EFFECT OF FLUORIDE AND EUGENOL CONCENTRATION ON THE CORROSION BEHAVIOR OF TITANIUM IN ARTIFICIAL SALIVA

Latifa Kinani, Abdelilah Chtaini*

Equipe d'Electrochimie et des Matériaux Inorganiques, Faculté des Sciences et Techniques, Université Cadi Ayad, BP 523, Beni Mellal, Maroc

*Corresponding author: chtainia@yahoo.fr, Fax 00 212 23 48 52 01

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Abstract: The purpose of this study was to investigate the effect of fluoride and eugenol concentration on the corrosion behavior of titanium (grade 2) alloy in artificial saliva using potentiodynamic polarization and spectroscopy impedance. Chemical analyses of the surface were characterized by SEM. The results showed that either the NaF or the presence of eugenol in medium saliva had a significant influence on the corrosion rate (J_{corr}) and polarization resistance (R_p): the J_{corr} value increased and R_p decreased in medium containing fluoride, but the presence of eugenol in media improved the corrosion resistance of this alloy.

Keywords: *fluoride, saliva medium, eugenol, corrosion inhibition, dental alloy*

INTRODUCTION

Titanium and titanium alloys are chosen for dental implantology because of their resistance to corrosion and their biocompatibility [1-3]. Titanium and its alloys form a strong passive film on their surfaces. It was reported however that this resistance is significantly reduced in the presence of fluoride, which is also often clinically used in the prevention of dental caries [4-15]. The corrosion resistance of Ti depends largely on the environmental solution that they are placed in.

Due to restrictive environmental laws, inorganic corrosion inhibitors such as chromate or nitrites are replaced by organic compounds [16], organic inhibitors being less or not toxic and so presenting a good compromise between alloying efficiency and environment and human health protection [17-18]. The role and mechanisms of corrosion prevention by most of inhibitors are well-known [19], but all research in this field consists now to design new environmental friendly inhibitors.

Eugenol was constitutive of the studied inhibitor, it is considered like an inhibitor of titanium in fluoride containing environments [20-21].

The aim of this study was to determine the effect of eugenol at different concentrations on the corrosion behavior of Ti alloys in artificial saliva with and without fluoride content.

MATERIALS AND METHODS

Eugenol was prepared in the laboratory following the usual extraction procedure. The specimens used were titanium plates (1 x 1 cm). The electrochemical cell was constituted of three electrodes, platinum was used as the counter electrode, saturated calomel electrode (SCE) as reference electrode, and the working electrode with a titanium plate (1 cm^2). The potentiodynamic control of the working electrode was provided by a potentiostat/Galvanostat (Voltalab 10 PGC 100), and assisted by Master 4 software. The experiments were carried out at 37 °C by circulating the water bath through the double wall of the cell. The surface of specimens was observed using a scanning electron microscope (SEM).

The elctrolyte reference used was Fusayama Meyer artificial saliva. The solution composition is KCl (0.4 g/L), NaCl (0.4 g/L), $CaCl_2$. $9H_2O$ (0.906 g/L), NaH_2PO_4. $2H_2O$ (0.690 g/L), Na_2S. $9H_2O$ (0.005 g/L), urea (1.00 g/L). The pH of this reference saliva (MS) was 7.3.

The second medium (MS + F) used had the MS solution enriched with fluoride ions with a concentration of 0.1 %, corresponding to the average fluoride concentration of the odontological gels mentioned above. Different concentrations (10^{-5}M, 10^{-3}M, 10^{-1}M) were added to these mediums.

RESULTS AND DISCUSSIONS

Similar polarization curves were obtained for titanium in MS, MS + F and MS + F + eugenol mediums (Figs. 1 and 2).

In a fluorinated saliva medium, the alloy also deteriorated and the corrosion rate value was extensively increased. (Table 1).

The corrosion parameters, including E_{corr} ,I_{corr} and R_p obtained from potentiodynamic polarization tests are listed in Table 2.

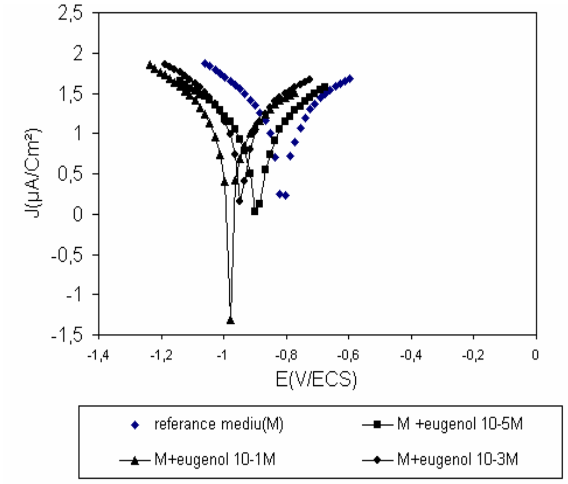

Figure 1. *Polarization curves of titanium in MS and MS + eugenol mediums, with different concentrations of eugenol*

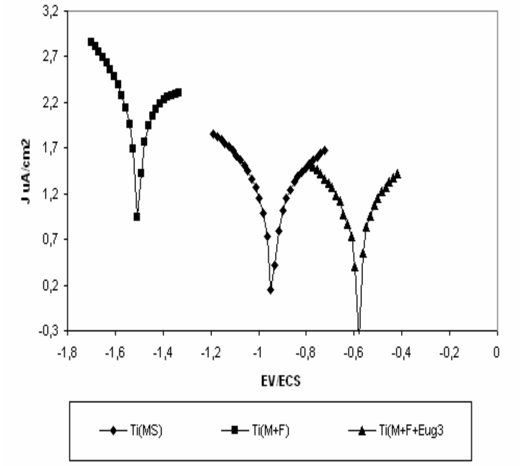

Figure 2. *Polarization curves of titanium in MS, MS + F and MS +F + eugenol mediums*

Table 1. *Electrochemical parameters of titanium in artificial saliva containing fluoride*

Medium	Jcorr [μA/cm^2]	Rp [ohm.cm^2]	E (i = 0) [mV]
Artificial saliva	13.37	5220	-795.3
Artificial saliva + fluoride	131.33	841.59	-1500

Table 2. *Electrochemical parameters of titanium in saliva medium containing different concentration of eugenol*

Eugenol concentration	Jcorr [μA/cm^2]	Rp [ohm.cm^2]	E (i = 0) [mV]	E [%]
0	13.37	5220	-795.3	-
10^{-5}M	13.34	5490	-974.2	0.22
10^{-3}M	8.10	6120	-891.3	39.41
10^{-1}M	7.22	7220	-764.2	45.99

These values show that the current density decreases by increasing the concentration of eugenol, whereas the resistance of polarisation increases in the presence of eugenol. The inhibition efficiency was calculated as following:

$$E[\%] = \left[1 - \frac{i_{corr(inh)}}{i_{corr}}\right] \times 100$$

Figure 3 showed the EIS data, in the form of Nyquist plot, of titanium electrode in artificial saliva containing different concentration of eugenol. The corresponding Rp values are listed in Table 3. As shown in Figure 3, all the plots revealed only one semicircle. The diameter of the semicircle was increased with the eugenol concentration increasing. As listed in Table 3, the Rp was over 6 kΩ, while that of eugenol concentration 10^{-1}M.

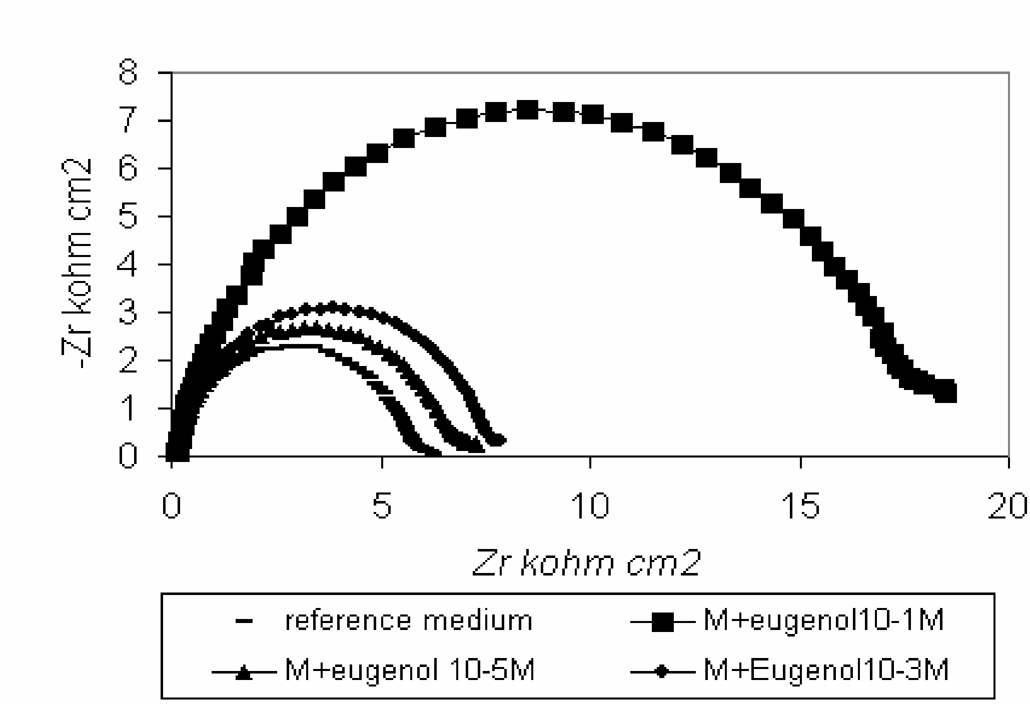

Figure 3. *EIS data of titanium in artificial saliva containing different concentrations of eugenol*

Table 3. *Values of Rp (polarization resistance) and C (Capacity of double layer) obtained from EIS measurements*

Medium	**R [kΩ.cm^2]**	**C [µF/cm^2]**
Artificial saliva (MS)	6.795	6.46
MS + eugenol 10^{-5} M	6.792	8.24
MS + eugenol 10^{-3} M	7.540	8.34
MS + eugenol 10^{-1} M	17.78	9.958

Figure 4 showed the EIS data, in the form of Nyquist plot, of the three mediums, MS, MS + F, and MS + F + Eugenol. Table 4 shows the corresponding Rp values. We noted that the Rp presented smaller values in the MS + F medium. The diameter of semicircle was much larger in MS + F + eugenol medium than in MS and MS + F medium.

Table 4. *Electrochemical parameters of titanium obtained from EIS measurements*

Medium	**R [kΩ.cm^2]**	**C [µF/cm^2]**
MS +Fluoride	0.708	940
MS + F+ eugenol 10^{-5} M	1.647	7.500
MS + F +eugenol 10^{-3} M	2.787	9.960
MS +F +eugenol 10^{-1} M	9.691	9.740

The surface micrographs obtained are shown in Figures 5 – 8. They show a general change in the surface of the titanium in Fusayama Meyer saliva medium, while in the much more fluoridated saliva medium the metal is characterized by localized pitting. The addition of eugenol to fluoridated medium provoked a high corrosion resistance in the titanium grade 2. Eugenol performs well as a no toxic inhibitor in artificial saliva containing fluoride.

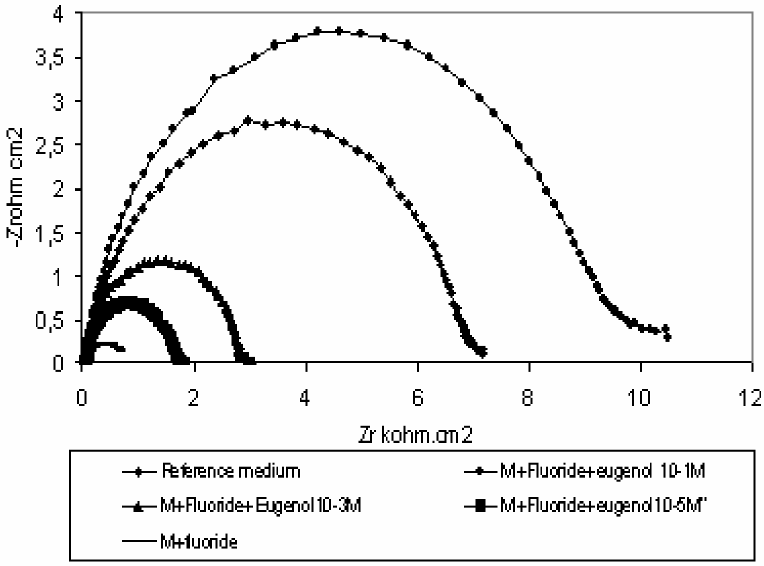

Figure 4. *EIS data of titanium in MS, MS + F and MS + F + Eugenol environments*

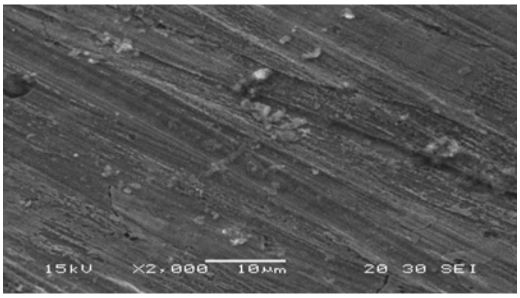

Figure 5. *SEM photomicrograph of grade 2 Ti after electrochemical test in MS medium*

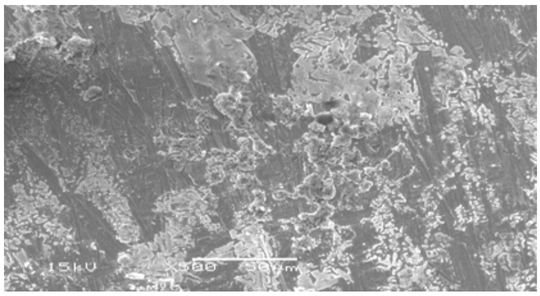

Figure 6. *SEM photomicrograph of grade 2 Ti after electrochemical tests in artificial saliva containing fluoride*

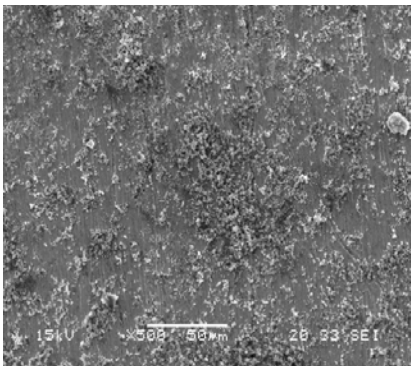

Figure 7. *SEM photomicrograph of grade 2 Ti after electrochemical tests in artificial saliva containing fluoride and eugenol*

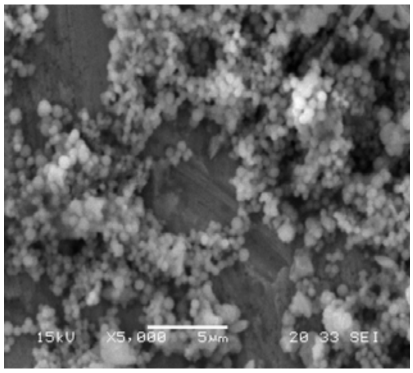

Figure 8. *SEM photomicrograph of grade 2 Ti after electrochemical tests in artificial saliva containing eugenol*

CONCLUSIONS

The electrochemical tests revealed an interaction between the fluoride and titanium, which caused changes to the protective layer of the metal. The main conclusion obtained is as follows:

- the addition of eugenol to artificial saliva medium containing fluoride resulted in high corrosion resistance in the Titanium surface;
- eugenol performs well as an inhibitor in saliva medium containing fluoride.

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