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Effect of commercial mouthwashes on the corrosion resistance of Ti-10Mo experimental alloy

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Abstract The purpose of this work was to evaluate the effect of three commercial mouthwashes on the corrosion resistance of Ti-10Mo experimental alloy. Experiments were made at $37.0 \pm 0.5°C$ in a conventional three-compartment double wall glass cell containing commercial mouthwashes. Three mouthwashes with different active ingredients were tested: (I) 0.05% sodium fluoride +0.03% triclosan; (II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride; (III) 0.12% chlorohexidine digluconate. The assessment of the individual effect of active ingredients was studied by using 0.05% sodium fluoride. Commercially pure titanium (CP Ti) was used as control. Microstructures from Ti-10Mo experimental alloy and CP Ti were also evaluated using optical microscopy. Ti-10Mo as-cast alloy shows the typical rapidly cooled dendrites microstructure (β phase) while CP Ti has exhibited a metastable martensitic microstructure. Electrochemical behavior of dental materials here studied was more affected by mouthwash type than by Ti alloy composition or microstructure. In both alloys passivation phenomenon was observed. This process may be mainly related to Ti oxides or other Ti species present in spontaneously formed film. Small differences in passive current densities values may be connected with changes in film porosity and thickness. Protective characteristics of this passive film are lower in 0.05% sodium fluoride +0.03% triclosan mouthwash than in the other two mouthwashes tested.

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1 Introduction

Several metals and its alloys have been used in dentistry in manufacture of crowns, bridges, casting, inlays and denture bases. Nickel-chromium and cobalt-chromium are alloys most commonly used. Recently, titanium and titanium alloys have been used for these applications [1, 2].

Although Ti-6Al-4V alloy and V free $\alpha + \beta$ type alloys such as Ti-6Al-7Nb and Ti-5Al-2.5Fe have been extensively used in dentistry [3, 4], studies have shown that the release of aluminium and vanadium ions from these alloys might cause some long term health problems, such as peripheral neurological diseases [5, 6].

Many attempts have been made to develop titanium alloys of different compositions to achieve better performance in terms of biocompatibility [7, 8]. Ho *et al.* [9] studied a series of binary Ti-Mo alloys with molybdenum contents ranging from 6 to 20 wt.%. Experimental results have indicated that both crystalline structure and microstructures of the cast alloys are sensitive to their molybdenum contents. Bending strength of Ti-10Mo alloy was 1750 MPa the highest among all Ti-Mo alloys. This value was a little lower than Ti-6Al-4V (1860 MPa) and twice higher than that found for commercially pure titanium (884 MPa). Also Ti-10Mo has exhibited the highest modulus (94 GPa) between Ti-Mo system. Despite this value to be lower than Co-Cr alloys and Ni-Cr alloys it is near Ti-6Al-4V (105 GPa) and higher than commercially pure titanium making this alloy a candidate for dental applications.

The high corrosion resistance of titanium and its alloys in various test solutions, such as artificial saliva and other physiological media, is due to formation of a very protective oxide layer on implant surface. There is an increased use of dental gels and rinses containing fluoride for caries dental prevention applications. Fluorides are inimical to all reactive metals such as titanium and its alloys, especially in acidic media, causing corrosion due to destruction of their passivity and loss of mechanical properties [10].

In a previous work, corrosion resistance of Ti-10Mo experimental alloy in fluoridated physiological serum was studied and compared with Ti-6Al-4V alloy [11]. Similar electrochemical response has been obtained. In naturally aerated physiological serum, corrosion rate is mainly controlled by dissolution process of a complex passive film. On the other hand, relatively few researches have been carried out to analyze the influence of fluoridated mouthwashes on corrosion resistance of dental alloys [12].

In the present work, microstructural characteristics and corrosion resistance of Ti-10Mo experimental alloy for dental applications in three commercial mouthwashes were evaluated and compared with commercially pure titanium (CP Ti).

2 Materials and methods

Each button of Ti-10Mo experimental alloy was made by melting of commercially pure titanium (CP Ti) grade 1 and commercially pure molybdenum (99.9%) into one 15 g button (∼1.3 cm diameter and ∼2.6 cm length) in an argon-arc melting furnace. The ingots were remelted ten times in order to improve chemical homogeneity.

2.1 Microstructural analysis

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 provide their handling. After this, specimens were ground for analysis using the following technique: wet grinding up to 2400 grit with SiC using water plus paraffin. Chemical polishing was done with fluid formed by two solutions: solution A (50 ml of H_2O, 25 ml of HNO_3 and 15 ml of HF) plus solution B (30 ml of colloidal silica and 30 ml of water). Samples were etched with Kroll's reagent and microstructures were observed in optical microscope (Epiphot 200, Nikkon, Japan).

2.2 Electrochemical studies

Cylinders (with cross-section of 1 cm^2) were machined from ingots of Ti-10Mo experimental alloy. These cylinders and CP Ti discs with 1.1 cm diameter were mounted in polyester resin and employed as working electrodes. Before each experiment, working electrodes were ground with 600 and 1200 grade emery papers, rinsed with distilled water and dried in air. The counter electrode was a platinum wire and reference electrode was an Ag/AgCl, KCl saturated electrode. The open circuit potential measurements, potentiodynamic and chronoamperometric curves were performed by means of an EG&G PAR Potentiostat/Galvanostat Model 283 (PerkinElmer Instruments Inc., USA).

Experiments were made at $37.0 \pm 0.5°C$ in a conventional three-compartment double wall glass cell containing commercial mouthwashes. Three mouthwashes with different active ingredients were tested: I) 0.05% sodium fluoride +0.03% triclosan pH = 5.1; II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride pH = 7.3; III) 0.12% chlorohexidine digluconate pH = 5.7. The assessment of individual effect of active ingredients was studied by using 0.05% sodium fluoride pH = 6.0. Corrosion behavior was studied in naturally aerated conditions. Open circuit potential measurements were recorded during an immersion time of 8 h. Potentiodynamic polarization curves were recorded in electropositive direction at a sweep rate of 0.02 V/min starting from −1.00 V up to 2.50 V. Chronoamperometric curves were recorded at different potential values into the anodic potential range (0.50 and 2.00 V).

3 Results and discussion

3.1 Microstructural characterization

In order to correlate the corrosion behavior of alloy under study, metallographic examination was performed. Micrographs of CP Ti and Ti-10Mo alloy in as-cast condition are showed in Figs. 1a and 1b. Samples have exhibited different microstructures. For Ti-10Mo (Fig. 1b), a typical rapidly cooled dendrites microstructure (β phase) was observed while CP Ti has exhibited a metastable martensitic microstructure (Fig. 1a). Evidence that these materials have distinct matrix and phases suggests that there should be local differences in composition and microstructure of surface film. In this sense, the corrosion behavior will depend not only on the microstructure of CP Ti and Ti-10Mo alloy, but also on the physical-chemistry characteristics of passive film formed on the metallic surfaces.

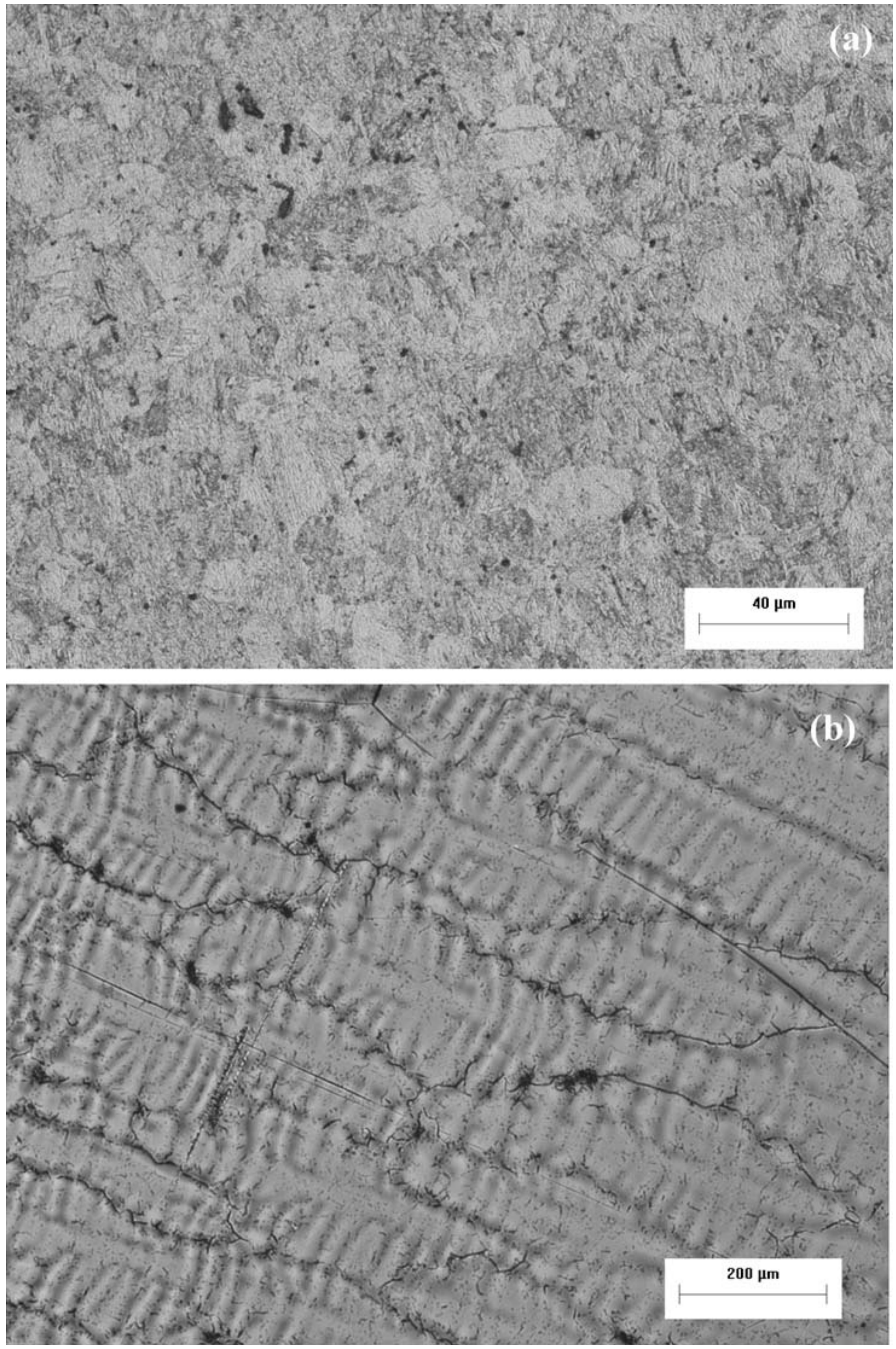

Fig. 1 Microstructures of Ti cp (a) and Ti-10Mo experimental alloy (b).

3.2 Electrochemical studies

Figures 2a and 2b shows an open circuit potential variation with time for CP Ti and Ti-10Mo alloy in naturally aerated mouthwashes. It is observed that these electrochemical measurements are more affected by mouthwash type than by Ti alloy composition or microstructure. Positive drift of open circuit potentials can be associated to the decrease of active surface area due to the growth of a passive film during immersion time. Ti alloys in 0.05% sodium fluoride rapidly attain a steady state potential value (~0.25 V) while in mouthwashes a similar potential value appears to be more slowly reached. Stable potential in an open circuit measurement is obtained after passivation process is completed. Ability for titanium or titanium-based alloy to passivate during a long period of time depend on rates of several processes such as formation

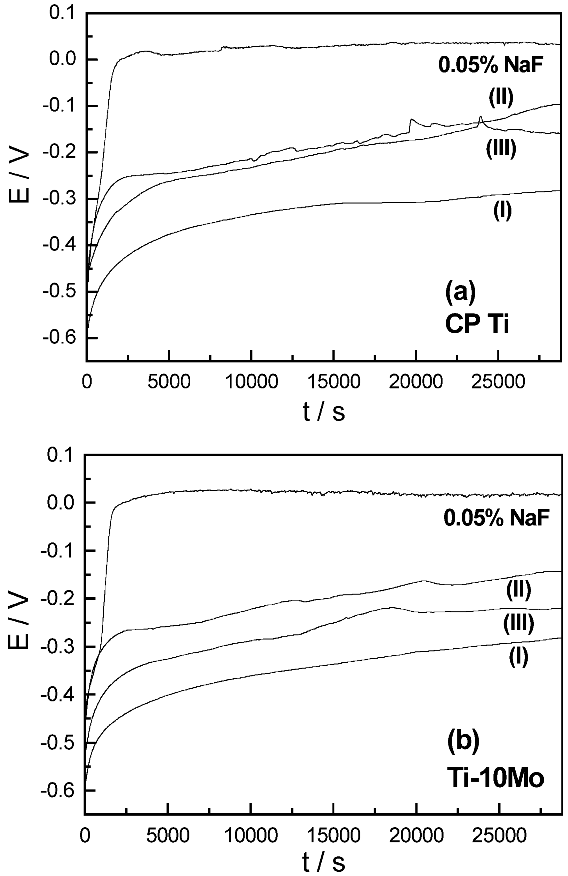

Fig. 2 Open circuit potential measurements for CP Ti (a) and Ti-10Mo alloys (b) in commercial mouthwashes: (I) 0.05% sodium fluoride +0.03% triclosan; (II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride; (III) 0.12% chlorohexidine digluconate.

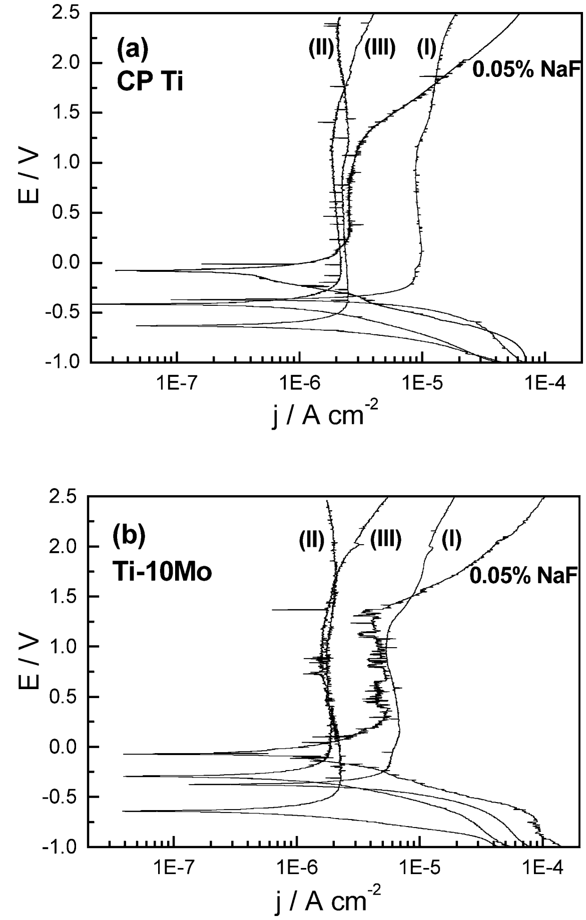

Fig. 3 Potentiodynamic polarization curves for CP Ti (a) and Ti-10Mo alloys (b) in commercial mouthwashes: (I) 0.05% sodium fluoride +0.03% triclosan; (II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride; (III) 0.12% chlorohexidine digluconate.

of oxide at the metal/oxide interface, ionic transport across oxide and dissolution of oxide at the oxide/electrolyte interface [14, 15]. In this context, curves slopes in Fig. 2 have revealed organic active ingredients effect on the passive film mechanism formation.

Potentiodynamic polarization curves of CP Ti and Ti-10Mo alloy in naturally aerated mouthwashes have been recorded at a sweep rate of 0.02 V/min, between −1.00 and 2.50 V. All curves exhibit similar general features (Figs. 3a and 3b). Cathodic branches exhibit a current density that decreases, as applied potential is less negative. Cathodic reaction is assumed to be proton and/or oxygen reduction. Anodic branches show apparently two passive regions, the first one up to ~1.20 V and the other observed at potentials more positive than 1.20 V. These regions may be associated with formation of one or more protective films [11]. Small oscillations of current density are related to the consecutive formation and repassivation of microsize pits [13]. These metastable pits may be promoted by fluoride or chloride presence in mouthwashes. For present alloys, lower passive current density values (~2 $\mu A/cm^2$) were observed in 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride and 0.12% chlorohexidine digluconate mouthwashes.

Titanium and titanium-based alloys tends to become covered with an oxide film in non-complex solutions of pH ranging from 3.5 to 7.5. Those oxides are predominately TiO_2 with small amounts of Ti_2O_3 and alloying elements oxides. Fluoride ions though their complex action, can cause localized corrosion and partial dissolution of this protective film [14–16]. However, our results suggest a non-predominant fluoride effect, rather than a combined effect of this anion with organic active ingredients on the passive behaviors of Ti alloys. In particular, triclosan seems to be more aggressive than cetylpyridinium chloride in fluoride medium.

Passivation phenomenon may be better studied by cronoamperometric technique. Chronoamperometric curves obtained for the two alloys in naturally aerated mouthwashes are shown in Figs. 4 and 5. At 0.50 V these curves initially exhibit a rapid decrease of current and then a slowly decay to attain a steady state current value (Figs. 4a and 4b). Similar curves have been observed at 2.00 V (Figs. 5a and 5b) but a steady state current value is more slowly attained. This

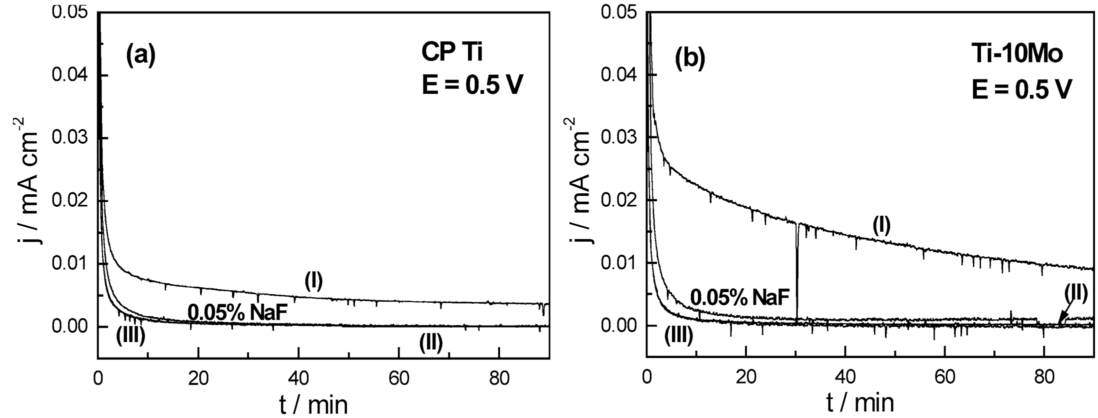

Fig. 4 Chronoamperometric curves at 0.50 V for CP Ti (a) and Ti-10Mo alloys (b) in commercial mouthwashes: (I) 0.05% sodium fluoride +0.03% triclosan; (II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride; (III) 0.12% chlorohexidine digluconate.

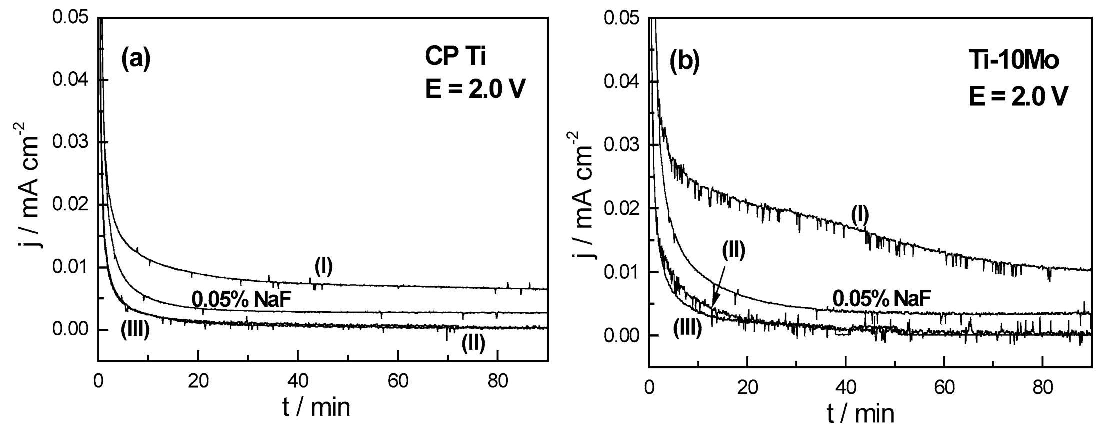

Fig. 5 Chronoamperometric curves at 2.00 V for CP Ti (a) and Ti-10Mo alloys (b) in commercial mouthwashes: (I) 0.05% sodium fluoride +0.03% triclosan; (II) 0.5 g/l cetylpyridinium chloride +0.05% sodium fluoride; (III) 0.12% chlorohexidine digluconate.

general behavior may be explained by reduction in active area due to the growth of a passive film, which grows more slowly on Ti-10Mo alloys in 0.05% sodium fluoride +0.03% triclosan mouthwash (Figs. 4b and 5b). It is interesting to notice that dental implants are susceptible to mechanical disruption of passive film and the repassivation rate is an important parameter. In a recent study [17], CP titanium has showed also a tendency to repassivation faster than Ti-6Al-4 V alloy in inorganic buffer solutions. This result was attributed to the higher catalytic activity towards hydrogen evolution reaction on pure metal in comparison with the alloy.

4 Conclusions

Electrochemical behavior of materials here studied is more affected by mouthwash type than by Ti alloy composition or microstructure. Passivation phenomenon was observed in CP Ti and Ti-10Mo alloys. This process may be mainly related to Ti oxides or other Ti species present in spontaneously formed film. Small differences in passive current densities values may be connected with changes in film porosity and thickness. Protective characteristics of this passive film are lower in 0.05% sodium fluoride +0.03% triclosan mouthwash than in the other two mouthwashes tested.

On the basis of the results obtained, we would recommend that patients with Ti alloys restorations in the mouth should be advised to use preferentially non-fluoridated mouthwashes.

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