

Study of Anodization of Ti-12 in 0.1M Sodium Bisulphite

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Abstract: Anodization of Ti-12 in 0.1M aqueous sodium bisulphite has been studied under different anodizing parameters. The effect of temperature on the kinetics of film formation was studied at constant current density, 8 mA/cm² at different temperatures varying from 298 to 338K. The rate of film formation decreased with increase in temperature. The effect of added anion impurities, carbonate (CO₃⁻²), sulphate (SO₄⁻²), phosphate (PO₄⁻³) and fluoride (F⁻) in milli molar concentrations has been investigated. It was observed that the rate of anodizing Ti-12 was decreased in the presence of carbonate (CO₃⁻²), sulphate (SO₄⁻²) and fluoride (F⁻) anion impurities except in phosphate (PO₄⁻³) impurities. It has also been studied the solvent (glycerol) effect of 20%, 40%, 60% and 80% of glycerol volume on anodization of Ti-12 in 0.1M aqueous sodium bisulphite solution at room temperature under galvanostatic conditions. As the percentage of glycerol increases the rate of formation and breakdown voltage increased.

Keywords: Anodization, Titanium-12, Rate of formation, Sodium bisulphate, Glycerol

Introduction

Titanium falls into the category of valve metals such as Al, Zr, V, W, Nb, Hf and Ta, because of it immediately forms natural oxide layer on its surface when it is exposed to its surroundings containing oxygen. This oxide layer inhibits further rate of reactions on the metal surface and shows high corrosion and wear resistance^{1,2}. Anodization is one of the best methods to improve the thickness of this native oxide layer. Anodized Ti and its alloys³ are widely used in aerospace, sports, marine, chemical, optics, solar energy conversion⁴, photo catalysis⁵⁻⁶, automobile, consumer goods and biomedical applications^{7,8} due to their high specific strength, light weight, high corrosive resistance, non magnetic character, biocompatibility⁹ and other surface related properties. On anodization they easily generate an array of different colors without using dyes¹⁰. The color formation predominantly controlled by electrolyzing potential¹¹.

In this work, anodization of Ti-12 in 0.1M aqueous sodium bisulphite has been studied under different anodizing parameters.

Experimental

Titanium-12, an alloy of 98% pure titanium with other trace elements used for research work purchased from Mishra Dhatu Nigam Limited (MIDHANI), Hyderabad. The chemical composition of titanium-12 alloy is shown in table 1.

Table 1. Chemical composition of Ti-12 alloy (w %)

Fe	Mo	Ni	N ₂	C	O ₂	H ₂	Ti
0.30%	0.2-0.4%	0.6-0.9%	0.03%	0.08%	0.025%	0.015%	Balance

Titanium-12 foil samples of 0.2 mm thickness were used to offer better interfacial barrier properties for the growth of TiO₂ nano structures¹². These foils were cut into flag shaped specimens of 1 cm² working area on both sides and 1½ cm long tag with the aid of a punch. Prior to anodizing, these foils were degreased by soaking in acetone and rinsing with deionized water for several times. Then they were applied for chemical polishing. The chemical polishing mixture used was consisting of a mixture of acids such as HNO₃, H₂SO₄, HF and water in a definite volume ratio of 2:1:1:1. For anodization process, a closed double walled glass cell of 200 mL capacity was used. Platinum foil of 20 cm² superficial area was used as cathode.

Sodium bisulphite used as an electrolyte. The influence of temperature, milli molar concentrations (0.001M) of added anion impurities, carbonate (CO₃²⁻), sulphate (SO₄²⁻), phosphate (PO₄³⁻) and fluoride (F⁻¹) and aquo-glycerolic media effect on the anodization of Ti-12 in 0.1M aqueous sodium bisulphite solution has been investigated (Table 2) under galvanostatic conditions (at constant current density, 8 mA.cm⁻²).

Table 2. Parameters of Ti-12 anodizing

Parameter	Value
Anion impurities (CO ₃ ²⁻ , SO ₄ ²⁻ , F ⁻¹ , PO ₄ ³⁻)	0.001 M
Electrolyte (sodium bisulphite)	0.1 M
Temperature	298K to 338K
Current density	8mA/cm ²
Solvent (Glycerol)	20%, 40%, 60% and 80%
Voltage	Up to breakdown

Results and Discussion

The effect of temperature, added anion impurities and solvent on anodization of Ti-12 in 0.1M aqueous sodium bisulphate electrolyte has been investigated under galvanostatic conditions and the corresponding results were reported.

Effect of temperature

The effect of temperature on the anodization of Ti-12 in 0.1M aqueous sodium bisulphate electrolyte has been studied at different temperatures ranging from 298 to 338K by using thermostat under galvanostatic condition (at constant current density of 8mA/cm²). The rate of film formation and breakdown voltages were decreased with the increase in temperature. Similar trends of decreasing in the rate of formation and breakdown voltage with the increase in temperature were reported earlier by many others¹³⁻¹⁵. It is may be due to dissolution of the already formed oxide film with increase in temperature and may be the decrease in the incorporation of anions into the film. The rate of film formation and

breakdown voltages were calculated and reported in the Table 3. The plots of formation voltage vs. time are shown in the Figure 1.

Table 3. Temperature effect on anodization of Titanium-12 in 0.1 M aqueous sodium isulphate solution at constant current density 8mA/cm^2

S No.	Temperature(K)	Formation rate $dV/dt(\text{V/s})$	Break down voltage $V_B(\text{volts})$
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

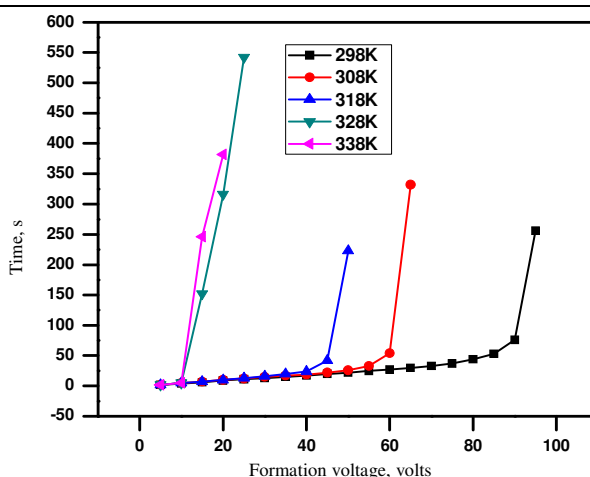


Figure 1. Plots of formation voltage as a function of time at different temperatures in 0.1 M aqueous sodium isulphate solution under constant current density 8 mA/cm^2

Effect of added anions

An attempt has been made to study the effect of added anion impurities on the kinetics of anodization of Ti-12 in 0.1 M aqueous sodium isulphate electrolyte. The change in the rate of film formation and breakdown voltage has been investigated by adding carbonate (CO_3^{-2}), sulphate (SO_4^{-2}), phosphate (PO_4^{-3}) and fluoride (F^{-1}) anions in milli Molar concentrations to the electrolyte solution at constant current density, 8 mA/cm^2 . It has been observed that the rate was decreased by the addition of carbonate (CO_3^{-2}), sulphate (SO_4^{-2}) and fluoride (F^{-1}) anion impurities except in the case of phosphate (PO_4^{-3}) impurities. It is may be due to their depassivative/dissolution effect on anodic film. The kinetic results are given in the Table 4 and Figure 2.

Effect of solvent

Anodization of Ti-12 in 0.1M aqueous sodium isulphate has been performed by adding glycerol with various proportions *i.e.* 20%, 40%, 60% and 80%. As the percentage of glycerol increases, improvement in the kinetics was observed but there is no proper improvement in the rate of formation at 80% of glycerol and beyond it. It is may be due to the electrolyte solution at this stage becomes more viscous by the addition of more glycerol which in turn prevents the free mobility of oxide ions to form oxide film. As the percentage of glycerol increases the

dielectric constant of the electrolyte solution which is responsible for solvent-ion interactions decreases. The kinetics of anodizing Ti-12 in 0.1M aqueous sodium bisulphate solution at various proportions of glycerol was reported in the Table 5 and Figure 3.

Table 4. Effect of anion impurities on anodization of Titanium-12 in 0.1 M aqueous sodium bisulphite solution at constant current density, 8 mA/cm²

S No.	Electrolyte	Formation rate dV/dt(V/s)	Break down voltage V _B (volts)
1	0.1M SBS	1.88	90
2	0.1M SBS +0.001M CO ₃ ⁻²	1.50	78
3	0.1M SBS +0.001M SO ₄ ⁻²	1.39	71
4	0.1M SBS +0.001M F ⁻¹	1.30	67
5	0.1M SBS +0.001M PO ₄ ⁻³	2.35	118

* SBS= Sodium bisulphite

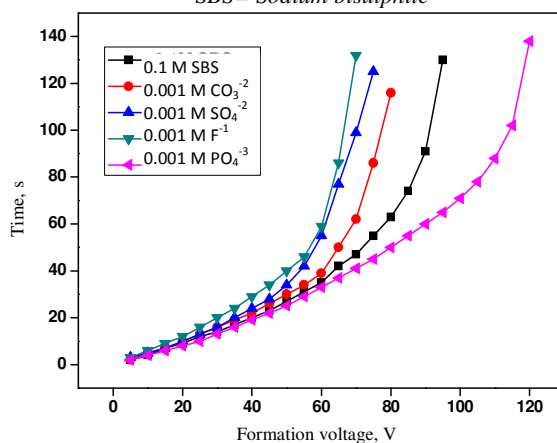


Figure 2. Plots of formation voltage as a function of time at different anion impurities in 0.1 M aqueous sodium bisulphite solution under constant current density 8 mA/cm²

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is very useful in the study of surface morphology of anodic oxide films. By using SEM micrographs we can find out surface nature of the film. Some of the SEM images of anodized Ti-12 in 0.1M aqueous sodium bisulphite solution at different anodizing conditions are shown in the Figures 4a-f. In the presence of solvent (glycerol) anodic films with good number of nanotubes array obtained.

Table 5. Effect of solvent on anodization of Titanium-12 in 0.1M aqueous sodium bisulphite solution at constant current density, 8mA/cm²

S No.	Electrolyte	Formation rate dV/dt(V/s)	Break down voltage V _B (volts)
1	0.1M SBS	1.88	90
2	0.1M SBS +20% gly	2.31	145
3	0.1M SBS +40% gly	2.90	180
4	0.1M SBS +60% gly	3.44	265

* SBS= Sodium bisulphite, gly= glycerol

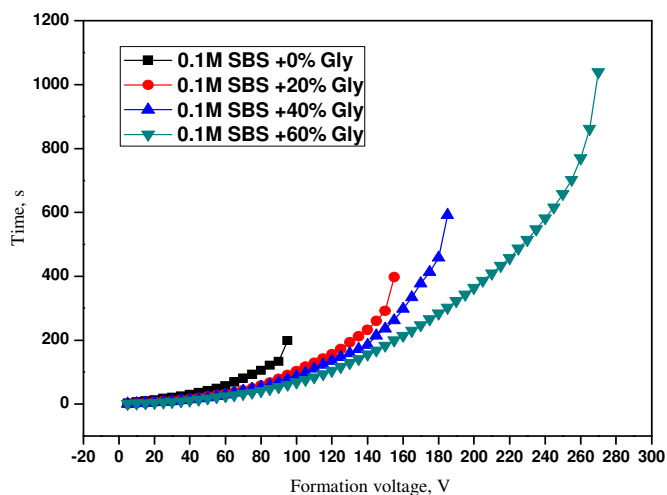


Figure 3. Plots of formation voltage as a function of time at different proportions of glycerol in 0.1 M aqueous sodium bisulphate solution under constant current density 8 mA/cm^2

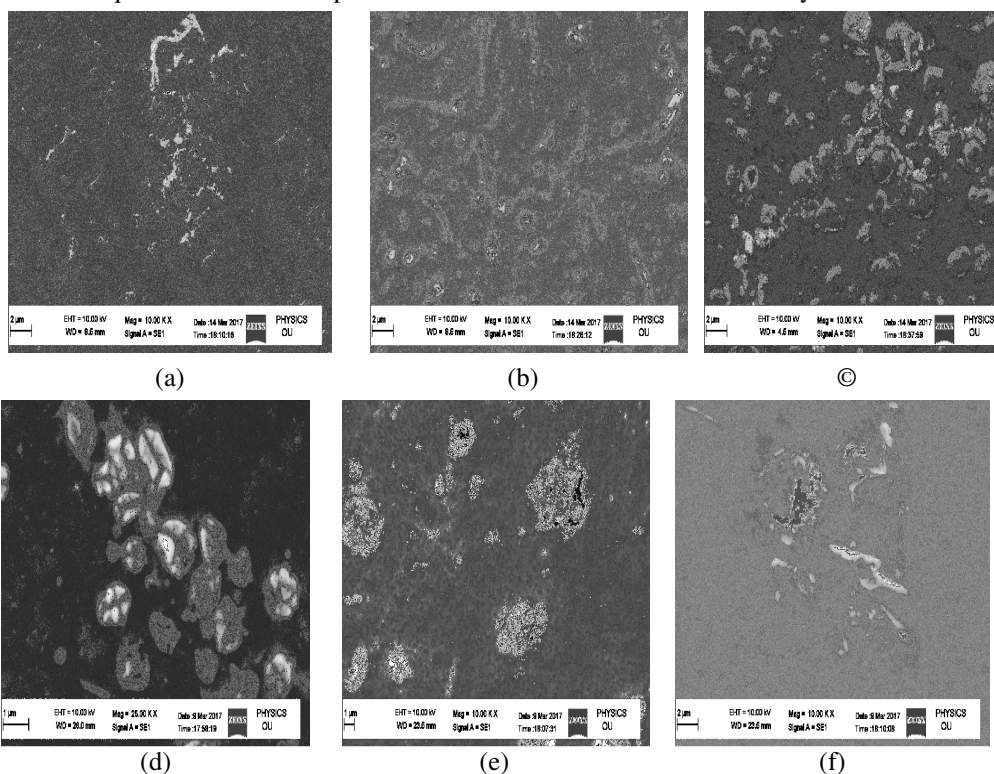


Figure 4. SEM images of anodized Ti-12 foil surface at 8 mA/cm^2 in 0.1 M aqueous solution of sodium bisulphite in the presence of (a) 20% glycerol up to 150V (b) 40% glycerol up to 185V (c) 60% glycerol up to 270V (d) 0.001 M Phosphate anion impurities up to 120V (e) at room temperature up to 95V and (f) at 338 K up to 20V

Conclusion

Anodization of Ti-12 has been carried out in 0.1 M aqueous sodium bisulphite solution at different anodizing parameters. The rate of film formation and breakdown voltages were decreased with the increase in temperature. It is attributed to the dissolution of oxide film with increase in temperature. The kinetics of anodization of Ti-12 in 0.1M aqueous sodium bisulphite were improved to some extent in the presence of milli molar concentration of phosphate anions while decreasing in the presence of fluoride, carbonate, sulphate anions in milli molar concentrations. The addition of glycerol in different proportions to the electrolyte solution increases anodizing kinetics up to 80% glycerol addition due to decreases in dielectric constant which in turn increases non polar nature of electrolyte. At higher proportions of glycerol (80% and above) the kinetics were decreased due to increase in the viscosity of electrolyte which restricts the free mobility of oxide ions to form anodic films.

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