Anodic Behaviour of Ti-12 in Various Electrolytes

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Abstract

Anodization of Ti-12 alloy has been carried out in various electrolytes at different constant current densities and temperatures. Kinetics of anodic films was studied in different electrolytes at different constant current densities ranging from 4mAcm^{-2} to 64mAcm^{-2} and at different temperatures ranging from 298 to 338K. From the plots of formation voltage (V) vs time (t), rates of formation were calculated. The rate of film formation and breakdown voltage increase with increase in constant current density while decrease with increase in temperature. The kinetics were found better in sulphamic acid electrolyte at room temperature compared to other electrolytes at the same anodizing conditions.

Keywords: Anodization, Constant Current Density, Formation Rate, Titanium-12

1. Introduction

Anodization is an electrolytic passivation process used to increase the thickness of the natural oxide layer formed on the surface of metal parts. Despite the fact that Al is well suited for anodizing, other metals like Zr, Nb, Ta and Ti can also be anodized. Titanium and its alloys [1- 2] easily form stable, constant, and highly adherent oxide layers which show tremendous corrosion and wear resistance. On account of this there has been a growing importance for titanium and its alloys in various fields. They are widely used for the fabrication of dental and orthopaedic implants [3-5] because of their high corrosion resistance in physiological media, biocompatible nature, high mechanical strength and low density [6-7]. Highly ordered titania nanotube layers were shown to enable interlocking of titanium implants with bone cells [8]. They are also used in electrosynthesis, photoelectrochemical activity, and solar energy conversion [9]. On anodizing titanium and its alloys, they generate an array of different colors without using dyes [10]. Hence, they are preferred in art and architecture, costume jewelry, body piercing jewelry and wedding rings [11]. The color formed is controlled by electrolyzing voltage and dependent on the thickness of the oxide layer, interference of light reflecting off the oxide and the underlying metal surfaces [12-13].

In this article, an attempt is made to study anodizing of Ti-12 in 0.1M solutions of sulphamic acid, sodium bisulphite and ferrous ammonium sulphate at different constant current densities and temperatures under galvanostatic conditions. The formation rates were calculated from the plots of formation voltage vs time at all anodizing conditions for these three electrolytes. All the results are reported in Table 1 - 6.

2. Materials and Methods

In this work, Titanium-12 an alloy of 98% pure titanium with other trace impurities was purchased from Defense Metallurgical Research Lab, Hyderabad to study anodic behavior in various electrolytes. The chemical composition of titanium-12 is: Fe, 0.30%; Mo, 0.2-0.4%; Ni, 0.6-0.9%; N$_2$, 0.03%; C, 0.08%; H$_2$, 0.015%; O$_2$, 0.25% and the rest is titanium. Titanium foils with 0.2mm thickness were used to offer better interfacial barrier properties for the growth of TiO$_2$ nano structures [14]. These foils were cut into flag shaped specimens of 1 cm^2 working

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area on both sides, and 1½ cm long tag. These foils were degreased by soaking in acetone and rinsing with de-ionized water for several times. Then they were chemically treated with a solution consisting of acids such as HNO_3, H_2SO_4, HF and water in the volume ratio of 2:1:1:1. For anodization, a closed double walled glass cell of 200ml capacity was used. The Platinum foil of 20 cm^2 superficial area was used as cathode. Galvanostatic mode DC power was used to supply constant current across the cell. Anodization of Ti-12 studied in 0.1M solutions of sulphamic acid, sodium bisulphite and ferrous ammonium sulphate at different constant current densities ranging from 4mA/cm^2 to 64mA/cm^2 and temperatures varying from 298K to 338K. All the experiments were carried out under galvanostatic conditions. Rates of film formation were calculated in V/sec from the plots of formation voltage vs time. Surface morphology of the anodized Ti-12 in 0.1M solution at constant current density, 8mA/cm^2 was investigated using Scanning Electron Microscopy.

3. Results and Discussion

3.1 Effect of Current Density

Anodization of Ti-12 has been studied in 0.1M solutions of sulphamic acid, sodium bisuphite and ferrous ammonium sulphate by applying constant current densities across the anodization cell by using DC power supply. The applied current densities varied from 4mA/cm^2 to 64mA/cm^2. The formation rates and breakdown voltages for all the three electrolytes were increased with increase in the constant current density. The plots of formation voltage as a function of time are shown in Figures 1 to 3. The formation rates and breakdown voltages calculated at constant current density for these three electrolytes are reported in Table 1 to 3. The plots of logarithm of formation rate *vs* logarithm current density were found to be linear as shown in Figure 4. Jyothi *et al.* [15] for Zr-2 alloy, Anjaneyulu [16] for Ti and Raghunathreddy *et al.* [17] for Zr-4 reported similar trends in different electrolytes.

Figure 2. Formation voltage – time profiles at different constant current densities in 0.1M aqueous sulphamic acid solution at room temperature.
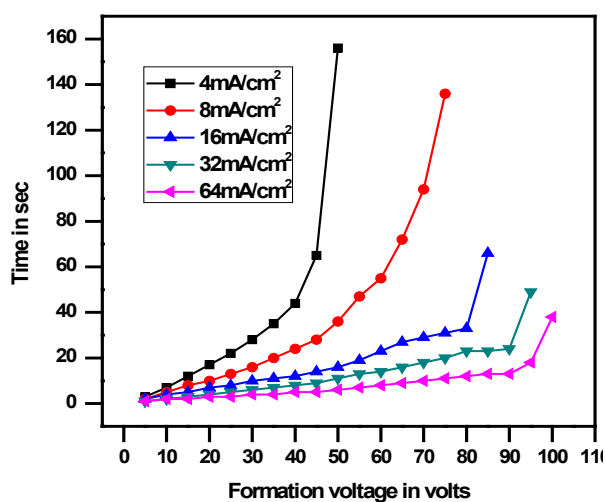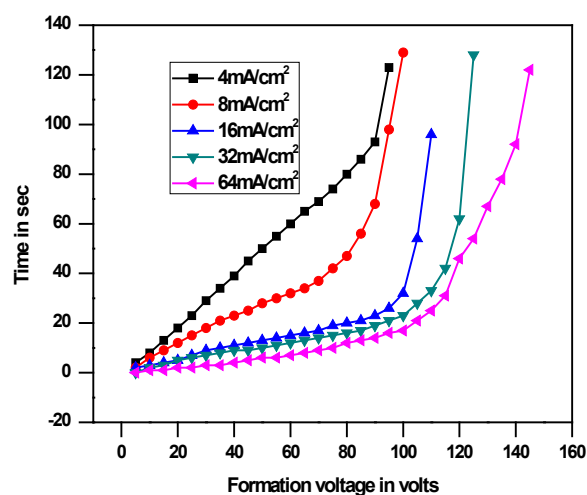
Figure 1. Formation voltage – time profiles at different constant current densities in 0.1M aqueous ferrous ammonium sulphate solution at room temperature.
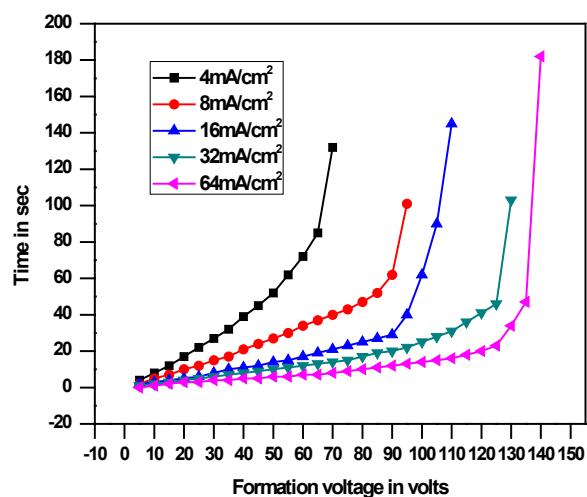
Figure 3. Formation voltage – time profiles at different constant current densities in 0.1M aqueous sodium bisulphite solution at room temperature.
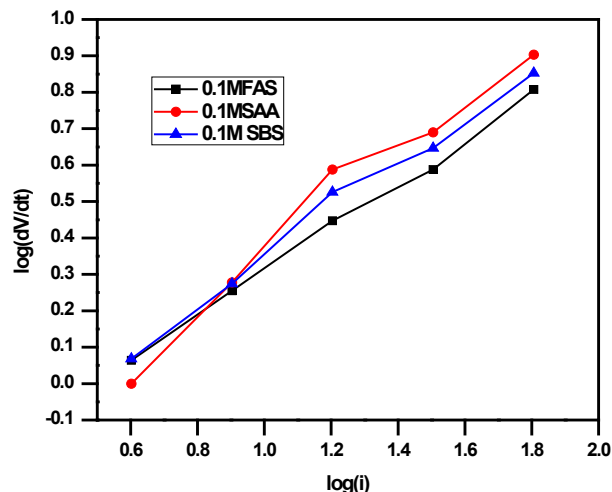
Figure 4. Formation rate - current density profiles FAS=Ferrous Ammonium Sulphate; SAA=Sulphamic Acid; SBS=Sodium Bisulphite

Table 1. Current density effect on anodization of Titanium-12 alloy in 0.1M aqueous ferrous ammonium sulphate solution at room temperature

Sl.No	Current density (mA/cm²)	Formation rate dV/dt(V/sec)	Break down voltage V_B(volts)
1	4	1.16	50
2	8	1.80	75
3	16	2.80	82
4	32	3.88	95
5	64	6.44	104

Table 2. Current density effect on anodization of Titanium-12 alloy in 0.1M aqueous sulphamic acid solution at room temperature

Sl.No	Current density (mA/cm²)	Formation rate dV/dt(V/sec)	Break down voltage V_B(volts)
1	4	1.00	89
2	8	1.90	95
3	16	3.88	112
4	32	4.90	120
5	64	8.00	138

Table 3. Current density effect on anodization of Titanium-12 alloy in 0.1M aqueous sodium bisulphite solution at room temperature

Sl.No	Current density (mA/cm²)	Formation rate dV/dt(V/sec)	Break down voltage V_B(volts)
1	4	1.17	68
2	8	1.88	90
3	16	3.36	97
4	32	4.44	125
5	64	7.14	136

3.2 Effect of Temperature

Anodization of Ti-12 has been done in 0.1M solutions of sulphamic acid, sodium bisuphite and ferrous ammonium sulphate at different temperatures ranging from 298 to 338K at constant current density of 8mA/cm². The rates of formation and breakdown voltages decreased with increasing temperature for these electrolytes. Reddy *et al.* [18] observed similar trend of decreasing kinetic results with increased temperature in 0.1M potassium tartarate. It was due to dissolution of the already formed oxide film with temperature and decreased incorporation of anions into the film. The rates of formation were calculated at each temperature from the plots of formation voltage vs time shown in Figures 5 - 7. The kinetic results are reported in Table 4- 6.
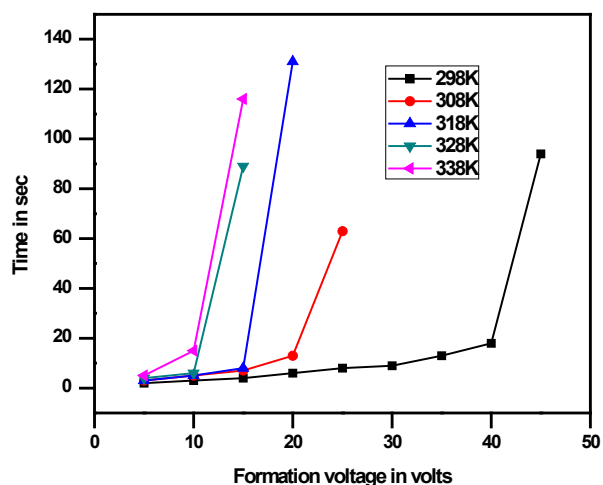

Figure 5. Formation voltage – time at different temperatures in 0.1M aqueous ferrous ammonium sulphate solution under constant current density 8mA/cm².
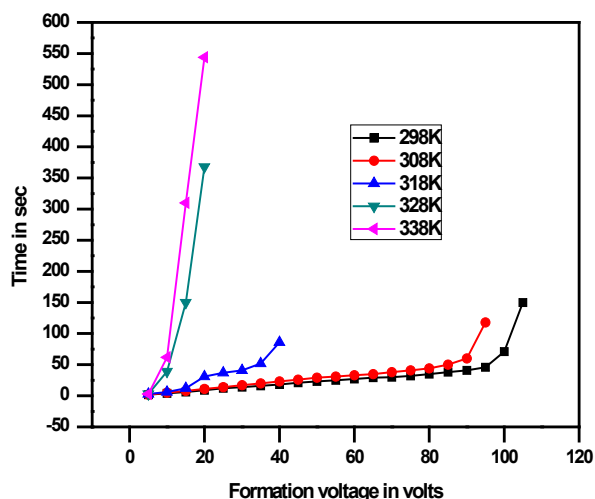
Figure 6. Formation voltage – time profiles at different temperatures in 0.1M aqueous sulphamic acid solution under constant current density 8mA/cm^2.
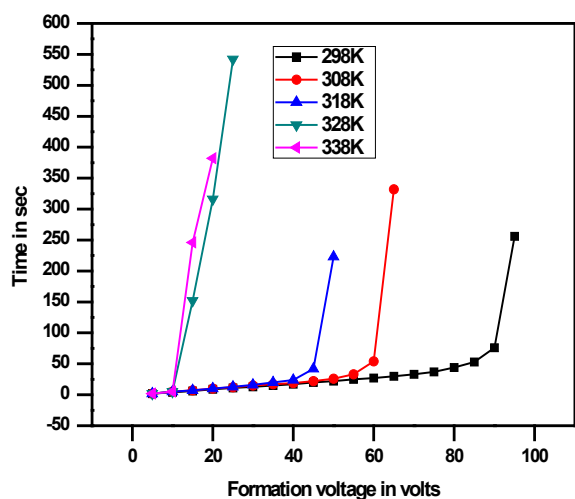

Figure 7. Formation voltage – time profiles at different temperatures in 0.1M aqueous sodium bisulphite solution under constant current density 8mA/cm^2.

Table 4. Temperature effect on anodization of Titanium-12 alloy in 0.1M aqueous ferrous ammonium sulphate solution at constant current density 8mA/cm^2

Sl.No	Temperature(K)	Formation rate dV/dt(V/sec)	Break down voltage V$_B$(volts)
1	298	3.18	41
2	308	2.12	22
3	318	1.83	15
4	328	1.60	11
5	338	1.00	09

Table 5. Temperature effect on anodization of Titanium-12 alloy in 0.1M aqueous sulphamic acid solution at constant current density 8mA/cm^2

Sl.No	Temperature(K)	Formation rate dV/dt(V/sec)	Break down voltage V$_B$(volts)
1	298	2.06	96
2	308	1.75	82
3	318	1.68	35
4	328	1.50	16
5	338	1.17	09

Table 6. Temperature effect on anodization of Titanium-12 alloy in 0.1M aqueous sodium bisulphite solution at constant current density 8mA/cm^2

Sl.No	Temperature(K)	Formation rate dV/dt(V/sec)	Break down voltage V$_B$(volts)
1	298	2.12	86
2	308	1.95	58
3	318	1.65	42
4	328	1.40	15
5	338	1.14	10

Aerts *et al.* [19] studied the influence of the anodizing temperature on the porosity and the mechanical properties of the anodic oxide films and found that the micro hardness of the anodic films progressively decreased with increasing temperature. Michal *et al.* [20] reported that the electrolyte temperature was the key parameter that controled the thickness of the anodic aluminium oxide layer.

3.3 Scanning Electron Microscopy

Scanning Electron Microscopy is a well-known technique for studying surface morphology of the anodic films. SEM images of the anodized Ti-12 foil in 0.1M solutions of sulphamic acid, sodium bisulphite and ferrous ammonium sulphate at constant current density 8mA/cm^2 were studied and compared. From these micrographs it was clear that surface with large number of pores was obtained for sulphamic acid compared to other two electrolytes. Corresponding SEM images are shown in Figure 8 (a) - (c).

4. Conclusions

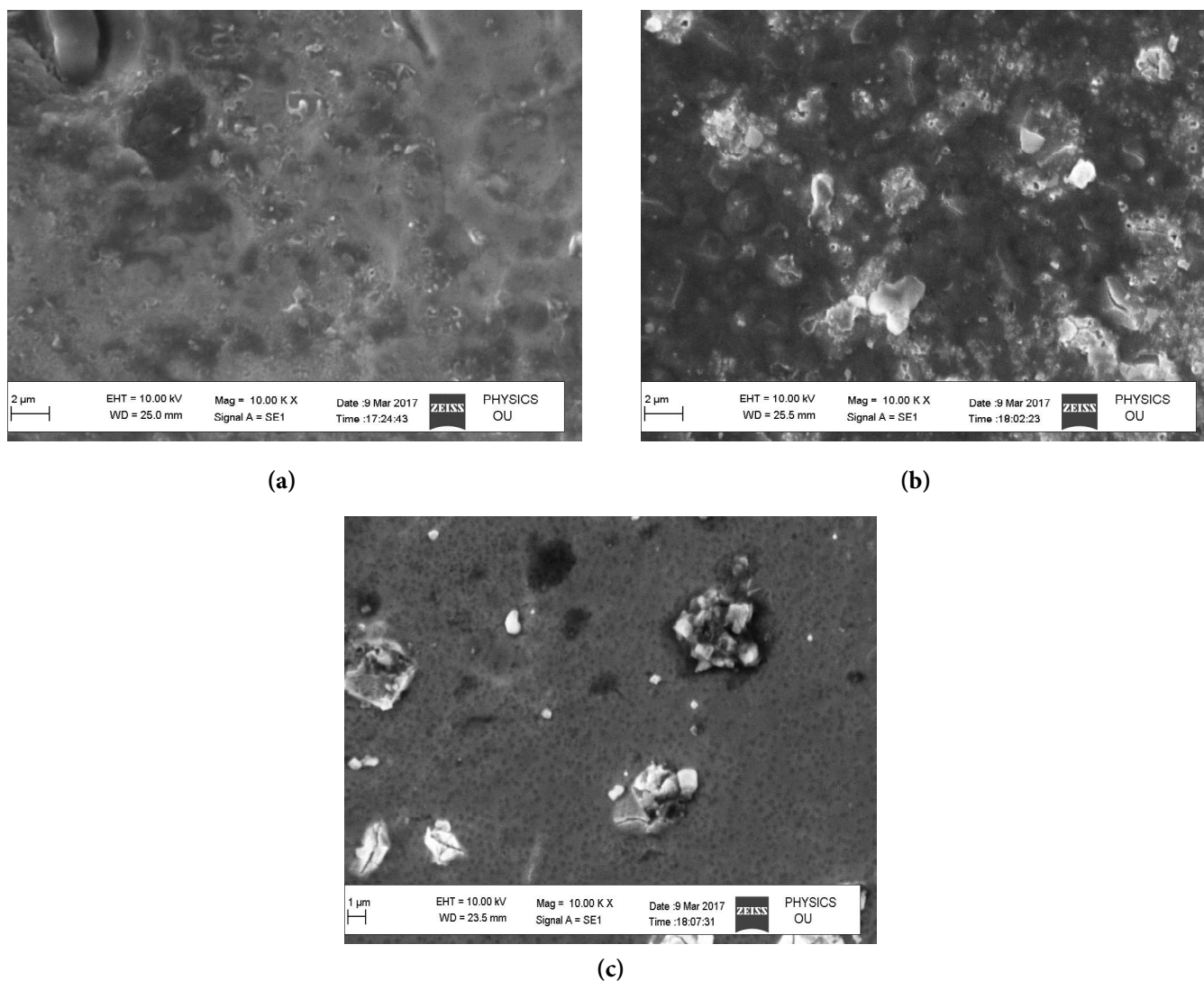Anodization of Ti-12 has been investigated in 0.1M solutions of sulphamic acid, sodium bisulphite and ferrous

(a)

(b)

(c)

Figure 8. SEM images of anodized Ti-12 foil surface at 8mA/cm^2 in 0.1M solutions. **(a)** Ferrous ammonium sulphate, **(b)** Sulphamic acid, **(c)** Sodium bisulphite.

ammonium sulphate. From the results of this work it was concluded that anodic oxidation of titanium-12 was better in sulphamic acid at room temperature compared to sodium bisulphite and ferrous ammonium sulphate at the same anodizing conditions. It was observed that the film formation rate and breakdown voltage decreased with the decrease in current density but increased with the decrease in temperature. It was due to dissolution of the already formed film, and the decrease in the incorporation of anions into the film.

5. Acknowledgements

6. References

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