Surface Properties of Ti6Al4V Modified by Simple Thermo-Chemical Modifications

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Abstract— Alloys place a premium on metals because of their diverse microstructures which can be obtained easily via elementary methods. Microstructure engineering of the alloys plays a key role in material science and engineering as it can produce a wide range of physical, chemical and biomechanical properties. In this study, Ti-6Al-4V alloy, as a common bio-alloy, was chemically modified to alter its surface characteristics. Surface microstructure and chemistry were characterized with the aid of a SEM / FESEM with EDS analysis. Surface topography was probed using SPM and stylus profilometer. The surface wettability was also evaluated via contact angle measurement. According to the results, the selective etching of α or β phases are obtained by double-acid and alkali treatment. From the topographical point of view double-acid treated samples make uniform sharp peaks on the surface whereas alkali etching creates partially uniform sphere protuberance. Treated samples present the lower contact angle as well as higher wettability after 30 min etching. Among the immersion treatment, alkali treated samples have the highest surface wettability.

Keywords— Chemical modification, Ti-6Al-4V alloy, Surface properties

I. Introduction

TITANIUM (Ti) and its alloys are extensively used as biomaterials, especially dental and orthopedic implants [1]-[5]. One of the most significant parameters of implants is their surface property such as surface topography and surface wettability. Protein adhesion, osseointegration and finally long-term implant survival are greatly affected by these surface properties [6]. Hence, numerous methods have been applied on the implants to modify their surfaces [7]. These techniques can be classified into three major groups including physio-chemical treatments, surface coating methods, and surface texturing approaches [4]. Among them, immersion corrosion treatment using acid or alkaline etchants is widely used to modify the surface mainly due to the time and/or cost saving. Immersion corrosion treatment creates a random topography on the surface and alters the surface roughness and wettability; therefore it can improve implants biocompatibility [8].-[9]. The aim of the present work is to characterize the surface properties and compare the acid and alkali etching of Ti-6Al-4V alloy as a common bio-alloy.

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II. Materials and Methods

A. Samples Preparation

Ti-6Al-4V alloy samples with dimensions of $10 \times 10 \times 4$ mm3 mainly contained 89% wt% Ti, 6.3 wt% Al, 3.6%V. The samples were firstly ground with 320, 500, 600, 800, 1000, 2000, 2500 and 3000 grit abrasive papers. Following polishing with alumina (2µm), the samples were ultrasonically cleaned in deionized water, acetone, and ethanol before drying. Then, different chemical treatments were conducted. The samples were then immediately rinsed with deionized water to stop the reactions before the further drying process.

B. Acidic Etching

Ti-alloy samples were submerged at three different acidic etchants including: 4% H2SO4, strong Kroll (3HF+2HNO3+95H2O), and weak Kroll (2HF+3HNO3+95H2O). The etching time was 3, 15 and 60 min. Etching was arrested after desired times by adding distilled water.

C. Alkali Etching

Samples were etched using piranha solution (an equal volume of H2SO4 97%, equivalent to 36 N) and 30% aqueous H2O2. Following cooling of the fresh solution in ice to 20 ºC, samples were immersed in it. After 3, 15 and 60 min, etching was stopped and samples were rinsed with distilled water and ethanol for 15 min, and then dried in air.

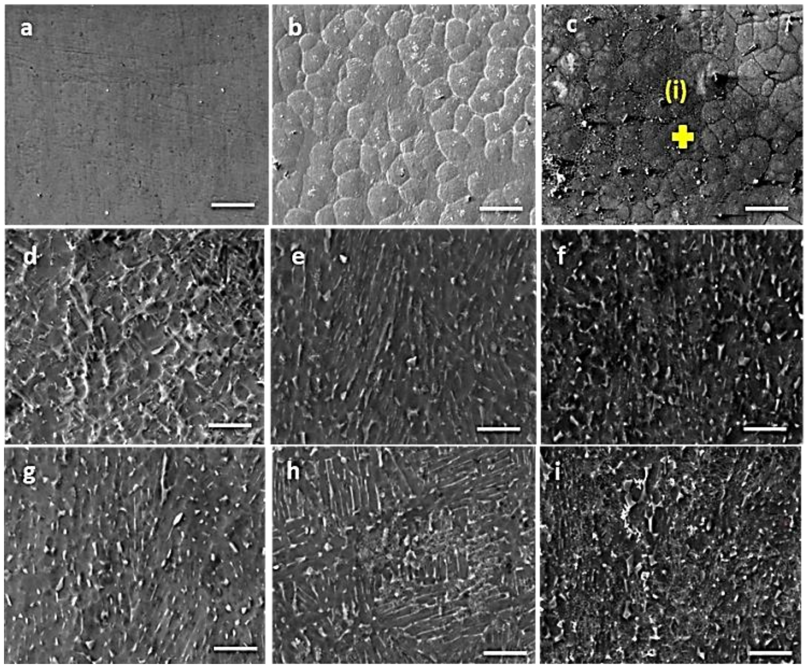

Fig.1 Acid etching of Ti-6Al-4V alloy. FESEM micrographs of Ti-6Al-4V alloy after exposing to single acid a-c) (H_2SO_4) and double acid-etching d-f) weak Kroll, g-i) strong Kroll for 15, 30 and 120 min, respectively. Scale bars are 50 μm.

D.Characterization

Surface morphologies were observed by field emission scanning electron microscopy (VEGA3-TESCAN FE-SEM). Surface chemical elements were examined by EDS analysis. The topography and roughness of the surface were evaluated using Scanning Probe Microscopy (AFM; SPM-9600, Shimadzu, Kyoto, Japan) and a Pocket Surf Make Mahr, GMBH- EMD 1500 profilometer. Surface wettability was also analyzed by contact angle measurement using static method and direct measurement of pure water drops using high-resolution camera. To measure the advancing contact angle 4μL droplets were used.

III. Results and Discussion

Fig.1 shows the SEM micrographs of Ti-6Al-4V alloy after single (H_2SO_4) and double acid etching (Kroll reagents) at room temperature. Etching of the sample with sulfuric acid up to 15 min did not exert significant on its surface morphology (Fig 1a), however, long time etching of the sample presents the concave-convex morphology containing micro-size hillocks (Fig 1b-c). Applying double-acid etching in a different order results in a similar surface morphology. As expected, α-phase is corroded with a higher rate than β-phase which seems to be due to its cathodic nature and higher corrosion tendency [10]. Although, treating with strong and weak Kroll reagents initially did not show significant differences in microstructure designing, it is obvious that β-phase showed protuberance the surface after long time etching with strong Kroll.

Fig. 2 shows the FESEM micrographs of Ti-6Al-4V alloy subjected to alkali etchant, piranha solution. As seen, the microstructure consists of surface pores that their size increases with the etching time.

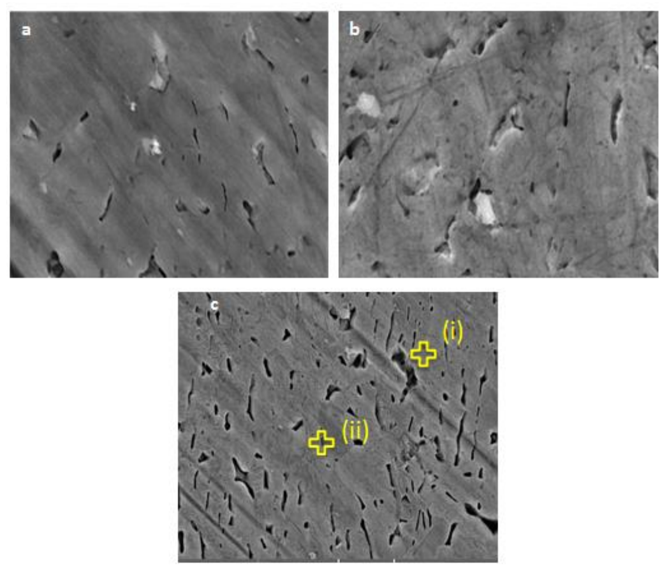

Fig.2 Alkali etching of Ti-6Al-4V alloy. Selective etching of β–phase. FESEM images of Ti-6Al-4V alloy etched by piranha solution for a) 15, b) 30 and c) 120 min. Scale bars are 2 μm.

As shown in Fig. 3, the surface chemistry of modified Ti-6Al-4V alloys with acidic or alkali reagents are different. Treating of the alloy with sulfuric acid demonstrates the lower V content and higher Al as well as S on the surface. The EDS analyses of modified samples with double-acid etchant and alkali solution reveal the Al-rich and V-rich phases. Therefore, selective etching of α- and β-phase can achieve by double-acid etching and alkali etching respectively [10]. This seems to be due to the different electrochemical potential of these phases in these reagents.

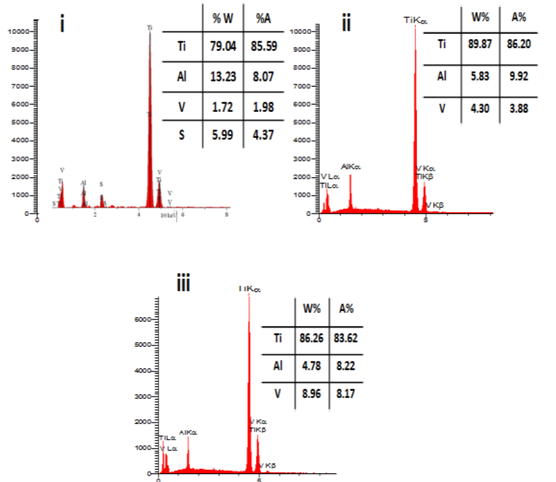

Fig.3 EDX analysis of point (i) showed in Fig.1.ii) black zone pointed as (ii) and iii) matrix pointed as (iii) in Fig.2.

Surface topographies of the modified Ti-6Al-4V alloy before and after etching were demonstrated in Fig. 4. As it can be seen, polished sample depicts relatively smooth topography (Fig. 4a). Double acid etching treatments depict uniform distribution of very sharp peaks (Fig. 5b-c). However, single etching sulfuric acid fabricates disorder peaks on the surface (Fig. 5d). Alkali etching shows rounded peaks with lower sharpness (Fig. 5e).

The effect of etching time on the topography of modified Ti-6Al-4V alloy by weak and strong Kroll is presented in Fig. 5. As demonstrated, the average roughness of 15 min-etched Ti-6Al-4V alloy with weak Kroll was 1.30 nm. Raising the etching time to 30 min increases the nano-roughness to 1.50 nm; however, long time etching shows a reduction to 1.38 nm. Higher nonmetric roughness is obtained by strong Kroll reagent compared to weak ones. Moreover, modified Ti-6Al-4V alloy by strong Kroll reagent shows similar variations in the surface roughness by etching time.

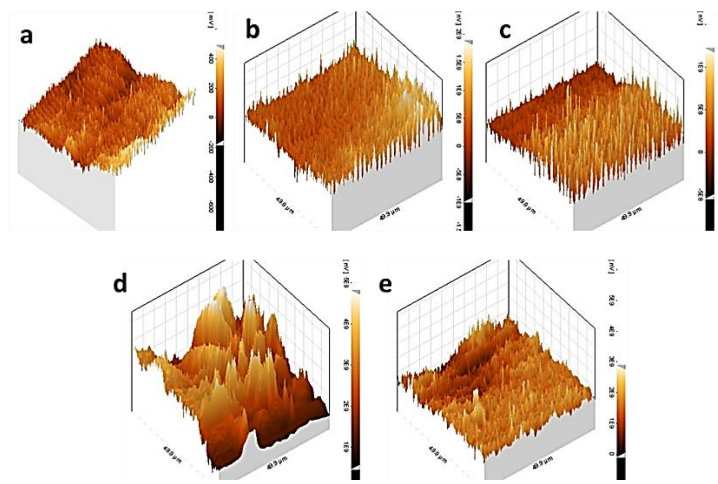

Fig. 4 Topography of Ti-6Al-4V after wet etching. SPM micrographs of Ti-6Al-4V alloy after a) polishing, etching with b) strong Kroll, c) weak Kroll, d) sulfuric acid and e)alkali etching for 60 min

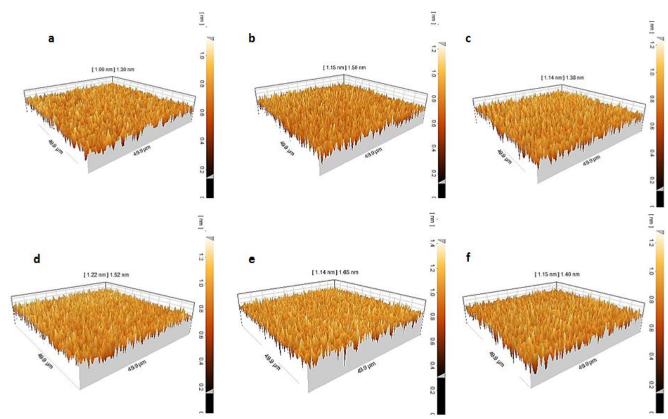

Fig. 5 Effect of etching time on the topography of modified Ti-6Al-4V alloy. SPM micrographs of Ti-6Al-4V alloy after etching with a-c) weak Kroll and d-f) weak Kroll after 15-60 and 120 min, respectively.

Fig. 6 shows the surface roughness of Ti-6Al-4V alloy before and after etching. As expected, acidic etchant leads to increasing the surface roughness [8]- [9]; however, Piranha solution remarkably decreases it [10]. Alkali modification etching β-phase greatly enhances the material ratio. As shown, more than 80% of engineering surfaces can bear the load.

a — raw

R_a (µm)	0. 33
R_q	0.37
R_{sk}	0.009
R_{ku}	1.86
R_z	1.66

b — Acidic etching

R_a (µm)	0.40
R_q	0.46
R_{sk}	0.01
R_{ku}	1.96
R_z	1.84

c — Alkali etching

R_a (µm)	0.05
R_q	0.07
R_{sk}	0.021
R_{ku}	2.89
R_z	0.41

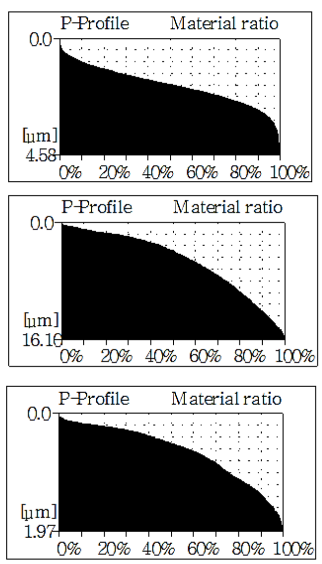

Fig. 6 Roughness results of a) polished and modified Ti-6Al-4V alloy with b) Strong Kroll, c) piranha for 60 min.

The water contact angles were used to investigate the wettability of modified samples as shown in Fig.7. The highest values of contact angels are present in the polished samples (Fig. 6), while the lowest values are obtained in the alkali-etched samples. Generally, alkali etching presents more hydrophilic structure than acid etching. By longer etching times to 30 min the wettability is improved. However, etching for long time slightly decreases it.

IV. Conclusion

The surface morphology and chemistry studies of immerged Ti-6Al-4V alloy in different reagents show some remarkable alteration. Treatment with double-acid leads to selective α-phase etching whereas alkali reagent results in selective β-phase corrosion. Moreover, long-time immersion increases the surface protuberances and the holes depth of β-phase in presence of strong Kroll and alkali treatment, respectively. It should be noted that although treated alloy with the single acid etchant produces lower V content; this sample does not show desired microstructure for biomedical application due to its ineffective morphology.

Furthermore, result shows that surface wettability of alkali treated samples via Piranha greatly improves rather than polished samples due to the uniform topography of sphere protuberance as well as lower roughness. Increasing of the immersion time up to 30 min leads to decreasing the surface wettability that is a desired result [11].

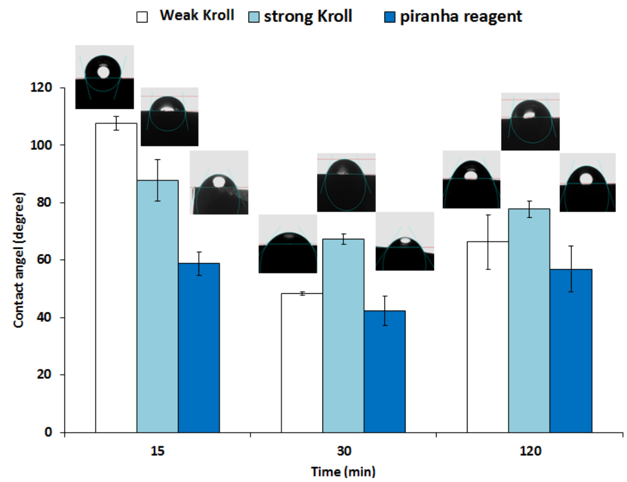

Fig. 7 Contact angel of pure water on modified Ti-6Al-4V alloy.

Acknowledgment

We would like to acknowledge funding from Iran National Science Foundation.

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