CHAPTER- VII

EFFECT OF SURFACE TREATMENT ON QUALITY OF PASSIVE OXIDE FILM OF TITANIUM AND TITANIUM-5%TANTALUM ALLOY.

NTRODUCTION

The excellent corrosion resistance of titanium is a result of its ability to form a stable, continuous, protective and adherent oxide film. This film generates almost instantly on exposure to air, water or any other source of oxygen. The growth of this natural oxide film in neutral/oxidizing media improves the corrosion resistance of metal, as evident from the slow shift in rest potential towards nobler direction. A freshly prepared-polished surface of titanium will form oxide film instantly, in air or water, having thickness ~ 1 to 4 nm. It will grow with time to ~ 5 nm in 7-days to ~ 7 to 9 nm in a year and will reach to 25 nm after 4- years [1].

Any surface treatment, which will thicken and improve stability of this film, will enhance the corrosion resistance. Unsophisticated and economic treatments like; thermal oxidation and anodizing have been thought to thicken and strengthen the film. Surface treatment will also change the structure of the surface oxide. However, the structure of surface oxide formed by different treatments is a matter of controversy [2]. Depending upon oxidation temperatures and anodizing voltages, varieties of oxides are formed on titanium metal/alloy surface. Titanium, being transition element, will exhibit different valence states and accordingly different levels of oxides of Titanium are expected to form. To fully understand the passivity and corrosion behaviors of titanium metal/alloy, it is important to understand the nature of oxide film forms on its surface. Equilibrium diagram of Ti – Oxygen system [3] depicted in figure-7.1 reveals that, variety of oxides formed at different temperatures and different levels of O_2 The most stable one is TiO_2, in readily available O_2 media. Similarly, E – pH diagram [4] shown in figure-3.2, which is reproduced here as figure-7.2, indicate that, within the stability limits of water, most stable oxide is TiO_2. In either case, under laying layer/s of lower oxides may be present. Equilibrium diagram of Ti–Ta system is shown in figure-7.3, which depicts phases preset in the alloy and transformations occur at various

temperature. Yet another interesting aspect of this system lies in the fact that, TiO_2 exhibits many structural forms. Anodically formed oxide at low voltage, i.e., less than 50V, shows glassy or amorphous, between 50V and 80V it shows quasi-amorphous while above 80V anatase TiO_2 [5-7]. Similarly oxide film formed on titanium by thermal oxidation has been reported to be microcrystalline 'anatase' type TiO_2 at low temperatures and crystalline 'rutile' type TiO_2 at high temperatures of oxidation [8-10].

The titanium dioxide is modeled as n-type semiconductor [10], but rutile is denser, more crystalline and having smaller band-gape energy than anatase[11,12]. Although there is a disagreement but most researchers accept the band gape energy value for rutile as 3.0eV and that for anatase is 3.2eV [13]. Moreover, Thermal oxide film is significantly strong, tough and more tenacious, need sand blasting for effective removal, but is poorly covering the surface. Anodized film, on the other hand, is uniformly coated and improves corrosion resistance. But can be rapidly removed by a simple acid pickle, light abrasion or mishandling [14]. In the present work an attempt has been made to study the nature and quality of oxide film formed on Ti & Ti-5Ta alloy after anodizing and thermal oxidation surface treatments.

Experimental Procedure: The same procedure, as described in chapter 4th, was also adopted here to evaluate passivity and corrosion data. The specimens after wheel polishing were subjected to the following surface treatments to modify the passive films on metal and alloy;

- Thermal Oxidation: - Heating at 680°C in Air, for 30 minutes, Air cool to room temperature [15].
- Anodizing: - Electrolytic anodizing at 80 V, 1Amp, for 90 seconds, in 10% $(NH_4)_2SO_4$ bath [16].

These specimens were then studied using EIS, PDP, SEM, EDAX and XRD techniques, the same manner as in case of previous studies.

7.1 Results and Discussions:

The application of titanium and its alloys is usually limited in reducing acid media owing to the instability and breakdown of otherwise stable-protective surface oxide film. Such media are, therefore, excellent test media for detecting any

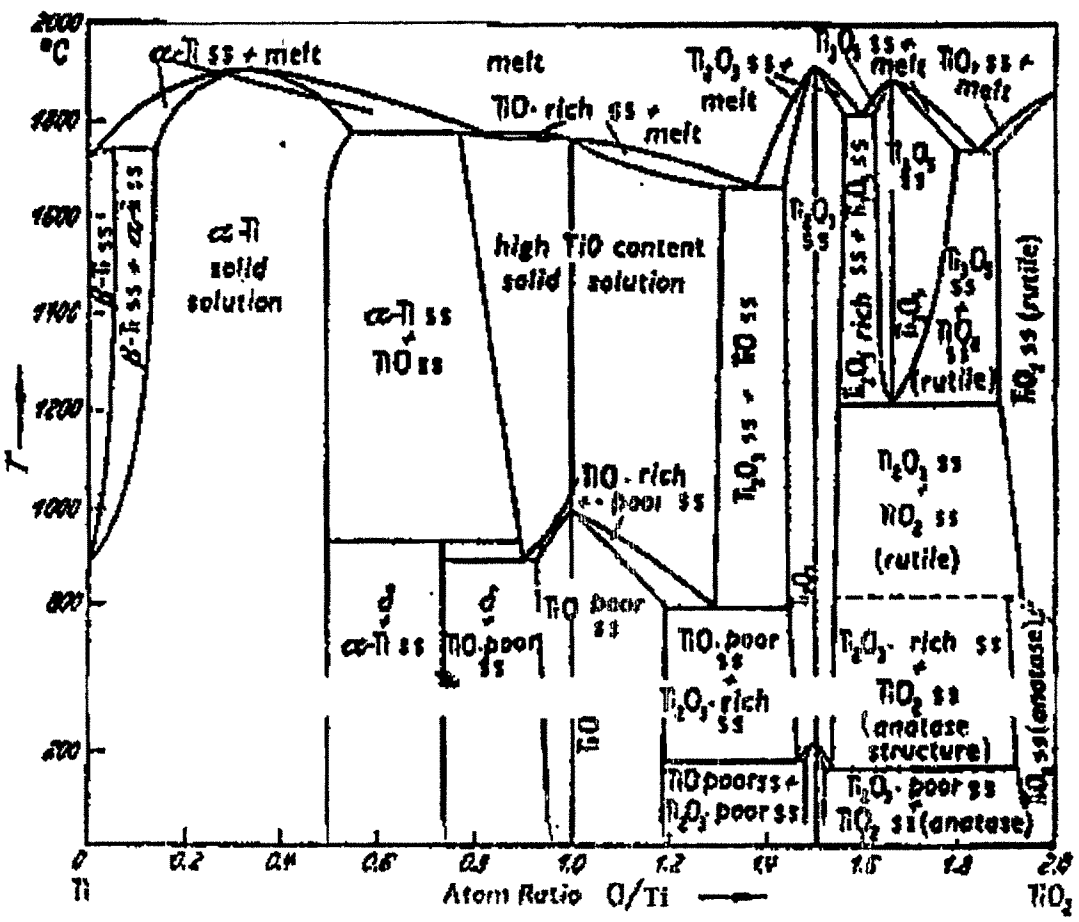

Figure-7.1 Ti – O_2 Equilibrium System

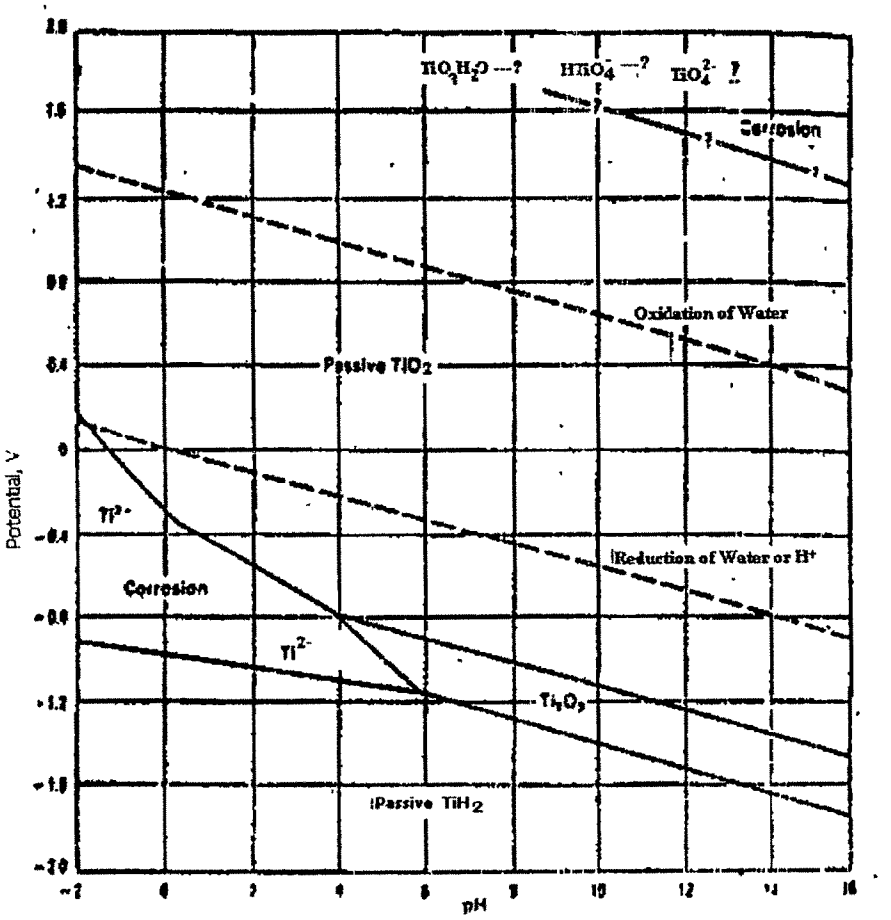

Figure 7.2 Ti – H_2O System

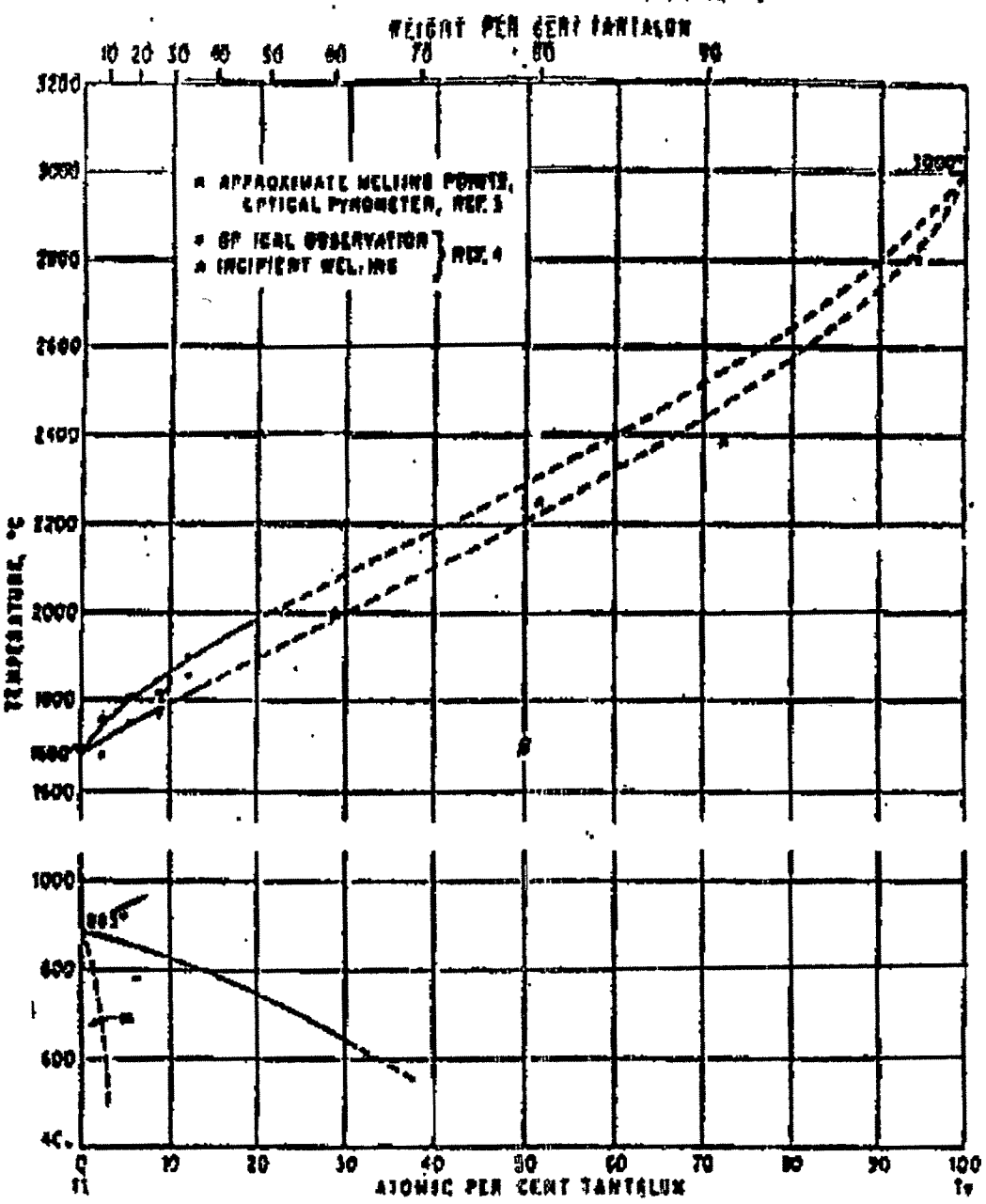

Figure 7.3 Ti-Ta Equilibrium System

improvement in passive film and corrosion resistance as a result of surface treatments Also it is generally occurring medium in many industrial process streams.

7.2 Untreated Ti & Ti-5ta Alloy:

Anodic polarization curves for titanium and Ti-5%Ta alloy, without any surface treatment, in 10% HCl solution are shown in fig.7.4. Improvement in the corrosion resistance by addition of 5%Ta in Ti is clearly seen here. The passive current value of Ti-5%Ta alloy is less than that of Ti by about 2.0 orders of magnitude. This indicates that the presence of 5%Ta must have improved the film characteristics and reduced the flow of corrosion current.

Fig.7.5 shows the Nyquist plot/EIS curves for Ti & Ti-5%Ta alloy. Here both $|Z|_{real}$ and $|Z|_{img}$ components of impedance of 5% Tantalum alloy exhibit superior values than those of metallic titanium, $|Z|_{real}$ rises from 32 ohm to almost 60 ohm and $|Z|_{img}$ from ~5.0 to ~16.0 ohm.

This may be attributed to the fact that, Ta is also an active-passive metal and forming passive film in general environment conditions. This film is resistant to corrosion attack of reducing-acid type environments especially in different concentration of HCl- solutions at ambient temperature. Initially Ti dissolves actively but soon Ta, being nobler than Ti, get exposed on the surface and protect the underneath titanium like Pt in Ti-Pt alloy [17]. Such diffusion of Ta-atom is fissible, as in reducing conditions Ti exhibits +3 valency having coordination 6 and ionic radius 0.67°A and Ta exhibits same coordination number with ionic radius 0.68°A and valency + 4[18].

X-Ray Diffraction results of these samples are given in fig. 7.6 and 7.7, providing qualitative analysis, show no peaks of oxides in either case. In fact surfaces are bare, owing to high reducing nature of acid, which diminishes the oxides forming on the surfaces of these samples. But tantalum being more prone to oxide formation continuously forms thin layer of oxide, using whatever small amount of naturally dissolved O_2 in HCl solution at ambient temperature [17].

Scanning Electron-photomicrographs of Ti metal and Ti-5%Ta alloy, photomicrographs-4 & 5, reveal the same facts. In case of Ti-5Ta only fewer area are covered with corrosion product. This must be due to exposure of Ta on the surfaces,

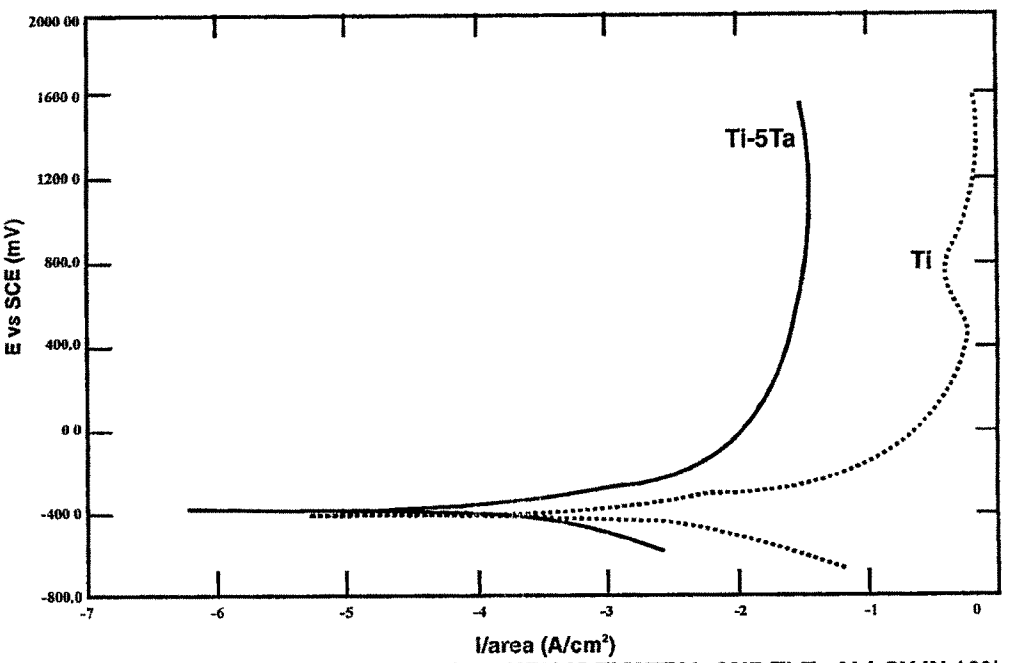

FIGURE 7. 4 : POLARIZATION CURVES TI METAL AND TI-Ta ALLOY IN 10% HCl SOLUTIONS

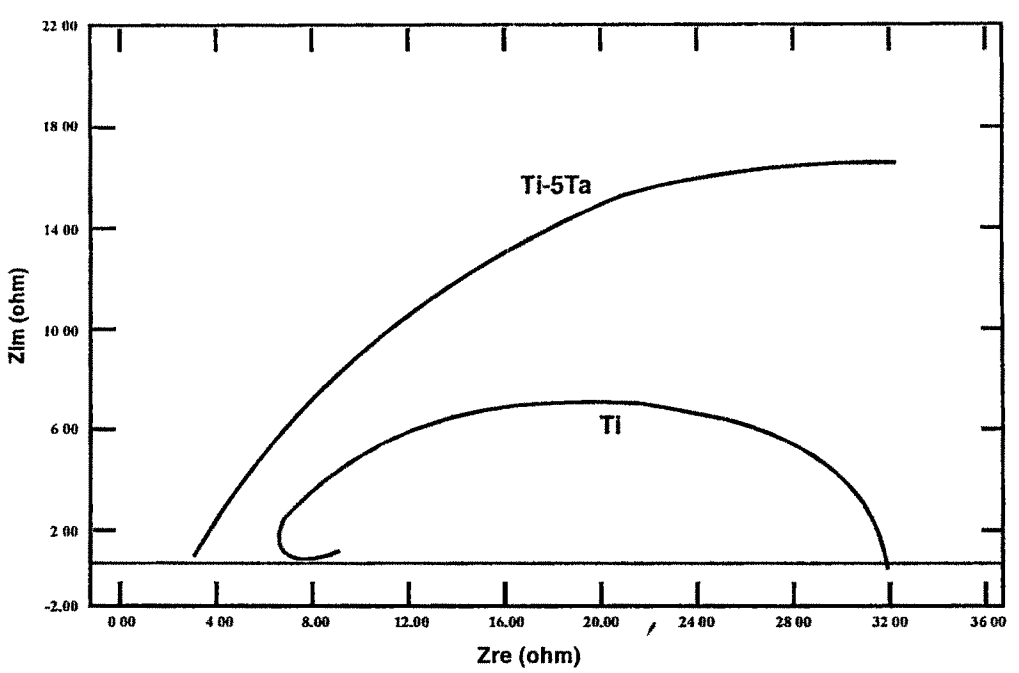

FIGURE 7. 5 : NYQUIST PLOTS FOR TI METAL AND TI-Ta ALLOY IN 10% HCl SOLUTIONS

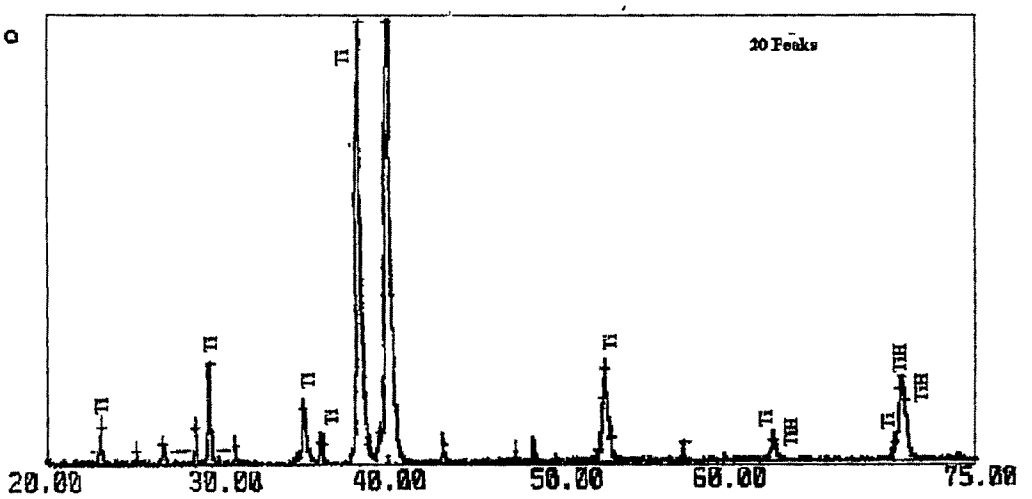

Figure 7.6: XRD of Untreated Titanium

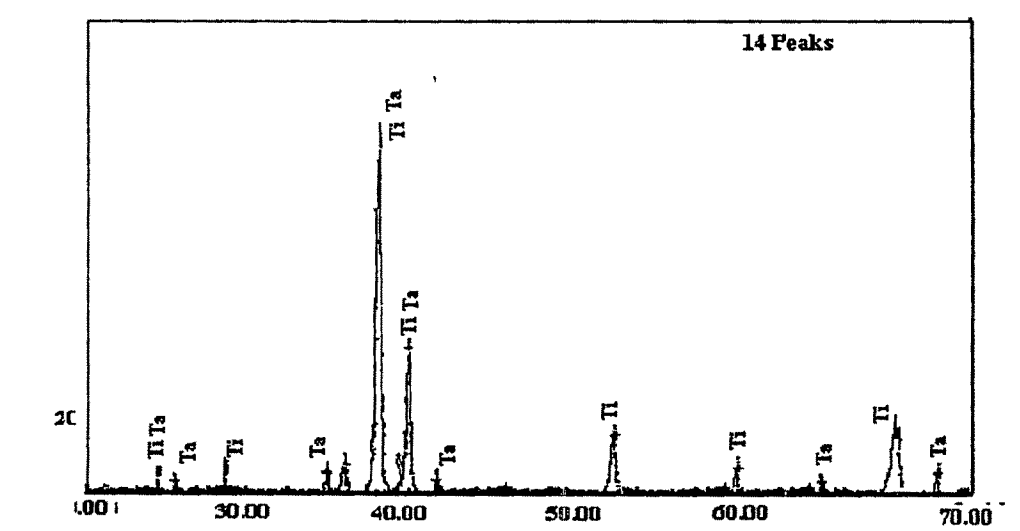

Figure 7.7 : XRD of Untreated Ti-5Ta Alloy

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EDS TEST REPORT

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Label:Ti in HCl

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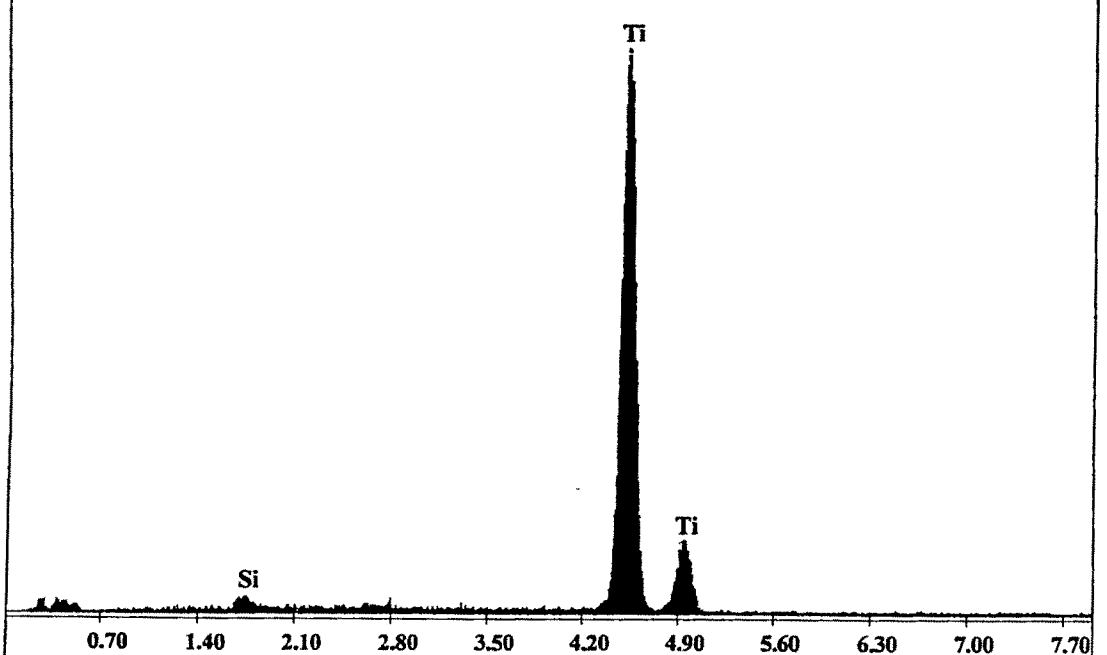

EDAX ZAF Quantification (Standardless)
Element Normalized

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:7.8

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EDS TEST REPORT

C:\EDAX Results\2211sr4a.spc

Label:Ti 5% Ta in HCl

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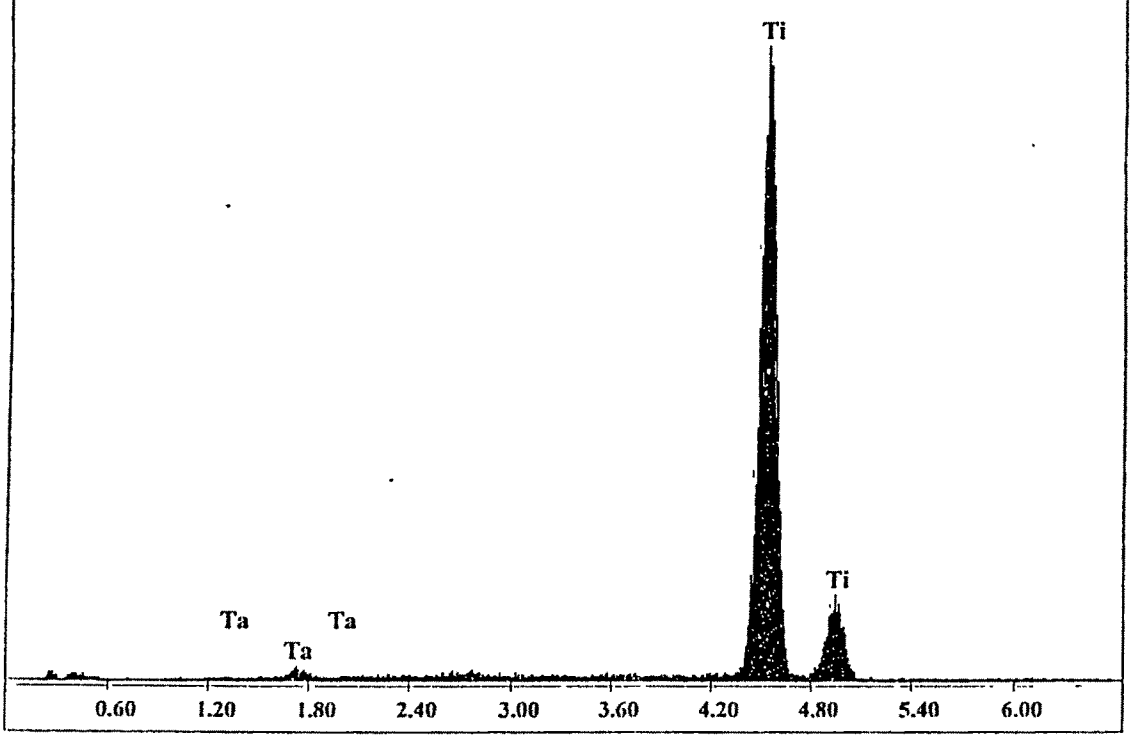
FS : 2106	Lsec : 6			22-Nov- 0	13:48:17



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:7.9

after initial dissolution of Ti, in case of alloy. Whereas in case of Ti many cavities of different sizes with relatively large affected areas are seen. Inferring that higher resistance to the attack is due to presence of Ta in the alloy, which continuously replenishing the passive film in small amount.

EDAX result (fig. 7.8 and 7.9) of alloy specimen is also supports these facts, giving average quantitative analysis of the surfaces. Indicating that 5.38%Ta is present on the surface but no traceable amount of O_2 is available, i.e., in reducing acid almost all the O_2 consumes in depolarization at cathodic areas on the surface

SURFACE TREATED Ti:

The anodic polarization curves for Ti in anodized and oxidized conditions are shown in figure-7.10 along with untreated Ti metal. It is clearly observed from the figure that, both the treatments raise the rest potential of the Titanium toward nobler side. This is expected as film thickness increases ionic diffusion becomes more difficult and metal behaves nobler than its previous condition. This fact is also presented by reduction-shift in passive current density by 3 to 4 orders of magnitude (10^{-3} to 10^{-4}) in anodized as well as oxidized coupons (fig.-7.10). Among these, oxidation treatment turns out to be little better than anodizing one, owing to the fact that, oxidation at 680°C forms rutile type film, which is more compact and impervious than the film-containing anatase. Thus a reduction in corrosion current is expected in oxidized specimen compared to anodized one.

The Nyquist plots of untreated metal, oxidized and anodized coupons are given in figure-7.11. It displays significant difference in the impedance values of these coupons, which in turn characterize the film quality with respect to passivity attained and resistance to corrosion. Both $|Z|_{real}$ and $|Z|_{img}$ components of impedance exhibit superior values, in case of anodized and oxidized titanium than those of untreated titanium. $|Z|_{real}$ rises from 32 ohm to almost ~900 ohm in anodized sample and ~1400 Ohm in oxidized one. Similarly $|Z|_{img}$ increases from ~5.0 Ohm for untreated metal-coupon to ~350.0 ohm and to ~670 ohm in anodized and oxidized coupons respectively. This increase in impedance values is clearly due to the increase in thickness of the films in both of the treated samples, offering more resistance to ionic

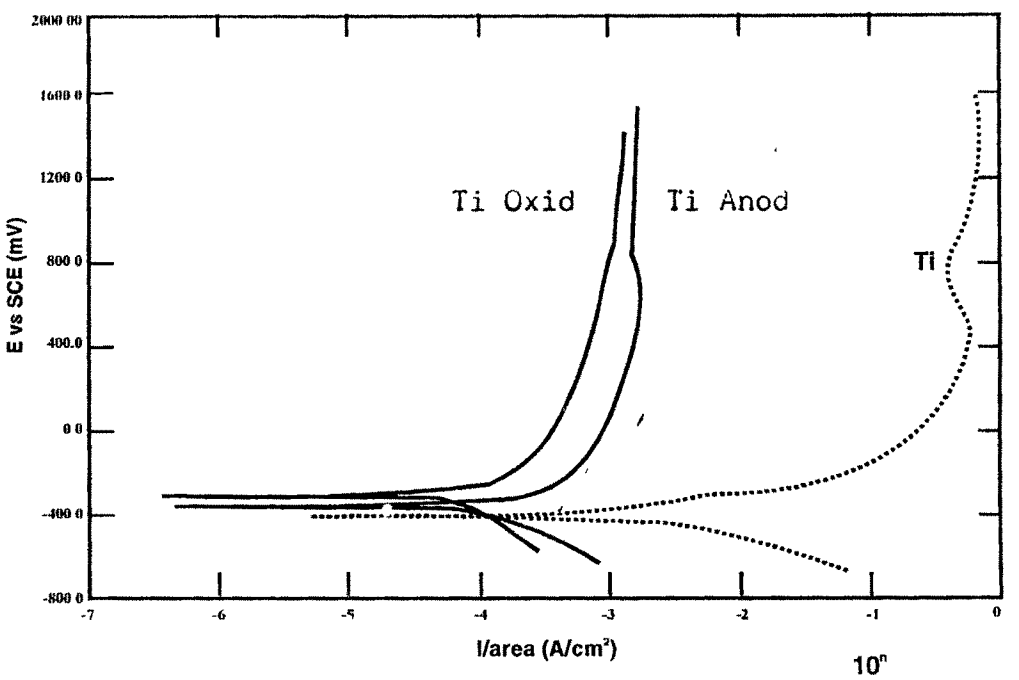


FIGURE 7.10 : POLARIZATION CURVES FOR UNTREATED, OXIDIZED AND ANODIZED TI-METAL IN 10% HCl SOLUTIONS

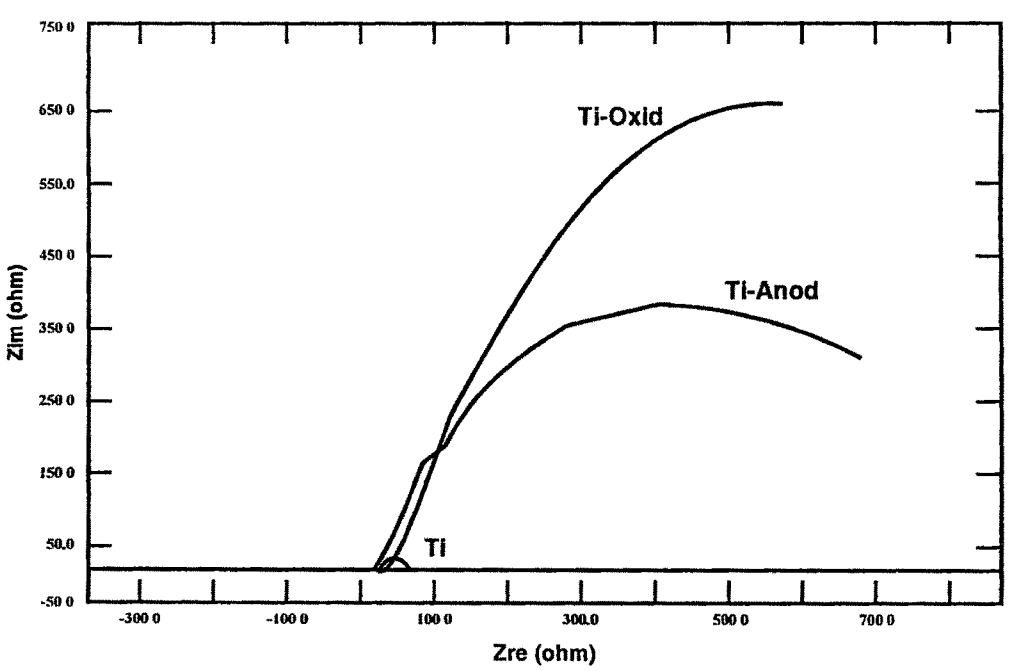


FIGURE 7.11 : NYQUIST PLOTS FOR UNTREATED, OXIDIZED AND ANODIZED TI-METAL IN 10% HCl SOLUTIONS

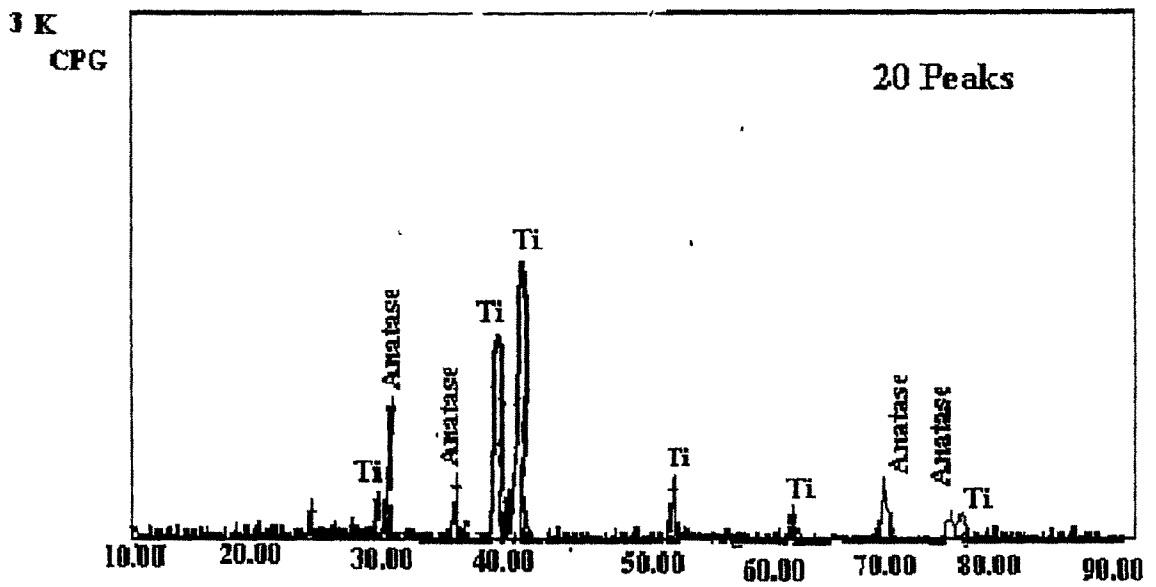


Figure-7.12: XRD of Anodized Ti

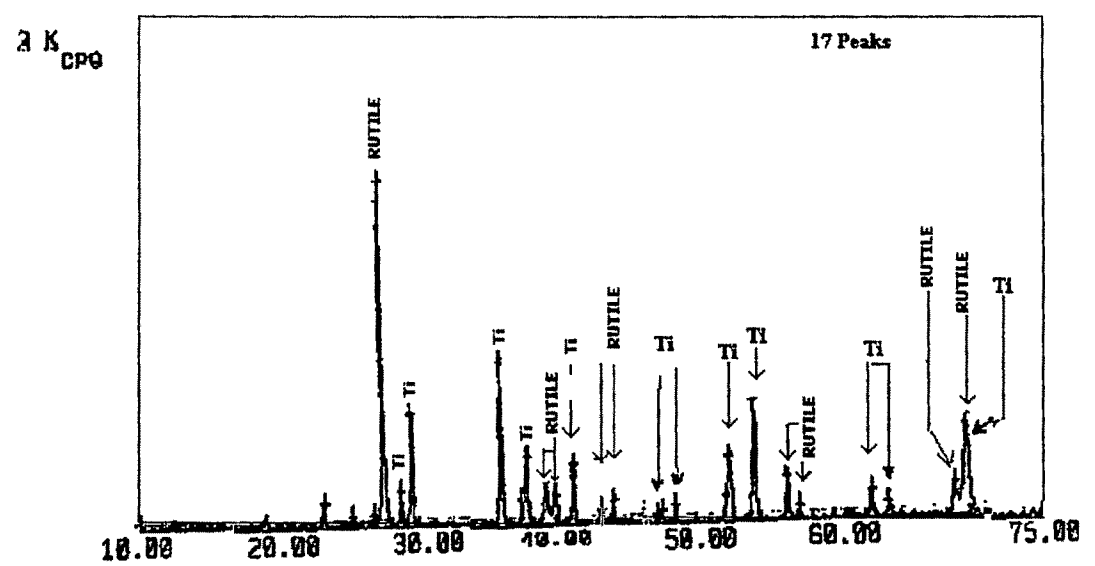


Figure 7.13: XRD of Oxidized Titanium

diffusion and anodic polarization. The superior results in thermally treated coupon is consistence with the findings that thermal oxidation produces dense, highly crystalline rutile oxide film. Whereas anodizing provides anatase oxide film, which is less dense, low crystalline and hence slowly dissolves in reducing acid.

The XRD-results of anodized and oxidized coupons are shown in figures 7.12 and 7.13 respectively, which reveal the presence of anatase and rutile oxide films respectively. These results are in agreement with previous findings that depending upon treatment, either anatase or rutile containing oxide film will form on the surface of titanium.

The scanning electron micrograph of anodized specimen of titanium is shown in microphotograph-2, exhibits the fact that film coating is more uniform in case of anodizing, but film is having cracks. This is due to high amount of O_2 intake during the course of anodizing. As Ti has high affinity for oxygen, forming anatase oxide having relatively distorted structure [11&12]. It is classed as n-type oxide and exhibiting inward movement of O-ions for conduction [19]. These aspects impart internal stresses causing cracks in the film. While the oxide film generated by thermal oxidation, though exhibiting non-uniform coating but it is intact/undistorted rutile type film. Obviously impairing O_2 intake and giving better masking to underneath metal from environment.

SURFACE TREATED Ti –5Ta ALLOY:

The polarization curves of anodized and thermally oxidized Ti-5Ta alloy coupons together with un-treated alloy coupon are displayed in the figure 7.14. Here no much shift of rest potential is observed, indicating that oxide film formed, of anatase type or rutile type, does not change passivity of the surface. But it is interesting to note that reduction in passive current density is more in case of anodized alloy than thermally oxidized alloy. While in anodized alloy the passivity current density reduces by almost 2.5 orders of magnitude as compare to that of untreated alloy. In case of thermally oxidized alloy this reduction is of the order of 2.0 magnitudes. Thus, anodizing provides a better corrosion resistant film than thermally oxidized one.

Electrochemical impedance measurements of these coupons characterize these films and enlighten the above findings. Figure-7.15 exhibits Nyquist plots of treated coupons. Wherein both $|Z|_{real}$ and $|Z|_{img}$ components of impedance are having, highest values in case of anodized film, intermediate values for thermally oxidized one and least for untreated alloy. $|Z|_{real}$ rises from ~32 ohm for untreated alloy to almost ~240 Ohm in anodized sample and ~100 ohm in oxidized one. Similarly $|Z|_{img}$ values increases from ~16 ohms, for untreated alloy, to almost ~30.0 ohms in thermally oxidized alloy and to approximately ~60.0 ohms in anodized alloy.

Both the polarization curves and Nyquist plots focus on the same fact that, anodizing treatment is giving most resistant film. Such behavior of films, in case of Ti-5%Ta alloy, can be explained on the basis of types of oxides formed in the film. The most stable oxide of Ta is of Ta_2O_5 type, having free energy of formation ~ -1970 J/mole which is much less compare to ~ -883.59 J/mole of TiO_2 [20], thus Ta has higher tendency to oxidize than Ti. Presence of Ta_2O_5, which is more resistant to corrosion attack, inhibits generation of thick film. Rather a thin film containing both types of oxide is formed in case of Ti-5%Ta alloy. This tenacious, highly impervious and well adherent film of admixture oxides, now present on the surface, inhibits the inward diffusion of oxygen ions even if the temperature is high during thermal oxidation.

This explanation is confirmed by EDAX results, shown in figures 7.16 and 7.17 The amount of oxygen present in the film formed by thermal oxidation of Ti metal is as high as 37.33%. Whereas in case of thermally oxidized Ti-5%Ta alloy, under same conditions of treatment, film contains only 10.39% oxygen.

The same phenomenal events occur during anodizing, since intake of O_2 is now less than in case of pure titanium metal because of Ta presence. This results in crack free film with higher uniformity and better quality film. It is having more corrosion resistance than the film generated by thermal oxidation, as latter gives relatively poor, non-uniform film coating. The titanium-oxide formed on thermal oxidized Ti-5Ta alloy may be rutile or anatase, but is coupled with Ta_2O_5 and has relatively low amount. As Ta_2O_5 forms first, which impair diffusion of O_2 for generating larger amount of TiO_2

XRD results of anodized and thermally oxidized alloy coupons (figure 7.18 and 7.19), confirm the existence of Ta_2O_5 and TiO_2 in the surface films. Presence of admix oxides is clearly seen in scanning electron photomicrograph of anodized Ti-5%Ta alloy in photomicrograph-1. Also comparing this micrograph with that of thermally oxidized alloy coupon, photomicrograph-3 showing globules of oxide loosely held on surface giving non-uniform coating. Thus it can be concluded that anodizing treatment provides more uniformly coated film than thermal oxidizing.

It is concluded from the above results that, the surface treatments like anodizing and thermal oxidation improves the quality of passive film in pure Titanium and latter showed significantly better quality film than former treatment. Although Ta presence in Ti-5Ta alloy showed better quality film, the surface treatment did not show drastic improvement in the passivity of the film due to TaO5. However, anodizing treatment showed better passivity than that of thermal oxidation.

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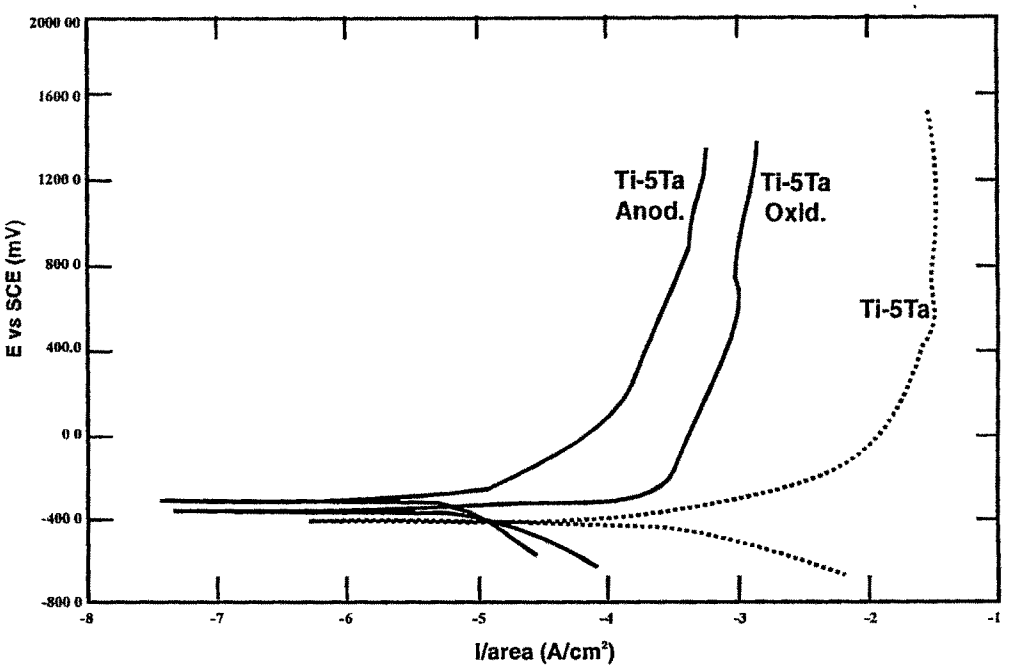

FIGURE 7.14 : POLARIZATION CURVES FOR UNTREATED, OXIDIZED AND ANODIZED Ti-5Ta ALLOY IN 10% HCl SOLUTIONS

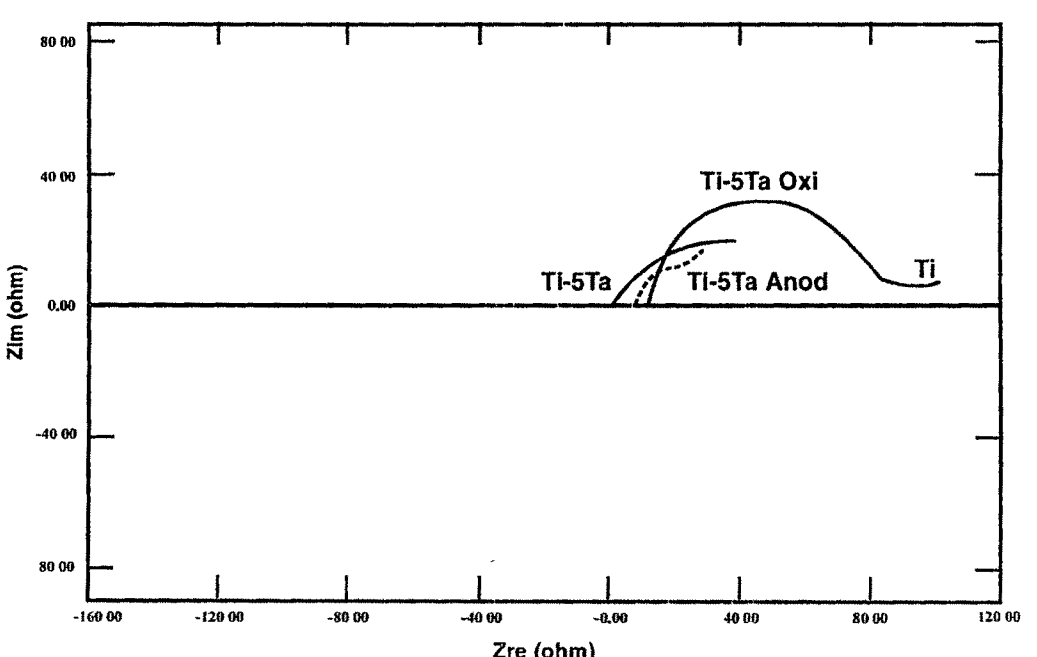

FIGURE 7.15 : NYQUIST PLOTS FOR UNTREATED, OXIDIZED AND ANODIZED Ti-5Ta ALLOY IN 10% HCl SOLUTIONS

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EDS TEST REPORT

C:\EDAX Results\2211SR3a.spc

Label:Ti Oxidised

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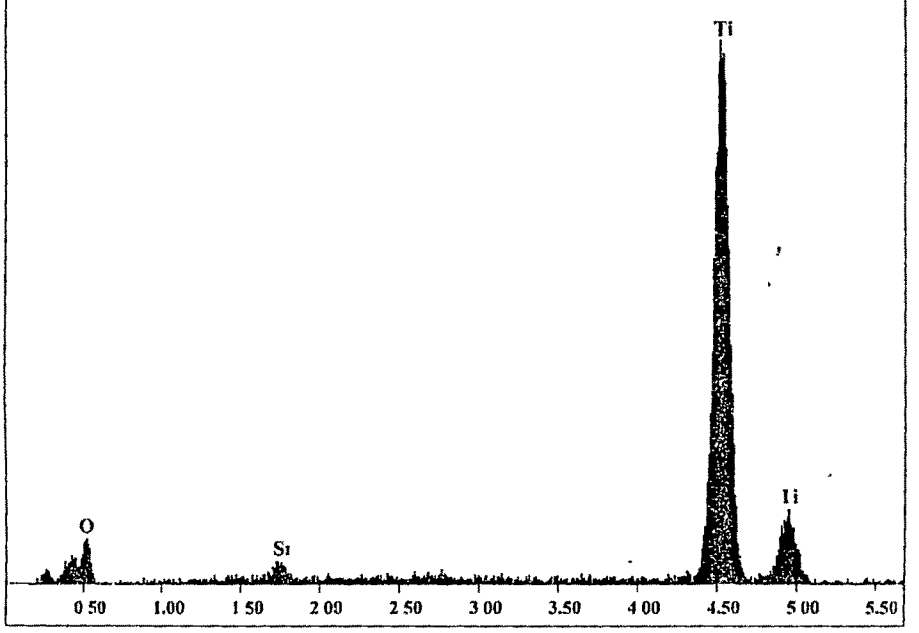

EDS TEST REPORT

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	37 33	63.51	0 0360	1.0843	0.0889	1.0001
SIK	2.21	2.14	0.0106	1.0458	0.4577	1.0062
TiK	60.46	34 35	0.5732	0.9563	1.0126	1.0000
Total	100 00	100 00				

Element	Net Inte	Bkgd Inte	Inte. Error	P/B
O K	67.14	1 16	5.41	57.83
SIK	41 22	10.45	7.67	3.94
TiK	1491.29	8.90	1.14	167.54

Fig:7.16

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EDS TEST REPORT

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Label:Ti 5% -Ta Alloy Oxidized

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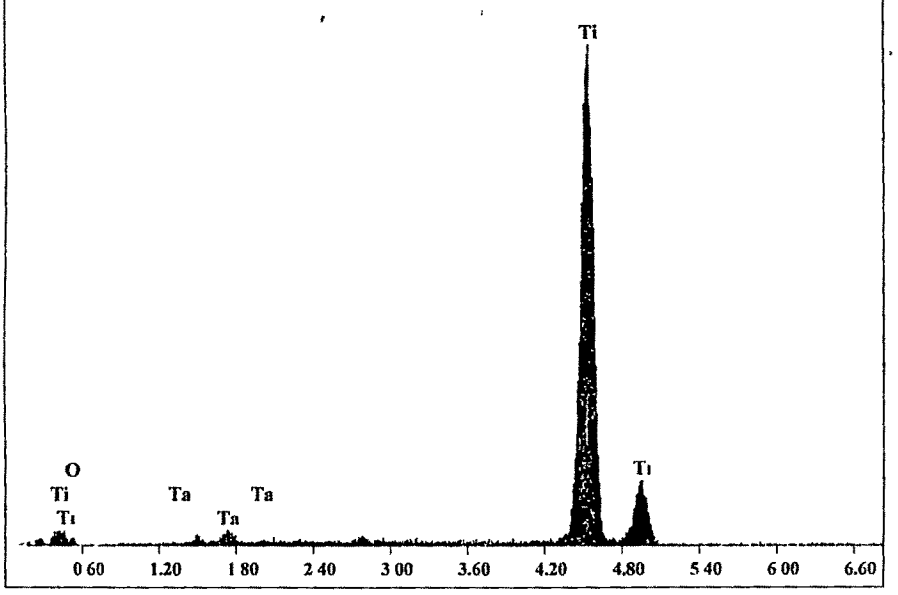
FS : 1750	Lsec : 9			22-Nov- 0	12:22:42



EDS TEST REPORT

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
O K	10 39	26.88	0.0078	1.1398	0.0662	1.0001
TaM	6.80	1.56	0 0480	0.8696	0.8099	1.0011
TiK	82.81	71.57	0.7897	0.9893	0.9619	1.0021
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte	Inte. Error	P/B
O K	9.99	0.64	10.70	15.50
TaM	22 14	6 88	7.98	3.22
TiK	1402 86	7 31	0.88	191.99

Fig:7.17

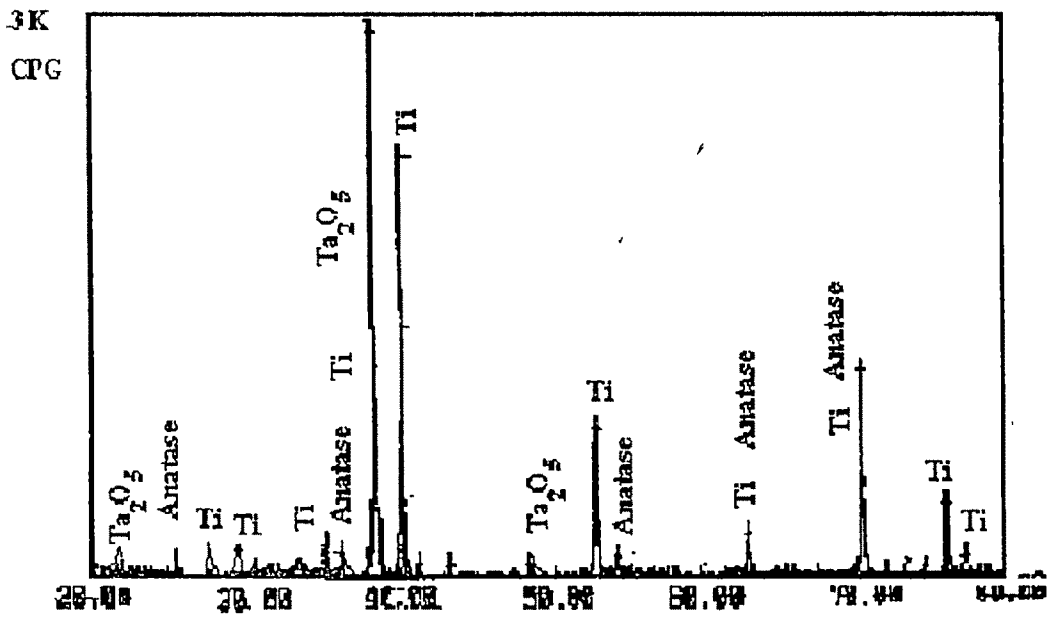


Figure 7.18: XRD of Anodized TI-5Ta

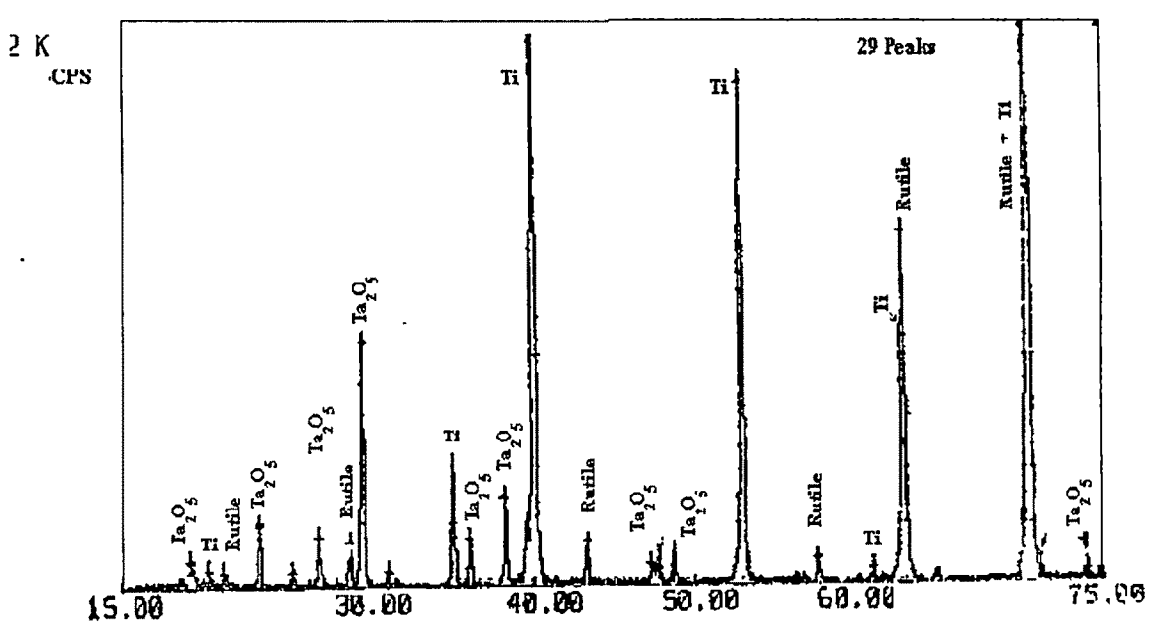


Figure 7.19: XRD of Oxidized Ti-5Ta