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# CORROSION RESISTANCE OF Ni-Cr ALLOYS IN DIFFERENT MOUTHWASHES

## *RESISTÊNCIA À CORROSÃO DE LIGAS DE NI-CR EM DIFERENTES ENXAGUATÓRIOS BUCAIS.*

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**SUMMARY:**
Several alloys have been used for prosthodontics restorations in the last years. These alloys have a number of metals that include gold, palladium, silver, nickel, cobalt, chromium and titanium and they are used in oral cavity undergo several corrosion. Corrosion can lead to poor esthetics, compromise of physical properties, or increased biological irritation. The objective of this study was evaluated corrosion resistance of two alloys Ni-Cr and Ni-Cr-Ti in three types of mouthwashes with different active ingredients: 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride, 0.05% sodium fluoride + 0.03% triclosan (with fluor) and 0.12% chlorohexidine digluconate. The potentiodynamic curves were performed by means of an EG&G **PAR 283** potentiostat/galvanostat. The counter electrode was a platinum wire and reference electrode was an Ag/AgCl, KCl saturated. Before each experiment, working electrodes were mechanically polished with 600 and 1200 grade papers, rinsed with distilled water and dried in air. All experiments were carried out at 37.0°C in conventional three-compartment double wall glass cell containing mouthwashes. The microstructures of two alloys were observed in optical microscopy. Analysis of curves showed that Ni-Cr alloy was less reactive in the presence of 0.12% chlorohexidine digluconate while Ni-Cr-Ti alloy was more sensitive for others two types of mouthwashes (0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride ® and 0.05% sodium fluoride + 0.03% triclosan). This occurred probably due presence of titanium in this alloy. Microstructural analysis reveals the presence of dendritic and eutectic microstructures for Ni-Cr and Ni-Cr-Ti, respectively.
**UNITERMS:** Corrosion, titanium, mouthwashes.

## INTRODUCTION

Metallic biomaterials have been widely used in dental applications because their excellent properties such as good processability, weldability and satisfactory mechanical properties. Several alloys have been used for prosthodontics restorations in the last years. These alloys have a number of metals that include gold, palladium, silver, nickel, cobalt, chromium and titanium. The most commonly used base metal alloy in dentistry is nickel-chromium-based alloy, which is commonly used of crown, bridge casting, inlays and denture bases. Chromium as an alloying element is used to form a passive film on the surface protecting the alloy against corrosion. Titanium is also added to the alloy to enhance to mechanical properties and corrosion resistance [1].

However, the main inconvenience of these materials is their degradation upon interaction with body fluids. Corrosion of the dental alloys, may exhibit biological, functional and aesthetic effects. Metal ions are released and may come into contact with cells and tissues in the close environment, or be distributed throughout the entire body. If these ions are not biocompatible, the organism may be injured [2-3].

Huang [4, 5] investigated the compositional influence on the corrosion behavior of Ni-Cr-based alloys dental casting in acidic artificial saliva. Cyclic potentiodynamic and potentiostatic tests were used to evaluate the corrosion in deaerated artificial saliva with pH 5 at 37°C. Ni-Cr-Mo alloys with higher Cr (21%) and Mo (8%) contents had a much larger passive range in the polarization curve and were immune to pitting corrosion due to presence of high Cr and Mo contents in the surface passive film. The presence of Ti lower than 4% in the Ni-Cr-Mo casting alloy had no effect on corrosion resistance.

According Bayramoglu [6] the corrosion characteristics of metals and alloys are dependent on

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the composition of the alloy, surface roughness, temperature and pH of media and presence of inhibitors.

Actually, there is an increased use of dental gels and rinses containing high fluoride concentration (10,000 ppm) and a pH range between 7.2 and 3.2 [7]. The effects of fluoride on titanium and its alloys have been investigated for many researchers [8-11]. However, the effect of fluoride solutions over Ni-Cr alloys has not been reported.

The purpose of the present study was to compare the electrochemical behavior and corrosion resistance of two Ni-Cr-based alloys in three commercial mouthwashes.

## MATERIALS AND METHODS

Two dental casting alloys were used as test specimens, Ni-Cr (Verabond II) and Ni-Cr-Ti (Tilite) alloys. Compositions, specifications and manufacturer information are listed in Table I.

The wax patterns (5 x 20 mm and cross-section of 1 $cm^2$) were invested in phosphate-bonded investment and cast in centrifugal casting machine with base-metal alloys. After casting, cylinders were mounted in polyester resin and employed as working electrodes. The counter electrode was a platinum wire and reference electrode was an Ag/AgCl, KCl saturated electrode.

| Metal Alloy | Composition (wt%) | Manufacturer |
|---|---|---|
| Verabond II | Ni 75.0; Cr 11.5; Mo 3.5; Si 3.5; Al 2.25; Nb 4.25 | Aalba Dent, Cordelia, Calif |
| Tilite | Ni 63.5; Cr 13.5; Mo 6.0; 4.0 Ti | Talladium Inc, Valencia, Calif |

Table 1- Commercial metal-base alloys

| Mouthwashes | Active ingredients |
|---|---|
| 0.05% sodium fluoride + 0.03% triclosan® | 0.05% sodium fluoride + 0.03% triclosan, pH = 5.1 |
| 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride ® | 0.5 g $l^{-1}$ cetylpyridinium chloride + 0.05% sodium fluoride, pH = 7.3 |
| 0.12% chlorohexidine digluconate ® | 0.12% chlorohexidine digluconate, pH = 5.7 |

Table 2- Chemical composition of commercial mouthwashes

Experiments were made at 37.0 ± 0.5 °C in a conventional three-compartment double wall glass cell containing commercial mouthwashes. Three mouthwashes with different active ingredients were used as the corrosion test electrolyte (Table II) according previous study [12]. For comparison, electrochemical behavior of Ni and Cr pure in inorganic active ingredient (0.05% Na F pH = 6.0) was also studied.

Potentiodynamic polarization curves were performed by means of an EG&G PAR Potentiostat/Galvanostat Model 283 (PerkinElmer Instruments Inc., USA). These curves were recorded in electropositive direction at a sweep rate of 0.02 V $min^{-1}$ starting from –1.00 V up to 2.50 V. Corrosion behavior was studied in naturally aerated conditions. Before each experiment, working electrodes were ground with 600 and 1200 grade emery papers, rinsed with distilled water and dried in air.

For microstructural analysis, ingots were sectioned using a cut-off machine (Accuton, Struers, Denmark) with diamond/CBN (cubic boron nitride) wafering blade and embedded in resin to facility their handling. After this, the cold mounting specimens was ground for analysis wet grinding up to 2400 grits with SiC using water. Samples were etched with Kroll's reagent and microstructures observed in optical microscope (Epiphot 200, Nikon, Japan).

## RESULTS AND DISCUSSIONS

Micrographs of Ni-Cr and Ni-Cr-Ti alloys in the as-cast condition are showed in Fig. 1 (A and B). Metallographic examination of alloy Ni-Cr, without Ti, reveals the presence of dendritic microstructure while Ni-Cr-Ti alloy exhibited eutectics regions. Eutectic alloys are very interesting for dental applications because these alloys exhibit casting temperature lower than pure elements (Ni, Cr and Ti).

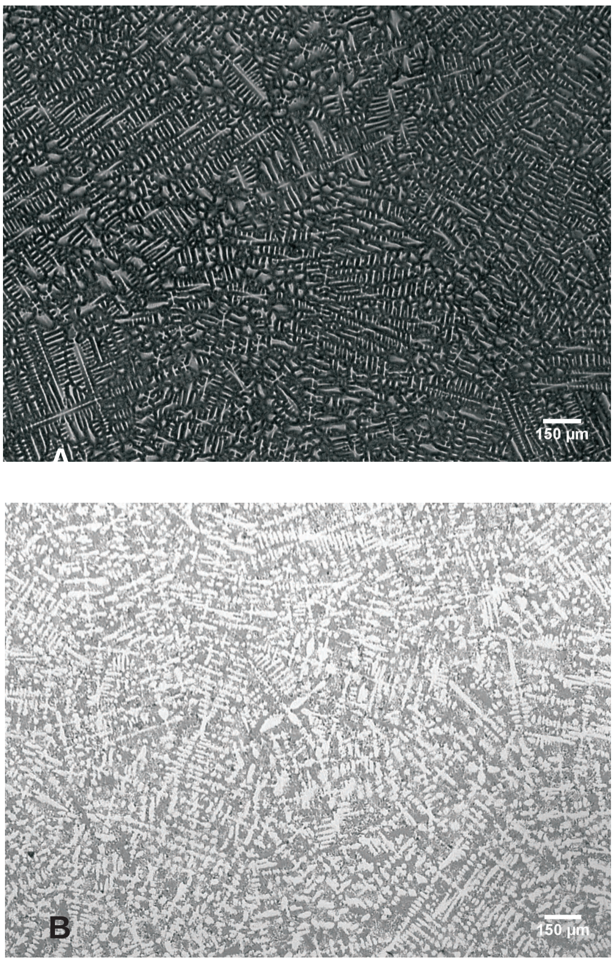


FIGURA 1 - Microstructures of Ni-Cr (A) and Ni-Cr-Ti alloys (B)

Potentiodynamic polarization curves of Ni-Cr and Ni-Cr-Ti alloys in naturally aerated mouthwashes have been recorded at a sweep rate of 0.02 V $min^{-1}$, between –1.00 and 2.50 V. All curves exhibit the similar general features (Fig. 2a and b). Cathodic branches exhibit a current density that decrease, as applied potential is set less negative. Cathodic reaction is assumed to be proton and/ or oxygen reduction. Anodic branches show passive and transpassive regions. These regions may be associated with formation and breakdown of one or more protective films. From potentiodynamic polarization curves of nickel and chrome pure in 0.05% NaF only in chrome a passive electrochemical behavior was confirmed (Fig. 3). Passivation process of Ni-Cr-based alloys in aqueous solutions was mainly related to chromium oxides present in the spontaneously formed film [5].

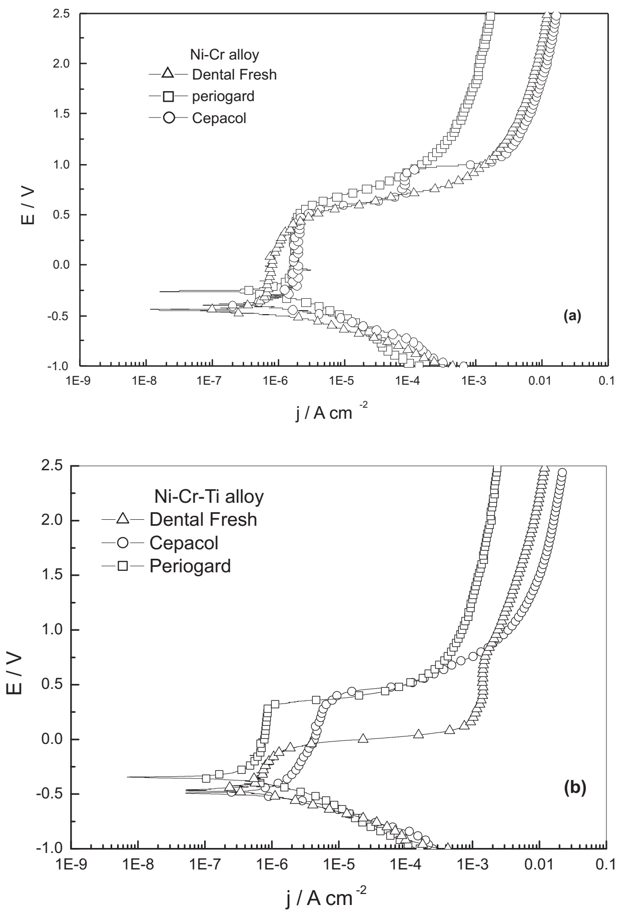


FIGURA 2- Potentiodynamic polarization curves for Ni-Cr (a) and Ni-Cr-Ti alloys (b) in commercial mouthwashes

The electrochemical behavior of Ni-Cr alloy in 0.12% chlorohexidine digluconate, 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride and 0.05% sodium fluoride + 0.03% triclosan mouthwash was similar (Fig. 2a). This alloy presents itself passive with a passive current density ~1 μA $cm^{-2}$ and a breakdown potential ~0.46 V. In the transpassive region at 2.50 V, the current density due to the electrooxidation and dissolution of the alloy elements was about ten times smaller with 0.12% chlorohexidine digluconate .

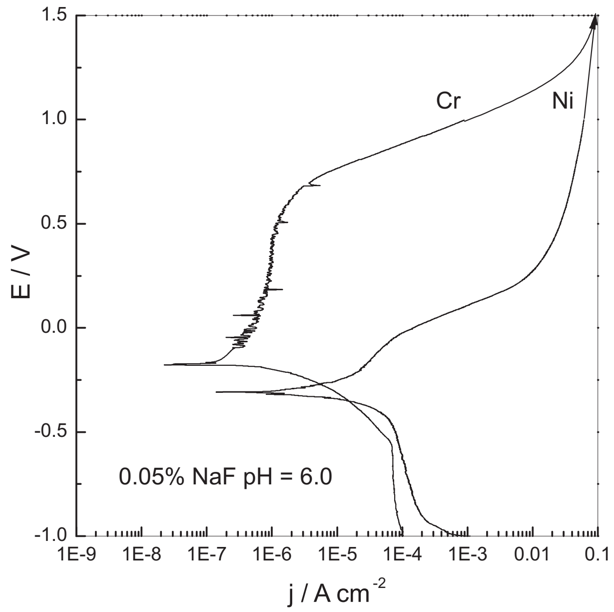


FIGURA 3 - Potentiodynamic polarization curves for Ni and Cr in 0.05 % sodium fluoride

On the other hand, the electrochemical behavior of Ni-Cr-Ti alloy was different in the three mouthwashes (Fig. 2b). In 0.12% chlorohexidine digluconate and 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride , this alloy also presents itself passive with a passive current density ~1 μA $cm^{-2}$ and ~3 μA $cm^{-2}$, respectively. Similar breakdown potential were observed (~0.35 V). In the transpassive region at 2.5 V, the current density due to the electrooxidation and dissolution of the alloy components was again about ten times smaller with 0.12% chlorohexidine digluconate (without fluoride) than with 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride . In 0.05% sodium fluoride + 0.03% triclosan, this alloy exhibits a relatively poor passivation and after film dissolution, the electrooxidation and dissolution of the less noble elements rapidly happens.

Corrosion behavior of these alloys is more affected by alloys compositions and microstructure than by mouthwash type. Passive film on Ni-Cr alloy appears to be more stable that on Ni-Cr-Ti alloy. Complex action of fluoride ions on titanium or titanium species [8-11], can provoke localized attack and partial dissolution of this protective film.

## CONCLUSIONS

Corrosion behavior of dental materials here studied is more affected by Ni-Cr alloy composition and microstructure than by mouthwash type. Passivation phenomenon was observed in both alloys in the three mouthwashes. However, spontaneously formed passive film on Ni-Cr alloy appears to be more stable. Differences in passive current densities values may be connected with changes in film porosity and thickness in each mouthwash. Protective characteristics of passive film on Ni-Cr-Ti alloy are significantly lower in 0.5g/l cetylpyridinium chloride + 0.05% sodium fluoride and 0.05% sodium fluoride + 0.03% triclosan than in 0.12% chlorohexidine digluconate mouthwashes. Probably, fluoride ions presents in the first mouthwashes provoke a selective attack on titanium or titanium species in the passive film.

**RESUMO:** *Várias ligas têm sido utilizadas na confecção de restaurações protéticas nos últimos anos. Essas ligas apresentam na sua composição ouro, paládio, prata, níquel, cobalto, cromo e titânio; quando na cavidade bucal são passíveis de corrosão, a qual pode empobrecer a estética e comprometer as propriedades físicas e biológicas. O objetivo deste trabalho foi avaliar a resistência a corrosão de duas ligas odontológicas, Ni-Cr e Ni-Cr-Ti em três tipos de colutórios bucais com diferentes ingredientes ativos: colutório I – 0.5g/l de cloreto de cetilpiridíneo +0.05 de fluoreto de sódio; colutório II -0.05 de fluoreto de sódio + 0.03% de triclosan e colutório III – 0.12% de diclonato de clorexidina. Curvas potenciodinâmicas foram realizadas por meio de potenciostato PAR283 e célula de vidro convencional de parede dupla para termostatização. Utilizou-se eletrodo de referência Ag/ AgCl, KClsat e auxiliar espiral de platina. A microestrutura das duas ligas foi observada por meio de microscopia ótica. Análise das curvas obtidas mostraram que a liga Ni-Cr foi menos reativa na presença de digluconato de clorexida a 0.12%, enquanto a liga Ni-Cr-Ti foi mais sensível para os outros dois tipos de colutório. Isto ocorreu , provavelmente, devido a presença de titânio na composição desta liga. Análise microestrutural revelou microsestrutura dendrítica na liga Ni-Cr e eutéticos na liga Ni-Cr-Ti.*

**UNITERMOS:** Corrosão, titânio, antisséptcos bucais

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