CHAPTER – VIII

Analogy Between Passivity Behavior of Stainless Steel, Titanium and Titanium – Tantalum Alloy In Reducing Environment

Present research deals with evaluation of quality and nature of passive film formed on austenitic stainless steel and titanium before and after alloy additions like Mo in stainless steel and Ta in Ti. Both austenitic stainless steel and titanium show good passivity in oxidizing environment, which is attributed to formation of strong, well adherent Cr_2O_3 and TiO_2 films respectively on ASS and Ti. The nature and quality of the passive film is important when environment is aggressive, contains Cl^- ions in reducing acid [1]. Presence of 2%Mo and 5%Ta in 18-8 (type 304) stainless steel and Titanium respectively seems to improve the quality of existing passive films and show better passivity in this aggressive environment. A lot of literature are available [2] about superiority of austenitic stainless steel with 2%Mo (type 316) and Ti –5%Ta alloy [3] over 304 type stainless steel and titanium metal respectively with respect to pitting corrosion and high temperature conditions. However very little information is readily available about the nature and quality of the film formed on these alloys.

A.C.Impedence (EIS) technique is used to reveal polarization resistance and double layer capacitance of these strong films formed on alloys, while potentiodyne is used to measure general corrosion and passivity behavior in different reducing acidic conditions viz. hydrochloric acid, lower concentration of sulfuric acid and phosphoric acid with/without impurities, as these are considered to be aggressive environment. Addition of alloying elements seems to enhance the quality of film, and thereby corrosion resistance, which further improves by adding small amount of oxidizing agent HNO_3 (1%) in the medium in case of Ti and Ti-5%Ta alloy.

In this chapter an endeavor is made to evaluate change in passivation behavior in presence of Mo in stainless steel and Ta in titanium.

8.1 Passivity behavior of SS 304 and Titanium in Hydrochloric Acid in Presence of 2% Mo and 5% Ta respectively.

The Polentiodynemic plots of SS 304 and SS 316 in 5% and 10% HCL solutions are show in figure 8.1. In both concentrations of acid, the SS 316 shows better passivity than SS 304. The current density value for SS 316 is approaching less than 10^{-3} A/cm^2 compare to 10^{-2} A/cm^2 value of SS 304. The effect is more predominant in lower concentration of acid compare to higher concentration (10%) of HCl solution. The EIS (Nyquist) plot for these steels is given in figure 8.2, which reveals that value for $|Z|_{real}$ and $|Z|_{img.}$ are 82.8Ω and 68.7Ω for SS 316 and are 47.2Ω and 22.5Ω for SS 304 in 10% HCl solution, indicating that films formed on SS 316 is of better quality than that formed on SS 304. Moreover there is a presence of W-component in SS 316 as indicated by the nature of Nyanist plot. Thus additional parallel resistance – conductance loop is present in the basic electric equivalent circuits. This confirms the presence of additional diffusion mechanism in case of SS 316, which may be due to the formation of Mo_2O_3 over and above Cr_2O_3 film on the surface of SS 316, imparting better quality and improved nature of the passive film in this case. The EDAX results already given previous chapter also confirm the presence of Mo and Oxygen in the surface of SS 316.

Figure 8.3 shows potentiodynemic results of titanium and titanium-5 Tantalum alloy is 5% and 10% HCl solutions. No passivity breakdown is observed in either case up to 1600mV, showing better nature and quality of Ti and Ti-5Ta than stainless steel. The passive current density in titanium is around 10^{-4}, which shifts to 10^{-5} in case of Ti-5Ta alloy. This reduction of one magnitude indicates that Ti-alloy is having more corrosion resistance than metallic Ti. This fact is confirmed by evaluating the quality of the film formed on these materials with the help of EIS (figure 8.4). The $|Z|_{rcal}$ and $|Z|_{img.}$values for Ti and Ti-5Ta in the figure indicates that R_p is around 120Ω and Cdl is 40Ω in Ti and the corresponding value for Ti-5Ta are more than 150 Ω and 120 Ω respectively. It means the quality of film formed on alloy surface is superior to that of Ti metal and imparting better corrosion resistance to the alloy. The film formed on alloy is seems to be more intact and adherent due to Ta-oxide formation, which is confirmed by presence of double loop in the Nyunist plot. The second loop confirms

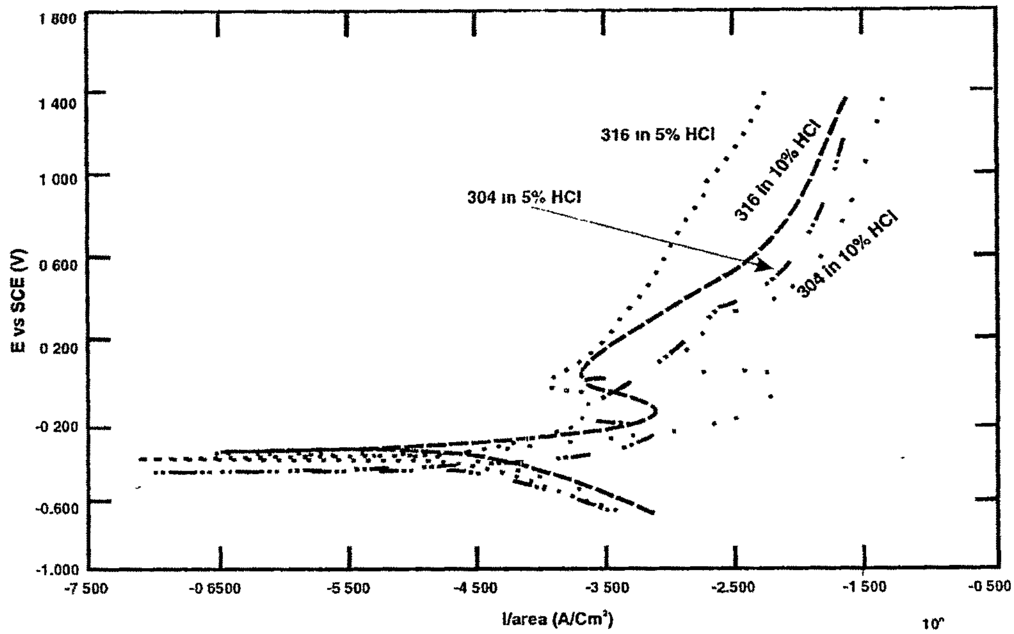


FIGURE 8.1 : POLARIZATION CURVES FOR SS 304 AND 316 IN 5% & 10% HCl SOLUTIONS

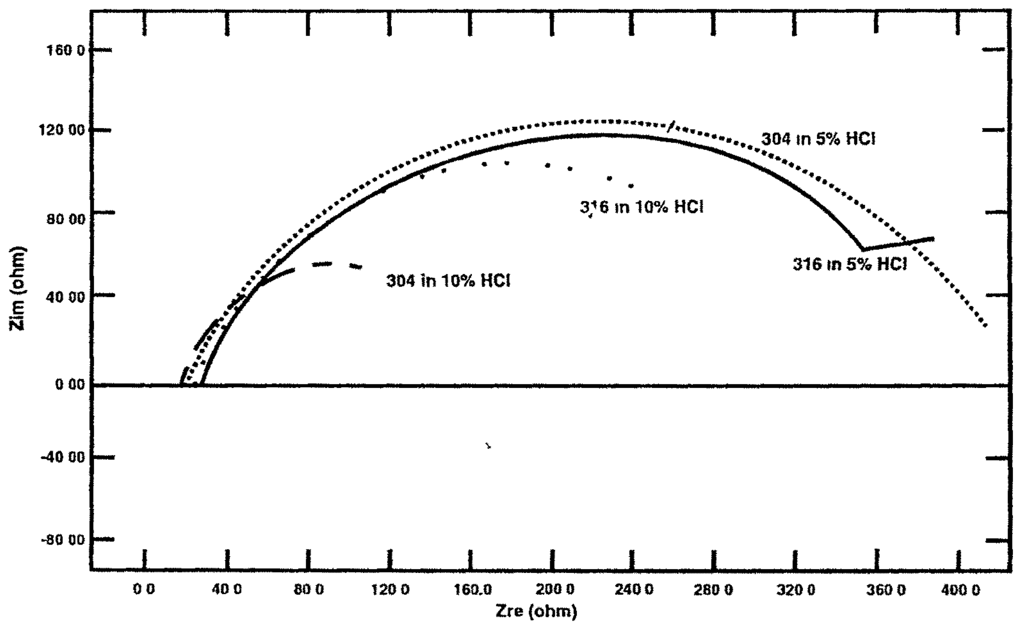


FIGURE 8.2 : NYQUIST PLOTS FOR SS 304 AND 316 IN 5% & 10% HCl SOLUTIONS

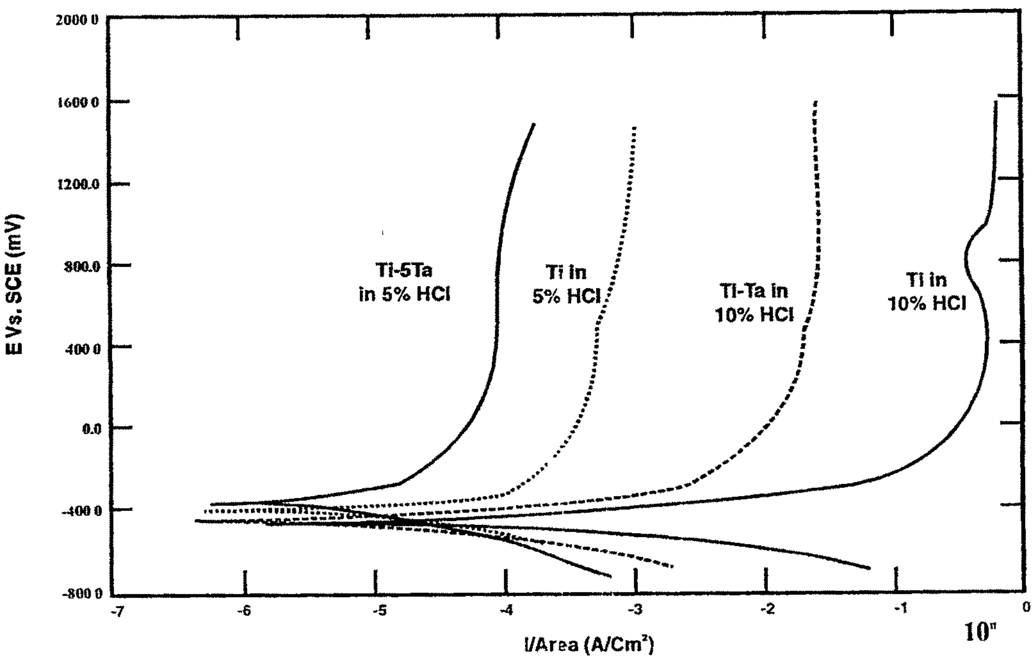


FIGURE 8.3 : POLARIZATION CURVES FOR TITANIUM AND Ti-5Ta IN 5% AND 10% HCl SOLUTIONS.

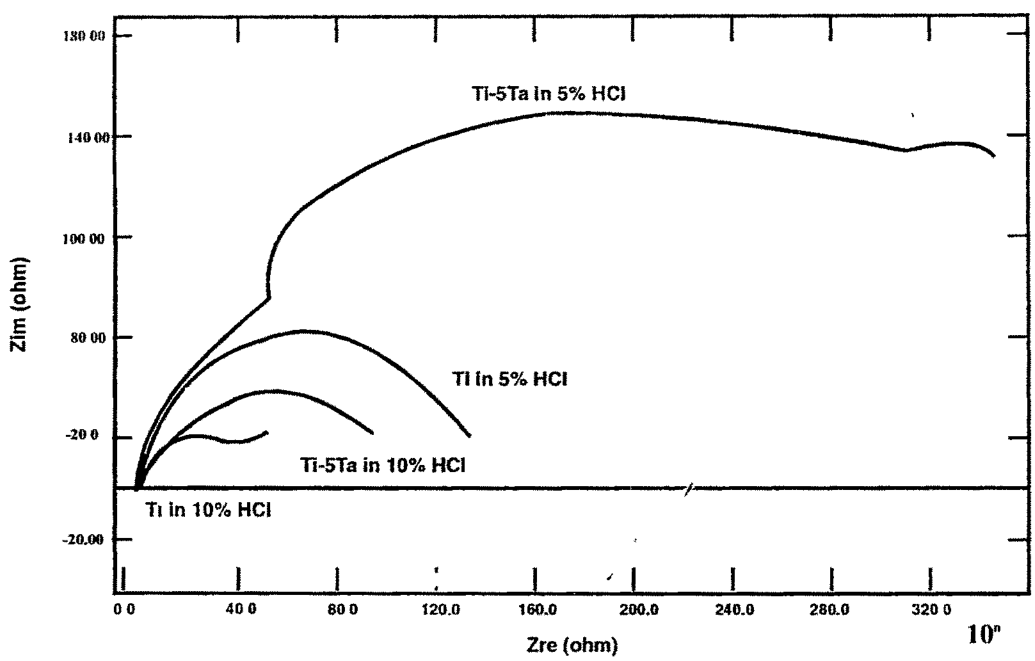


FIGURE 8.4 : NYQUIST PLOTS FOR TITANIUM AND Ti-5Ta IN 5% AND 10% HCl SOLUTIONS.

firstly the presence of w-impedance and secondly formation of oxide of Ta, which stabilizes the existing TiO_2 film.

The increase in concentration of the acid reduces the oxygen availability for generation of films [4]. Hence nature and quality of films deteriorates. However the effect of Mo and Ta is still observed towards enhancement of quality of film even in this higher concentration acid too.

8.2 Passivity behavior of SS 304 and Titanium exposed to Sulfuric Acid in Presence of 2% Mo and 5% Ta respectively.

The Polentiodynemic plots of SS 304 and SS 316 in 10% and 20% H_2SO_4 solutions are show in figure 8.5. In both concentrations of acid, the SS 316 shows better passivity than SS 304. The passive current density value for SS 316 is approaching less than 10^{-3} A/cm^2 it is similar to that of SS 304, but the curve is more uniform in case of SS 316 than in case of SS 304. Further the potential of SS316 is little nobler than of SS 304, these facts indicate that passive film formed on 316 is superior and more stable compare to film formed on SS 304. The effect is more prominent in lower concentration of acid compare to higher concentration (20%) of H_2SO_4 solution. The EIS (Nyquist) plots for these steels are given in figure 8.6, which reveals that value for $|Z|_{real}$ and $|Z|_{img.}$ are 382.6Ωfor 157.3Ωfor SS 316 and are 189Ω and 66.8Ωfor SS 304 in 20% H_2SO_4 solution, indicating that films formed on SS 316 is of better quality than that formed on SS 304. Moreover there is a presence of W-component in SS 316 as indicated by the nature of Nyanist plot. Thus additional parallel resistance–conductance loop is present in the basic electric equivalent circuits. This confirms the presence of additional diffusion mechanism in case of SS 316, which may be due to the formation of Mo_2O_3 over and above Cr_2O_3 film on the surface of SS 316, imparting better quality and improved nature of the passive film in this case.

Figure 8.7 shows potentiodynemic results of titanium and titanium-5 Tantalum alloy is 10% and 20% H_2SO_4 solutions. Here again no passivity breakdown is observed in either case up to 1600mV, showing better nature and quality of Ti and Ti-5Ta than stainless steel. The passive current density in titanium is around $10^{-3.5}$, which is almost same in case of Ti-5Ta alloy, but a rise in E_{corr} in case of alloy coupled with

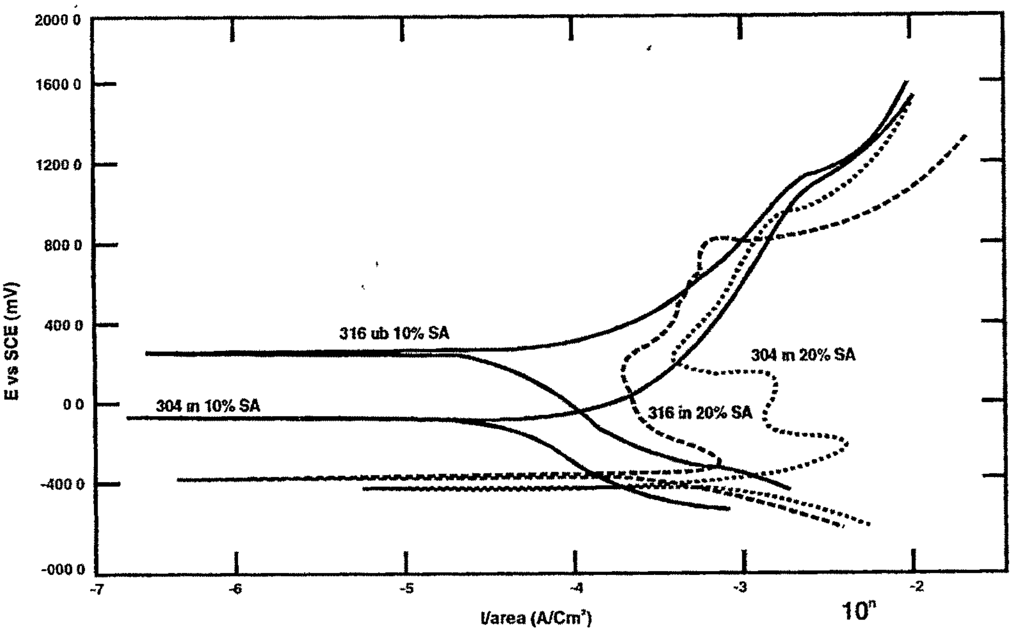


FIGURE 8.5 : POLARIZATION CURVES FOR SS 304 AND 316 IN 10% & 20% H_2SO_4 SOLUTIONS

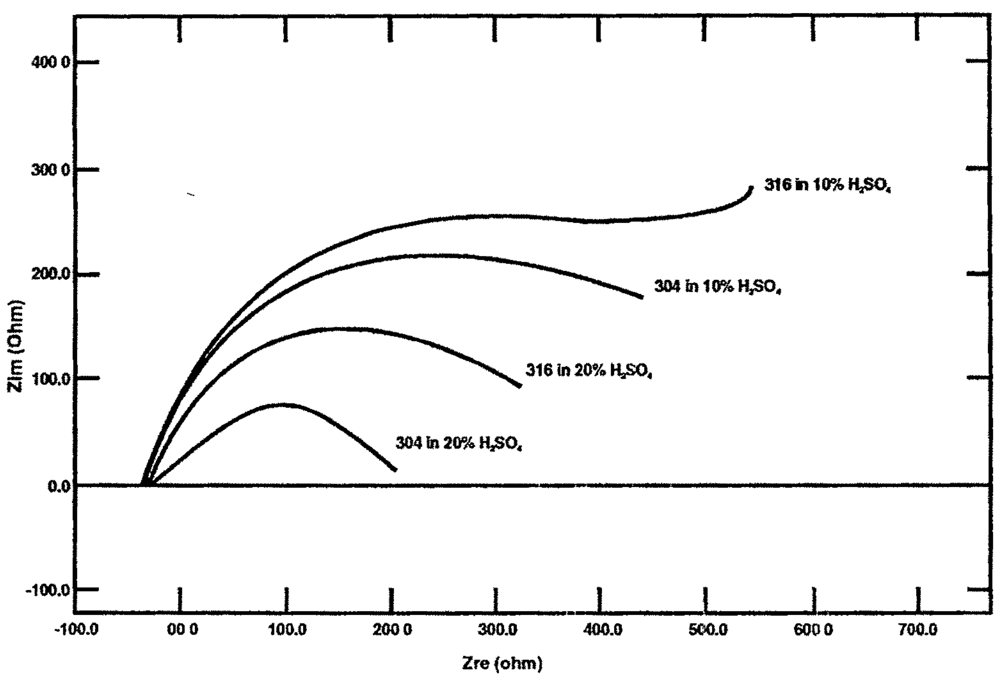


FIGURE 8.6 : NYQUIST PLOTS FOR SS 304 & 316 IN 10% & 20% H_2SO SOLUTIONS

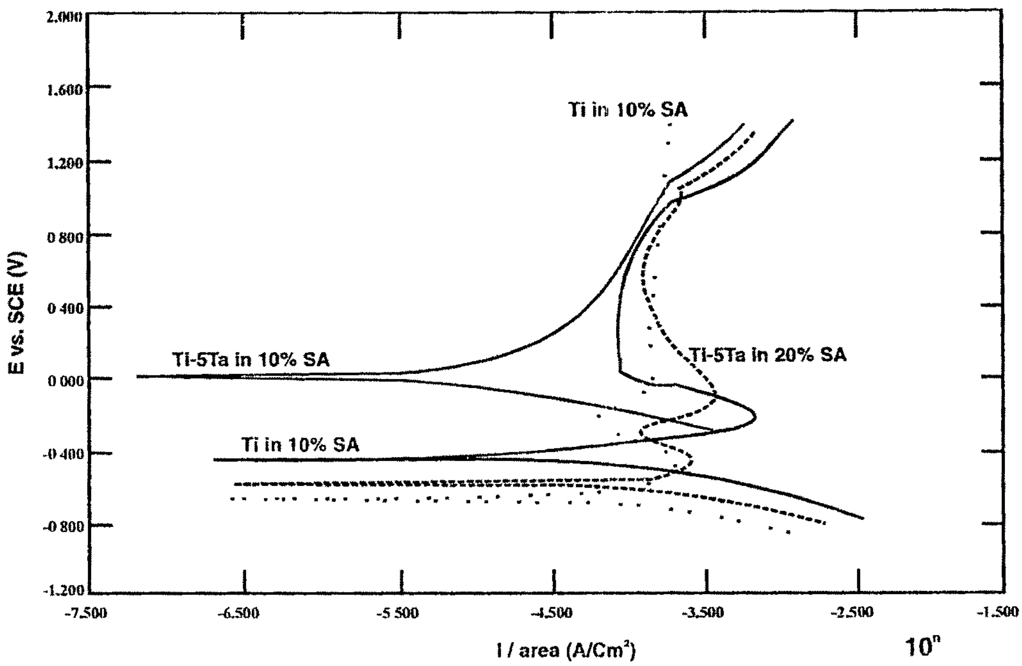


FIGURE 8.7 : POLARIZATION CURVES FOR Ti AND Ti-5Ta IN 10% & 20% H_2SO_4 SOLUTIONS

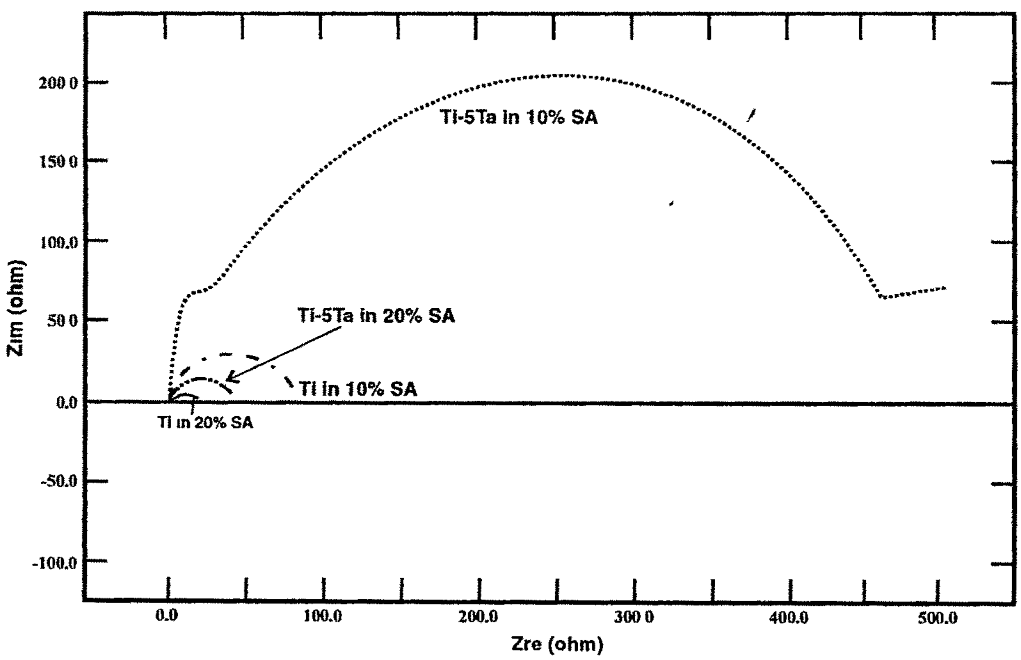


FIGURE 8.8 : NYQUIST PLOTS FOR Ti AND Ti-5Ta IN 10% & 20% H_2SO_4 SOLUTIONS

similarity in passive range indicates that Ti-alloy is having little better corrosion resistance than metallic Ti. This fact is confirmed by evaluating the quality of the film formed on these materials with the help of EIS (figure 8.8). The lZl_{real} and lZl_{img}. values for Ti and Ti-5Ta in the figure indicates that R_p is 13.6Ωand Cdl is 3.78Ωin Ti and the corresponding value for Ti-5Ta are more than 37.3Ωand 13.5 Ωrespectively. It means the quality of film formed on alloy surface is superior to that of Ti metal and imparting better corrosion resistance to the alloy. The film formed on alloy contains both Ti-oxide and Ta-oxide; therefore it seems to be more intact and adherent which is confirmed by presence of double loop in the Nyunist plot in dilute acid solution. The second loop confirms firstly the presence of w-impedance and secondly formation of oxide of Ta, which stabilizes the existing TiO_2 film.

The increase in concentration of the acid makes the solution more aggressive for dissolution of films. Hence nature and quality of films deteriorates. However the effect of Mo and Ta is still observed towards the improvement of quality of film.

8.3 Passivity behavior of SS 304 and Titanium exposed to Pure and Impure Phosphoric Acid in Presence of 2% Mo and 5% Ta respectively.

The Polentiodynemic plots of SS 304 and SS 316 in Lab. Gr. and Comm. Gr. H_3PO_4 solutions are show in figure 8.9. In both concentrations of acid, the SS 316 shows better passivity than SS 304. The passive current density value for SS 316 is approaching less than A/cm^2 it is less than that of SS 304 ($10^{-2\,5}$), but the curve is more uniform in case of SS 316 than in case of SS 304 particularly in passive range. These facts indicate that passive film formed on 316 is superior and more stable compare to film formed on SS 304. The effect is more prominent in lab. Gr. acid compare to comm. Gr. H_3PO_4 solution. The EIS (Nyquist) plot for these steels expose to two grades of acids are given in figure 8.10, which reveals that value for lZl_{real} and lZl_{img}. are 193.73Ω and 89.64Ω for SS 316 and are 63.33Ω and 17.7Ω for SS 304 in lab grade H_3PO_4 solution, suggesting that films formed on SS 316 is of better quality than that formed on SS 304. Moreover there is a presence of double loop in SS 316 as indicated by the nature of Nyanist plot. Thus the basic electric equivalent circuit involves additional parallel resistance–conductance loop. This confirms the presence of additional diffusion mechanism in case of SS 316, which may be due to the

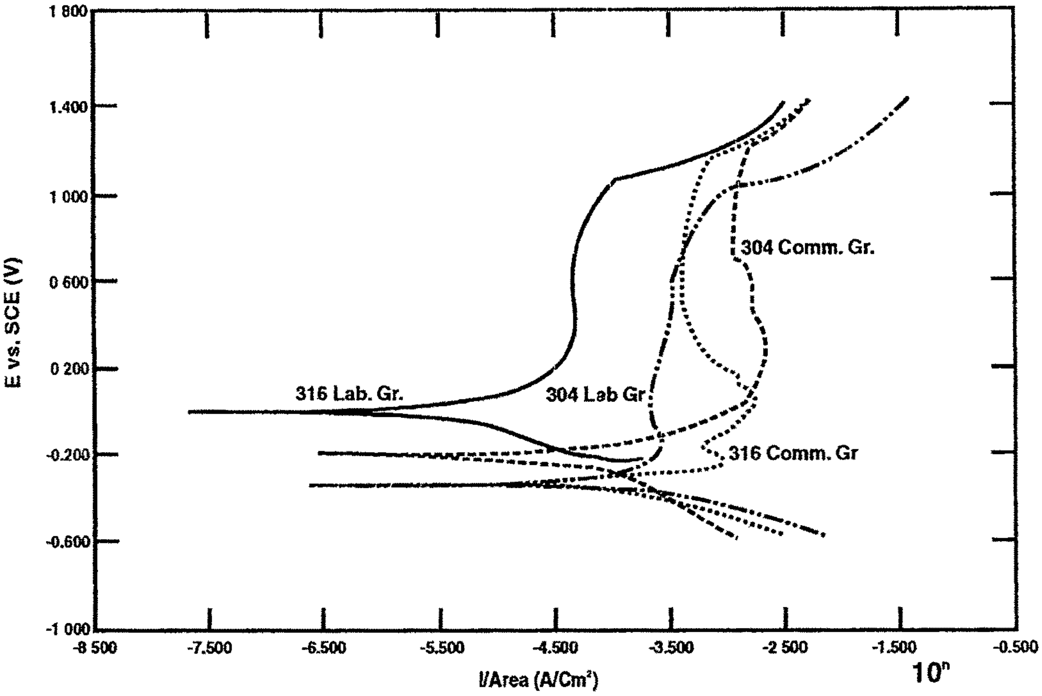


FIGURE 8.9: POLARIZATION CURVES FOR SS 304 AND SS 316 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS

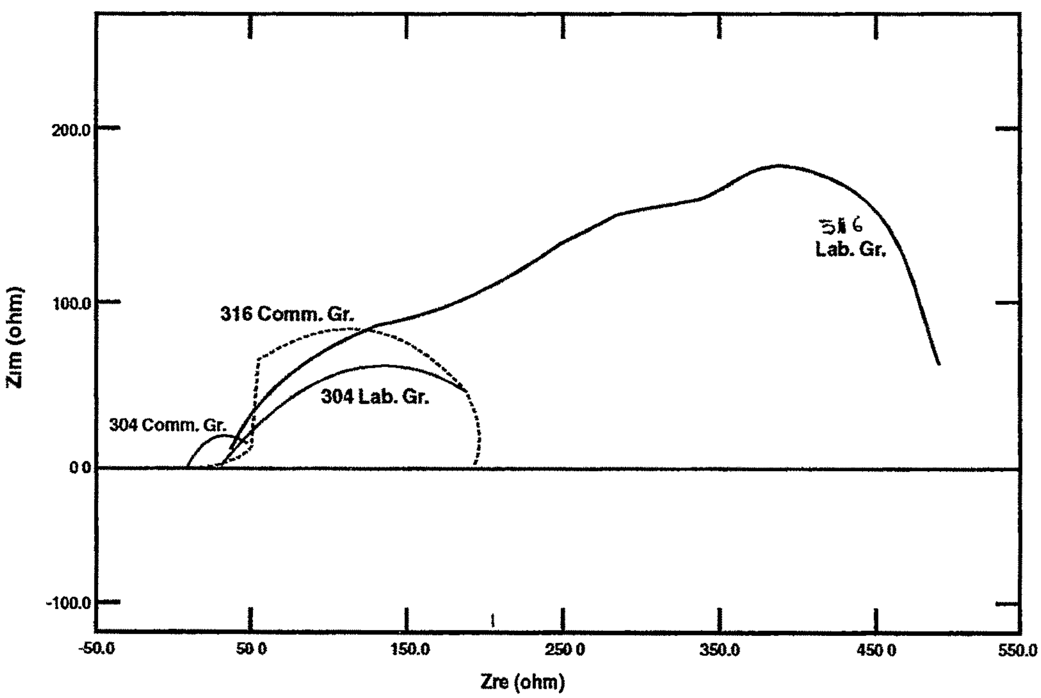
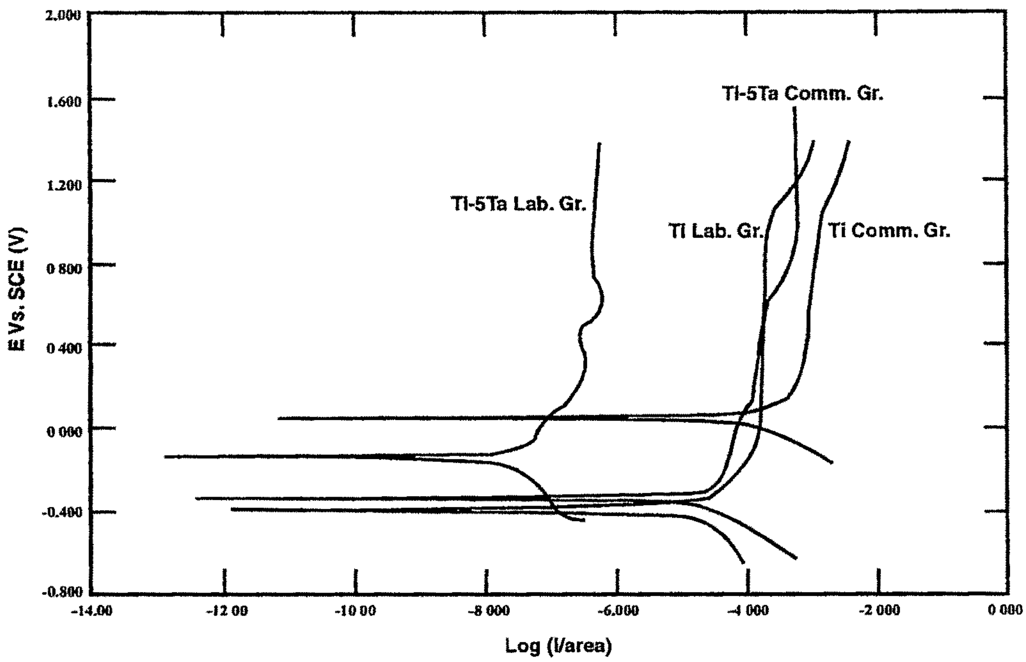
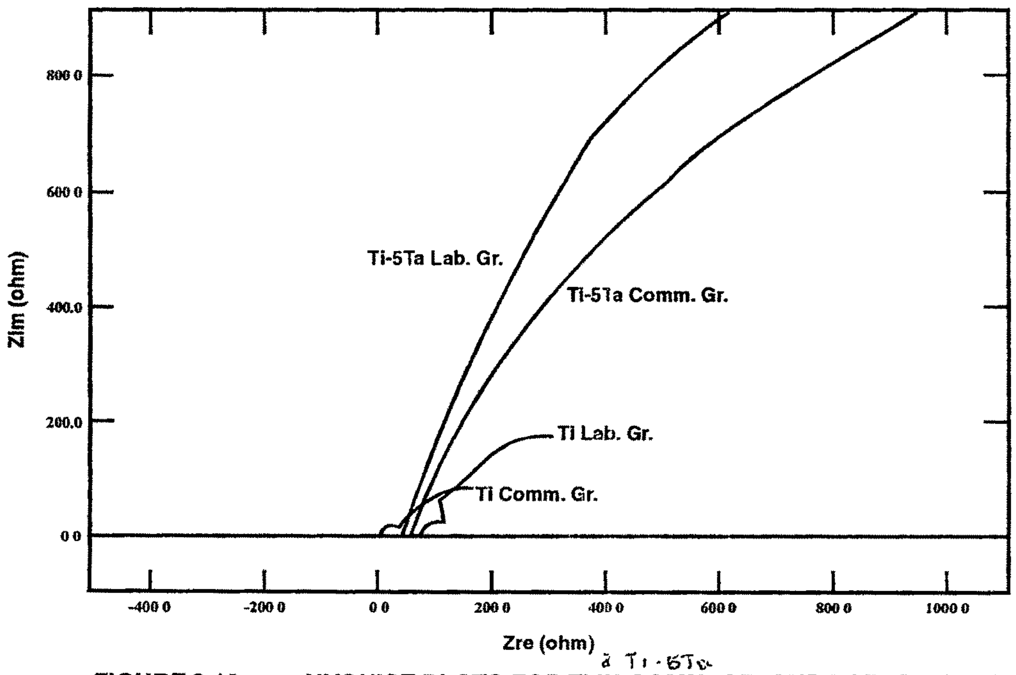


FIGURE 8.10: NYQUEST PLOTS FOR SS 304 AND SS 316 IN LAB. GRADE AND COMM. GRADE PHOSPHORIC ACIDS.



& Ti-5Ta

FIGURE 8.11 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.



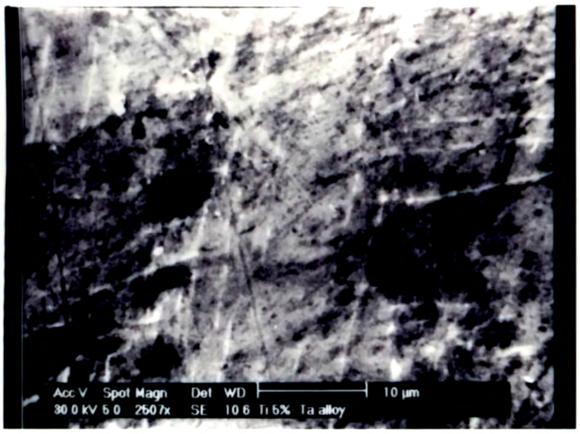
& Ti-5Ta

FIGURE 8.12 : NYQUIST PLOTS FOR Ti IN COMM. GR. AND LAB. GR. H_3PO_4 SOLUTIONS.

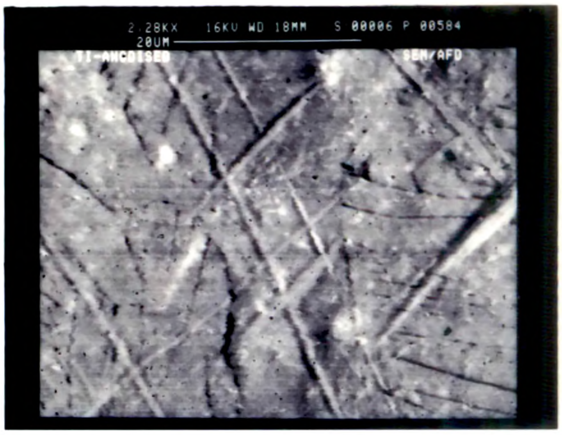
formation of Mo_2O_3 along with generation of Cr_2O_3 film on the surface of SS 316, rendering the passive film an admix of oxides giving better in quality and nature in this case.

Figure 8 11 shows potentiodynemic results of titanium and titanium-5 Tantalum alloy in Lab. Gr. and Comm. Gr. H_3PO_4 solutions Here again no passivity breakdown is observed in either case up to 1600mV, exhibiting better nature and quality of passive films on Ti and Ti-5Ta than in case of stainless steel. The passive current density in titanium is approaching less than 10^{-4} A/cm^2 compare to 10^{-3} A/cm^2 value of SS 304, which is higher by one magnitude, also reduction in i_{corr} in case of alloy coupled with stability in passive range indicates that Ti-alloy is having little better corrosion resistance than metallic Ti This fact is confirmed by evaluating the quality of the film formed on these materials with the help of EIS (figure 8.12) The $|Z|_{real}$ and $|Z|_{img}$ values for Ti and Ti-5Ta in the figure indicates that R_p is 138.6Ωand C_{dl} is 73 99Ω in Ti and the corresponding value for Ti-5Ta are 4.41kΩand 1 22k Ω respectively. It means the quality of film formed on alloy surface is much superior to that of Ti metal and imparting very high corrosion resistance to the alloy. The film formed on alloy contains both Ti-oxide and Ta-oxide; therefore it seems to be more intact and well adherent, which is confirmed by presence of double loop in the Nyunist plot in comm.Gr.H_3PO_4 acid solution. The second loop confirms both, the presence of w-impedance and formation of oxide of Ta, which seems to stabilizing the existing TiO_2 film.

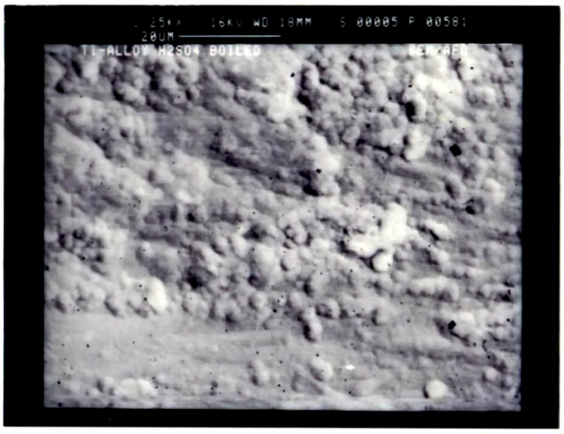
The increase in concentration of the acid makes the solution more aggressive for dissolution of films. Hence nature and quality of films deteriorates. However the effect of Mo and Ta is still observed towards enhancement of quality of film.



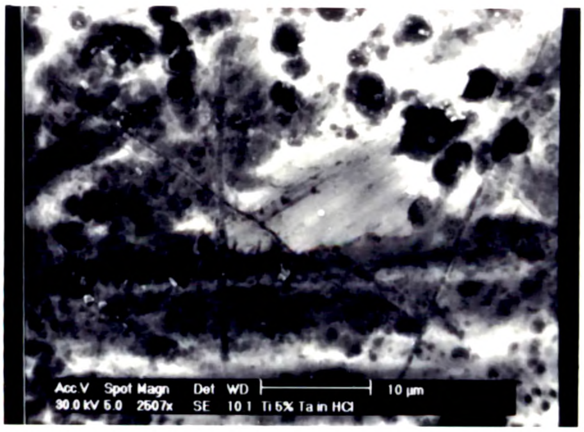
Photomicrograph - 1
Ti-5Ta Anodize



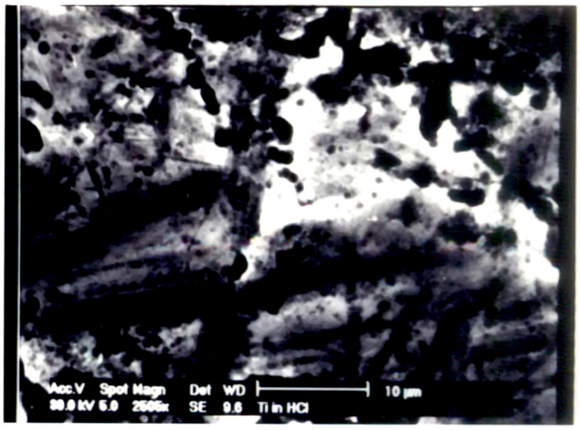
Photomicrograph - 2
Ti-Anodize



Photomicrograph - 3
Ti-5Ta Oxid



Photomicrograph - 4
Ti-5Ta in HCl



Photomicrograph - 5
Ti in HCl

CONCLUSIONS: -

The following conclusions prove the analogy between SS & Ti in means of Mo & Ta

1. Both stainless steel with Mo & Titanium with Ta show similar type of corrosion behavior in reducing acids like at lower concentration HCl, H_2SO_4, and in H_3PO_4 acids with imparities.
2. The nature and quality of passive film changes drastically with the addition of Mo & Ta respectably in SS and Ti.
3. The polarization resistance (Rp) and double layer capacitance C_{dl} balances increase tremendously with addition of Mo & Ta in SS and Ti respectably.
4. Both SS and Ti show `w` impedance in presence of Mo & Ta respectably indicated by Nyqust plot.
5. The stainless steel with Mo & Titanium with Ta shows Mo rich side layer (Mo_2O_3) and Ta rich side layer (Ta_2O_5) on the surfasc, which gives better quality of passive film and stabilizer effect.
6. The Zig Zag nature of passive curve is reduced with addition of these metal in SS and Ti.
7. The stabilizing effect of passive film is confirmed by reduction in passive current density to the order of 2 to 3 depending on concentration of the reducing environment.
8. The nature of passivity is superior in both SS and Ti with additions of these alloying matels
9. The increase of concentration of reducing acid deceases the oxygen availability for development of passive film & hence reduces the quality. But still additions of Mo & Ta show better performance

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