible even at this magnification (dark regions). These must be as weak areas on the surface and there is no regular pattern is followed in which damage has taken place. This is because of the fact that, polarization curve clearly indicates that substantial passive range is attained by this steel, further corrosion product is seen in and around the damage portion like in case of HCl solutions. Pits of fine and large sizes are seen in scattered fashion. The reasoning for the formation of pits in the film may be that, any non-uniformity prevailing on the metal surface has a direct bearing on the film, as film is too thin and replenishment or thickening is not possible in an environment lacking in oxygen.

Thus, resulting pits are also non-uniform in size, depth and location depending upon the nature of metal surface beneath it. Note that there are some pits free regions.

It can be concluded that 20% H2SO4 solution furnishes more of localize type than general type corrosionas seen in 304 type steel.

Photomicrograph 5.18 is of S.S. 316 in the same solution at X700 magnification. It clearly indicates the presence of film unlike in case of steel type 304and the damage appears to be general type. Few bright spots observed within dark region are of corrosion product of metal, as metal gets bare in these area after reductive dissolution of passive film. It is neatly observed that, irregular shape holes (dark) of large and small sizes have been formed throughout the surface containing shiny particles of corrosion product well within themselves. Such general uniform type damage is due to presence of molybdenum in the steel, which can resist reducing acid and known to avoid localize corrosion.

EDAX Results of S.S. exposed to H_2SO_4 Solutions:

Average of 3 readings of EDAX results are depicted in figures-5.19 & 5.20. The elemental analysis shows the presence of 19.46%Cr and 11.13%Ni on the surface of steel type-304. While in steel type-316: Cr is 18.19%, Ni is 10.76% and Mo is 2.04%.

These results reflect that the amount of Cr decreases in presence of molybdenum. Thus, as said before formation of Mo-oxide is thermodynamically favorable and comparable to chromium oxide. On the other hand nickel does not readily transfer to the oxide form, resulting in very nominal difference in its amount.

During the above discussions of electrochemical spectroscopy and polarization results, emphasis is given that existence of Mo in conjunctions with chromium improves the characteristics of passive film. This in tern enhances the corrosion resistance of the material. EDAX- elemental analysis clearly indicates the presence of molybdenum on the surface-in the passive film of S.S. 316. This fact confirms the correctness of results obtained by the electrochemical spectroscopy and polarization techniques as well as explanation put forth.

5.3 Passivity Behavior of S.S. 304 & S.S.316 in Phosphoric Acid.

The nature of phosphoric acid is similar to that of sulfuric acid. Accordingly highly concentrated and very dilute acids can be handled safely. While intermediate

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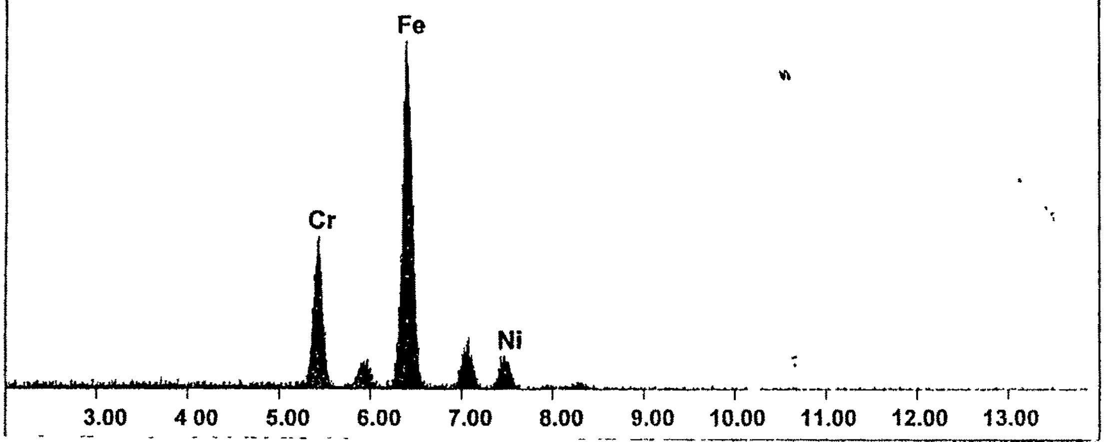
EDS TEST REPORT

C:\EDAX Results\2002\May\0507304H2SO4.spc

Label:304 in 20% H_2SO_4

kV:30.0	**Tilt:0.0**	**Take-off:34.8**	**Det Type:SUTW+**	**Res:127**	**Tc:100**
FS : 1349	**Lsec : 22**			**5-Jul- 2**	**12:24:05**



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
CrK	19.46	20.72	0.2247	0.9942	0.9777	1.1880
FeK	69.41	68.79	0.6545	0.9986	0.9287	1.0168
NiK	11.13	10.49	0.0891	1.0188	0.7860	1.0000
Total	100.00	100.00				

Fig:5,19

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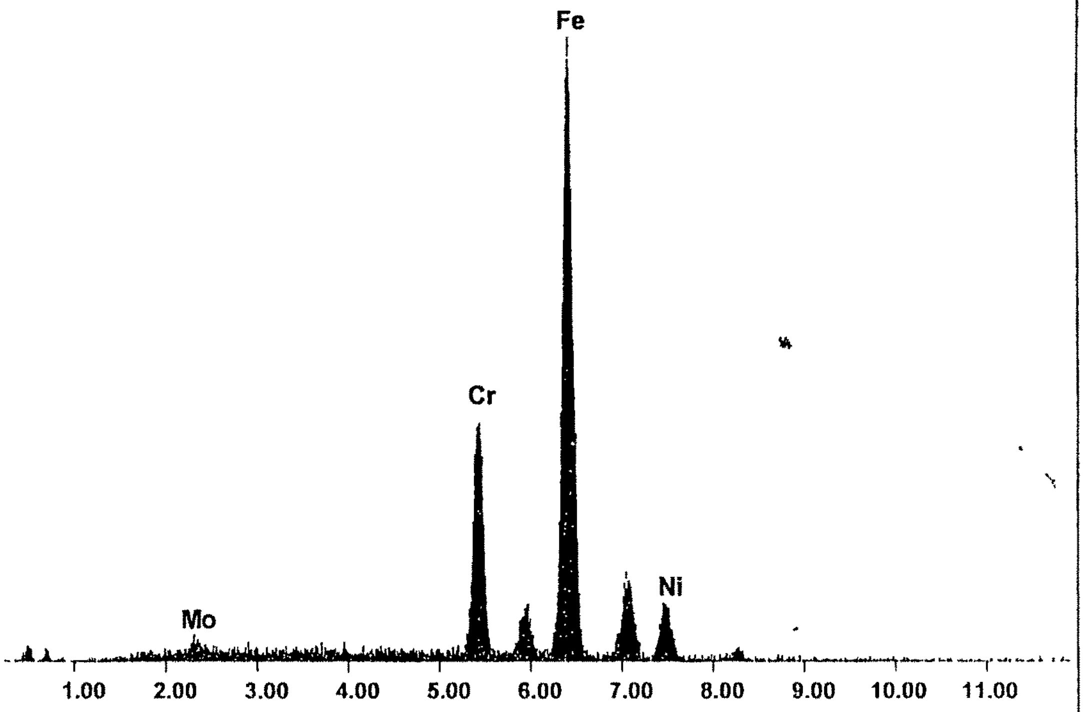
C:\EDAX Results\2002\May\0507316H2SO4.spc

Label:316 in 20% H2SO4

kV:30.0 Tilt:0.0 Take-off:34.8 Det Type:SUTW+ Res:127 Tc:100

FS : 1349 Lsec : 32 5-Jul- 2 12:31:51



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
MoL	2.04	1.19	0.0127	0.9320	0.6670	1.0025
CrK	18.19	19.54	0.2082	0.9956	0.9709	1.1843
FeK	69.01	69.03	0.6517	1.0000	0.9293	1.0163
NiK	10.76	10.24	0.0865	1.0204	0.7875	1.0000
Total	100.00	100.00				

Fig:5.20

range of concentrations of this acid is very corrosive. But the allowable ranges of concentration and temperature are somewhat greater for phosphoric acid than that for H_2SO_4. Besides this, most of the metal phosphates are insoluble in aqueous medium.

In wet process phosphoric acid manufacturing, environmental impurities derived from phosphate rock, such as chlorides, fluorides and H_2SO_4 are invariably present. These halogens make the acid more active and aggressive.

5.3.1 Passivity Behavior of S.S. 304 in Phosphoric Acid.

The Nyquist plots of this steel in pure laboratory-grade ortho-phosphoric acid (85% concentration) and commercial grade impure acid are given in fig.5.21. It clearly indicates that characteristics of the passive film formed in pure 85% concentrated phosphoric acid are more stable than that formed in commercial acid. This film has both $|Z|_{real}$ and $|Z|_{img}$ peak-values 211.5 Ω and 62.15 Ω, much higher (nearly 4-times) than the latter one, having $|Z|_{real}$ and $|Z|_{img}$ values 63.3Ω and 17.76Ω respectively. This may be explained by theory of passivity (17), when Cl^- ions are present, they get adsorbed on the metal surface in preference with dissolved oxygen/phosphate ions. This is due to the facts that, relative size of Cl^- ions is small and phosphoric acid is viscous-offering higher ohmic resistance than solution of other two types of acids (20.5Ωas compare to 0.5 Ωfor 20% sulfuric acid and 8.14 Ωfor hydrochloric acid). This adsorption increases both, the exchange current density and the critical current density for anodic dissolution, leading to poor/ breakdown potential of passivity.

Extrapolations of both the plots exhibit semi-circle nature. Thus, S.S.304 does not have W-impedance element in its equivalent circuits in either of the environments. The semi-circle fit has diameter 263.1 Ωfor ss-304 in lab-grade acid. For SS-304 in commercial-grade diameter is only 67.9 Ω Thus, calculated values of R_p from semi-circle intercepts clearly indicate the superiority of the film forms on S.S.304 on its immersion in 85% pure phosphoric acid.

These aspects, as revealed by EIS, are the indications of deterioration of film, when halides and other impurities are present in the acid. Yet Nyquist plot for commercial acid is smooth. It imparts that general corrosion is pronounced rather than localized, like pitting, as expected when halide ions, especially F^-, are present as impurity (17).

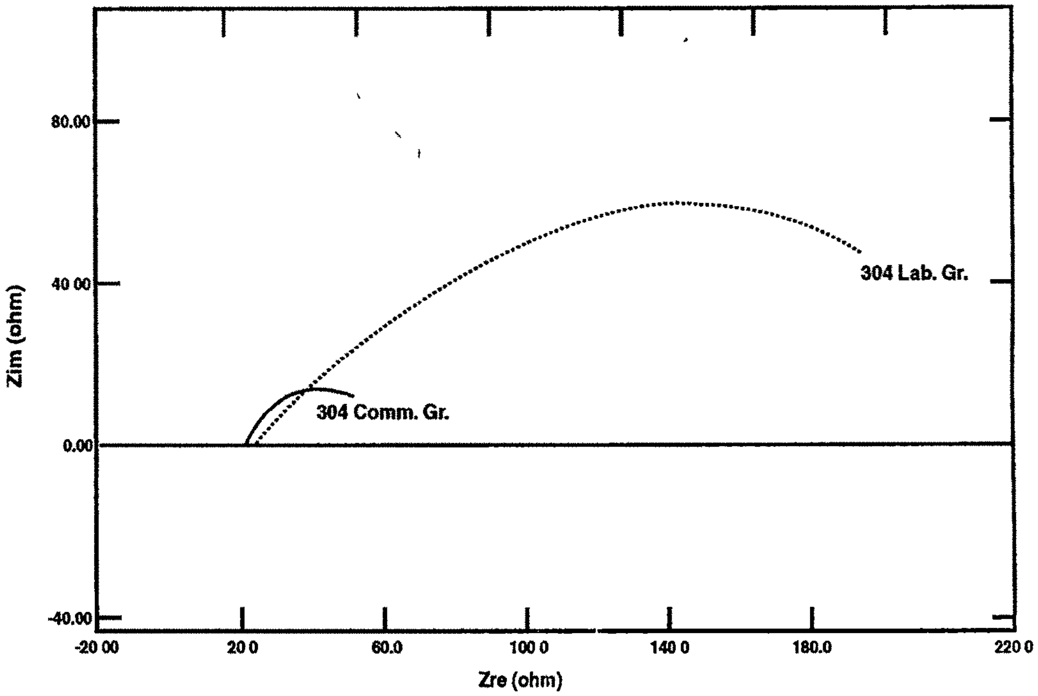


FIGURE 5.21 : NYQUIST PLOTS FOR SS 304 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS

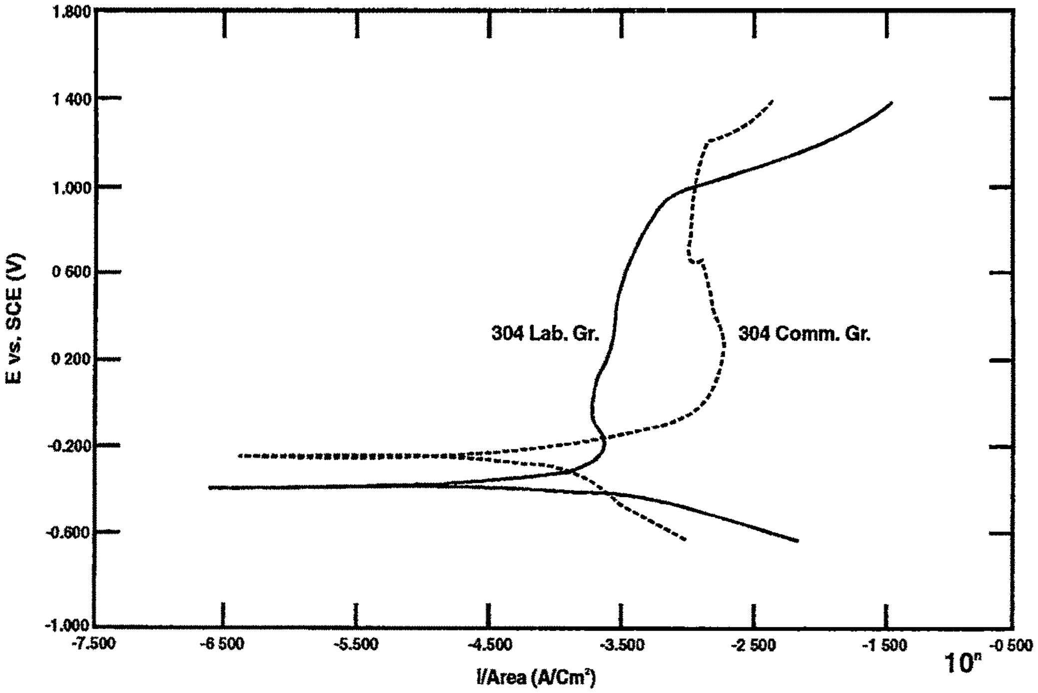


FIGURE 5.22 : POLARIZATION CURVES FOR SS 304 IN LAB GRADE AND COMM.GRADE PHOSPHORIC ACIDS

These differences in characteristics of the passive films formed in lab grade pure 85% H_3PO_4 and impure commercial grade acid have marked effect on corrosion behavior of SS 304. This is exhibited by polarization curves as shown in figure 5.22. Here a large reduction in passive current density values (of almost 3.5 orders of magnitude) between SS 304 in pure acid system and SS 304 in commercial acid system is clearly seen. The passive potential values are similar in both the cases, viz. 0.018 and 0.02V, which is a clear-cut indication of early (at low critical current, value namely 0.0011mA/Cm^2) and stable film formation in pure 85% H_3PO_4 compared to that in the case of commercial grade acid. Alloy in pure acid behaves little nobler than in commercial grade acid as exhibited by small shift in rest potential towards nobler direction. Comparing corrosion rates [0.4064 & 73.75mpy], for these two systems also infers that corrosion behavior of SS 304 in pure lab-grade 85% H_2PO_3 acid is much better. All these potentiodynamic polarization results confirm the results of EIS studies.

5.3.2. Passivity Behavior of S.S. 316 in Phosphoric Acid.

Figure 5.23 depicts the Nyquist plots of S.S.316 in pure lab-grade and commercial grade phosphoric acids. Figure clearly indicates that the presence of Mo significantly improves passive behavior of steel, particularly in lab-grade ortho-phosphoric acid. Here the maximum values of $|Z|_{real}$ and $|Z|_{img}$ are very high (table 5.1) compared to those of S.S.304. While in the case of commercial grade phosphoric acid, containing halides ions and H_2SO_4, significant role is played by Mo present in the steel. In an environment of low pH containing halide ions, particularly F^- ions, and having reducing nature, Mo seems to replenish the damage of passive film. In general commercial grade phosphoric acid passivate the S.S.316 to some extent and Mo has significant contribution in strengthening the film as observed in this study. The $|Z|_{real}$ and $|Z|_{img}$ values in pure lab. grade acid are 1538Ω and 565.34Ω, where as in commercial acid $|Z|_{real}$ and $|Z|_{img}$ values are 49.68Ω & 11.64Ω respectively. Both the presence of halide ions, particularly F ions and 3-valance state of phosphate anions can be assumed to be responsible for effectiveness of Mo addition. In such conditions molybdenum forms bonding with F-ions giving a protective layer $^{(18)}$.

Nature of the Nyquist plots, depicted in figure 5.24, is semi-circle type indicating absence of W-impedance element in the equivalent circuits of both pure and

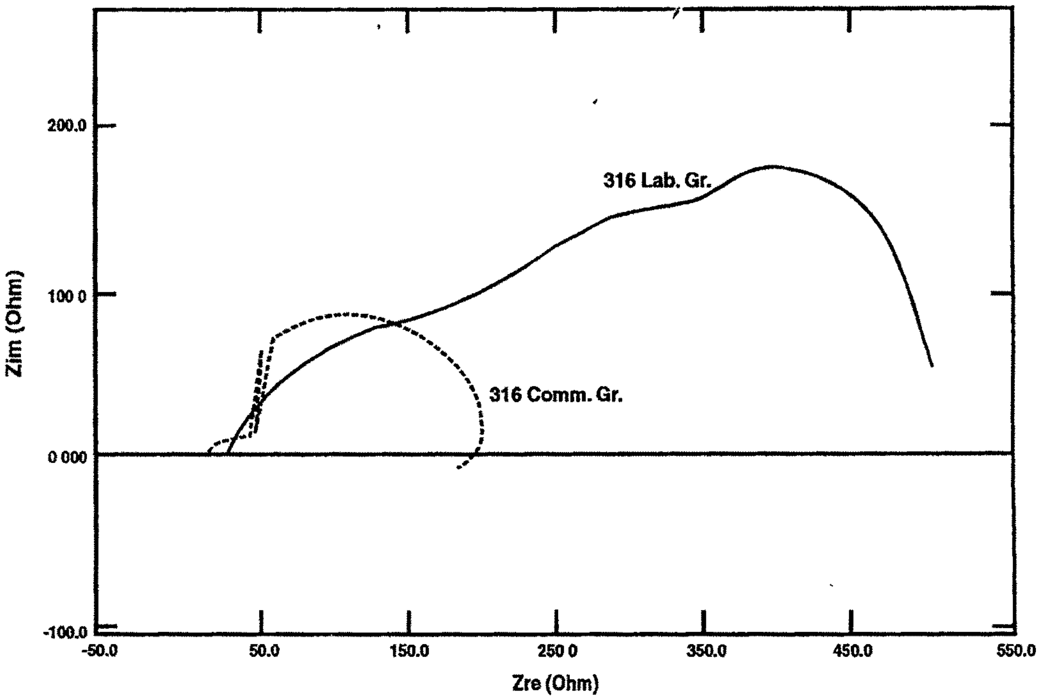


FIGURE 5.23 : NYQUEST PLOTS FOR SS 316 IN LAB. GRADE FOR COMM. GRADE PHOSPHORIC ACIDS.

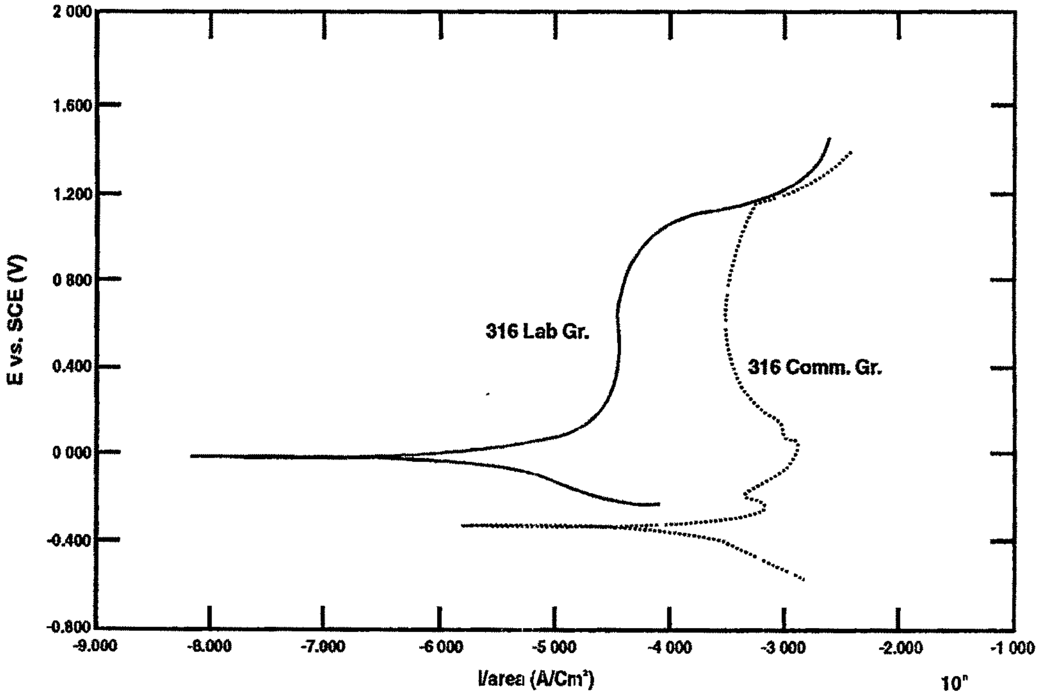


FIGURE 5.24 : POLARIZATION CURVES FOR SS 316 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS.

commercial grade phosphoric acids environments. Enhanced characteristics of film in pure acid than in commercial grade phosphoric acid is due to high thickness of film generated, which induces more impedance in the film and curtail corrosion rate.

Polarization curves for SS 316 in lab-grade and commercial grade phosphoric acids are exhibited in figure 5.24. Again like in case of SS 304, tremendous reduction in passive current density of the order of almost 2 orders of magnitude is observed. But now steel becomes passive as environment changes. This is indicated by shift in rest potential of the steel, in passive direction with change in environment. Effect of presence of halide ions is clearly seen here. Anodic polarization curve of S.S.316 in commercial grade acid have zig-zag nature, indicating poor quality of passive film compared to the curve in lab-grade acid, which is very smooth owing to stable passive film. Accordingly the reduction in corrosion current density & corrosion rate and the rest potential increases in lab-grade acid, these values are E_{corr}= -8.55mV, I_{coor}=1.851μA/Cm^2 and corrosion rate is 0.8552 mpy.

As described before, such nature of polarization curves is due to the presence of Mo in steel, particularly shift in rest potential. Uneven nature of curve in commercial grade acid can also be explained with same reasoning. Molybdenum being nobler and more resistant to corrosion in reducing environment containing Cl-ions through formation of insoluble Mo-chloride (5), replenish the damages but Mo cannot withstand the effect of F-ions. Thus the effort of Mo to generate the film is spoiled by the action of small amount of F-ions present, which damages the film. Thus passivity curve takes up the zig-zag shape.

5.3.3. Comparison of S.S. 304 and S.S. 316 in Phosphoric acid:

Over laying of Nyquist plots for 304 & 316 in lab-grade and commercial grade phosphoric acid is shown in figure-5.27. As per this figure the nature of plot increases in size as environment change from commercial grade acid to 85% lab-grade acid and steel changes from S.S. 304 to S.S. 316. Lowest values of impedance components are from SS 304 in commercial grade acid and highest are for S.S.316 in pure 85% acid [see table-5.2].

Therefore, passive film formed is best in case of steel containing Mo in pure 85% acid environment. This is purely due to the fact that this acid is free from F-ions and H_2SO_4 and presence of Mo in S.S. Maximum values of polarization resistance and capacitance for steels 304 & 316 in pure and impure acids are given in table-5.1.

Furthermore, all of the 4 plots have almost semicircular shape. This indicates that there is no w-impedance existing for corresponding equivalent circuit, and quality of passive film formed depends only on thickness of the film, which therefore resist the charge flow required for corrosion current. But quality wise they are poor. The presences of fluoride ions in ppm level in commercial grade phosphoric acids deteriorate the film. Though the presence of Mo in steel enhances the quality of film in both types of phosphoric acid. This improvement in film quality is very small in phosphorus rock acid, containing impurities. In general Mo being relatively more resistant to halide ions and reducing acids, tries to protect the film from damages.

Figure 5.28 depicts polarization curves of S.S. 304 and S.S. 316 in two types of phosphoric acid. In case of commercial grade acid, owing presence of Mo, rest potential of steel 316 is more positive (noble) than that of steel 304. Also the polarization curve is relatively smoother than in case of steel 304. Similarly, I_{corr} value is also less in S.S. 316 as compared to that of S.S. 304. These aspects result in diminishing the corrosion rate by almost half in S.S. 316. The values of electrochemical parameters values are given in table 5.2. But passive current density is little less in steel S.S. 304 than that for S.S. 316. This might be explained by the nature of impurities present in the acid and susceptibilities of Mo to oxidizing conditions. High concentration of impurities in phosphoric acid like sulfuric acid is exhibiting slightly oxidizing behavior (19). In both the steels the passive ranges are similar and break down occurs at about 1100 mV.

These two types of stainless steels in lab-grade phosphoric acid exhibit a similar trend. But now their rest potentials are nobler (+ve) and I_{corr} and I_{pp} values shift towards left side (lower values). Although corrosion rates are slightly differing and is less for 304, curve for 316 is much more smooth than curve for 314. But in both the cases rate is less than 1.0 mpy and both the steels have equal usefulness in so far as general corrosion is concerned. All these polarization results are in agreement with the EIS results.

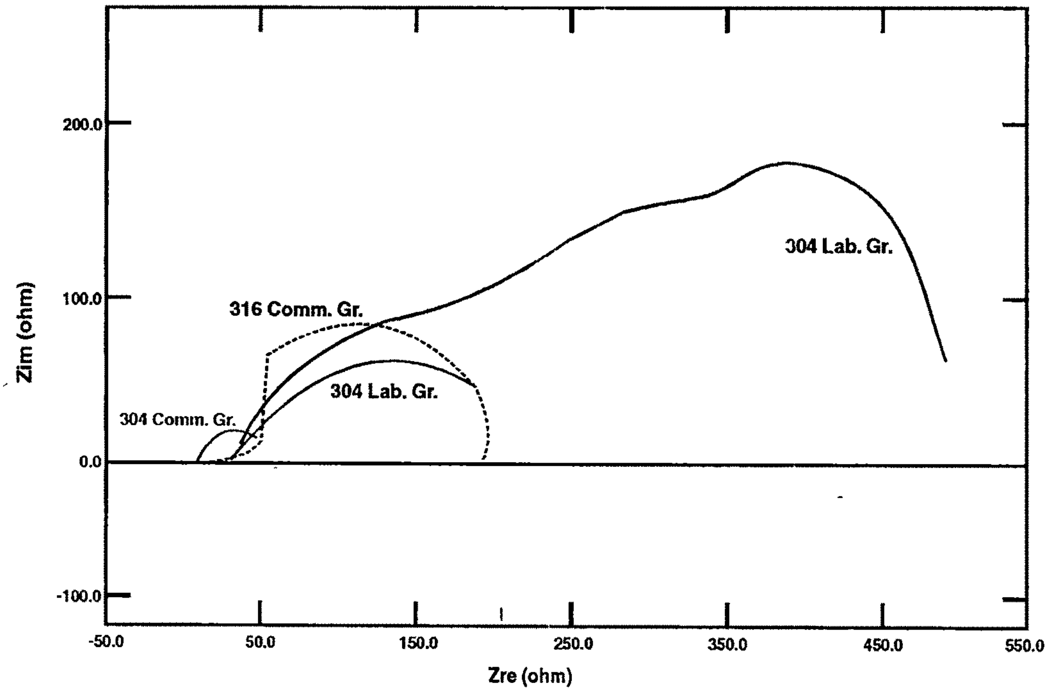


FIGURE 5.25: NYQUEST PLOTS FOR SS 304 AND SS 316 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS.

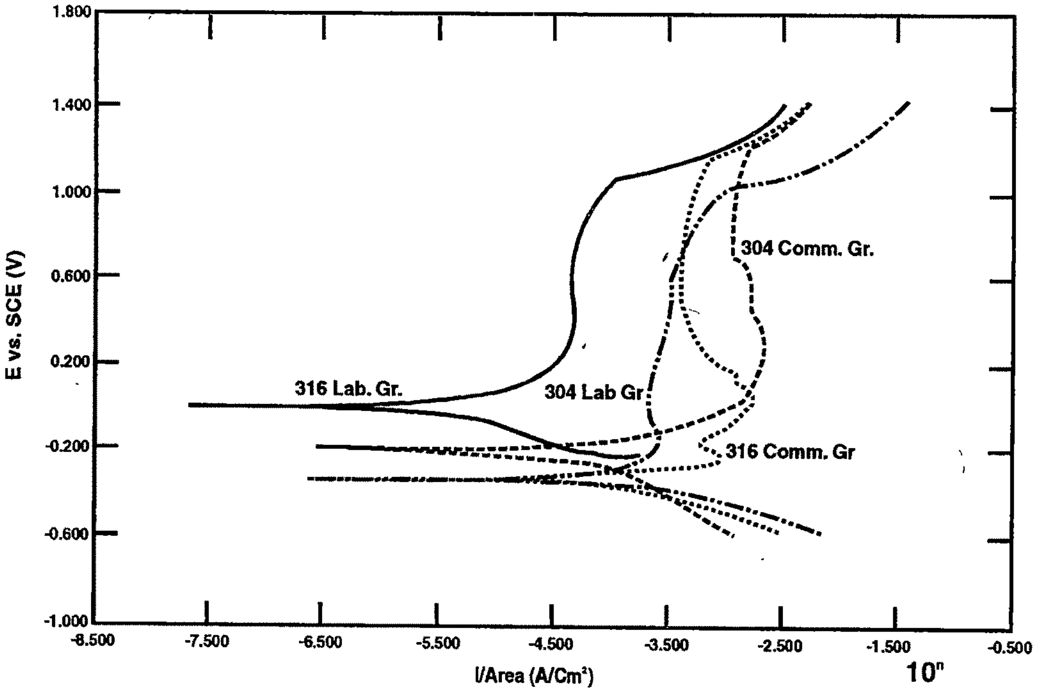


FIGURE 5.26: POLARIZATION CURVES FOR SS 304 AND SS 316 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS

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EDS TEST REPORT

C:\EDAX Results\2002\May\0507304CPH3PO4.spc

Label:304 CP H3PO4

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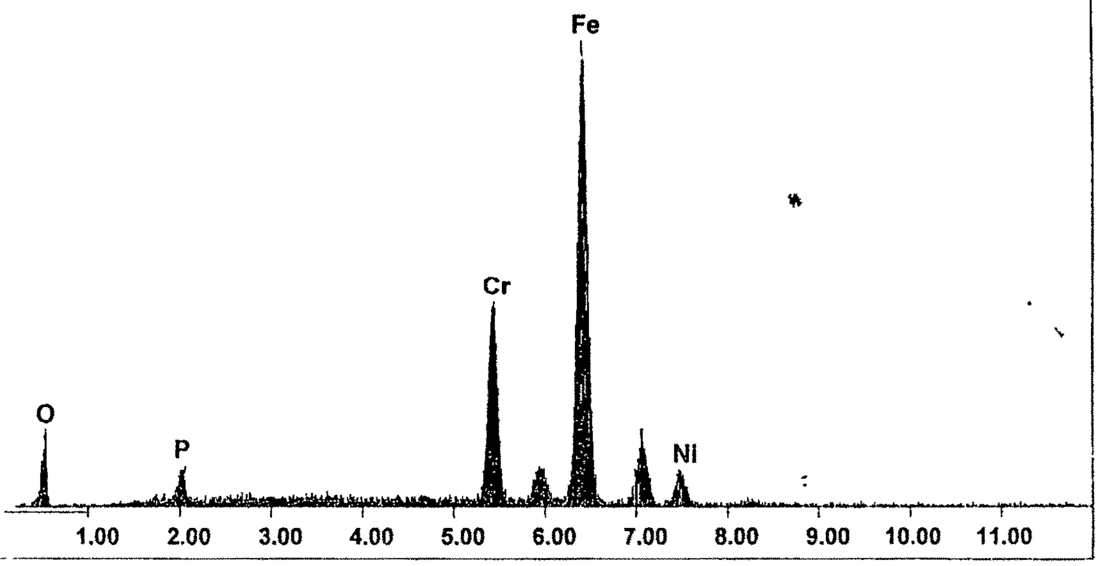

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	9.49	26.01	0.0373	1.1245	0.3485	1.0032
P K	3.43	4.86	0.0142	1.0487	0.3946	1.0037
CrK	17.67	14.90	0.1986	0.9762	0.9808	1.1740
FeK	61.92	48.63	0.5756	0.9805	0.9367	1.0122
NiK	7.50	5.60	0.0605	1.0000	0.8066	1.0000
Total	100.00	100.00				

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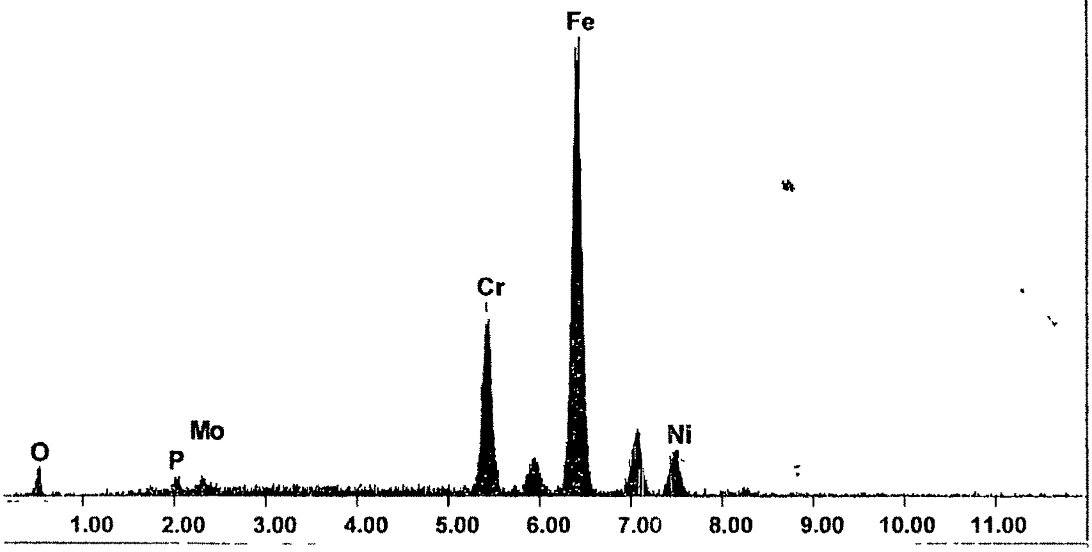
EDS TEST REPORT

C:\EDAX Results\2002\May\0507316CPH3PO4.spc

Label:316 CP H3PO4

kV:30.0 Tilt:0.0 Take-off:34.8 Det Type:SUTW+ Res:127 Tc:100

FS : 1349 Lsec : 24 5-Jul- 2 13:02:04



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	4.39	13.70	0.0161	1.1362	0.3218	1.0034
P K	1.37	2.21	0.0056	1.0594	0.3797	1.0045
MoL	2.17	1.13	0.0135	0.9247	0.6734	1.0024
CrK	17.14	16.45	0.1936	0.9872	0.9719	1.1772
FeK	64.82	57.92	0.6095	0.9915	0.9335	1.0159
NiK	10.10	8.59	0.0816	1.0115	0.7989	1.0000
Total	100.00	100.00				

Scanning Electron Microscopy of H_3PO_4 exposed Stainless Steels:

SEM photomicrographs of steels S.S. 304 and S.S. 316 in commercial grade phosphoric acid are given here. As it is more aggressive than lab-grade acid and affects the passive film more.

Photomicrograph-5.28 is of S.S. 316, at high magnification (3300 X) shows that film is peeling off locally. But being well compact, peeling give rise to rosette leaves like appearance. That is, it does not detached off from alloy-film interface and damage is only within the film. In adjoining region film is visible quite clearly, which covers the underneath metal. Thus in case of S.S. 316 the film is providing better passivity and low corrosion rate.

Phosphate in variety of forms is used as one or the other type of inhibitor, like condensed phosphate acts as cathodic inhibitor, through formation of protective film (20). Besides this, phosphates of most metals are insoluble in aqueous solutions, giving protection by adhering on the surfaces.

SEM micrograph for S.S. 304 is shown in photomicrographs 5.27 at high (X2700) magnifications. Again the coating of film appears but now it is more deteriorated than in case of S.S. 316. At such a high magnifications more uniform surface appears in S.S.316 as compared to in steel type 304. At 2700X damage of passive film in the form of plate like tunnels is clearly observed. This leads to a corrosion rate of 304 almost double to that for steel 316

EDAX-RESULS:

Elemental analysis using EDAX technique reveals following results.

S.S.304 on its surface contains; 17.67% Cr, 7.50% Ni, 9.49% O_2, and 3.43% P. While S.S.316 on its surface possesses, 17.14% Cr, 10.10% Ni, 4.39% O_2, 1.37% P and 2.17% Mo. This analysis indicates presence of phosphate in the surface layer, which might have formed through any one of the two mechanisms viz, formation of insoluble metal phosphate or cathodic inhibitive film, mentioned below. Also it is worth noting that amount of P and O_2 are less in Mo containing steel than Mo free steel, which must be the effect of Mo, as this is the only difference between the two steels.

REFERENCES:

1. I. I. Tingley, corrosion, Vol. 14, pp- 273t, (1958)

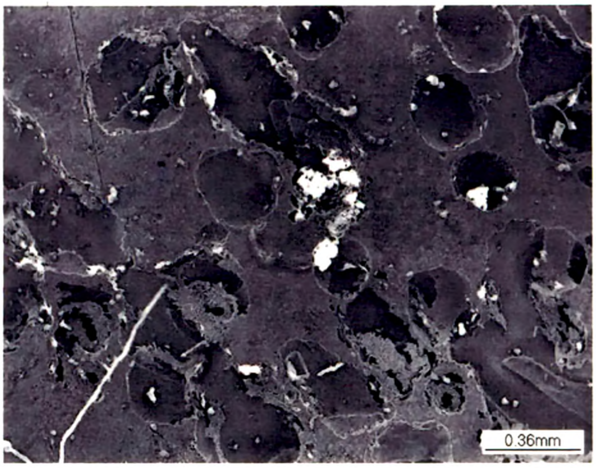


Figure - 5.7 :
SEM Photomicrograph
of SS 304 in 10% HCl

Figure - 5.8 :
SEM Photomicrograph
of SS 316 in 10% HCl

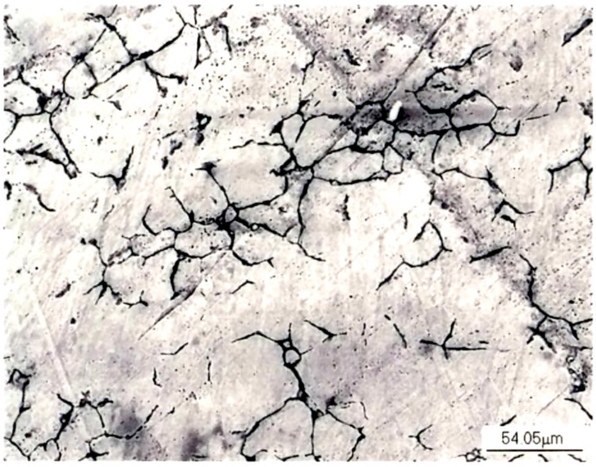


Figure - 5.17 :
SEM Photomicrograph
of SS 304 in 20% H_2SO_4

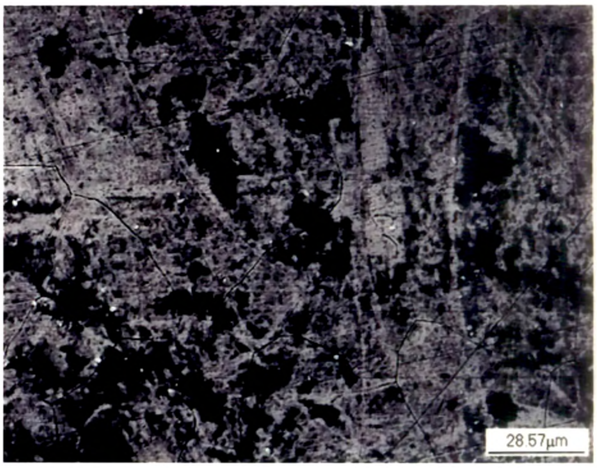


Figure - 5.18 :
SEM Photomicrograph
of SS 316 in 20% H_2SO_4

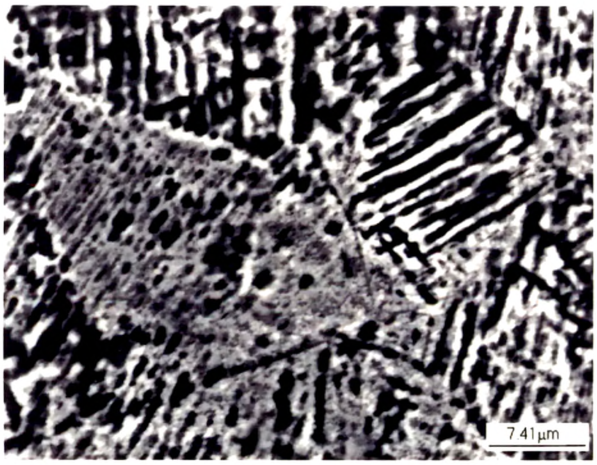


Figure - 5.27 :
SEM Photomicrograph of
SS 304 in Comm. Gr. H_3PO_4

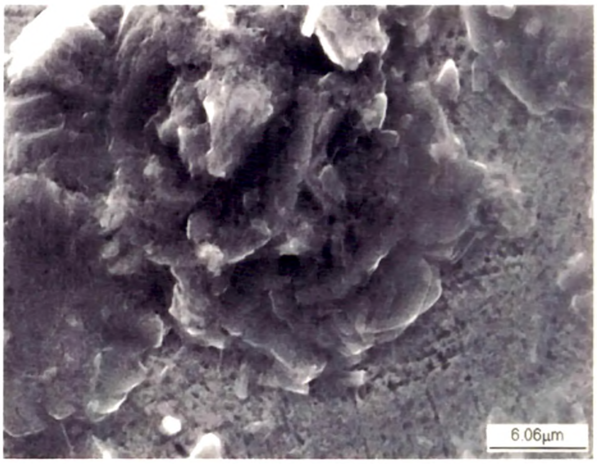


Figure - 5.28 :
SEM Photomicrograph of
SS 316 in Comm. Gr. H_3PO_4

2. Raphl M., Terry Debold and Mark J. Johnson, ASM Metals Hand Book, Vol.13, 9th Edition, pp. 550, 1987.
3. U.R.Evans, "The corrosion and Oxidation of Metals", Edward Arnold. London. pp. 346-352, (1977).
4. G.V.Samsonov Ed., "The Oxide Handbook", Ifi/Plenum Publisher, pp. 85, 1973.
5. A.Alon, J.Yahamol and M.Schorr, "Influence of Halides in Phosphoric Acid on the Corrosion Behavior of Stainless Steels", Corrosion, Vol.31, No.9, pp. 318, 1975.
6. H.H.Uhlig, "Corrosion and Corrosion Control" John Wiley & Sons, pp.70-71, 1963.
7. ASM Metal handbook, "properties and selection" Irons, steel and high performance alloys, vol. 1, 10th edition, pp. 842-847., (1990).
8. Donald Peckner and I.M.Berstein, "Handbook of stainless steel", Me Graw Hill book company, pp. 10.16, (1977).
9. N.D.Tomashov. and G.P.Chemova, "Passivity and Protection of Metals Against corrosion". Plenum Press, New York pp. 78-80, 1967
10. H.H.Uhlig, "Corrosion and Corrosion Control", 2nd Edition, John Wiley & Sons,
    1. pp.310, (1973).
11. Te-Lin Yau, " Selecting Performance Alloys for Chemical Processing", Web: www/chemical processing .com/protected/cp 1099/ocp_metals.html. (1999).
12. H. Campbell, J. Appl. Chem., vol. 4, pp. 633, (1954).
13. C.B. Bargeron and R.B. Givens, "Precurcive Blistering in Localized Corrosion of Aluminum", Corrosion, vol. 36, No. 11, pp. 620, Fig-4, (1980).
14. Edeleanu, "Nature", vol. 173, No. 739, (1954).
15. V. R. Evans, " The corrosion & oxidation of metals", Edward Arnold (Pvt.) Ltd
    1. pp. 346, (1977).
16. M. Prazak and V. Cihal, Z. Elekrtochem., 62739, (1958).
17. Kotaro Ogura and Takahiko Ohama, "Pit Formation in Cathidic Polarization of Passive Iron", Corrosion, vol. 37, No.10, pp.569, (1981).

18. G. H. Cartledge, J Electochemsoc, vol 104, pp-420 (1957)
19. G.Okamoto, T. shibata. Passivity of metals. Corrosion monographs series, R.P.Frankenthal, J.Kruger, Eds., Electrochemical society, Pennington, New Jersy, p. 646 (1978).
20. David Thompson Ed., " Insight into Specialty Inorganic Chemicals", Royal Society of Chemistry, p.396, (1999).
21. L. Mitra, " Inorganic Chemistry", Publ. Ghosh & Co., 35th Edition, p.494, (1951)