

SOME PROPERTIES OF BIOMEDICAL Ti6Al4V ALLOY IN DIFFERENT SOLUTIONS

Jassim Mohammad Salman Mohammad Luay Aziz

jmsmaterials@yahoo.com eng88mla@yahoo.com

University of Babylon ,Materials Engineering College, , Babylon, Iraq.

ABSTRACT

The aim of the present investigation is to study the effect of different simulated solutions on wear behavior, chemical properties and ion release of Ti-6Al-4V alloy which used in human body. For this purpose three solutions have been used (Hank's solution, 0.9NaCl and artificial saliva). The corrosion properties of Ti-6Al-4V implant alloy were examined at 37ºC by using electrochemical techniques, such as the potentiodynamic method and open circuit potential (OCP). The electrochemical corrosion characteristics of Ti-6Al-4V implant alloys in three biological solutions were measured in terms of the corrosion potential (Ecorr) and the corrosion current density (icorr).Wear behavior was investigated by using pin-ondisc tribometers at human temperature under different loads (10,15,20)N. The wear test consisted of measuring the weight loss of samples. The metal ion release of base and alloying element by immersed specimens into various solutions for 7 days (168 hours) at 37ºC. The result found that the Ti6Al4V implant alloy in three biological solutions exhibited a characteristic of a good behavior. The superior corrosion resistance these alloy which current density measured in $(nA/cm²)$. The weight loss of samples by wear test increase with increase load and time. After applied heat treatment, about 40% enhancement in the wear behavior of alloy. The quantity of Al element metal release of implant alloy with variation fluids which increase with decrease the value of pH and little amount of vanadium element in hank's solution.

KEYWORDS: Biomedical Alloy, TiAlV alloy, Different Solution, Mechanical Properties.

بعض خ٘اص اىسبينت اىحياتيت تيتاّي-ً٘ اىَْي-ً٘ فْاديً٘ في ٍختيف اىَحاىيو

جاسم محمد سلمان محمد لؤي عزيز

الخالصة

حقل استخدام المواد الطبية بدأ يأخذ حيزا واسعا كما ان هذه المواد بإمكانها ان تحسن نوعية وإدامة اكثر لحياة البشر . هذه الدراسة تزكز بصوره اساسية على سبيكة التيتانيوم – الومنيوم – فناديوم المستخدمة في المجال الطبي. تتضمن در اسة السلوك التاكلي لسبيكة التيتانيو مفي ثلاث محاليل صناعية تحاكي السوائل الموجوده في جسم الانسان حيث يتم تحضير ها مختبريا ويتم الاختبار بدرجة حرارة جسم الانسان . كذلك دراسة البلي الانزلاقي الرطب في ثلاث سوائل مختبرية وباحمال مختلفة (10,15,20) نيوتن عند درجة حرارة 37ºC . يتضمن البحث ايضا اجراء اختبار التحلل الايوني بغَمر السبيكة لمدة اسبو ع بثلاث سوائل (سلايفا ، 0.9 كلوريد الصوديوم ،هانك)وبدرجة حرارة جسم الانسان باستخدام جهاز الالتزاسونك ومن ثم قياس العناصر المتحررة في السائل باستخدام جهاز التحلل الايوني . النتائج اظهرت قوة تأكل عاليه للسبيكة في فحص التآكل حيث تقاس بالنانو امبير . اوضح فحص البلي الانز لاقي ان معدل البلي يزداد مع زيادة الزمن والحمل المسلط عليها ولـجميع المحاليل المستخدمة وان الصلادة تؤثر على مقاومة البلبي وهذا ماتوضح لسبيكة تيتانيو م-الو منيو م-فناديو م إما بعد اجراء المعاملة الحرارية تبين زيادة الصلادة للسبيكةمما ادى الى نقصان واضح في معدل البلي . ان مقدار التحلل الايو ني ظهر وبتر اكيز قليله جدا مما يجعلهما ً من السبائك التو افقيه والقابله للتكيف بجسم الانسان ولفتر ات طويلة.مقدار تحلل عنصّر الالمنيوم للسبيكة باختلاف السوائل يزداد كلما نقص مقدار الpH مع ملاحظة تحرر كميات قليلة لعنصر الفناديوم في محلول المانك .

الكلمات المفتاحيه : السبيكه الحياتيه . السبيكه تيتانيوم-المنيوم –فناديوم. محاليل مختلفه. الخواص الميكانيكيه

INTRODUCTION

Titanium and its alloys are getting much attention for biomedical applications. In both medical and dental fields because of excellent biocompatibility, light weight, excellent balance of mechanical properties, excellent corrosion resistance, etc[Kim, S. K. (Ed.)., 2015]. They are mainly used for implant devices replacing failed hard tissue, for example, artificial hip joints, artificial knee joints, bone plates, dental implants, etc.**[** Niinomi, M. ,2002**]**. The demand for titanium and its alloys has grown considerably as they have been known since the 1970s to have a lower density, low modulus of elasticity of Titanium alloy as compared with 316-stanless steel and cobalt- $Cr - Mo$ alloys, the density for this alloy is just (4.5 g/cm³))) comparing to (7.9 g/cm³.)))(8.3 g/cm³) for 316-stainless steel and Cobalt-Cr-Mo alloys respectively. Titanium and its alloys as example Ti-6Al-4V are recognized for their superior both strength of tensile and the resistance of pitting corrosion. Ti alloys are appropriate for specific application like dental, repair wiring since it's alloyed with Nickel, having shape memory effect **[**Polmear, 2017**]**. Excellent corrosion resistance and high strength [Manam, N. S., 2017]. Ti6Al4V alloy commonly used for biomedical implant as up implants for dental product, such as crowns, bridges, and dentures, which are mainly produced by the precision casting method. and part for orthodontic surgery, bone fixation material as nails, knee, shoulders, spine, wrist and elbow, joint replacement parts for hips, screws, nuts and plates, housing devices for the pacemaker and artificial heart valve, surgical instrument and component in high-speed blood centrifuge [Geetha, M.,2009]. Ti-6Al-4V alloy with $\alpha + \beta$ phases, which suitably treated, have an exceptional mixture of strength and ductility. They usually are stronger than the α or the β alloy individually **[**Kutz, M. (Ed.),2006**].**Titanium alloy have to be higher biocompatibility as a compared with stainless- steel and cobalt-based alloy and that return superior resistance of corrosion for titanium **[**Landuci, M. C.,2016**]**.Muta- genicity ,as determined by in vitro mutation assays, signifying that Ti alloys are not dangerous for humans and animals **[**Landuci, M. C. ,2016**]**.The biomaterial surface is a chief issue effect undesirable reactions of the body, because the primary contact of the body is among the surface. The chemical compositions on the surface and its topography are supposed to be essential in implants contacting bone. Titanium is discovered to be good tolerated and just about an inert materials in the human body environments. In an optimum state titanium has the ability for osseointegrations with bones **[**Niinomi, M., 2002**]**.Also one of the specific properties of titanium oxide film (TiO2) in addition to its excellent stability in the surface that if the protective layer removed or damaged, it's rebuilt immediately. The aim of this work is to investigate the behavior of famous implant titanium alloy (Ti6Al4V) in different simulated body fluid.

EXPREMINTAL WORK

Preparation of Samples

The materials used in this research prepared as a cast are (F136) Ti-6Al-4V (Company: Shanxi Joint industry co., ltd) which tested in Science and Technology Ministry. Table 1 show the chemical composition of (Ti6Al4V) alloy. After received alloy as a cast rod , cutting it to samples by turning machine with slow cutting speed and flow rate also used cutting fluid to avoid the heating result from the cutting . The thickness of the samples determines according to the required test.

Microstructure Characterization

Microstructure Observation

The microstructure of a specimen of alloy was observed and studied using optical microscope and scanning electron microscope (SEM). Samples after cutting were grinded by using (180, 220, 320, 600, 800, 1000,1200,1500,2000 and 2500) grit silicon carbide papers, then polished with a diamond past of 15 μm to get a bright mirror finish for the final step. Specimens were etched using the following solutions shown in Table 2**[**Iijimaa, D.T., 2003]. The prepared samples are immersed in etching solution for 5-10 seconds, then washed with distilled water and dried, finally samples was ready for microstructure observations

X-Ray Diffraction Analysis

X-ray diffraction analysis has been performed on specimen to determine the existing phases. X-ray diffraction device used is (Lab X, XRD – 6000) with 40 Kv and 30 mA .Scanning speed 2° per minute was used. The range of the diffraction angle was $(20^{\circ} - 80^{\circ})$.

Mechanical Properties

Hardness Test

Hardness is a basic mechanical property of a materials can be suitably defined as the resistance existing by the materials to indentation, i.e., permanents deformations and cracking **[**Askeland D.R, 2005**]**. Microhardness Vickers's tester which used to measure the hardness of the samples with (500 gm) as applying weight and the incubation time was (10-15 sec) in state applied weight. Three measurements for every sample (before and after solution treatment) had been taken and the average values used to analysis behavior of the alloys. The measurement of Vickers hardness was done by using a micro-hardness tester HVS 1000/China agreeing with ASTM E9282.

• Wear Test

Before wear test the samples were dried at $(50 °C)$ for (2 hours) and cooling in the furnace, this process had been done by using vacuum drying furnace, then the samples are saved in well- knit boxes with silica gel material to keep them completely dry. To determine the weight loss of biomedical (Ti6Al4V) alloys specimens, (0.0001) accuracy digital balance Type (L220S– D) with Germany Origin. was used for weighting the specimens before and after the wear examination. The wear apparatus is a rotational type micro-tester (Pin-on-Disc) MT 4003 version 10 was adopted, a martensitic steel disc was used with Ra=0.265 μ m and HV= 852 **[**ASTM, G, 2000**]**. The test was carried out using (10N, 15N and 20 N load). Disc rotates at a constant speed of 350 rev/min and constant radius (6mm). Wet wear experiments(as shown in figure 1) were performed by using pin-on-disc tribotester in Saliva, Hank's solution and SBF Solution, the composition of later solutions is indicated in table 3, table 4 and table 5 respectively at 37 ºC. The durations of the tests were 5, 10, 15, 20, and 25 min. The sample test is weighted and the sliding wear rate had determined according to equation (1). The test method had been covered according to ASTM G 99**[**ASTM, G., 2000**]**.

Wear rate=weight $\cos(g)/\rho(g)$ (1) where:

Weight loss (g) = quantity loss after(5,10,15,20 and 25)min.

 ρ (g/cm³) = theoretical density of the element formed for the specimen calculated from following equation:

 The wear test also applied for specimens which affect heat treatment under protective atmosphere vacuum–furnace by using vacuum tube furnace type MTI-(GSL1600X). The solution treatment by heating specimen of alloy at(850ºC) for one hour then cooling in air, after that aging treatment at (550 ºC) for three hours .

Corrosion Test

The corrosive behavior of Ti-6Al-4V alloy studied in three different solutions includes (simulated human body fluid (0.9% NaCl), artificial saliva, and Hank's solution). The chemical composition of artificial saliva, Hank's solution and 0.9NaCl is illustrated in table (3), (4) and (5) respectively. The preparation of solution was done by adding the specific amount of each constituent for each solution to a liter of deionized water and stirred for about 30 minutes at room temperature on a magnetic stirrer.

Open Circuit Potential (OCP)

The tests were carried out with the samples immersed in artificial saliva a,(0.9 NaCl) and Hanks solution. A 500 ml capacity glass electrolytic cell is used individually. The potential of working electrode is measured respecting a saturated calomel electrode (SCE). A voltmeter is connected saturated between the working electrode and the reference electrode. For each specimen (2-4) hours opencircuit potential measurement was performed. The first record was taken immediately after immersion then the voltage was monitored for the intired period of test at an interval of (5min).

Potentiodynamic polarization

"Electrochemical experiments were performed in three electrode cell containing and electrolytes similar to nature saliva, (0.9NaCL) and Hank's solution. The counter electrode was Pt electrode and the reference electrode was SCE and working electrode (specimen) according to the American society for testing and materials (ASTM G 61-86). The potentiodynamic polarization curves were plotted and both corrosion current density (Icorr) and corrosion potential were estimated by Tafel plots by using anodic and cathodic branches. The test was conducted by stepping the potential using a scanning rate 0.4 mV/s from initial potential of 350 mV below the open circuit potential and the scan continued up to 350 mV above the open circuit potential **[**jabber. H.H., 2014**]**.

Corrosion rate (CR) was calculated by the following equation **[**Cramer, S. D., 2003**]**.

Corrosion Rate (mpy) = 0.13. (icorr).(EW)/ ρ (2)

Where: (icorr) is corrosion current density $(\mu A/cm^2)$

 $(mpy) =$ Corrosion rate (mils per year)

 0.13 = metric and time conversion factor

EW is equivalent weight (g/eq.). ρ is density (g/cm3)

Metals Ion Release

The investigated the release metals of both base and alloying element, (Ti–6Al–4V)alloys by immersed in different solution: artificial saliva, Hank's solution and(0.9NaCl) which illustrated in tables (3), (4) and (5) respectively. The test of static immersions was recognized in agreement with the currently specified JIS T- 0304 standards for metallic biomaterial

[Hanawa, 2004**]**. Samples were immersed in glass containers with 50mL of each solution for one week in an ultrasonic cleaner to keep the temperature at 37˚C. Assessing the metals ion Ti ,Al , V, Nb concentration by Atomic Absorption flame (Nov AA 350).The test has been done in university of Baghdad (college of education)**[** Z. J. Ridha ,2016**]**.

RESULTS AND DISCUSSIONS Microstructure Characterization

Optical Microscope and Scanning Electron Microscope (SEM)

Light optical microscope and scanning electron microscope (SEM) have been used to get the microstructure of the etched samples. The specimens have been etched to show the grain boundaries in the microstructure. Figure (2) illustrates the microstructure of etched Ti6Al4V alloy with magnification (400x, 600x). Explanation of the Ti6Al4V alloy more a domain of magnifications spanning so low to high revealed a duplex microstructure consisting of the near equiaxed alpha (α) (white phase)and transformed beta $(β)(dark phase)$ phases.

SEM pictures are extremely responsive to chemical composition consequently, the microstructure of samples displayed a multiphase structure in which the two phases (α and β) which α represent α stabilizing element as (Al)element and β phase represent β stabilizing element as (v)element , thus confirming the XRD results. Figures (3)(A)(B) showed SEM images for Ti6Al4V alloy with different magnifications(3.030 x -10.181x).

X-ray diffraction analysis

 X-Ray diffraction test was prepared Ti6Al4V alloys. XRD test are used to determine the phases present in samples. Figures (4) shows the XRD diffraction of alloy (Ti-6Al -4V) with two phases $(α+β)$ which α represent α stabilizing element as (Al)element and β phase represent β stabilizing element as (v)element .

MECHANICAL PROPERTIES

Hardness Test

In the current study the hardness of the samples of all alloys are measured by using Vickers hardness test and the results as we show in table (6). From this table notice the hardness of these alloy increased after the heat treatment. As shown in figure (5) ,the microstructure of titanium alloy after the solution treatment which consist of more fine near equiaxed alpha (α) (white phase)and transformed beta (β)(dark phase) phases and that as we knew leading to more the resistance existing by the materials to indentation.

Wear Test

From the figures $((6)... (8))$, it can be note that the wear rate decrease with decreasing of the load applied of the samples. The reason behind this variation is very clear. This is due to increase in friction at the surface as the load on the material increases. In addition, the wear rate increase as the time increase for all tasted specimen, this is certainly because more time of friction tend to remove more material from the surface, this increases in wear rate that has been attributed to increase the plastic deformation for the material on the surface , particles of the material pull out [Aseel safe hemza ,2013]. The normal of load applied is also one of the factors that effect on the weight loss as well as the distance from slip, which losing of weight measure the wear of soft body one a stiff surface. When we have two unworn surface which first undergo sliding one relative to other ,the wear happened for the material which contain a rough surface by eliminate initial oxide layer . Generally, material with more hardness is capable to hold a thicker oxide layer tightly comparative to one with softer material [Cvijovic (2011)]. The oxidative wear can be described through the construction of surface oxides

which are incessantly created and worn. Path. On the possibility that the oxide scale .on the worn: surface are in-adequately reinforced by the fundamental strain-hardened. Materials and don't adheres to the substrate. They have a. tendency to be continuously disjointed. Consequently, they are not defensive and subsequent wear is harsh because the surface of specimens in these examination is under nonstop touch, one reason for reduced resistance of wear for researched alloys returns incapacity to .produce defensive oxide film through wear [Mamoun Fellah, (2014)].

The Effect of Heat Treatment on Wear Resistance

 It is famous that the tribological property of Titanium alloys, as wear resistance is extremely dependent on its microstructural characteristics. Heat treatment variation are usually used to control the alloy microstructure and in turn its performance. With the purpose of get improved performance in terms of the wear behavior, it is highly essential to choose suitable heat treatment procedure. The wear behavior was studied in two simulated body fluid solution (Hank and Saliva solution). The effect of experimental parameters, including applied load on the wear rate of heat treated alloy was also presented. Figures (9) (10) show the effect of heat treatment on wear rate of Ti6Al4V alloy. In all cases, a significant variation of the wear rate with solution treatment is observed. It is clearly evident that the wear loss is lower in the treated alloy. This indicates that the wear resistance of Ti alloy is very sensitive to heat treatment, which modifies the microstructure.

 Archard's law explain that the relation between volumetric loss of materials comparative inversely with the value hardness of materials. This mean that materials with more hardness, a smaller amount in volume loss. The treated alloy display difference value of hardness as mentioned above in table (6). The wear resistance of treated (Ti-6Al-4V) alloy is higher of untreated (Ti-6Al-4V alloy). As can be seen, the treated alloy (Ti- 6Al -4V) its weight loss lower than that in the case of untreated (Ti6 -Al- 4V) alloy. This elucidation compatible as mentioned from the law of Archard which exhibit higher hardness of these alloys leading to lesser volume of weight is loses [Mamoun Fellah, 2014]. From figures (10)(11) show the wear rate of treated alloy with hank's solution little as compared with the effect of saliva solution in spite of the same time and applied load .

CORROSION TEST

Open Circuit Potential (OCP)-**Time Measurement**

The OCP-time was measured with respect to SCE in artificial saliva, (0.9NaCl) and Hank's. Solution at 37 ± 1 C \degree for tested alloys. Figure (11) displays the evolution of corrosion potential of the alloys throughout time. The time period from (0 to \pm 180) minutes and with interval of 5 minutes were potentially reported. Observed that initial time for few minute, the potential in the active direction, after that become continuous rise in the way of noble direction with passage of time even reach to the steady state potentials. These behavior can be explained that there's competition between the dissolution of the protective film and the formation of these layer. End of this process obtained a surface film with enough thickness for self-healing .The variant rate of potential, which reflects the rate of oxide formation, decreased after such of time and arrived to the steady state [Gurappa. I. 2002].

 From Figure (11) it can be seen that the steady state of the alloy is a slightly more positive potential with saliva and hank's solution than potential of 0.9 NaCl. The reason of that depend on the value of pH for each solution, more number of pH represent more positive potential were pH of hank's and saliva were 7.4 and 6.62 respectively while pH of 0.9NaCl at 37C° 6.2 [Singh. R, (2007)].

Potentiodynamic polarization

 The obtained result of corrosion current densities (*i*corr) by tafel curves extrapolation method as exhibit in table (7). Observed a very low *(i*corr) values for the tested Ti-based alloy and ideal of passive materials. The electrochemical tests indicate that tested Titanium alloy at different solutions acted in a comparable way. This behavior happened since passive film created in such alloys is basically of the equal nature, which produced by a titanium oxide, probably TiO2. The existence of alloying elements and creation passive films on the surface are greatly affected to the corrosion behavior of an alloy. The constructional varies in the film or the changing in the electrical or ionic conductivity of the film alters the resistance of passive films against corrosion [Geetha, M., 2009]. From the table (7) it can be seen that there is a slightly increasing in corrosion current and corrosion rate for sample in 0.9NaCl solution with comparison to samples in artificial saliva and Hank's solution. The PH of artificial saliva, Hank's solution and 0.9NaCl at 37°C were 6.62, 7.4 and 6.2 respectively, these results agreement with fact that the corrosion resistance of pure metal or an alloy strongly depends on the environment where it is exposed, the chemical composition, viscosity and so forth [Singh. R, 2007]. It's noted in figure (12) which represents polarization curve for alloys in three solutions, represent the voltage and the corrosion current decreases.

The character for the corroded surface has been taken by using SEM in order to show the corrosion effect on the surface of the alloy .Figure (13) observed that the color of the surface has changed because of the corrosion products, and from that color it can be estimated that the corrosion has occurred on the surface.

Metals Ion Release

 The behavior of metal release from each base and alloying elements constructing the metallic biomaterial must be tested using different solutions: Hank's solution, artificial saliva and 0.9NaCl [Yoshimitsu Okazakia, 2005].In this research, we executed static immersion tests with Ti alloys (Ti6Al4V) implant material to get quantitative data necessary for selection appropriate materials in accordance with a variety of medical usage condition. Figure (14) showed the amount of metals ion released after immersion in Hank's solution, artificial saliva and 0.9NaCl solutions for 7 days.

Titanium is a reactive metal, and disruption or damage to the oxide film is repaired immediately in the presence of air or oxidizing media, as would occur in the human body. In applications where there is no oxygen or in reducing media, such as would occur in a crevice, titanium cannot form the passive film and would not be corrosion resistant. From the figures (14) it can be seen that there is a slightly increasing in quantity of released aluminum metal for all samples in 0.9NaCl solution with comparison to samples in artificial saliva and Hank's solution. The PH of artificial saliva, Hank's solution and 0.9NaCl at 37C° were 6.62, 7.4 and 6.2 respectively, consequently the quantity of Aluminum released from the alloy (Ti-6Al-4V) gradually decrease with increase pH .Hank's solution with fewer released metals as a compared with other solutions. The release of V ions in minute quantity tended to be enhanced at a pH of about 6 or lower.

CONCLUSIONS

1- Observed that the corrosion rate for (Ti-6Al-4V) alloy very low, tested in different artificial solutions which showing a passive behavior.

2-Formation spontaneous passivity for alloy in nature aerated solutions at 37 ºC.

3-The wear performance of alloy under different loads according to the curves are something similar, in spite of the fact the difference in the used solution.

4-The heat treatment has a significant effect on wear properties which increase the hardness of the alloy leading to lower loss of weight.

5- Titanium alloys exposed development in the resistance of passive film with immersion in solutions. The quantity of Al released from the Ti–6Al–4V alloy step by step decreased with increasing PH. A small amount of V was released into Hank's solution.

Table (1): Illustrates the chemical composition analysis of the used alloy.

Table (2): Chemical composition of etching solution

NO.	Constituent	ml
1	HF	10
2	HNO ₃	5
$\overline{\mathbf{3}}$	Water	85

Table (3): Composition of artificial saliva [Giacomelli F. C., 2004]

NO.	Constituent	(g/L)
	NaCl	8.035
2	MgCl.6H ₂ O	0.311
3	$K2HPO4 .3H2O$	0.231
4	NaHCO ₃	0.355
5	CaCL ₂	0.292
6	Na2SO ₄	0.072

Fig.(1) : Shows the Wear Apparatus and Working Method.

Fig. (2): Microstructure for Ti6Al4V alloy after etching A(400x), B(600x)

 Fig.(3)(A)(B) SEM images for etched Ti6Al4V alloy with different magnification

Fig.(4): XRD pattern for Ti6Al4V alloy showing $(\alpha)(\beta)$ phases

Figure (5): Microstructure for Treated Ti-6Al-4V Alloy after Etching

Table (6): Vickers hardness of alloys

	Alloy	Vickers hardness (HV)
As a Cast	Ti6Al4V	317.147
Solution treatment $aging +$	Ti6Al4V	362.552

Fig. (6) : Wear rate vs time for Ti6Al4Valloy at (Hank solution) various loads

Fig. (8) : Wear rate vs time for Ti6Al4Valloy at (saliva solution) various loads

Fig. (9) : Wear rate vs time for treated Ti6Al4V alloy at (Hank solution) various loads

Fig. (10): Wear rate vs time for treated Ti6Al4V alloy at (saliva solution) various loads

Fig.(11): OCP-time in different solutions at 37 ± 1 °C for tested alloy **(A) (B)**

Fig. (12): potentiodynamic polarization for Ti6Al4V alloy (A) 0.9NaCl, artificial saliva and (c) Hank's solution

Fig.(13): SEM Micrograph of Ti6Al4V alloy (a) Hank's solution,(b) saliva solution, (c) 0.9NaCl solution.

 (A) (B)

 (C)

Fig.(14) : Quantity of each metal element released from Ti–6Al–4V alloy by (ppm)into various solutions at 37ºC after 1 week: (A) released Ti ,(B) released Al, (C)released V"

REFERENCES

Alher M. A. (2013) 'Ni ion release of $TiO₂$ and $TiO₂$ / Hydroxyapatite composite coatings formed on shape memory alloy produced by powder metallurgy' Ph.D. thesis, Production Engineering and Metallurgy Department, University of Technology, Baghdad-Iraq,.

Aseel safe hemza (2013)' study of microstructure, corrosion and dry sliding wear of copper – aluminum- nickel shape memory alloys '' , MS.C thesis , materials engineering college , university of Babylon / Iraq

Askeland D.R., P.P. Phulke,(2005)'The Science and Engineering of Materials' Fifth ed, Thompson Publishers, USA, p. 520.

ASTM, G. (2000). 99–95a Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus. ASTM International.

Cramer, S. D., Covino Jr, B. S., Moosbrugger, C., Sanders, B. R., Anton, G. J., Hrivnak, N Scott Jr, W. W. (2003). ASM handbook. Corrosion: environments and industries, 13.

Cvijovic I. ´-Alagic´, Z. Cvijovic, S. Mitrovic´ c, V. Panic, M. Rakin b(2011)' Wear and corrosion behaviour of Ti–13Nb–13Zr and Ti–6Al–4V alloysin simulated physiological solution Corrosion Science '53 PP:796–808.

Geetha, M., Singh, A. K., Asokamani, R., & Gogia, A. K. (2009)' Ti based biomaterials, the ultimate choice for orthopaedic implants–a review'Progress in materials science, 54(3),PP: 397-425.

Giacomelli F. C., C. Giacomelli and A. Spinelli(2004) 'Behavior of a Co-Cr-Mo Biomaterial in Simulated Body Fluid Solutions Studied by Electrochemical and Surface Analysis Techniques' J. Braz. Chem. Soc., Vol. 15, No. 4, PP. 541-547.

Gurappa. I.(2002)' Materials Characterization' 49 PP:73-79.

Hanawa. T.(2004)'Metal ion release from metal implants'. Elsevier materials science and engineering. Vol: 24, PP: 745-752,

Iijimaa, D.T. Yoneyamab, H. Doib, H. Hamanakab, N. Kurosakia(2003)' Wear properties of Ti and Ti–6Al–7Nb castings for dental prostheses' Department of Oral Diagnosis and General Dentistry, Graduate School, Tokyo Medical and Dental University, 1-5-45 YushimaBunkyoku,Tokyo 113-8549, Japan.

Jabber. H.H.,(2014) 'The Effect of Admixed Ti on Corrosion Resistant of High Copper Dental Amalgam' journal of Babylon University, vol. 22, no. 2.pp. 413-421.

Kim, S. K. (Ed.). (2015). Springer handbook of marine biotechnology. Springer.

Kutz, M. (Ed.). (2006). Materials and Mechanical Design. John Wiley & Sons

Landuci, M. C. (2016).' Characterization of mechanical properties of biomaterials . Mamoun Fellah,1 Mohamed Laba\z,1 Omar Assala,1 Leila Dekhil, Ahlem Taleb,1 Hadda Rezag,1 and Alain Iost. (2014) 'Tribological behavior of Ti-6Al-4V and Ti-6Al-7Nb Alloys for Total Hip Prosthesis Surface Engineering and Tribology' Group, Laboratory of Metallurgy and Engineering Materials, BADJI Mokhtar-University.

Manam, N. S., Harun, W. S. W., Shri, D. N. A., Ghani, S. A. C., Kurniawan, T., Ismail, M. H., & Ibrahim, M. H. I. (2017)' Study of corrosion in biocompatible metals for implants': A review. Journal of Alloys and Compounds.

Niinomi, M. (2002)' Recent metallic materials for biomedical applications' Metallurgical and materials transactions A, 33(3), PP:477-486.

Polmear, I., StJohn, D., Nie, J. F., & Qian, M. (2017) Light alloys: metallurgy of the light metals. Butterworth-Heinemann.

Ridha Z. J. (2016)'Preparation and Studying Properties of NiTi Shape Memory Alloys Coated with Biocompatible Layer' A Thesis Submitted to The Council of The College of Materials Engineering/ University of Babylon in Partial Fulfillment of The Requirements for the Degree of Master of Science in Metallurgical Engineering .

Singh. R.And N. B. Pahotre, (2007) 'Corrosion Degradation and Prevention by Surface Modification of Bio Metallic Materials', J Mat. Sci: Mater, Vol. 18 PP: 725 – 751.

Xu. J.L., L.Z. Bao , A.H. Liu , X.F. Jin , J.M. Luo , Z.C. Zhong and Y.F. Zheng(2015) 'Effect of pore sizes on the microstructure and properties of the biomedical porous NiTi alloys prepared by microwave sintering' Journal of Alloys and Compounds,Vol. 645, PP: 137–142.

Yoshimitsu Okazakia, ,Emiko Gotohb(2005)' Comparison of metal release from various metallic biomaterials in vitro Institute of Mechanical Systems Engineering, National Institute of Advanced Industrial Science and Technology.