



Corrosion Behavior and Mechanisms of Co-Cr-Mo Alloy Fabricated by Powder Metallurgy Route in Ringer's Solution

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Abstract

The current research is aimed to study the corrosion behavior and mechanism of Co-Cr-Mo alloy fabricated by powder metallurgy route in Ringer's solution with 7.4 and 37°C for pH and temperature values, respectively.

The research was done by using a potentiostat to obtain the potentiodynamic and cyclic polarization to measure and calculate some significant parameters of the alloy corrosion. The cyclic polarization curve is indicated the resistance of the fabricated samples to the pitting and crevice corrosions. Optical, SEM and SEM-Mapping observations were revealed that the corrosion of the tested alloy was due to inter-particle and inter granular corrosion.

Introduction:

Co-Cr-Mo alloys (CCMAs) have been extensively and effectively used for orthopedic implants, for instance knee and hip joints and in dentistry. The reasons are due to their excellent wear and corrosion resistances, owing to the inactive film of chromium oxide that forms spontaneously on the alloy surface ⁽¹⁻⁵⁾. This oxide formation was assigned to the high concentration of Cr ⁽⁶⁾. The oxide will

avoid ions release in the mouth. They are consequently capable to be used as framework for consolidation fixed partial denture ⁽³⁾. The resistance to corrosion is one of the most substantial properties that control the biocompatibility of CCMAs. Accordingly, it was used in the bulk form for clinical application for long durations of time because of its good biocompatibility⁽⁷⁾.The enough high

mechanical properties of CCMAAs which make them to bear the stresses induced by mastication without danger of falling-out which is another enhancing factor for the utilization as implants ^(2,3,6). The powder metallurgy route (PMR) and foundry as examples for the elaboration routes to obtain parts for dental prostheses from CCMAAs ⁽³⁾. While, several other researchers used PMR in their studies. The CCMAAs were fabricated by casting have been used for numerous years to attain partial dentures, substituting nearly all alloys of gold. Meanwhile, 1949 it has been assessed that above 80% of partial dentures were made of CCMAAs, and next 1969, more than 87%. In present-day nearly all the metal plates of partial dentures are made of CCMAAs ⁽⁸⁾. The ordinary pressing followed by sintering powder metallurgy route is a favorable way to obtain a CCMAA for biomedical application by using suitable parameters ⁽⁹⁾. Parts made by compactions of the powders in a die to the wanted shape then sintered in protecting atmosphere ⁽¹⁰⁾. Parts with different complexity with densities arranged between (80-90) percent of the theoretical density with final dimensions made with high fabrication rates. The behavior of CCMAAs within corroding media is effected by numerous factors which include characteristics related to the material and fabrication situations ⁽¹¹⁾. Under usual situations most body fluids pH and temperature are 7.4 of 37°C respectively. Most in vitro experimentations have been done in 0.9% NaCl, Ringer's or Hank's solution ⁽¹²⁾. It is important before implantation in a human body the materials must be tested in vitro. It is desirable to replicate as closely as possible the natural environment the metal will be exposed to after implantation. Therefore, corrosion study is important for a basic understanding of the behavior of metallic material in biological media from point view of determining the characteristics of this passive film and biocompatibility. It represents a first step toward the more realistic situation encountered in clinical situations ^(5, 13). Mainly the interested researchers about the corrosion of CCMAAs are probably due to

the local breakdown of the passivity as a consequence of localized forms of corrosion such as pitting or crevice corrosion, or fretting corrosion under high oxidizing conditions. These corrosion failure mechanisms as informed by ⁽⁴⁾ and ⁽¹⁴⁾. P. Süry was one of the earlier researchers who studied the corrosion behavior of forged and cast CCMAAs using Ringer's solution as corrosive media. He stated that the forged alloy displays greater pitting and crevice types' corrosion resistance in chlorides containing media than the cast alloys. Because of more regular and smaller grained structure than castings. This was probably reflected in its more stability ⁽¹⁵⁾. Josianne Cassar et al. work was aimed to improve the corrosion resistance of wrought ASTM F1537 CCMAA by carburizing treatment. The treated and untreated samples were examined in Ringer's type solution with 7.4 pH. The solution was kept at 37°C ($\pm 1^\circ\text{C}$). The researchers stated that the treated CCMAA has higher polarization resistance ⁽¹⁶⁾. In turn Murat Songür et al. inspected the corrosion behavior of CCMAA in the Ringer lactate at 37°C by the use of mixed potential and Tafel plots. They pointed out that the tested CCMAA has a substantial corrosion resistance in the biological solutions. Also, they suggested that owing to CCMAA as well as strength and cost usefulness it may be a good substitute as an implantation material ⁽¹⁷⁾. J. C. Mirza studied in vitro corrosion behaviour in Ringer's solution with pH equal to 6.8 two types of CCMAAs: Vitallium and VeraPDI. They tested by polarization of potentiodynamic type and electrochemical impedance spectroscopy. The alloys showed good corrosion resistance as a result of the highly protective oxide layer and converted to a passive region, without showing the active-passive evolution ⁽¹⁸⁾. C. Montero et al. studied the electrochemical properties for ASTM-F75 as-cast cobalt-based alloys with different carbon content (0.05–0.25) %C in Ringer's solution. The cast alloy with low C content displayed the highest pitting resistance which was as a result of the superior chemical and microstructural similarity ⁽¹⁴⁾. The goals of the present

research were to study the corrosion behavior and mechanism of Co₂₉Cr₆Mo alloy fabricated by powder metallurgy route in Ringer's solution

Materials & Experimental Methodology:

Samples preparation

Pre-alloyed spherical shape CCMA powder supplied by China Jincan Chemicals and Alloy Limited Company. Its Particle size distribution and chemical composition were examined by Uniq-Tech company-Turkey using Malvern laser particles size analyzer instrument and Bruker S8 Tiger XRF spectrometer respectively. Also (C and S) elements contents were detected by NCS C-S analyses instrument according ASTM E1019 C-S which was made by Metal Quality Control Laboratory/Istanbul-Turkey. Table (1) illustrates the chemical composition of the CCMA powder. Fig. (1) shows the CCMA powder particles shape afterward of ball milling. The samples prepared by PMR. Each sample was double pressed under 1000 MPa as a best applied pressure due to the greater gotten value of the green density. Then sintering was made in electric resistance furnace type CARBOLITE-UK in a continuously applied argon gas stream from the commencement of the sintering process until room temperature. Sintering performed firstly by heating the compacts to stearic acid debinding temperature which was 500°C for 2 hrs then heated to 1200°C and soaked for another 2 hrs⁽¹⁹⁾. The heating rate was fixed at 10°C/min. The furnace switched off and the samples left to slowly cool inside it. Optical microscopy using invert microscope type OPTIKA-Italy, SEM-EDS and SEM-Mapping using TESCAN instrument (VEGA3LM) were used for microstructure analyses.

Electrochemical measurements

The corrosion tests were performed for the CCMA sintered samples. The tests measuring techniques were involved, open circuit potential (OCP), Potentiodynamic and cyclic polarization. They were

performed in the Ministry of Science and Technology-Bagdad/Corrosion laboratory using the cell which was consisted of 1000 capacity fully transparency beaker and three electrodes immersed in the corrosion solution by a special holding facility as shown in the Fig. (2). The electrodes were an inert platinum auxiliary electrode (A.E) and saturated calomel electrode (SCE) type reference electrode. The later was utilized to measure the potential of the working electrode (W.E.) which were CCMA samples with (1±0.05) cm² testing area, The two circular parallel faces of the sample were wet ground using silicon carbide emery papers with (240, 600, 1000, 2000 and 3000) grit then polished using 5µm alumina suspension solution, washed with distilled water and dried in laboratory oven type LHT/60-UK at 120°C for half an hour. A polymeric covered copper wire was joined to one of the two faces then it was isolated carefully by pouring cold mounting acrylic resin on it. The samples uncovered face with the resin was exposed to a final ground by (3000-grit) SiC emery paper, cleaned by acetone then washed with distilled water and dried by the same mentioned drying procedure. Finally the samples were covered with several layers of dry cotton then kept inside polyethylene containers which were closed tightly and opened directly before the usage. The electrochemical cell is attached to Wenking-M lab type special software interface that enables the variations record for each test parameter in the connected computer as a numerical values and as a diagrammatic sketches. The tests were performed at (37±1°C) in Ringer's type. It was prepared freshly just before the tests commencement by dissolving 4 Ringer's tablets with specification and chemical composition illustrated in the Table (2) in a half of a litter of distilled water to obtain a full strength solution. The pH value was measured by portable pH meter type ecotester pH2. The (6.9 pH) value was obtained then equalized to (7.4 pH) by NaCO₃ addition. The pH value of the immersing electrolyte was also measured after the end of the tests. The range of the cyclic polarization test was carried out between (+ 2000 and - 2000) mV. The

scan rate was 1 mV/sec. The principal result for OCP was measured for the duration of 3600 Sec in the electrolyte before execution the experiment. Besides, the corrosion current density (i_{corr}) and potential (E_{corr}) moreover the Tafel slopes were measured by Tafel extrapolation method.

Results & Discussion:

OCP Measurement

The potential at the alloy electrolyte interface is intensely depends upon the nature of the electrolyte and its concentration, surface conditions besides, pH value. Hence, the reactions change with the time at the interface. Fig. (3) shows potential-time curve for CCMA. The potential was increased from (-600 mV) with the time and reached to (-103 mV) at the end of the measurement period. The potential rise displays that the alloy become thermodynamically further stable with time. This is because of Cr_2O_3 passive film formation and/or the thickening of the previously existed film that acts for an extent as a barrier for metal dissolution and reduces the corrosion rate whenever it is unbroken ⁽²⁰⁾. The red color curve shows the trend of the variation of OCP which has been drawn by the aid of Curve Expert software program.

Potentiodynamic Polarization

The main results found were stated in the terms of the corrosion current density (i_{corr}) and corrosion potentials (E_{corr}) and the Tafel slopes. Fig. (4) shows the polarization behavior of CCMA in Ringer's solution, at (pH=7.4 and Temp. =37°C). Potentiodynamic and Tafel extrapolation method is a modest scheme for assessing the rate of the corrosion. It is adequately sensible even to measure low rates of corrosion as Ali and his coworkers were referred ⁽²¹⁾. The obtained (i_{corr}), (E_{corr}) and the Tafel slopes values are listed in the Table (3). However, the value of ($i_{corr} = 8.41 \mu A/cm^2$) is comparable to those measured by C. Montero et al. for CoCrMo alloy fabricated by investment casting with chemical composition near to that one used in the present work but with

low, medium and high carbon content. Their i_{corr} measured values were (0.058, 0.063 and 0.079) mA/cm² respectively, when tested in Ringer's solution ⁽¹⁴⁾. Also, it is important to inform that the alloy was translated directly into a steady passive state, without revealing the traditional active-passive transition. The rate of corrosion (CR mpy) in a test solution is directly proportional with its current density of corrosion (i_{corr}) according to the equation ⁽²¹⁾:

$$C_R(mpy) = 0.13 \frac{e}{\rho} i_{corr} \dots \dots \dots (1)$$

Where:

CR: Corrosion rate in (mpy) unit,
 e : equivalent weight of CCMA alloy (gm), and ρ : density of alloy (gm.cm⁻³).

Cyclic Polarization

Cyclic polarization is highly useful method for determining the susceptibility of a metal or an alloy to pitting ⁽²²⁾. From Fig. (5) the apex potential for CCMA is 2050 mV, the contrary scan curve onsets to the left of the forward scan, that is, towards the lower current density state. This behavior is recognized as a resistant to locally type corrosion ⁽²³⁾. The potentials for the contrary scan curve are more positive than that for the forward one. These results demonstrate that a steady oxide film was formed throughout the forward scan. The cyclic polarization result is also, ensure that CCMA would not be disposed to crevice corrosion or pitting under in vitro condition.

Optical and SEM Microscopy

The corroded sample after completion of potentiodynamic and cyclic polarization tests was observed by optical and SEM microscopes in order to analyze what was happened actually to the surface of the tested samples during corrosion process. Fig. (6-A and B) indicates optical images for CCMA sample surface before and after corrosion tests. It is clearly seen the huge differences between them. The inside zone of some particles with dark colour was corroded. Also, the particles exposed to intergranular corrosion which detected from departing of individual particles to

several portions due to the corrosion occurrence at those grain boundaries that forms each particle. Besides, the corrosion was occurred at particle boundaries. This is due to chromium element depletion as a result of Cr_2O_3 oxide formation at the particles boundaries. The SEM image of the same sample is illustrated in the Fig. (7). It is clarify with more detail the reflection of the harmful effect of the intergranular corrosion on the appearance of the examined area. After departing each particle to several portions the electrolyte continually penetrated inward at those positions. Also, at particles boundaries which in turn tend to rippling off some grains which forms each individual particle due to their detaching from the bulk of the particle. Finally they left their positions as a large cavities as shown in the upper portion of the image. The Ringer's solution also acted as etching media where some particle surface was roughened at those zones contained dendrite phase. But pitting corrosion does not revealed by optical microscope and SEM examination. This observation is compatible with the cyclic polarization test result for the alloy. The SEM-mapping technique offered the capability to observe the chromium element depletion at particles boundaries and at the boundaries of the grains that are form particles as shown in the Fig. (8). This phenomenon has its greater effect on the corrosion rate

increase of the CCMA more than pitting and crevice corrosion. Hence, the protection of the alloy from the intergranular corrosion will be very necessary by find out the way to remove or to reduce it.

Conclusions:

Followings are the main conclusions:

1-Tafel slopes data specify that the rate of charge of the current with change of potential during cathodic and anodic polarization is approximately the same for CCMA in Ringer's solution.

2- Cyclic polarization result indicates that CCMA that was fabricated by PMR would not be prone to crevice or pitting corrosion during in vitro test conditions.

3-The non-vertical passivity line with alignment to the rightward indicates the continuous ions release with the time and their amounts were became more particularly, at potential values more than 960 mV.

4-Optical, SEM and SEM-Mapping observations revealed the corrosion of CCMA was due to inter-particle and intergranular corrosion. The responsible reason is the Cr-element depletion from near to particles and grain boundaries within each particle.

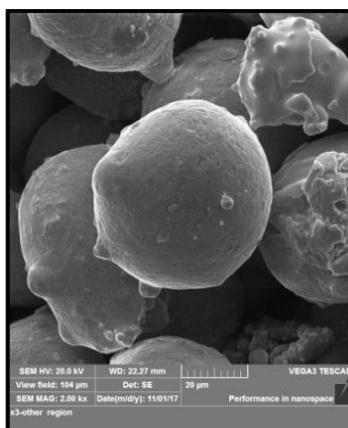


Fig. (1): SEM image for CCMA powder after ball milling.

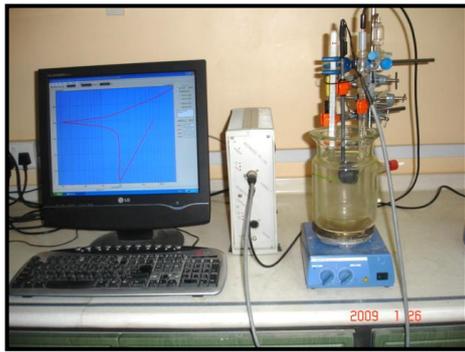


Fig. (2): Electrochemical system used.

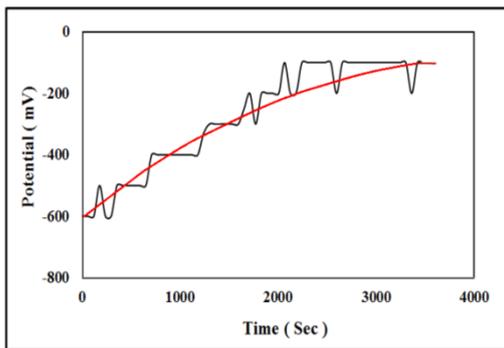


Fig. (3): OCP curve for CCMA in Ringer's solution for 60 min immersion duration.

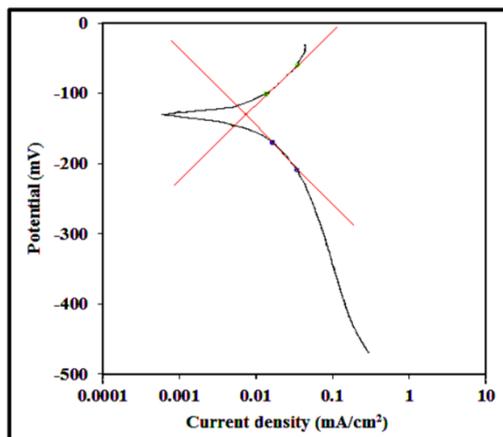


Fig. (4): Potentiodynamic polarization plot curve CCMA in Ringer's solution.

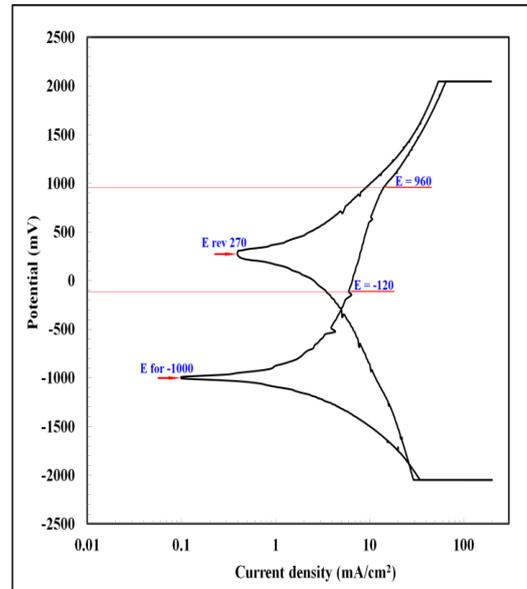


Fig. (5): Cyclic polarization curve for CCMA in Ringer's solution.

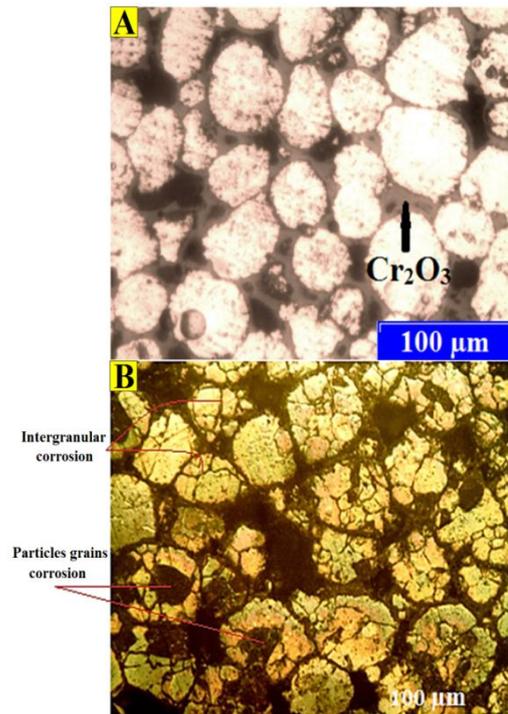


Fig. (6): Optical microscope image for CCMA corroded in Ringer's solution.

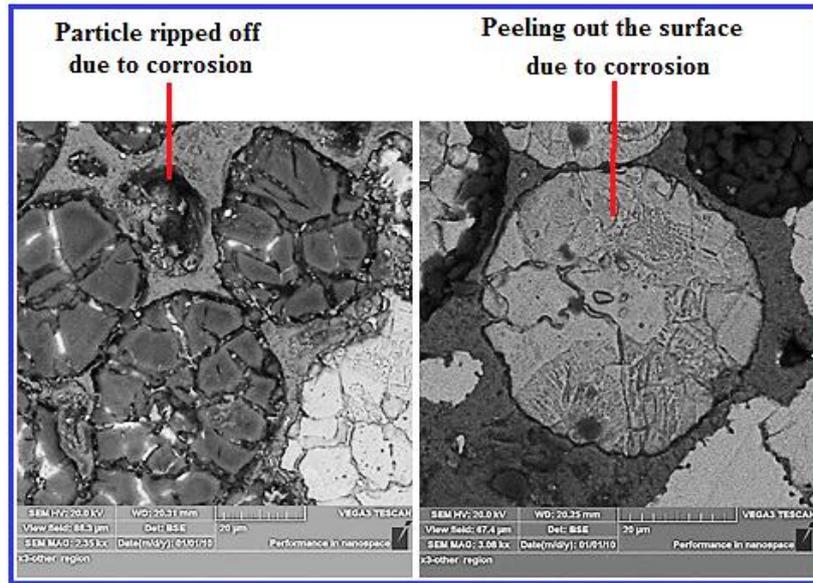


Fig. (7): SEM image for CCMA corroded in Ringer's

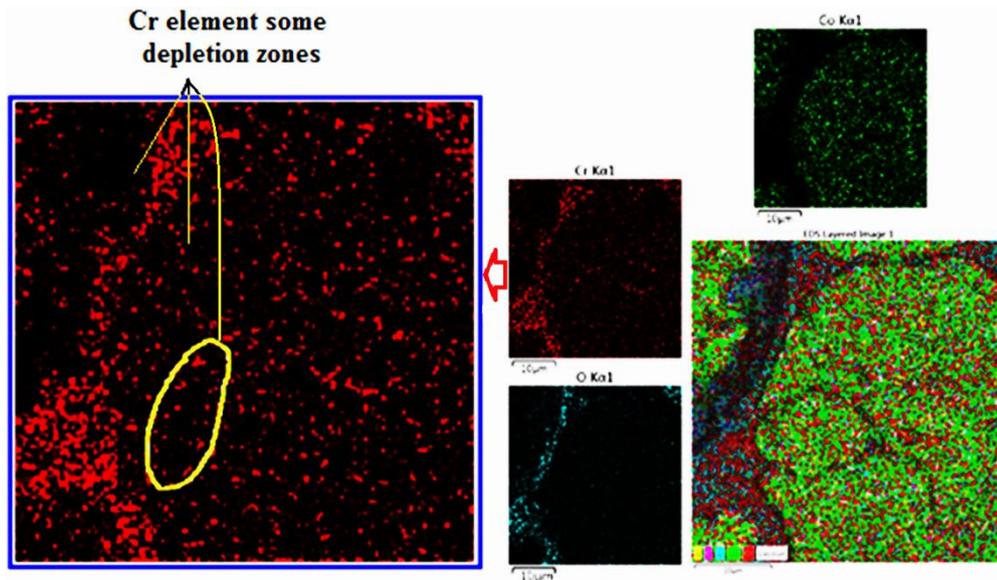


Fig. (8): SEM-Mapping image for CCMA corroded in Ringer's

Table (1): Chemical composition analysis of the CCMA powder used.

<i>Element wt%</i>	Co	Cr	Mo	Si	Mn	O	C	S
<i>A</i>	Bal.	28.52	5.95	-	-	0.035	-	-
<i>B</i>	62.97	29.2	6.612	0.38	0.319	-	-	-
<i>C</i>	-	-	-	-	-	-	0.036	0.0071

A: Manufacturer specification B: XRF analyses result C: C-S analyses

Table (2): The used Ringer's tablets specification and chemical composition.

Specifications		Typical Composition (g/tablet)	
Appearance of solution after autoclave)	clear	NaCl	1.125
pH-value (after autoclave)	6.8 - 7.2	KCl	0.0525
Weight (min)	≥ 1.47 g	CaCl₂, anhydrous	0.03
Weight (max)	≤ 1.79 g	NaHCO₃	0.025

OCP (mV)	I _{corr} (μA/cm ²)	-E _{corr} (mV)	β _a (mV/dec)	-β _c (mV/dec)	CR mpy
-103	8.41	127.1	102.7	128	3.987

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