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Characterization and Corrosion Study of Titanium Anodized Film Developed in KOH Bath

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ABSTRACT:
Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. Aluminum is ideally suited to anodizing, although other nonferrous metals, such as tantalum and titanium, can also be anodized. 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, 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 KOH at different voltage ranges. The anodized film is characterized by visual observation, SEM & EDAX analysis & A.C impedance spectroscopy, while the corrosion studies were performed using salt spray test & potentiodynamic studies. Result of various studies shows that Anodized film was mainly consisting of TiO_2 and Ti_2O_3, having spectrum of colors from Blue-Yellow-Purple-Green. The film is more compact, adherent and more uniform due to which it exhibits good corrosion resistance.
***Keywords*:** Anodizing of Titanium, Coloring Effect, Potentiodynamic Test, AC Impedance Test, Salt Spray Test, and SEM & EDAX analysis

I. INTRODUCTION

1.1 Anodizing:

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. It increase wear resistance and provides better adhesion for paint primers and glues on base metal [1, 2]. Generally, anodizing is carried out on metals like Aluminum, Titanium, Tantalum and alloy like Stainless Steel. 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. Coatings are normally porous, which can be sealed to achieve better corrosion resistance [3].

1.2 Titanium Anodizing:

Anodized Titanium often used in the medical devices, orthopedic implants, dental implants, and device components of aerospace industries. It offers coloring effect without altering the mechanical properties of metal [4].Anodized film of Titanium offer 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, NaH_2PO_4, and Na_2HPO_4 [5-7]. In present work, the pure Titanium plate was anodized using different baths of KOH 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 qualitative evaluated by salt spray test according to ASTM B 117 standard in 5 % NaCl solution while quantitatively 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 perfume 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% KOH	20-22	10
2	10% KOH	40-42	10
3	10% KOH	50-52	10
4	10% KOH	70-72	10

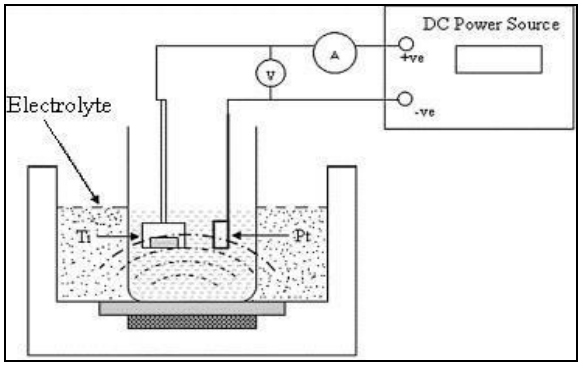

Fig 1: Experimental set up of anodizing process

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 Salt Spray Test (Fog Test):
It was performed on anodized Ti samples according to ASTM B-117 standard in 5% NaCl solution at 30 to 35^0C temperature with exposure period of 72 hours.

3.3.2 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, Blue-Yellow-Purple-Green.

Table 4: Result of visual inspection

Sr. No	Sample No	KOH bath voltage range (V)	Color
1	7	20-22	Blue
2	5	40-42	Yellow
3	2	50-52	Purple
4	6	70-72	Green

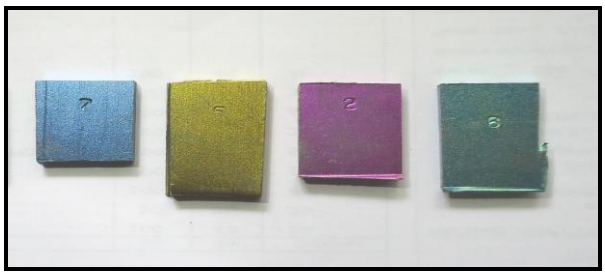

Fig 5: Titanium Spectrum at different voltage ranges in KOH bath

4.2 Microscopic Evaluation by SEM:

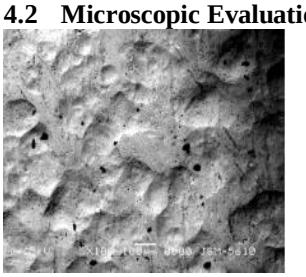

Fig 6(a)

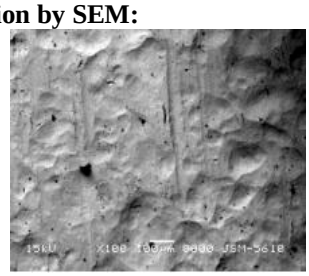

Fig 6(b)

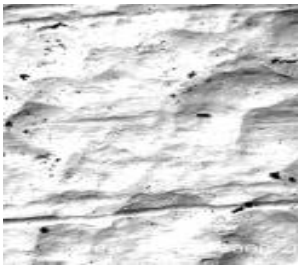

Fig 6(c)

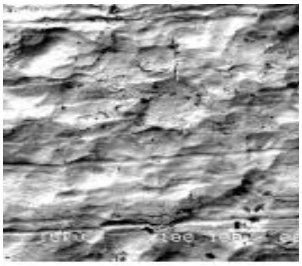

Fig 6(d)

Fig 6(a), Fig 6(b), Fig 6(c) & Fig 6(d) shows microstructure of anodized Sample No- 2, Sample No-5, Sample No-6, and Sample No- 7 respectively by SEM at 1000X magnification. SEM analysis shows that film developed on all samples were uniform and compact.

4.3 EDAX Analysis:

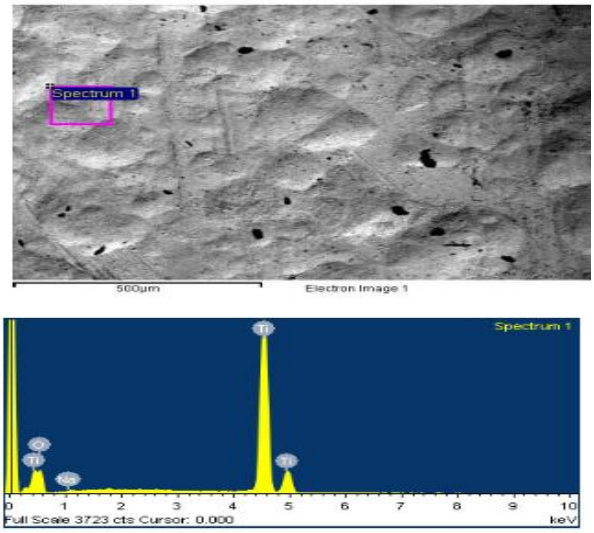

Fig. 7 EDAX analysis of Sample No -2 (1000 X magnification)

Table 5: Percentage amount element present on the film

Element	Weight%
O K	27.65
Na K	0.34
Ti K	72.01
Totals	100.00

EDAX analysis show that film is mainly consists of Titanium oxide.

4.4 Result of Salt Spay Test:

Fig.8(a)

Fig.8(b)

Fig.8(c)

Fig.8(d)

Fig.8 (a), (b), (c) and (d) show the result of salt spray test on anodized film Sample No- 2, Sample No-5, Sample No-6, Sample No- 7 respectively after 72 hour of exposure period. It reveals that all samples do not show any corrosion product even after exposure period of 72 hour.

4.5. Result of Potentiodynamic study:

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

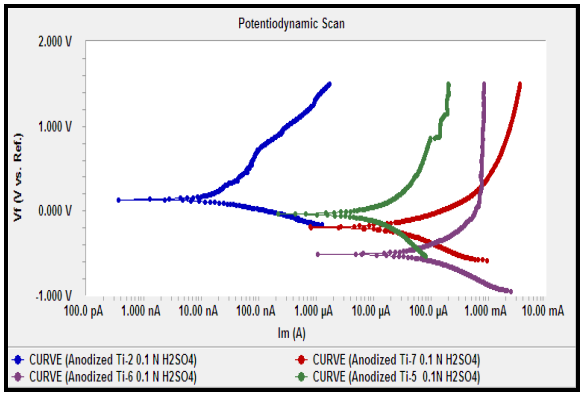

Fig. 9: Potentiodynamic scans of anodized film in 0.1N H_2SO_4 solution

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

Sr. No.	KOH bath voltage range (V)	E_{corr} (mV)	I_{corr} (µA)	Corrosion rate (mpy)
1	50-52	-137	0.017	0.0237
2	20-22	-192	9.41	13.11
3	40-42	-35.1	37.2	51.76
4	70-72	-510	71.8	100.1

Fig. 9 shows the potentiodynamic scan of anodized film 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 (50-52V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-52 V voltage range.

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

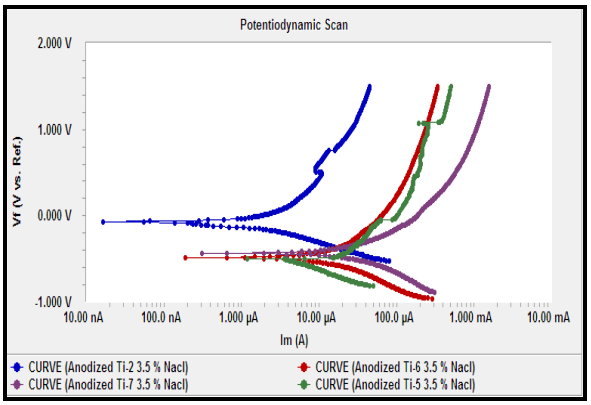

Fig. 10: Potentiodynamic scans of anodized film in 3.5% NaCl solution

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

Sr. No.	KOH bath voltage range (V)	E_{corr} (mV)	I_{corr} (µA)	Corrosion rate (mpy)
1	50-52	-68.9	0.354	0.493
2	20-22	-432	5.4	7.521
3	40-42	-493	23.3	32.41
4	70-72	-483	39.2	54.59

Fig. 10 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 (50-52V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-52 V voltage range.

4.6. Result of AC Impendence Spectroscopy (EIS):

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

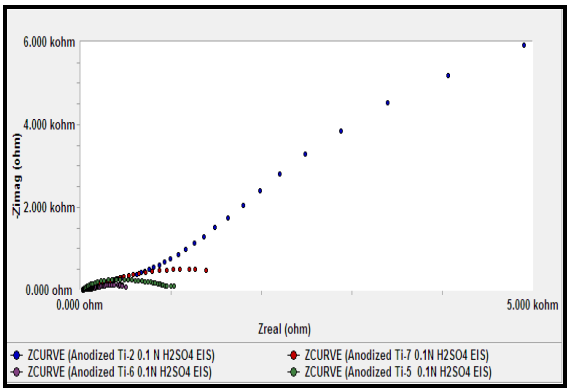

Fig. 11: Electrochemical Impedance spectroscopy scans of anodized film in 0.1N H_2SO_4 solution.

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

Sr. No.	KOH bath voltage range (V)	Capacitance value(Ω)
1	50-52	5923
2	20-22	519.0
3	40-42	261.9
4	70-72	127.8

Fig. 11 shows the Electrochemical Impedance Spectroscopy scan of anodized film in 0.1N H_2SO_4 solution. Film developed at, 20-22V, 40-42V and 70-22 V 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 50-52 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.

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

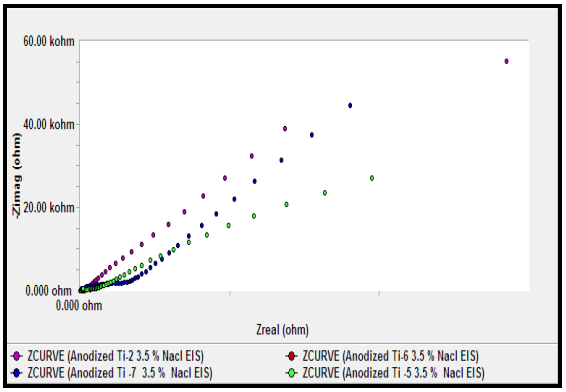

Fig.12: Electrochemical Impedance spectroscopy scans of anodized film in 3.5% NaCl solution.

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

Sr. No.	KOH bath voltage range (V	Capacitance value(Ω)
1	50-52	55100
2	20-22	44550
3	40-42	27320
4	70-72	2082

Fig. 12 shows the Electrochemical Impedance Spectroscopy scan of anodized film in 3.5 % NaCl solution. Film developed at 20-22V, 40-42V and 70-22 V 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 50-52 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 Blue-Yellow-Purple & Green with increasing the voltage step by step from 10-70 Volts in KOH bath.
2. Anodized film developed using KOH bath consist mainly of Ti – Oxide layer.
3. All the samples exhibit good atmospheric corrosion resistance even after 72 hours of exposure in NaCl fog.
4. Anodized film developed at voltage range (50-52V) exhibits best corrosion resistance, while the corrosion resistances were decreases below as well as above 50-52 V voltage range in 0.1N H_2SO_4 and 3.5% NaCl solutions.
5. Film developed at voltage range (50-52V) is more compact, uniform, high capacitance while films produced below as well as above 50-52 V voltage ranges are less compact and lower capacitance value.

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