

Study of Corrosion Resistance of Co-Cr-Mo Surgical Implants Alloy in Artificial Saliva

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Received on: 4/12/2013

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Accepted on: 13/5/2014

ABSTRACT

Co-Cr-Mo alloy has been used for biomedical implant for a number of years. In this study, ASTM F-75 Cobalt-base substrate specimen was immersed in artificial saliva at 37 ± 1 °C to study the corrosion resistance properties. Surface of specimen before and after the immersion was analyzed by optical microscope and Scanning Electron Microscopy (SEM). X-Ray Diffraction (XRD) was used to study the phase structure present. The metallic ions in the artificial saliva were analyzed after the corrosion test by Absorption Spectrophotometer (AAS). Electrochemical Measurements by polarization experiments were performed to study the corrosion resistance, the main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method, and also cyclic polarization are used in artificial saliva solution. The results of galvanic corrosion show that the Co-Cr-Mo alloy had localized corrosion in artificial saliva at 37 ± 1 °C.

Keywords: corrosion of Co-Cr-Mo alloy, surgical implants, artificial saliva

دراسة مقاومة التآكل لسببكية الزوارع الجراحية ذات اساس كوبلت-كروم- موليبدنيوم
في اللعاب الاصطناعي

الخلاصة

تستخدم سببكية كوبلت - كروم - موليبدنيوم في زراعة المواد الطبية لسنوات عديدة . في هذه الدراسة ، غمرت نماذج سببكية ASTM F-75 ذات الاساس كوبلت في اللعاب الصناعي بدرجة حرارة 37 ± 1 درجة مئوية لدراسة مقاومتها للتآكل. تم تحليل سطح النماذج قبل وبعد التآكل باستخدام المجهر الضوئي والمجهر الالكتروني الماسح (SEM). وكذلك تم دراسة حيود الاشعة السينية (X-Ray Diffraction) لدراسة الاطوار الموجودة في السببكية. واجراء تحليل للأيونات المعدنية في سائل اللعاب الصناعي بعد اختبار التآكل. أجريت القياسات الكهروكيميائية بواسطة تجارب الاستقطاب لدراسة مقاومة التآكل، والنتائج الرئيسية التي تم الحصول عليها بعد التعرض لللعاب الصناعي تتمثل بجهد التآكل (E_{corr}) وكثافة تيار التآكل (i_{corr}) بالإضافة إلى قياس ميول تافل لمنحنيات تافل (Tafel)

بطريقة تافل للاستقراء وكذلك الاستقطاب الحلقي في اللعاب الاصطناعي. تبين نتائج التآكل الكلفاني بان سبيكة كروم- موليبيدينوم المطلية تتآكل موضعيا في اللعاب الاصطناعي عند درجة حرارة 37 درجة مئوية.

INTRODUCTION

Metallic biomaterials consist of stainless steel, Cobalt-base alloys, and titanium alloys are widely used for dental alloys, orthodontic wire and manufacturing of orthopedic prosthesis due to their biocompatibility, good mechanical properties and excellent corrosion resistance. Co-Cr and Co-Cr-Mo alloys are the safest materials used in hip and knee prosthesis development and dental alloys. However, these materials are classified as bio-inert materials, because they cannot bond to living bone [1]. The most common process for manufacturing of Cobalt-base ASTM F-75 alloy orthopedic and dental implants is investment casting to obtain the desired area or shape [2]. Cobalt-based alloys have been widely used in implant components, especially in orthopedic implants. Two types of cobalt-based alloys are the most common implant materials (high and low carbon Co-Cr-Mo alloy). They both have a composition of cobalt with approximately 28% chromium and 5% molybdenum. The difference between them is that one has higher carbon content (0.15–0.35%) than the other (0.00–0.14%). The biocompatibility of Co-Cr-Mo alloy is related closely to the material's excellent corrosion resistance, obtained by a thin passive chromium oxide layer with some minor contributions from Co and Mo oxides. Once implanted and exposed to the aggressive body environment, Co-Cr-Mo alloys tend to corrode over time, releasing Co, Cr and Mo ions into body fluids (serum, urine, etc.). Implant components fabricated from Co-Cr-based alloys have been reported to produce elevated Co and Cr concentrations in body fluids. Over time the level of metal ions may become clinically significant [3].

Many authors investigated the corrosion of dental and orthopedic alloys. Duncan et al.(2011) studied the effects of thermal treatments on protein adsorption of Co–Cr–Mo ASTM-F75 alloys. Adsorption of proteins from (foetal bovine serum) FBS onto Co–Cr–Mo ASTM-F75 has been studied using X-ray photoelectron spectroscopy (XPS).The bonds formed by proteins on an AC Co–Cr–Mo ASTM-F75 substrate are significantly stronger than those formed by proteins onto heat treated Co–Cr–Mo ASTM-F75 alloys[4]. Rosentha et al.(2012) [5] studied the phase characterization in as-cast F-75 Co–Cr–Mo–C alloy, and indicated that the presence of coarse and fine lamellar cellular colonies, grain boundary film carbide, and different types of coarse block particles, including single-phase σ , dual-phase $\sigma/M_{23}C_6$, a binary eutectic comprised of σ and Co- α phases, and a three-phase feature comprising the binary eutectic and solid state formed $M_{23}C_6$. The carbide has probably formed during cooling from casting due to σ metastability. Majed R. A. (2013) [6] studied the galvanic corrosion potentials and currents of some dental alloys (amalgam, Co-Cr-Mo, Ni-Cr-Mo, SS 316L, Ti-6Al-4V alloys) by measuring polarization curves in artificial saliva containing citric acid with three concentrations 3,6 and 9 g/l at 37°C. From her result conclude that the metallic contact of amalgam as filling with Ti-6Al-4V alloy give better galvanic corrosion resistance than the coupled of Co-Cr-Mo, Ni-Cr-Mo, and SS 316L with amalgam in the absence and presence of citric acid.

In this work, the corrosion resistance of Cobalt-base ASTM F-75 alloy in artificial saliva on vitro via electrochemical method was investigated, and analyzed the surface of specimens after and before the corrosion test.

Experimental Procedure

Specimen Preparation of ASTM F-75 Co-base alloy

Samples were prepared by cutting into 1x1 cm² pieces and then mounting them into epoxy base, thus leaving only one side of specimen area into contact to the test electrolyte. Samples were grinded with successively finer grade of emery papers (up to 1200 grit) and polished using 0.5 μm alumina past. Then cleaned with acetone (10 min), ethanol (10 min), rinsed with distilled water (10 min) and dried. **Table 1** shows standard and analytical chemical compositions of ASTM F-75 alloy used as a working electrode. **Figure 1** shows the photograph of the epoxy mounted Co-base alloy samples.

Table (1): Standard and analytical chemical compositions of ASTM F-75 Co-base alloy obtained by XRF.

Element (wt%)	Cr	Mo	Mn	Si	Co
Standard	27-30	5-7	1.0	1.0	Balance
Analytical	28.0	6.00	1.0	1.0	Balance

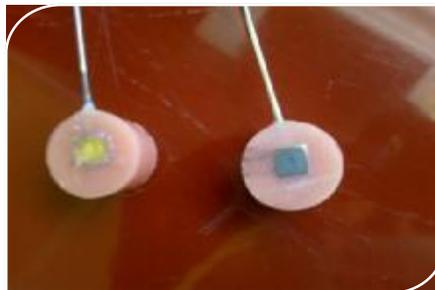


Figure: (1) shows the photograph of the epoxy mounted Co-base alloy samples.

In Vitro Evaluation:

For in vitro evaluation, the electrolyte reference used was modified Fusayama artificial saliva [7], which closely resembles natural saliva, with composition shown in **Table 2**, and pH is 5.2 before the corrosion test and 5.7 after the corrosion test. Specimens were immersed in artificial saliva and hold in a water bath at 37±1°C.

Table (2) : Composition of artificial saliva [7]

Element	KCl	NaCl	CaCl ₂ .2H ₂ O	NaH ₂ PO ₄ .2H ₂ O	Na ₂ S.9H ₂ O	Urea
Conc.(g/L)	0.4 g/l	0.4 g/l	0.906 g/l	0.69 g/l	0.005g/l	1g/l

Electrochemical Measurements:

Polarization experiments were performed in WINKING M Lab 200 Potentiostat/Galvanostat from Bank-Elektronik with electrochemical standard cell with

provision for working electrode (ASTM F-75 Cobalt-base), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with saturated calomel electrode SCE reference electrode, as shown in the **Figure 2**. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate $0.5 \text{ mA}\cdot\text{sec}^{-1}$. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slopes by Tafel extrapolation method.

a. Open Circuit Potential (OCP): Open circuit potential was measured in the electrolyte before carrying out the experiment. The OCP was measured for duration of 720 s.

b. Tafel Studies: Tafel plot of Co-base alloy was obtained by exposing it into respective electrolyte and polarizing from E -2000 mV to +2000 mV vs. SCE with scan rate of $0.5 \text{ mA}\cdot\text{sec}^{-1}$.

c. Cyclic Polarization Study: The specimen was polarized in a cyclic manner from -2000 mV from OCP to a vertex potential of 1200mV and final potential of the cyclic scan was 2000 mV . Scan rate during the experiment was $0.5 \text{ mA}\cdot\text{sec}^{-1}$.



Figure (2) : Potentiostat for electrochemical corrosion measurement

Characterization Methods

X-Ray Diffraction (XRD) technique in Ministry of Science and Technology was used to analyze and study the phase structure present in the surface of specimen, the sigma (σ) and $M_{23}C_6$ carbide were the only secondary phases formed in the face centered cubic cobalt-base alpha matrix (Co- α), as identified by X-ray diffraction, as shown in **Figure 3**. The diffractometer was operated at 40 kV and 30 mA at a step size of 0.05.

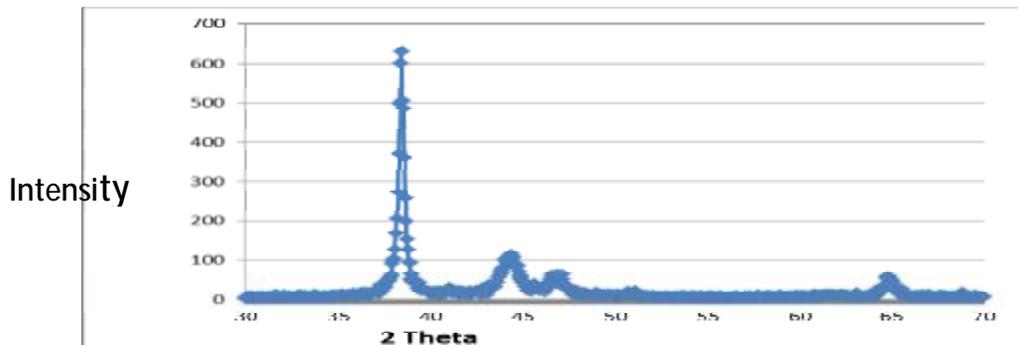


Figure (3) : XRD analysis results for Co-base alloy.

ASTM F-75 alloy substrate microstructure was studied before and after corrosion by quantitatively analyzed by Image Tool software as shown in **Figure 4**.

Scanning Electron Microscopy (SEM) was used to study the surface of specimens before and before corrosion, as shown in **Figure 5**.

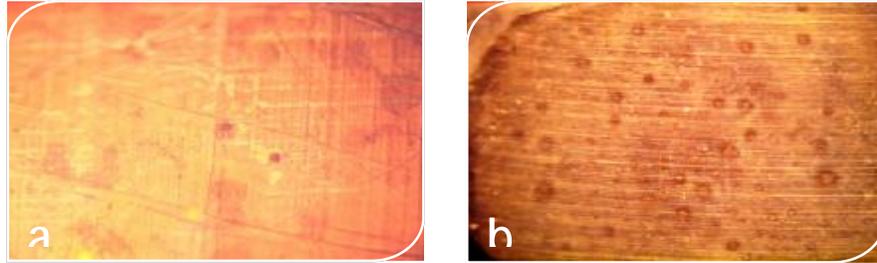


Figure (4) : Micrographs of specimens of ASTM F-75 Co-base alloy
 (a) Specimen surface before corrosion test, b) Specimen surface after corrosion test.

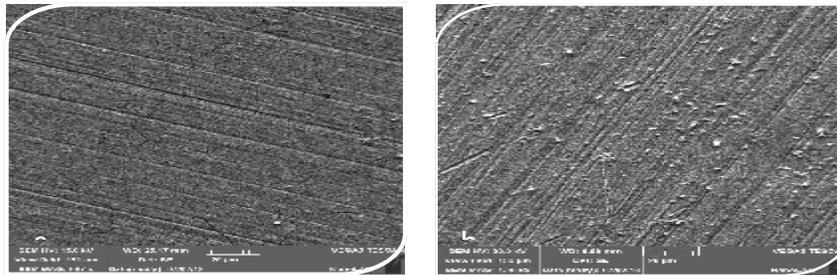


Figure (5) : SEM micrographs of Co-base alloy at 1000x.
 a) Before corrosion test , b) After corrosion test

Analyze the Metallic Ions in Artificial Saliva Solution

The metallic ions in artificial saliva were analyzed after the corrosion test by Atomic Absorption Spectrophotometer (AAS) in Ministry of Industry and Minerals / IBN SINA STATE COMPANY/ Baghdad. The metallic ions analysis results are shown in **Table 3**.

Table (3) : Analyze the ions of the artificial saliva after corrosion test.

No	Item	Result
1	Co	0.01 ppm
2	Cr	0.004 ppm
3	Mo	0.2423 ppm

Micro Hardness Test

The Micro hardness test of the Cobalt-base ASTM F-75 alloy was done in Materials Eng. / University of technology by using digital Micro Vickers hardness tester “LARYEE“ at (1 kg) for (15 sec.) is (538Kg/mm²) , as shown in **Figure 6**.



Figure (6) : Digital Micro Vickers hardness tester “LARYEE“.

Results and Discussion

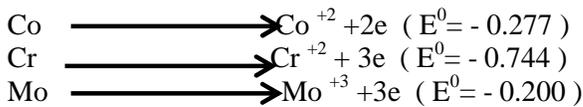
Figure 7 shows the potential-time plot of Cobalt-base ASTM F-75 alloy exposed to artificial saliva solution. Upon exposure of this sample in artificial saliva (modified fusayama solution), it was shown that a shift in the potential from noble to active direction to reach the steady state. The E_{ocp} shifts from -300mV to -700mV and then to stable at -675mV. This is possibly due to breakdown of passive film to the alloy.

Figure 8 shows the current density-potential characteristics (Tafel plot) of Co-base ASTM F-75 alloy exposed to artificial saliva solution. It is evident from the figure that the Tafel behavior of this alloy is highly distinct. These results are shown in **Table 4** which indicate that the corrosion current density (i_{corr}) equals to 597 μA/cm² and corrosion potential(E_{corr}) equals to -938.4 mV. It can be seen from the figure that the corrosion resistance of Co-base ASTM F-75 alloy was good.

The Tafel plot shows the electrochemical reactions of Co-base alloy in artificial saliva, at cathodic site, the reduction of hydrogen take place according to the following equation due to the acidity of medium:



While at anodic sites, the dissolution of metals can occurs according to their activity as follow :



In spite of chromium has most active potential , yet , it is the lowest to dissolve because it's form stable chromium oxide (Cr_3O_2) as protection layer , this result is enhanced by AAS as shown in **Table 3**. Corrosion resistance can be calculated by using the following equation:

$$\text{Corrosion Rate(mpy)} = 0.13 * i_{\text{corr}} * [e/\rho] \quad \dots(1)$$

Where:

$$i_{\text{corr}} = \text{corrosion rate } (\mu\text{A}/\text{cm}^2)$$

$$e = \text{atomic weight for cobalt} = 28.59$$

$$\rho = \text{density of cobalt} = 8.59 \text{ gm}/\text{cm}^3$$

$$R_p = \frac{b_c * b_a}{2.3 * i_{\text{corr}} (b_c + b_a)} \quad \dots(2)$$

Where :

R_p = polarization resistance ($\Omega \cdot \text{cm}^2$) , b_c and b_a are cathodic and anodic Tafel slopes respectively, i_{corr} is corrosion current density.

Cyclic polarization study of uncoated and coated Cobalt-base ASTM F-75 alloy exposed to modified Fusayama solution is shown in **Figure 9**, showed active-passive behavior , then on reversing the potential, the scan initially follows a lower current path and intersects the forward scan just above the pitting potential and there after traces a higher current path, possibly indicating a poor re-passivation by this alloy in artificial saliva. Therefore this alloy has tendency for localized corrosion (pitting corrosion), because of carbide forming during solidification take up chromium away from the matrix.

The presence of Cr improves the corrosion resistance of alloys in a corrosive environment due to the formation of a Cr-rich, passive oxide film which is highly resistant to acid attack. Similarly, presence of molybdenum in the Co based alloy increases the resistance to localized corrosion in the chloride containing environment. Therefore, for Co-based dental alloys, the addition of 12% Cr (minimum value) and 2-5% Mo to the alloy bulk is well recommended from the corrosion resistance point of view [8].

On the other hand , the increasing of corrosion for alloys containing chromium due to rapidly converting of Cr^{6+} to Cr^{3+} and this phenomenon decreases the concentration of chromium ions at surface and then increases the dissolution of metal atoms. Otherwise, the carbide will give different results for ASTM F-75 Co-base alloy castings, carbides themselves which are very good at resisting corrosion resistance , but during solidification of the alloy carbides take up chromium away from the matrix which deprives it of a highly corrosion resistant element. This preferential leaching of chromium causes a chromium depleted zone adjacent to carbide, which is known as sensitization. These surrounding areas of the carbide are then open to localized attack . Pits and crevices can then form in the matrix which can accelerate the rate of corrosion[9].

Table (4) : Corrosion parameters of Co-Cr-Mo alloy in artificial saliva at temperature 37°C .

Alloy	$-E_{oc}$ (mV)	$-E_{corr}$ (mV)	i_{corr} ($\mu A.cm^{-2}$)	$-b_c$ (mV.dec ⁻¹)	b_a (mV.dec ⁻¹)	CR (mpy)	$R_p \times 10^3$ $\Omega.cm^2$
Co-Cr-Mo alloy	675	938.4	597.4	811.2	2586.4	9.558	0.4488

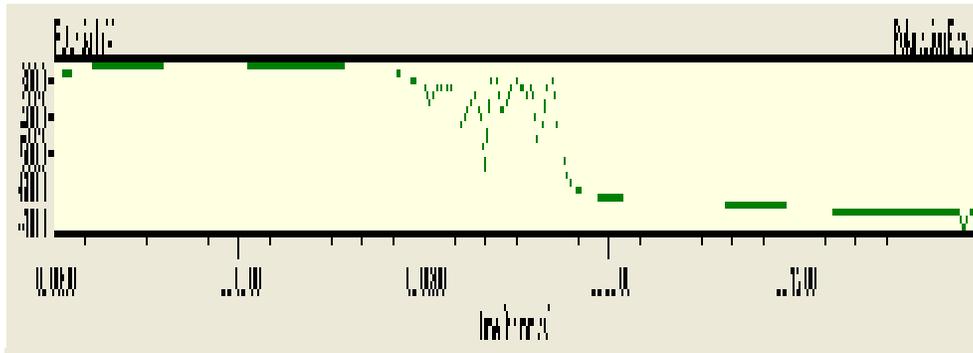


Figure (7): Galvanostate curve for Co-base ASTM F-75 alloy in artificial saliva.

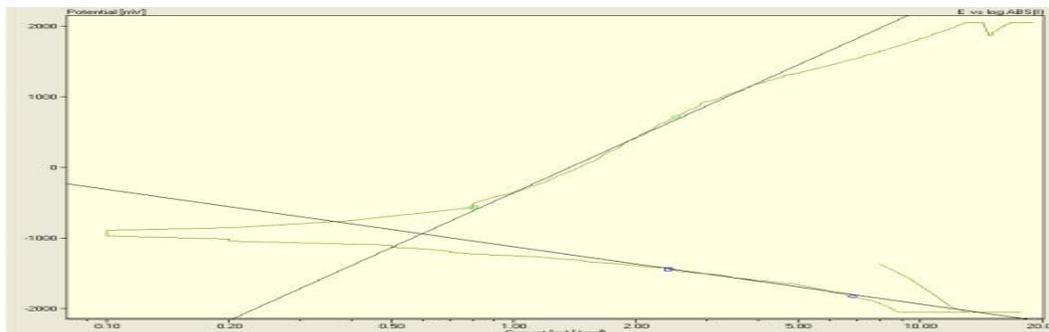


Figure (8): Tafel plot for ASTM F-75 Co-base alloy in artificial saliva.

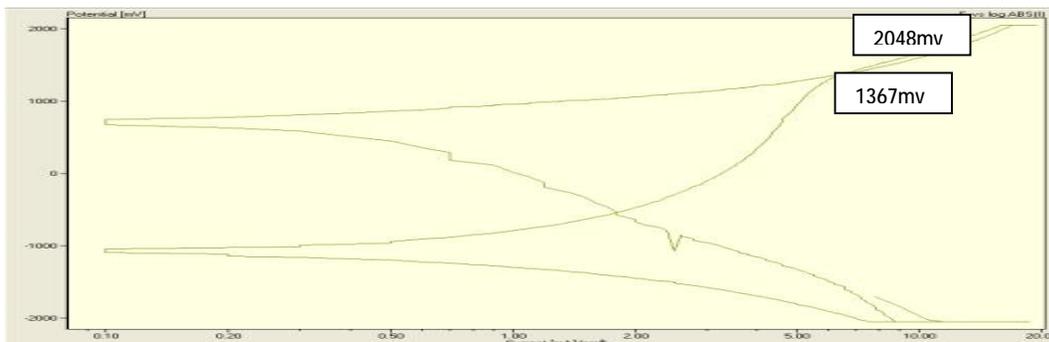


Figure (9): Cyclic polarization for ASTM F-75 Co-base alloy in artificial saliva.

Conclusion

From the data of corrosion of ASTM F-75 Cobalt-base alloy castings, we can conclude that this alloy has localized corrosion in the artificial saliva at $37 \pm 1 \text{ }^\circ\text{C}$, because of carbide forming during solidification take up chromium away from the matrix which deprives it of a highly corrosion resistant element.

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