

Corrosion and Structure Characterization of Anodized Ti-6Al-7Nb Alloy

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ABSTRACT

Electrochemical and structural properties of titanium implant materials with a nanotube surface treatment and heat treatment were examined. Amorphous TiO₂ nanotubes were grown homogeneously on α phase of Ti-6Al-7Nb alloy.

Amorphous TiO₂ nanotubes were partially crystallized to rutile by heat treatment at 800^oC for 2 hrs. The corrosion potential (E_{corr}) of the annealed sample had value of -162.881mV due to the stable TiO₂ crystal phase compared to the -343.629 mV observed in the untreated sample. At 0.5 V, where a passive layer had formed, the corrosion resistance of the annealed sample was approximately ten times that of the untreated sample.

خصائص التركيب والتآكل لسبيكة Ti-6Al-7Nb المونونه

الخلاصة

فحصت الخواص التركيبية والكهروكيميائية لزروعات التيتانيوم بعد تكوين انابيب نانوية على سطحها ومعالجتها حراريا. تكونت انابيب نانويه ذات تركيب عشوائي من ال TiO₂ بصورة منتظمة على طور α لسبيكة Ti-6Al-7Nb. هذه الانابيب النانوية تبلورت جزئيا الى طور Rutile بعد التسخين الحراري بدرجة 800^oC لساعتين. جهد التآكل للنموذج الملدن هو -162.881mV بسبب الطور البلوري المستقر ل TiO₂ بينما كان هذا الجهد للنموذج الغير معامل -343.629 mV . عند 0.5 V حيث تكونت الطبقة المانعة للتآكل فان مقاومة التآكل للنموذج الملدن كانت اكبر بعشرة مرات من تلك للنموذج غير المعامل.

الكلمات المفتاحية: التاكل , انابيب نانوية , زوارع التيتانيوم , التلدين , سبيكة Ti-6Al-7Nb.

INTRODUCTION

From the biological point of view the surface is the most important part of the implants. The surface has direct contact with human tissue and is responsible for acceptance of the implant. Surface reactions can lead to good acceptance and cooperation of the implant with the surrounding tissue. [1]

In the last years different types of surface modifications were developed with the aim of improving the osteointegration ability of titanium alloys. The chemical composition, crystallographic structure and morphology of a surface layer can be modified in order to obtain a better interaction between the implant, the cells and the organic fluids. The final goal is to obtain a more efficient bone growth also in critical clinical cases.[2] Titanium and its alloys are the most used metallic materials for biomedical applications, due to their excellent mechanical, biological and chemical properties. Ti-6Al-7Nb and Ti-6Al-4V are probably the best known titanium alloys and they are meanwhile well-established metallic materials for implants, especially on replacement of hip joints.[3] Ti-6Al-4V was the most popular alloy in biomedical industry until the recognition of adverse tissue reactions and toxicity arising from in-vivo release of vanadium ions. To overcome this drawback, a new alloy, Ti-6Al-7Nb, has been developed by substituting niobium with vanadium [4]. Ti-6Al-7Nb alloy was developed to achieve the following objectives [5]:

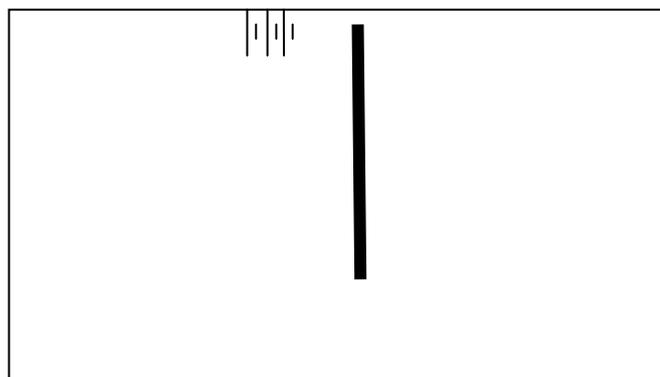
- a dense and stable passive surface layer with the presence of all alloying elements;
- high resistance to corrosion;
- $\alpha+\beta$ grain structure with the possibility of superplastic deformability;
- mechanical properties comparable with those of the high-strength, wrought Ti-6Al-4V alloy;
- Economical production of semifinished material and of implant components.

The fabrication of ordered oxide nanotube arrays on Ti and Ti alloys has been investigated extensively in recent decades for application in water purification, photocatalysis, photoelectrolysis, gas sensors and orthopedic implants, due to their high photocatalytic activity and self-cleaning properties, good corrosion resistance and high strength, enhanced biocompatibility[6].

In this contribution we try to investigate the corrosion characteristics and structural properties of Ti-6Al-4V alloy before and after anodizing and annealing processes.

EXPERIMENTAL PART

5 mm thickness circular samples were cut from Ti-6Al-7Nb rod of 25mm diameter, using wire cut machine. A mirror-finished surface was then obtained by grinding progressively finer down to 2400 grit with SiC papers. The specimens were then polished with 3µm diamond suspension. For the purpose of removing debris and contamination from the polished samples, ultrasonic cleaning bath (Sonomatic/170-2-T80, Germany) with ethanol and acetone of 75:25 wt% ratio was carried out. This process was performed for 15 minutes, and all samples were dried at 100°C. A schematic representation in Figure (1) shows the design of the electrochemical cell used in this work. The cell consists of graphite disc acted cathode and disk of titanium alloy as anode.



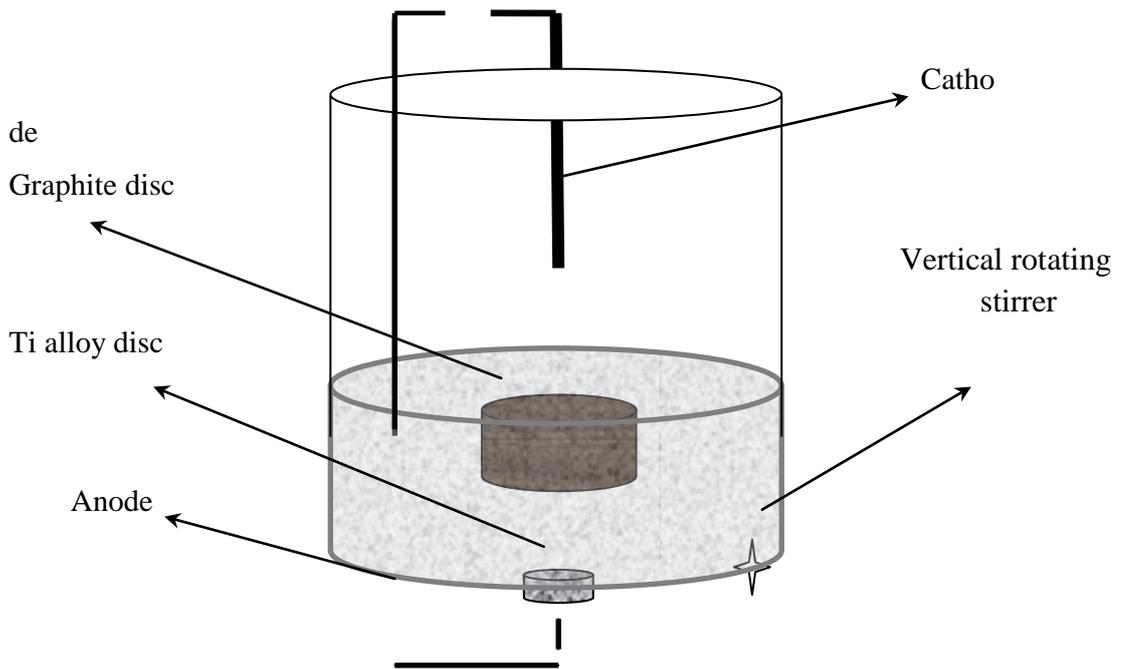


Figure (1) Anodic process cell works at Room temp and Voltage difference 30 V.

The chemical solution of the anodization process consists of $\text{NH}_4\text{F}:\text{H}_2\text{O}$: glycerol at a ratio of 1:20:79 wt. %. The voltage difference between cathode and anode was maintained at 30 V during one hour of the process. During the surface modification by this method the chemical solution was kept with continuous stirring. After electrochemical process the samples were washed by ionized water and then dried at 100°C . Scanning electron microscope (VEGA II SBH MS 12) was used to explore the surface topology. Structural analysis for the modified surfaces was carried out using X-ray diffraction (SHIMADZU, XRD-6000, and Japan.) Annealing process was done for two hours at 800°C using tube furnace (Carbolite Type MTF 12/38A BAMFORD England). The electrochemical measurements were carried out using potentiostat / galvanostat (PARASATE 2273, Princeton Applied Research)

provided with electrochemical interface controlled by commercial POWER SUITE software. A three-electrode cell arrangement was used for the electrochemical measurements, with the Ti samples, saturated calomel electrode (SCE) and a large Pt screen as the working, reference and counter electrodes, respectively. The specimen was scanned in the positive direction at a sweep rate of 10 mV/sec and the current was monitored with respect to the potential. The corrosion measurements were done for the specimens under equilibrated conditions in simulated body fluid (SBF) as can be seen its constituents in Table (1) [7].

Table (1) the compositions of SBF.

| Order | Reagent | Weight(gm/l) |
|-------|----------------------------------|--------------|
| 1 | NaCl | 6.800 |
| 2 | KCl | 0.400 |
| 3 | CaCl ₂ | 0.200 |
| 4 | NaHCO ₃ | 2.200 |
| 5 | Na ₂ HPO ₄ | 0.126 |
| 6 | NaH ₂ PO ₄ | 0.026 |
| 7 | MgSO ₄ | 0.100 |

RESULTS AND DISCUSSION

The ternary titanium alloy studied in this work consist of two metallurgical phases (α and β). Figure (2) shows that the microstructure of the as cast Ti-6Al-7Nb alloy consists of parallel plates of α delineated by the β between them. The α phase consists of Al-rich (Hexagonal close packed-HCP-) and the β phase (Body center cubic-BCC-) which are enriched in Nb.[15].

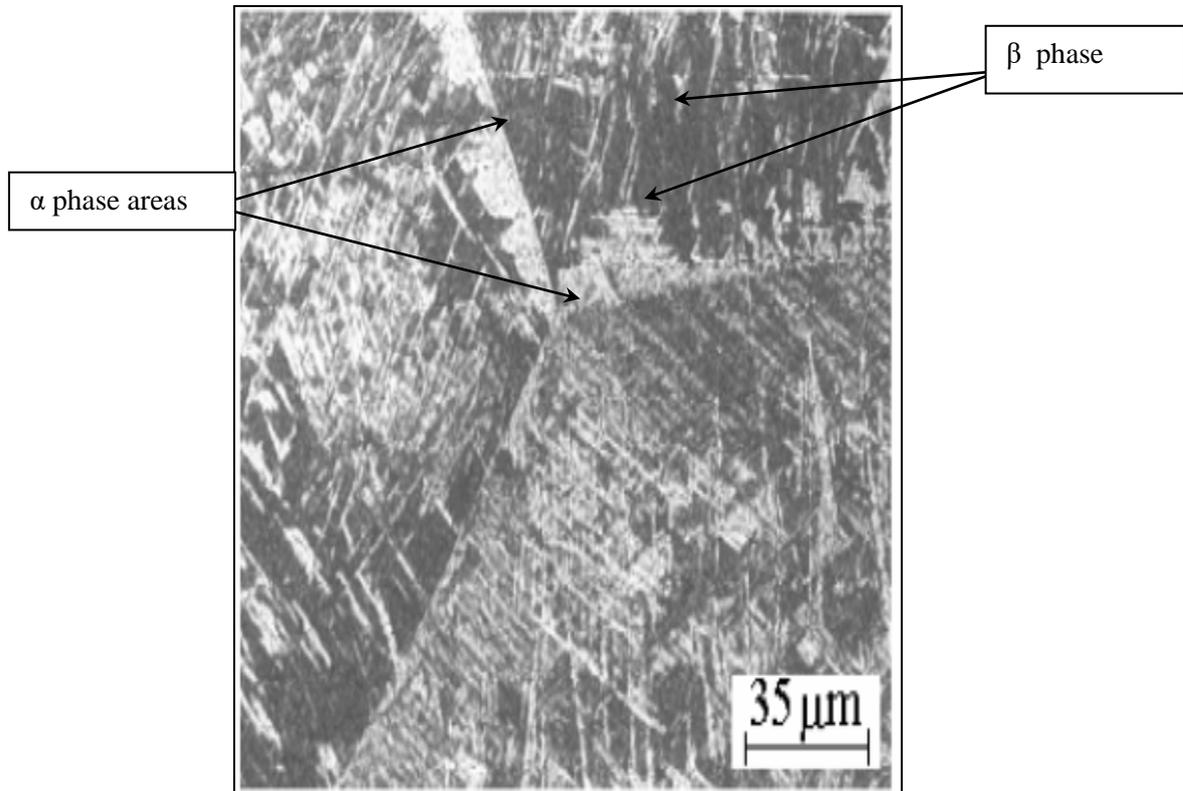


Figure (2) Optical micrographs of the as cast Ti-6Al-7Nb alloy.

Scanning electron microscopy was employed for the structural and morphological characterization of the Ti-6Al-7Nb sample surfaces after the anodization process. The SEM image of the alloy surface Figure (3) shows that the alloy phases are differently affected by the treatment in fluoride-containing solution. Under this condition only on the α -phase oxide annotate structure formed, while β phase seems to be just etched and less wide but did not present any porous structure. Emanuela et.al [8] found that the β -phase surface was just etched also when Ti-6Al-7Nb alloy was anodized in [1 M H_3PO_4 /0.1 wt% HF], for 40 minutes.

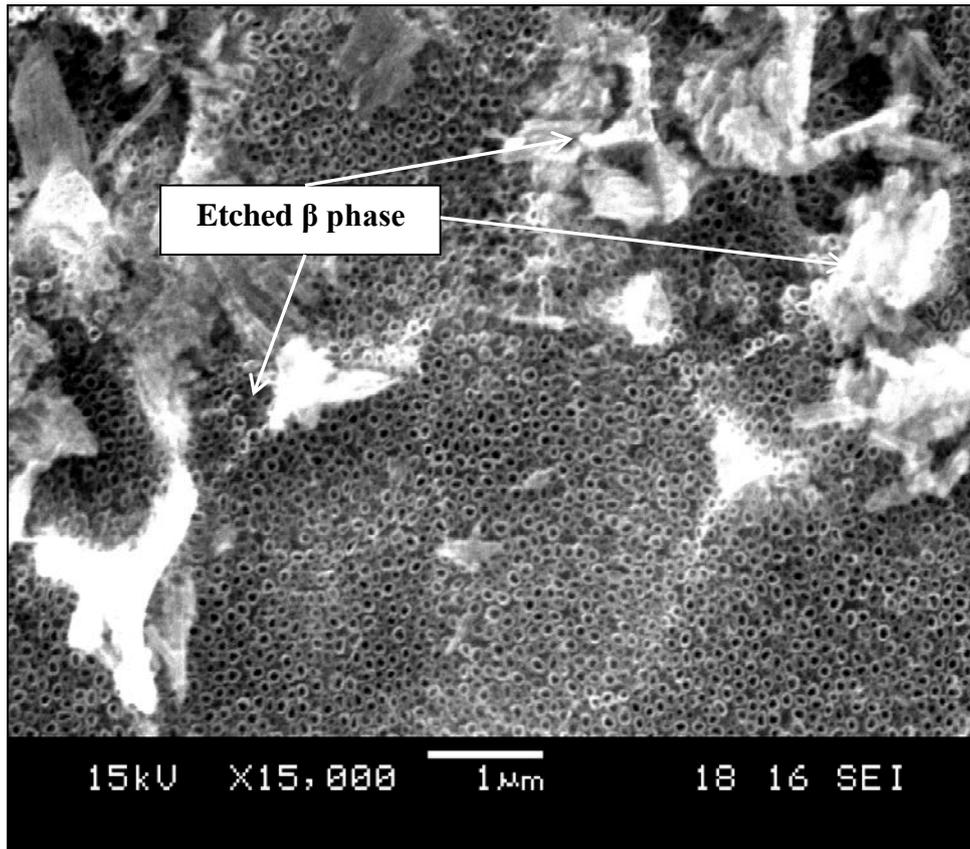


Figure (3) Formation of Titanium oxides nanotube on α phase of Ti-6Al-7Nb alloy surface.(the α phase is dark;the β phase is bright).

Figure (4) shows the XRD patterns recorded for the untreated, as-formed and the heat-treated (800⁰C for 120 min) nanotubular alloy. There was no large observable changing on the XRD pattern of as anodized alloy compare with that of untreated sample, only the peaks corresponding to the titanium were obtained, which probably indicates the amorphous nature of the nanotubes.[9]. After annealing, strong new reflections appear, indicating that the as-annealed nanotubes layers are crystallized. These peaks can be assigned to crystal phases of TiO₂ (Rutile), (JCPDS file no. 211276), α phase of Ti (JCPDS file no.441294) and β phase of Ti (JCPDS file no.441288). The presence of α -Ti and β -Ti peaks in the XRD pattern is due to the penetration of X rays beyond the oxide layer. Niobium was classified as beneficial alloying element,

according to its effect on oxidation resistance of titanium alloys. Oxygen is a strong α stabilizer in titanium alloys [10], therefore accompanying the inward diffusion of oxygen atoms by annealing process, the retained β would transfer into stable α , thus leading to a reduced content of β phase in the near surface area, this phenomena is clear for β -Ti (110) peak in Figure (4). The beneficial effect of niobium was correlated with the stabilization of the oxide layer as a consequence of annihilation of anion vacancies in the crystal lattice of TiO_2 [11]. In this respect Jiang et al. [12] reported that niobium in the solid solution of the oxide layer improves the oxidation resistance but high niobium levels may lead a reduction in oxidation resistance by inducing additional oxide phases such as TiNb_2O_7 or AlNbO_4 , which were not detected in the present study.

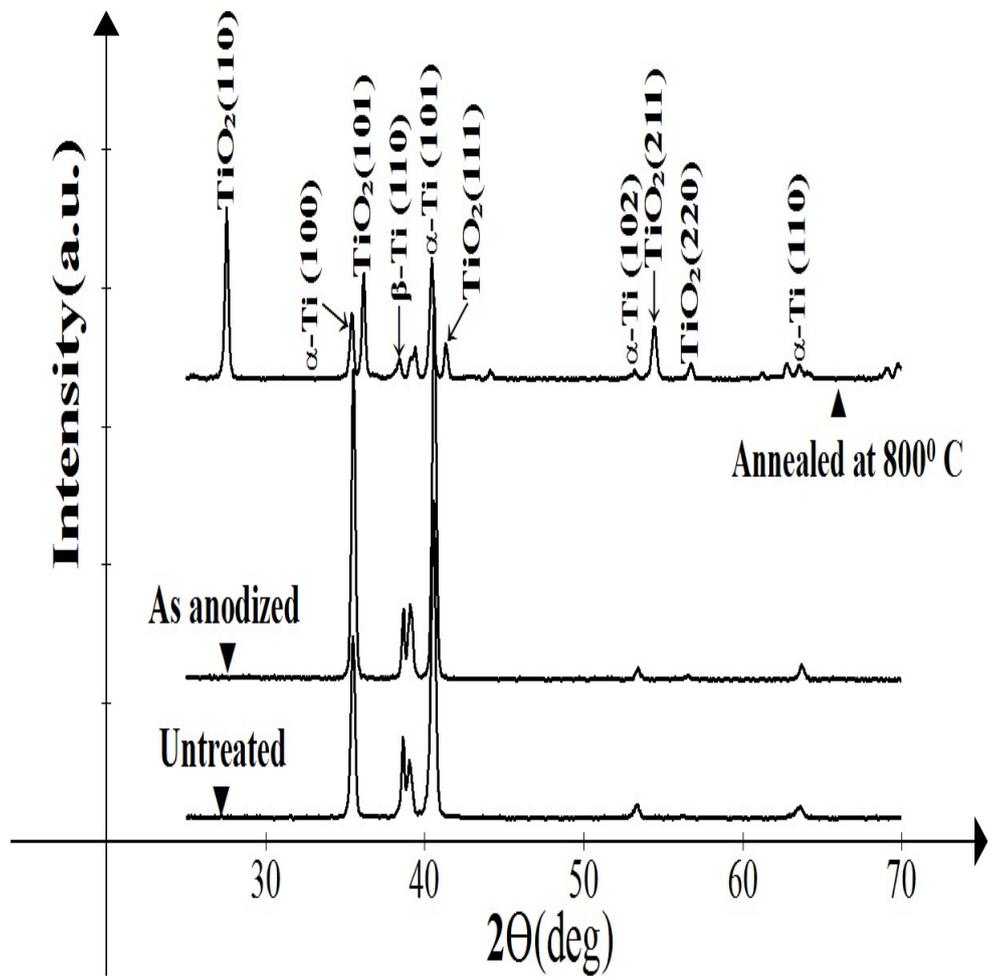


Figure (4) XRD patterns of Ti-6Al-7Nb alloy with various Surface treatments.

In order to investigate the chemical composition of the oxide tubes, the as-anodized sample was further characterized by energy dispersive X-ray spectrometer (EDS). Figure (5) illustrates the composition of as anodized sample. Quantitative evaluation of the results are tabulated in Table (1).

Table (2) Concentration of Ti-6Al-7Nb alloy elements.

| Element | atomic number | Energy (KeV)of $K_{\alpha 1}$ lines | spot A | | spot B | | spot C | | spot D | |
|---------|---------------|-------------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| | | | wt% | at% | wt% | at% | wt% | at% | wt% | at% |
| O | 8 | 0.523 | 10.63 | 25.43 | 7.645 | 19.18 | 9.673 | 24.58 | 10.238 | 24.51 |
| Ti | 22 | 4.51 | 78.50 | 62.72 | 82.935 | 69.51 | 81.43 | 66.81 | 81.17 | 64.92 |
| Al | 13 | 1.487 | 4.266 | 6.054 | 4.664 | 6.942 | 3.733 | 5.23 | 3.64 | 5.181 |
| Nb | 41 | 2.166 | 5.187 | 2.137 | 3.915 | 1.692 | 4.031 | 1.92 | 3.58 | 1.478 |

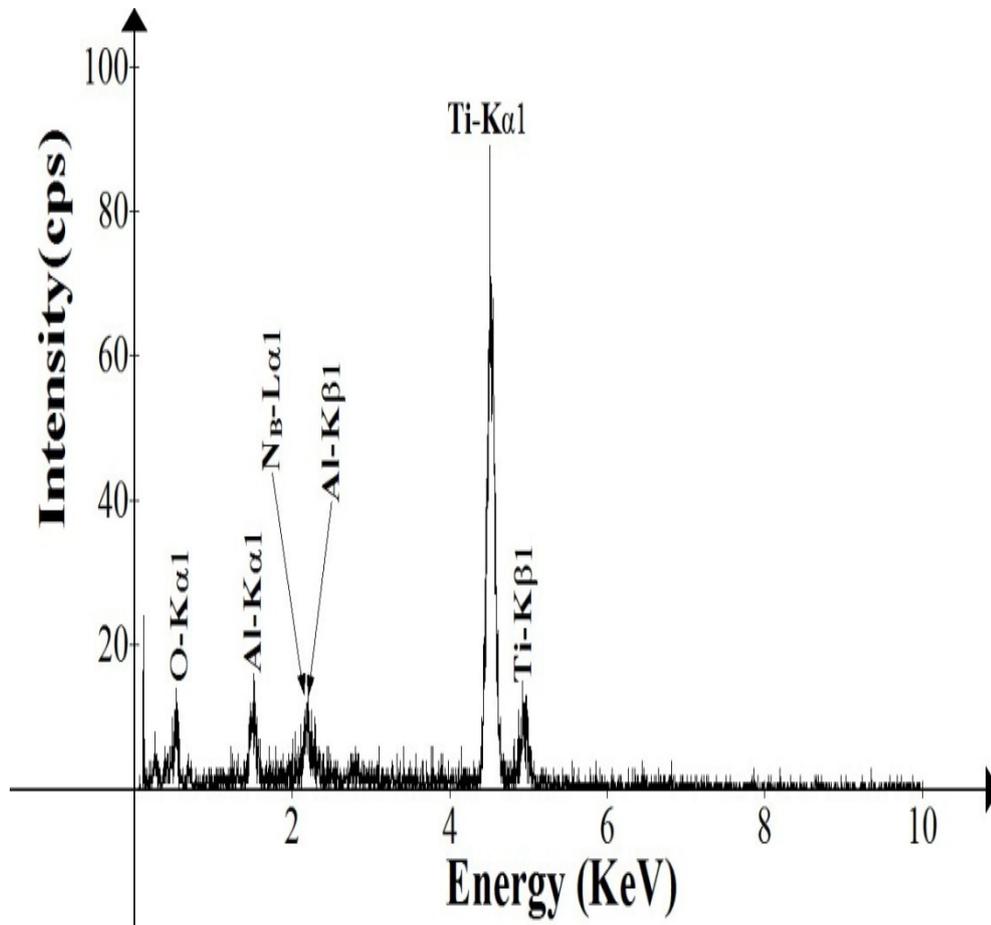
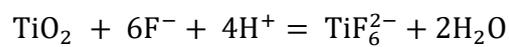


Figure (5) ED's spectra of as anodized Ti-6Al-

The difference between the weights of alloy's elements before and after anodic process might be attributed to dissolution of these elements during this process as a result to reactions with a chemical solution. The reduction of Ti element after anodic process was seen by Qingyun CAI et.al. [13] And they confirmed that the decrease in anode mass indicates that the chemical dissolution is significant in the presence of F^- :



Weight's variation of each element over different spots over the surface of as anodized sample is a direct result to inhomogeneous distribution of α and β phases as SEM's image in Figure (3) showed. Among multiple titanium oxides, only TiO_2 (Rutile) is formed after anodic process as it was confirmed by XRD pattern. Also from this pattern, there is no Aluminum or Niobium oxides; so most of atomic percent (at%) of oxygen in Table(1) react with Ti to form TiO_2 . The rest of titanium which did not react with oxygen was α -Ti or β -Ti phase, as XRD pattern in Figure (4) showed. Figure (6) shows the results of potentiodynamic polarization curve analyses of each sample in the SBF electrolyte. Table (2) shows the corrosion parameters obtained from each sample. The corrosion current density (I_{corr}) and corrosion parameters, such as the anodic and cathodic Tafel slopes (Ca (β) and an (β)), were calculated from the polarization curves by a Tafel extrapolation. With the untreated sample, the corrosion progressed rapidly in the initial stage. A passive region was observed at a potential of >0.35 V, which was quite effective against further corrosion due to formation of a stable oxide layer, and no further corrosion occurred. For anodized sample, the formation of a passive layer was broken and re-formed in a three-step process, this suggests that the TiO_2 nanotube oxide layer provided good corrosion resistance at the initial corrosion stage whereas the corrosion progressed through an unstable anatase oxide layer with immersion time. This behavior is similar to potentiodynamic polarization curves in the SBF electrolyte of untreated and anodized Ti-6Al-4V alloy samples observed by Hyeoung et.al. [14]. Due to the stabilized crystallization of the TiO_2 layer, the heat treatment sample showed good corrosion resistance compared to other samples, all its corrosion parameters are improved as the numerical values of corrosion parameters shows in Table(3).

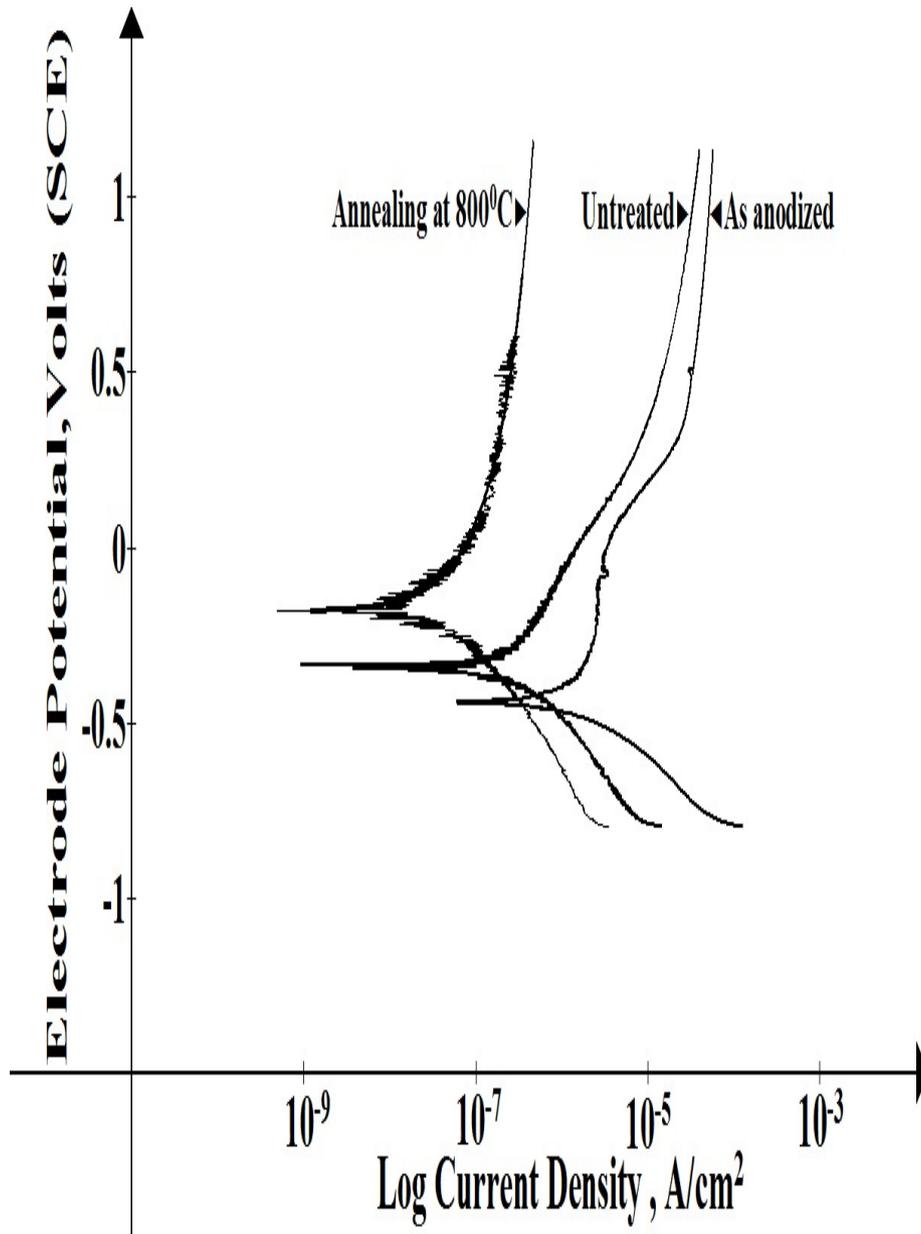


Figure (6) Tafel plots for Ti-6Al-7Nb with various surface treatment in SBF at room temperature.

Table (3) Corrosion parameters of Ti-6Al-7Nb with various surface treatments.

| Sample's type | E(I=0)(mV) | I _{corr.} (μ A) | Co.Rate(mmpy) *10 ⁻³ | Ca(β)(mV) | An(β)(mV) |
|---------------|------------|-------------------------------|------------------------------------|-------------------|-------------------|
| Untreated | -343.629 | 0.39 | 3.349 | 306.239 | 579.123 |
| As anodized | -429.323 | 0.1148 | 9.83 | 165.406 | 501.415 |
| Annealed | -162.881 | 0.044 | 0.38 | 302.6 | 576.072 |

At 0.5 V, all three samples formed a passive layer; here, the current density of annealed sample was $0.3\mu\text{A}/\text{cm}^2$, whereas it was $10.48\mu\text{A}/\text{cm}^2$, $30\mu\text{A}/\text{cm}^2$ with untreated and anodized sample respectively. This suggests that the corrosion progress was more than tentimes faster on untreated than on annealed sample.

CONCLUSIONS

In cases of an anodic oxidation process forming a nanotube structure, heat treatment would be necessary to maintain an electrochemically stable status during long-term implantation into a host body.

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