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Evaluation of Corrosion Rate and Surface Oxides Formed of Zr-2.5%Nb as an Implant Material in Ringer's Solution

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Abstract

Background/Objectives: Corrosion causes complications such as toxicity and inflammation by making changes in metals, fracture, relaxation and loss of implant strength. In biomaterial science, we try to select and combine materials to construct and design the implants that have less corrosion and consequently reduce complications as much as possible. **Methods/Statistical analysis:** In this study, Zirconium-2.5 Niobium alloy was heat-treated to remove its residual stress after rolling operations. Surface oxides were diagnosed by XPS analysis on the desired alloy which had been kept for two years in Ringer's solution. To measure the corrosion rate parameter on the desired sample, corrosion test was conducted using a three-electrode cell method. **Findings:** Surface oxides Nb_2O_5 and ZrO_2 were diagnosed by XPS analysis. The results showed that the corrosion rate in this alloy was less than the usual corrosion rate of Titanium implant and its alloys. **Application/Improvements:** Biocompatible oxides alongside high in vitro corrosion make Zr-2.5Nb alloy as favorable surgical implants.

Keywords: Corrosion rate, Implant material, Ringer's solution, Surface oxides, Zr-2.5%Nb

1. Introduction

Metals and alloys should be almost inert for the sake of using them as biomaterials in orthopedics and dentistry applications. Because of their physical-chemical properties and compatibility with biological surroundings, these inertmetallic biomaterials are being to a great extent used[1]. Owing to the surrounding medium when electrochemical attacks, a metal will lose its quality and consequently corrosion occurs[2]. Implant materials or their surface oxide may be corroded or worn, which causes the creation of erosion particles, thereby causing local and systemic biological responses[3]. Zr and Nb are known as valve metals on which an oxide layer is formed at room temperature, that is a protector between the metal and the surrounding environment, an electrical insulation and resistant against acids, bases and inorganic materials[4]. Due to Zirconium oxidation, the created oxide layer deactivates the lower level. By injecting ZrO_2 into the body of mouse and investigating the internal organs, researchers have concluded that these particles do not cause any adhesion and scar in the internal organs[5]. In terms of mechanical properties, Zirconium alloy has a modulus of elasticity close to the bone, is very stable and resistant to cracking and causes self-healing of its surface imperfections[6]. Moreover, Zirconium has been more considered than titanium in bone fixation devices, because it has less identification with bone and has reduced further surgery. On the other hand, Titanium has a poor shear strength and is more susceptible to pitting corrosion than Zirconium[7]. While combined with Zirconium, Niobium improves the mechanical properties of zirconium effectively[8]. It is a shiny, soft and flexible metal, has low yield strength and is accordingly well-shaped. Samples of Niobium- Zirconium alloy weighing 2 grams and containing 2.5, 5 and 10 wt% Niobium in 0.5 M sulfuric acid solution at 37 °C were compared with pure Zirconium, and the corrosion potential versus time diagram showed that by increasing the percentage of Niobium alloy, the corrosion resistance of the alloy

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increased[9]. Zirconium -2.5 Niobium alloy has an elongation of 22%[10], while the popular Ti-6Al-7Nb alloy has an elongation of 8-15%[11], hence, this factor makes this alloy important for formation of implants. Corrosion is one of the biochemical factors whose behavior has been improved by using engineering technologies such as suitable coatings, thermomechanical operations and desired heat operations to remove residual stresses. Residual stresses created in various stages of construction and operation increase stress level in the parts during labor and make them more sensitive to cracks, which can be destructive and have adverse effects on performance of the parts; therefore, stress relief operations are recommended to be performed on the parts. The correct stress operations minimize the possibility of development of defect and increase the dimensional stability and corrosion resistance, especially stress cracking.

Therefore, in this study, according to the aforementioned valuable properties and characteristics which provide basic needs for an implantable material, surface oxidation agents that play an important role in protecting the substrate have been specified. Moreover, since corrosion rate reflects the strength of implant, we have examined this factor and compared it with Titanium and its alloys used widely today.

2. Materials and Methods

Delivery bars of Zirconium-2.5 Niobium alloy from Isfahan UCF complex underwent stress relief process to remove their residual stress. This stage included the heating operation in a furnace with a maximum temperature of 1200° C conducted for 2 h with 10° C/min velocity. Then, the furnace was turned off and samples were cooled under the cooling condition of furnace. Using a rolling mill machine (Cavallin -M120, OttoFrei Co,USA), the samples were placed under cold rolling operations under the force of 55 kN. To remove the applied stresses, thermal stress relief operations were applied on the samples again. This process involved heating the samples for 15 min at 1000°. To determine the type of surface oxides on Zirconium-2.5 Niobium alloy, X-Ray Photoelectron Spectroscopy (XPS) test was used. To this end, some of the disc-shaped specimens were placed in closed plastic containers in Ringer's solution for 2 years. The device used to perform the analysis was Bistec, made in Germany.

To evaluate the corrosion test and to obtain the polarization curve, the potentiostat device (PARSTAT 2273 Ame.Tek, Inc, USA) was used to plot the graphs. A three-electrode cell, with Kalomel electrode as the reference electrode, Platinum electrode as a neutral electrode, Zr-2.5Nb electrode as working electrode with an area of 6.0 square centimeters and an electrolyte, was used to prepare the Ringer's solution. Polarization test was performed at 37° C.

3. Results

According to the results of XPS test, the peaks of basic Zirconium element and oxides forming the surface of Zirconium -2.5 Niobium alloy, immersed in Ringer's solution for 2 years, were determined (Figures 1. and 2).

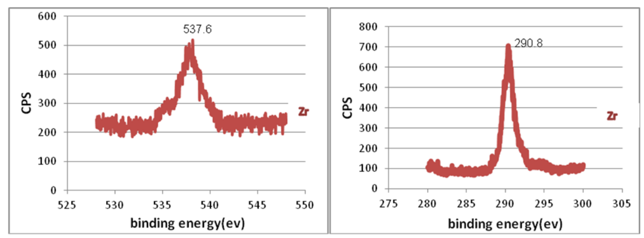

Figure 1. The magnified two achieved main peaks of Zirconium element in XPS analysis in the range of 550 eV-275 eV.

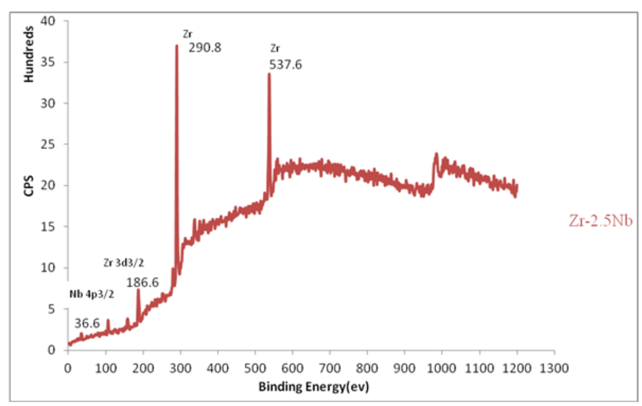

Figure 2. The oxides forming the surface of Zirconium -2.5 Niobium alloy immersed in Ringer's solution for 2 years.

The peaks of 290.8 and 537.6 eV were associated with the Zirconium base metal in this alloy, because they were seen in both XPS spectra associated with Zr-2.5Nb alloy and XPS spectra of pure zirconium metal (Figure 1). XPS spectra have been investigated according to NIST (National Institute of Standards and Technology) standards. The binding energy 36.6 eV is associated with energy level Nb4p3/2 which has led to Nb_2O_5, compound and binding energy 36.6 eV is associated with energy level Zr3d3/2 which has created ZrO_2 compound.

Polarization curve of Zr-2.5Nb in Ringer's solution is plotted in Figure 3. In polarization curve, there is a zincoid area in anodic polarization part that indicates the formation of a stable film on the surface. An important factor in corrosion is corrosion rate, which is provided in Table 1 with respect to the corrosion potential parameter (Ecorr) and corrosion current parameter (Icorr).

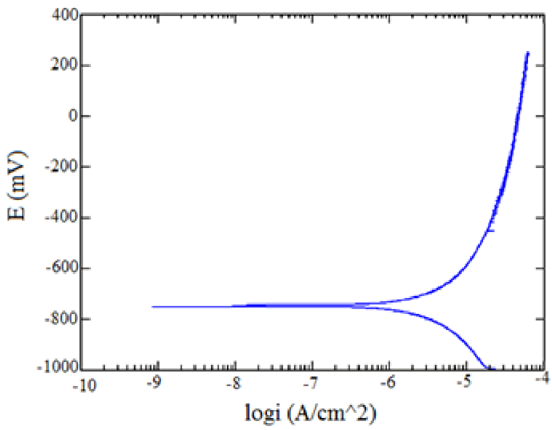

Figure 3. Polarization curve of Zr-2.5Nb in Ringer's solution.

Table 1. Biological corrosion parameters of Zirconium -2.5 Niobium alloy

Material	Ecorr(mv)	Icorr (µA/cm2)	Corrosion Rate(mm/yr)
Zr-2.5Nb	-749.1	5.25	5.9×10^{-3}

The corrosion rate for the desired alloy after 2 years (17,520 hours) of immersion in Ringer's solution in accordance with the following formula was reported to be 5.9×10^{-3} mm/yr.

$CR = 3.27 \times 10^{-3} \times i\ corr \times Ew/A \times d$ (mm/ yr)

i (µA): Current density, Ew (g): Highest equivalent, A (m^2): Cross-section used in the cell, d(g/cm^3): Alloy density.

4. Discussion

The main reason for the instability of the parts is residual stresses over the time. Also, residual stresses decrease the load-bearing of parts and reduce fatigue life. These stresses are like excess forces on the piece and in many cases cause the demolition of structures. Next, the samples were immersed in Ringer's solution for two years, and XPS analysis was carried out afterward to investigate their forming surface oxides. According to the results of XPS, Zirconium oxide and Niobium oxide were formed on the surface of the alloy. Zirconium oxide is a bioinert ceramic and is not considered as a threat to the surrounding tissue. Also, the amount of bone formed adjacent to the implant made of ZrO_2 has been reported to be 68% and has the esteoconductive property[12]. Niobium oxide is also very stable and resistant to corrosion. The researchers showed that Niobium oxide coating on Titanium implants increased the implant connection rate[13]. The biocompatibility of Zirconium-2.5 wt% Niobium alloy exposed to bone cells[3] suggests that surface oxides (ZrO_2 and Nb_2O_5) are biocompatible with the adjacent tissue. Comparing the corrosion potential of Zirconium-2.5 wt% Niobium alloy in Ringer's solution at 25 and 37° C with pure Zirconium sample, the researchers showed that the corrosion potential of Zirconium-2.5 wt% Niobium alloy was higher than Zirconium[14]. Table 2 presents a comparison of corrosion rate of Zirconium -2.5 Niobium alloy with Titanium and the popular alloy Ti-6Al-4V in Ringer's solution at pH=7. Zr-2.5Nb has shown lower corrosion rate in comparison with Ti and Ti-6Al-4V. Lower corrosion rate of Zr-2.5Nb may be associated with its passive film because Zr^{4+} in ZrO_2 is chemically more stable than Ti^{4+} in TiO_2[15].

Table 2. Corrosion rate of Zirconium -2.5 Niobium alloy, Titanium and the popular alloy Ti-6Al-4V in Ringer's solution at pH=7(15)

Material	Time(h)	Corrosion Rate (mm/yr)
Zr-2.5 Nb	17520	5.9×10^{-3}
Ti[16]	12000	$6.51\text{x}10^{-3}$
Ti-6Al-4V[16]	12000	6.48×10^{-3}

5. Conclusion

To put everything in nutshell, with regard to the preceding paragraphs it can be stated that:

- Rolling Zirconium-2.5 wt% Niobium sample was done by rollers, and then heat treatment was performed to reduce residual stresses.
- According to results of XPS, Zirconium oxide and Niobium oxide have been formed on the surface of the alloy and they were biocompatible and non-toxic. This is an important factor for longstanding implants.

- Zr-2.5Nb has higher corrosion resistance than Titanium in the longer time which makes this alloy more prominent in comparison with Titanium in implants application.

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