Influence of Fluoride on Titanium in an Acidic Environment Measured by Polarization Resistance Technique

Gert Boere

Academic Centre for Dentistry Amsterdam (ACTA), Department of Dental Materials Science, Amsterdam, The Netherlands

The effect of sodium fluoride on the polarization resistance of titanium was investigated. Titanium plates were exposed to sodium chloride solutions with increasing fluoride concentrations. This was done at pH 7 and 4 at 37 °C. The polarization resistance technique was chosen because it is the only electrochemical corrosion test procedure that allows sequential measurements of the same specimen and provides a quantitative basis to estimate corrosion currents unlike measurements of the potential. The results showed a large decrease in polarization resistance with increasing fluoride concentration at pH 4. The polarization resistance at pH 7 remained constant after a slight decrease at a very high value, even with a high fluoride concentration. The results clearly confirm that titanium is attacked by fluoride in an acidic environment. The clinical implications are that fluoride rinses or fluoride gels must have a neutral pH if there is a titanium containing device in the oral environment despite the less prophylactic effectiveness. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Titanium (Ti) is well known for its excellent stability in oral and body liquids and for this reason it is the metal of choice for dental implants. From its position in the periodic table of the elements, it is evident that titanium is in fact a very active metal with an $E°$ (standard reduction potential) approaching that of aluminum. Hence, the surface of titanium will always react with water or air and become covered with a protective oxide layer. Access of electrolyte to the metal is possible only through the pores of the oxide layer. With the protective layer, titanium behaves as a noble metal. It is very resistive to the action of strong acids.

Titanium is rapidly dissolved by hydrofluoric acid (HF); and furthermore, it is rapidly dissolved by strong, and even weak acids such as acetic, formic, and phosphoric acid if the solution contains soluble fluorides. Hydrofluoric acid is known to dissolve the oxide layers present on the metal surface according to the reactions:

$$Ti_2O_3 + 6\ HF \rightarrow 2\ TiF_3 + 3\ H_2O, \quad or$$

$$TiO_2 + 4\ HF \rightarrow TiF_4 + 2\ H_2O,$$
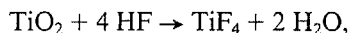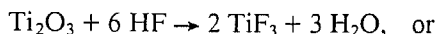
thus exposing the metal to attack by the acid and causing the metal to exhibit a low negative potential.

The metal goes into solution as a trivalent ion: Ti →

$Ti^{3+} + 3e$. The reactivity of a metal is closely associated with the potential of that metal; measured potentials are not equilibrium but corrosion potentials. As such they depend on the nature and composition of the protective oxide layers, their thickness, electrical conductivity, and porosity. Hence a poor reproducibility of potential measurements is to be expected.[1]

Prophylactic fluoride gels with a low pH are known to be more effective than the neutral gels.[2] This low pH is prepared by addition of citric or phosphoric acid to the gel. These gels with a pH as low as pH 4 could be harmful to titanium devices in the mouth.[3,4]

This study evaluates the behavior of titanium in fluoride containing solutions at different pH values as measured by the polarization resistance technique. Because the reproducibility of the potential measurements is expected to be poor, the linear polarization resistance (R_p) is chosen as the variable to characterize the surface of the metal. This technique is based on the phenomenon of a linear relationship between potential and applied current at potentials only slightly removed from the corrosion potential.[5,6] R_p is the slope of this straight line at $\Delta E \rightarrow 0$. Although the polarization resistance is time dependent for passivating metals,[6] an advantage of this method in respect to other electrochemical corrosion test procedures is the nondestructive character of the technique. Sequential measurements of the same specimen are possible and changes in corrosion currents can be detected through changes in the polarization resistance.

The corrosion current, i_{corr}, is related to R_p by the expression $i_{corr} = B/R_p$. [$B = b_a b_c / 2.303 (b_a + b_c)$, in which b_a is the anodic Tafel slope and b_c is the cathodic Tafel slope.] The theoretical value of B can range from 6.5 to 52.1 mV. A value of 26 mV for B represents the average of all corrosion systems.[5] The accuracy of this technique

depends on the Tafel slopes. The maximum error is a factor of 3.

MATERIALS AND METHODS

Corrosion Cell

A titanium plate was mounted in the flat cell corrosion cell K0235 (EG&G Princeton Applied Research, Princeton, NJ), which was adjusted with a second sample end plate.

Specimens

The titanium was of 99.99% purity (catalogue no. 34,881-3, Aldrich Chemical Company, Inc., Milwaukee, WI). The titanium was used as delivered after cleaning with acetone and washing with distilled water and drying. The area of metal exposed to the liquid was 0.94 cm^2.

Test Solution

The test medium was a sodium chloride (NaCl) solution of 9.0g L^{-1}. The solution was buffered by a hydrion buffer (catalogue no. 23,903-8, Aldrich) with pH 4.00 at 25 °C or a hydrion buffer (catalogue no. 23,908-9, Aldrich) with pH 7.00 at 25 °C. The temperature for all experiments was 37 °C. The actual pH values of the buffer solutions at 37 °C were 3.9 and 6.7; for convenience they are referred to as pH 4 and 7.

Polarization Resistance Measurements

The specimens were tested in a temperature controlled, three electrode flat cell K0235. A saturated calomel electrode with a luggin capillary was used as a reference, and a carbon rod as a counter electrode. The solutions were left undisturbed and unstirred for 1 h before each scan.

The equipment consisted of an electronic potentiostat (model 273, EG&G) with Soft Corr corrosion software (model 342, rev 2.38). The normal range in which the straight line is automatically determined was −10 to +10 mV around E_{corr}. Because of fluctuations in E_{corr}, this range was not always found. In these cases a range from 0 to +20 mV with respect to E_{corr} was used to determine a straight line with a linear regression method.

E_{corr} Versus Time

Another electrochemical testing method was executed to measure the potential as a function of time without applying any tension or current and without addition of sodium fluoride. Equipment and solutions were the same as with the polarization resistance measurements.

Test Procedures

During the experiments a specific amount (0.5, 1.0, or 5.0 mL) of sodium fluoride (NaF) solution was added at regular times with a pipette. Two different NaF solutions contained, respectively, 1.00 and 2.50 g/100 mL. The fluoride concentrations were calculated from the total amount added and the total volume of the solution. Just before and 1 h after each addition, R_p and E_{corr} were determined. In one experiment the first addition was made at the beginning of the experiment; in another the titanium was allowed to set for 100 h before starting the addition of the sodium fluoride solution, and in a third the titanium was allowed to set for 3 weeks before adding the fluoride.

Graphical Reproduction

The relationship between R_p and E_{corr} on the one hand and NaF concentration on the other is depicted graphically with R_p on the left Y axis written as log R_p (pR_p). In this way the graph with pR_p is conveniently arranged and the maximum error of a factor of 3 is a constant of 0.5 on this scale.

The E_{corr} versus time relationship is reproduced as an E-log t curve.

Calculations

The experiments were executed twice and the values were averaged. The standard deviation was in all cases smaller than the 300% theoretical error. All values of R_p have been calculated with the least squares line. Values of R_p with the correlation coefficient of this line smaller than 0.9 were neglected.

RESULTS

The pR_p values and the corresponding E_{corr} values as a function of the NaF concentration in a NaCl solution with pH 4 are shown in Figure 1. The NaF solution was added from the onset of the experiment.

The same is shown in Figure 2, where the additions were made after 100 h of setting in the NaCl solution with pH 4. Figure 3 shows the pR_p values as a function of the fluoride concentration after a setting time of 3 weeks in the NaCl solution with pH 4. In this case the R_p values without or with only a small quantity of fluoride, were beyond detectability. The pR_p is ≥ 7.

The R_p values as a function of the NaF concentration at pH 7 are shown in Table I. This relationship is not graphically depicted.

The E_{corr}-log t curve made during a setting time of 100 h where no fluoride was added, shows a linear relationship (Fig. 4).
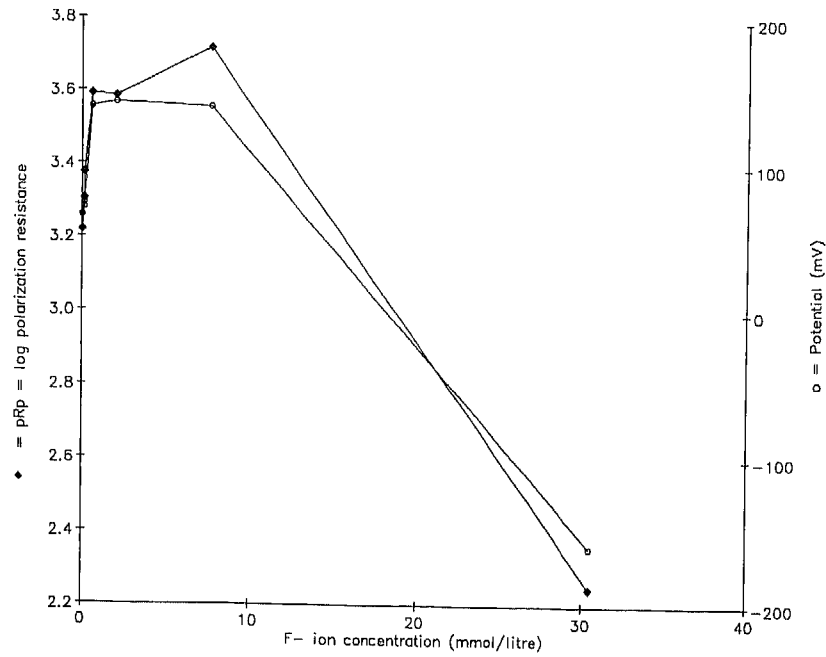
Figure 1. The pR_p and potential (E_{corr}) of titanium vs. F^- concentration. The NaF was added from the onset.

DISCUSSION

From Figure 1, it seems that there is a limiting value for the NaF concentration where concentrations below this value do not influence the E_{corr} or the R_p, which would mean that at low concentrations titanium is not attacked by HF. From Figures 2 and 3 it is observed that the R_p

values are higher and the influence of HF is detected at lower concentrations of fluoride.

A closer evaluation of the E_{corr} and R_p values recorded after a time interval where no sodium fluoride was added revealed an increase for both values (Figs. 2, 5). In the E-log t curve, this relationship is linear with a slope of 78 (Fig. 4). This linear relationship points to an oxide layer
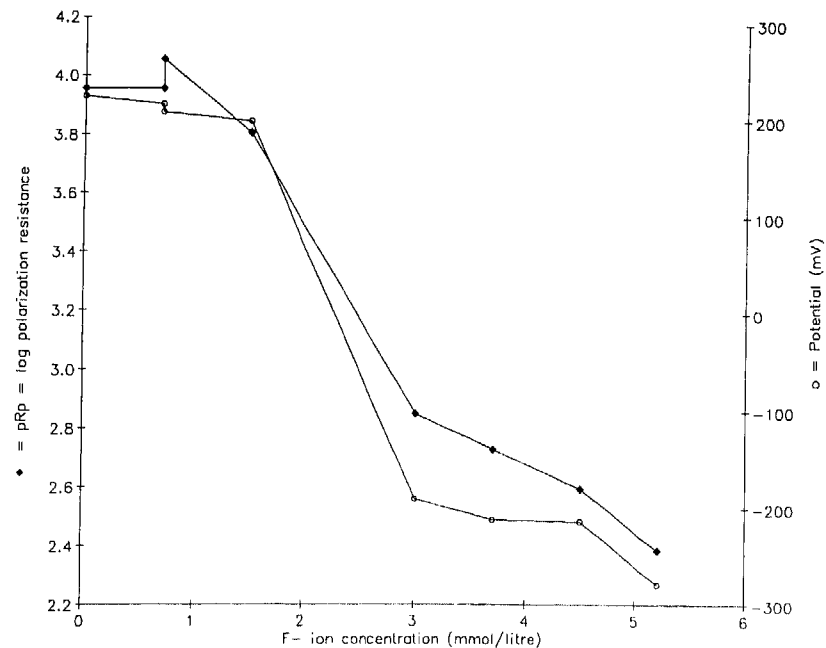

Figure 2. The pR_p and potential (E_{corr}) of titanium vs. F^- concentration. The NaF was added after 100 h.
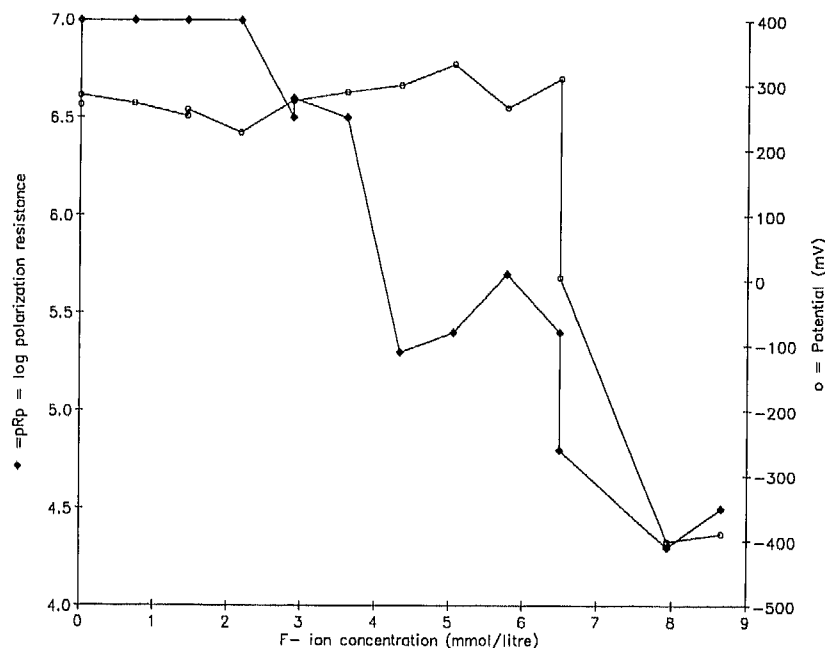
Figure 3. The pR_p and potential (E_{corr}) of titanium vs. F^- concentration. The NaF was added after 3 weeks.

formation.[7] In the experiment where NaF was added from the onset, the slope of the straight line, in a period where no fluoride was added, is 37 (Fig. 5). The influence of NaF was established as a smaller R_p. If the NaF is added from the onset, the potential and R_p rise due to the oxide layer formation is counteracted by the dissolution reaction with HF. The conclusion from these results is that the addition of NaF influences the E_{corr} and R_p even at low concentrations and that there is no limiting value for NaF concentrations at low pH to attack titanium. Figure 3 also shows that the potential of titanium, which was allowed to set for 3 weeks, remains relatively constant at low fluoride concentrations where the R_p is already descending. A possible explanation for this behavior is that after 3 weeks, the oxide layer is very thick and titanium reacts as a nobel metal, in which case the titanium might function as a hydrogen electrode.[7] With the Nernst equation it can be calculated

that the E_{H^+}/H_2 is +240 mV at pH 4, which is close to the constant value; so it might be that titanium functions as a hydrogen electrode and remains to do so even if the oxide layer already suffers some damaging influence of the fluoride. The attack of fluoride in a neutral solution is not so dramatic. The R_p values, although somewhat lower than without the NaF, are the same order of magnitude as the R_p of the noble metals. The attack by NaF at low pH and not at pH 7, means that the initiation of the attack is by the molecule HF and not by the ion F^-. The dissociation constant K of HF is 3.53×10^{-4} ($K = [H^+][F^-]/[HF]$). At pH 4 the ratio $[F^-]/[HF] = 3.53$ meaning that 22% of all the fluoride in the solution is in the HF form. This explains the small effect at pH 7 because at that pH only 0.03% of all the fluoride is in HF form; it also makes clear the effect of fluoride ions in weak acids like orthophosphoric acid where even moderate concentrations of these acids form buffers with a pH of 4 or even lower. The presumed mechanism is that the small undissociated molecule HF diffuses into the pores of the oxide layer, attacks this protective layer, and partially dissolves it. This process increases the pore diameter and makes the unprotected titanium vulnerable to attack by the H^+ ions.

It is interesting to look at the concentrations of fluorides in the oral environment after use of toothpaste, fluoride rinse, or fluoride gels. The concentration of fluoride in saliva is from 8.4 mg L^{-1} (0.2 mmol)[8] to 62 mg L^{-1} (1.5 mmol),[9] depending on the concentration of fluoride in the toothpaste and the amount used. After rinses the fluoride concentration is from 49 mg L^{-1} (1.2 mmol) to 120 mg L^{-1} (2.9 mmol) in saliva.[10–12] When

TABLE I. R_p Values of Ti in 0.9% NaCl at 37°C and pH 7 with Different NaF Concentrations

pR_p	NaF Concn L^{-1} (mmol)
5.9	0
5.8	11
5.7	21
5.6	31
5.6	40
5.5	50
5.6	60

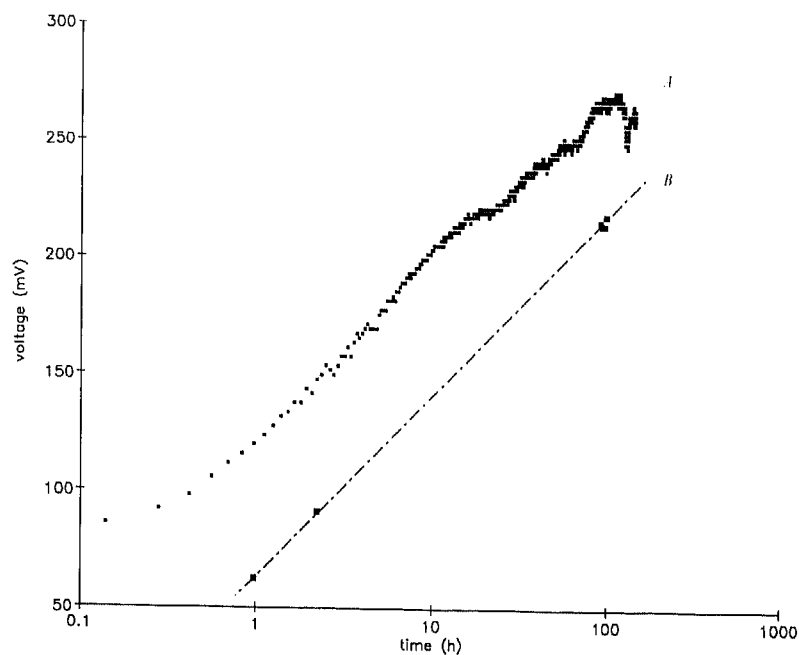The values of R_p are written as log $R_p = pR_p$ (R_p in ohm cm²).

Figure 4. The potential of titanium vs. time. Curves A and B are independently measured in different solutions with different plates. The E values of curve A were measured with a 0.5 min interval during a 500.000 s scan. Line B is drawn through the E values determined during polarization resistance scans.

topical fluoride gels are used the fluoride concentration in saliva is up to 300 mg L^{-1} (7 mmol). Especially the concentration of fluoride after application of topical gels deserves attention because this concentration is such that damage to the titanium is very well possible.

In plaque rich areas where the pH is below neutral the attack might be severe. With this in mind it is advisable to use the neutral fluoride topical gels in patients where titanium is used for implants or other prosthetic provisions.
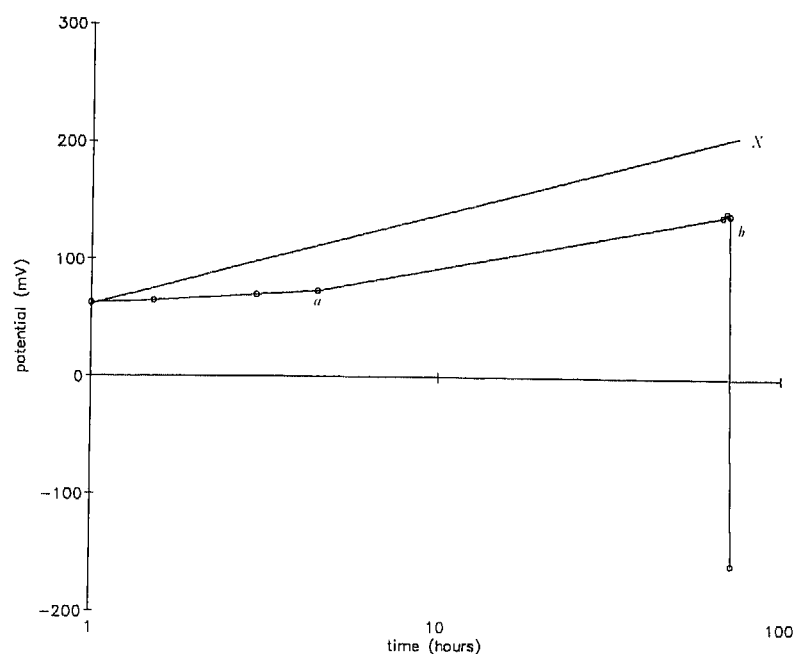

Figure 5. The potential of titanium vs. time. The NaF was added from the onset. In the time interval between a and b no additions of NaF were made. Line X is the same line as line B in Figure 4, projected here to emphasize the difference in slope.

CONCLUSION

The results of this study clearly show that the use of fluoride containing rinses or gels might be harmful to titanium devices such as implants, if the pH of these very useful prophylactic aids is below neutral. The use of home-care gels must be discouraged unless the precise pH value is known. The results from the polarization resistance technique indicate that this technique provides information for a better understanding and a quantification of the corrosion process of titanium in a fluoride containing environment.

REFERENCES

1. James, W. J.; Straumanis, M. E. Titanium. Bard, A. J., ed. Encyclopaedia of electrochemistry of the elements, New York: Marcel Dekker; Vol. V. 1976:305–395.
2. Dawes, C. Fluorides: Mechanisms of action and recommendations for use. J. Can. Dent. Assoc. 55:721–723; 1989.
3. Cohen, F.; Chemla, M.; Burdairon, G. Propriétés corrosives des gels odontologiques fluorés à l'égard du titane. CR. Acad. Sci. Paris 313(II):501–508; 1991.
4. Weber, H.; Pröbster, L.; Geis-Gerstorfer, J. Titan als prothetischer werkstoff. Dtsch. Zahnärztl. Z. 47:473–481; 1992.
5. Fontana, M. G.; Green, N. D. Corrosion engineering, 2nd ed. Tokyo: McGraw–Hill; 1983:297–346.
6. Mansfeld, F. The polarization resistance technique for measuring corrosion currents. Montana, M. G.; Staehle, R. W.; eds. Advances in corrosion science and technology, Vol. 6. New York: Plenum Press. 1976:163–262.
7. Muller, A. W. J. Corrosion of dental NiCrMo alloys. University of Amsterdam; Ph.D. Thesis (ISBN 90-9003639-3); 1990.
8. Duckworth, R. M.; Morgan, S. N.; Gilbert, R. J. Oral fluoride measurement for estimation of the anti-caries efficacy of fluoride treatments. J. Dent. Res. 71(Special Issue):836–840; 1992.
9. Afflito, J.; Schmid, R.; Esposito, A.; Toddywala, R.; Gaffar, A. Fluoride availability in human saliva after dentrifice use: Correlation with anticaries effects in rats. J. Dent. Res. 71(Special Issue):841–845; 1992.
10. Zero, D. T.; Raubertas, R. F.; Fu, J.; Pedersen, A. M.; Hayes, A. L.; Featherstone, J. D. B. Fluoride concentrations in plaque, whole saliva, and ductal saliva after application of home-use topical fluorides. J. Dent. Res. 71(11):1768–1775; 1992.
11. Vogel, G. L.; Carey C. M.; Ekstrand, J. Distribution of fluoride in saliva and plaque fluid after a 0.048 mol/L NaF rinse. J. Dent. Res. 71:1553–1557; 1992.
12. Vogel, G. L.; Mao, Y.; Carey, C. M.; Chow, L. C.; Takagi, S. *In vivo* fluoride concentrations measured for two hours after a NaF or a novel two-solution rinse. J. Dent. Res. 71(3):448–452; 1992.