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Research Article

Surface modification of Ti-6Al-4V by electrochemical oxidation

Chandan Kumar*, Amit Biswas

Department of Biotechnology & Medical Engineering, National Institute of Rourkela, Odisha, India

Email: ckumar.rs.bme13@iitbhu.ac.in

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Abstract: Titanium is a metallic biomaterial having multidimensional properties, highly sophisticated function and a wide range of applications in the biomedical field, especially as implants. Titanium is a useful biomaterial for biomedical implants because of its biocompatibility and nontoxicity. Ti-6Al-4V has been used as a substrate in the electrochemical process of anodic oxidation. Two different compositions of electrolyte have been chosen for the present study. The first electrolyte consists of CH_3COOH and HF and the second electrolyte consist of H_2SO_4 and HF. After deposition, the sample was dried at room temperature for 24 hours and the oxide layer was later analyzed by different characterization techniques. The surface morphology and phase analysis of the coated surface were examined by scanning electron microscope (SEM) and X-ray diffraction (XRD). SEM images show the presence of uniformly distributed oxide layer on the Ti-6Al-4V surface. The microhardness test of the electrolytically grown oxide was also carried to determine the hardness of the coating, which confirms that after treatment hardness of Ti-6Al-4V increases with the time duration. Lastly, the wettability test was performed on the surface of the coated Ti-6Al-4V to evaluate the wetting property of the surface.

INTRODUCTION

Pure titanium and titanium alloys are the most attractive metallic materials for biomedical applications. Ti-6Al-4V has been a primary biomedical titanium alloy since an extended period. [1]. Biomedical titanium alloys with enhanced biocompatibility have been proposed and are currently under development [2]. These are mainly β type alloys and are composed of n on-toxic elements. The β type alloys, also have greater biocompatibility because their moduli are much less than those of α+β type alloys as that of Ti–6Al–4V. These alloys are also able to gain much greater strength and toughness balance. Titanium alloys, especially Ti-6Al-4V are expected to be in much more increased use as implant materials in medical and dental fields due to their superior biocompatibility, corrosion resistance and specific strength compared to other metallic implant materials. [3]. Pure Titanium is not as strong as the different alloys of titanium. Maintenance of the long-term stability of implants grafted onto the bone requires good bio-affinity of the biomaterial. Close adhesion with the bone is also mandatory for a prolonged period [4].

Anodizing is a passive electrolytic process, which is used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is termed anodizing since the metal to be treated forms the anodic electrode of an electrical circuit. Anodizing increases the corrosion resistance as well as wear resistance. Anodic films can also be used for various cosmetic effects with porous coatings quite thick so that they can absorb dyes and also with transparent coatings that can add interference effects to reflected light. Anodic films can be most commonly applied to protect aluminum alloys, although similar processes exist for titanium, zinc, magnesium, niobium, and tantalum. Anodization changes the microscopic surface texture and also changes the metal crystal structure near the surface. Thick coatings are usually porous; therefore a sealing process is typically needed to enhance the corrosion resistance that was previously being obtained. Anodic films are much stronger and much more adherent than most types of paints and metal platings that make them less susceptible to crack and peel from aging and wear.

The high affinity of Ti-6Al-4V for oxygen results in several oxides of differing crystalline structures. Natural conditions and a stable atmosphere promote the formation of a thermodynamically stable oxide; i.e. TiO2, which exists in three crystalline phases which are anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [5]. The anatase structure is usually obtained by anodic oxidation whereas the rutile structure is obtained by anodic oxidation followed by a heat treatment [6]. The surface morphology and the thickness of the oxide depend mainly on the methods applied for the formation of the oxide layer. The implant-environment interaction is maintained by morphology and the thickness of the oxide film. [7].Usually, the color of the oxide produced in the process of anodic oxidation is a measure of the thickness of the film. This relation between color and thickness depends upon on the anodization process as well as the electrolyte [8].

A slight modification of these parameters enables the changes of the coloration of the titanium oxide surface.

MATERIALS AND METHODS

Materials required

Square pieces of Ti-6Al-4V are used as anode material [9]. A pure graphite rod acted as the cathode. Acetone, ethanol(absolute) and Magnesium Sulphate, and Magnesium Chloride, Sodium Chloride and D-glucose, Sodium hydrogen carbonate while Di-sodium hydrogen Phosphate is used to prepare Hank's solution. Hydrofluoric acid (48%), Glacial Acetic acid and hydrogen fluoride are used for making electrolytes. All the solutions and the glassware were autoclaved before being used, and the desired reagents were prepared in de-ionized water.

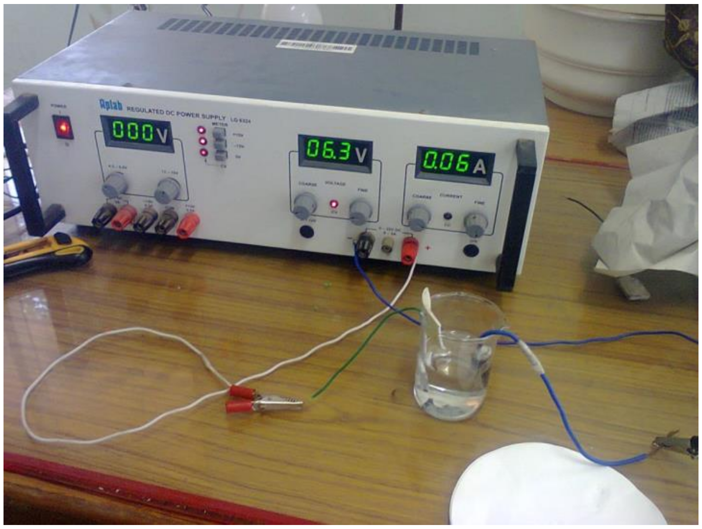

Figure 1: Working Set-up for Anodic Oxidation

Sample preparation for anodic oxidation

Cutting: Ti-6Al-4V samples were cut from a titanium sheet in the dimension of 12mm×10mm×5mm using a hex blade.

Grinding: Grinding of crude and rough samples was done on a belt grinder. Grinding was done to produce smooth edges.

Paper polishing: Paper polishing was done using four types of emery paper graded as 1/0, 2/0, and 3/0. These papers have abrasive particles on their surface. 1/0 has more roughness than the other two papers. The roughness of the paper decreases from 1/0 to 3/0. Effective polishing was achieved by using two consecutive emery papers in the perpendicular fashion on the Ti-6Al-4V samples. Paper polishing was done to remove roughness of the material received.

Cloth Polishing: The next step after paper polishing was Cloth polishing. Cloth polishing was done on a velvet pad on a cloth polishing wheel. Also known as buffing; this was used as a pre-requisite for finishing the polishing process. Alumina paste was used as a polishing material in the cloth polishing. This cloth polishing was done to remove minor scratches that remained after paper polishing.

Diamond polishing: Diamond polishing was the last step after cloth polishing. Diamond polishing was done only for removing very fine scratches that remained after cloth polishing. In, this procedure, the diamond paste was used along with Hi-Fin spray. Finally, a mirror-like surface was produced after diamond polishing was done.

Experimental procedure for anodic oxidation

The experimental set-up for anodic oxidation used in this work is a 2-electrode system depicts below in figure 1. The oxidation was carried out using a graphite rod as the cathode and the titanium samples as anode respectively. The temperature of the experimental set-up was maintained at a constant room temperature. [10].In this work, TiO2 layer deposition on titanium substrates was achieved by carrying out the anodic oxidation at a constant voltage [11]. A DC supply was provided by APLAB regulated DC power supply.

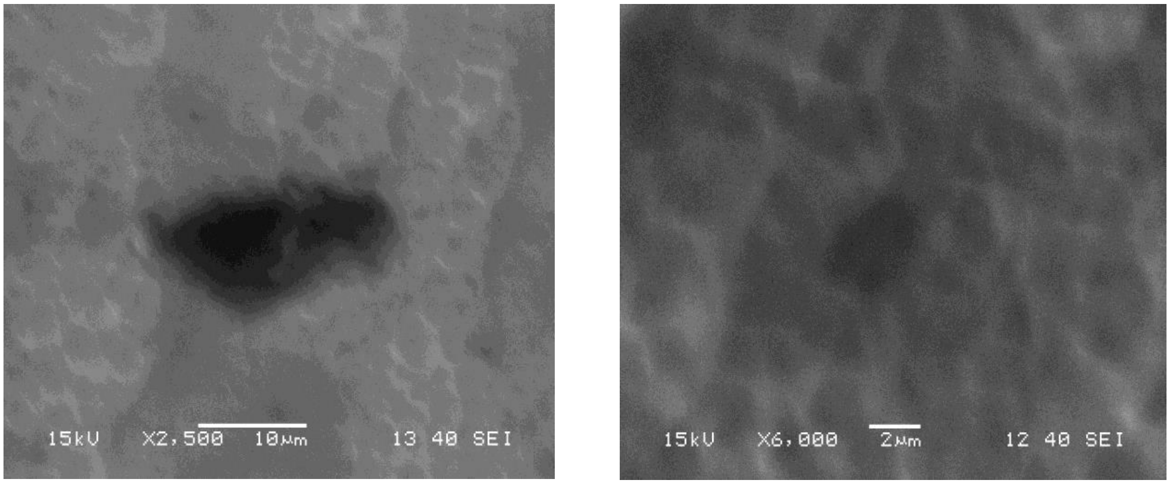

Figure 2: SEM images of the Titanium oxide surfaces obtained on Ti-6Al-4V substrate with CH_3COOH+0.5M HF at different Magnification at (a) 1,500X and (b) at 6,000X for 4 h.

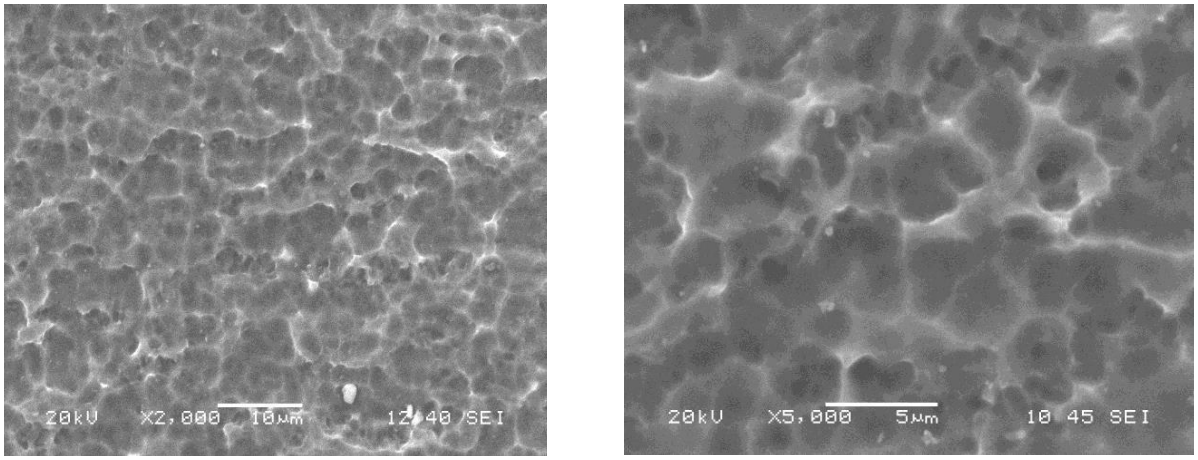

Figure 3: SEM images of the Titanium oxide surfaces obtained on Ti-6A-l4V substrate with 1M H2SO4+0.15 %M HF at (a) 2,000X and (b) at 5,000X for different magnification for 4 h.

Characterization techniques

The scanning electron microscope (SEM) is used for to study the surface morphology ofTi-6Al-4V. SEM characterization of the oxide layers was performed using JEOL JSM-5300 microscope (acceleration voltage 15 kV). The oxide samples were placed in the SEM‟s sample holder using graphite impregnated adhesive conductive black "carbon tape". This sample holder was then ushered inside the instrument. Finally, these samples were visualized under SEM at various magnifications e.g. 1500X, 2500X, 5000X, and 7500X. The X-ray diffraction patterns of the samples were recorded on a Philips Analytical Ltd, Holland (PW3040) using Ni-filtered Cu-Kα radiation. The range for XRD characterization was selected as 20-80 degree with a scan speed of 2 degrees per minute using Bragg-Brantano configuration. After deposition, the oxide layer so obtained was examined by X-ray diffraction (XRD) to consider the phases formed in the oxide layer. A similar study was also carried out on the on the as received Biomaterial. XRD was performed in the 2θ range of 20-80 and 2-3 degrees per minutes scan rate using Cu-Kα (α= .15406 nm) radiation in a Philips X'pert system.

The hardness of the titanium oxide layer on the Ti-6Al-4V surface has been measured using LECO LM700 micro hardness tester. The test was carried out with 10 gf load for 15 seconds to ensure that the indentation is up to the coating surface only. The hardness values were taken at 5 different places on the surfaces and average of these values were considered in this result. Wettability of the sample is being done by an apparatus designed the degree of wetting, or the wettability is determined by a force balance between adhesive and cohesive forces.

RESULTS AND DISCUSSION

Morphological characterization

It has been observed that in anodic oxidation, the morphological nature of the oxide grown on the surface depends on real-time parameters such as the operating voltage, reaction time, and current density. In this work, the nature of the working electrolyte and the reaction time have used as the varying parameters.Ti-6Al-4V surface has been polished and anodically oxidized in different solutions. The detailed study of oxide surface is discussed under this section.

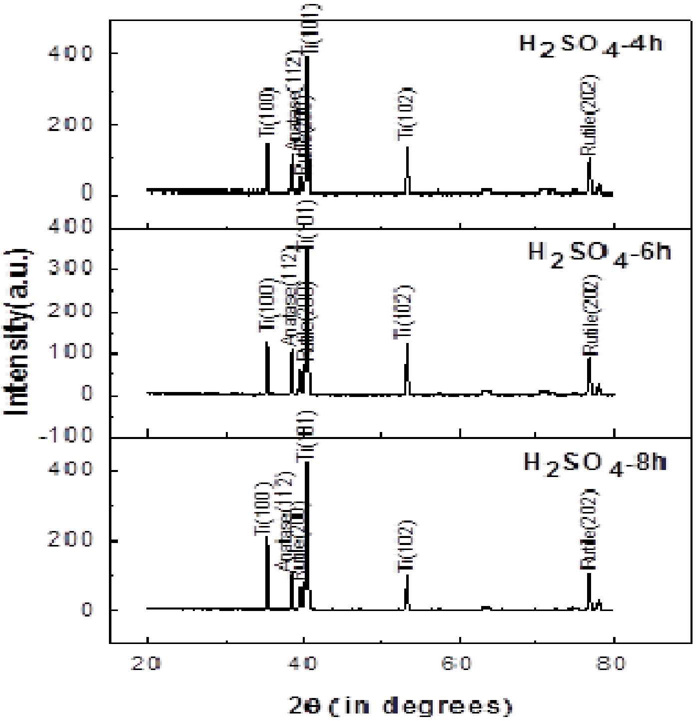

Figure 4: XRD spectra of Ti-6A-4V upon treated with H2SO4 on different time duration

Scanning electron microscopy (SEM)

Figure 2 shows scanning electron micrograph of the Ti-6Al-4V surface after anodic oxidation using CH_3COOH +0.5M HF as the electrolyte .Ti-6Al-4V has treated anodically for three different time duration such as 4, 6 and 8 h. From the figure, it has been observed that coating is continuous, uniform and crack-free. The oxide layer is deposited throughout the surface in a globular form. At higher magnification, numerous pores can be seen, and the grain diameters are found to be 2 micrometers.

Figure 3 shows scanning electron micrograph of the Ti-6Al-4V surface by anodic oxidation in 1M H_2SO_4 +0.15 % HF for 4h. From the figure, it has been observed that coating is continuous, uniform and crack-free. The oxide layer is deposited throughout the surface in a globular form. At higher magnification, numerous pores can be seen, and the grain diameter is found to be 5 micrometers.

XRD profile of the oxide layer on Ti-6Al-4V treated with 1 M H_2SO_4 +1.5%HF at various time durations are shown in figure 4. All the peaks for the anatase have been matched with JCPDS database reference no. 84-1286, while the peaks for the α-Titanium have been matched with that of reference no. 44-1284. It can be seen that the patterns at 35 deg. And 48 deg. ascribed to the Ti (100) and Ti (101) crystal plane on the surface of the Ti-6Al-4V. The peaks correspond to the 38 deg. and 76 deg. confirms the presence of anatase and rutile phase respectively. It is evident from the graph that as we increase the time of reaction the intensities increases.

Table 1: Vicker's Hardness No. for the untreated Ti-6Al-4V and anodically oxide Ti-6Al-4V is mentioned as a reference value.

Sample	Vicker's Hardness No. (VHN)
Bare titanium (as received)	330
CH_3COOH+0.5M HF (30 V, 4 h.)	263
CH_3COOH +0.5M HF (30 V, 8 h.)	396
1M H_2SO_4 +0.15 %M HF (30 V, 4 h.)	388
1M H_2SO_4+0.15 %M HF (30 V, 6 h.)	477
1M H_2SO_4+0.15 %M HF (30 V, 8 h.)	505

The micro-hardness of the oxide layer is measured by vicker's hardness tester by applying 100 gF. The values taken in the above table represent the average of the 5 values obtained for each sample. The increased in the hardness may be attributed to the formation of the oxide layer over the surface. The table compares the different hardness values for the anodic oxidation reactions performed in various reaction period .As can be inferred from the table, the VHN increases as the time for the reaction increases. This suggests that with time, the depth of the oxide layer on the sample substrate increase and an increase in hardness is attributed to the formation of a more uniform oxide layer on the surface. Table 1 shows the hardness number upon treatment of sample in different solution.

Table 2: Showing the contact angle (all in degree) obtained by treatment with the solution shown above with voltage 20 and 30 V respectively

Sample	20 V	30 V
CH_3COOH + 0.5M HF (4h.)	69	66
CH_3COOH + 0.5M HF (8h.)	56	53
1M H_2SO_4 + 0.5% HF (4h.)	68	63
1M H_2SO_4 + 0.5% HF (6h.)	62	60
1M H_2SO_4 + 0.5% HF (8h.)	60	57
Bare Titanium (as Received)	74	74

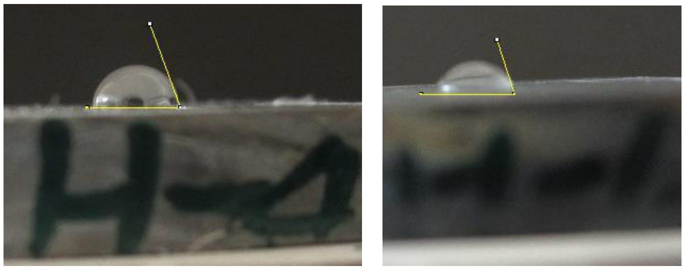

Figure 5: Images of contact angle over Ti-6Al-4V treated with sulfuric acid 4 h. and 6 h.

Wettability analysis was carried out through measuring Contact angle by using Hank's solution onto the surface of the oxide layers. The wettability of the titanium dioxide films with different morphologies was investigated by Hank's solution contact angle (CA) measurement depicts below in figure 5. For the as-prepared films, the CA exhibits a clear trend of decrease with the increase of anodizing voltages and time of treatment. When the anodizing voltage was 30 V, the samples became more wetted than 20V also with the increase in time the samples show less contact angle. The CA on a polished Ti-6Al-4V sample is normally observed around 74deg [12]. Table 2 below depicts the contact angle in degrees upon treatment with different solutions at a different duration of time. Much higher CA are due to the increase of roughness. The CA of an oxidized sample at 20V was approximately 65deg. The drop spread up to 60deg. when a sample oxidized at 30V was used for the test. Therefore, it can be concluded that increase in voltage above 30 V improves the hydrophilicity of the surface due to the formation of highly polar O–Ti–O bonds. The titanium dioxide surfaces, therefore, exhibit little CA at voltages near 30V.

CONCLUSIONS

Surface polishing was a crucial step to produce a mirror-like surface. This helped in a better oxide layer. Usually, titanium dioxide can exist in three crystalline forms, in which the anatase and rutile phases are more useful than the brookite phase. The crystalline form of the titanium dioxide prepared by electrochemical anodization under the specified condition was investigated by XRD, which confirmed the presence of anatase and rutile form of TiO2. The microhardness studies also confirmed the fact that the hardness of the sample oxidized for the maximum duration of time was the highest. The wettability studies confirmed the hydrophilicity of the oxide surface at a voltage of 30V. This hydrophilicity is advantageous regarding better cell growth and adhesion. On soaking in Hank's solution after anodizing with sulfuric acid a dense appetite layers formed on the titanium surface. Highly hydrophilic titanium dioxide coating is of great interest for various applications like biocompatible implants, anti-fog coating, and self-cleaning surfaces. As a further application of anodic oxidation of Ti-6Al-4V, a higher voltage condition can be provided so that nanotubular structures are formed with much ease and convenience. Titania nanotubes are of great significance in the field of biomedical science, drug delivery, photocatalytic activities and biosensor devices.

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COMPETING INTEREST

The authors have declared that no competing interests exist.

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About Author

Mr. Chandan Kumar is doing his Ph.D. at School of Biomedical Engineering, Indian Institute of Technology (BHU), Varanasi. He has received M. Tech degree from Department of Biotechnology & Medical Engineering, National institute of Rourkela, Odisha and B. Tech in Electronics and Instrumentation Engineering from Institute of Technology and Management (ITM), RGTU, Gwalior, MP, India. Currently he is working on energy scavenging through human motion.