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FE-SEM and EDX Characterization of Sand Blasted and Sulfuric Acid Etched of Novel Biomaterial (Ti13Nb13Zr)

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Abstract: Titanium and its alloys areutilized as superior biocompatible materials in recent decades. Surface treatment is crucial in terms of osseo integrations, tissue re-formation and great biocompatible attributes of implants. Manufacturer uses sequential sand blast and acid etch (SLA) procedure on titanium alloys surfaces in order to create great biocompatible and textured surface. Evaluation surface morphology after surface modifications have been said is vital in biomedical performances. In this research, novel titanium alloy (Ti13Zr13Nb) has been studied by means of Field Emission Scanning Electron Microscope (FESEM) and Energy dispersive X-ray (EDX). Surface treatment was carried out from cutting using diamond-coated wheel cutter, polishing by automatic machine in 3 steps, sandblasted 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, and followed in etching process using 66 % sulfuric acid solution at 25ºc for 20 s. Surface morphology, element concentration and distribution were investigated after sandblasting and acid etching. Interpreting the data reveals that the capacity of novel biomaterial surface in term of biocompatibility and osseo integration of SLA treated surface was improved. Cut surface showed the surface with tendency to unidirectional cell growth. Poor capacity to osseo integration was observed on polished surface. The alumina sand blasting process changed Ti13Zr13Nb surface with large number of peak and valleys with sharp edges, active for corrosion and poor in biocompatibility. Fine pits, less sharp edge and morphology desirable for cell proliferation was observed in SLA surface.Sulfuric acid was more effective in terms of maintaining the amount of embedded Al2O3 particles, which is worthy for osseointegration. Remarkably, concentration and distribution of the alumina weresignificantly affected by sulfuric acid etching. In addition, it has been illustrated that other elements of the material (Ti, Zr, Nb) were affected by sulfuric acid solution in form of homogeneous elements distribution. In present research, the importance of specific acid selection and the sequence of processhave shown. This performance played the main role in preparation of the textured and biocompatible novel titanium implant.

Key words: Titanium alloys, Alumina sandblasting, Sulfuric acid etching, Morphology, Biocompatibility.

INTRODUCTION

The Field Emission Scanning Electron Microscope (FESEM) is a microscope using electron scanned beam in raster mode. This equipment used as a replacement for SEM because of the need to achieve detailed images of implant surfaces(Suzuki, 2002; Brabazon and Raffer, 2010). Energy dispersive X-ray (EDX) used an analytical model depending on the X-ray excitation of samples for characterizing peaks of X-ray spectrum based on atomic structure(Lausmaa et al., 1990).

Biotic response of implant devices is highly dependent on surface. The composition of the biomaterial can be fully different from surface(Lacefield, 1999; Oshida, 2007). It has illustrated that surface treatment is vital for improving the biological, chemical and mechanical properties of titanium and its alloys used in biomaterials(Liu et al., 2004). Zirconium and Niobium has been used for generating new titanium alloys as in Ti-Zr-Nb for increasing in its biocompatibilities and bio-applications(López et al., 2001; Geetha et al., 2009).

Sandblasting with alumina abrasive particles are proposed for producing complex reaction on substrate surfaces, to make changes in the composition and morphology of the metal surface with new element at the substrate surfaces(Oshida, 2007; Son and Choe, 2011). Osseo integration of modified biomaterials is crucial in terms of restoration, tissue re-formation and great biocompatible attributes of implants. Osteoblast adhesion is the main reason to create bone on the implant surfaces(Le Guéhennec et al., 2007). Manufacturer uses sequential sand blast and acid etch procedure on titanium substrate surfaces for creating rougher surface due to the aid of strong Osseo integration(Le Guéhennec et al., 2007). In addition, it has been reported that acidic components have the ability to make chemical bonding with newly created bones(Lamolle et al., 2009). Furthermore, type and concentration of acid are the main factors in determining rate of etching on titanium. To improve biological applications, sulfuric acid treated biomaterials surface is effective in term of creation three-dimensional pores to promote cell growth(Martin et al., 1995; Ban et al., 2006).

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In present work common surface modification (sand blasting and acid etching) have been done using biocompatible Alumina abrasive particles and sulfuric acid solution for two purpose: First, evaluating the surface morphology in terms of surface capacity of biocompatibility and osseo integration on novel Ti13Zr13Nb material. Second, this is the first time EDX analysis has been used after SLA process on Ti13Zr13Nb alloy in term to characterize elements distribution and their percentages on the surface. Surface capacity and topography are crucial, in determining short and long term healing time in biomedical engineering.

MATERIAL AND METHODS

Substrate Material Preparation:

The substrate used in this research was Ti13Zr13Nb in the shape of rod with 10 mm diameter and 150 mm length. In the initial stage of preparation, the Ti13Zr13Nb was cut by using diamond wheel precision cutter to 10 mm in diameter and 2 mm thickness. The contaminant and dust were removed using steam cleaning, in next step. The burr free surface of the substrate was selected for treatment. The specimens were cured by cold mounting so it can be manipulated easier for succeeding steps. 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 of130 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:

Sulfuric acid (H2SO4 66%) was used to etch substrates at temperature 25ºC, etching time 20 second and 1 atmosphere pressure. Heating of acid solution was done via ultrasonic heater with ±1 ºClearance. The substrate was cleaned and dried at each stage of treatment via high-pressure airflow.

Surface Characterization:

The Field Emission Scanning Electron Microscope (FESEM) was used for characterizing surface morphology of Ti13Zr13Nb substrates surface after treatment. This machine was able to take images with high resolution. Chemical composition of the alloys were measured with the aid of an EDX micro-analyzer, which was assembled to FESEM. The distribution of bombarded particles was detected via EDX map in different color.

Results:

The irregular tool feed marks were created using precision diamond cutter. The small pits, lamellar structure and textured surface was observed, as a result of friction between cutting tool and substrate surface. The surface morphology of cut surface at 3000X magnification is shown in figure 1-a with numerous undesired cutting line from cutter. After polishing surface morphology of substrate became smooth. Even at higher magnification of 3000 X, no feed marks were formed on the polished substrates in terms of time and force that cause noticeable change in morphology of substrate from the cut surface (see figure 1-b). Deep valleys and peaks were observed on the surface via sand blasting process with large particle. It can be seen in figure 1-c, the sand blasting process deformed polished surface entirely and caused extreme rough surface. Peak with lighter color, and pit with darker region was identified base on initial evaluation of FE-SEM. Large width for pits (almost 8-13µm) were observed on the sandblasted surface. These three dimensional peaks and pits formed textured surface from sand blasting procedure even in micro scale. Subsequent process as sulfuric acid etching created significantly high wavy surface and even changes the size of peaks and pits width to less than 3 µm. Sulfuric acid is corrosive, it could control abruptness in the micron via controlling the number and size of tiny holes (see figure 1-d).

Chemical composition of Ti13Zr13Nb biomaterial was evaluated on atomic percentage and weight percentage via EDX. The percentage of oxygen, aluminum, titanium zirconium and Niobium was involved 21.27, 8.08, 47.86, 8.46, 14.33 wt.%, respectively on a sandblasted surface. The EDX map characterization has shown that alumina distribution was not homogeneous on the surface in comparison with other elements (see figure 2). Surprisingly, the EDX data after sulfuric acid etching has shown extensive contrast with non-etched surface. It was observed that oxygen, aluminum and niobium concentration changed greatly from 21.27, 8.08, 14.33 to 43.26, 17.60, 22 wt.%, respectively. Remarkably, the distribution of the oxygen and aluminum on the surface significantly changed to homogeneous form. Titanium and zirconium percentage has shown a reduction in wt. %, specifically for titanium. The surface has homogenized in elements distribution because of sulfuric acid attacks on the alumina particles (see figure 3).

Discussion:

Low electrical charge and low kinetic energy electron enable FESEM take images in higher resolution in comparison with SEM. The morphology and element composition was investigated in four stages: cutting, polishing, sandblasting and SLA on the treated surface in order to distinguish biological signal proper for cell proliferation. This signal recognition is necessary to characterize proper condition for bone formation. The surface morphology has important role particularly in adhesion of osteoblast. The feature of interaction between biomaterial surface and cell will determine capacity of cell attachment and spreading(Donoso et al., 2007). To enhance this ability acid etching after alumina sandblasting is utilized to increase osseo integration in implant manufacturing.

Zirconium and niobium elements in Ti13Zr13Nb produced tougher alloy in comparison to other titanium alloys, this effect was distinguished by tool feed marks on the surface of substrate in form of heat-deformed surface. These elements cause a resistance to cutting in titanium as lamellar structure and small pits from tool friction on the surface. This surface with heterogeneous morphology will cause a reduction in osseo integration and cell proliferation. On this surface, there exist trend to unidirectional cell growth since cells have inclination to follow this heterogeneous orientation, which cause delay in healing time(Elias et al., 2008).

Surface morphology of polished surface have shown great smooth surface without pits, grooves and deformity from cut surface. Osteoblast cells trend to be secured in rough surface in titanium bio implants. Implant manufacturer are removing polished surfaces and cut surfaces from bio-markets which lack surface treatment, because of inferior biomedical performance of these kind of implants.

The modified morphology of biomaterial will change the capacity of osseo integration on surface via surface roughness, energy and wettability. Some texturing treatment methods such as plasma spraying and hydroxyapatite coating suffer from late osseo integration(Buser et al., 2004). However, sand blasting and acid etching have more tendencies to bone contact with implant. To produce fine surface morphology, sand blasting with large particle was done to create rough surface then followed by acid etching process to form textured surface due to better implant interface surface for bone. Sulfuric acid solution cause slightly different surface with complex and undamaged form, involving fine pits in micro size. The sharp edge was eliminated and depth of holes was reduced because of sulfuric acid attack on bombarded titanium alloy surface. The texturing of the Ti13Zr13Nb alloy developed after etching process (see figure 1-d).

The above-mentioned surface has voids edges and isotropic morphology, observed on SLA treated surface in comparison with cut and polished surface. These edges create desired condition for cell integration on the implant surfaces. These kind of morphology (SLA morphology) formed on the novel Ti13Zr13Nb will cause fibrin retention and development in osseo integration as stated by manufacturer(Elias et al., 2008). Cell growth and proliferation will be high on Ti13Zr13Nb because of fluctuated morphology including micro pits, coarse surface, negative biased surface and positive obliqueness(Rosales-Leal et al., 2010)(see figure 1-d).

Weight ratio was used for calculating alumina as wt. %. Retention of Al_2O_3 fragment can be quantified based on the percentage of alumina, which covered the surface(Al Jabbari et al., 2012). Alumina, which covered the surface on Ti13Zr13Nb biomaterial surface observed large amount of Al_2O_3 with 8.08 wt. %. This amount of involvement illustrated the embedding of fractured alumina on Ti13Zr13Nb surface, using proper alumina mean grit size and airflow pressure (see figure 2).

Sulfuric acid solution affected elements (Ti, Zr, Nb) composition on the surface in order to homogenize element distribution which is illustrated in figure 3. Meanwhile, surface characterization base on surface roughness, fractal study and investigational wettability examination is extremely advised for future research on Ti13Zr13Nb alloy.

Conclusions:

The surface of novel biomaterial (Ti13Zr13Nb) is characterized in four stages: 1-Cut, 1-Polished, 3-Sand blasted, 4-SLA. Cut surface showed the surface with tendency to unidirectional cell growth. Poor capacity to osseo integration was observed on polished surface. The alumina sand blasting process changed Ti13Zr13Nb surface with large number of peak and valleys with sharp edges, active for corrosion and poor in biocompatibility. Fine pits, less sharp edge and morphology desirable for cell proliferation was observed in sulfuric acid etched surface. Surprisingly, alumina concentration and distribution significantly increased. Ti, Zr, Nb percentages and their distribution were affected by sulfuric acid, creating homogeneous form. In this research biocompatibility and textured surface rise on SLA treated novel biomaterial was observed, although high number of research is necessary to authenticate biological response of this novel biomaterial.

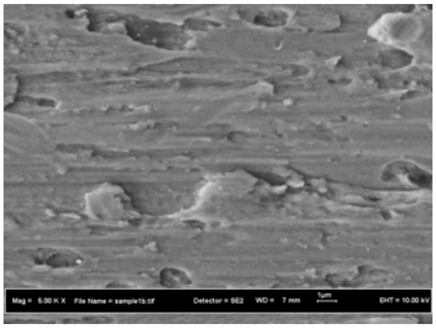


Fig. 1-a)

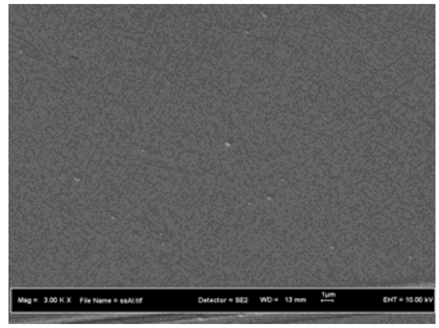


Fig. 1-b)

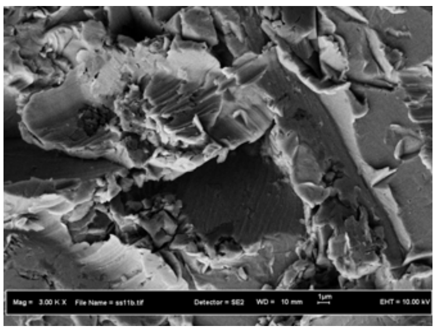


Fig. 1-c)

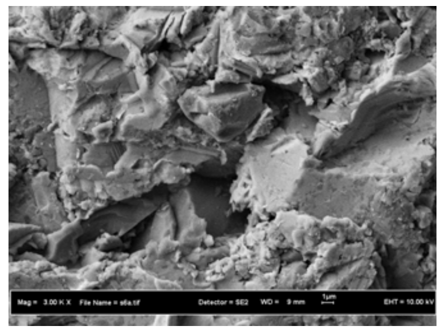
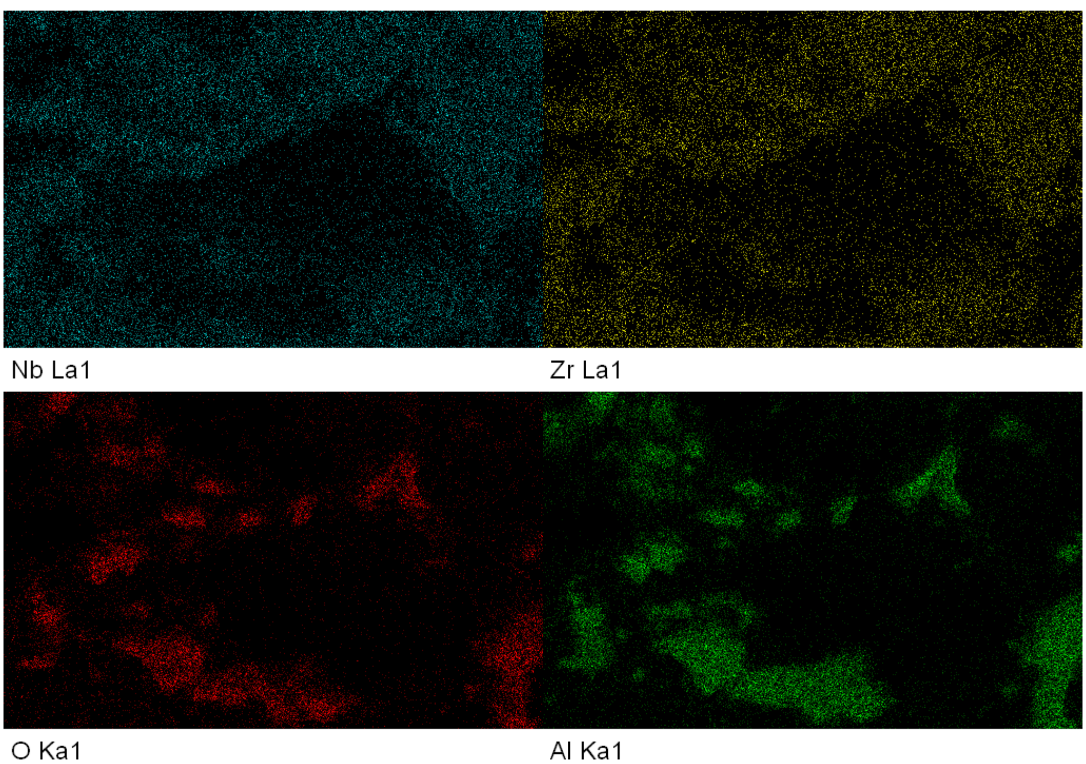
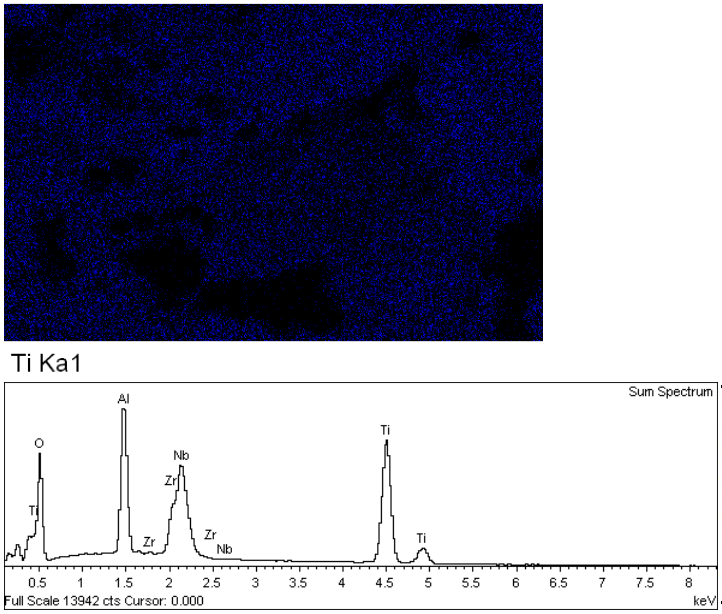


Fig. 1-d)

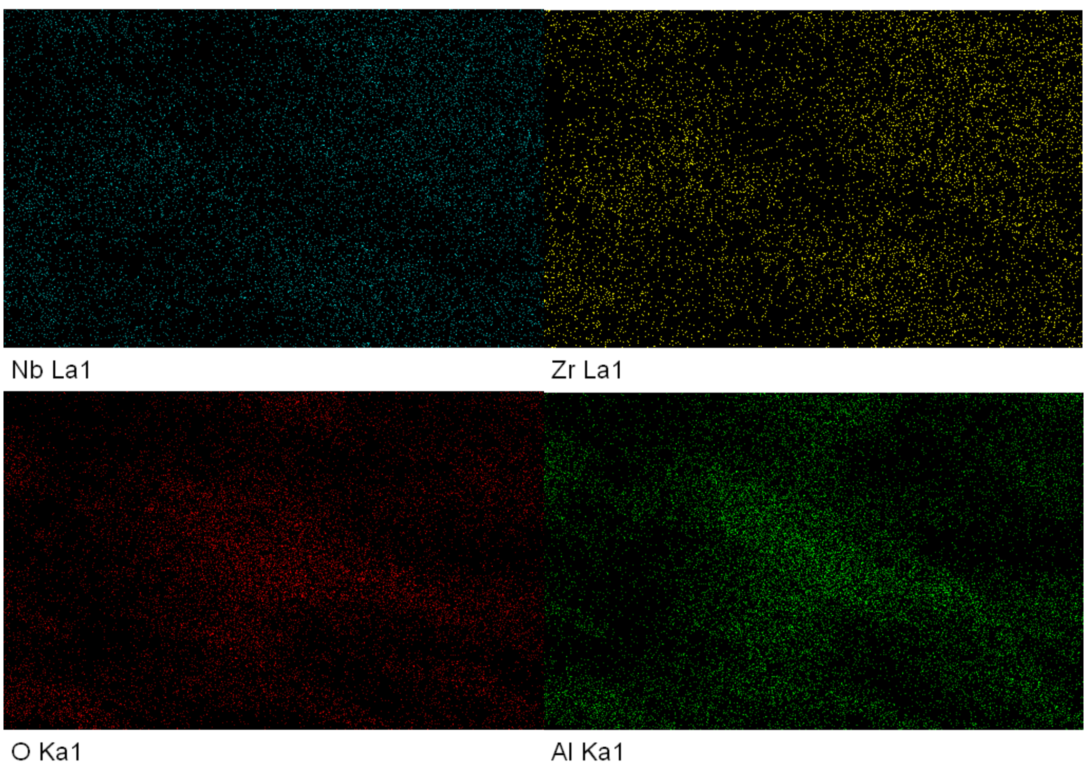
Fig. 1: FE-SEM images of a) Cut, b) Polish, c) Sandblasted, d) Alumina sandblasted and sulfuric acid etched surfaces.

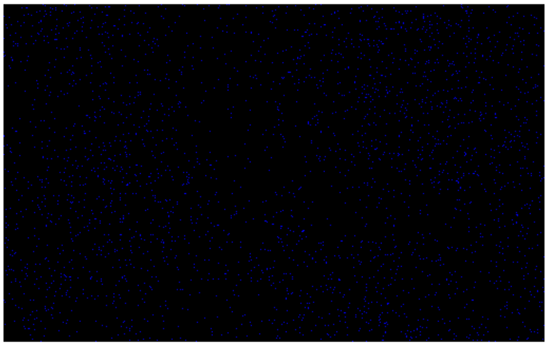




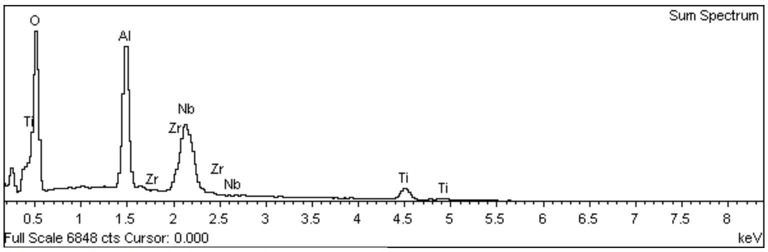
Element	Weight%	Atomic%
O K	21.27	46.24
Al K	8.08	10.41
Ti K	47.86	34.75
Zr L	8.46	3.23
Nb L	14.33	5.37
Totals	100.00	

Fig. 2: EDX map and composition percentages analysis of sand blasted Ti13Zr13Nb.





Ti Ka1



Element	Weight%	Atomic%
O K	43.26	69.65
Al K	17.60	16.80
Ti K	10.19	5.48
Zr L	6.94	1.96
Nb L	22.00	6.10
Totals	100.00	

Fig. 3: EDX map and composition percentages analysis of sand blasted and sulfuric acid etched Ti13Zr13Nb.

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