Journal of Applied Electrochemistry **30**: 95–100, 2000.

Electrochemical behaviour of titanium in fluoride-containing saliva

M. FERNÁNDEZ LORENZO de MELE[1] and M.C. CORTIZO[2]
[1]*INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 16, Suc. 4, 1900 La Plata, Argentina*
[2]*Cátedra de Materiales Dentales, Facultad de Odontología, Universidad Nacional de La Plata, 1900 La Plata, Argentina*

Received 3 March 1999; accepted in revised form 8 July 1999

Key words: corrosion, dental materials, fluoride, saliva, titanium, titanium oxide

Abstract

The effect of fluoride on the electrochemical behaviour of titanium was studied. Open circuit potentials, breakdown potentials (E_b) and potentiostatic transient currents were measured in synthetic salivas of different compositions. Optical and scanning electron microscopic observations were also made. Results show that the growth rate of Ti oxide layer is affected by fluoride anions and tensile stresses are developed. The OCP/time relationship of Ti immersed in salivas A and B obeys a logarithmic law which depends on the saliva composition. The E_b value is influenced by the thickness of the oxide layer, by the composition of the saliva (including fluoride concentration), and by the technique utilised for its evaluation. Thus, results reported in the literature, which seem to be contradictory, could be explained taking into account the experimental conditions assayed. A careful control of the titanium-containing dental materials should be made after long treatments with fluoride-containing prophylactic products or when fluoride-releasing restorative materials are present in the vicinity.

1. Introduction

The high corrosion resistance of titanium and its alloys in biotic media [1–3] as well as their biocompatibility are reasons for the acceptance of these metals as dental materials [4, 5]. They are widely used in the dental implant field and are gaining increasing importance as corrosion resistant materials for bridges and crowns. However, in the latter case it is necessary to improve the bond between titanium and polymers by activation of the titanium surface [5].

Titanium is highly colonized by bacteria present in natural fluids [1, 2, 6–8]. NaF and other fluoride compounds are frequently used as prophylactic products in dental treatments to prevent dental plaque formation and caries development [9, 10]. Their caries prevention mechanism is not well understood and a variety of mechanisms have been implicated including chemical effects on enamel hydroxyapatite resulting in the formation of fluorapatite [11], local effects influencing the demineralization and remineralization of enamel, interference with ionic bonding during pellicle and plaque formation and the inhibition of the production of acid enzymes by the microorganisms [12]. However, the prophylactic action may be accompanied by the corrosion of metallic dental materials by this aggressive anion [13, 14]. Infiltration of fluoride containing saliva into the implant supported structure or contact between crowns and bridges with the saliva containing this anion may be the cause of the corrosive attack.

Titanium owes its high corrosion resistance to the presence of a thin surface layer of TiO_2 [15]. The growth of this layer is generally accompanied by the development of internal stresses in the oxides [16, 17]. Breakdown of these films in halide solutions has been described by several authors [15–19] who found that this process occurs above 1 V, the exact potential being dependent on the identity of the halogen ion. In the case of bromide solutions pitting occurs at lower potentials than in iodide or chloride solutions. Casillas et al. [15] suggested that in this case the shift of the breakdown potential could be related to a chemical interaction between the titanium oxide and the halogen ion. High current densities arose from scratch testing and thin-film fracture testing made in NaCl solutions. The high charge involved in the repassivation process was attributed to a dissolution process [20, 21] which is often related to the formation of titanium halide compounds that are very soluble in the electrolyte solutions [22].

A significant dependence of the breakdown of barrier films formed on valve metals on the concentration of fluoride has been found [13, 16, 17]. Fluoride level in the oral cavity varies according the prophylactic treatment: fluoride is used up to 1% in the tooth-pastes and mouth-rinses and close to 2% with the aim of eliminating enamel stains. Simultaneously, chloride ions are also present in saliva together with organic acids. Consequently, it can be inferred that titanium/fluoride-containing saliva is a very complex system.

Several research works about the effect of fluoride on titanium/saliva electrochemical system have been published [22–26]. Some authors concluded that fluoride could produce deleterious effects on titanium surface [23, 24] while no increase in titanium corrosion attack could be found by others [22, 25, 26].

The aim of this work is contributing to the understanding of the effect of fluoride on titanium based dental materials. With this purpose, open circuit potentials (OCP), breakdown potentials (E_b) and potentiostatic transient currents were measured in synthetic saliva of different compositions. Optical and scanning electron microscopic (SEM) observations were also made.

2. Experimental details

Titanium grade 1 cylindrical coupons were used for electrochemical studies. They were embedded in an epoxy resin leaving an exposed area of 0.385 cm^{-2}. Prior to each run, pre-treatment of samples was made by polishing down to alumina 1 μm size, degreased with acetone, and rinsed in distilled water. Microscopic observations (magnification: 100×) made after this pretreatment showed intrinsic micrometric imperfections (3 ± 1 micrometric imperfections per $10^6 \mu m^2$) which could not be eliminated by polishing.

Electrochemical measurements were performed in a conventional double wall electrochemical cell configuration using a Pt counter-electrode and a saturated calomel electrode (SCE) as reference. A synthetic saliva, A [27], (NaCl 6 g dm^{-3}; KCl 0.3 g dm^{-3}; $CaCl_2$ 0.2 g dm^{-3}; lactic acid 3.1 g dm^{-3}, pH 6.5) with and without NaF in the 0.8 to 8 g dm^{-3} concentration range was used as electrolyte. Experiments with another synthetic saliva, B [28], (NaCl 0.58 g dm^{-3}; Na_2HPO_4 0.34 g dm^{-3}; KH_2PO_4 0.34 g dm^{-3}; $KHCO_3$ 1.5 g dm^{-3}; $MgCl_2$ 0.014 g dm^{-3}; $CaCl_2$ 0.166 g dm^{-3}; citric acid 0.029 g dm^{-3}, pH 6.8) and with a therapeutic oral solution C (hydroxypropyl methyl cellulose 1 g; xylitol (sol. 70%) 4.3 g; KCl 0.1 g; NaCl 0.2 mg; $MgCl_2$ 5 mg; $CaCl_2$ 15 mg; K_2SO_4 40 mg; pH 7, double-distilled water up to 100 ml) were also made with the aim of comparison. All solutions were prepared from analytical grade chemicals.

Polarization curves were performed at a constant scan rate of 0.01 V min^{-1} from −1.0 V up to different anodic limits. Current–time curves were obtained at the preset constant potentials after holding the electrode at −1.0 V for 60 s. Open circuit potential (OCP) was measured against a SCE. Optical and scanning microscopic observations of the samples were made after performing the electrochemical experiments.

3. Results

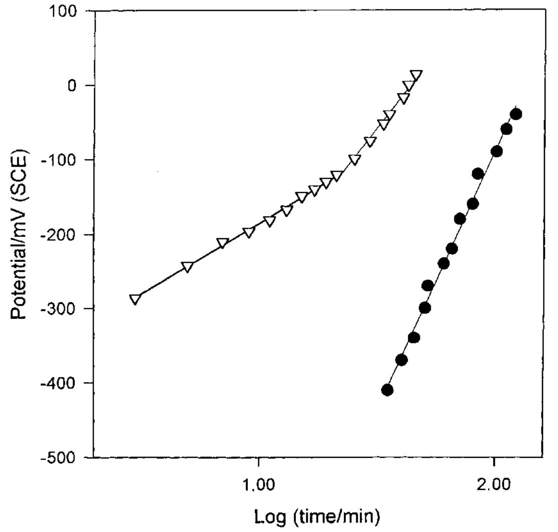

Fig. 1. Open circuit potential against log time plot of titanium immersed in different synthetic salivas: (●) saliva A ($r_A^2 = 0.992$), (▽) saliva B (r_B^2 (initial) = 0.997, r_B^2 (final) = 0.989).

Figure 1 shows the OCP evolution of titanium immersed in saliva A and B. The OCP against time relationship is dependent on the electrolyte composition and shows a linear dependence with the log of time in the −0.4 V to −0.1 V potential range. In the case of saliva B a change in the slope of the curve is evident. After long immersion periods (longer than 24 h) the OCP achieves a constant value of about 0.01 V. Saliva C showed scattering values (±20 mV) probably related to its viscous characteristic which made the measurements difficult. When fluoride anions are added to the synthetic saliva A 100 h after the immersion, the OCP values are not altered. However, when the addition is made a few minutes after the immersion the OCP decreases abruptly from 0.01 V to −0.4 V (Figure 2). Thus, fluoride ions interfere in the titanium oxide formation at the early stages. If the

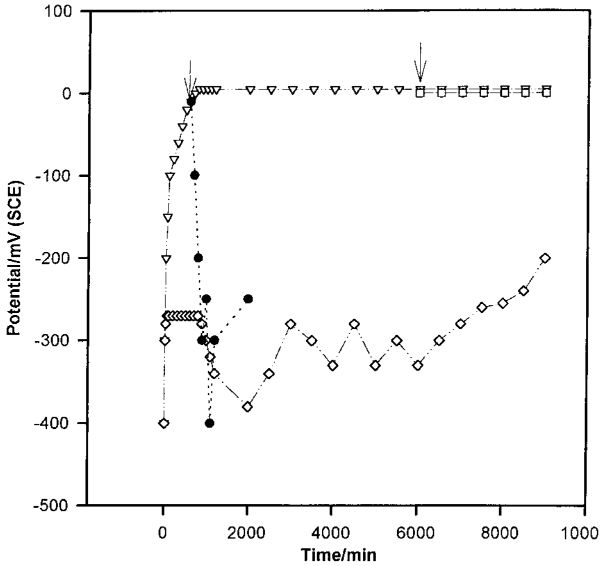

Fig. 2. Open circuit potential against time plot of titanium immersed in saliva A with and without 0.2 M NaF addition: (▽) without fluoride addition, (□) fluoride addition after 6000 min, (●) fluoride addition after 40 min, (◇) fluoride containing saliva.

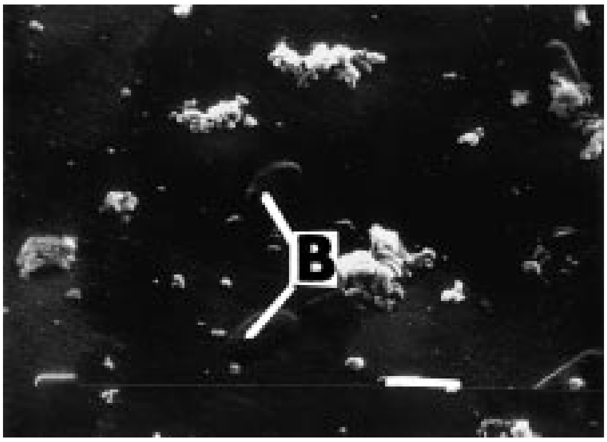

Fig. 3. SEM microphotograph of titanium immersed in 0.2 M NaF solution at open circuit potential condition. Blisters (B) can be seen on the surface. Horizontal bar indicates 2 μm, and **B** the blisters.

fluoride addition is made before the immersion of the titanium electrode the OCP remains unstable at low values (−0.32 V ± 0.05 V) and then increases. SEM observations reveal the formation of blisters at the titanium surface (Figure 3).

Polarization curves made at different fluoride concentrations are shown in Figure 4. It can be seen in the case of 0.02 M NaF solution that titanium remains passive up to 0.4 V and then the current density increases. At higher fluoride concentrations the E_b value is lower. In the absence of fluoride (Figure 5) the current density remains at the 0.0 μA cm^{-2} value but when fluoride is added current increases (see arrow).

To improve the E_b evaluation potentiostatic current transients were recorded. A typical series of current–time curves obtained in saliva A containing NaF (0.2 M) at potentials in the −0.1 V to 0.1 V potential range is shown in Figure 6. It can be observed that after a sudden increase current density decreases and remains close to 0.0 μA cm^{-2} during different periods according to the potential value. In the case of the −0.1 V current transient, no current increase occurs during a 3 h period. At higher potential values, transient currents reach a maximum at a time t_m, which is longer than 2 h at potential values lower than 0.1 V (Figure 6 only shows the maximum of 0.1 V current transient due to the magnification of the plot). Thereafter current density decreases following a roughly linear $i/t^{1/2}$ relationship in each case. The time t_m after which the maximum is achieved is shorter when fluoride is initially present in the electrolyte medium than when it is added 10 s after the beginning of the curve (Figure 7).

SEM microphotographs show the presence of blisters (Figure 8) with corrosive attack beneath some of them (Figure 9). Certain zones reveal the faceting of the surface which is crystallographically etched after anodizing (Figure 10).

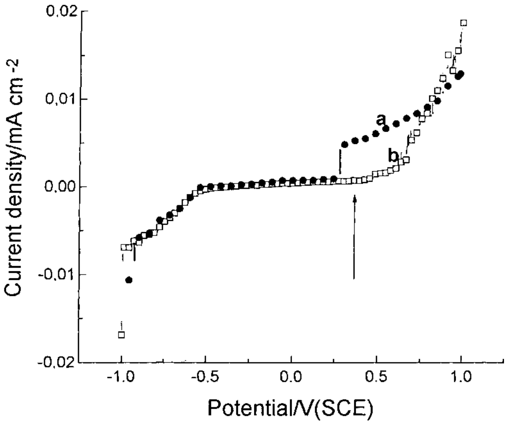

Fig. 5. Polarization curves of titanium immersed in: (a) (●) saliva A + 0.2 M NaF, (b) (□) saliva A initially without NaF and then added (see arrow).

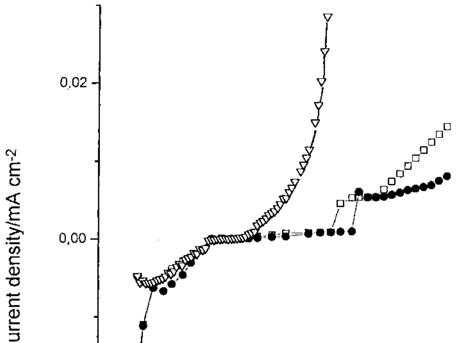

Fig. 4. Polarization curves of titanium immersed in saliva A with different fluoride concentrations: (●) 0.02 M NaF, (□) 0.2 M NaF, (▽) 0.5 M NaF.

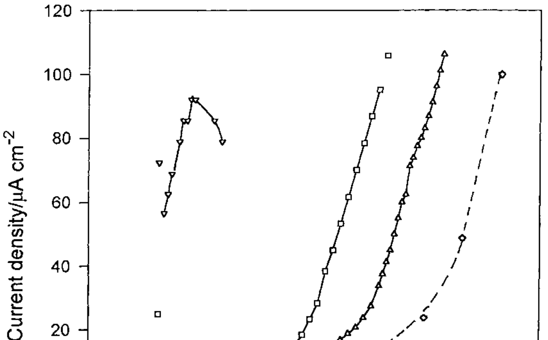

Fig. 6. Potentiostatic current transients of titanium in 0.2 M NaF synthetic saliva A made at different potentials: (●) −0.1, (◇) −0.05, (△) 0.0, (□) 0.05 and (▽) 0.1 V.

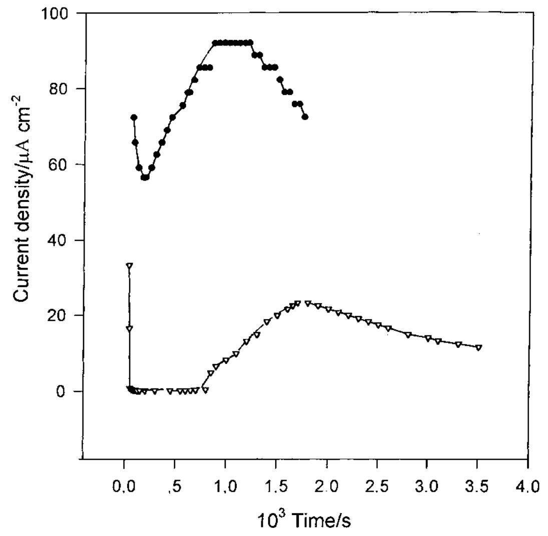

Fig. 7. Potentiostatic current transients of titanium in 0.2 M NaF synthetic saliva A made at 0.1 V in: (●) synthetic saliva A + 0.2 M NaF added before the immersion of titanium, (▽) synthetic saliva + 0.2 M NaF added 10 s after starting the anodization.

4. Discussion

The increase in the open circuit potentials of the valve metals to more noble values is attributable to growth of barrier film on the metal surfaces [29]. According to capacitance measurements [30, 31], titanium oxide films can be considered as three-dimensional. The present results show that the OCP of titanium in salivas A and B obeys a direct logarithmic law of growth, in agreement with those reported by El-Kader [32, 33] for barrier films formed on Hf, Ti, Mo and Ta. Barrier films may grow at different rates, the magnitude of which depend on the solution composition. The change in the rate of the film growth (Figure 2, saliva B) may be attributed to processes like adsorption of anions on the film, accumulation of soluble anodic products, the change from two dimensional to three dimensional films or the formation of a layered structure [31].

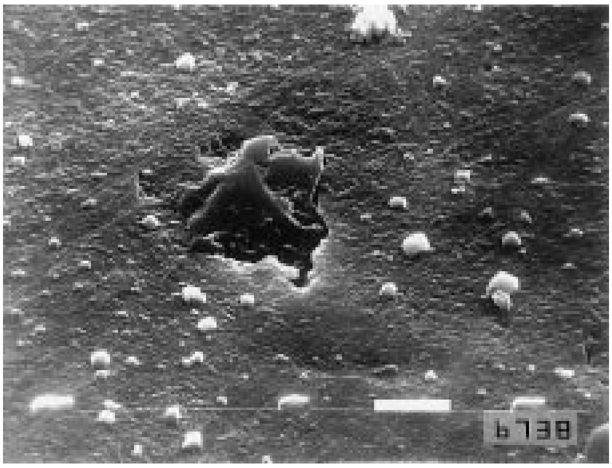

Fig. 9. SEM microphotograph of titanium immersed in 0.2 M NaF solution and held at 0.1 V for 2 h. Blisters and localized attack beneath them can be seen in the middle of the picture. Horizontal bar indicates 2 μm.

The susceptibility to localized attack of the passive film was more significant in those samples with higher number of imperfections detected by microscopic observations. Thus, susceptibility seems to be associated with defect structures in the oxide film such as inclusions, mechanically formed defects and structural crystallographic defects, as well as line defects at steps and terraces, and defects in grain boundaries [15, 18, 19]. In the case of bromide solutions the microscopic sites at which breakdown occurs showed higher conductivity than the surrounding film [15]. Ti, Zr, Al or Ta oxide layer rupture may also be caused by the development of stresses. These stresses may be either tensile or compressive in nature and range from zero to values high enough to disrupt the film [17]. The jumps in current density values observed during the polarization curves may be associated with these disruptions (Figures 4 and 8). SEM microphotographs of the films formed under OCP conditions show the development of blisters on the titanium oxide layer as

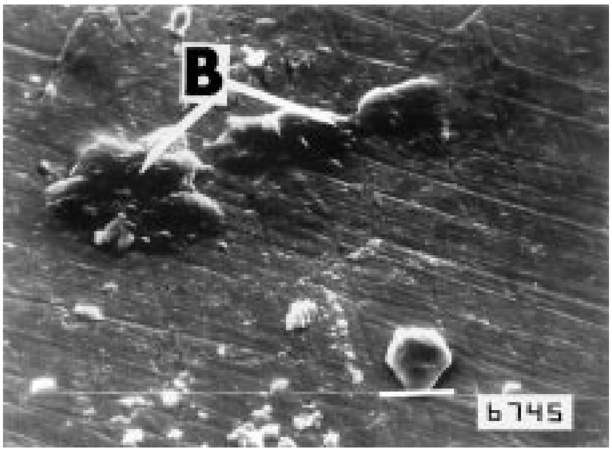

Fig. 8. SEM microphotograph of titanium immersed in 0.2 M NaF solution and held at 0.1 V for 2 h. Blisters (B) can be seen on the surface. Horizontal bar indicates 2 μm, and **B** the blisters.

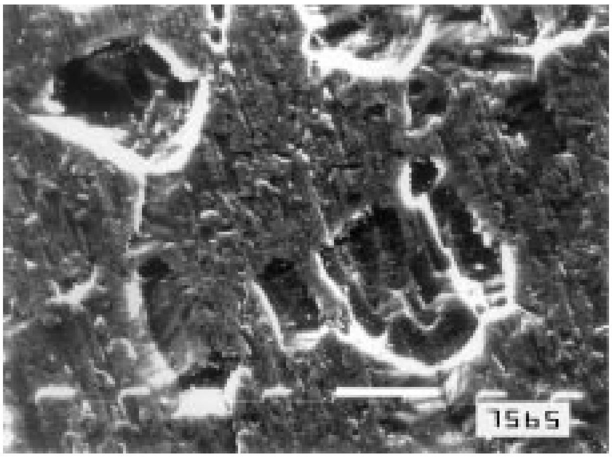

Fig. 10. SEM microphotograph of titanium immersed in 0.2 M NaF solution and held at 0.1 V for 2 h. Faceting of the crystallographic etched surface can be seen. Horizontal bar indicates 10 μm.

a consequence of internal stresses in the oxide layer (Figure 3). The nature and magnitude of the stresses are affected by the rate of growth of the film and by the presence of fluoride during the oxide formation [16, 17]. Changes in the stresses from tensile to compressive were found when Zr was etched in a HF-containing solution. The transport fraction of the migrating ions seems to be altered during anodizing under these conditions [17].

Present results (Figures 2 and 7) show that thin oxide films are very liable to fluoride attack. Conversely, the aggressive action of fluoride anions is hindered when a thick oxide layer is formed after long exposure periods. It has been reported that the influence of the anion is insignificant for oxide films thicker than 7 nm [15]. Accordingly, open circuit potential experiments show no noticeable change when fluoride ions are added several hours after the immersion of titanium, where a thick oxide layer has developed (Figure 2). However, the decrease in the corrosion potential occurs immediately if the fluoride ions are added a few minutes after the immersion of the titanium coupon.

It has been found [15] that there is an approximately linear dependence between the breakdown potential and the oxide thickness in the case of bromide solutions. Polarization curves and potentiostatic current transients also show the breakdown of passivity when fluoride is added to the solution in which a passive electrode was immersed (Figures 5 and 7).

A significant dependence of the breakdown potential with the fluoride concentration was found (Figure 4). Consequently, the potential at which breakdown occurs in fluoride containing saliva can be related to: (a) the number of imperfections of the titanium surface prior to anodizing, (b) the applied current density and the thickness of the oxide developed in this condition, and (c) the fluoride concentration. These parameters control the internal stresses in the oxide. If the stress level is high enough, the oxide will fracture and corrosion is initiated within the cracks. If the solution within the cracks is sufficiently acid [21] and strong in fluoride ions, soluble species may be formed and may precipitate on the surface of the specimen outside the cracks [18]. A significant dissolution taking place over the length of the current decay transient was also reported. The large majority of anodic charge during repassivation seems to contribute to dissolution of titanium and not to film formation [20, 21]. There is a potential-dependent dissolution of the oxide layer in the presence of fluoride leading to the faceting of the electrode after two hours of potentiostatization (Figure 10). Similar faceting was also found for titanium immersed in halide solutions [18]. Little difference was detected in the repassivation of titanium and titanium alloys in acidic, alkaline and neutral chloride solutions. There is also no apparent alloy-specific difference in repassivation behaviour of titanium alloys [20, 21]. However, breakdown of passivity was observed in solutions containing bromide. In the case of fluoride containing saliva several anions seem to be involved in the dissolution process because the electrochemical behaviour changes when the composition of the saliva changes.

It is interesting to consider that localized attack in fluoride containing saliva, in which chloride and organic acids anions are present, is observed at lower potentials than in other saliva containing the halide as the sole anion added to the solutions [17, 18]. Notwithstanding that the passivity region in the polarization curves made with 0.2 M NaF solutions extends up to 0.2 V, the breakdown of the oxide film at potentiostatic conditions occurs at a lower potential after long exposure periods. Thus, the breakdown potential values are strongly affected by the technique utilised for its evaluation. The time t_m shows a significant dependence with potential, being shorter at higher potentials.

High levels of fluoride anions in the mouth can be supplied by mouth-rinses or toothpastes. Additionally, fluoride-containing restorative materials (composites, glass ionomer cements) have the ability to release fluoride with the aim of preventing the caries development in the surrounding areas. Thus, care must be taken to prevent titanium deterioration during long treatments with fluoride-containing compounds and when titanium dental materials are within the inhibition area of the fluoride-containing restorative materials. Although the latter have different rates of fluoride release, most of the fluoride release usually takes place in the first day or week in the oral cavity. After these periods, a careful examination of the titanium dental materials should be made.

5. Conclusions

The growth rate of titanium oxide layers is affected by fluoride anion concentration. Internal stresses leading to blister formation were detected at the oxide layer in the presence of fluoride.

The OCP/time relationship of titanium immersed in salivas A and B obeys a logarithmic law. The magnitude of each slope depends on the saliva composition.

Titanium oxide film formation and the rupture of titanium passivity are influenced by the composition of the saliva (including fluoride concentration) and by the number of imperfections in the titanium surface. The breakdown process is also influenced by the thickness of the oxide film.

The E_b values of the titanium immersed in fluoride containing synthetic saliva are lower than those found in fluoride solutions. E_b is also significantly affected by the technique utilized for its evaluation.

Care must be taken during long treatments with fluoride containing prophylactic products or when fluoride-releasing restorative materials are present in the vicinity of the titanium-containing dental materials.

Acknowledgements

The authors acknowledge the technical assistance of Paula Caregnato and Vanina Fracaroli. This research work was financially supported by the National Council of Scientific and Technical Research of Argentina (CONICET) and by the National University of La Plata.

References

1. G. Brankevich, M. Fernández Lorenzo de Mele and H.A. Videla, *Marine Technol. Soc. J.* **24** (1990) 18.
2. H.A. Videla, M. Fernández Lorenzo de Mele and G. Brankevich, *Corrosion* **44** (1988), 1988 423–6.
3. S.G. Gómez de Saravia, M. Fernández Lorenzo de Mele and H.A. Videla *OEBALIA*, **XIX**, Suppl. (1993) 231–58.
4. J. Gilbert, C.A. Buckley and E. Plautenshalger, *J. Dent. Res* **74** (IADR Abstracts) Abstract 645 (1995) 492.
5. J. Meyer, W.D. Müller, K. Seliger and J. Gilbert, *J. Dent. Res* **74** (IADR Abstracts) Abstract 590 (1995) 474.
6. A. Mombelli, D. Buser and N.F. Lang, *Oral Microbiol. Immunol.* **3** (1988) 113.
7. A. Leonhardt, J. Olsson and G. Dahlén, *J. Dent. Res.* **74** (1995) 1607.
8. M.C. Cortizo and M. Fernández Lorenzo de Mele, 'Biofilm formation on dental metallic materials. Effect of fluoride anions', Proc. 3rd. Latin American Symposium of Biodeterioration and Biodegradation (edited by C.C. Gaylarde, T.C.P. Barbosa, N.H. Gabilan), Br. Phycol. Soc., UK (1998), p. 18.
9. W.M. Edgar, M.A. Cockburn and G.N. Jenkins, *Arch. Oral Biol.* **26** (1981) 615.
10. G.H.W. Bowden and I.R. Hamilton, *Oral Microbiol Immunol.* **4** (1989) 57.
11. Y.H. Li and G.H. Bowden, *J. Dent. Res.* **73** (1994) 1615.
12. E.D. Hamilton and J. Arends, *in* E. Ekstrand, O. Fejerskov, L. Silverstone, (Eds.) 'Fluoride Dentistry' Munsksgoord, Copenhagen (1991), p. 77.
13. M.C. Cortizo and M. Fernandez Lorenzo de Mele, 'Biodeterioration of Dental Metallic Materials', 2nd NACE Latin Am. Reg. Corrosion. Congress (1996), paper LA96149.
14. M.C. Cortizo and M. Fernandez Lorenzo de Mele, 'Corrosion of Dental Alloys in Synthetic Saliva of Different Compositions. Effect of Biofilms', International Materials Research Congress, Symposium 11 Biomaterials, Cancún, Sept. (1998), paper 4.
15. N. Casillas, S. Charlebois and W.H. Smyrl, *J. Electrochem. Soc.* **141** (1994) 636.
16. L.C. Archibald and J.S.L. Leach, *Electrochim. Acta* **22** (1977) 21.
17. L.C. Archibald and J.S.L. Leach, *Electrochim. Acta* **22** (1977) 15.
18. T.R. Beck, *J. Electrochem. Soc.* **120** (1973) 1317.
19. T.R. Beck, *J. Electrochem. Soc.* **120** (1973) 1310.
20. D.G. Kolman and J.R. Scully, *J. Electrochem. Soc.* **142** (1995) 2179.
21. D.G. Kolman and J.R. Scully, *J. Electrochem. Soc.* **143** (1996) 1847.
22. I. Reclaru and M. Meyer, *J. Dent. Res* **74** (IADR Abstracts) Abstract 585 (1995) 474.
23. P. Wiig, J.E. Ellingsen and K. Videm, *J. Dent. Res. IADR Abstracts* **72** (1993) 195.
24. N. Rozenbajghier and L. Probster, *J. Dent. Res. IADR Abstract* **72** (1993) 227.
25. O. Riesgo and G. Duffo, 'Corrosion of Titanium caused by Topical Fluoride', Proc. of the XXV Annual Meeting of the Int. Assoc. Dental Research (Div. Argentina), Tandil (1993).
26. O. Riesgo and G. Duffo, 'Corrosion of Titanium caused by Topical Fluoride', Proc. of the XXVI Annual Meeting of the Int. Assoc. Dental Research (Div. Argentina), Cordoba (1994).
27. C. Baron, C.M. Marschoff and P.J. Aragon, *J. Life Sci.* **8** (1978) 105.
28. E. Quezada Castillo, MS thesis, Universidad Nacional General San Martin, Argentina (1997).
29. U.R. Evans, 'The Corrosion and Oxidation of Metals' (Arnold, London, 1960), p. 898.
30. M.S. El-Basiouny, A.M. El-Dot and M.M. Hefny, *Corrosion* **35** (1979) 566.
31. A.G. Gad-Allah and H.A. Abd El-Rahman, *Corrosion* **43** (1987) 698.
32. J.M. Abd El-Kader and A.M. Shams El-Din, *Brit. Corros. J.* **14** (1979) 40.
33. J.M. Abd El-Kader, F.M. Adb El-Wahab, H.A. El-Shayeb and M.G.A. Khedr, *Brit. Corros. J.* **16** (1981) 111.