Electrochemical behavior of the commercial Ni-Cr-based alloy Wiron 99 in 0.05 mol/L sulphuric media

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Palabras clave: Aleación en base a Ni-Cr, comportamiento electroquímico, potencial a circuito abierto, resistencia de polarización
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RESUMEN. Durante las últimas dos décadas ha sido cada vez más frecuente el uso de las aleaciones Ni-Cr como una alternativa de las aleaciones de metales nobles en aplicaciones dentales, debido a que poseen mejores propiedades mecánicas y además, el costo intrínseco es despreciable comparado con los materiales tradicionales sobre la base de Au. La biocompatibilidad de materiales metálicos está íntimamente relacionada con su comportamiento corrosivo. La corrosión y la disolución de capas superficiales son dos mecanismos que introducen iones en el cuerpo humano. Por esta razón, en el presente trabajo se han estudiado 5 muestras de la aleación comercial de Ni-Cr Wiron 99 en disolución 0,05 mol/L de H_2SO_4 realizando mediciones de potencial a circuito abierto en el tiempo y de curvas de polarización potenciodinámicas. También se realizó un análisis químico de las disoluciones después de dejar un tiempo las muestras en ella y por último se hicieron estudios de microscopia electrónica. Se utilizó un sistema especial de mini-celda para realizar las determinaciones de potencial a circuito abierto (E_{OC}) y de resistencia de polarización (Rp). Para calcular Rp, se trazaron curvas de polarización potenciodinámicas 20 mV alrrededor de E_{OC} en la región anódica y catódica. Se obtuvieron micrografías de la superficie de las muestras después de ser sumergidas por separado, en una solución 0,05 mol/L de H_2SO_4 por varios días. Los valores de E_{OC} muestran que evidentemente existen dos comportamientos (llamados comportamiento G y F). Este resultado sugiere que existe un proceso de disolución complejo para las muestras con comportamiento G, donde los valores de E_{OC} varían rápidamente en el tiempo y por lo tanto la velocidad de disolución cambia también rápidamente en el tiempo. Sin embargo, las muestras con comportamiento F mostraron una velocidad de disolución más estable, debido a que los valores de E_{OC} se mueven ligeramente en el tiempo. Los resultados de la determinación de Rp indican que las muestras con comportamiento G tienen el valor más alto de Rp (alrededor de 4-5 veces), lo que demuestra que estas muestras tienen una superficie más pasiva que las muestras con comportamiento F. Con estos resultados se concluye que las muestras presentaron dos comportamientos diferentes, llamados comportamiento F y G. El segundo de éstos, manifiesta una superficie pasiva y por lo tanto más estable que el primero. Este resultado se pudo confirmar con el análisis químico y los estudios de microscopia.

ABSTRACT. During the last two decades, Ni-Cr-based alloys have become frequently used in dental applications as an alternative to alloys based on noble metals, because their mechanical properties are best and the intrinsic cost is negligible compared to the traditional gold-based materials. The biocompatibility of metallic materials is closely related to their corrosion behavior. Corrosion and surface film dissolution are two mechanism to introduce additional ions into the human body. For this reason in this work, the corrosion behavior of five samples the commercial Ni-Cr-based alloy Wiron 99 in 0,05 mol/L H_2SO_4 solution have been studied by means of open circuit potential time measurements, potentiodynamic polarization curves, chemical analysis of the solutions after exposure and SEM studies. A special mini-cell was used for open circuit potential (E_{OC}) and polarization resistance (Rp) determination. Potentiodynamic polarization curves were made in order to calculate the polarization resistance 20 mV around open circuit potential in the cathodic and anodic region. After all samples were individually immersed in 0,05 mol/L H_2SO_4 solution for several days, micrographs of the surface were made and the concentration of Ni was determined by atomic absorption analysis. The E_{OC} values showed that evidently there exist two behaviors (named F- and G-behavior). This result suggests a complex dissolution process for G-behavior samples, where the E_{OC} values fast move with time and therefor the dissolution rate changes fast with time. However, the F-behavior samples showed a more stable dissolution rate, because the E_{OC} values slowly move with time. The Rp results indicate that the G-behavior samples have the higher Rp value (around 4-5 times), which means that these have a more passivated surface than the F-behavior samples. With these findings it was concluded that the samples show two different behaviors, called F-behavior and G-behavior. The second one suggests a passivated and consequently, a more stable surface than the first one. This fact was confirmed by microscopic studies and chemical analysis.

INTRODUCTION

During the last two decades, Ni-Cr-based alloys have become frequently used in dental applications as an alternative to alloys based on noble metals, because their mechanical properties are best and the intrinsic cost is negligible compared to the traditional gold-based materials. The amount of nickel in these alloys ranges between 65 and 81 % by weight and the amount of chromium between 11 and 22 % by weight. Elements such as molybdenum, aluminium, copper, beryllium and titanium are added in order to obtain carefully controlled properties.[1]

The biocompatibility of metallic materials is closely related to their corrosion behavior. Corrosion and surface film dissolution are two mechanism to introduce additional ions into the human body. Since nickel is a known allergen an even a suspected carcinogen metal,[2] the rates of corrosion of dental Ni-Cr alloys are of high interest.

Kuhn and Rae[3] has recently critically reviewed the literature on this matter. Although the majority of these investigations have been designed to determine the uniform corrosion rates of these alloys in artificial saliva,[4-9] only few attempts have been made to determine the potentiodynamic characteristic in alkaline[10-11] and chloride[11] solutions or the physical and mechanical properties of different Ni-Cr-based alloys,[12] but no studies have been made to determine the corrosion behavior in acidic media.

Depending of the casting process during the production of a dental prosthesis, these alloys may show different phases, ones may be more stable than others. 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 high interest.

In the present work the corrosion behavior for a commercial Ni-Cr-based alloy Wiron 99 has been investigated in 0,05 mol/L H_2SO_4 solution by means of open circuit potential time measurements, potentiodynamic polarization curves, chemical analysis of the solutions after exposure and SEM studies.

MATERIALS AND METHODS

Five samples of a commercial Ni-Cr-based alloy Wiron 99 have been investigated in 0,05 mol/L H_2SO_4 solution. The composition of the alloy is shown in Table 1. The samples were wet polished with No. 500 emery paper, 6 micron and 3 micron diamond suspension and finally with an oxide polisher suspension. Prior to starting the measurements they were degreased in acetone.

Table 1. Composition (wt %) of the commercial Ni-Cr-based alloy Wiron 99

Ni	Fe	Cr	Mo	Nb	Si	Ce
65	0,5	22,5	9,5	1	1	0,5

A special mini-cell[13] with a volume of about 5 mL was used for open circuit potential (E_{oc}) and polarization resistance (Rp) determination. The exposed area of the samples was 0.8 mm^2. The composition of the used solution was 0,05 mol/L H_2SO_4. During the measurements the solution was not stirred. A saturated calomel electrode (SCE) was used as reference electrode. All potentials are referred to SCE. After the samples were immersed in the solution to obtain a constant value of E_{oc}, potentiodynamic polarization curves were made in order to calculate the polarization resistance (Rp) 20 mV around Eoc in the cathodic and anodic region with a speed (scan rate) of 0,1 mV/s. The experiments for one sample were repeated at least 3 times. All electrochemical measurements were made on a EI-SI 1286 (England) and controlled by a computer using the Correware 1.2 program.

In some cases, after the electrochemical measurements had been completed, micrographs of the surface were made by a Light Microscope METAVAL (Karl-Zeiss, Jena, Germany). After all samples were individually immersed in 0.05 mol/L H_2SO_4 solution for several days, micrographs of the surface were made by a AMRAY 1810 SEM Microscope (USA) and the concentration of Ni was determined by atomic absorption analysis.

RESULTS AND DISCUSSION

Figure 1 shows the E_{oc} values plotted against time for different samples (F, G, H, I, K) of Wiron 99 exposed in 0,05 mol/L H_2SO_4. Evidently there exist two behaviors. At the beginning of the experiment, the E_{oc} values are less anodic for samples which named in the following text as G-behavior. This suggests a complex dissolution process in these samples, where the E_{oc} values fast move with time and therefor the dissolution rate changes with time too. In contrast, the shape of the curves of the other group of samples, later named as F-behavior, indicates a more stable dissolution rate, because the E_{oc} values slowly move with time. In the G-behavior group, the E_{oc} values show a minimum (after 0.5-1 hour) and approach to a more anodic state from the active to the passive zone. However the E_{oc} value for an exposure time of 3-4 hours is the same for both behaviors (Table 2). These results are consistent with earlier investigations[9] of other Ni-Cr-based alloys in artificial saliva. So the E_{oc} vs. t curves give an acceptable information about differences of the electrochemical stability in a short time scale.

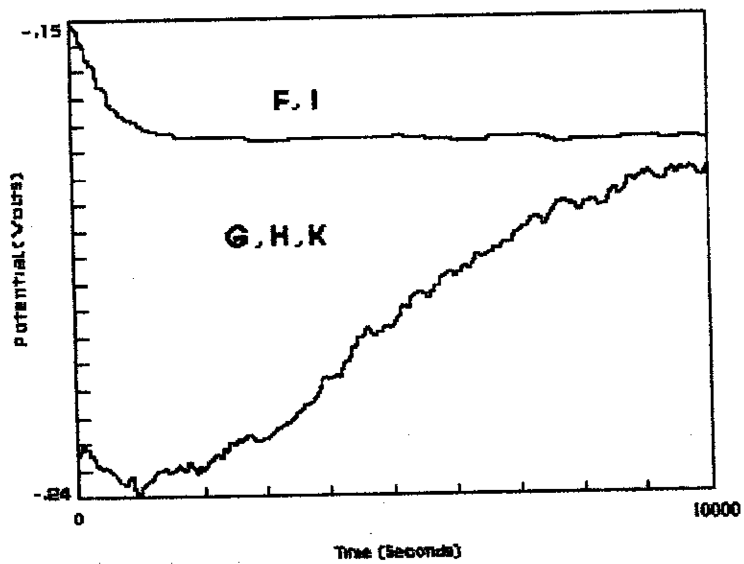


Fig. 1. *The values of E_{oc} plotted against time for different samples (F, G, H, I, K) of Wiron 99 exposure in 0.05 mol/L H_2SO_4*

Table 2. E_{oc} value of Wiron 99 for an exposure time of 3-4 hours in 0.05 mol/L H_2SO_4

Sample	Mean value of E_{oc} (mV)	Number of values (n)	Standard deviation (S) (mV)	Standard error (ε) (mV)
F	–201*	27	3.835	0.74
I	–201*	3	4.725	2.73
G	–187*	11	20.27	6.11
H	–198*	5	17.57	7.86
K	–202*	6	16.32	6.66
Wiron 99	–198	52	13.00	1.80

*The means are NOT significantly different at the 0.05 level (ANOVA test)

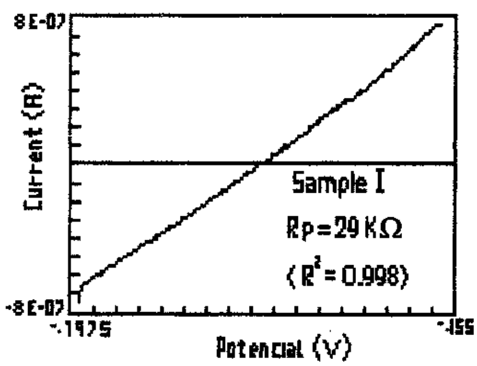
At the end of the E_{oc} monitoring, potentiodynamic polarization curves for Rp determination in F-behavior and G-behavior samples (Fig. 2) were obtained. Table 3 gives the Rp mean and other statistical values. These results indicate that the G-behavior samples have the higher Rp value (around 4-5 times), which means that these have a more passivated surface than the F-behavior samples.

After all samples were separately introduced in 0.05 mol/L H_2SO_4 solution for 4 days, the E_{oc} and the potentiodynamic polarization curves for Rp calculation, were determined immediately afterwards. Figure 3 shows these curves for two experiments. These results indicate a more passivated surface for the G-behavior samples (E_{oc_2} = 320 mV, Rp = 1 059 kΩ · 0.8 mm^2 = 8.5 kΩ · cm^2), than for the F-behavior samples (E_{oc_2} = –197 mV, Rp = 10 Ω · 0.8 mm^2 = 80 Ω · cm^2). A similar behavior is shown by the latter for a 3-4 hours exposure in the same solution (Fig. 1). In contrast, the G-behavior samples show a more passivated surface with a more anodic E_{oc} value (around 400 mV) and a higher Rp value (around 5-6 times).

In order to confirm these results several micrographs by light and (or) SEM microscope to determine the structural characteristic of the sample surface were undertaken. Figures 4 and 5 show SEM micrographs displaying the structure of the I and K samples respectively after 2 days of exposure in 0.05 mol/L H_2SO_4 solution. The samples were partially immersed in this solution. In Figure 4 the corroded area of the I sample is shown. There are two phases, one more sensitive to corrosion than the other. It was not possible to determine the composition of these phases. In Figure 5 only a little corrosion is observed. Few pits can be seen in the whole display for the K sample.

To confirm that the dissolution rate of F-behavior samples is higher than dissolution rate of G-behavior samples, atomic absorption analysis of the solutions after 12 days of exposure was made. The results (Table 4) show that Ni dissolution in the F-behavior samples was 100-300 times higher than in the other ones.

All these results are consistent ones with others and show that the F-behavior samples are more corroded than the G-behavior ones.



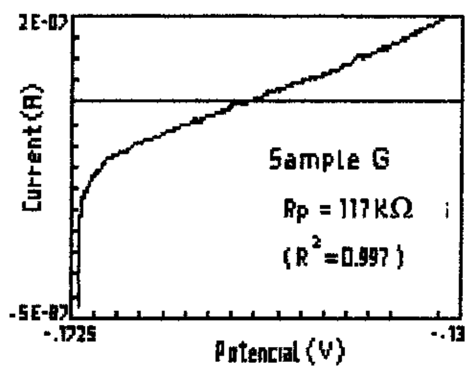


Fig. 2. *The potentiodynamic polarization curves for Rp determination in F-behavior and G-behavior samples of Wiron 99*

Table 3. Rp value of Wiron 99 for a exposure time around 3-4 hours in 0.05 mol/L H_2SO_4

Sample	Mean value of Rp (MΩcm^2)	Number of values (n)	Standard deviation (S) (MΩcm^2)	Standard error (ε) (MΩcm^2)
F-behavior	3.2*	12	0.572	0.2
G-behavior	15*	19	5.125	1.0

*The means are significantly different at the 0.05 level (ANOVA test)

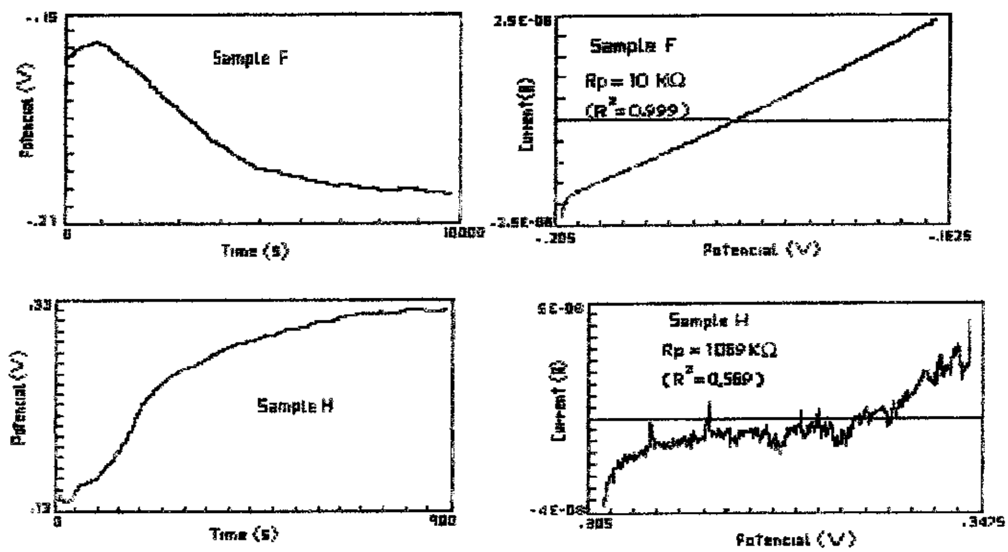


Fig. 3. *The E_{oc} and the potentiodynamic polarization curves for Rp determination in F-behavior and G-behavior samples of Wiron 99 after 4 days exposure in 0.05 mol/L H_2SO_4*

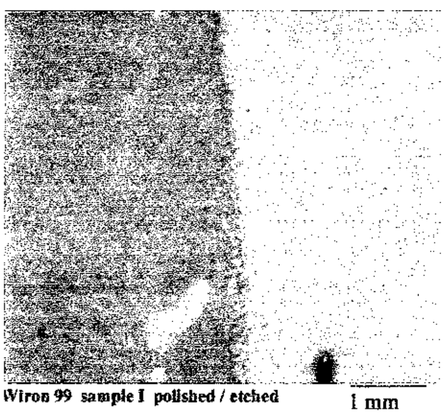


Fig. 4. *SEM micrographs of I sample after 2 days of exposure in 0.05 mol/L H_2SO_4 solution. Magnification 1 040 x*

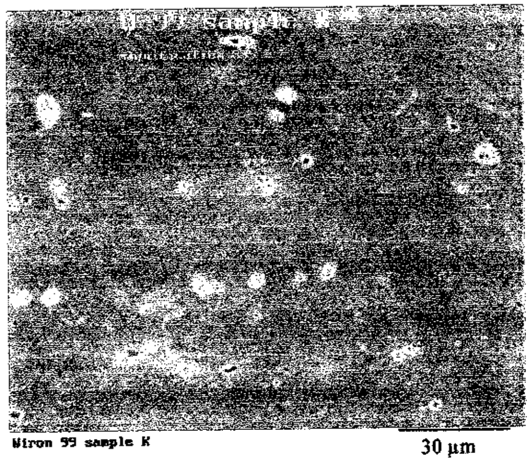


Fig 5. *SEM micrographs of K sample after 2 days of exposure in 0.05 mol/L H_2SO_4 solution. Magnification 835 x.*

Table 4. Concentrations of Ni dissolved from different samples of Wiron 99 in 0.05 mol/L H_2SO_4. Exposure time of 12 days

	Samples			
	F	I	K	G
Ni conc. (ppm)	1 100	1 100	9.8	3.8

CONCLUSIONS

The monitoring of the E_{oc} values as a function of exposure time and the polarization resistance determination give an acceptable information of the dissolution rate of the commercial Ni-Cr based alloy Wiron 99 and could be used as a control method in the production of dental prosthesis.

The investigated samples show two different behaviors, the called F- and G-behavior. The F-behavior samples have a low Rp value (less resistant to corrosion) and a more corroded surface, because the E_{oc} value is in practice constant, at least during the first 3 days of exposure. This value corresponds with a intensive corrosion process in the active zone.

The G-behavior samples have a more irregular E_{oc} curve. The surface was slowly corroded with time and at the end of the experiment (4 days) higher Rp values and more anodic E_{oc} values, were obtained, which correspond with a passivated surface.

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