RESEARCH ARTICLE OPEN ACCESS

Corrosion Behaviour and Colour Properties of Anodized Titanium

Mr. Ashutosh R Singh (Temporary Assistant Professor), Dr. Sunil D. Kahar
(Metallurgical & Materials Engg. Dept., Faculty of Technology & Engineering, The M.S.University of Baroda, Vadodara-390001, India)

ABSTRACT:
Anodizing is an electrolytic passivation process used to increase the thickness of the oxide layer on the surface of metal parts. Aluminium is also 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, 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 TiO2 or mixtures of TiO2 & Ti2O3 etc.
The present study is focused on analyzing the change of colour of anodized titanium and effects of electrolytic voltage on corrosion behaviour of titanium. In the present work, Pure Titanium plate has been anodized using bath of citric acid at different voltage ranges from 17 to 32 volts. The anodized film is characterized by visual observation, AC Impedance Spectroscopy, while the corrosion studies were performed using potentiodynamic studies in 3.5 % NaCl solution & 1 M H2SO4 Solution. Anodized film was mainly consisting of TiO2 and Ti2O3, having spectrum of colors from violent-sky blue-light gray with increases in voltage from 17 to 32 volts. Corrosion resistance of the film has been improve with increases in voltage from 17 to 32 volts in both solution i.e. 3.5 % NaCl solution & 1 M H2SO4 Solution due to increase in the capacitance value of the film.
Key word: Anodizing, Titanium oxide; colouring effect, potentiodynamic study, EIS study

---

DATE OF SUBMISSION: 03-01-2020 DATE OF ACCEPTANCE: 18-01-2020

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, corrosion resistant, durable film. It increase wear resistant and provides better adhesion for paint primers and glues on base metal. Generally, anodizing is carried out on metals like Aluminium, Tantalum, Titanium and alloys like Stainless Steel. It has 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 resistant.

1.2. Titanium Anodizing:

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, H2SO4, Coke, H3PO4, NaH2PO4, and Na2HPO4.[1] In Present work, the pure Titanium(Grade-II) plate was anodized using bath of Citric Acid at various voltage ranges to obtain different spectrum of colors[3][2]. The anodized film characterized by A.C. Impedance Spectroscopy &Potentiodynamic test. 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 behaviours were quantitatively evaluated by Potentiodynamic testing according ASTM G-5 standard in 3.5% NaCl& 1M H2SO4 using Gamry Reference 600 Potentiostat.

II. RESEARCH SIGNIFICANCE

Anodizing of Pure Titanium (Grade-II) plate gives good appearance to the metal surface. So that one can use it as a decorative purpose. During anodizing process oxide layer form on the metal surface, that prevents corrosion. By using different voltages during anodizing process it gives different spectrum of colour without altering the mechanical properties of metal. So by using this one can get metal surface with different colour without using colours and coating. This process reduces the time for colouring. It reduces the cost to protect the metal surface from atmosphere. Anodized Titanium often used in the medical devices, orthopedic implants, dental implants, and device components of aerospace industries.

III. EXPERIMENTAL WORK

3.1 Materials &Method

Pure Titanium (Grade-II) plate has been cut in the size of 25mm X 20mm X 2mm to carry out anodizing process using experimental set as shown in fig. 1. It consists of DC power source, beaker for electrolytic bath and carbon electrode as cathode and test samples of anode.

3.1.1Pre-treatment:

Samples are subjected to degreasing and etching in the mixture of 37% HNO3, 3.5% HF & 210ml H2O for 4-5 minutes.

3.1.2 Design of Experiments:

Anodizing process were perfume using bath parameters as tabulated in Table-1.

Table 1: Bath Parameters of Anodizing Process

Sr. No.	Bath Composition	Voltage (V)	Time (min.)
01	20g/l Citric acid & 20g/l Baking soda	17	15
02		25	15
03		32	15

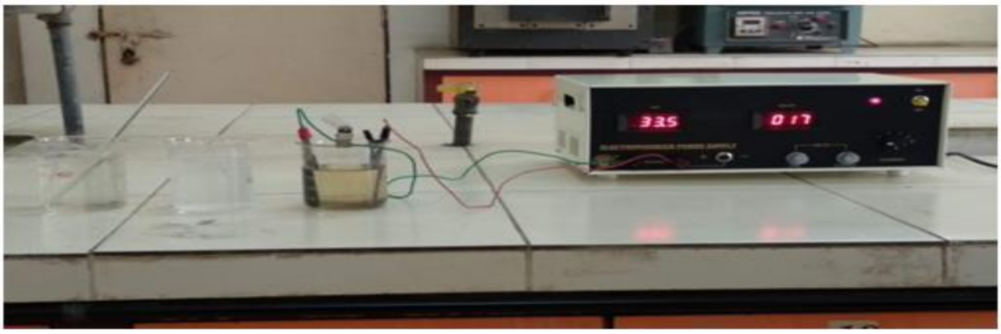


Fig 1: Experimental set up of anodizing process

3.1.3 Post Treatment:

It was subjected to hot water sealing at 80-85ºC
For 2-3 minutes and then quickly dried using a Dryer.

3.2 Testing & Evaluation

3.2.1 Visual Observation:

Anodized film was visually observed to view the coloring effect.

3.2.2 Corrosion study:

3.2.2.1 Potentiodynamic Test:

Corrosion behaviour of anodized Ti samples were study as per ASTM G – 5 standards in 3.5% NaCl solution and 1M H2SO4 solution using potentiostatGamry 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
01	Initial voltage: -0.5 V w.r.t reference electrode
02	Final voltage: 1 V w.r.t reference electrode
03	Conditioning time: 30 sec
04	Initial delay: 30 sec
05	Scan rate: 5mV/sec
06	Sample area: 0.25 cm2
07	Density: 4.506 gm/cm3
08	Equivalent weight: 23.93 gm

3.2.2.2 AC Impedance Test:

Film was characterized by AC impedance spectroscopy in 3.5% NaCl and 1M H2SO4 solutions using potentiostate Gamry reference 600. The operating parameters of AC impedance spectroscopy are tabulated in Table-3.

Table 3: Operating parameters for AC Impedance Test

Sr. No.	Operating Parameters
01	DC voltage: 0 V w.r.t OCP
02	AC voltage: 10 mV rms
03	Initial frequency: 100000 Hz
04	Final frequency: 0.2 Hz
05	Sample area: 0.25 cm2
06	Conditioning time: 30 sec
07	Initial delay: 30 sec
08	Density: 4.506 gm/cm3
09	Equivalent weight: 23.93 gm

IV. RESULTS & DISCUSSIONS

4.1 Visual Inspection:

In this test, we observed different colors on anodized Titanium plate. Here below is the list that we observed.

Table 4: Result of Visual inspection

Sr. No.	Voltage (V)	Colour
01	17	Violet
02	25	Sky Blue
03	32	Light Grey

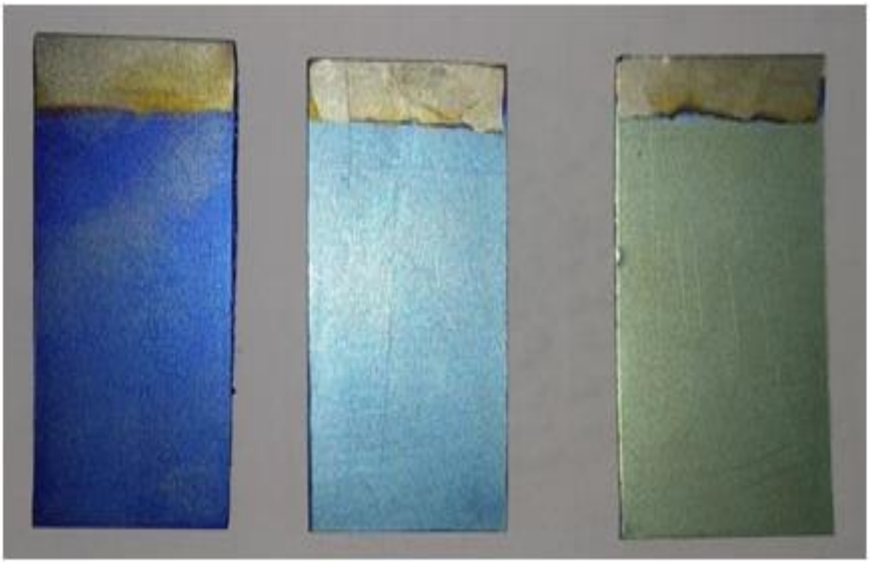


Fig 2: Titanium Spectrum at different voltage ranges in Citric acid bath

4.2 Result of Potentiodynamic study:

4.2.1 Effect of voltage variation on corrosion behaviour of anodized film in 3.5% NaCl solution:

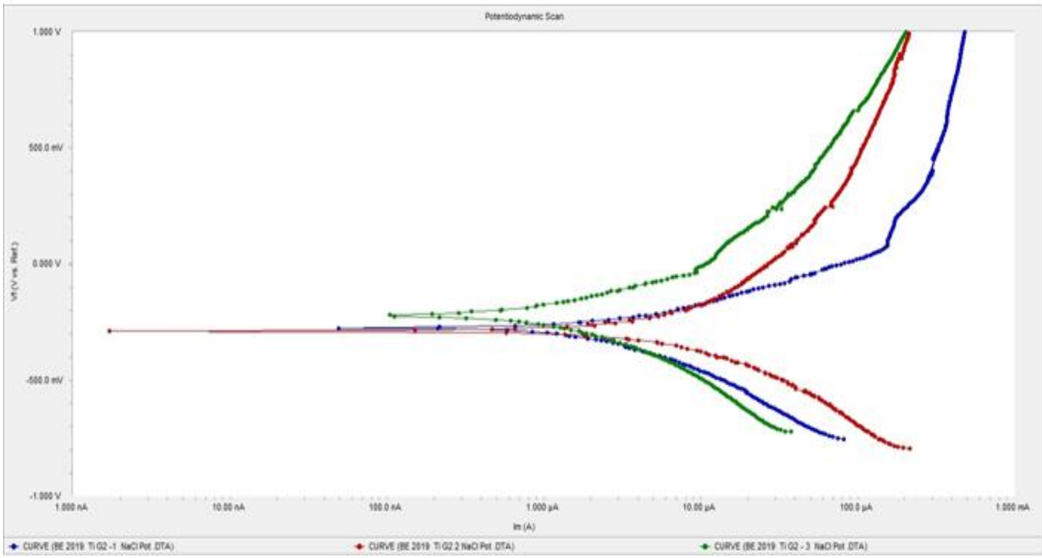


Fig 3: Potentiodynamic scans of anodized film in 3.5% NaCl solution

Table 5: Electrochemical parameters of potentiodynamic scans of anodized film in 3.5% NaCl solution

Sr. No.	Voltage (V)	Ecorr (mV)	Icorr (µA)	Corrosion rate (mpy)
01	17	-275.00	2.750	7.516
02	25	-288 00	1.460	3.994
03	32	-222.00	1.190	3.258

Fig. 3 shows effect of voltage variation on corrosion behaviour of Ti anodized film in 3.5% NaCl solution. All samples exhibit active potential in given environment. It was observed that with increase in voltage from 17V to 25V the corrosion rate was decreases. With increase in voltage from 25V to 32V the corrosion rate was also decreases. So it can be concluded that with increasing in voltage from 17V to 32V the corrosion rate was decreases in 3.5% NaCl solution.

4.2.2 Effect of voltage variation on corrosion behaviour of anodized film in 1 M H2SO4 solution:

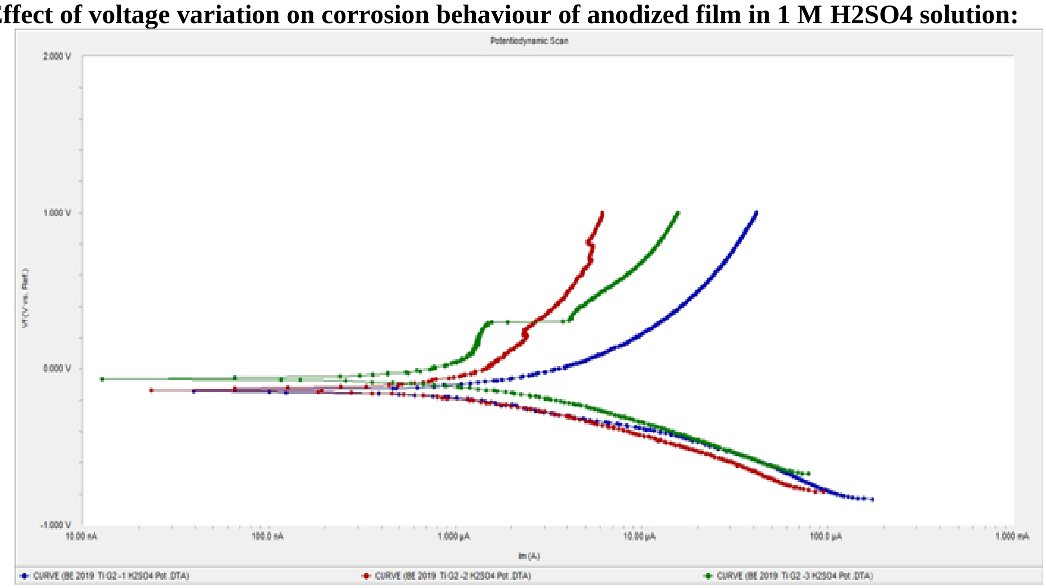


Fig 4: Potentiodynamic scans of anodized film in 1 M H2SO4 solution

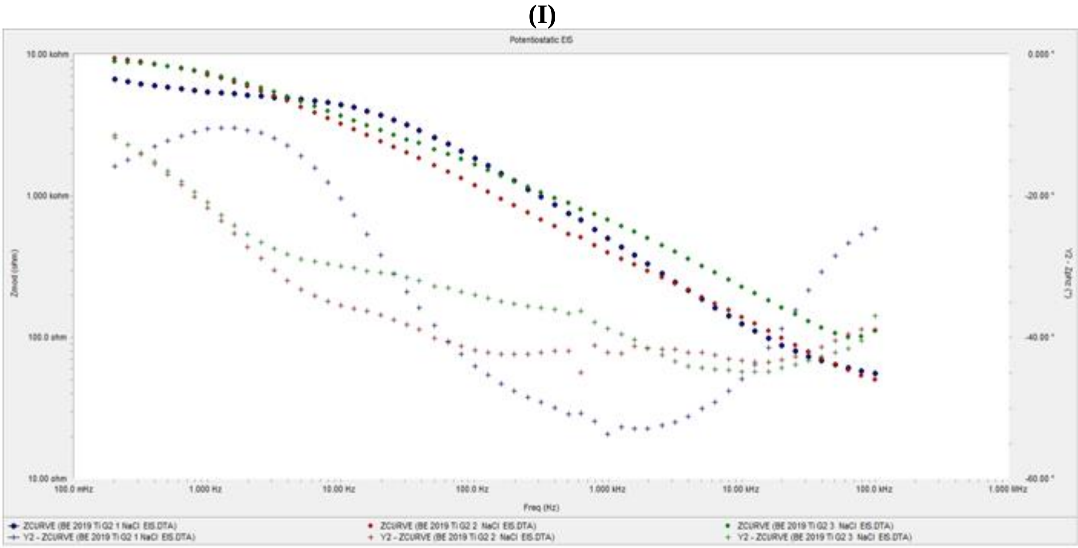
Table 6: Electrochemical parameters of potentiodynamic scans of anodized film in 1 M H2SO4 solution

Sr. No.	Voltage (V)	Ecorr (mV)	Icorr (µA)	Corrosion rate (mpy)
01	17	-141.00	2.950	8.077
02	25	-61.90	2.140	5.866
03	32	-62.00	1.600	4.365

Fig. 4 shows effect of voltage variation on corrosion behaviour of Ti anodized film in 1M H2SO4 solution. All samples exhibit active potential in given environment. It was observed that with increase in voltage from 17V to 25V the corrosion rate was decreases. With increase in voltage from 25V to 32V the corrosion rate was also decreases. So it can be concluded that with increasing in voltage from 17V to 32V the corrosion rate was decreases in 1M H2SO4 solution.

4.3 Result of AC Impedance Spectroscopy (EIS):
4.3.1 Effect of voltage variation on anodized film by AC Impedance Spectroscopy in 3.5% NaCl solution:

(I)



(II)

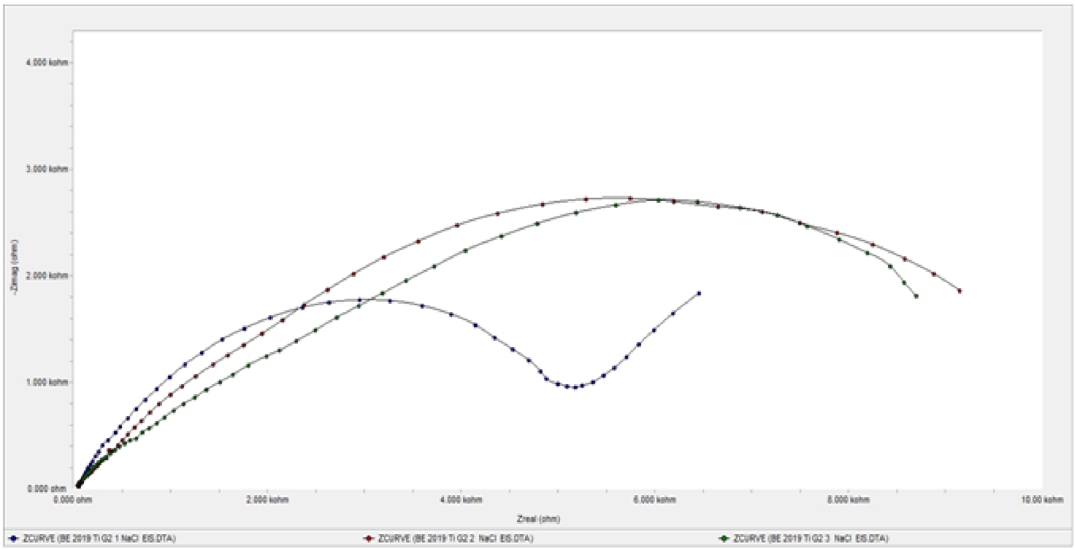


Fig 5: (I) & (II) Nyquist& Bode plot of Ti anodized film in 3.5% NaCl solution respectively

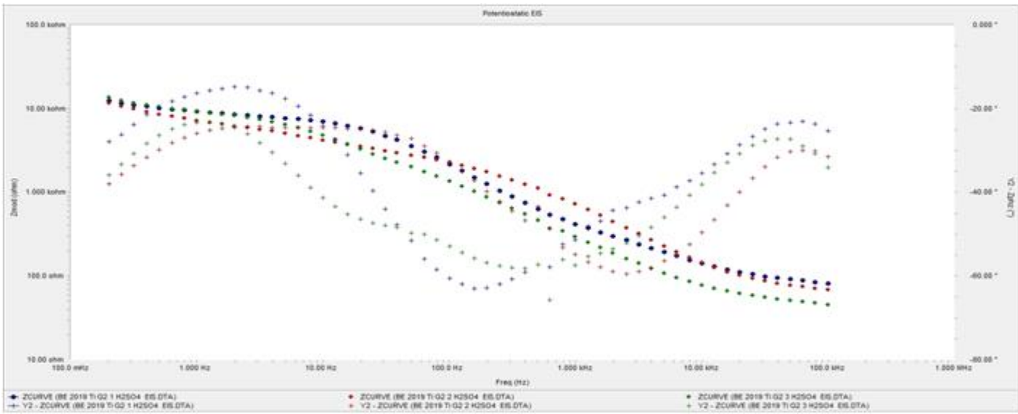
Table 7: Electrochemical parameters of EIS scans of anodized film in 3.5% NaCl solution

Sr. No.	Voltage (V)	Capacitance value (Ω)
01	17	1.833
02	25	2 704
03	32	2.717

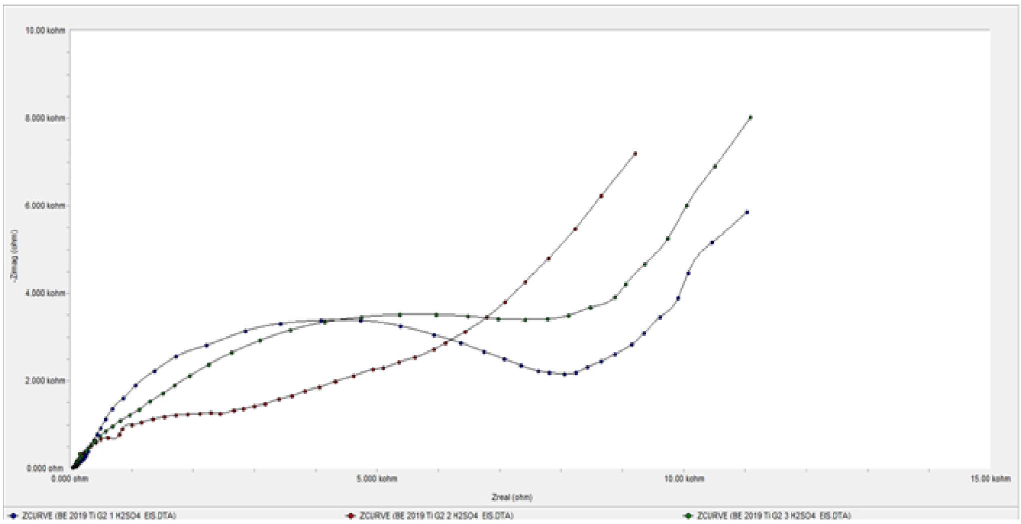
Fig. 5 shows the effect of voltage variation on Capacitance value of Ti anodized film in 3.5% NaCl solution in form of Nyquist plot & Bode plot respectively. Film developed with 17V has lower Capacitance value which indicates that film is slightly porous and the semicircle in the higher and middle frequency region of EIS curve which indicate higher rate of dissolution of film due to which its corrosion resistance were decreases. Film developed with 25V & 32V has almost similar Capacitance value but 32V film exhibit higher Capacitance value. With the value 2.717KΩ which indicates that film was uniform and also has higher value of imaginary part of the impedance in the lower frequency region which indicates that formation of protective film.

4.3.2 Effect of voltage variation on anodized film by AC Impedance Spectroscopy in 1 M H2SO4 solution

:



(I)



(II)

Fig 6: (I) & (II) Nyquist& Bode plot of Ti anodized film in 1 M H2SO4 solution respectively

Table 8: Electrochemical parameter of EIS scans of anodized film in 1 M H2SO4 solution

Sr. No.	Voltage (V)	Capacitance Value (Ω)
01	17	5.85
02	25	7.19
03	32	8.09

Fig. 6 shows the effect of voltage variation on Capacitance value of Ti anodize film in 1 M H2SO4 solution in form of Nyquist plot & Bode plot respectively. Film developed with 17V has lower Capacitance value which indicates that film is slightly porous and the semicircle in the higher and middle frequency region of EIS curve which indicate higher rate of dissolution of film due to which its corrosion resistance were decreases. Film developed with 32V exhibit higher Capacitance value. With the value 8.09KΩ which indicates that film was uniform and also has higher value of imaginary part of the impedance in the lower frequency region which indicates that formation of protective film.

V. CONCLUSION

(1) Pure Ti-Grade-II metal shows spectrum of color from Violet – Sky Blue – Light Grey with increasing in voltage step by step from 17V to 32V in Citric acid bath.
(2) Anodized film developed with 32V bath of Citric acid exhibit best corrosion resistance in 3.5% NaCl solution.
(3) Anodized film developed with 32V bath of Citric acid exhibit best corrosion resistance in 1M H2SO4 solution.
(4) Film developed with 32V is more compact, uniform & having higher Capacitance in 3.5% NaCl solution.
(5) Film developed with 32V is more complete, uniform & having higher Capacitance in 1M H2SO4 solution
(6) Finally it can be concluded that Ti-Grade-II shows coloring effect in anodizing using Citric acid bath at different voltage ranges and increases in corrosion resistance with increase in voltage from 17V to 32V.

REFERENCES

Journal Papers:

[1]. **Mr. Sunil D. Kahar, ArpitMacwan, Ms. RiddhiOza, VrundOza, SmitShah** Characterization and Corrosion Study of Titanium Anodized Film Developed in KOH Bath. (2013). Vol. 3, pp. 441-442

[2]. **G.Napoli,M.Paura,T.Vela,A.DiSchino** Colouring Titanium alloys by anodic oxidation (2018)

[3]. **AliKarambakhsh,AbdollahAfshar,ShahramGhahramani, and Pejmanmalekinejad** Pure Commercial Titanium Color Anodizing and Corrosion Resistance(2010)

[4]. **J.L. Delplancke, M. Degrez, A. Fontana and R. Winand,** Self colouring of Titanium, Surface Technology, 16 (1982) pp 154-158

[5]. **A.K. Sharma**, Anodizing Titanium for Space Applications, Thin Solid Films. (1992), P 48

Books:

[6]. **S.Narain,** An introduction to electrometallurgy p. 193

[7]. **Mars G. Fontana & Norbert D. Green,** “Corrosion Engineering”, Mcgraw Hill International Book Company, New Delhi p.154

Mr. Ashutosh R Singh "Corrosion Behaviour and Colour Properties of Anodized Titanium" *International Journal of Engineering Research and Applications (IJERA*), vol.10(01), 2020, pp 17-23.