COMUNICACION CORTA

Electrochemical methods as control test for casting dental alloy individual prosthesis

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RESUMEN. Algunos autores han demostrado que las técnicas electroquímicas convencionales con solo algunas modificaciones relacionadas con las condiciones biológicas, han sido efectivas en la disolución de algunos problemas relacionados con la biocompatibilidad de algunos materiales. Las aleaciones preciosas no pueden ser utilizadas en todos los casos como material dental, por tal motivo se han empezado a utilizar aleaciones del tipo Ni-Cr y Co-Cr, aunque la biocompatibilidad de estas ha sido cuestionada por sus propiedades corrosivas, alérgicas e incluso mutagénicas. El factor primario que controla el comportamiento corrosivo es la naturaleza de la capa pasiva en metales y aleaciones. Existe poca información sobre el efecto de factores físicos y químicos en la respuesta de un tejido al implante metálico y en la relación que puedan tener con la liberación de iones como resultado de la interacción célula-material. Estas aleaciones pueden presentar diferentes fases, que pueden ser unas más estables que otras en dependencia del proceso de fundido, durante la producción de piezas dentales metálicas. Por esta razón, a recibido atención particular el desarrollo de un método sencillo y rápido que sirva para certificar el comportamiento corrosivo después de la preparación de estas piezas. El objetivo de este trabajo es presentar algunos resultados sobre el comportamiento corrosivo de dos aleaciones comerciales: Wiron 99 (aleación Ni-Cr) y Aurolloyd kf (aleación de Au). Estos resultados fueron obtenidos por varias técnicas electroquímicas: Potencial a circuito abierto–tiempo (E_{oc}) y voltametría de barrido lineal (Rp) para la aleación Wiron 99, y potencial a circuito abierto–tiempo y voltametría cíclica (VC) para la aleación Aurolloyd kf. Se concluye que con la aplicación de métodos electroquímicos usando un sistema de mini-celda, es posible determinar cómo es el comportamiento corrosivo después del proceso de fundición de prótesis dentales individuales. En el caso de la aleación de Au, se concluye que las diferencias en el comportamiento electroquímico dependen fuertemente de los óxidos superficiales formados. Estos resultados demuestran que diferentes métodos electroquímicos pueden ser seleccionados como prueba de control después del proceso de fundición de las prótesis individuales.

ABSTRACT. Extensions and modifications of standard electrochemical techniques, accounting for unique conditions related to biological considerations, have proved useful in attacking some problems related to biocompatibility of the Biomaterial. Some authors have demonstrated that modern electrochemical techniques can be used to clarify some difficult problems in the field of biomaterials. Precious alloys can not be apply for all cases especially such as long range bridges or prosthesis. For this reason, Ni-Cr as well as Co-Cr casting alloys have been used for dental application as alternatives to precious alloys. The biocompatibility of Ni-Cr alloys have been questioned because of their corrosive, allergenic, and even mutagenic potentials. The nature of passive films on metals and alloys is the ultimate factor which controls their corrosion behavior. There is little reliable information on the effects of the physical and chemical factors involved in the tissue response to an implant and the associated ionic release on the cell-material interaction. Depending on the casting process during the production of a dental prosthesis, these alloys may show different phases, ones may be more stable than other. For this reason, the development of a fast and simple method for determination of the corrosion behavior as a control test in the production of a metallic dental devices is of great interest. The purpose of this work was to present some results on the corrosion behavior of two different commercial alloys: Wiron 99 (Ni-Cr alloy) and Aurolloyd kf (Au alloy). These results were obtained by several electrochemical methods: open circuit potential–time and liner sweep voltammetry for Wiron 99, and open circuit potential–time and cyclic voltammetry for Aurolloyd kf. It is concluded that with the application of electrochemical methods in a mini cell-system , it is possible to know how the corrosion behavior of casting dental alloy individual prosthesis is. In the case of Au alloy, it is concluded that the differences in electrochemical behavior strongly depend of surface oxides formed. These results showed that different electrochemical methods could be selected as control test after casting of individual prosthesis.

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INTRODUCTION

There are various problems regarding compatibility of biomaterials which, although interesting and important, have received relatively little attention because of difficulties associated with conventional approaches to study them. Some authors[1] have demonstrated that modern electrochemical techniques can be used to clarify some problems in the field of biomaterials. Bundy et al.[1a] concluded that electrochemical methodology can be used both for measurements *in vivo* and for measurements attempting to simulate *in vivo* conditions. Bumgadner *et al.*[2] showed that the Ni-Cr-Be alloys have a nonhomogenious surface oxides and they are less resistant to corrosion attack than the non-Be containing Ni-based alloys and Hugot-Le Goff *et al.*[3] demonstrated that the passive film in a Be-containing Ni-Cr alloys is not insulating enough and the anodic current enhances. Pan *et al.*[4] investigated the corrosion resistance of different non-Be and Be-containing Ni-Cr-Mo dental alloys by different electrochemical methods: open-circuit potential methods, potentiodynamic method at low scan rate, and impedance spectroscopy and concluded that the dissolution rate of Be and Ni are closely correlated with the Be-content in the alloys. In order to eliminate the potential health hazards of Ni and Be, Co-Cr alloys can be used to replace Ni-Cr-Be alloys without sacrificing the good physical properties of the metal framework, including yield strength, flexural strength and modulus of elasticity.

Rubo *et al.*[5] demonstrated that tin-electroplating increased the bond strength of metal-ceramic gold alloy to a level comparable to the Ni-Cr alloy, but had a harmful effect on the IV type gold alloy, and Matsumura *et al.*[6] compared heating, Tin-electroplating and ion coating for some dental alloys to create a strong bond between a composite resin and metal frameworks with a new adhesive resin. The metal specimen were type III gold, Ni-Cr and Co-Cr alloys.

Smith *et al.*[7] studied the influence of the preparation procedure on different dental implant materials and concluded that each procedure generated an individualistic composition for the outermost surface of each material and these differences could be significant for tissue response.

It has been reported[8] that various metal ions leach from dental castings or from dental restorations due to the corrosion of the metal into environmental tissues. An improper heat treatment or the placement of prosthetic appliances made of different metals increases the dilution of metal ions. Many studies[9-11] have been done showing the influences of dissolved metal ions on dental tissues, oral bacteria, and on allergic reactions.

There is a little precise knowledge of the actual interface between implant and tissue and of the factors which influence host response and a long-term integrity of the implant system. More fundamental research is needed on both materials and design for rational progress.[12]

The aim of this research was to develop a fast and simple electrochemical method for determination of electrochemical, at least the corrosion behavior as a control test in the production of a individual dental prosthesis. The purpose of this work is to show some results on the corrosion behavior of different dental alloy. These results were obtained by several electrochemical methods, which could be used as a control test for characterization of dental alloys after casting of individual prosthesis.

MATERIAL AND METHODS

The alloys were a commercial Ni-Cr alloy, Wiron 99 (65 % Ni; 22.5 % Cr; 9.5 % Cr; 0.5 % Fe; 1 % Nb; 1 % Si; 0.5 % Ce) and a commercial Au alloy, Aurolloyd kf (55 % Au, 29 % Ag, 10 % Pd, 3.3 % In). Always the exposed area was 0,8 mm^2. The following pretreatment were made before the experiments: wet polished with No. 500 emery paper, 6 µm and 3 µm diamond suspension and finally with an oxide polisher suspension, and degreased in acetone. The solutions were 0,1 N H_2SO_4 (Ni alloy) or 1 % NaCl (Au alloy), without stirring. The experiments were made in a special 5 mL mini-cell.[13] Reference electrode was a saturated calomel electrode (SCE). The following methods were used: Open Circuit Potential (E_{oc})–time, Liner Sweep Voltammetry (LSV) near E_{oc} with a scan rate of 0,1 mV/s or Cyclic Voltammetry (CV) with a scan rate of 1 mV/s .

RESULTS AND DISCUSSION

Open circuit potential-time and liner sweep voltammetry

Figure 1 shows the E_{oc}–time curves for different samples (F, G, H, I, K) of Wiron 99 exposed in 0,1 N H_2SO_4. Evidently there exist two different behaviors,* because in one case the potential moves to the cathodic region and in the other, to the anodic region. These different behaviors indicate that there are two different surfaces. Since this is a simple but no a fast test we made another experiment to confirm the results.

Figure 2 shows the LSV curves to calculate the polarization resistance (R_p) 20 mV around E_{oc} (Rp determination). These results indicate that the G-behavior samples have a higher Rp value, that is, a more passivated surface than the F-behavior samples and therefore they are in agreement with those of figure 1. It can be concluded that with any of both methods, it is possible to know how the corrosion behavior of casting individual dental prosthesis is, but the spent time for both methods is completely different; in LSV curves it spent no more than 30 min, but in E_{oc}–time curves the spent time was more than 2.5 h . For this reason, a fast and easy procedure to know the corrosion behavior of this dental alloy could be the LSV method.

Open circuit potential-time and cyclic voltammetry

Figure 3 shows the E_{oc}–time curves for different areas at the surface of Aurolloyd kf in 1 % NaCl solution. As in Ni-alloy, there are two different curves that means two different behavior. This difference could be due to the degree of oxidation at the surface. This result suggests that the potential is strongly dependent on the surface oxide formed on the alloy, that means on the kind of compound formed during the casting procedures.

Figure 4 shows the CV curves for the same two different surface points of Aurolloyd kf in 1 % NaCl solution. There are three cathodic peaks (at other superficial areas, only two peaks are observed) and only one anodic peak just before 0.0 V (vs Calomel Electrode). The peaks, Pc2 and Pc3, could be associated with the reduction of surface oxides,

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* *Named for authors F- behavior (F and I samples) or G-behavior (G, H and K samples).*

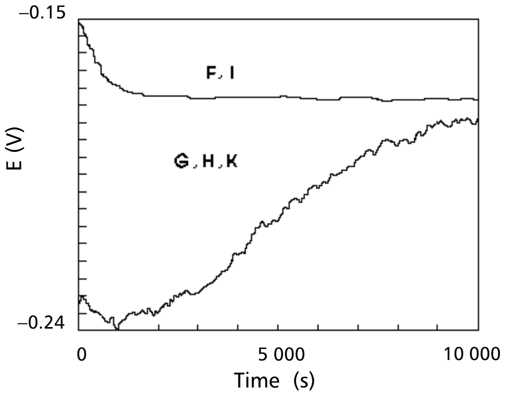

***Fig. 1**. $E_{oc-time}$ values for different samples (F, G, H, I, K) of Wiron 99 exposed in 0,1 N H_2SO_4.*

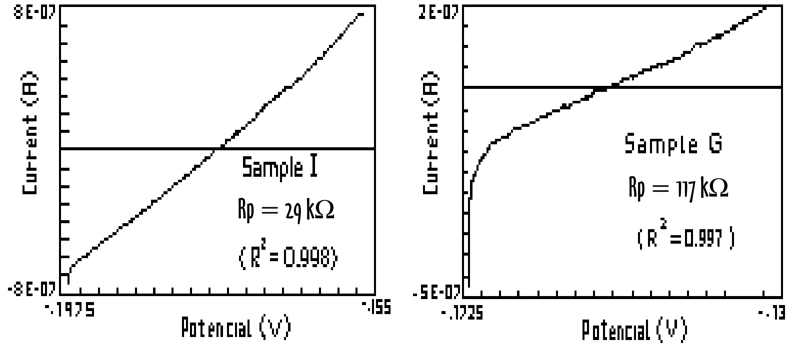

***Fig. 2**. LSV curves to calculate the polarization resistance (R_p) 20 mV around E_{oc}.*

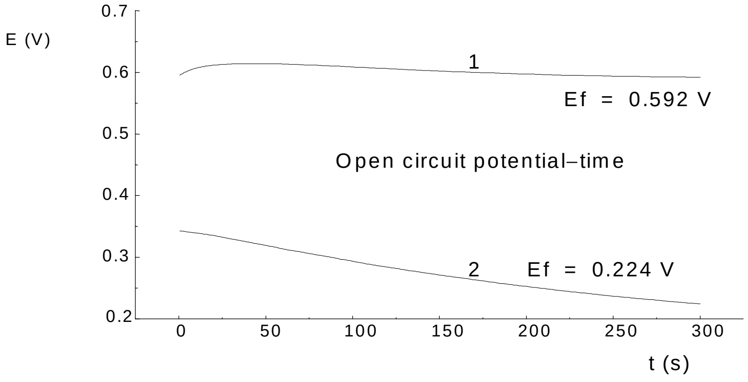

***Fig. 3**. Open circuit potencial (Eoc)–time for a sample of Aurolloyd fk in 1 % NaCl solution. Curves 1 and 2 represent different surface areas.*

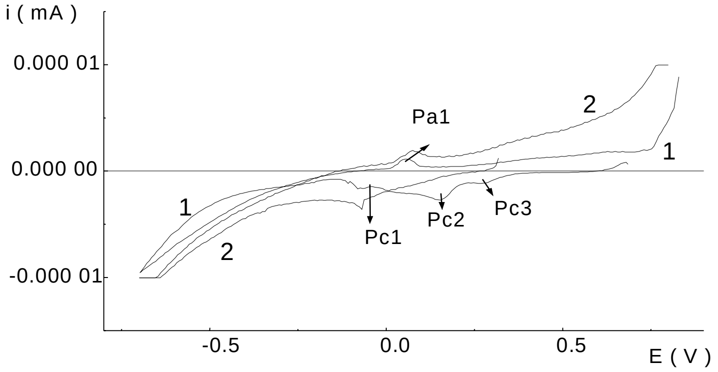

***Fig. 4**. CV curves for different surface points of Aurolloyd kf in 1 % NaCl solution. Curves 1 and 2 represent the same surface areas that in figure 3.*

that is, with the chemically adsorbed oxygen on the surface. This experiment demonstrated that these picks are strongly dependent on the end Eoc value (Fig. 3). The peaks Pc1 and Pa1 should be the reduction and oxidation of Ag in chloride solution, because these values are in agree with potential values of the electrode Ag(II)/Ag, but it should be confirmed. Comparing figures 3 and 4, it can be concluded that the results are similar.

Since this is a noble alloy (Au, Ag and Pt), the differences in electrochemical behavior strongly depend on surface oxides formed. For a better electrochemical characterization of this noble alloys a strong pretreatment that allowed a more homogeneous surface should be developed.

For a definitive conclusion, all these results have to be analyzed by the light of the Mixed Potential Theory.

CONCLUSION

These investigations show that LSV or CV methods can be usefull for the description of the electrochemical behavior of dental casting alloys. In case of non-precious alloys an assessment of the corrosion stability is given by the application of the mini cell-system. The characterization of precious alloys demonstrated also the partial inhomogeneity of the surface composition caused by casting procedures.

These kinds of measurement can be improved the knowledge about the corrosion behavior of dental alloys and can be used as check for the quality of them.

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