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Corrosive properties of fluoride-containing odontologic gels against titanium

F. Toumelin-Chemla*, F. Rouellet† and G. Burdairon*
**Laboratoire de Biomatériaux de la Faculté de Chirurgie Dentaire de l'Université Paris V and*
†Laboratoire d'Electrochimie de l'Université Paris VI, France

ABSTRACT

Objectives: The purpose of this study is to determine, on a quantitative basis, the kinetics of ionization of pure and alloyed titanium in various electrolytic media including commercial dental gels containing fluoride ions (Fluogel).

Methods: The experimental method is a linear sweep voltammetric analysis, making use of a rotating disc electrode. Several successive analyses of different titanium samples are carried out, particularly as a function of the nature of the electrolytic solutions. The current corrosion I_{cor} is measured by the determination of linear polarization resistence R_p.

Results: R_p and I_{cor} measurements by the voltammetric and analysis confirm the excellent resistance of titanium in physiological solutions; they also show that a fluoride-containing dental gel, which is a fluoridated and acidic preparation, is significantly harmful with respect to the corrosion process of titanium.

Conclusion: The results of this study must draw our attention towards the use of prophylactic gels in which pH is acidic. Indeed titanium suffers an important corrosion process in fluoridated acidic media. Recommendations for the prescription and for the optimized composition of the dental gels could be derived.

KEY WORDS: Titanium, Corrosion, Fluoride ions, Dental gels

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INTRODUCTION

Most metallic alloys used for dental restoration, permanently maintained in the saliva electrolyte, undergo a slow and progressive degradation, as a result of an electrochemical corrosion. The degree of resistance to corrosion, therefore, constitutes a good criterion in the utilization of a metallic biomaterial in the oral medium. Therefore, a large number of studies, most of the time performed *in vitro*, have led to the production of materials which are increasingly resistant to corrosion.

Titanium, which is widely used in surgical restoration, is currently considered to be the best possible material in the constitution of oral implants. Despite its extremely high melting point, titanium is already used for the realization of prosthetic elements, and several investigations are underway to optimize the mechanical and corrosive properties of the alloys[1].

It should be remembered that corrosion is caused by metallic ionization, in terms of its dissolution tension and on the characteristic potential which occurs when a metallic sample is placed in an electrolytic solution. However, different factors, such as the formation of a passivating layer, can considerably modify the properties. Therefore, despite titanium being strongly electronegative, its electrochemical potential E° being equal to -1.63 V SHE^{-1} (ref. 2), it is universally established that its behaviour in ionic solution is superior to that of the other metals. Titanium stability in a corrosive medium results from the formation on the surface of a highly protective passivity film, the thickness of which is between 10 and 20 nm[3]. Pure titanium, which is very reactive and extremely oxidisable when perfectly bare, could develop several oxides of different stoichiometries (TiO, Ti_2O_3, TiO_2); amongst these, TiO_2 is the most commonly seen[4,5].

This phenomenon is being widely used in many procedures for the manufacture of dental implants. The procedure being established by Adell *et al.* has been described by Hench[6]. Therefore, the contact between the metallic implant and the receiving tissues is made through the medium of the oxide-coated surface[7]. In fact, the chemical properties of the external atomic layers condition the osseointegration process. The proven titanium biocompatibility, as an implant material, is then another consequence of its oxide surface properties[4], which accounts for the large

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Correspondence should be addressed to: Dr F. Toumelin-Chemla, Department of Restorative Dentistry, Academie de Paris, Université René Descartes, Faculté de Chirurgie Dentarie, 1 rue Maurice Arnoux, 92129 Montrouge, France.

number of authors who have extensively studied the electrochemical behaviour of titanium alloys used in odontology. The mechanical characteristics of these alloys, whose titanium proportion varies between 85% and 95%, are improved by the addition of aluminium, nickel, copper or vanadium, but the passivity is maintained nearly equal to that of pure titanium[5, 9-11].

Theoretically, this passivation layer should not break down under the conditions surrounding the implant in an oral medium. Moreover, even in more aggressive conditions, i.e. concentrated solutions containing strong acids such as HCl or H_2SO_4, the titantium corrosion remains extremely low[12].

However, within the scope of odontological practice, our attention has been brought to the fact that in a fluoridated medium, and especially in acid-fluoridated solutions, titanium is easily degraded[12,13]. This phenomenon is interpreted as being the result of the incorporation of F^- ions in the oxide layer, whose protective properties are then considerably reduced.

A low quantity of fluoride, in the presence of acid medium, induces the following chemical reaction[12]

$$NaF + CH_3\text{-}COOH \rightarrow HF + CH_3\text{-}COONa.$$

The fluorhydric acid molecules can then react on the titanium oxide:

$$TiO_2 + 2\,HF \rightarrow H_2O + TiOF_2,$$

and give rise to titanium oxyfluorides in solid state. The lattice parameter of these compounds is such that they induce many structural defects in the oxide coating, whose protection is considerably loosened.

Yamaguchi and Otsuda, cited by Bard[12], were the first to describe the titanium disintegration, when submitted to 48% HF solutions action during short periods of time.

On the other hand, we notice a rapid development of the utilization, that is more and more widespread in the odontological field, of fluoridated prophylactic gels. During the past 40 years, the prophylactic application, at regular time intervals, of gels and solutions containing high concentrations of fluorides has indeed become more frequent, reaching a noticeable impact on the dental caries prevention[14].

Owing to the large number of favourable results, the utilization of concentrated fluoridated gels by the professional odontologists has obtained the approval of the US Food & Drug Administration[15], and a number of commercial preparations have been accepted by the Council on Dental Therapeutic of the American Dental Association[16].

These approved dental gels constitute fluoridated and acidic preparations. The pH range of gels generally used is between about 3.2 and 7.7, although it is known that acidic preparations lead to the fast formation of fluorhydric acid. Moreover, according to Dawes[17], one could increase the fluoridated topics' effectiveness by diminishing their pH even more, thus encouraging the formation of calcium fluoride on the tooth surface. Likewise, a recent study carried out by Titanoff *et al.*[18] reveals a significant reduction of gingivitis depending upon brushing twice a day using a SnF_2 gel containing 1000 p.p.m. F^-, 2950 p.p.m. Sn^{++}, the pH being equal to 3. A NaF gel, of the same fluoride concentration but with a pH = 7, reaches twice the inferior results. This study therefore highly recommends the utilization of strongly acidic dental gels.

In this context, many manufacturers have commercialized highly fluoridated gels whose fluoride ion content can reach 10,000 p.p.m. with a pH = 5.5 (Fluogel, Labo. Dentoria, France). However, such a concentration may have some harmful results on corrosion resistance.

We think that the use of any preventive therapy makes it necessary to take into account, not only the favourable effects, but also the potential risks. Therefore, a fundamental study dealing with metallic dental alloys, and particularly titanium, in fluoridated media, is necessary, since there is a large number of pharmaceutical preparations based on concentrated fluorides with an acid pH.

MATERIALS AND METHOD

First, we studied the electrochemical behaviour of spectroscopically pure titanium (Johnson Matthey, U.S.A.). Then, the same procedure was being extended to a titanium alloy produced by Pechiney (France), which is generally recommended for biomedical applications (*Table II*).

The linear sweep voltammetric method, using a rotating electrode, ensures a perfect control of the physicochemical parameters. This permits the duplication under identical conditions of the experiments, thus leading to comparable and reproducible results[19,20]. Each experiment has been repeated four times, the results being identical within the precision of the corrosion current measurements which is ±5%.

The rotating disc electrode device (EDI 101 T Tacussel), comprises an adaptable Teflon tip inside which the titanium specimen is built, so that the metallic surface in contact with the electrolyte is a flat disc with a diameter of 3 mm. The rotation speed has been fixed to 2500 r.p.m.

The electrochemical device used for this study is a Solea Polaroprocesseur 220 T—computerized equipment (*Fig. 1*). It ensures several functions:

- The successive generation of potential values, at predetermined increments. In our experiments, the scan rate was most often 10 mV per second.
- The acquisition as digital data of current values as a function of the potential.
- The automatic adjustment of a sensitivity and of a measurement scale with respect to the studied sam-

ple, followed by the automatic tracing of the current/tension curve, at the most relevant scale.

— The implementation of a curve smoothing program, as well as an interpretation of voltammogram software. For the measurement of the corrosion parameters, the voltammogram is exploited by a mathematical program which determines the linear polarization resistence R_p from the slope $\Delta F/\Delta I$ near the zero current rest potential of the metal. Then the corrosion current is defined from the relationship $I_{cor} \approx RT/FRp$.

In our first experimentations, for a clear objectivation of the current values, the excursion in potentials is carried out inside the interval −500 to +1500 mV versus the Saturated Calomel Electrode. The procedure conditions are similar to those defined by Sarkar[21,22]. Our purpose is to verify in which condition the electrolytic medium has an influence on the corrosion of titanium; then we studied its behaviour in five different media, following a logical programme:

1. Physiological solution of which the composition is simple and known: Ringer's solution[25]:

NaCl	9.0 g
KCl	0.4 g
$CaCl_2, 6H_2O$	0.2 g
$NaHCO_3$	0.2 g
distilled water q.s.p.	1000 ml
pH	7

2. Fluoridated odontological gel Fluogel (Labo, Dentoria) of which the composition is:

NaF	0.553 g
NH_4F	1.126 g
Potassium sorbate	0.553 g
Excipient (pH = 5.5) q.s.p	100 g

3. Ringer's solution with added fluorides, characterized by:

Ringer	20 ml
NaF	0.2 g
NH_4F	0.2 g
pH	6.75

This solution, which is pH neutral, has a fluoride concentration identical to that of Fluogel (10 g l^{-1}).

4. Non-fluoridated Ringer's solution, with added lactic acid, in order to attain an acid pH, which equals 4.
5. Fluoridated Ringer's solution (10 g l^{-1}) acidified by the addition of lactic acid (pH = 5.5).

The titanium samples' shape is defined by the requirements of the voltammetric analysis method. We use Teflon tips which are perfectly adaptable to the working electrode.

The titanium surface initially smoothed down on an electrical polishing machine, using abrasive papers of decreasing granulometries. This surface treatment is machined to a polished mirror finish, using a felt impregnated with aluminum oxide milk of 0.1 µm.

The sample, in which the lateral linings are protected by the Teflon support, is then ready to undergo the voltammetric analysis. Several successive analyses of the same sample are carried out, in particular as a function of the nature or composition of the electrolytic solution. Before each analysis, one only needs to

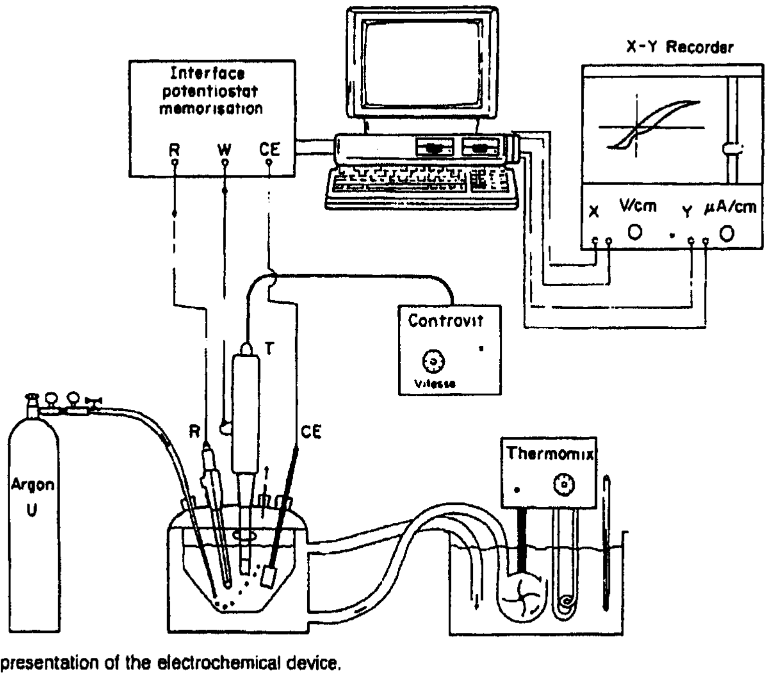

Fig. 1. Diagramatic representation of the electrochemical device.

perform another polishing in order to regenerate a new metallic surface.

RESULTS

Figures 2–6 represent the characteristic titanium voltammograms in the different electrolytic media defined here with:

1. The voltamperometric analysis of titanium in a Ringer solution is representative of a perfectly passivable metal (*Fig. 2*). The first scanning (a) shows a low current, less than 4 μA, which corresponds to the growth of the oxidation film. The second scanning (b), on the same electrode, reveals the characteristic passivation of titanium, since the measured current is virtually zero between −500 and +1000 mV SCE^{-1}. The examination of the electrode surface confirms this result; titanium appears intact and perfectly bright, thus demonstrating its perfect resistance to the electrochemical corrosion, after the formation of a passivating film a few nanometres thick.
2. When we replace the Ringer's solution by a dental fluoridated gel of pH = 5.5 Fluogel for topic applications, we observe a quite different behaviour of the titanium electrode (*Fig. 3*). The first voltamperogram indeed shows an oxidation current which is clearly much higher, already 70 μA at 0 V SCE^{-1}, and which rises very fast, reaching 160 μA at +1500 mV SCE^{-1}. On the other hand, the study of the successive voltamperograms does not show any decrease in the current intensities, thus revealing the absence of the metal passivation. In this acid and fluoridated environment produced by the Fluogel medium, the protecting oxide film has been degraded, thus leading to a fast corrosion process of the metal. The observation of the electrode surface, under the microscope confirms this result, since the titanium shows a completely rough surface due to the formation of crevices resulting from the metal dissolution.

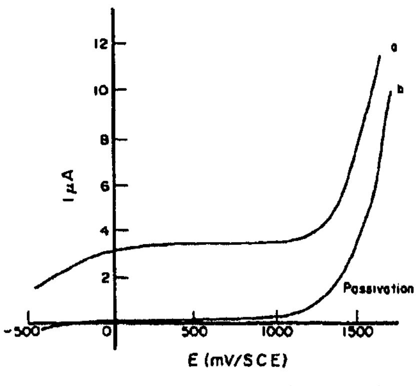

Fig. 2. Voltammograms of pure titanium (J. Matthey) in Ringer's solution. Scan b shows achievement of passivation.

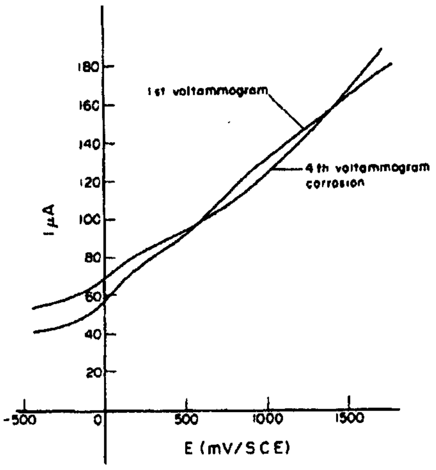

Fig. 3. Voltammograms of pure titanium (J. Matthey) in Fluogel. Successive scans demonstrate a strong corrosion process.

3. In order to determine the eventual influence of the acidity in a fluoride-free electrolyte on the behaviour of titanium, we then studied the electrochemical response of the metal in Ringer's solution made acidic by the adjunction of a small quantity of lactic acid (pH = 4). The analysis of the two successive voltamperograms reveals a titanium behaviour which is quite similar to that observed in the pure Ringer's solution with a neutral pH, i.e. the response is characteristic of the passivation phenomenon (*Fig. 4*). This result confirms the literature data, since titanium remains unattacked even in an acidic medium.
4. It is then logical to determine the degree of contribution of fluorides ions in terms of titanium corrosion. For this purpose, we have studied the metal behaviour in Ringer's solution mixed with fluorides, NaF and NH_4F, in which the concentration is the same as in the Fluogel preparation, that is to say 10 g l^{-1}; the solution pH being virtually neutral, equal to 6.75.

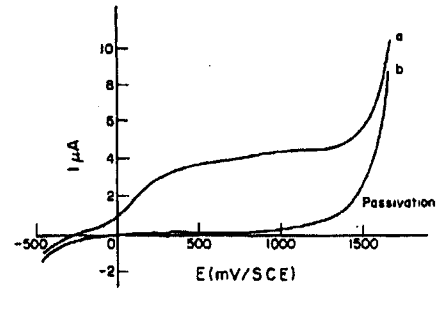

Fig. 4. Voltammograms of pure titanium (J. Matthey) in Ringer's solution acidified to pH = 4 with lactic acid.

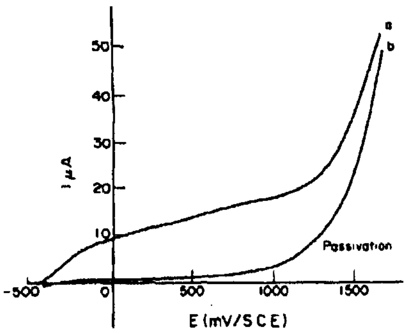

Fig. 5. Voltammograms of pure titanium (J. Matthey) in neutral (pH 6.75) fluoridated solution (10 g l⁻¹).

The first voltamperogram shows oxidation current values which are superior to those obtained in the pure Ringer's solution, 10 μA at 0 V SCE^{-1}, reaching approximately 30 μA at +1400 mV. However, during the second and subsequent scannings, we observe a decay of the oxidation current to less than 1 μA. We could then conclude that the presence of F$^-$ ions in a neutral solution does not hinder the formation of a protecting layer (*Fig. 5*).

5. The last operation lies in studying the titanium electrode behaviour in the same 10 g l^{-1} fluoridated solution, but now mixed with lactic acid, until an acid pH equal to 5.5 is obtained. The electrolytic medium prepared in this way, therefore, has a composition similar to that of a fluoridated gel, Fluogel.

The results which have now been obtained (*Fig. 6*) are significant of the corrosion of titanium, which is not protected anymore; the first voltamperogram shows an oxidation current of 100 μA at 0 V SCE^{-1}, which then increases to reach approximately 200 μA at +1400 mV. The second scanning reveals even higher currents, 200 μA at 0 V SCE^{-1}, which then rise above 600 μA at about 1400 mV. Therefore, in this fluoridated and acidic environment, titanium is undergoing an electrochemical corrosion, which gradually worsens the structure of the metal, the reactive surface increasing as the metal ionization is taking place.

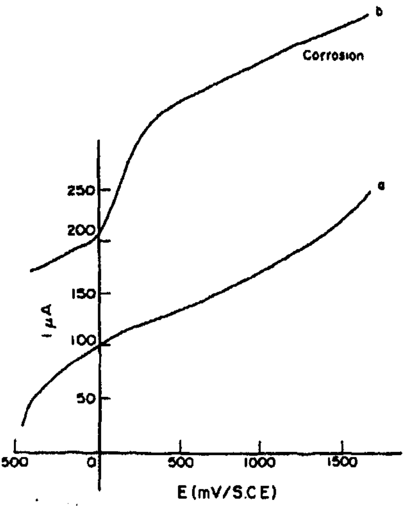

Fig. 6. Voltammograms of pure titanium (J. Matthey) in fluoridated solution (10 g l⁻¹) plus lactic acid (pH=5.5).

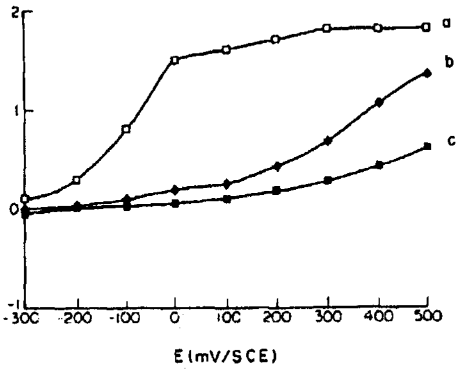

Fig. 7. Voltammograms of Bränemark alloy in Ringer's solution.

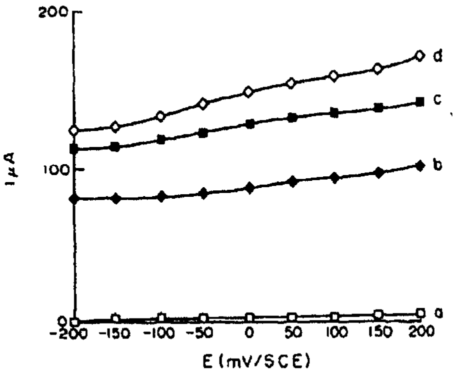

Fig. 8. Four successive voltammograms of first passivated Bränemark alloy in Fluogel.

The whole of the data which are contained in the curves of *Figs 2–6* can be translated into numerical data, which represent the polarization resistance R_p, and the corrosion current i_{corr}; these data are given in *Table I*.

6. In order to complete this study, we have conducted a similar experiment with a few titanium alloys such as Bränemark (commercially pure titanium, i.e. impurities <0.25%) and Ti 6Al 4V (Pechiney, *Table II*), which are frequently used in the making of oral implants. In Ringer's solution, even if we reduce the scan range, the successive voltammograms of Bränemark titanium are characteristics of a perfectly passivable metal (*Fig. 7*). On the other hand, when the same Bränemark alloy samples are immersed in Fluogel, the results are characteristic of a fast and severe corrosion (*Fig. 8*). Quite similar

Table I. Results of the electrochemical measurements

Electrolyte	*R_p Ω·cm²*	*i_{co}, μA·cm⁻²*
Neutral Ringer	$4 \cdot 10^6$	0.006
Acidic Ringer	$2.5 \cdot 10^6$	0.01
Fluogel 1st scanning	$1.2 \cdot 10^4$	2.14
Flueogel 4th scanning	10^4	2.57
Fluorodated neutral Ringer	$5 \cdot 10^5$	0.05
Fluorodated acidic Ringer	$4 \cdot 10^3$	6.0

Table II. Composition of the Ti 6A1 4V alloy (Pechiney)

Elements	*Values*	*Unit*
A1	6.05	%
C	101	p.p.m.
Fe	1612	p.p.m.
H	45	p.p.m.
N	80	p.p.m.
O	1465	p.p.m.
V	3.92	%

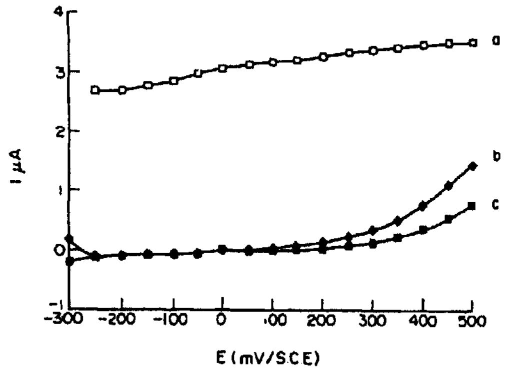

Fig. 9. Three successive voltammograms of Ti 6Al 4V Pechiney alloy in Ringer's solution.

results and conclusions are obtained with the Ti 6A1 4V alloy (*Figs 9, 10*).

Finally, we left a Bränemark implant in Fluogel for 7 days, for spontaneous reaction without any applied potential. The surface of this sample revealed an important crevice corrosion (*Fig. 11*).

DISCUSSION AND CONCLUSION

The results from this study[23] are in accordance with those of Wiig *et al.*[24] and must draw our attention towards the use of prophylactic gels in which the pH is acidic. Indeed titanium, which is a metal known for its excellent resistance to corrosion, suffers an important degradation in fluoridated acidic media. Furthermore, several complementary experiments, undertaken in a similar programme, are enabling us to reveal the harmfulness of the fluoridated acidic gel towards most passivating alloys, such as dental nickel-chromium alloys.

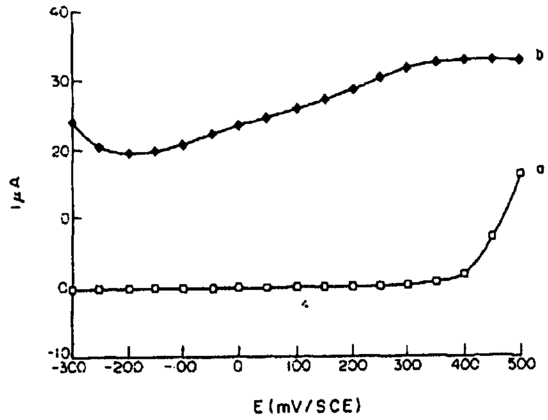

Fig. 10. Two successive voltammograms of first passivated Ti 6Al 4V Pechiney alloy in fluogel.

The free delivery of these dental gels, and their non-controlled utilization, are thus likely to lead to very noticeable side-effects, which are strongly prejudicial to the durability of the metallic prostheses which are present in the oral medium. At the present time, it would be advisable to prescribe these concentrated fluoride gels very carefully, to patients who do not show any metallic restoration nor implant denture. Nevertheless, taking into account the established prophylactic nature[15] of fluoridated constituents against dental decay, some complementary studies, based both on the electrochemical corrosion of the alloys used in odontology, and on preventive measures involving fluorides, is most desirable. These studies should lead to the optimization of the fluoridated gels' formulation, with particular attention being drawn to the pH of these preparations.

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Fig. 11. Microscope photograph (×200) of the surface of Brånemark alloy maintained for 7 days in Fluogel.

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