In vitro Study of Biomimetic Apatite Behavior on Titanium Alloy Implants

Abdulsalam Khashan Swadi **Thair Latif Al-Zubaidi** **Ismaeel Khalil Hasan**
Ministry of Science and Technology,Materials Research Directorate
Baghdad-Iraq

Abstract

This study show the corrosion behavior obtained from potentiodynamic polarization measurements for type of Ti-13Nb-13Zr specimens which has been heat treated with (solution treatment & ageing STA at 950°C and air cooled) in comparison with other specimens deals with same heat treatment but different cooling rates.

The EDXA spectra showed compounds containing phosphor and calcium to precipitate on substrate alloy surface, this state may be belonged to the mechanism of the positively charged Ca^{2+} which may act as nucleation site for the formation of hydroxyapatite by attaching with the negatively charged $(PO_4)^{3-}$ to form Ca-P enriched surface layer which crystallizes to form bone-like apatite.

Key words: Titaniun alloys , Biomimetic processes and Ceramics

دراسة مختبرية حول امكانية ترسيب مركب الابتايت على سطح سبيكة التيتانيوم المستخدمة في التطبيقات البايلوجية

عبدالسلام خشان سوادي **ثائر لطيف الزبيدي** **اسماعيل خليل حسن**
وزارة العلوم والتكنولوجيا – دائرة بحوث المواد
بغداد – العراق

الخلاصة

هذه الدراسة تتعامل مع سلوك التاكل للسبيكة (تيتانيوم– 13نيوبيوم– 13زركونيوم) المعاملة حراريا بدرجة 950 م° وبثلاث اوساط تبريد مختلفة باستخدام تقنية الاستقطاب الديناميكي فقد تبين بان سلوك السبيكة في تلك الدرجة الحرارية وفي حالة التبريد بالهواء (STA) اظهرت نتائج فعالة ومتميزة بالمقارنة مع العينات الاخرى ولكن باوساط تبريد مختلفة.

اظهرت فحوصات تشتيت الطاقة لفلورة الاشعة السينية قابلية السبيكة في تلك الحالة (STA) لترسب عنصري الكالسيوم والفوسفور على سطحها وهذا يعود الى ميكانيكية التفاعل التي تبديها ايونات الكلسيوم الموجبة والتي تعمل كنواة لاجل تكوين مايشبه مركب الهيدروكسي ابتايت وذلك من خلال التماس مع الفسفور ذو الشحنة السالبة مما يكسبها طبقة تحمي السبيكة من التاكل وتزيد من التوافقية البيولوجية وهي نفس الفعالية التي تبديها العظام في الجسم

الكلمات المفتاحية :سبيكة تيتانيوم و السيراميك

Introduction

Human bone is a composite material made up of collagen and calcium phosphate mineral. The mineral phase of bone comprises 60–70% of total dry bone weight. Bone mineral is an apatitic calcium phosphate containing carbonate and small amounts of sodium, magnesium, fluorine and other trace elements (Aziz-Kerrzo *et al.* 2001).

Artificially prepared HAP, with the same structure as that of apatitic phosphate of natural bone has good biocompatibility with the human organism. It forms chemical bond with the host hard tissue and for this reason, it is widely used in medical applications as implants, as coating on prostheses or as bone filling material (Jonasova *et al.* 2004).

Titanium is widely used for making orthopedic implant devices as it can form a stable passivity surface in the bio-medium that is compatible with the tissue surroundings. (Khan *et al*. 1999 and Thair *et al*. 2002). Ti and its alloys consist mainly of amorphous titanium dioxide, which is responsible both for their corrosion resistance and their biocompatibility (Aziz-Kerrzo *et al*. 2001 and Lavos *et al*. , 2004)

Bio-inert titanium based materials are generally encapsulated after implantation in to the living body by fibrous tissue that isolates them from the surrounding bone. Chemical stability, mechanical behavior and biocompatibility have been making titanium and its alloys known to be among the best biocompatible materials due to their passivation characteristics (the passive film can occur at time 10^{-9}sec.) (Koike and Fujii 2001 and Won-Hoon *et al*. 2003). The alloys currently used as orthopaedic biomaterials are protected from accelerated corrosion rate by a passivation oxide layer that acts like an electrical resistor to retard the anodic dissolution of metal atoms (Thair *et al.* 2004). Alloy modifications of titanium were found to be high effective to improve the corrosion resistance of the materials. Surface modification of Ti and its alloys with calcium- phosphor bio ceramics plays a twin (dual) role both in preventing the release of metal ions (rendering it more corrosion resistant) and also in making the metal surface bioactive (Yu *et al*. 1999 and Mudali *et al.* 2003). The aim of present work was to obtain further information about the passive film and weight gained formed on the substrates surface of Ti-13Nb-13Zr alloy by immersion for relatively long period in Hanks solution compared with the results obtained by potentiodynamic polarisation studies.

Experimental Samples preparations

According to the manufacture instructions preparation sheet by DMRL (Defense Metallurgical Research Laboratories, Hyderabad-India), the as rolled alloy were cut to make samples at size 11 x 11 x 3 mm, Then these samples were heat treated under solution treatment ST at 950 °C for 1hr and then cooled at different cooling conditions [water quench (WQ), air cooled (AC) and furnace cooled (FC)]. Aging was made for all specimens WQ and AC at 550 °C for 4hr. The specimens for optical observations were prepared following the metallographic techniques for titanium alloys.

Potentiodynamic Polarization Measurements

Potentiodynamic polarization was carried out in Hanks solution at pH adjusted to 7.4 and temperature 37.4±1^{o}C for both tests to as rolled and heat treated specimens. Nitrogen gas was continuously purged into the electrolyte throughout the tests to eliminate the dissolved oxygen. All the potential measurements were made with reference to a standard calomel electrode (S_{CE}). A platinum foil was used as counter electrode and potentiostate device was used used for conducting the polarization experiments.

When the specimen attained a constant potential, potentiodynamic polarization was started from an initial potential of 250 mV below the open circuit potential and the scan was continued up to 1500 mV. The specimen was scanned in the positive direction at a sweep rate of 1 mV/sec and the current was monitored with respect to the potential.

Electrolyte

Hank's solution with analytical grade chemicals (BDH and Fluke) was used as the electrolyte given in table 1.

Table (1): Chemical Composition Wt% of Hank's Solution

Chemical Composition	Wt%
KCl	0.40
$CaCl_2$	0.14
$NaHCO_3$	0.35
Glucose	1.00
NaH_2PO_4	0.10
$MgCl_2$	0.10
Na_2HPO_4	0.06
$MgSO_4$	0.06

Results and Discussion

It is very important to evaluate the susceptibility to localized corrosion of the material under study, which can be determined by means of potentiodynamic polarization curves. The main parameters that can be obtained from these curves are the corrosion potential (E_{corr}) and the passivation current density (i_p).

The potentiodynamic polarization curves of the specimens- solution treated and aged (STA), are presented in figure 1.

The passivation current density at 500 mV_{SCE} [Thair et al 2004 and Lavos etal 2004] measured for the solution treated and aged (STA) specimens are given in table 2.

The specimens ST at 950°C followed by air cooling and aged show the lowest passivation current density (0.533 $\mu A/cm^2$) as compared to other specimens indicating stability of the passive film of the specimen against any dissolution. The potentiodynamic polarization curves show that Ti-13Nb-13Zr specimens heat treated under different conditions are passive in a wide potential region up to the breakdown occurrence at $E_b \approx 1$ to 1.1 V_{SCE}. It has been reported [Thair et al.2002, 2004] that the primary α is softer than the matrix structure, irrespective of whether the matrix consisted of Martensitic, Widmanstätten α, or fine secondary α (figure 2). This implies that elemental distributions are same in the two phases of AC specimen.

Based on this observation, it may be stated that FC and WQ specimens have high elemental partitioning compared to the air-cooled structure. Thus, the recorded passive current densities of these specimens are high due to selective dissolution of the alpha phase. On the other hand, due to the identical distribution of the elements in the air-cooled structure selective dissolution of either α or β phase has not occurred resulting in low corrosion current density. Based on this it may be concluded that the major reason for the different corrosion rates observed with different microstructures in the as rolled and solution treated Ti-13Nb-13Zr is due to differences in the phases [Mudali etal 2003 and Jonasova etal 2004].

Table (2): Passive Current Density (i_p) at 500 mV_{SCE} of Alloy Specimens Ti-13Nb-13Zr In Hank's Solution STA at 950 °C.

Heat treatment	Passive Current Density (i_p) at 500 mV_{SCE} in Hank's Solution ($\mu A/cm^2$)		
	W Q	AC	FC
950°C	1.812	0.533	2.731
As Rolled	1.497	1.489	1.502

Energy Dispersive X-Ray Fluorescence spectra

The EDXRF spectra of the as rolled and heat treated specimens obtained at various cooling conditions, has been noticed that as the heat treatment temperature increased toward the α/β transformation temperature, the calcium and phosphate concentration were increased so that the specimen ST at

950^{o}C, aged and air cooled shows higher concentration of phosphor and calcium than other specimens. It has been found that the formation of apatite on the surface of oxidized Ti in the simulated body fluid (SBF) appears to be closely related to the Ca and P containing compounds

Won-Hoon et al 2003 conformed that the Ca and P containing phases includes, β-$Ca_2P_2O_7$, $CaTiO_3$, α-$Ca_3(PO4)_2$, and $Ca_2Ti_5O_{12}$. They have found that at Ti surface coated biomimetically, the $CaTiO_3$ was undergone hydrolysis to form Ca^+, OH^- and $TiO(OH)_2$ in the SBF. The hydrolated titanium oxide is concerned to be insoluble and yields a TiOH surface which might act as nucleation sites.

Conclusions

The results of potentiodynamic curves have been clearly revealed that compositional variation in the phases plays a major role on the corrosion behavior of the hot rolled specimens. The specimen STA at 950^{o}C and air cooled exhibits interesting corrosion behavior due to the absence of selective dissolution of the phases.

The electrochemical investigations on the rolled and heat-treated specimens show that the alloy Ti-13Nb-13Zr remains in passive state over more than 1.0 V_{SCE} under various cooling conditions whereas, 0.5 V_{SCE} above –0.25 V_{SCE} is adequate for satisfactory performance of orthopedic implants.

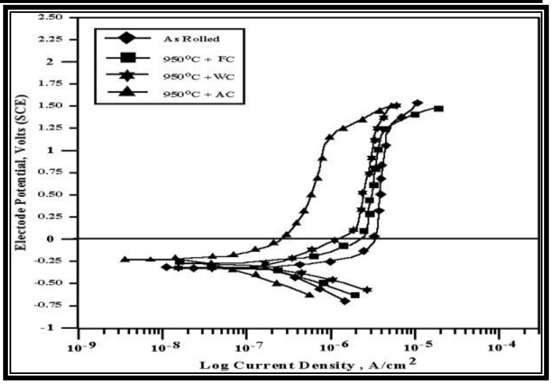

Fig. 1: Potentiodynamic polarization curves of the hot rolled and heat treated Ti-13Nb-13Zr specimens at 950°C with different cooling conditions.

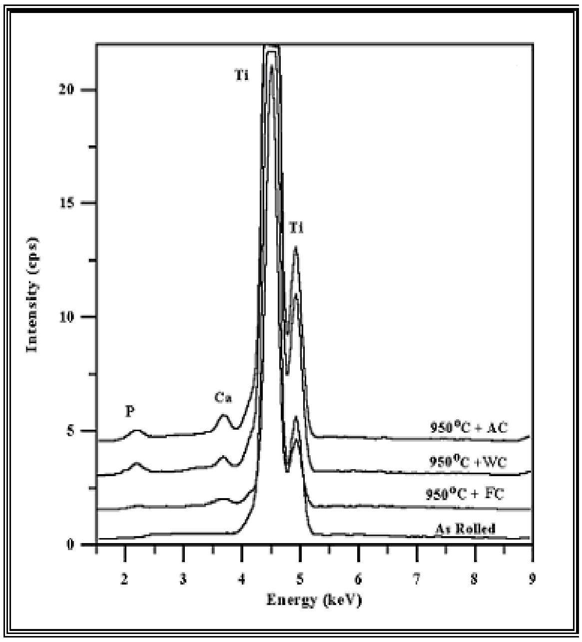

Fig 2: EDXRF spectra of the specimen hot rolled and heat treated at 950 °C, cooled at different conditions.

References

Aziz-Kerrzo Maan; Conroy Kenneth G.; Fenelon Anna M.; Farrell Sinead T. and Breslin Carmel B. (2001), 'Electrochemical Studies on the Stability and Corrosion Resistance of Titanium-Based Implant Materials', Biomaterials, 22, 1531-1539.

Jonasova L.; Muller F. A.; Helebrant A.; Strand J. and Greil, P. (2004), Biomemitic Apatite Formation on Chemically Treated Titanium, Biomaterials, 25, 1187-1194.

Koike Marie and Fujii Hiroyuki. (2001), The Corrosion Resistance of Pure Titanium in Organic Acids, Biomaterials, 22, 2931-2936.

Lavos-Valereto, I. C.; Wolynec, S.; Ramires, I.; Guastaldi, A. C. and Costa, I. (2004), Electrochemical Impedance Spectroscopy Characterization of Passive Film Formed on implant Ti-6Al-7Nb alloy in Hank’s Solution, J. Mater. Sci., Mater. In Med. 15, 55-59

Mudali, U.K.; Sridhar, T.M.and Baldev, R. (2003), Corrosion of Bioimplants, Sadhana,.28 (3 and 4), 601-637. Printed in India.

Thair, L.; Kamachi, M. U.; Bhuvaneswaran N.; Nair, K.G.M.; Asokamani, R. and Baldev, Raj. (2002), ‘Nitrogen Ion Implantation and *In Vitro* Corrosion Behavior of As-Cast Ti-6Al-7Nb Alloy’, Corrosion. Science, 44, (11), 2439-2457.

Thair, L.; Kamachi, M. U.; Asokamani, R. and Raj, B. (2002), Corrosion Properties of Surface Modified Ti-6Al-7Nb Alloy under Pulsed Plasma Nitriding and Nitrogen Ion Implantation Conditions , Surface Engineering,. 20, (1), 11-16.

Won-Hoon, S.; Youn-Ki J.; Yong, H. and Seong-Hyeon, H., (2003) Biomemitic Apatite Coatings on Micro-arc Oxidized Titania's, Biomaterials, Article In Press.

Yu, S.Y.; Brodrik, C.W.; Rayan, M.P. and Scully, J.R. (1999), Effect of Nb and Zr Alloying Additions on the Activation Behavior of Ti in Hydrochloric Acid, J. Electrochemi. Soc, 146, (12) 4429- 4438