Electropolishing and Mirror-like Preparation of Titanium in Choline Chloride-Ethylene Glycol Mixture Liquid

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ABSTRACT
This report presents simple, rapid and an efficient electropolishing of Ti metal in choline chloride-based ionic liquid (so called Ethaline) at 20 °C. This electrolyte is relatively benign and environmentally friendly which is desirable for electropolishing. Potentiostatic method was applied to Ti electropolishing in this electrolyte. Under an electrochemical condition of 6–10 V for 30 min. and at 20 °C, a promising electropolishing process was performed without obvious gas evolution. To characterize the electropolished surface, atomic force microscope (AFM) and scanning electron microscope (SEM) were used. The achieved an apparent mirror-like finished surface with an average surface roughness (Ra) was 5.7 nm which is considerably different from that of unpolished one (Ra = 118.8 nm). The microscopic results showed leveling and brightening of the surface of Ti by carrying out the current procedure. This electrolyte provides sufficient environment to dominate the mass transport mechanism which is responsible for reduction in the surface roughness.

1. Introduction
Titanium and titanium alloys are lightweight materials with relatively high corrosion resistance. These are used in medical applications, aerospace and electrocatalysis because of their interness and biocompatibility.© The Author(s) 2020. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.20-00038]. Uploading "PDF file created by publishers" to institutional repositories or public websites is not permitted by the copyright license agreement.

Keywords : Ionic Liquid, Deep Eutectic Solvent, Electropolishing, Titanium
Over last two decades, deep eutectic solvents as relatively benign electrolytes have attracted attention of some research groups to be utilised in a number of applications, such as bioplastic synthesis and desulfurization. These electrolytes are either composed of mixture of fully ions or ion/molecule. These electrolytes have wide applications, especially in electrochemistry field, such as electro-polishing, electrolyzing and anodic reactions.

In the present report, it is shown that electropolishing of Ti in choline chloride-based ionic liquid is successfully carried out. This electropolishing of Ti is incredibly important and the used liquid is comparatively benign and non-corrosive compared to the current aqueous acid counterparts. It is also motivation to take into consideration the corrosion resistance improvement of Ti surface. The electrolytic condition of the electropolishing is at a relatively low potential (6 V) and for 30 min. The mirror-like finished surface is clearly shown in the microscope images.

2. Experimental

2.1 Chemicals

The Ti sheet was purchased Alfa Aesar (Alfa Aesar 99%, USA). Prior to use, the Ti sheet is cleaned in mixture of dilute sulfuric acid and hydrochloric acid and then inserted into acetone with sonication to remove impurities. Ethylene glycol (EG, 99%) and choline chloride (ChCl, 99%) were purchased from Sigma Aldrich (Sigma Aldrich, USA) and used as received.

2.2 Instruments

The current density-voltage ($I-V$) and current density-time ($I-t$) plots were drawn using digital multi-meters (Widewing AN8008 True-RMS). Scanning electron microscopy (SEM) was used to examine the morphology of the surface (Philips XL30 ESEM). The atomic force microscopy (AFM) image acquisitions were recorded using a Digital Instruments Nanoscope 4 run using contact mode. The AFM images of titanium recorded in resonant mode at a frequency (300 Hz) at a scan rate of 0.5 Hz. The potential acquisition was performed using AC/DC Laboratory Power Supply DC: 0–30 V.

2.3 Preparation of deep eutectic solvent

The preparation of deep eutectic solvent was performed by mixing choline chloride (ChCl) and ethylene glycol (EG) in a 1:2 molar ratio. The mixture was heated with continuous stirring until a homogeneous clear electrolyte was obtained.

2.4 Electrochemical polishing

In the electropolishing process, 1 cm$^2$ Ti disk (thickness of 2 mm) and cylindrical platinum electrode were used as working and counter electrodes, respectively in 10 ml Ethaline at a constant voltage of 6 V for 30 min. at room temperature. The distance between the working and the counter electrodes is usually maintained in the range of 1–5 cm. In this work, 1 cm distance was chosen between the electrodes in order to minimize the resistance and less usage of electrolyte.

3. Results and Discussion

3.1 Electrochemical titanium electropolishing in EG/ChCl

Figure 1a shows the polarisation response of Ti sheet in the 2 EG:1 ChCl mixture at 20°C. In this experiment the electrode system of Ti sheet was utilised as working electrode and cylindrical platinum gauze as counter one.

The responses reveal three distinct areas: slow current rise, steady state and huge current rise. The first area which is the current rises slowly, it is an current that results mainly as Ti dissolution steadily. The second area is a steady state current, as this steady state comes as a consequence of effective electropolishing of Ti surface where mass transport is the rate limiting factor at the voltage range of 6–10 V. The final stage is the potential range (ca 10–14 V) where a remarkable current rise occurs. This is due to gas evolution, such as H$_2$ and might be owing to electrolyte decomposition. On the one hand, in the first and third regions, there were pitting at the Ti surface as which can be correlated to migration that accompanying diffusion of dissolved Ti into bulk electrolyte region effectively. On the other hand, at the plateau region, the cation of Ti dissolves regularly under mass control into the bulk electrolyte through viscose layer at the interfacial region.

The current-time transient curve indicates reaching steady-state beyond 10 min. of potential holding at 6 V as presented in Fig. 1b. At this stage, mass-transport dominates through the film formed at the interface between the Ti sheet and the electrolyte that lasts 20 min. It is strongly believable that Cl$^-$ ion is species that form complex with dissolved Ti at the interfacial region as shown below:

$$\text{Ti}^{4+} + 4\text{Cl}^- \rightarrow \text{TiCl}_4$$

Figure 2 shows a schematic mechanism of electropolishing process where as the film forms at the interfacial region, the metal dissolution commences at three surface locations, a, b and c. At a and c locations, the Ti dissolution and diffusion into bulk electrolyte region are faster under electrochemical course than b location as logically higher distance is seen for the former ones.

3.2 Surface morphology

Figure 3 shows the SEM micrographs of the Ti surface; polished and parent surfaces. Before exposing Ti sample to electropolishing regime, the sheet was masked where the desired area confined.

**Figure 1.** shows electrochemical studies of Ti sample in Ethaline; a) Polarisation curve determined and b) i-t curve measured at constant voltage of 6 V for 30 min.
SEM image of the polished part showed that there is an apparent mirror-like finished surface. The polished area is relatively much smoother with no trace of the crystal grains exist in the unpolished one.

In a comparison to other electrolyte enriched in Cl⁻ ion, there is a recorded SEM image where small etching seen clearly. It is noteworthy, the deep eutectic mixture used in the present study has provided brilliant and with no defect at the Ti surface.

Figure 4 shows an ex situ AFM image of Ti sheet before and after electropolishing in ChCl:EG (1:2) mixture at 20 °C. This is to determine the quality of the surface after electropolishing. Figure 4a shows the parent surface with Ra value of 118 nm. From Fig. 4b, it is obviously seen that the average surface roughness $R_a = 5$ nm and surface morphology is consistent. The resolution of grain boundary features is satisfactory indicating that the tip was controlled and no problem with surface scanning the tip in both polished and unpolished surfaces.

Figure 4c exhibits single line trace within 5 µm alongside x-axis where large number of surface roughness fluctuations are observed with 560 nm. alongside the y-axis. It is also seen that the surface SEM image of the polished part showed that there is an apparent mirror-like finished surface. The polished area is relatively much smoother with no trace of the crystal grains exist in the unpolished one.

Figure 2. shows typical graphical representation of mechanism of metal surface electropolishing process indicating the influence of valley and protrode.

Figure 3. SEM image at the boundary between the polished and unpolished region of Ti sample.

Figure 4. AFM images with single line traces alongside, of Ti sample recorded in resonant mode at a frequency (300 Hz) in air at a scan rate of 0.5 Hz, 256 lines. a and c) before electropolishing, b and d) after electropolishing.
prior to electropolishing is relatively very rough with an average grain size of 560 nm which dull optically. The polished region exhibits much lower roughness of 350 nm on the AFM scale (Fig. 4d). It is worth-mentioning to say that the mean values of Zmax (over 5 measurements) before and after electropolishing of Ti are 118 and 5 nm, respectively.

Despite of much smoother of the polished area, there is a large variation in height across the scan region. Recently, the current electrolyte was utilised in the electropolishing Al that a bright variation in height in both cases is comparable; however, the scale is much smaller in length in the case of polished one.

A photograph of Ti before and after electropolishing in the Ethaline electrolyte is shown in Fig. 5. Over the whole photograph, a boundary separates the polished and unpolished region where the polished one is clearly visible. It is obviously seen that a mirror-like finished surface was gained, showing effective optical reflectivity.

4. Conclusions

In conclusion, an apparent mirror-like surface of Ti can be obtained using a relatively benign electrolyte, the deep eutectic solvent (Ethaline). It is comparably low volt voltage (10 V) and reasonably short period of time (30 minutes) were required to electropolishing the Ti surface in this electrolyte with no obvious gas evolution. This eutectic solvent as promising medium provides sufficient viscose medium to dominate mass transport of ionic species that created at the interface as a result of dissolution electrochemically. The eutectic solvent functions very well in the electropolishing process, and 5 nm roughness of smooth metallic surface was obtained. Electropolishing method in ionic liquid showed a promising strategy to overcome problems that encountered in electropolishing in aqueous media.

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