



## Anodic Behaviour of Titanium-12 in 0.1 M Ferrous Ammonium Sulphate under Different Anodizing Conditions

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### ABSTRACT

Anodization of Titanium-12 alloy has been studied in aqueous ferrous ammonium sulphate electrolyte at different current densities, temperatures and electrolyte concentrations under galvanostatic conditions. The surface morphology of the anodic films formed were studied by using Scanning Electron Microscopy. From the plots of formation voltage vs. time, the rates of film formation were calculated. Kinetics of film formation was studied in aqueous ferrous ammonium sulphate electrolyte of different concentrations ranging from 0.1 M to 0.00625 M and at different temperatures ranging from 310 K to 350 K under galvanostatic conditions. It was also studied the anodization at different current densities ranging from 4 mA.cm<sup>-2</sup> to 64 mA.cm<sup>-2</sup>. From the results it was found that the rate of film formation and breakdown voltage decrease with decrease in electrolyte concentration and increase in temperature. But they increase with increase in constant current density. It has also been observed the significant change in film surface morphology from SEM studies at different anodizing conditions.

**Keywords:** Titanium-12; Anodic oxidation; Ferrous ammonium sulphate; Surface morphology; Formation rate

### INTRODUCTION

The interest in titanium and its alloys keeps growing on account of their peculiar engineering properties, which find wide range of applications from architecture to bioengineering [1], from automotive to photovoltaic cells and photo catalytic devices [2], as well as to produce self-cleaning surfaces. All surface-related properties of Titanium and its alloys namely aesthetic appearance, corrosion resistance and interactions with the working environment [3], including human body can be fine-tuned as a function of the final application desired by oxidizing the metal surface, which is generally performed by anodic oxidation. An anodized oxide layer has a thickness in the range of 30 nanometers to several micrometers. Anodizing titanium generates an array of different colors without dyes [4], for which it is sometimes used in art, costume jewelry, body piercing jewelry and wedding rings. The color formed is dependent on the thickness of the oxide.

Luckey H and Kubli F [5] explained how effectively titanium and its alloys are useful as surgical implants than stainless steel and Co-Cr-Mo alloys. Omidrar H and Goodarzi S [6] studied influence of anodization parameters on the morphology of TiO<sub>2</sub> nanotube arrays. They found that the rate of film formation increased as increase in electrolyte pH and decrease in temperature. Krasicka-Cydzik E [7,8] reported formation of thin anodic layers on titanium and its alloys and also investigated influence of Phosphoric acid on the rate of titanium alloys anodization. Hensler KE [9] published a paper on the influence of electrolyte composition on the formation and dissolution of passivating films. De-Sheng K [10] examined the deleterious/depassive effect of fluoride ions on physicochemical properties of anodic oxide films formed on titanium surfaces and explained that the anodic films formed at higher potentials (>2.5 V) significantly show high stability towards fluoride attack than those formed at lower potentials (<2.5 V). Toccafondi C et al. [11] briefly explained the optical properties of nanogrannular and highly porous TiO<sub>2</sub> thin films.

In the present work, an attempt is made to study the kinetics of anodization of titanium-12 alloy in aqueous ferrous ammonium sulphate at different current densities, temperatures and electrolyte concentrations. Results were reported in Tables 1-3 and respected film formation rates were calculated from the plots of formation voltage vs. time. Surface morphology of the anodic films at different anodic conditions has been compared and studied by using Scanning Electron Microscopy micrographs.

### MATERIALS AND METHODS

Titanium-12 is an alloy of 98% pure titanium with other trace impurities, purchased from Defence Metallurgical Research Lab, Hyderabad. The chemical composition of titanium-12 is: Fe-0.30%; Mo-0.2-0.4%; Ni-0.6-0.9%; N<sub>2</sub>-0.03%; C-0.08%; H<sub>2</sub>-0.015%; O<sub>2</sub>-0.25% and the balance is titanium. In the present work, the foil samples with 0.2mm thickness used were cut with the aid of a punch into flag shaped specimens of 1 cm<sup>2</sup> working area on both sides and 1 ½ cm long tag. The chemical polishing mixture used was a mixture of acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF and water in a definite volume ratio of 2:1:1:1. For anodization process, a closed double walled glass cell of 200ml capacity was used. The cathode used was Platinum of 20 cm<sup>2</sup> superficial area to make double layer capacitance as large as possible. Ferrous ammonium sulphate was used as an electrolyte. The current densities applied were ranging from 4 mA.cm<sup>-2</sup> to 64 mA.cm<sup>-2</sup>, temperatures ranging from 310 K to 350 K and electrolyte concentrations vary from 0.1 M to 0.00625 M. All the experiments were carried out under galvanostatic conditions. The experimental procedure for the anodization is given elsewhere [12]. The rate of film formation was calculated in VSec<sup>-1</sup> from the conventional plots of formation voltage vs. time. The surface morphology of anodic films was studied by using SEM.

### RESULTS AND DISCUSSION

Anodic oxidation of Titanium in aqueous ferrous ammonium sulphate at various current densities, temperatures and in different electrolyte concentrations was studied and the corresponding results were reported. VD Shukla [13] studied kinetics and surface morphology of the anodic films formed on Nb in 0.1 M aqueous ferrous ammonium sulphate at different temperatures. In the case of Ti-12, it is observed that the formation rate and breakdown voltage are low when compared with Nb at corresponding anodizing conditions.

#### Effect of Current Density

In the present work, anodic oxidation of titanium-12 alloy was performed in aqueous ferrous ammonium sulphate electrolyte at different constant current densities applied across the cell using DC Power supply. Muzushima [14] studied the formation of anodic films on titanium in 10% ammonium borate in glycolic medium at constant current densities ranging from 12.5 mA/dm<sup>2</sup> to 200 mA/dm<sup>2</sup> and at various temperatures and found that the rate of thickness per volt (A/V) was found to increase with increase in current density. Rates of film formation were calculated from the plots of V Vs. t. at various current densities ranging from 4 mA.cm<sup>-2</sup> to 64 mA.cm<sup>-2</sup>. As the current density increases the rate of film formation and breakdown voltage increase linearly as shown in the Table 2. Intensity of colors of anodic films diminishes as current density increases. SEM images of the yielded titania films in 0.1 M aqueous ferrous ammonium sulphate at low (4 mA.cm<sup>-2</sup>) and high (64 mA.cm<sup>-2</sup>) constant current densities and the corresponding plots of formation voltage vs. time were shown in the Figure 1.

#### Effect of Electrolyte Concentration

Anodic oxidation of titanium-12 is also performed by changing electrolyte concentration under galvanostatic conditions (at a constant current density of 8 mA.cm<sup>2</sup>). It is observed that the rate of film formation and breakdown voltage gradually decrease with decrease in electrolyte concentration from 0.1 M to 0.00625 M as shown in the Table 3. It is attributed to the decrease in the number of available free anions per cubic centimeter. Intensity of colors of anodic films also decreases as the electrolyte concentration decreases. SEM images of the resulted titania films in 0.1 M and 0.00625 M aqueous ferrous ammonium sulphate at room temperature and the corresponding plots of formation voltage vs. time were shown in the Figure 2.

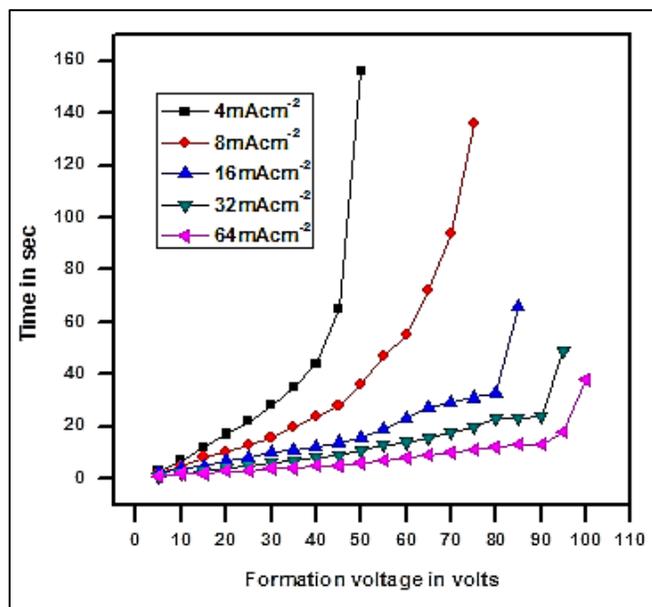


Figure 1: Plots of formation voltage as a function of time in 0.1 M aqueous ferrous ammonium sulphate solution at different current densities

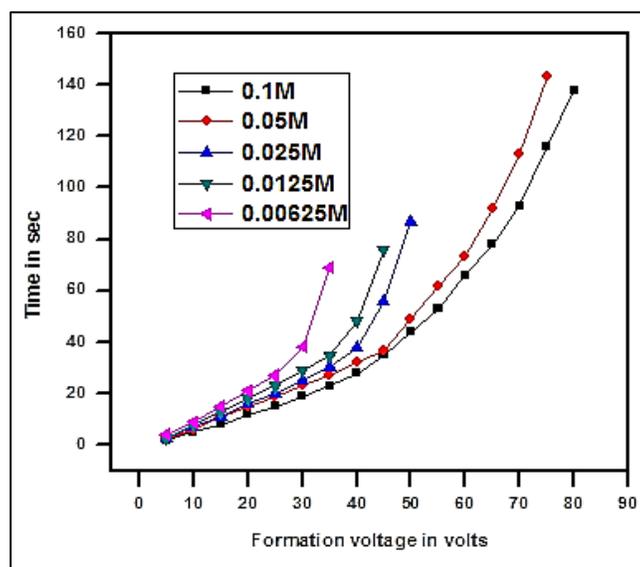


Figure 2: Plots of formation voltage as a function of time at different concentrations of aqueous ferrous ammonium sulphate solution at room temperature

### Effect of Temperature

The effect of temperature on the kinetics of anodic oxidation of titanium-12 has also been studied in 0.1 M aqueous ferrous ammonium sulphate electrolyte at constant current density of  $8 \text{ mA}\cdot\text{cm}^{-2}$ . Various temperatures applied for anodic oxidation of titanium-12 were ranging from 310 K to 350 K. The conventional plots were drawn as shown in Figure 3. From these plots, the formation rates were calculated. It was observed that the formation rate and breakdown voltage were found to be increasing linearly with the decrease in temperature as shown in the Table 1.

The decrease in the formation rate and breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may be due to the dissolution of the film with the increase in temperature. SEM images of the anodized films in 0.1 M aqueous ferrous ammonium sulphate at low (310 K) and high (350 K) temperatures and the corresponding plots of formation voltage vs. time were shown in Figure 3.

Colton and Wood [15] reported that the breakdown voltage was decreased with increase in temperature in the case of titanium oxide films and explained the observation based on dissolution of the film. Nigam et al. [16] studied anodic growth of films on tantalum in aqueous solutions of citric acid and oxalic acid at different temperatures.

Bhaskar reddy et al. [17] observed the similar trend of decreasing kinetic results with increase in temperature in 0.1 M potassium tartarate. Similar trends were reported by many others [18-23] (Figures 4-6).

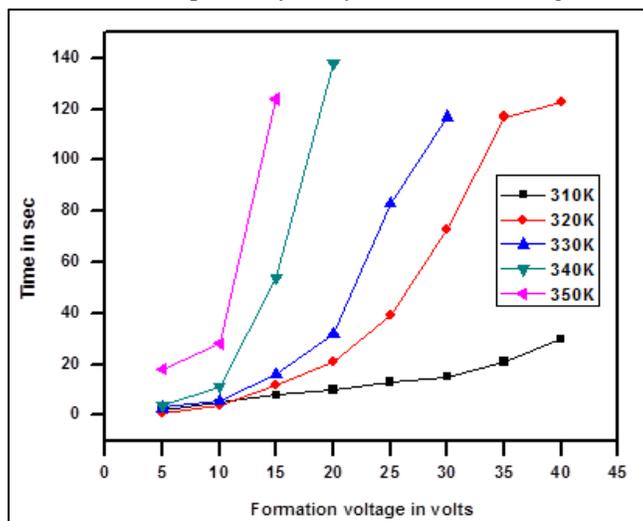


Figure 3: Plots of formation voltage as a function of time in 0.1 M aqueous ferrous ammonium sulphate solution at different temperatures

Table 1: Temperature effect on anodization of Titanium-12 alloy in 0.1 M aqueous ferrous ammonium sulphate solution at constant current density  $8 \text{ mA.cm}^{-2}$

Sl. No	Temperature (K)	Formation rate $dV/dt$ ( $\text{V.s}^{-1}$ )	Break down voltage $V_B$ (volts)
1	310	1.67	45
2	320	1.33	37
3	330	1	28
4	340	0.72	20
5	350	0.33	13

Table 2: Current density effect on anodization of Titanium-12 alloy in 0.1 M aqueous ferrous ammonium sulphate solution at room temperature

Sl. No	Current density ( $\text{mAcm}^{-2}$ )	Formation rate $dV/dt$ ( $\text{V.s}^{-1}$ )	Break down voltage $V_B$ (volts)
1	4	1.16	50
2	8	1.8	75
3	16	2.8	82
4	32	3.88	95
5	64	6.44	104

Table 3: Effect of electrolyte concentration on anodization of Titanium-12 alloy under constant current density  $8 \text{ mA.cm}^{-2}$  at room temperature

Sl. No	Electrolyte concentration (M)	Formation rate $dV/dt$ ( $\text{V.s}^{-1}$ )	Break down voltage $V_B$ (volts)
1	0.1	1.4	80
2	0.05	1.11	76
3	0.025	0.83	53
4	0.0125	0.68	45
5	0.00625	0.53	36

### Scanning Electron Microscopy

Scanning Electron Microscopy is the best technique for studying surface morphology of anodic films. Figures from 4-6 are the scanning electron micrographs of anodic films formed on titanium-12 in aqueous solution of ferrous ammonium sulphate at various anodizing conditions. From these SEM reports, it is clear that as increase in electrolyte concentration and current density anodic films with improved surface morphology were obtained at low temperatures. As temperature increases dissolution of anodic film takes place. Hence rough surface with least number of nanotube array obtained.

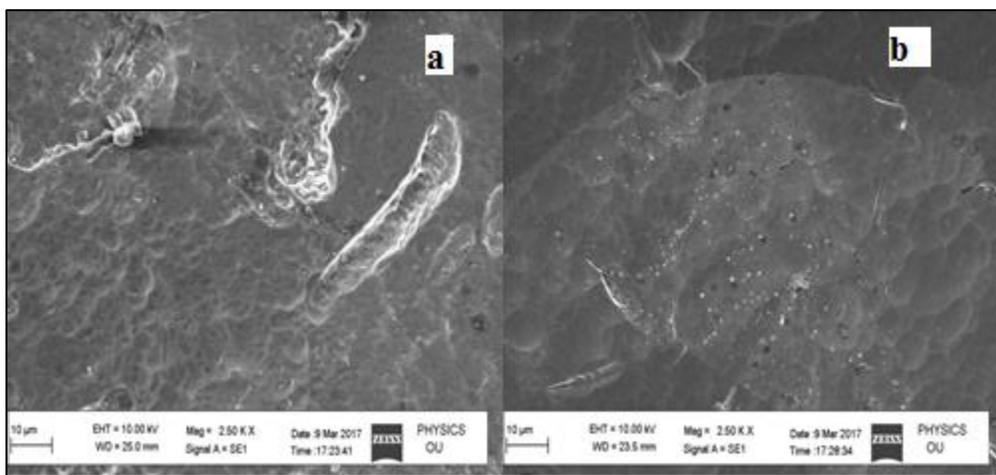


Figure 4: SEM images of Ti-12 foil sample anodized (a) up to 80 V in 0.1 M aqueous ferrous ammonium sulphate at  $8 \text{ mAcm}^{-2}$  at R.T. and (b) up to 36 V in 0.00625 M aqueous ferrous ammonium sulphate at  $8 \text{ mAcm}^{-2}$  at R.T

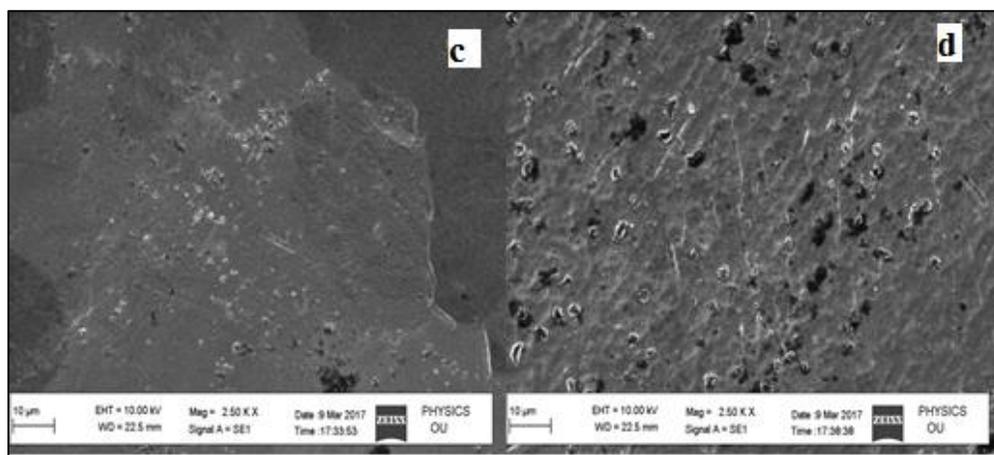


Figure 5: SEM images of Ti-12 foil sample anodized (c) up to 50 V in 0.1 M aqueous ferrous ammonium sulphate at  $4 \text{ mAcm}^{-2}$  at R.T. and (d) up to 104 V in 0.1 M aqueous ferrous ammonium sulphate at  $64 \text{ mAcm}^{-2}$  at R.T

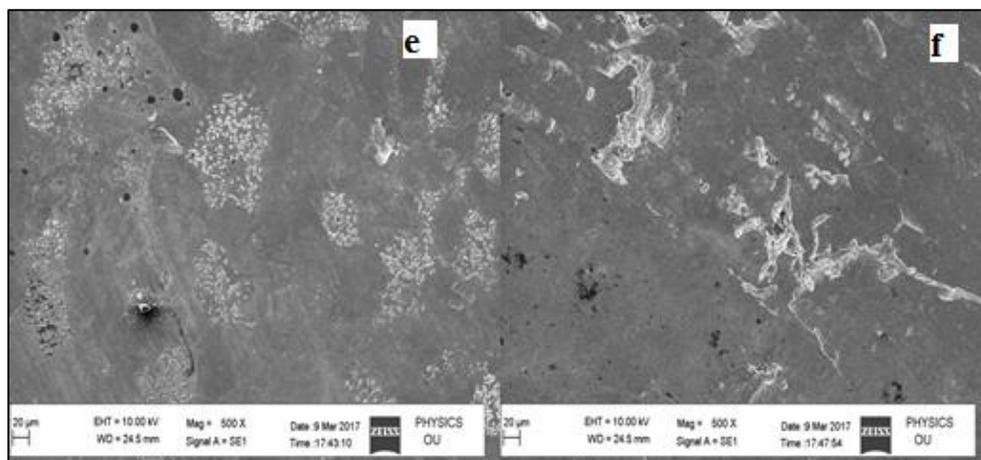


Figure 6: SEM images of Ti-12 foil sample anodized (e) up to 45 V in 0.1 M aqueous ferrous ammonium sulphate at  $8 \text{ mAcm}^{-2}$  at 310 K and (f) up to 13 V in 0.1 M aqueous ferrous ammonium sulphate at  $8 \text{ mAcm}^{-2}$  at 350 K

## CONCLUSION

It is concluded that the kinetics of anodic oxidation of titanium-12 varied with the variation of anodizing conditions. It has been observed that the film formation rate and break down voltage decrease with the decrease in electrolyte concentration and current densities.

It has also been observed that the kinetics was good at low temperatures and the formation rate and breakdown voltages were found to be increasing linearly with the decrease in temperature. It may be attributed to the decrease in the incorporation of anions into the film and may be due to dissolution of the film with the increase in temperature.

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