Some ideas about electrochemical characterization of dental alloys

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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 solución de algunos problemas relacionado 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 mutagenicas. 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 producto de la interacción celula-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 prótesis dentales. Por esta razón, ha recibido atención particular el desarrollo de un método rápido y sencillo que sirva para certificar el comportamiento corrosivo después de la preparación de estas prótesis.

El objetivo de este trabajo es mostrar 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 vs tiempo (E_{oc}) y Voltametría de Barrido Lineal (Rp) para la aleación Wiron 99, y Potencial a Circuito Abierto vs tiempo y Voltametría Cíclica (VC) para la aleación Aurolloyd kf. En el caso de la aleación Ni-Cr se concluye que con la combinación de ambos métodos es posible conocer como es el comportamiento corrosivo para una prótesis fundida de forma individual. Para la aleación de Au se concluye que la diferencia en el comportamiento electroquímico depende fuertemente de los óxidos superficiales formados. Estos resultados señalan que una de las combinaciones estudiadas, E_{oc}-Rp o E_{oc}-CV pudiera ser seleccionada como test de control después del proceso de fundido como certificación del comportamiento corrosivo de la prótesis dental.

Summary

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 prostheses. 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 of 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 quick and simple method for determining the corrosion behavior as a control test in the production *of a dental prosthesis is of great interest.*

The purpose of this work was to show 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 vs time and Liner Sweep Voltammetry for Wiron 99, and Open Circuit Potential vs time and Cyclic Voltammetry for Aurolloyd kf. In the case of the Ni-Cr alloys, it is concluded that with the combination of both methods, it is possible to know how the corrosion behavior of casting individual dental Ni-Cr alloy prosthesis is, and 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 one of the studied combination, E_{oc}-Rp or E_{oc}-CV characterization, could be selected as control test after casting of individual prosthesis.

Key Words: electrochemistry, dental alloy, corrosion behavior, biocompatibility.

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 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 elution of metal ions. Many studies have been done showing the influences of eluting metal ions on dental tissues, oral bacteria, and on allergic reactions.

As a result of the development of the past few years, a variety of endosseous dental implant systems has become available with widely different designs, surface textures, and material construction. A few systems have received official sanction for clinical use but, in general, there is little scientific evidence for the safety and efficiency of the majority of systems available. 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

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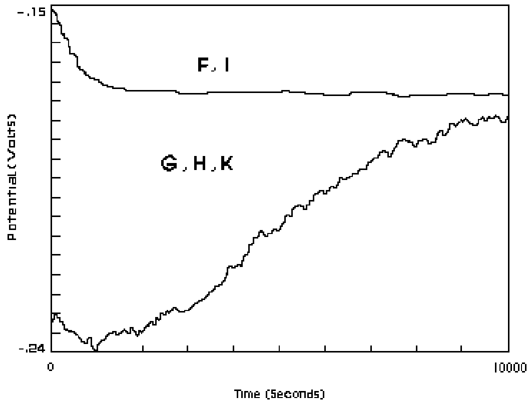


Figure 1 $E_{oc\ vs\ time}$ values for different samples (F, G, H, I, K) of Wiron 99 exposed in 0,1 N H_2SO_4 .

system. More fundamental research is needed on both materials and design for rational progress (9).

The aim of our research group is to develop a quick and simple electrochemical method for determining 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.

Materials and methods

The alloys were a commercial Ni-Cr alloy, Wiron 99 and a commercial Au alloy, Aurolloyd kf. Always the exposed area was 0,8 mm^2. The following pre-treatment were made before the experiments: wet polished with No. 500 emery paper, 6 micron and 3 micron diamond suspension and finally with an oxi-de 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(10). The reference Electrode was a saturated calomel electrode (SCE). It were used the following methods: Open Circuit Potential (E_{oc}) vs time, Liner Sweep Voltammetry (LSV) near E_{oc} or Cyclic Voltammetry (CV).

Results and discussion

Open Circuit Potential vs time and Liner Sweep Voltammetry

Figure 1 shows the E_{oc} values plotted against time 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, named F- or G-behavior. The E_{oc} values indicated that there are two different surfaces. Since this is a simple test we made another test to confirm our results.

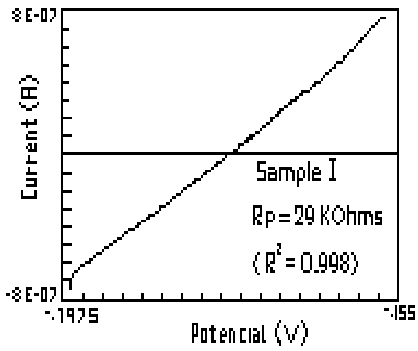
Figure 2 shows the LSV curves to calculate the polarization resistance (R_p) 20 mV around E_{oc} (Rp determination). These results indicate that the G-behavior samples have the higher Rp value, that is, a more passivated surface than the F-behavior samples and therefore they are in agreement with those of Figure 1.

The time spent for both methods is no more than 30 minutes, that means, it is a quick and easy procedure. With the combination of both methods, it is possible to know how the corrosion behavior of casting individual dental prosthesis is.

Open Circuit Potential vs time and Cyclic Voltammetry

Figure 3 shows the E_{oc} values plotted against time for different surface points of Aurolloyd kf in 1 % NaCl solution. There are 2 different curves. This difference is due to the degree of surface covering by oxygen. This result suggests that the potential is strongly dependent on the surface oxide formed on the alloy.

Figure 4 shows the CV curves for different



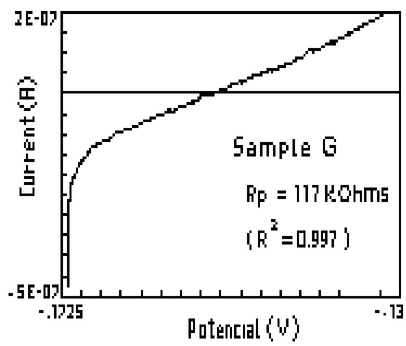


Figure 2 LSV curves to calculate the polarization resistence (R_p) 20 mV around E_{oc}

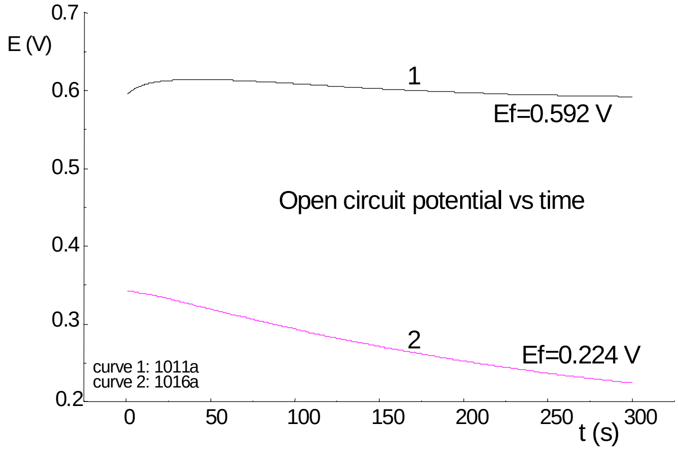


Figure 3 Open circuit potencial (Eoc) vs time for a sample of Aurolloyd fk in 1% NaCl solution. Curves 1 and 2 represent different surface points.

surface points of Aurolloyd kf in 1 % NaCl solution. There are 3 cathodic peaks (in other superficial points, only 2 peaks are observed) and only 1 anodic peak just before 0.0 V. The peaks, Pc2 and Pc3, are associated with the reduction of surface oxides, that is, with the chemically adsorbed oxygen. This experiment demonstrated that they depend on the end Eoc value . The peaks Pc1 and Pa1 should be the reduction and oxidation of adsorbed hydrogen, because they are near 0.0 V potential. It should be experimentally confirmed. These results are consistent with those of Figure 3.

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 pre-treatment that allowed a more homogeneous surface should be developed.

Conclusion

One of the studied combination, E_{oc}-Rp or E_{oc}-CV characterization, could be selected as control test after casting of individual prosthesis. It is necessary to find better conditions to decrease the experimental error of these methods. It is believed that these results will enhance the understanding of the corrosion behavior of dental casting alloys.

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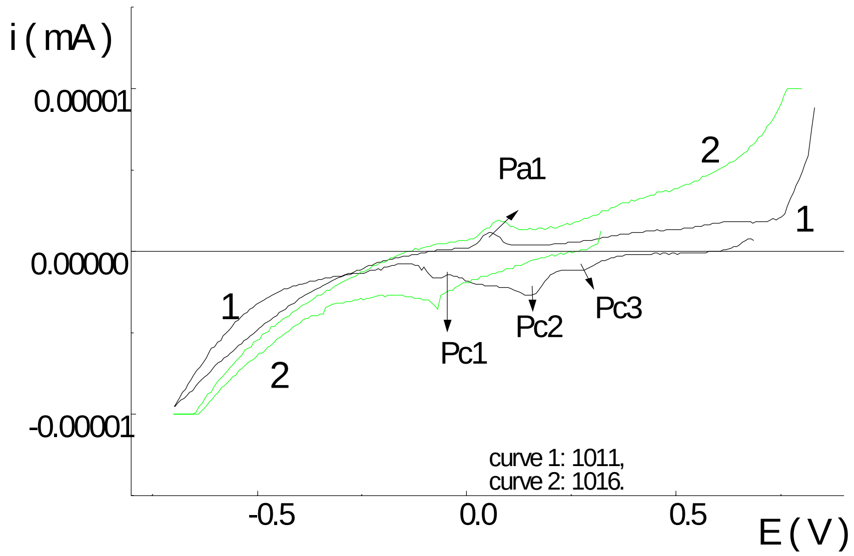

Figure 4 CV curves for different surface points of Aurolloyd kf in 1 % NaCl solution. Curves 1 and 2 represent the same surface points that in Fig. 3.

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