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The Influence of Two Different Acid Solutions on Surface Texturing of Alumina Sandblasted Novel Non-Toxic Biomaterial

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Abstract: Titanium alloys identified as excellent materials in biomedical applications. The biocompatibility greatly depends on properties and morphology of biomaterial surfaces. Surface modification and texturing are effective on osseo integrations and increase biocompatibility. In biomedical engineering, sand blasting and acid etching (SLA) process on titanium alloys surface performed to increase texturing of surface. It has to be noted that surface texture and roughness characterization are important in biomedical performances. In this research, vanadium free titanium alloy (Ti13Zr13Nb) has been studied in terms of surface texturing and roughness variation. Rod shape materials were cut using diamond wheel precision cutter and were polished by automatic machine in three stages. Sandblasting process was performed with alumina particles of 150 µm mean size by a laboratory shot-blasting machine, at 2.5MPa-pressure for 30 s at10 mm nozzle distance. Kroll's etchant (3ml HF+6ml HNO_3+100 ml H_2O) and Sulfuric acid (H_2SO_4 66%) solutions were used to etch substrates. Two etching conditions as low and high conditions were conducted for both solutions. Low condition would be defined as low time and temperature (10s, 25ºC) and also high condition is defined as high time and temperature (30s, 60ºC). Surface texture was evaluated by Field Emission Scanning Electron Microscope (FESEM) and the mean surface roughness Ra (nm) measured by a contact mode profilometer.Cut and polished surfaces exhibited the poor capacity to osseo integration and cell growth. The sand blasting process affected on Ti13Zr13Nb surfaces by creating peaks and valleys with sharp edges, texture form, active for corrosion and poor in biocompatibility. These surfaces significantly changed using Kroll's etchant solution in high condition to smooth surface. After SLA, at high condition of sulfuric acid and low condition of Kroll's etchant, observed fine textured surface including fine pits, less sharp edge and desirable morphology for cell proliferation and osseo integration. The surface roughness fluctuated significantly after cutting, polishing and sand blasting process. Both acid solutions caused a reduction in surface roughness. The Kroll's etchant at 30s, 60ºC caused Ra reduction significantly by 290 nm. This present research, demonstrates the importance of specific acid and condition selection in terms of surface texturing and roughness reduction. These reflections are important to achieve desire signal in terms of rapid osseo integration, biocompatibility and short therapeutic time.

Key words: Titanium alloys, Morphology, Sandblasting, Acid etching, Biocompatibility.

INTRODUCTION

High biocompatibility, corrosion resistance and mechanical properties cause titanium alloys use as excellent materials for implant in large extent. Ti6Al4V is one of the most popular titanium alloys that have been utilized for long time. But the toxic element, vanadium, affected body due to corrosion (Liu al., 2004). Alloying process was performed with new elements in order to increase implant durability and cytocompatibility. Zirconium and Niobium have been used for generating new titanium alloys as Ti-Zr-Nb(Davidson *et al*., 1994; Assis *et al*., 2005).

Biomedical industry utilized smooth surfaces texture resulted from machining process for almost fifty years. However, these smooth surfaces suffer from long healing time in biology performances (Palmquist *et al*., 2010). The importance of surface treatment has been illustrated to improve the biological, chemical and mechanical properties of titanium and its alloys used in bio-implants. Characterizing and texturing of the surface have been used in order to increase osseo integration and cell proliferation (Liu *et al*., 2010; Möller *et al*., 2012).

Surface treatment is crucial in terms of restoration, tissue re-formation and great biocompatible attributes of implants. Sandblasting with alumina abrasive particles is recently employing to produce complex texturing and roughening on titanium alloy surfaces. Surface roughness and morphology influences on modified implant in order to osseo integration (Le Guéhennec *et al*., 2007; Elias *et al*., 2008). Manufacturers use sequential sand blast and acid etch (SLA) procedure on titanium alloys surfaces in order to create textured surface. It has been reported that acidic components have ability to make chemical bonding with newly created bones (Buser *et al*., 2004). Moreover, type and concentration of acid are well-known as the main factors in determining rate of texturing on titanium surface. To improve biological applications, sulfuric acid and hydrofluoric acid combined

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with nitric acid have been recommended for treating implant surface. These treating processes are effective in terms of creation three-dimensional pores to promote cell growth (Ban *et al*., 2006; Lamolle *et al*., 2009).

In present work, common surface modification, SLA, has been precisely done using biocompatible alumina abrasive particles and two different acid solutions. Consequently, condition of solution was changed in terms of temperature and time. The obtained results were evaluated in two cases: First, Ti13Zr13Nb surface texturing in terms of capacity in biocompatibility and osseo integrations. Second, surface roughness changes by applying SLA process. In implant manufacturing, surface capacity, morphology and texturing are crucial, in determining short and long term healing time.

MATERIALS AND METHODS

Substrate Material Preparation:

Ti13Zr13Nb rods were cut with 10 mm diameter and 150 mm length. The Ti13Zr13Nb was cut using diamond wheel precision cutter to 10 mm in diameter and 2 mm thickness. In next step, the contaminant and dust were removed using steam cleaning. The burr free surface of the substrate was selected for treatment. Polishing of substrates was done automatically via machine (Strus-Tegimn-25) to obtain identical surface finish. Firstly, grinding was done using SiC paper 320µm grit size with 30 N force, 1 min, upper spindle speed 150 rpm and down spindle speed of 130 rpm. Secondly, diamond polishing was performed using 9µm grit size for 1min and 20 sec in the same condition. Thirdly, OP-S polishing paper with MD-Chem solution was used for 1min and 10 sec in the same condition.

Sand Blasting:

The blasting process was carried out before acid etching pretreatment. This process was used mainly to roughen the substrate surfaces. Polished substrates were shot blasted with Al_2O_3-particles of 150 µm mean size. This was done using laboratory shot-blasting machine at 2.5MPa-pressure at10 mm nozzle distance for 30 seconds in order to saturate particles at the substrate surface. After shot blasting, samples were ultrasonically cleaned for 15min in acetone via Brason ultrasonic bath machine (Model 2510 with 55kHz frequency agitation).

Acid Etching:

Kroll's etchant (3ml HF+6ml HNO_3+100 ml H_2O) and Sulfuric acid (H2SO4 66%) solutions were used to etch substrates. Two etching conditions as, low and high condition were conducted for both solutions: low condition: low time and temperature (10s, 25ºC) and high condition: high time and temperature (30s, 60 ºC). Etching process was performed at one atmosphere pressure. Heating of acid solution was done using ultrasonic heater with ±1 ºClearance. The substrate was cleaned and dried at each stage of treatment via high-pressure airflow.

Surface Morphology:

The Field Emission Scanning Electron Microscope (FESEM) was used for characterizing surface morphology of Ti13Zr13Nb substrates surface after treatments. This machine was able to take images with high resolution. Surface roughness parameter in each stage was measured in contact mode by profilometer (Mitutoyoformtracer CS-5000 , Japan). This equipment is used a large LCD touch-panel for simple operating. The mean roughness value (Ra) in nanometer unit was taken as a typical height indicator, which is measuring in biomedical implants.

Results:

Tool feed mark created lamellar structure with low texture surface by precision diamond cutter. Undesired cutting line was observed on the surface at 1000X magnification (figure 1-a). Surface roughness was measured on rough-cut-surface as Ra (nm) for each sample. The roughness of cut surfaces were in the range from 687 to 953(Table 1). Polishing process caused high smooth surface. Surface become tool feed marks free even at high magnification of 3000X (figure 1-b). Polishing process in three states with mentioned adjustments exhibited excellent smooth surface. Surface roughness on polished surface showed significant reduction from cut surface. The roughness of polished surfaces were in the range from 42 to 55 nm (Table 1). It can be seen in figure 1-c that the surface was highly textured with large alumina particles in sand blasting process. Numerous valley and peak created on the surface. Peak region was identified with lighter color and valley with darker region based on preliminary evaluation of FE-SEM. In this experiment, sand blasting process presented high significant effect on the roughness increasing. The roughness of sand blasted surfaces were in the range from 620 to 759 nm (Table 1).

For SLA in extreme low condition, the surface texture was observed to be less with using sulfuric acid solution (figure 1-d), but surface roughness, Ra, reduced by 12 nm. Extreme high condition showed slight reduction in surface roughness and texturing on the surface (figure 1-e). In extremely high condition, the surface texture was observed to be affected explicitly using Kroll's etchant solution. Surface roughness reduced significantly by 290 nm (see figure 1-g and Table 1). In contrary, in extreme low condition, neither the surface texture nor roughness reduction were significant (see figure 1-f and Table 1).

In general, Kroll's etchant was more effective than sulfuric acid in terms of surface texturing and roughness reduction, at same condition. At 25 ºC in texturing surfaces, there was not observed significant discrepancy using both acid solutions in same etching time. Using Kroll's etchant, substrate's surfaces were influenced obviously changing from 25 ºC to 60 ºC. The temperature Changes from 25 ºC to 60 ºC of sulfuric acid solution displayed no significant effect on substrate's surfaces (see figure 1).

Discussion:

The surface texturing of biomaterials was studied after cutting, polishing, sandblasting and acid etching using two unlike solutions, with different conditions. Morphology and surface roughness are vital to achieve proper biological retort and cell proliferations (Donoso *et al*., 2007). It should be noted, the contact between implant and bone border is crucial to have short healing time in osseous implant. Surface texturing plays the most important role in implant bone response (Shalabi *et al*., 2006). In the implant manufacturing, the identification of biological sign is essential in titanium alloys surfaces.

The deformed surface caused by heating, observed on cut Ti13Zr13Nb surface, due to exist hard Zr and Nb alloyed elements. It will result to a slow osseous implant therapeutic. Polish surface without any texturing sign and low roughness value is not able to create high rate of cell proliferation. The polishing process displayed fine surface preparation prior to roughening process. The rough surface in biomaterials will lead to immobile osteoblast cells. This high rough surface was achieved via large alumina particles. However, this surface suffers from sharp edges, deep valley, large valley width and directional edges (figure 1-c). These imperfections influence on osseo's integration value and its direction (Elias *et al*., 2008).

In spite of the fact that the topography of implant surfaces is not the lone factor on biological reaction, the cell's adhesion and adsorption are influenced by surface roughness. It was report that in clinical performances, which were carried out in vivo test, using the roughen surface for more contact between bone and implant (Shalabi *et al*., 2006; Novaes *et al*., 2010). Ra is the arithmetic average value, which is utilizing to explain as well as possible in term of height variations. In this study, this value exhibited a reduction via both solutions, as the result of influencing acid on alumina bombarded Ti13Zr13Nb surfaces. Kroll's etchant solution had significant effect on the reducing roughness value. This reduction is because of the effect of hydrofluoric and nitric acid on the alumina blasted surface. It increased by increasing the exposure temperature and time. Sulfuric acid solution has influenced less than Kroll's etchant due to its nature in the exposing with sand blasted titanium surface and capacity to change textured titanium alloy. This result from high concentrated sulfuric acid can confirm the result of Ban who reported, the rough titanium implant surface via sulfuric acid etching process (Ban *et al*., 2006). Remarkably, its effect reduced by increasing temperature and time in contrary with Kroll's etchant. It can be illustrated by this study that hydrofluoric and nitric acids (which are useful in texturing of implants surface) are most effective on surface roughness value altering. This modifying should investigate as much as possible due to importance of the roughness value in term of biomaterials performance, which mentioned in above.

The novel biomaterials texturing showed a sensitive factor in terms of SLA treatment in different solutions and conditions. Sulfuric acid has textured the sand blasted surface slightly in both high and low condition. This partial effect on surface was as well as the surface roughness changing. The Kroll's etchant changed significantly in high extreme condition of SLA process. It showed almost similar surface morphology at low temperature and time condition to sulfuric etched surface. It can be declared, the sulfuric acid is capable to texture alumina blasted of Ti13Zr13Nb surface as same as low exposure condition of hydrofluoric and nitric acid solution.

SLA of titanium alloys surfaces has proper biocompatibility. In this research, SLA surface was created by applying different conditions. The micro pits creation using sulfuric acid solution in low condition did not show significant changes from sandblasted surface. While, sulfuric acid in high and Kroll's etchant in low condition exhibited the fine micro pit desire for osseo integration and cell proliferation. Considerably, in these cases were observed a reduction in sharpness, deep valley and width of valley (figure 1-e and 1-f). They lead to have high trend to biocompatibility, cell adhesion, great osseo integration and short time osseous implant therapy. The Kroll's etchant significantly attacked on the surface in high condition and it caused the smooth surface creation. It suffers from rapid osseo integration and short remedial time in titanium implants.

Conclusion:

The surface texturing of novel biomaterials (Ti13Zr13Nb) was investigated using different condition. These results can be concluded from this research: 1- The surface roughness showed a reduction in Ra value after SLA process using both sulfuric and Kroll's etchant acids. 2- The Kroll's etchant caused significant reduction in surface roughness and led to smooth surface in high etching condition. 3- The cut, polish and alumina sand blasted surfaces displayed some imperfections in term of biocompatibility. 4-high condition for sulfuric acid and low condition for Kroll's etchant exhibited desire signal for rapid osseo integration, biocompatibility and short healing time. However, further researches with vivo tests are essential to ensure the biological response of this new generation of biomaterials.

Table 1: Surface roughness Ra (nm) values after cut (a.c), after polish (a.p), after sand blasting (a.s.b), after sulfuric acid eching (a.s.a.e), roughness reduction (r.r), after Kroll's etchant etching (a.K.e.e).

Condition	a.c Ra (nm)	a.p Ra (nm)	a.s.b Ra (nm)	a.s.a.e Ra (nm)	r.r (nm)	a.c Ra (nm)	a.p Ra (nm)	a.s.b Ra (nm)	a.K.e.e Ra (nm)	r.r (nm)
Extreme low: 25 ºC and 10 s	687	42	759	747	12	784	45	686	630	56
Extreme high: 60 ºC and 30 s	735	55	723	719	4	953	55	620	330	290

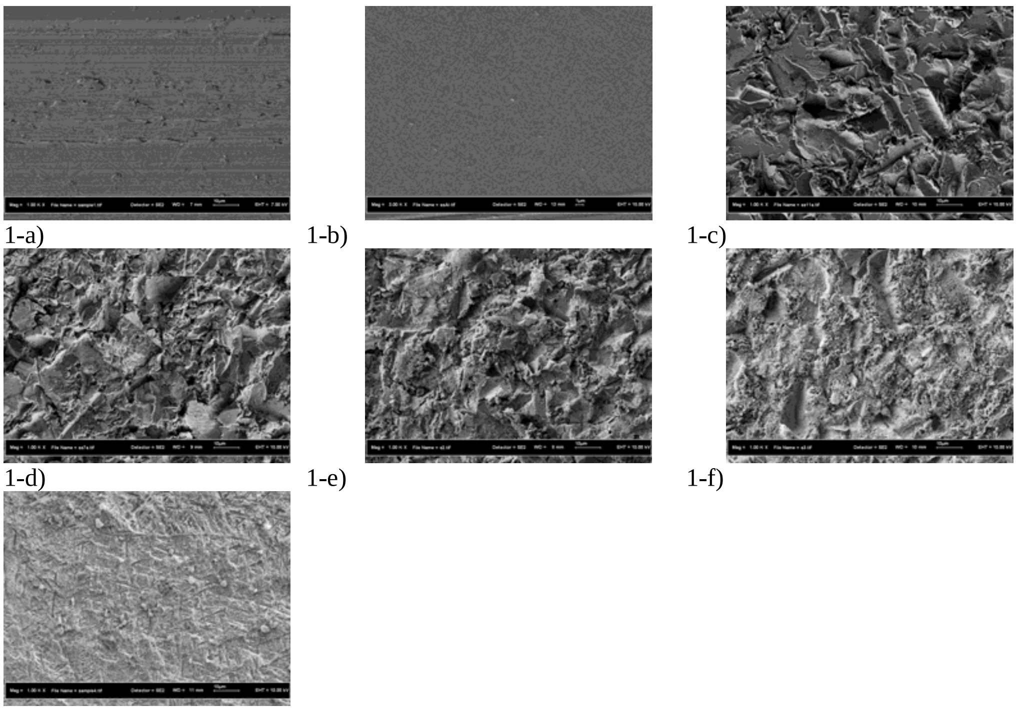

Fig. 1: Morphology of Ti13Zr13Nb surfaces after a) cut, b) polish, c) sandblast, d) SLA using sulfuric acid at low condition, e) SLA using sulfuric acid at high condition, f) SLA using Kroll's etchant acid at low condition, g) SLA using Kroll's etchant acid at high condition

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