CHAPTER VI

PASSIVITY BEHAVIOR OF TI AND TI-5%TA ALLOY IN DIFFERENT CONCENTRATIONS OF REDUCING ACIDS

RESULTS AND DISCUSSION

Titanium is an electronegative metal. It is active in the EMF series, the calculated standard potential of its dissolution with formation of Ti $^{2+}$ ions is -1.63V and Ti $^{3+}$ ions is -1.21V. In non-oxidizing acids, anodic dissolution and intense corrosion of titanium occur at potentials about 1volt more positive than above, i.e. at -0.45 and -0.25 V $^{(1)}$, indicating that anodic dissolution/corrosion of titanium is accompanied by the anodic inhibition.

The inhibition of corrosion is due either to anodic or cathodic polarization, as Ti has high affinity for both oxygen and hydrogen. Thus formation of both hydrides and oxides is thermodynamically possible depending on potential, providing passivity to Ti over a wide range of potential. Moreover, its flade potential region is relatively active ($E_f = 0.05$) indicating stable passivity $^{(2)}$. Most researches $^{(3,4\ \&\ 5)}$ consider that passive film on Ti is mainly oxide type.

On addition of nobler metal to titanium cathodic processes enhance, either by increase in cathodic area or in rate of cathodic reaction. This result in low cathodic over voltage and ensure stability of passivity. In the present work, to study such passivity behavior of titanium, an alloy Ti with 5% tantalum has also been investigated.

All three types of acids with different concentration and chemistry used in case ASS are also used in this case to evaluate the corrosion and passivity behavior of Ti and Ti-5Ta in these aggressive media. Results obtained are reported and discussed as under:

6.1 Passivity Behavior Titanium exposed to 5 and 10% HCl Solutions:

On immersing Ti in 5 and 10% HCl solutions the Nyquist plots (Figure 6.1) shows that superior quality of film generates in 5% solution than in 10% HCl. Both components of impedance $|Z|_{real}$ and $|Z|_{Img}$ are having values 129.78Ω and 61.24Ω respectively, which are almost three time greater as compared to those in 10%

solution, viz. $|Z|_{real}$ = 42.37Ω and $|Z|_{Img}$ = 19.23Ω. The semi circles fit for Ti in 5% and 10%HCl solutions are having diameters 142.94Ω and 59.87Ω respectively.

Nature of the plot in dilute solution is semicircle type, thus confirming a simple equivalent circuit consisting of a resistor in parallel to a capacitance. On increasing acid concentrations, values of these elements decreases. The nature of the plot changes to halfway semicircle with one end extends as the line having about 45° inclination. Hence in the equivalent circuit of this plot a W-impedance element must be present. But both the values, viz. resistor and capacitance of W-impedance are relatively small. This results in comparatively inferior type of film or poor passivity in concentrated acid solution.

Above results of EIS may be explained on the basis of fact that, titanium is vulnerable in reducing acid. It needs oxygen, in small amount, for generating passivity (4 6). However, in concentrated acid solution, amount of naturally dissolved air/oxygen is less than in case of dilute acid and number of negative ions are more and having small radius (Cl^- = 1.81 A), this in turn favor adsorption of Cl-ions in preference to oxygen ions at the interface. Both these factors increase charge per unit area at anode/solution interface and raise its polarizing power at the expense of the stability of passive film (3).

Polarization curves for titanium metal in 5% and 10% HCl solutions are depicted in figure 6.2. It shows that value of I_{corr} reduces from 1584.89 μA/Cm^2 to 19.95μA/Cm^2 ($10^{-2.8}$ to $10^{-4.7}$), i.e., 2 orders of magnitude and passive current density & I_{crit} by 3 orders of magnitude. These results clearly indicate the reduction in general corrosion rate from 61.37 mpy in 10%HCl to 29.12 mpy in 5%HCl solution.

Rest potential values of titanium in 5% and 10% HCl solutions are –0.3941V and -0.4125V, i.e., almost same and in the active range. Indicating that in hydrochloride acid solutions, titanium attains poor passivity and remains active. As environment is reducing type the only source of oxygen is naturally dissolved air at ambient temperature, which reduces as concentration of acid increases (7). Thus, the qualities of passive film further deteriorate as acid concentration increases, since pH and available oxygen both reduces.

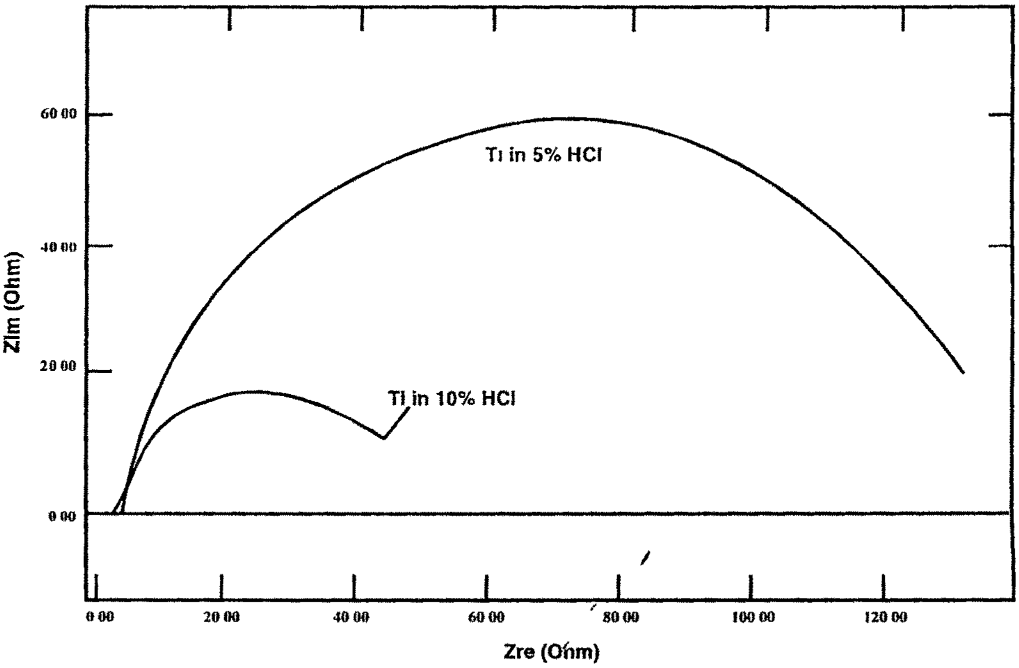

FIGURE 6.1 : NYQUIST PLOTS FOR TITANIUM IN 5% AND 10% HCl SOLUTIONS

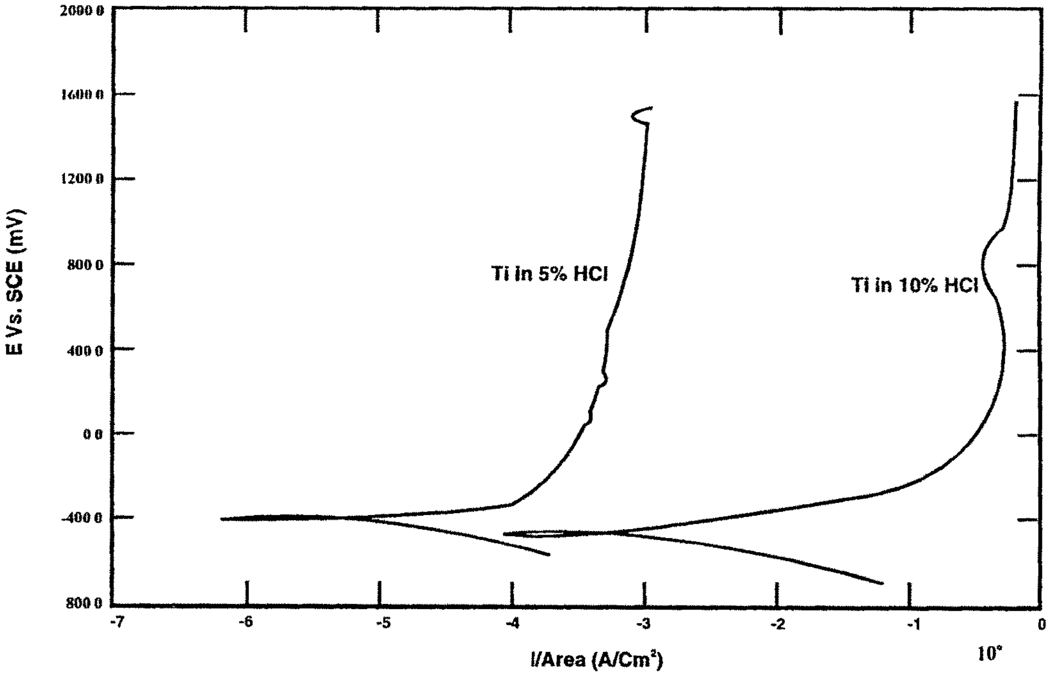

FIGURE 6.2 : POLARIZATION CURVES FOR TITANIUM IN 5% AND 10% HCl SOLUTIONS.

The third interesting information revealed by these curves is the basic characteristic of this metal. Note that although potential rises in +ve (anodic) direction up to 1.6 volts, there is no indication of transpassive or passivity breakdown. This is the intrinsic property of titanium that its breakdown potential is very high (8,9) compared to other active-passive type metals/alloys. In other words, Ti forms quickly a stable film on its surface, having low critical current density and does not show any decrease in current density values as a mark of passivity attainment when anodically polarized. This may be attributed to the facts that, titanium has affinity for hydrogen also and during cathodic polarization hydride forms, which covers the surface and provide passivity (1).

6.1.2. Passivity Behavior of Ti-5Ta Alloy exposed to 5 and 10% HCl Solutions

Figure-6.3 depicts the Nyquist plots for this alloy immersed in 5 and 10% HCl solutions. It reveals that passivity behavior of alloy is different than that of the metal. Alloy in 5% HCl bath generates the film, which gives a complex plot having parabolic nature, i.e., at low frequencies $|Z|_{img}$ component do not diminishes. In 10% HCl solution, on the other hand, alloy gives semi circular plot. In other words passivity attains in dilute solution is highly resistant to flow of current with $|Z|_{re} = 346.25\Omega$and $|Z|_{img} = 156.42\Omega$values of impedance components. But the barrier to charge flow is poor in concentrated bath with $|Z|_{re} = 123.96\Omega$ and $|Z|_{img} = 28.71\Omega$values of impedance components. Diameters of semicircle fit are 130.13 and 640.58 ohms in 10% & 5% HCL solutions respectively.

Equivalent electrical circuits correspond to these plots are modeled as: In case of 5%HCl bath the circuit is consisting of a small capacitance in series with usual resistor-capacitor loop, providing high values of $|Z|_{img}$ towards low frequency range. While in 10%HCl bath it consist usual resistor-capacitor circuit resulting in a semi-circle type plot. Besides, values of resistor and capacitance are relatively low in 10% HCl solution, thus passive film produced is having relatively inferior quality.

Figure-6.4 shows the polarization curves of the alloy in 5 and 10% HCl baths. Observe that alloy remains as active as metal with rest potentials -385 V and -410 V in 5% & 10%HCl solutions respectively. Also like titanium i_{corr}, reduces from 125.647 to 11.45 $\mu A/Cm^2$ and i_{crit} reduce from 3162.27 to 19.92 $\mu A/Cm^2$ and also i_{pp} by 2 to3

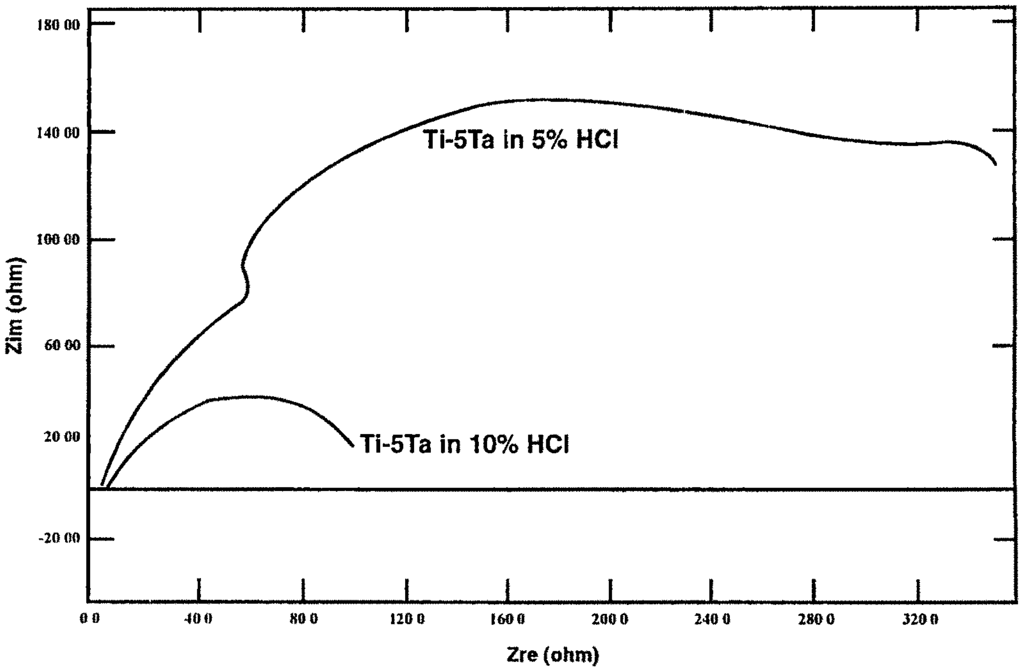

FIGURE 6.3 : NYQUIST PLOTS FOR Ti-5Ta ALLOY IN 5% AND 10% HCl SOLUTIONS

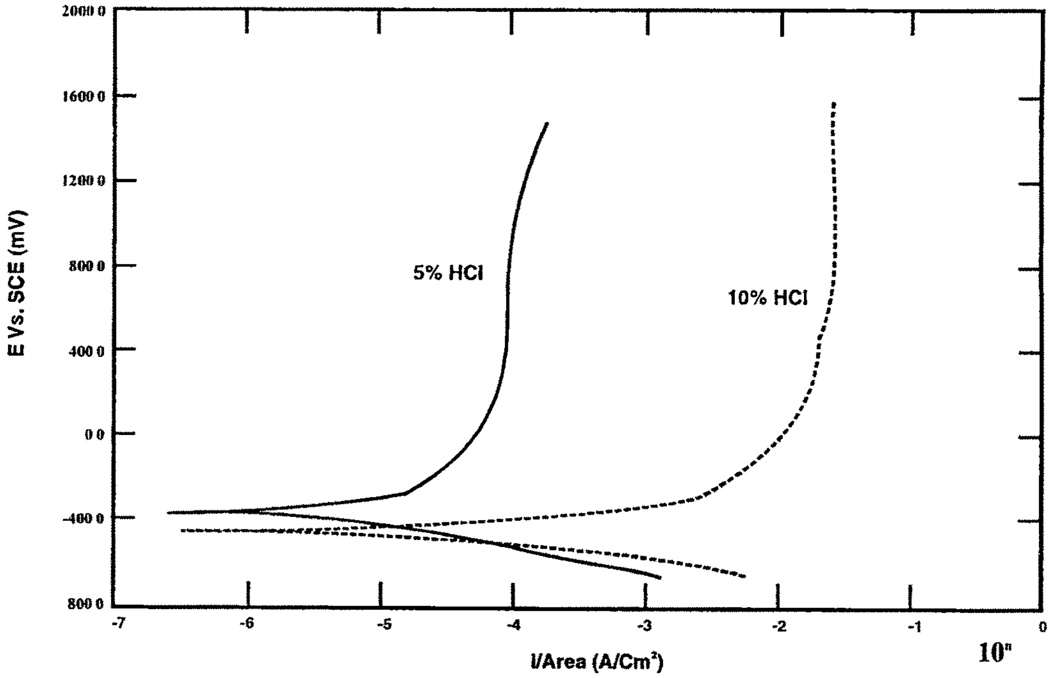

FIGURE 6.4 : POLARIZATION CURVES FOR Ti-5Ta ALLOY IN 5% AND 10% HCl SOLUTIONS

orders of magnitude, indicating rise in corrosion rate with concentration of acid from 19.05. to 49.61 mpy. Such a large reduction is clearly seen in the figure by shift of curve towards left side as the concentration of acid decreases. Obviously such corrosion behavior of alloy is due to deterioration of passive film in concentrated acid bath, as observed in EIS-studies.

Such passivity and corrosion behavior of Ti-5Ta alloy may be explained on the basis of characteristics of tantalum. Tantalum being nobler than titanium is resistant to practically all the acids and in alloy it increases cathodic area by enriching most of the surface with tantalum, after initial dissolution of anode like platinum in Ti-Pt alloy (10). Further tantalum also has high affinity for oxygen and forms thin oxides film imparting high resistance against many aggressive environments (11). These factors are responsible for the improvement of passivity and corrosion behavior of the alloy.

6.1.3 Comparison of Behavior of Ti And Ti-5ta in 5% & 10%HCl Solutions:

Nyquist plots of Ti and alloy in 5% land 10% HCl solutions are exhibited in figure 6.5. The superiority of passive film formed on the surface of Ti-5Ta in 5% acid medium amongst all is neatly visible. Behavior of alloy is also better than metal even in concentrated solution. Both Ti and Ta form variety of oxides, being transition elements, most stable are TiO_2 and Ta_2O_5 types respectively. Comparing free energy of formation of these oxides, data indicates that at room temperature both of the oxides can form and exist (12). Thus, the assumption of presence of both the oxides in the film is valid. And due to presence of admixture of oxides in passive film its characteristics improves as shown by EIS results.

Similarly, the polarization curve of Ti-5Ta alloy-5% HCl system turns out to be the best, giving lowest values of I_{crit}, I_{pp} and I_{corr} which gives lowest corrosion rate, amongst the all 4 types of system studies in this work. Such nobler behavior of alloy in dilute and concentrated bath is ascribed by presence of 5% Ta in it. In 10% HCl solution, dissolved natural air is less and acid is more aggressive than 5% HCl bath. Hence electrochemical parameters of alloy increases with concentration of bath, but Ti-5Ta alloy still remain superior to titanium metal. Here also it is observed that, though anodic potential has been raised up to 1.6 volts, passivity break down is not

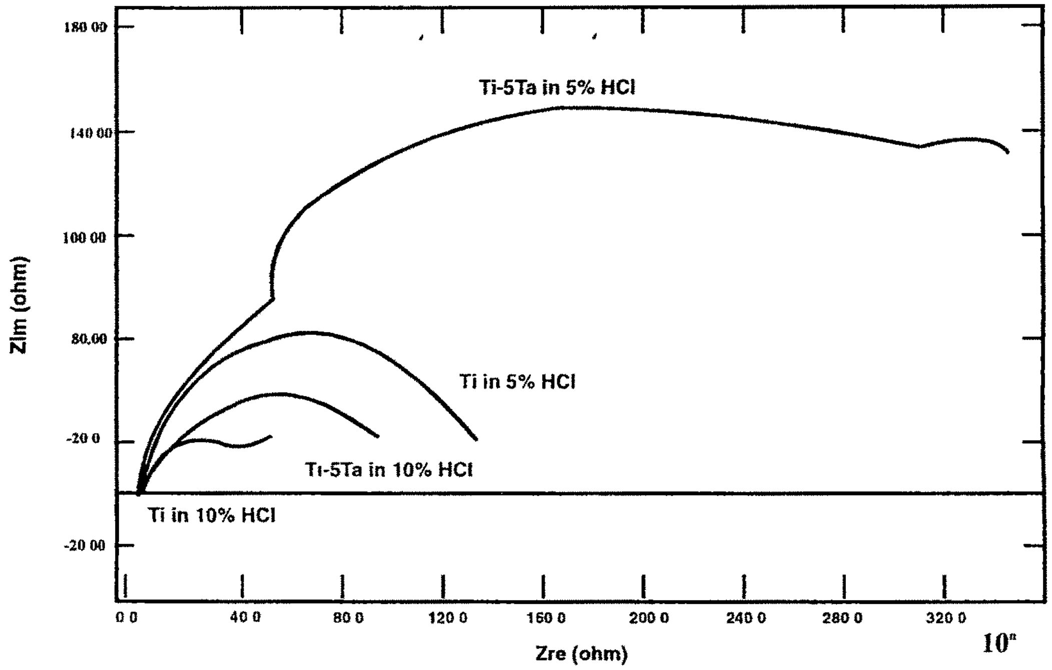

FIGURE 6.5 : NYQUIST PLOTS FOR TITANIUM AND Ti-5Ta IN 5% AND 10% HCl SOLUTIONS.

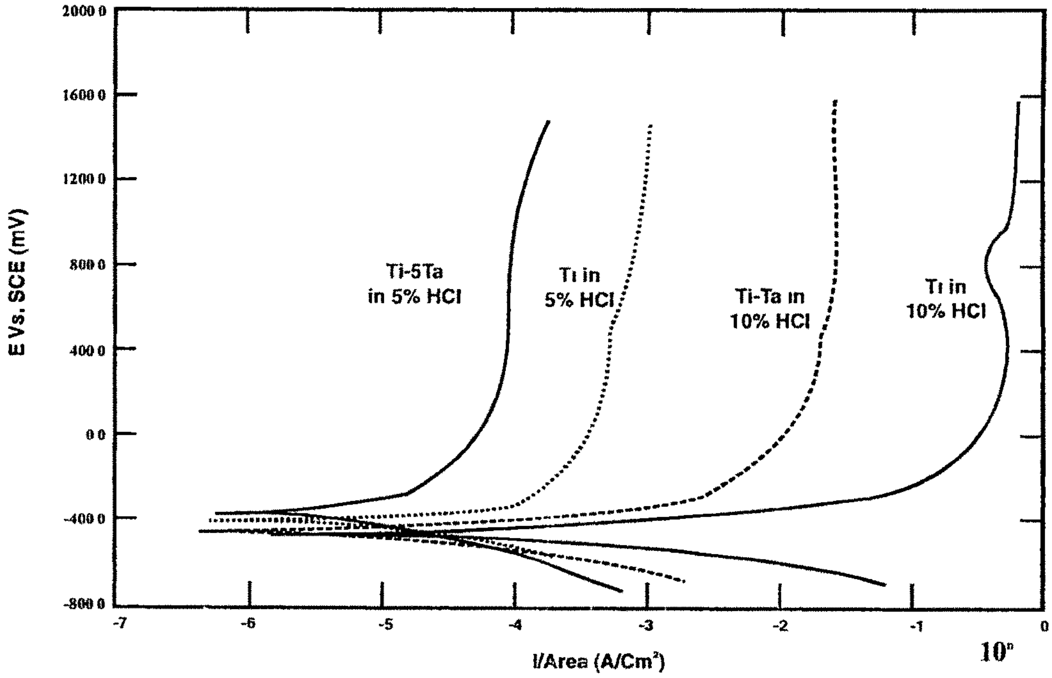

FIGURE 6.6 : POLARIZATION CURVES FOR TITANIUM AND Ti-5Ta IN 5% AND 10% HCl SOLUTIONS.

appearing even in case of alloy. Thus, like titanium metal, alloy also do not exhibit transpassive region, till high anodic voltage is reached.

In general small amount of addition of Ta improves the quality of passive film generating on the corroding surface. Such an improvement, in tern, reduces corrosion rate and extends the applicability of titanium in mild reducing environment.

6.1.4 Scanning Electron Microscopy of HCl exposed Ti and Ti-5Ta alloy:

SEM photomicrographs of Ti-metal and Ti-5Ta alloy are shown in figures 6.7 and 6.8. These micrographs are taken after exposing the metal and alloy to 10% HCl solution.

Surfaces appear to be uncovered with any film yet no grain boundaries are clearly visible in any photograph. Localized tunnel type corrosion is seen in both the micrographs. Such kind of corrosion is expected, as active-passive metals are prone to localize corrosion, particularly in the presence of small size anions like Cl-ions. On comparing the two micrographs higher amount of damage is seen on the metal surface than on alloy surface. In both the cases, dark regions are seen and on observing minutely, particularly in case of alloy, the surface is visible beneath this dark region. Hence, it must be the corrosion product or loosely held hydride. But hydride formation is controversial at high value of anodic polarization potential (1)(1.6V).

These results of SEM studies are in agreement with results of polarization and EIS that passive films formed are poor in HCl containing solution, which results in high corrosion rate. But passive film generates on alloy is relatively better than passivity of metal

EDAX Results of HCl Exposed Ti and Ti-5Ta Alloy:

Electron dispersion analytic X-ray reveals that, after anodically polarizing in 10% HCl solution, titanium surface contains 97.43% Ti 2.47%Si and no oxygen. In case of alloy 94.62% Ti 5.38%Ta and again no oxygen.

Above elemental analysis clearly indicate absence of oxide passive film on the surface of either specimen after exposing them to 10%HCl solution. Any other kind of film/deposition present on the surface results in poor quality of passivity in either case. In alloy, surface region contains Ta 5.38%, which is signifying the presence Ta on the surface and in turn higher passivity than on the metal surface. The presence of

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EDS TEST REPORT

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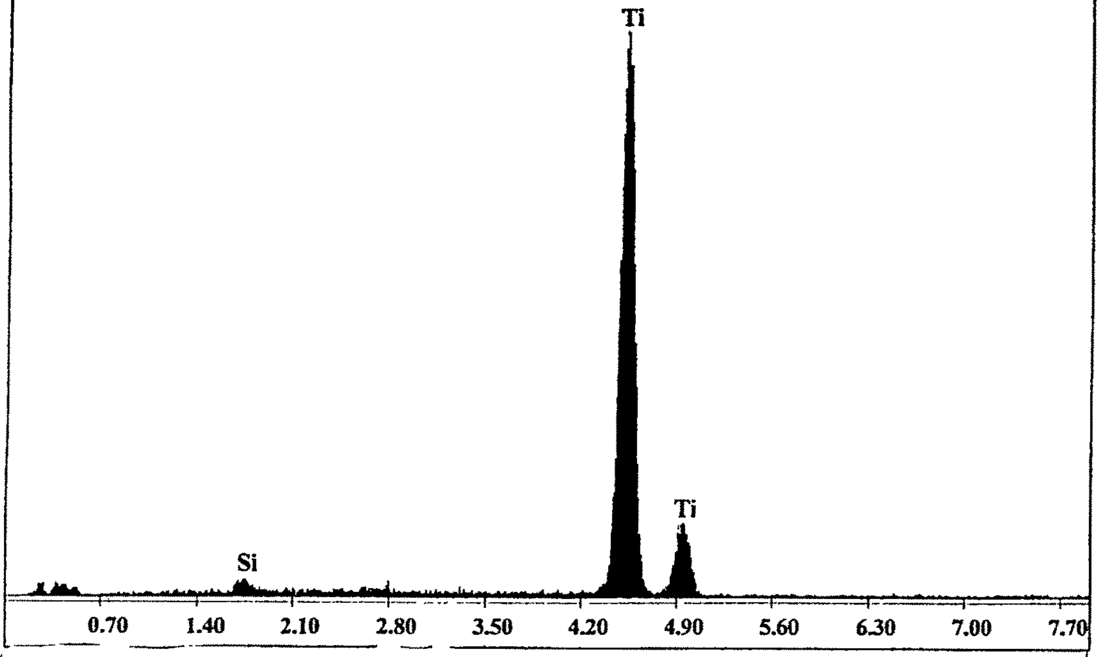
Label:Ti in HCl

kV:30.0 Tilt:0.0 Take-off:34.6 Det Type:SUTW+ Res:127 Tc:100

FS : 1597 Lsec : 4 22-Nov- 0 14:00:30



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
SiK	2.57	4.30	0.0119	1.1079	0.4148	1.0092
TiK	97.43	95.70	0.9653	0.9968	0.9939	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
SiK	41.62	14.14	8.06	2.94
TiK	2266.52	9.70	0.95	233.69

Fig:6.9

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EDS TEST REPORT

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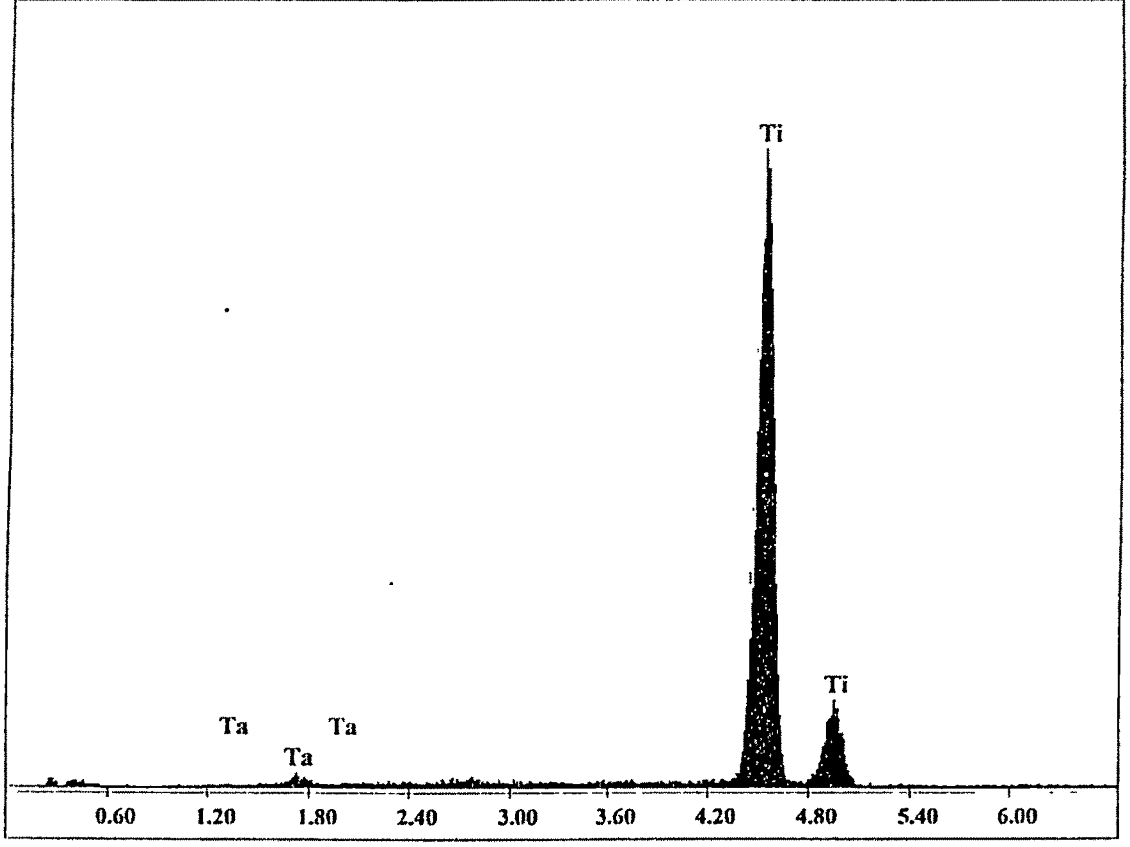
Label:Ti 5% Ta in HCl

kV:30.0	Tilt:0.0	Take-off:34.6	Det Type:SUTW+	Res:127	Tc:100
FS : 2106	Lsec : 6			22-Nov- 0	13:48:17



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
TaM	5.38	1.48	0.0373	0.8838	0.7831	1.0012
TiK	94.62	98.52	0.9212	1.0065	0.9657	1.0016
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
TaM	24.04	8.54	9.04	2.81
TiK	2286.56	12.16	0.80	187.99

Fig:6.10

silicon on the surface of titanium metal might be due to adhesion of some particle during polishing. (Fig 6 9 & 6 10)

6.2 Passivity Behavior of Ti & Ti - 5ta 10% And 20% in Sulfuric Acid Solutions:

Sulfuric acid is oxidizing reducing type acid, depending on concentration. Dibasic sulfuric acid has high ionization energy (13) and sulfate ions exert weak Vander walls' forces among themselves (14). Both the aspects indicate coagulation tendency of sulfate ions. These in tern, results in less aggressiveness of this acid compared to hydrochloric acid. Also the sulfate ions produced are doubly charged and larger than Cl-ions, therefore held strongly at the films/solution interface, the resulting electrostatic field increases the polarization voltage and penetration is possible at weak sites only. In the present work concentrations sulfuric acid used are same as in case of stainless steels and considered to be a reducing acid in nature.

6.2.1. Passivity Behavior of Ti exposed to 10 % and 20% H_2SO_4 Solutions:

Nyquist plots for Titanium in 10% and 20% H_2SO_4 Solutions are shown fig.6-11. The characteristics of passive film formed in 10% H_2SO_4 acid are better than those of film formed in 20% H_2SO_4 acid. The film formed in 10% H_2SO_4 has polarization resistance value 78.94 ohms and maximum capacitive-impedance value is 34.81 ohm. These are much greater than $|Z|_{re}$ and $|Z|_{img}$ values of the film generated in 20%·H_2SO_4 solution, in which respective values are 7.89 ohms and 3.27 ohms.

Both the plots are having semicircle type nature. Therefore, including a resistor with a parallel connection of capacitor in their equivalent electric circuits. In case of dilute solution $|Z|_r$ and $Z|_{img}$ values are more than those of in concentrated (20%) solutions, accordingly it has a larger semicircle. Reasoning for such passivity behavior is attributed to the double fold facts. Firstly, the aggressiveness of the H_2SO_4 increases with concentration in lower range of concentration. This leads to fixation of Ti ions by sulfate ions which in free state act as inhibitor for titanium dissolution (15). Secondly, the amount of naturally dissolved air/oxygen reduces at higher concentration of sulfuric acid (16), which inhibit the passive film formation. In general then, quality of

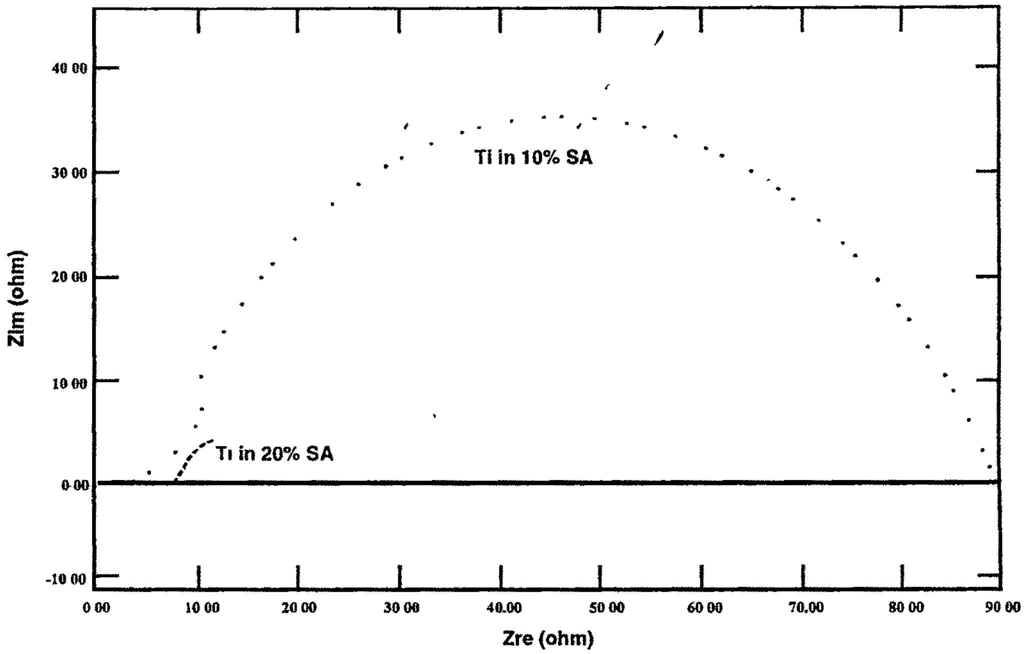


FIGURE 6.11 : NYQUIST PLOTS FOR Ti IN 10% & 20% H_2SO_4 SOLUTIONS

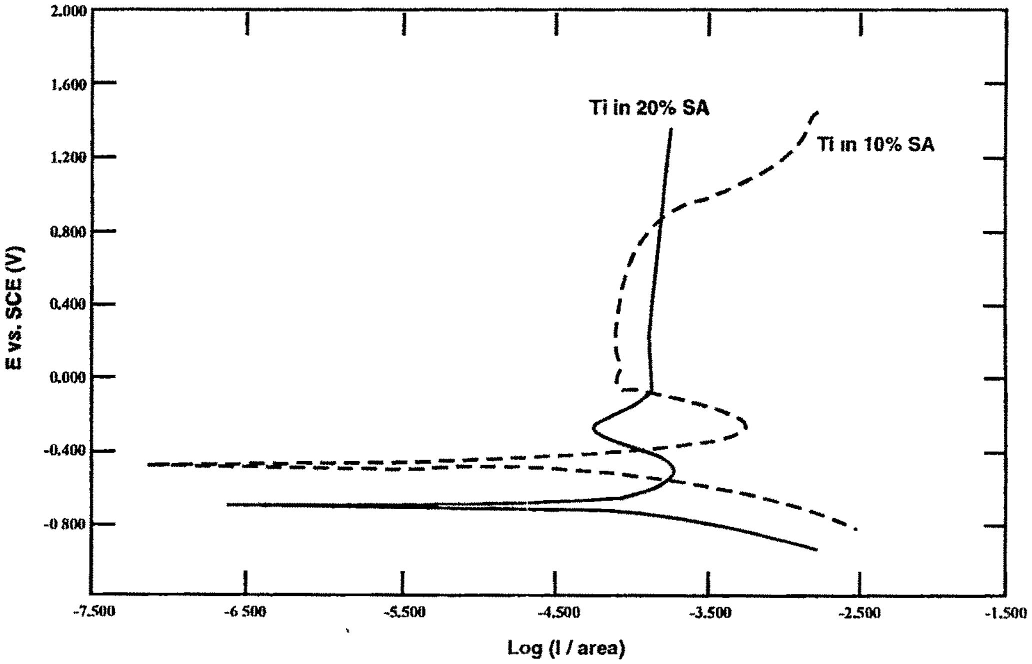


FIGURE 6.12 : POLARIZATION CURVES FOR Ti IN 10% & 20% H_2SO_4 SOLUTIONS

passive film producc in 10% acid solution is little superior than one generates in 20% acid solution.

Polarization curve for Titanium in 10 and 20% H_2SO_4 Solutions are given in fig. 6.12. It clearly shows that the metal is active in both the concentrations of acid. As rest potential values of metal are -0.4584V and -0.6616V, in 10 and 20% H_2SO_4 solutions respectively. Although critical current density (I_{crt}) is more in dilute acid but i_{corr} values are 0.7068 mA/Cm^2 & 0.801 mA/Cm^2 in 10 and 20% H_2SO_4 respectively, with corrosion rates are 54.66 and 72.86 mpy, differing by nominal amount in two cases. The passive current density-I_{pp} in case of dilute acid is less by relatively moderate amount. Thus overall corrosion rate, based on passive conditions is less in dilute than in concentrated acid solution. In other words, polarization studies point out that passivity attains in dilute sulfuric acid is better than in concentrated one by small amount. This is the same conclusion as drawn from EIS studies. But both the studies lead to the conclusion that titanium is resistance to reducing acid in low concentration range, like dilute sulfuric acid (< 10%) at room temperature. This inference matches with those reported in the literature (17,18).

6.2.2. Behavior of Ti-5Ta Alloy exposed to 10 % and 20% H_2SO_4 Solutions:

When this alloy is immersed in 10 and 20% sulfuric acid solutions and Nyquist plots are obtained, it is observed that they follow the same trend as titanium metal. That is plot in dilute acid (10%) has larger dimensions compared to plot for film engender in concentrated solutions (20%). Film on the surface of Ti-5Ta in 10% H_2SO_4 has $|Z|_{real}$ and $|Z|_{img}$ values 482.94 Ωand 272.0 Ωrespectively, which reduces to 37.36 Ωand 13.56 Ωas oncentration of solution increases from 10 to 20% acid. The values of Z_{ohmic} are 6.037Ωand4.022, where as diameter of semi circle fit are 487.9Ωand 40.16 Ωin 10 and 20% sulfuric acid solutions respectively.

Here again both the plots have semicircular nature, indicating a resistor and a capacitor in parallel connection in equivalent circuits of both the plots. But this time values of polarization resistance and double layer's capacitance are relatively higher than those of titanium metal.

This is obviously the effect of 5% tantalum present in the alloy. Being nobler than titanium, it increases cathodic reaction/s and reduces cathodic over voltage. Such cathodic depolarization increases the anodic reaction/s and promotes passive film formation, even in moderately severe conditions. Besides this tantalum is also prone to oxidation and the formation its stable oxide is thermodynamically feasible (12). Thus passive film generate on the alloy should be an admixture of oxides, imparting more impedance to flow of charge particles.

Since the available air/oxygen is less in concentrated acid solutions, film forms in this solution might be relatively thin or weak, resulting in the poor characteristics of it. Again, since Ti has poor resistance to corrosion in concentrated reducing acid, presence of 5% Ta which increases cathodic area/reactions, only nominally improves the passivity by increasing exchange current density or lowering cathodic over potential. When acid concentration is less (10%), a little more stable-strong passive film is available on the surface. Here more amount of naturally dissolved air is possible resulting in relatively thicker film formation and higher impedance values. Polarization curves for this alloy in 10% and 20% sulfuric acid solutions are shown in figure 6.14. Corrosion behavior of alloy in 10% H2SO4 solution is visible better than in 20% H2SO4 solution. The rest potential of alloy diminishes from +10.79 mV to -0.601 V as concentration of acid increases from 10% to 20%. Other electrochemical parameters, indicating corrosion rate like Icorr, Icrit and Ipp reduces with reduction in acid concentrations. Corrosion current density reduces from 57.54 MA/cm2 to 0.1245MA/cm2 whereas Icrit and Ipp diminishes by almost 2 to 1 order of magnitude respectively as acid concentration reduces from 20% to 10%. Here the reduction in Icorr and elevation of Icorr indicate that alloy behaves in more passive manner in dilute solution compared to in concentrated solution. At high anodic voltages both the curves slightly deviate which is not so sharp as to Cor considered as the indicative passivity breakdown. Thus in sulphusric acid alloy behaves like metal, exhibiting high potential for passivity breakdown.

This type of corrosion behavior of Ti-5Ta alloy is attributed to the fact that, tantalum present in the alloy makes it passive in dilute solution and therefore a rise in rest potential value by almost 0.6V is which is higher than the shift of Ecorr observed in case of metal. Moreover, it is exposure to environment

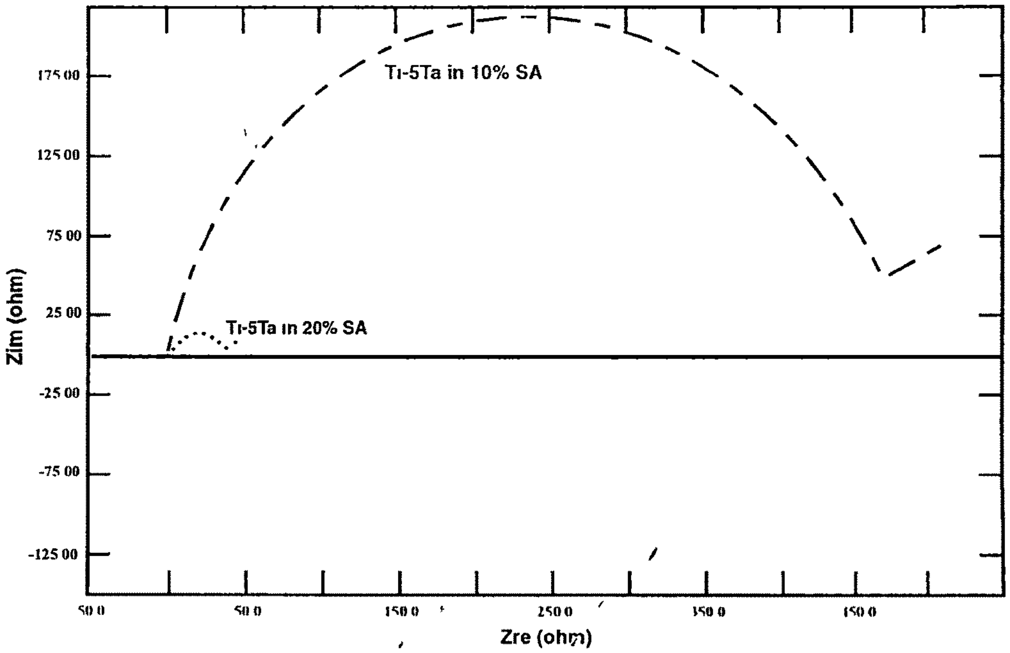


FIGURE 6.13 : NYQUIST PLOTS FOR Ti-5Ta ALLOY IN 10% & 20% H_2SO_4 SOLUTIONS

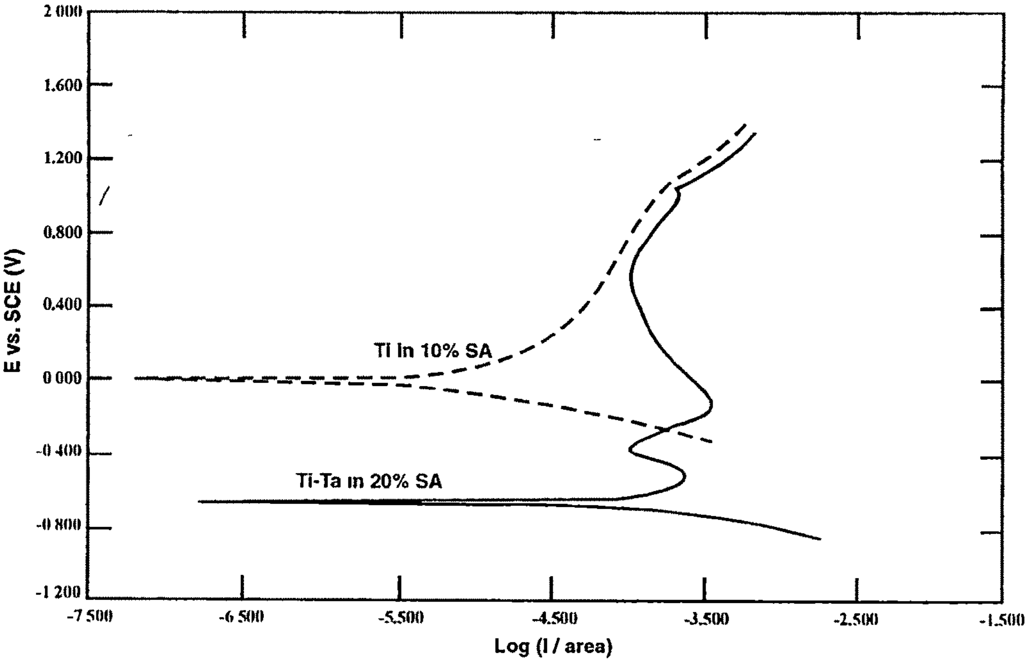


FIGURE 6.14 : POLARIZATION CURVES FOR Ti-5Ta ALLOY IN 10% & 20% H_2SO_4 SOLUTIONS

6.2.3 Comparison of Ti & Ti-5Ta in 10% & 20% H2SO4 solutions:

On super positioning the Nyquist plots of Ti and Ti-5Ta in 10% & 20% H2SO4, it is evident from figure 6.15 that the film formed at alloy Ti-5Ta on exposing to 10% H2SO4 provides best passivity surface, amongst all the seen Nyquist plot of this system is largest and involved W-element. On the other hand remaining three plots have semi-circular nature and much low values of impedances. Characteristics of passive film formed on both metal and alloy are better when exposed to 10% H2SO4. Also addition of tantalum provides further stability to the passivity with the result that, whether solution contains is 10% or 20% H2SO4 passivity attains by alloy is superior than that of metal in respective solution.

On comparing polarization curves of all four systems it is seen from the figure 6.16 that better passivity attains by both reducing concentration of acid and alloying the metal with 5% tantalum. Here the rest potential shifts towards nobler value in both the concentrations i.e. either alloying the metal or reducing the concentration of acid or both. At high voltages (+6V) although alloy show minor deflections in both the solutions, no significant indication of passivity break down is observed. That is intrinsic property of titanium is retained in all the systems.

This type of behavior of titanium metal and Ti-5Ta alloy is attributed to as mentioned before less aggressiveness of 10% H2SO4 and higher amount of naturally dissolved air/oxygen and cathodic depolarization owing to presence of tantalum in alloy.

Scanning Electron Microscopy of Ti and Ti-5Ta alloy in H2SO4:

SEM photomicrograph of metal Ti exposed to 20% H2SO4 shows intense corrosion. As shown in figure 6.17(X3300), deep tunnels are visible indicating high amount of dissolution of metal. There is no indication of presence of passive film and grain boundaries are also not seen. A couple of bright particles are present as corrosion product. Here again passivity is achieved at after going through making-breaking steps results in alternating to and fro shape of the polarization curve. But now final passive region (at high voltage) is accompanying with relatively higher current density, which is an indication of relatively poor quality of passive film.

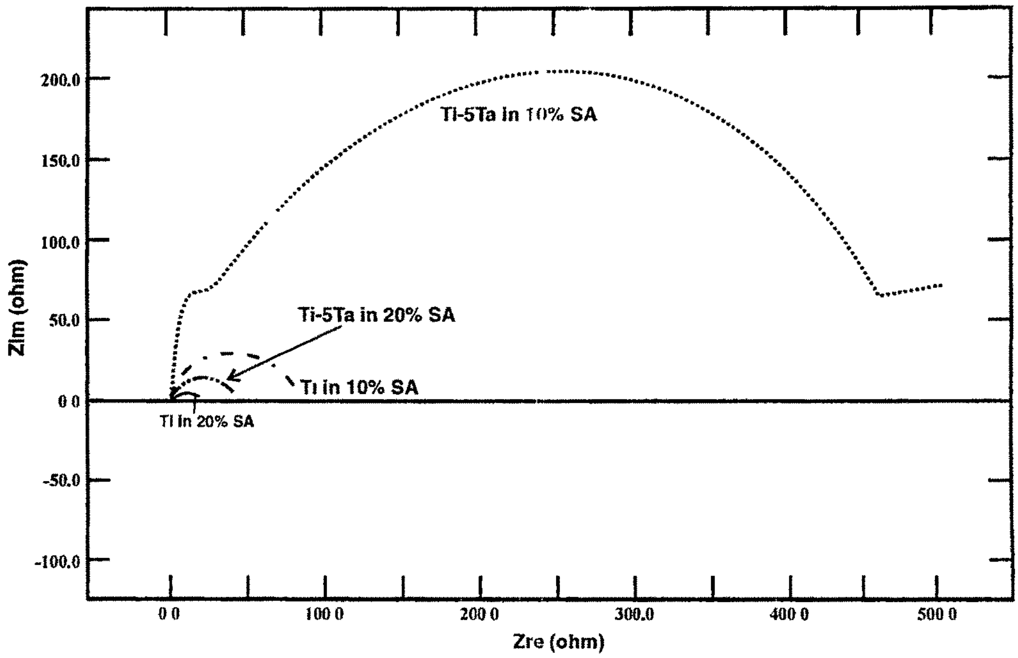


FIGURE 6.15 : NYQUIST PLOTS FOR Ti AND Ti-5Ta IN 10% & 20% H_2SO_4 SOLUTIONS

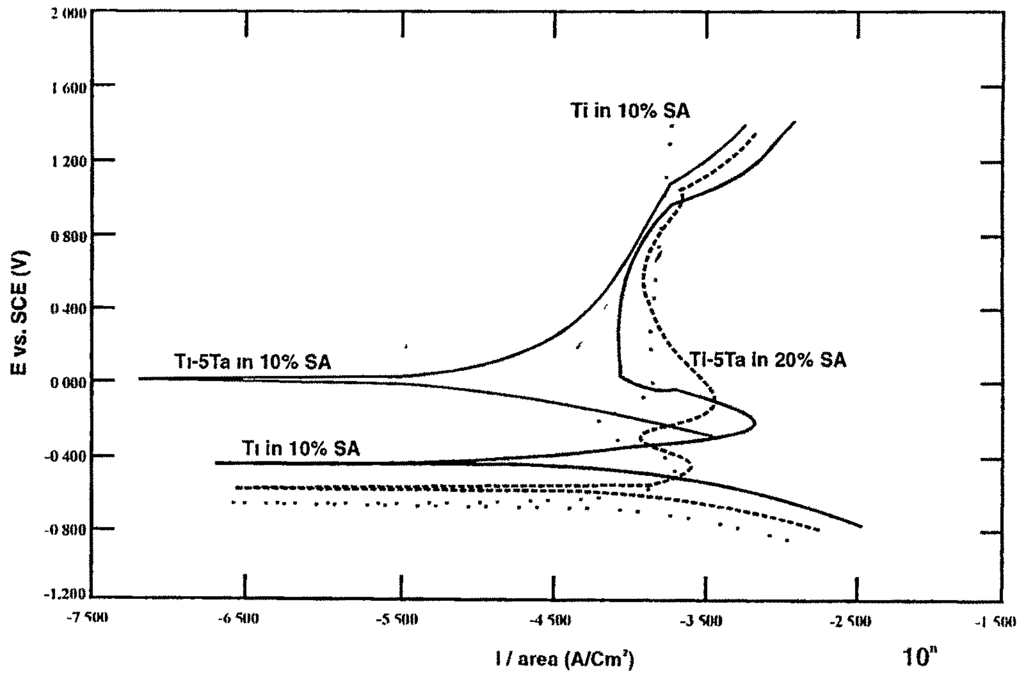


FIGURE 6.16 : POLARIZATION CURVES FOR Ti AND Ti-5Ta IN 10% & 20% H_2SO_4 SOLUTIONS

On the other hand, figure 6.18 shows SEM-photomicrograph of Ti-5Ta alloy at X1400 exposed to 20% H2SO4 solution. It shows hills & valleys type structure having feathery appearance on the top of the hills. Thus 20% H2SO4 attacks the alloy severely and passivity attains by the metal in this environment is very poor quality. It should be observed that no grain boundaries are visible indicating that some layer is present on the surface but being of poor quality it covers the surface only partially resulting in feathery nature at the hill's top. No such covering is seen in the valleys formed due to dissolution of metal. In short presence of this type of structure explain the polarization behavior of alloy. The representative polarization curve for Ti-5Ta exposed to 20% H2SO4 attains passivity with high current density and before this constant current density region, curve is having zig-zag shape, pointing out that film forms with difficulty and have poor quality even in final stage.

Thus, SEM photomicrograph of alloy infers that in sulfuric acid alloy is undergoing corrosion but attains better passivity than metal.

EDAX Results of Ti and Ti-5Ta alloy in H2SO4:

Both metal and alloy do not exhibit presence of any other element on their surface metal. Surface contains 100% Ti whereas alloy surface contains Ti and 5%Ta. It is therefore concluded that in 20% sulfuric acid environment both metal and alloy attain poor quality of passivity with high rate of corrosion. But relatively less in alloy than in metal due to presence of nobler alloying element tantalum.(Fig 6 19 & 6 20)

6.3 Passivity Behavior of Ti and Ti-5Ta in different grades of Phosphoric Acid.

Pure phosphoric acid at room temperature imparts passivity to titanium and its alloys. Therefore corrosion rate and electrochemical parameters indicate corrosion of titanium and titanium-5 tantalum alloy are having low values. But these values increase with temperature as breakdown of passivity occurs.

The impurities, particularly halide ions, in phosphoric acid also causes passivity break down and accelerate the corrosion rate. The change in corrosion rate depends upon concentration of halogenic acid and free halide ion concentration, their chemical reactivity and ionic size (17).

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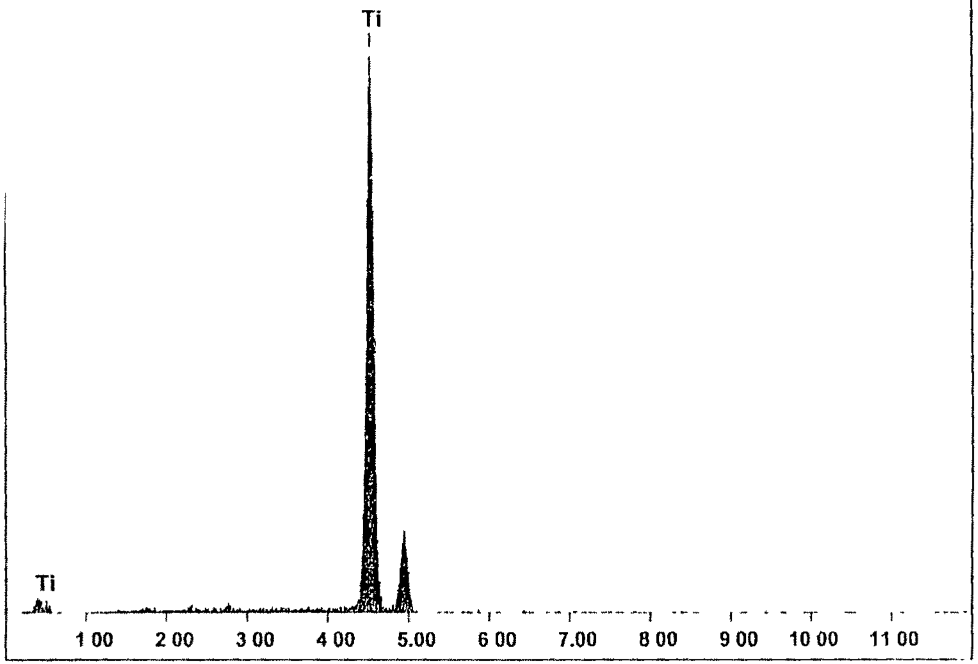
TEST REPORT

C:\EDAX Results\2002\May\0507TiH2SO4.spc

Label:Ti - H2SO4

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

FS : 1499 Lsec : 29 5-Jul- 2 15:52.10



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
TiK	100.00	100.00	1 0000	1.0000	1.0000	1.0000
Total	100.00	100.00				

Fig:6.19

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CHARUTAR VIDYA MANDAL
Vallabh Vidyanagar - 388 120

EDS TEST REPORT

C:\EDAX Results\2211SR1a.spc

Label:Ti 5% -Ta Alloy in H_2SO_4

kV:30.0 Tilt:0.0 Take-off:34.6 Det Type:SUTW+ Res:127 Tc:100

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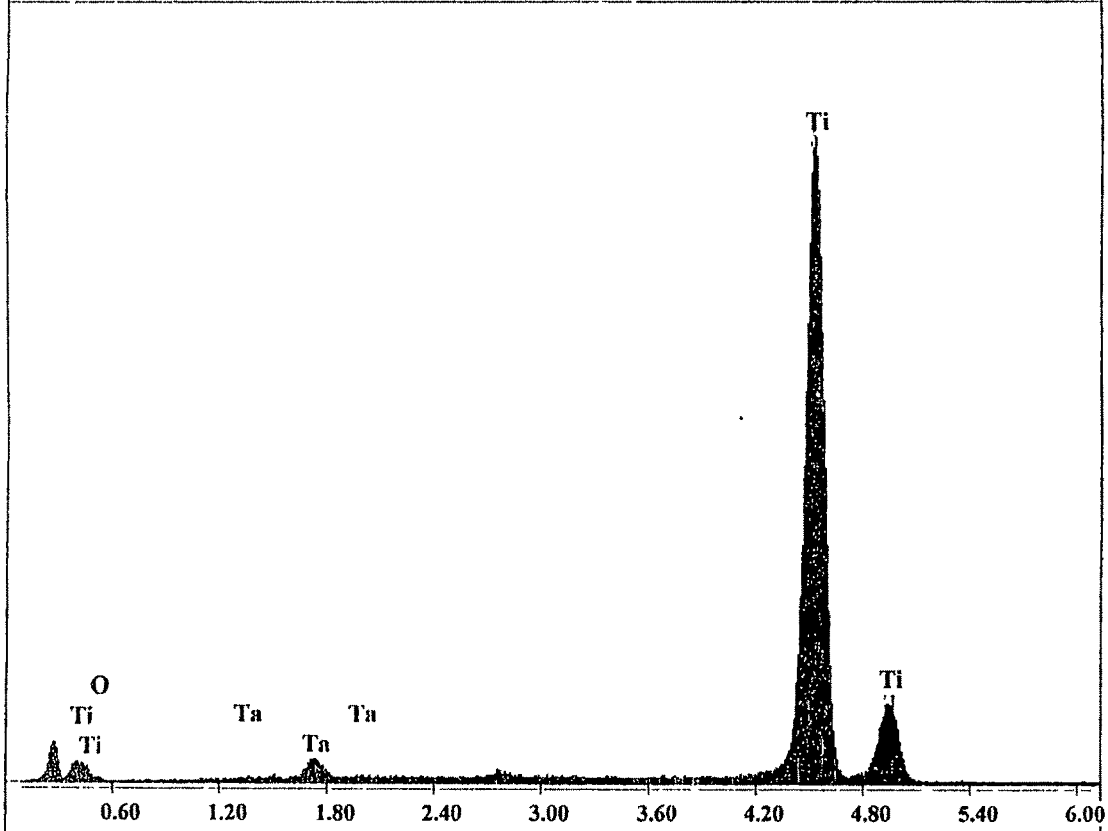

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	5.48	15.46	0.0039	1.1491	0.0627	1.0001
TiK	87.91	82.89	0.8445	0.9979	0.9607	1.0020
TaL	6.62	1.65	0.0537	0.8355	0.9708	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	4.54	0.97	9.31	4.67
TiK	1354.93	9.38	0.49	144.46
TaL	16.58	4.67	5.01	3.55

Fig:6.20

In manufacturing phosphoric acid by wet process method, based on digestion of phosphate rock in H_2SO_4, impurities like halides (particularly F and Cl) and sulfuric acid are invariably present. The degree of purity in the phosphoric acid finally obtained depends upon the phosphates rock composition and acid used. The corrosivity of halide ions (X^-) and halogen acid (HX), formed with H^+ ions present in strong mineral oxygenated-acids like H_3PO_4 $^{(17)}$ is related to their physico-chemical properties.

The net corrosivity of impure commercial phosphoric acid is a result of synergistic effect of all these factors. Hence the attainment of passivity and resulting corrosion rate are based on impurity level of phosphoric acid. Of course, in the same environment the metal and alloy behave differently.

6.3.1. Passivity Behavior of Titanium in phosphoric acid.

Nyquist plots obtained for Ti in Lab grade pure and commercial grade impure phosphoric acid, using EIS are shown in figure 6.21. According to this plot, passivity attains by titanium in Lab grade pure acid is much better and offers much higher impedance to flow of charge particles accountable for corrosion. This fact is indicated quantitatively by values of $|Z|_{real}$ and $|Z|_{img}$ components of titanium in two types of acids. In pure lab grade acid $|Z|_{real}$ is 323.41 Ω and $|Z|_{img}$ is 166.34 Ω where the values in impure commercial grade acid are $|Z|_{real}$ 138.50 Ω and $|Z|_{img}$ 73.99 Ω The $|Z|_{ohmic}$ values are 44.72 Ω and 18.77 Ω with diameters of semi-circle fit 543.15 Ω and 71.03 Ω respectively in lab grade pure and commercial grade impure acids. These quantitative figures clearly infer that, pure acid provides a passive film on titanium, which has much better characteristics than one generated in impure acid.

Considering nature of the plots none of the plots has regular semi-circle shape. In both the cases initially semi circle forms, but later on as frequency decreases, plots deviate and follow a path along the lines inclined by nearly 45°. Accordingly, both the plots should contain a 'W' element in their equivalent circuit. The main difference in these two plots is the values of real and imaginary components of w-impedance. When metal is immersed in lab-grade pure phosphoric acid, passive layer forms by secondary reactions/diffusion polarization is well compact, adherent and non-porous. Offering larger barrier to charge flow leading to higher total impedance and its

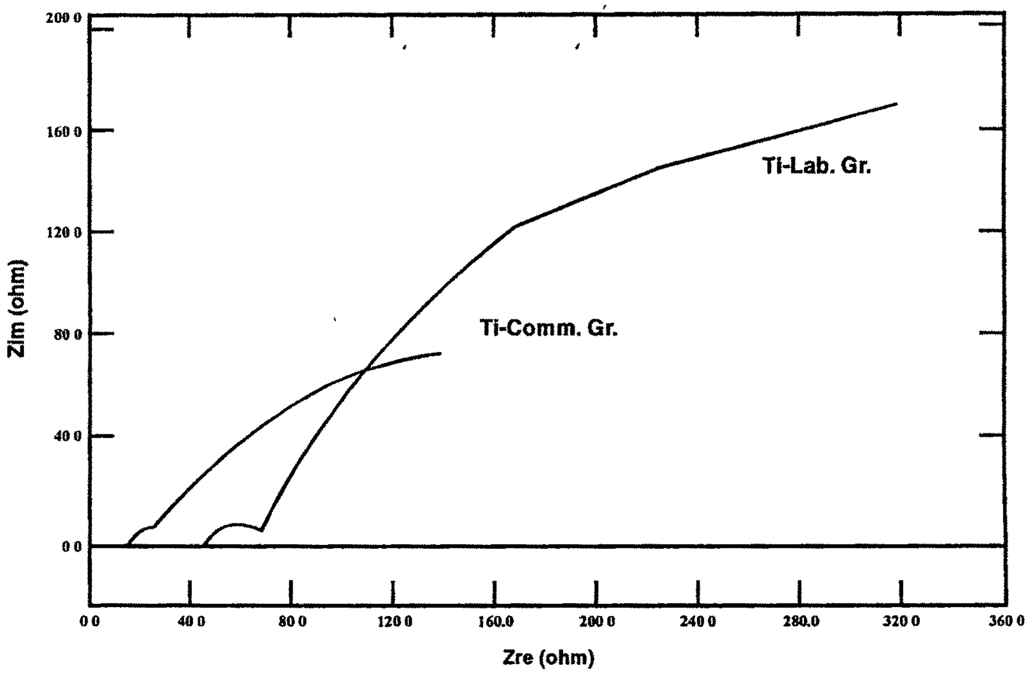

FIGURE 6.21 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

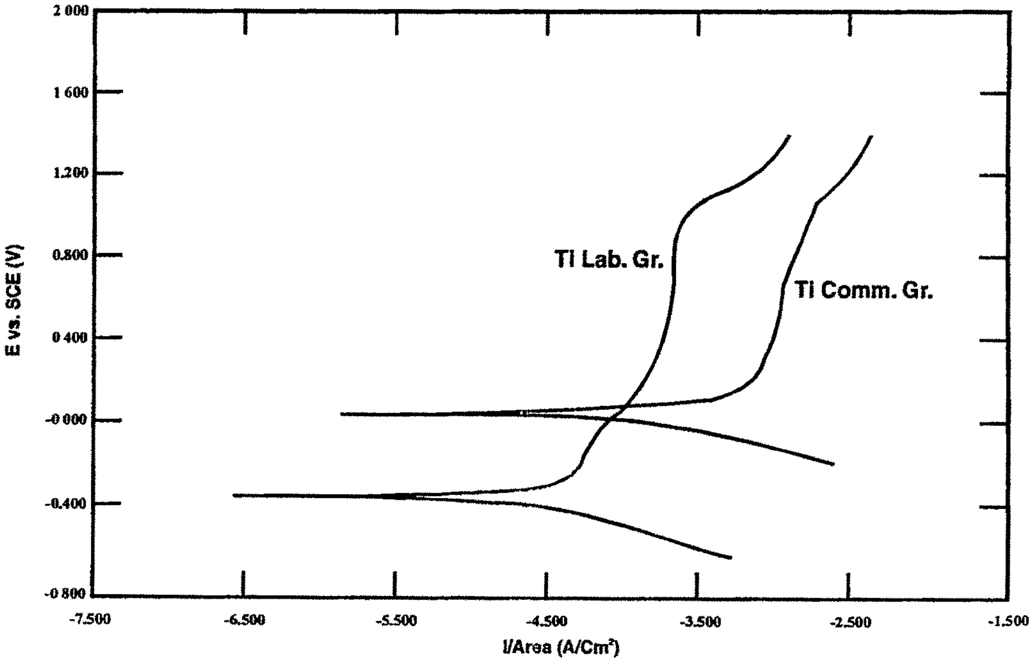

FIGURE 6.22 : POLARIZATION CURVES FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTION.

components. Whereas in commercial grade acid, these values are relatively very small. Indicating that film formed by secondary reactions is not of good quality. Thus in the former case, as observed from figure 6.21, W-element is much higher compared to that of in latter case of exposing metal to commercial grade acid system. Although initial semi circles in former system is smaller. In other words, firstly metal corrodes at high rate in pure acid but as the film grows it offers more impedance resulting in higher values of W-element compared to value of W-element in metal - commercial grade acid system.

Polarization curve of titanium in two grades of phosphoric acid are exhibited in figure 6.22. It can be observed that electrochemical parameters, which directly indicate corrosion, like I_{corr}, I_{crit} are decreasing in case of lab grade acid metal system. Except E_{corr} value, which is nobler in case of commercial grade acid-metal system, i.e., metal is passive in commercial grade acid. With E_{corr} value of 47.24 mV as compared to E_{corr} value equal to

- 0.2419V in lab-grade acid. This may be ascribed as by the fact that owing to higher concentration of acid in lab grade solution than commercial grade solution on exposure immediately metal exhibits active state and corrodes at faster rate, but as corrosion product build up and engender passive film, corrosion rate reduces with respective electrochemical parameters. Besides this, impurities present in grade-2 type titanium, particularly Fe and Al, form complexes with fluoride ions and reduce its aggressiveness (17). Thus initially titanium grade-2 behaves like a passive metal owing to presence of small amount of Fe. Such passive behavior of Titanium offers low corrosion rate of 9.350 mpy in lab grade acid compared to 37.36 mpy offered by impure commercial grade acid. Similarly, Icorr value is also less (27.38 $\mu A/cm^2$) in lab grade acid than in commercial grade acid (0.1089 mA/cm^2).

This explanation of passivity behavior matches well with Nyquist plots of two systems consist of small semi circle initially followed by divergence as described in previous paragraphs. In other words, polarization studies give the same inference as revealed by EIS studies.

Such behavior of Titanium in two types of phosphoric acid is due to formation phosphate of Ti which is insoluble and form an intact, adherent and stable film(18) on the surface. But in presence of halide ions, in the solution, they adsorb quickly on metal surface in competition with phosphate ion or dissolved oxygen, as both the molecules are relatively larger in size. This adsorption increases exchange current density and critical current density for anodic dissolution (3). In such conditions passivity break down occurs resulting in rise in corrosion rate in impure phosphoric acid. But in pure lab grade acid no such event takes place and resulting passive layer retains without any break down.

6.3.3. Passivity Behavior of Titanium-5 Tantalum Alloy in different grades of H_3PO_4.

Upon exposing this alloy to lab grade and commercial grade phosphoric acids, respective Nyquist Plots obtained are presented in figure 6.23. It can be observed that alloy follow the same trend as titanium metal, i.e. alloy attains better passivity in lab grade pure acid compared to that in impure commercial grade acid. In this case of alloy plots are having impedance components values in killo-ohms. The commercial grade acid system, shows peak value of $|Z|_{real} = 4.416$ KΩ and $|Z|_{img} = 1.299$ KΩ with ohmic resistance 15.41 ohm and diameter of semi circle fit is 5.41KΩ While in pure lab grade acid the $|Z|_{real}$ is 4.804 KΩ, $|Z|_{img}$ is 1.78 KΩ, ohmic resistance is 35.65 ohm and diameter of semi circle fit is 6.99 KΩ As far as nature of the Nyquist plots are concerned, both are running parallel to each other, one in lab grade acid has some what higher value than the other plot of commercial grade acid - alloy system. Both the plots are semi circle type and therefore they should be modeled as equivalent electrical circuit consisting of two parallel paths for flow of current. One path includes resistor - representing resistance of the passive film and the other includes double layer capacitance of the film.

Such nature of Nyquist plots, quite different than those of titanium is indicative of the fact that alloy, unlike metal, gets passive state as soon as it is exposed to other type of acid. In other words, alloy Ti-5Ta is passive in both kind of acid environments. This passivity grows further on application of anodic voltage.

Figure 6.24 shows the polarization curves for this alloy in two kinds of phosphoric acid. In lab grade acid, rest potential of alloy is - 0.1325 V, which is higher by about 0.26V than rest potential of alloy in commercial grade acid (-0.3948V).

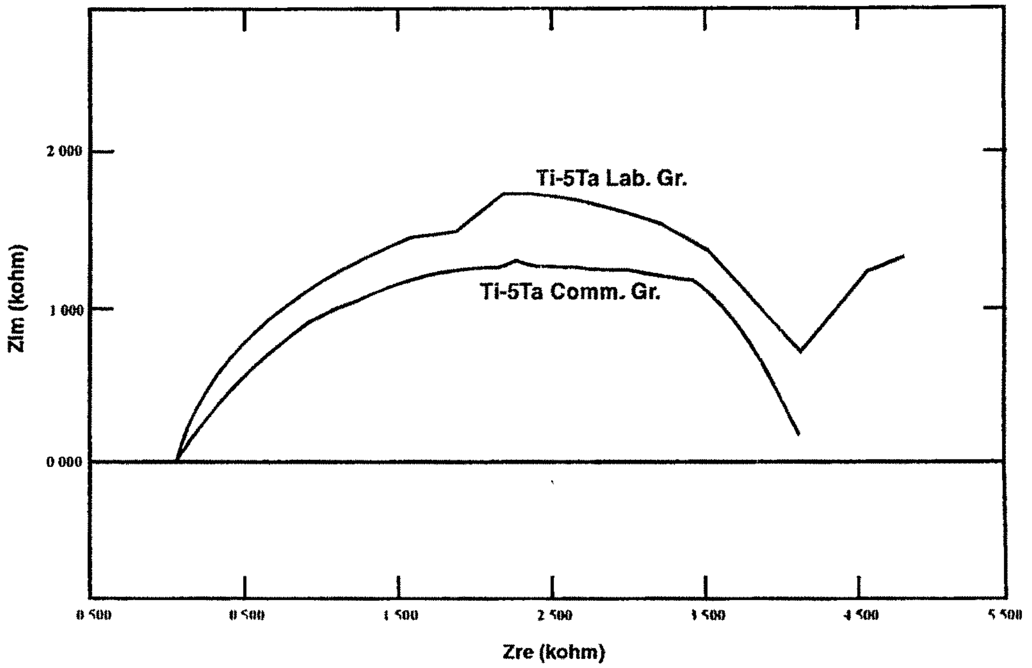

FIGURE 6.23 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

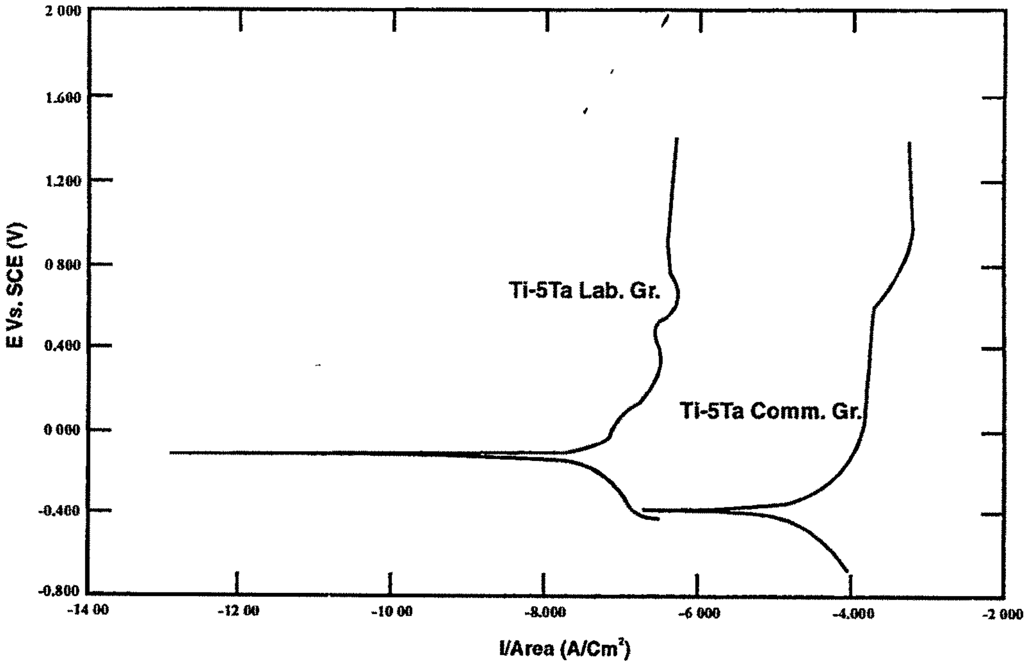

FIGURE 6.24 : POLARIZATION CURVES FOR Ti-5Ta IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

Likewise, I_{corr} is 120.90 μA in commercial grade acid, which reduces to 39.22 μA in lab grade acid i.e. by 3 orders of magnitude. The other parameters related to corrosion rate are also less in pure acid. All these values of electrochemical parameters indicate that corrosion rate in lab grade acid (13.47 x 10^{-3} mpy) is much less than in commercial grade acid (7.192 mpy).

In general, Ti-5Ta alloy attains much better passivity and very low corrosion rate in lab grade acid. Such behavior of alloy is ascribed by the presence of alloying element Ta. Being nobler metal and highly resistance to many environments, it provides large cathodic area on the surface and enhances cathodic depolarization and decrease in cathodic over voltage. These interlink phenomena lead to rise in anodic current density, which easily crosses the critical current density and approach stable passive region. Besides this, in commercial grade acid as halide ions get adsorbed on electrode surface, does not effect various current densities values as tantalum is nobler metal and having low critical and exchange current densities even in chloride and fluoride ion (at room temperature) environment (19). Also it is observed from the figure that passive current density shift toward reduced value by almost 2 orders of magnitude as environment changes from commercial grade to lab grade acid. It means the full passivity is attained by alloy and it practically becomes immune to the surroundings.

Thus it can be concluded that alloy exhibits very good corrosion resistance in both kind of acids but has better performance in lab grade acid. All these results of polarization studies match with results of EIS studies.

6.3.3. Comparison of Passivity Behavior of Ti and Ti-5Ta alloy exposed to H_3PO_4:

Overlaying of Nyquist plots for Ti on Ti-5Ta alloy is exhibited in figure 6.25. It clearly show the superior passivity behavior of alloy in both the acids with and without halide ions. This is solely due to the presence of 5% tantalum in the metal. Tantalum is otherwise a noble metal and is affected only by strong alkali and hydrofluoric acid in hot conditions i.e. it behaves like a glass with respect to its corrosion properties towards chemical environments. Moreover, in absence of halide ions both, titanium as well as alloy, are exhibiting better quality film. Hence amongst all four systems, alloy exposed to lab grade acid system has the best characteristics as indicated by figure.

Chemistry of passive film formed in phosphoric acid (18) reveals the formation of metal-phosphates, involving electro-negative metallic ions forming strong ionic bond with phosphate ions. In the present case metal Ti has high electro negativity (+3 in reducing environment) and phosphate ion also has high oxidation state (-3 in ortho-acid). Thus, resultant product namely, titanium phosphate must have good stability, under the favorable conditions and in presence of phosphorus probability of metal phoshpide formation also increases. Here also strong ionic bond exists between +3 oxidation state of metal and –3 oxidation state of phosphorus indicating the stability of product (20). Both phosphate and phosphide of many metals are insoluble in many aqueous media (21) and adhere well on substrate with strong ionic bond. Alloy involves tetra-valent tantalum along with titanium, which is having higher oxidation power. Therefore, forming more stable and stronger passive film having better impedance and less effect of fluoride ions, if present, than in case of titanium alone.

Super positioned polarization curves for Ti and Alloy, in lab grade and comm.-grade acids, are shown in figure 6.26. Accordingly the rest potential exhibited by titanium in comm. grade acid is the only exception and the reasoning for the same has given above. While all other electrochemical parameters, indicative of corrosion rate, are low in case of alloy exposed to lab grade acid resulting in corrosion rate of 11.59 $x10^{-3}$ mpy. It is also seen from the figure that behavior of metal in lab grade acid is almost similar to that of alloy exposed to comm. grade acid where as Ti in comm. grade acid exhibites least tability with highest corrosion rate (37.36 mpy).

These types of corrosion behavior of metal and alloy in lab and comm. grade H_3PO_4 acids have been0 already explained above. This is due to, nullifying effect of most aggressive F-ion by complex formation, cathodic depolarization leading to shift in potential to passive region and ensuring stability of film in case of alloy, formation of insoluble phosphates/ phosphides films, which are strongly bonded with surface and normally stable and other aspects mentioned therein. In short such corrosion behavior of metal and alloy confirms the results obtained by EIS studies.

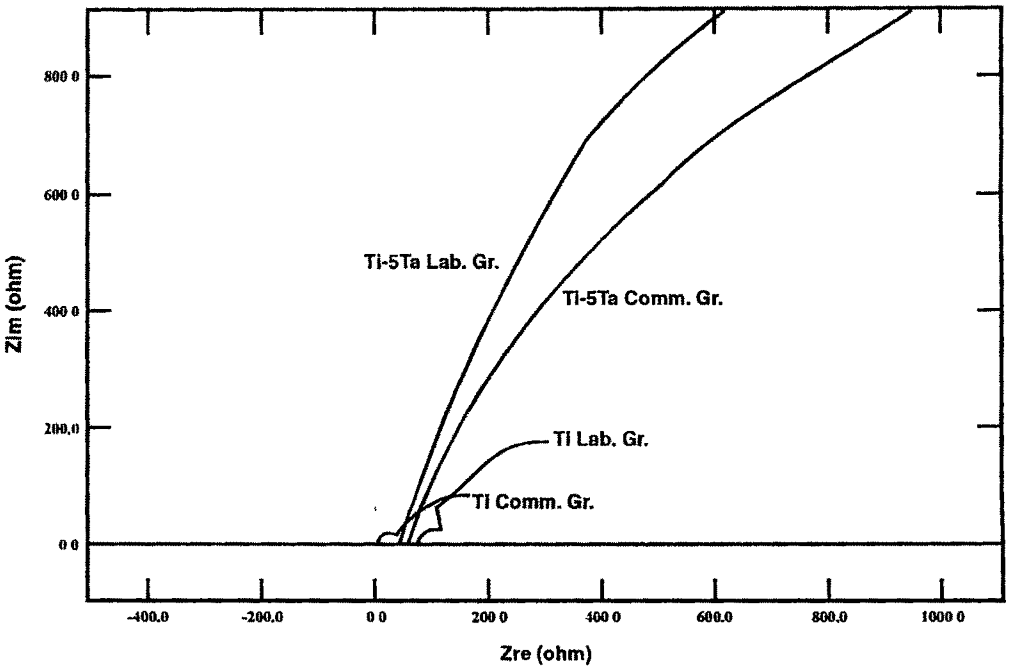

FIGURE 6.25 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

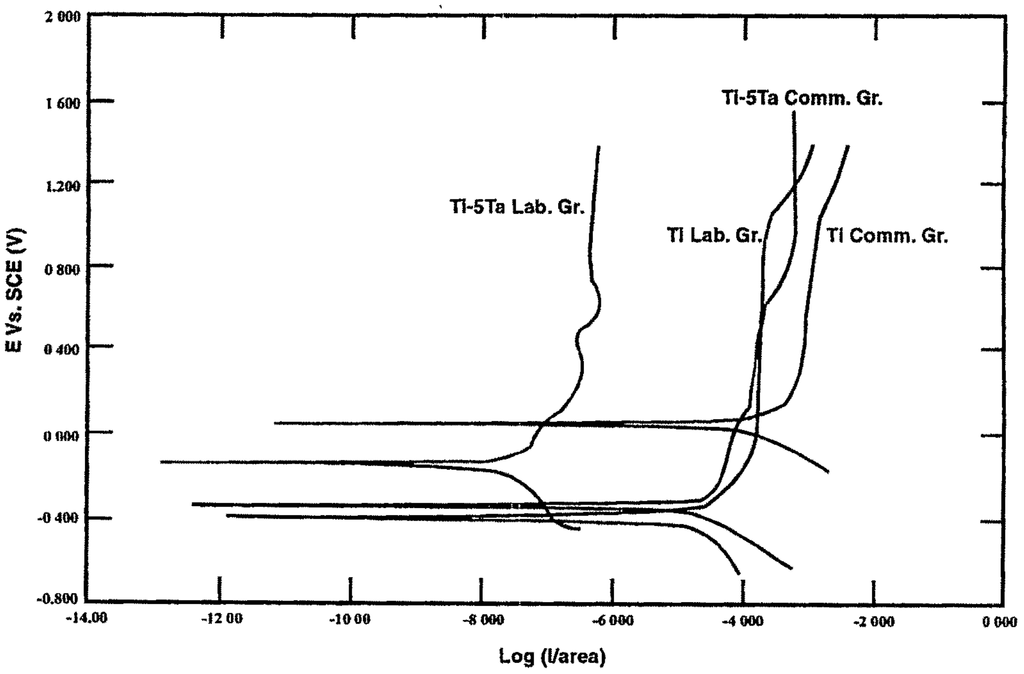

FIGURE 6.26 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

Scanning Electron Microscopy of Ti and Ti-5Ta Alloy Exposed to H_3PO_4:

Figure 6.27 shows the SEM-photomicrograph of metal titanium exposed in commercial grade phosphoric acid at X4500, it shows two distinct regions A and B. In A region, film formed on the specimen of Ti is clearly revealed from this part of figure. Here each grain has been coated with the film but at grain boundaries film deposition is poor and therefore are neatly seen in the micrograph. In the second region, B, the micrograph shows the deterioration of the film and it is consisting of corrosion product (bright).

As described earlier that many metals form insoluble phosphate in this acid and if metal is having high electro negativity, then it will also form phosphide in favorable conditions. It is, therefore, most like that chemistry of the film generated on grains must be of metal-phosphate or phosphide type or both. As titanium is active and possess high electro negativity (member of IVth A group) so it is apt to form phosphate.

Again, as passive film formation depends upon the corresponding structural homogeneity of the surface on which it forms. Poor film is forming along the grain boundary. The damage of film is seen more clearly by focusing this area at the same magnification (X4500). Almost similar SEM photomicrograph for Crevice Corrosion in 904L steel has been narrated by.

Figure 6.28 is presenting SEM micrographs of alloy Ti-5Ta at high (X3300) magnifications. Passive film is neatly observable with some pit holes. Some corrosion product also appears adjacent to holes as bright particles. It is interesting to note that holes are neither uniform in shape nor in depth. Some holes are shallow in depth while others are deep. But overall their number is less; passive film is more uniform and exhibits less damage compared to micrograph of metal. Thus it can be concluded that phosphate passive film forms in both metal and alloy surfaces and it is more uniform and less damaged in case of alloy than in the case of metal.

EDAX Results of Ti and Ti-5Ta Alloy Exposed to H_3PO_4:

Elemental analysis of alloy surface reveals presence of 17.87% O, 1.11% P, 8.02% Ta and balance Ti. This result confirms the presence of phosphate on the surfaces. As amount of oxygen present is higher than that needed for merely the formation of phosphate ion (PO_4). Hence it indicates formation of oxides of Ti, Ta or both on the surface along with phosphate. It is also interesting to note that; surface gets enriched with Ta as its concentration rises from 5% to 8%.

On the other hand analysis of titanium surface proclaim presence of 15.27% O, 7.26% P and 77.47% Ti. According to this analysis, amount of phosphorus is on higher side and of oxygen is on lower side than that needed for formation of Ti-phosphate. Therefore formation of phosphide is established, as this is the most likelihood alternate event.Thus, EDAX results also point out the same facts as revealed by Polarization, EIS and SEM studies. (Fig 6.29 & 6 30)

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EDS TEST REPORT

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Label:Ti H3PO4

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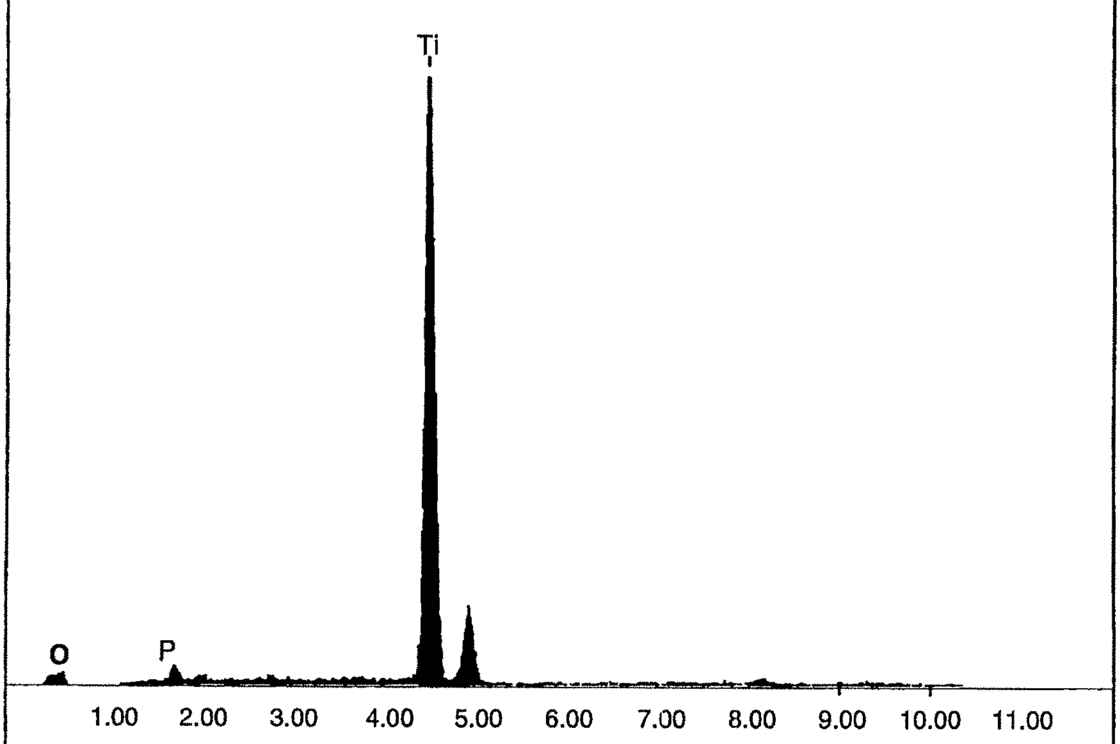

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	15.27	36.54	0.0121	1.1310	0.0703	1.0001
P M	7.26	1.54	0.0516	0.8630	0.8225	1.0010
Ti K	77.47	61.93	0.7328	0.9813	0.9616	1.0024
Total	100.00	100.00				

Fig:6.29

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EDS TEST REPORT

C:\EDAX Results\2002\May\0507TiH3PO4.spc

Label:TiH3PO4

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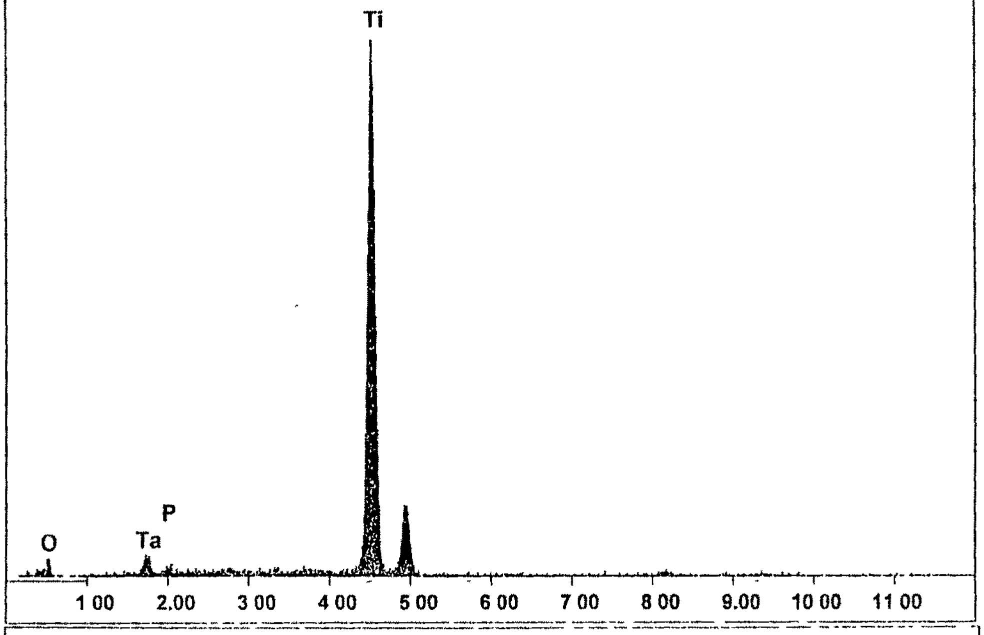

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	17.87	41 05	0.0148	1.1260	0 0736	1.0001
TaM	8 02	1 63	0 0577	0.8592	0.8366	1.0010
P K	1.11	1.32	0.0057	1.0504	0.4860	1.0109
TiK	73.00	56.00	0.6828	0.9767	0.9552	1.0026
Total	100 00	100.00				

Fig.6.30

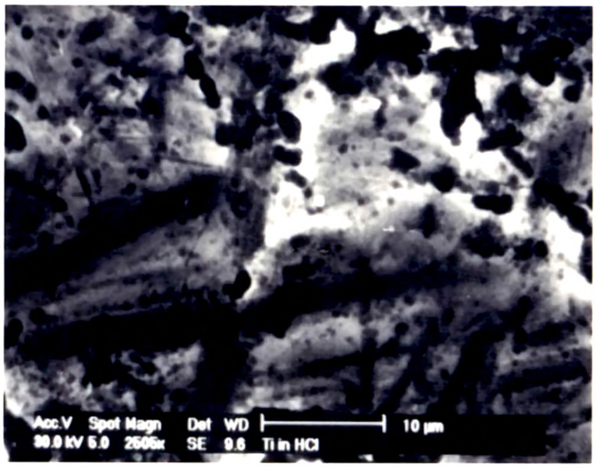

Figure - 6.7 :
SEM Photomicrograph
of Ti in 10% HCl

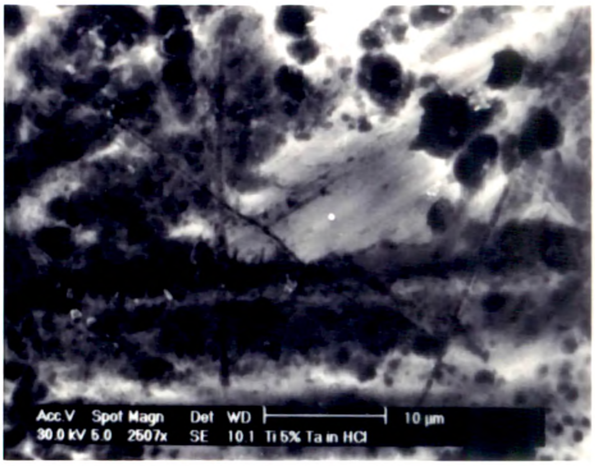

Figure - 6.8 :
SEM Photomicrograph
of Ti - 5Ta in 10% HCl

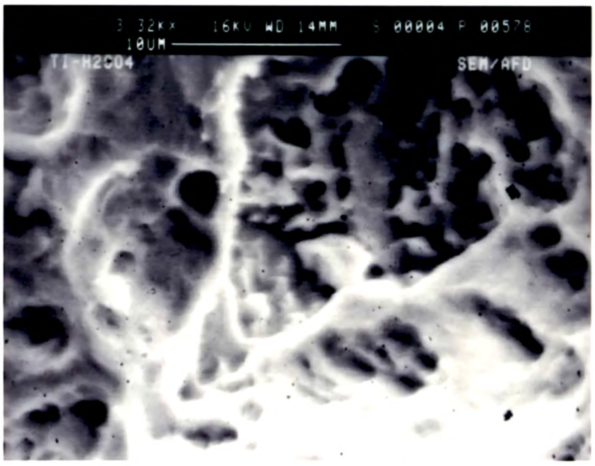

Figure - 6.17 :
SEM Photomicrograph
of Ti in 20% H_2SO_4

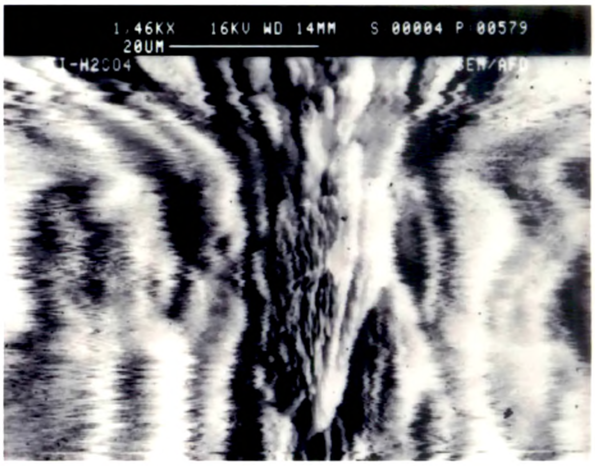

Figure - 6.18 :
SEM Photomicrograph
of Ti - 5Ta in 20% H_2SO_4

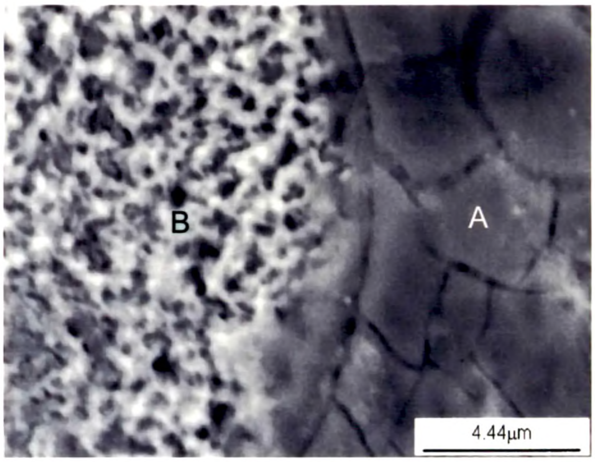

Figure - 6.27 :
SEM Photomicrograph
of Ti in Comm. Gr. H_3PO_4

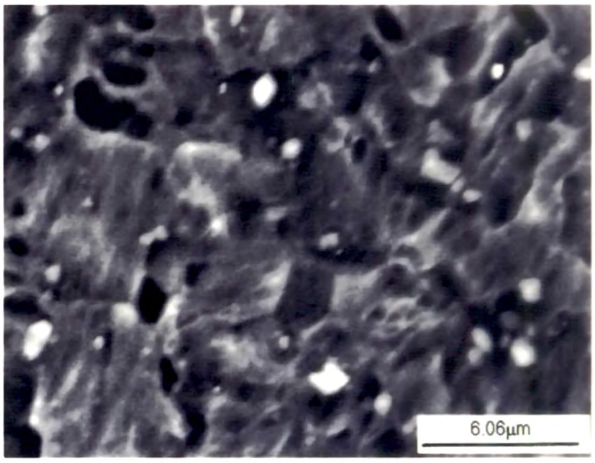

Figure - 6.28 :
SEM Photomicrograph of
Ti - 5Ta in Comm. Gr. H_3PO_4

TABLE -6.1: ELECTROCHEMICAL IMPEDANIC DATA FOR TITANIUM AND Ti – 5Ta ALLOY

	TITANIUM				TI-5Ta ALLOY			
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	129.78	61.24	4.61	142.94	346.25	156.24	5.12	640.58
10%Hcl	42.32	19.72	2.98	59.87	123.84	28.71	3.33	130.13
10%SA.	78.94	34.18	5.831	80.28	482.94	272.00	6.037	487.9
20%SA	13.68	3.727	4.517	22.24	37.36	13.56	4.022	40.16
Lab-grade PA	323.41	166.34	44.72	543.15	4.806 k	1.780 k	35.65	6.99 k
Comm. grade PA	138.50	73.99	18.77	71.03	4.416 k	1.229 k	15.41	6.416 k

Table 6.2 : ELCTROCHEMICAL POLARIZATION DATA FOR TITANIUM AND Ti-5Ta ALLOY.

MATERIAL	TITANIUM			TITANIUM+5%TANTALUM		
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	**- 0.3941**	**18.71 x10^{-6}**	**12.12**	**- 0.385**	**11.45 x10^{-6}**	**8.05**
10% HCL	**- 0.4125**	**48.71 x10^{-6}**	**16.37**	**- 0. 410**	**15.65 x10^{-6}**	**10.61**
10%H_2SO_4	**-0.4584**	**0.7068x10^{-3}**	**54.66**	**10.79 x10^{-3}**	**57.54x10^{-6}**	**19.74**
20%H_2SO_4	**-0.6616**	**0.8012x10^{-3}**	**72.86**	**- 0.601**	**0.1245 x10^{-3}**	**43.02**
Comm. Gr. H_3PO_4	**47.24 x10^{-3}**	**0.1089 x10^{-3}**	**37.36**	**- 0.3948**	**20.90 x10^{-6}**	**7.17**
Lab. Gr. H_3PO_4	**-0.3419**	**17.03 x10^{-6}**	**5.845**	**- 0.1359**	**33.78 x10^{-9}**	**11.59 x10^{-3}**