

Potentiostatic Evaluation of Co-Cr Alloy After Four Repeated Casting Procedure with the Addition of 50% New Alloy

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Abstract

Background: Potentiostatic polarization is one of the reliable method to evaluate the corrosion behavior of hard alloys. There many studies that were concerned with the physical properties of hard alloys while few studies were concerned with effect of electrochemical properties (corrosion behavior). On other hand, no studies have been reported indicating the effect of corrosion behavior after four repeated casting with the addition of new metal alloy. So the aim of study is to evaluate the effect of corrosion behavior of Cr-Co alloy after four repeated casting procedure with the addition of new metal alloy by 50%.

Materials and Method: A hard type of non-precious alloy which is (Remanium alloy) Co-Cr alloy was used in this study. This alloy is supplied by Dentaurum Company). A cylindrical specimen was designed in accordance to the ASTM. It was exposed to electrochemical evaluation before casting procedure and after each repeated casting procedure. In the fourth casting procedure a 50% of new metal alloy was added to compare the electrochemical behavior of this alloy with the other repeated casting procedures. A potentiostatic polarization measurement was used in this study.

Results: The results of polarization resistance (R_p) take the following order $R_p (\Omega \cdot \text{cm}^2)$ 2 casting > 4 casting + addition new metal > 1 casting > 3 casting of Co-Cr alloy. This means that second casting and addition of new metal with fourth casting increase resistance of alloy to corrosion through the new phase which produces at the surface of alloy.

Conclusion: It was concluded that the addition of new metal alloy by 50% has improved the corrosion resistance and this can be reflected on our practical practice in which we can recast old frames with the addition of new metals by 50% and this is economically a good benefit base in combination with scientific approach.

Keywords: (R_p) Polarization Resistance Ecoor; Icoor; Tafel Slopes; Cathode Region; Anode Region

Introduction

The term recasting in dentistry for hard and soft alloy started long time ago. Regarding the non-precious alloys (hard metal alloys), the subsequent demand for these alloys has now resulted in substantial increase in their prices. So, it would be economically advisable to reuse them in combination with new metal as is the practice when using precious metal alloys [1,2]. The most commonly used base metal alloys in dentistry are nickel-chromium and cobalt chromium alloys, which are commonly used for crowns, bridges, inlays and denture bases. The addition of chromium increases the corrosion resistance for these alloys while the addition of nickel increases the ductility and reduces the hardness [3].

Regarding the practical practice of recasting procedure, recasting of dental alloys are generally accomplished with addition of 50% new metal [4], however the non-precious metals might reused several times with the addition of one-third or one-half new metal each time.

Regarding recasting procedure concerned with mechanical properties, Jose *et al.* evaluated the effect of the condition of cp Ti (as received and re-cast) on its mechanical properties, microstructure and fractography. It was concluded that the use of recasting procedure can lower the costs of cp Ti castings and can be safely in dentistry [5].

Regarding the corrosion behavior of dental alloys after recasting, very few studies were reported which discussed the electrochemical behavior of Ni-Cr and Co-Cr dental alloys [6]. Jayant Palaskar, *et al.* in 2010 studied the effect of recasting of nickel–chromium alloy on its porosity. This study was designed to find out occurrence of porosities in new alloy and recasted alloy using a scanning electron microscope and not potentiostatic polarization measurement. Within the limitations of the study it was conducted that the porosities will not be affected by recasting of nickel-chromium alloy. But regarding Clinical Implication it was concluded that porosities in dental casting alloy can alter physical and mechanical properties of the metal which is in turn may lead to failure of crown and bridge, and also cast partial denture prosthesis [7].

Regarding the electrochemical behavior of dental alloys, many studies were carried out. Ameer, *et al.* in 2004 studied the electrochemical behavior of recasting of three types of alloys which are wironit, wiroloy 99 and wiron 99 in artificial saliva using different chemical and electrochemical techniques. It was concluded that the higher rate of wiron 99 compared to wiroloy is due to presence of high concentration of Mo. increasing casting number leads to decrease Rct value and increasing Cdi value [8]. On the other hand, Horasawa, *et al.* studied the effect of recasting on corrosion of silver-palladium alloy in artificial saliva by four times repeated casting procedure. The results indicated that recasting had little effect on the shape of the polarization curves, but the corrosion current density dramatically increased after the fifth cast [9] while Ayad, *et al.* studied the corrosion behavior of as-received and previously cast high noble alloy by using potentiodynamic polarization technique. The results showed that the elemental composition was significantly different among the casting groups and the interaction between casting protocols and electrolyte were not significant among all corrosion parameters [10]. still other researchers studied the corrosion behavior of Co-Cr-Mo dental alloy in solutions of different composition and different pH values. Rincic N., *et al.* carried out this research in 2003. The results indicated that leaching of the Co, Cr, Fe, Zn, and Ni was dependent both upon the nature of the solution and the duration of immersion [11]. On the other hand, Constaninos, *et al.* studied analytic and electrochemical evaluation of the in vitro corrosion behavior of Ni-Cr and Co-Cr casting alloys for metal ceramic restorations. The results showed that the corrosion rates of the Co-Cr alloy were lower than that of Ni-Cr alloy [12]. While Viswanathan S., *et al.* in 2009 studied the electrochemical behavior of Co-Cr and Ni-Cr dental cast alloys. The results showed that Co-Cr alloy exhibits more desirable corrosion resistance properties than Ni-Cr alloy [13]. Also, Qiu J., *et al.* in 2011 studied the Corrosion behaviour and surface analysis of a Co-Cr and two Ni-Cr dental alloys before and after simulated porcelain firing. It was concluded that the corrosion rate of the Be-free Ni-Cr alloy increased significantly after porcelain firing, whereas the firing process had little effect on the corrosion susceptibility of the Co-Cr alloy and the Be-containing Ni-Cr alloy [14]. In a very recent studies, R. A. Rodríguez-Díaz, *et al.* in 2015 studied the Electrochemical Corrosion Behavior of a Co20Cr Alloy in Artificial Saliva. It was concluded that the measured values of Rp at the end of the exposure time are related to a higher stability of the film composed by the corrosion products formed on Co20Cr alloy as compared with those of the 316 L SS, which is related to a minor corrosion rate of the Co-Cr alloy after the third day of immersion. Corrosion behavior is explained in terms of the stability of the corrosion products formed film [15].

As the time was passing some studies started to look for the improvement the galvanic corrosion behavior of dental alloys. These studied found that the use of some special composites, ceramics and metallic glass can improve the galvanic corrosion behavior of dental alloys. Such alloys were considered to be the materials of future [16,17]. In the last recent years many studies started to search for the effect of fluoride on the corrosion behavior of dental alloys and implant alloys. Anwar *et al.* considered the effect of fluoride ion concentration on the corrosion behavior of Ti and Ti-6Al-4V implant alloys, when coupled with either metal/ceramic or all ceramic superstructures can impair the corrosion resistance of these alloys [18]. Also Noguti, *et al.* and Rosalbino, *et al.* considered that the toothpastes, mouthwashes and prophylactic gels contains fluorides from 200 to 200,000 ppm F(-) can impair the corrosion resistance of dental alloys in the oral cavity [19,20].

Accordingly, only few studies were concerned with the corrosion behavior of cobalt chromium alloy after repeated casting procedure. Hence, the aim of this study is to evaluate the electrochemical behavior of Remanium alloy (Co-Cr alloy) in 0.9 sodium chloride solution by using potentiostatic polarization assessment after four castings procedures with the addition of new metal alloy of 50% and according to our knowledge no study has been reported concerned with the effect of corrosion behavior of this alloy after four repeated casting procedure.

Material and Methods

A hard type of non-precious alloy was used in this study which is (Co-Cr) alloy. This alloy is considered a base metal alloy. Table one refers to the type of this alloy while table two indicates the composition of this alloy according to the manufacture’s industry.

Alloy commercial name	Type	Supplier	Application
Remanium	Co-Cr	Dentaurum company	Denture base material for partial and complete denture + combination technique

Table 1: Type of dental alloy used in this study.

Alloy commercial name	Co	Ni	Cr	Mo	Other, Si, Mn and C
Remanium	63.3%	0	30%	5%	0.35%

Table 2: Composition of Co-Cr alloy used in this study.

Regarding sample preparation, a cylindrical disc-shaped test specimen design was used. This is in accordance to the ASTM (F-136) which was used by Lemon, *et al.* 1992 when they measured the intraoral corrosion behavior of various metallic materials [21]. Before corrosion testing, all samples were ground with 180-, 320-, and 600-grit Si carbide abrasive papers and then polished with 9-, 3-, and 0.05-µm diamond suspensions (Buehler, Germany) to produce mirror-like surfaces.

The casted specimen was re-casted again up to three times but in the fourth casting procedure a 50% of new metal alloy was added to compare the corrosion resistance for the four casting procedures. The electrical connection was made by crimping the slotted portion of the specimen onto a copper wire. A saturated calomel electrode (S.C.E.) was used as reference electrode which consists of a salt bridge (KCl). The solution used was 0.9% NaCl with a pH of 7 + 0.5 adjusted by sodium bicarbonate.

However, a controlled temperature water bath was used to control the temperature of the solution at 37 °C. The potentiostatic polarization measurements were performed by a potentiostat from a fixed potential of a -600 mV Vs., S.C.E. to a potential of 600 mV Vs., S.C.E [22]. The potential for the alloy was scanned at a rate of 600 mV/min. The test for each specimen after each recasting procedure was repeated up to the forth casting procedure.

Results and Discussion

The linear polarization test is a simple method for evaluating the corrosion rate, sufficiently sensitive to measure even a low corrosion rate; potentiostat with software program determines and displays the corrosion current as the ordinate of the intercept between the two Tafel lines extrapolated at the (i = 0). The test was conducted at a scanning rate of 0.5 mA/sec. The current densities were calculated with reference to the samples geometrical area.

During anodic or cathodic polarization, or at open circuit, ion transfer reaction of metal ions and oxygen ions will take place. A clear process is the anodic corrosion of a passive metal in the steady state. In such a case, metal ions travel through the oxide film with a constant rate and are transferred in an ion transfer reaction at the interface oxide/electrolyte. The rate of that passive film dissolution depends on the local potential drop at the interface, the pH and the activity of the metal ions at the oxide surface.

The polarizations test started at a cathodic potential in relation to the corrosion potential, therefore the surface passive film was at least partially removed due to the highly reducing initial potentials as shown in Figure 1 which illustrates the linear polarization of Co-Cr alloys after four casting processes.

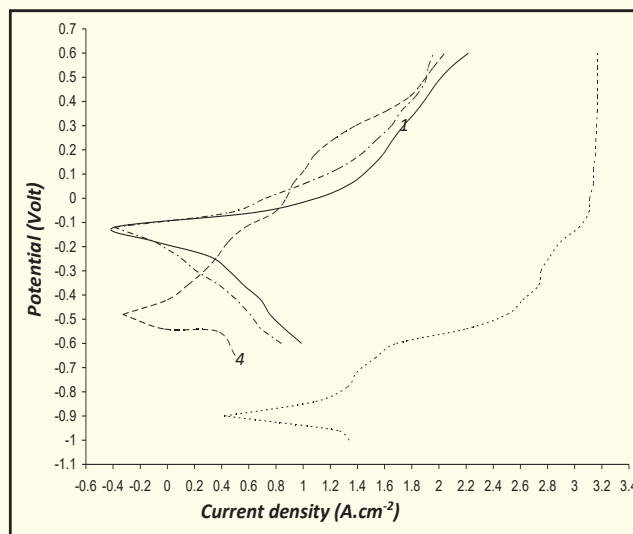
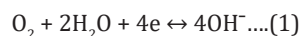
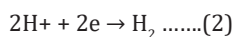


Figure 1: The polarization behavior of four casting Co-Cr alloy in 0.9% NaCl solution. 1-First casting Co-Cr alloy, 2-Second casting Co-Cr alloy, 3-Third casting Co-Cr alloy, 4-Co-Cr alloy with addition.

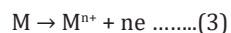
The polarization curves consist of two main regions, cathodic and anodic region. The section (ab) on the curve represents the reduction reactions accordance to pH of medium. In neutral and basic environment, reduction of oxygen can occur:



While in acidic environment, the hydrogen evolution reaction can occur:



Anodic dissolution of metals and alloys begin at point (c) and continue along (cde) accordance to the following reaction:



The corrosion potential (E_{corr}) of a material in a certain medium at a constant temperature is a thermodynamic parameter which is a criterion for the extent of the corrosion feasibility under the equilibrium potential (in opposite sign) of the cell consisting of the working electrode and the auxiliary electrode when the rate of anodic dissolution of working electrode material becomes equal to the rate of the cathodic process that takes place on the same electrode surface.

The data of corrosion potentials that listed in Table (3) indicate that increasing the casting process shift the E_{corr} toward active direction.

The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the value of (i_{corr}) results in an enhanced value of the corrosion rate on pure kinetic ground.

For deep analysis of polarization behavior Tafel slopes can be calculate for cathodic and anodic curve.

The reduction of the H_2O molecule is a common cathodic reaction for the corrosion of metals in neutral and alkaline solutions:



The hydrogen evolution reaction (h.e.r) has been the most widely studied electrode reaction.

However, it is important to note that the discharge step involves adsorption of hydrogen atoms at available sites on the metal surface, and is followed by desorption that may be either a chemical step, or an electrochemical step in which further charge transfer occurs. A value of the cathodic Tafel slope of (-0.120 V.decade⁻¹) may be diagnostic of a proton discharge-chemical desorption mechanism in which the proton discharge is the rate-determining step (r.d.s).

Values of transfer coefficient (α) have been calculated from the corresponding values of the Tafel slope (b) using the relation [23,24]:

$$\alpha = (2.303 RT)/bF$$

Table (1), in general, show that Tafel slopes are greater than expected 2.3x (2RT/F) (b = 0.120 V.decade⁻¹ or $\alpha = 0.5$ at 25°C) for the Volmer-Tafel mechanism.

The Tafel slopes greater than 2.3x(2RT/F) are usually regarded as anomalous since they cannot be predicted for any mechanism by the two well-known theoretical procedures, namely, the steady-state method and the quasi-equilibrium approach, without making assumptions which are easily contestable. During the preparation of the working electrodes to the corrosion test, exposure to air and therefore the electrodes undoubtedly had a thin oxide film on their surface before being introduced into the cell. It is clear, however, that the presence of a film can markedly influence the reduction process at the surface by affecting the energetic of the reaction at the double layer, or by imposing a barrier to charge transfer through the film, or both [25].

The polarization resistance (Rp) may be defined as the slope of a potential (E)-current density (i) as [26,27]:

$$R_p = \left(\frac{\partial \eta}{\partial i} \right)_{T,C} \quad \text{at } \eta \rightarrow 0$$

Where η , overpotential ($\eta = E - E_{\text{corr}}$), is the extent of polarization of the corrosion potential and (i) is the current density (c.d) corresponding to a particular value of (η). For low-field polarization [28].

The term (R_p) corresponds to the resistance (R) of the metal/solution interface to charge – transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed. The reaction resistance (R_p), which mainly depends upon the equilibrium exchange current density (i_0) determines what may be termed the polarizability, i.e., what overpotential ($\eta = E - E_{\text{corr}}$) a particular current density needs or produces.

The polarization resistance (R_p) can be determined from the Tafel slopes and according to Stern- Geary equation [29,30]:

$$R_p = \left(\frac{dE}{di} \right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c) i_{\text{corr}}}$$

The values of Rp which have been calculated from above equation are presented in table 3.

Sample	Corrosion		b (V.decade ⁻¹)		α		R _p /10 ⁶ Ω.cm ⁻²
	-E _{corr} (V)	i _{corr} /10 ⁻⁶ A.cm ⁻²	-b _c	+b _a	α _c	α _a	
1 casting Co-Cr alloy	0.13	0.4265	0.120	0.054	0.493	1.095	0.038
2 casting Co-Cr alloy	0.48	0.4898	0.136	0.200	0.435	0.296	0.072
3 casting Co-Cr alloy	0.90	4.7863	0.114	0.148	0.519	0.399	0.006
4 casting Co-Cr alloy	1.20	0.5623	0.250	0.080	0.236	0.739	0.047

Table 3: Values of corrosion potentials E_{corr} , corrosion current densities i_{corr} , cathodic and anodic Tafel slopes (b_c and b_a), cathodic and anodic transfer coefficients (α_c and α_a), polarization resistances R_p , and equilibrium exchange current density (i_0) for the polarization of Co-Cr alloy in 0.9% NaOH solution.

The results of polarization resistance (R_p) take the following order:

R_p ($\Omega \cdot \text{cm}^2$) 2 casting > 4 casting+ addition new metal > 1 casting > 3 casting of Co-Cr alloy

This means that second casting and addition of new metal with fourth casting increase resistance of alloy to corrosion through the new phase which produces at the surface of alloy.

Conclusion

It was concluded that the addition of new metal alloys by 50% can improve the corrosion resistance after repeated recasting procedure. From practical point of view, it can be stated that old frames can be re-casted with the addition of new metal alloys by 50% with no hazard on corrosion property. This can be considered a great benefit and economically wise advantage in the field of prosthodontics dentistry regarding cobalt-chromium frames of removable partial denture.

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