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Corrosion Behaviour of Titanium Anodized Film in Different Corrosive Environments

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ABSTRACT
Anodizing is an electrochemical process in which thickness of the natural oxide layer is increased and converted it into a decorative, durable, corrosion-resistant film. Titanium is used as a biocompatible material in human implants due to its excellent corrosion and wears resistance. Stable, continuous, highly adherent, and protective oxide films can be developed on titanium using various acid or alkaline baths. Anodizing of titanium generates a spectrum of different color without use of dyes. This spectrum of color dependent on the thickness of the oxide, voltage ranges, interference of light reflecting off the oxide surface and reflecting off the underlying metal surface. The anodized film of Titanium is mainly consists of TiO_2 or mixtures of TiO_2 & Ti_2O_3 etc. In the present work, Pure Titanium plate has been anodized using bath of Chromic Acid at different voltage range. The anodized film is characterized by visual observation, SEM & EDAX analysis & A.C Impedance Spectroscopy, while the corrosion studies were performed using Potentiodynamic studies were performed in 3.5% NaCl & 0.1N H_2SO_4. The Results show that the anodized film of Titanium show different spectrum of colors from Brown-Violet-Tea or Peacock. SEM & EDAX analyses show that the anodized film of Titanium is mainly made up of TiO_2 and Ti_2O_3. Potentiodynamic study implies that the film developed on Titanium using the bath of Chromic Acid exhibits good corrosion resistance. The A.C. Impedance study shows that the film is more compact, adherent and more uniform in chromic acid bath.

Keywords-Anodizing of Titanium, Coloring Effect, Potentiodynamic Test, AC Impedance Test, SEM & EDAX analysis

I. INTRODUCTION

Anodizing is carried out on metals like Aluminum, Titanium, Tantalum and alloy like Stainless Steel to provide decorative finishing, improve corrosion resistance and wear resistance & better adhesion for paint or primers. Coatings are normally porous, which can be sealed to achieve better corrosion resistance [1-3].Anodized Titanium often used in the medical devices, orthopedic implants, dental implants, and device components of aerospace industries. It having different microscopic texture of the crystal structure when it was developed on the metal surface due to which it shows different spectrum of colors from Grey-Brown-Blue-Yellow-Pink-Violet-Teal-Green in different baths such as NaOH, KOH, Chromic Acid, H_2SO_4, Coke, H_3PO_4, and Na_2HPO_4 at different voltage range without altering the mechanical properties of metal [4-8]. In present work, the pure Titanium plate was anodized using different baths of Chromic acid at various voltage ranges to obtain different spectrum of colors. The anodized films were characterized by SEM & EDAX an analysis which shows that the film was mainly made up of TiO_2 and Ti_2O_3. A.C Impedance Spectroscopy of the films reveals that the film exhibits good capacitance value which indicates that it was more compact and uniform. Corrosion behaviors were evaluated by potentiodynamic testing according ASTM G-5 standard in 3.5% NaCl & 0.1N H_2SO_4 using Gamry Reference 600 potentiostat.

II. EXPERIMENTAL WORK:

Pure Titanium Metal has been cut in the size of 3cm X 2cm X 0.5cm to carry out anodizing process using experimental set as show in fig. 1. It consists of DC power source, bicker for electrolytic bath and platinum as cathode and test samples of anode.

2.1 Pre-treatment:

Samples are subjected to degreasing in 40% NaOH solution for 2 minutes and then electrically etched in the mixture of 10% Nitric Acid and 5% HF solution for 2 minutes.

2.2 Design of experiments:

Anodizing process were performed using bath parameters as tabulated in table No 1.

Table 1: Bath Parameters of anodizing process

Sr. No	Bath composition	Voltage (V)	Time Sec
1	10% Chromic acid	10-12	10
2	10% Chromic acid	50-55	10
3	10% Chromic acid	60-62	10

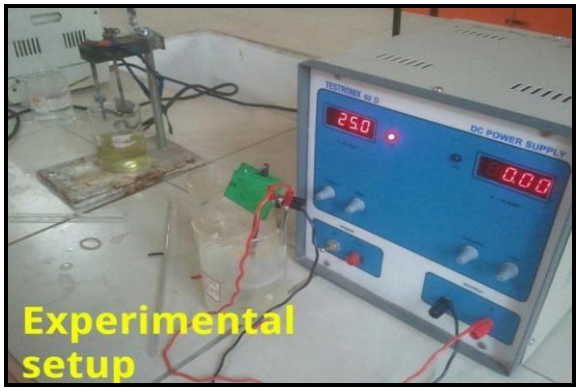


Fig 1: Experimental set up of anodizing process

2.3 Post Treatment:
It was subjected to hot water sealing at 70˚ C for 3-4 minutes and then quickly dried using a dryer.

III. TESTING & EVALUATION:

3.1 Visual observation: Anodized film was visually observed to view the coloring effect.

3.2 SEM & EDAX Analysis:
Morphological investigation of anodized film was carried out with the help of SEM while elemental analysis was done using EDAX analysis.

3.3 Corrosion study:
3.3.1 Potentiodynamic Test:
Corrosion behavior of anodized Ti samples were study as per ASTM G 5 standards in 3.5% NaCl solution and 0.1N H_2SO_4 solution using potentiostat Gamry Reference 600. Corrosion cell which consists of Calomel electrode as reference electrode, graphite rod as counter electrode and test samples as working electrode. The operating parameters of potentiodynamic study are tabulated in table 2.

Table 2: Operating Parameters of potentiodynamic Test

Sr.No	Operating Parameters
1	Initial voltage = -0.5 V w.r.t. reference electrode
2	Final voltage = 1.5 V w.r.t. reference electrode
3	Conditioning time = 60 sec
4	Initial delay = 60 sec
5	Scan rate = 5 mV / sec
6	Sample area = 0.25 cm^2
7	Density = 4.43 gm / cm^2
8	Equivalent weight =11.98 gm

3.3.3 AC Impedance Test:
Film was characterized by AC impendence spectroscopy in 3.5% NaCl and 0.1N H_2SO_4 solutions using potentiostat Gamry Reference 600. The operating parameters of AC impendence spectroscopy are tabulated in table 3.

Table 3: Operating Parameters for AC Impedance Test

Sr.No	Operating Parameters
1	DC Voltage = 0 V w.r.t. OCP
2	AC Voltage = 10 mV rms
3	Initial frequency = 100000 Hz
4	Final Frequency = 0.2 Hz
5	Sample area = 0.25 cm^2
6	Conditioning time = 60 sec
7	Initial Delay = 60 sec
8	Density = 4.43 gm / cm^2
9	Equivalent weight = 11.98 gm

IV. RESULTS & DISCUSSIONS:

4.1 Visual Inspection:
In visual test, we observed different colors on anodized titanium plate. Here below is the list that we observed, violet-brown- teal or peacock.

Table 4: Result of visual inspection

Sr. No	Sample No	Voltage range (V)	Color
1	3	10-12	Violet
2	4	50-55	Brown
3	8	60-62	Teal or Peacock

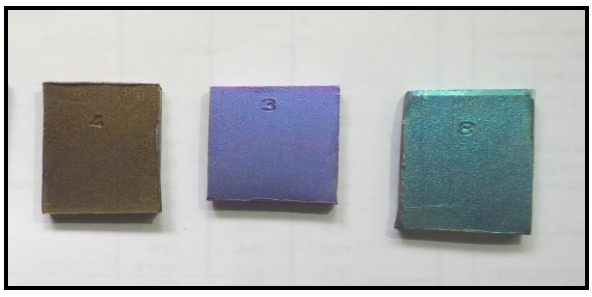


Fig 5: Titanium Spectrum at different voltage ranges in Chromic acid bath

4.2 Microscopic Evaluation by SEM

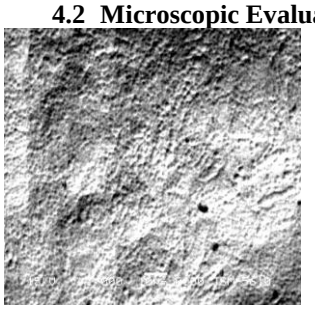


Fig 6(a): Sample 2

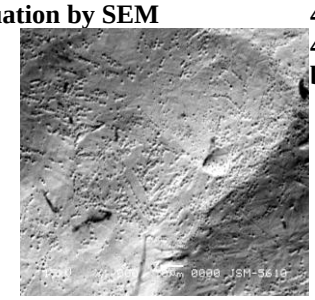


Fig 6(b): Sample 3

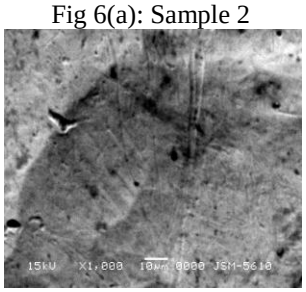
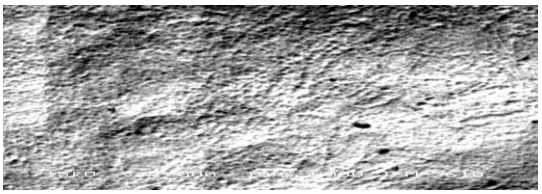


Fig 6(c): Sample 4

Fig 6(a), Fig 6(b), & Fig 6(c) shows microstructure of anodized Sample No- 2, Sample No-3 and Sample No-4, respectively by SEM at 1000X magnification. SEM analysis shows that film developed on sample No: 3 is thinner compared to all other films, while film developed on sample No: 4 is thicker and more compact than all other films.

4.3 EDAX Analysis:



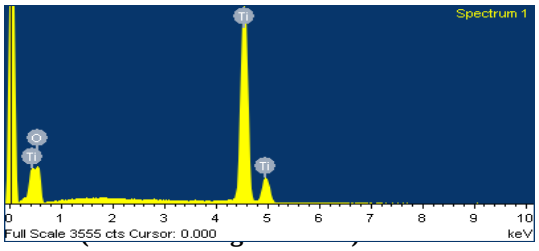


Table 5: Percentage amount element present in the film

Element	Weight%
O K	33.65
Ti K	66.65
Totals	100.00

Table -5 shows the EDAX analysis of anodized film is which indicate that it is mainly consists of Titanium oxide.

4.4. Result of Potentiodynamic study:

4.4.1 Effect of voltage variation on corrosion behavior of anodized film in 0.1N H_2SO_4 solution

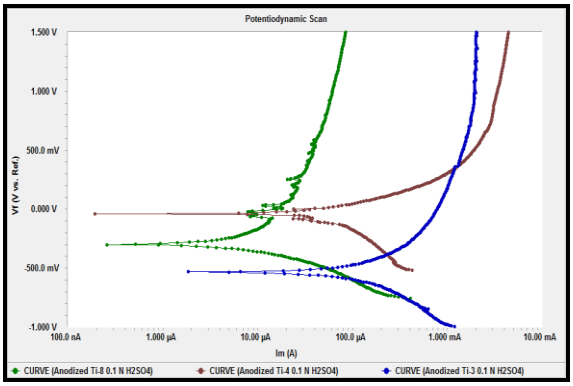


Fig. 8: Potentiodynamic scans of anodized film in 0.1N H_2SO_4 solution

Table-6: Electrochemical parameters of potentiodynamic scan of anodized film in 0.1N H_2SO_4 solution

Sr. No.	voltage range (V)	E_{corr} (mV)	I_{corr} (µA)	Corrosion rate (mpy)
1	10-12	-38.2	127	176.6
2	50-55	-532	18.5	25.8
3	60-62	-297	10.4	14.47

Fig. 8 developed at different voltage range in 0.1N H_2SO_4 solution. All samples exhibit active potential in given environment. Anodized film developed at voltage range (60-62V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-55 V voltage range.

4.4.2 Effect of voltage variation on corrosion behavior of anodized film in 3.5% NaCl solution

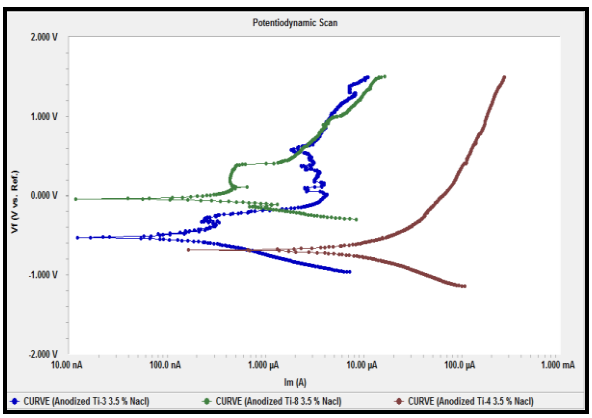


Fig. 9: Potentiodynamic scans of anodized film in 3.5% NaCl solution

Table-7: Electrochemical parameters of potentiodynamic scan of anodized film in 3.5 % NaCl solution

Sr. No.	voltage range (V)	E_{corr} (mV)	I_{corr} (µA)	Corrosion rate (mpy)
1	10-12	-688	60.6	84.4
2	50-55	-528	0.255	0.35
3	60-62	-38.1	0.548	0.76

Fig. 9 shows the potentiodynamic scan of anodized film developed at different voltage range in 3.5% NaCl solution. All samples exhibit active potential in given environment. Sample developed at voltage range (60-62V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-55 V voltage range.

4.5. Result of AC Impendence Spectroscopy (EIS):

4.5.1 Effect of voltage variation on anodized film by AC Impendence Spectroscopy in 0.1N H_2SO_4 solution

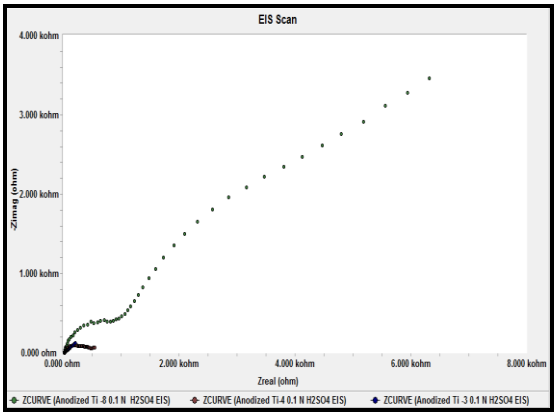


Fig. 10: Electrochemical Impedance spectroscopy scans of anodized film in 0.1N H_2SO_4 solution

Table -8: Electrochemical parameters of EIS scan of anodized film in 0.1N H_2SO_4 solution

Sr. No.	Voltage range (V)	Capacitance value(Ω)
1	10-12	95.24
2	50-55	121.4
3	60-62	3502 Ω

Fig. 10 shows the Electrochemical Impedance Spectroscopy scan of anodized film in 0.1N H_2SO_4 solution. Film developed at, 10-12V, 50-55V voltage range has lower capacitance value which indicated that film is slightly porous and the semicircle in the higher and middle frequency region of EIS curve which indicate the complete dissolution of the films due to which its corrosion resistance were decreases. Film developed at and 60-62 V voltage ranges higher capacitance value of which indicated that film was uniform and also has higher value of imaginary part of the impedance in the lower frequency region which indicates that the formation of protective film.

4.5.2 Effect of voltage variation on anodized film by AC Impendence Spectroscopy in 3.5 % NaCl solution.

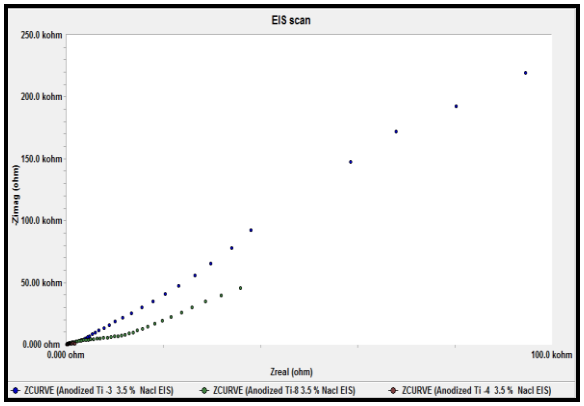


Fig.11: Electrochemical Impedance spectroscopy scans of anodized film in 3.5% NaCl solution.

Table -9: Electrochemical parameters of EIS scan of anodized film in 3.5% NaCl solution

Sr. No.	Voltage range (V)	Capacitance value (KΩ)
1	10-12	0.9183
2	50-55	219.8
3	60-62	45.53

Fig. 11 shows the Electrochemical Impedance Spectroscopy scan of anodized film in 3.5 % NaCl solution. Film developed at 10-12V, 50-55V voltage range has lower capacitance value which indicated that film is slightly porous and the semicircle in the higher and middle frequency region of EIS curve which indicate the complete dissolution of the films due to which its corrosion resistance were decreases. Film developed at 60-62 V voltage ranges higher capacitance value of which indicated that film was uniform and also has higher value of imaginary part of the impedance in the lower frequency region which indicates that the formation of protective film.

V. CONCLUSION

1. Pure Titanium metal shows spectrum of colors from Violet - Brown & Teal or Peacock with increasing the voltage step by step from 10-62 Volts in chromic acid bath.

2. Anodized film developed using chromic acid bath consist mainly of Ti – Oxide layer.
3. Anodized film developed at voltage range (60-62V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-55V voltage range in 0.1N H_2SO_4 and 3.5% NaCl solutions.
4. Film developed at voltage range (60-62V) is more compact, uniform & having high capacitance while films produced below as well as above 50-55 V voltage ranges are less compact and having lower capacitance value.

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