

COMPLEMENTARY TECHNIQUES IN THE EVALUATION OF ELECTROCHEMICAL DEGRADATION OF SOME IMPLANT METALLIC MATERIALS

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INTRODUCTION: The degradation of metals and alloys used as surgical implants is usually a combination of electrochemical and mechanical effects. Titanium is well known as metallic biomaterial in orthopaedics and odontology, having chemical inertia and mechanical resistance [1,2], being one of the best in the field.

The properties of titanium and titanium alloys passive films and their stability in Ringer 2 solutions are studied in this paper using chemiluminescence, infrared spectra and atomic absorption in order to complete electrochemical methods in the evaluation of implant behavior. [2]

MATERIALS AND METHODS:

The specimens were made from Ti, Ti6Al4V and Ti 6Al2, 5Fe.

The composition of titanium electrode is: 0.056% N₂; 0.015%Fe; 0.205%O₂; 0.015% H₂; 0.09% Al; Ti rest. The composition of alloys is 0,08%C; 0,05%N₂; 0,015%H₂; 0,02%O₂; 0,03%Fe, 6,7%Al; 4,5%V: Ti rest ,and 0,08%C; 0,05%N₂; 0,015%H₂; 0,02%O₂; 6,5% Al; 2,5%Fe; Ti rest respectively.

The electrodes were abraded first of all with emery paper, degreased in boiling benzene, chemically polished in 3% HF+20%HNO₃ for 3 minutes, and then thoroughly rinsed with tap and distilled water

The experiments were performed in Ringer 2 solution, at 37°C, taking into account that this is the normal temperature of the human body. Composition of the Ringer 2 solution is the following: NaCl 0.3 g/l, KCl 0.37 g/l, NaHCO₃ 2.44 g/l, MgCl₂.6H₂O 0.203 g/l, MgSO₄.7H₂O 0.123 g/l, Na₂HPO₄.12H₂O 0.07 g/l and NaH₂PO₄.H₂O 0.069 g/l. The pH is 7.4. It is to point out that the Ringer 2 solution is that with phosphate, this anion having a special effect on titanium film stability.

The experiments were performed using the following techniques:

- IR spectra FTIR JASCO 620 equipment was the instrument for the structure changes.

- Atomic absorption spectroscopy AAS 6 Vario with flame for ion release identification.
- Determinations of antioxidant activity of bioliquid by chemiluminescence.
- X- ray photoelectron spectroscopy using ESCALAB MK II.

RESULTS AND DISCUSSIONS:

Regarding the corrosion mechanism, in the case of Ti and titanium alloys, the good corrosion resistance is the result of formation of very stable oxide, typically TiO₂, the most stable oxide of titanium. The passive film is a mixture of oxides, but X-ray photoelectron spectroscopy demonstrated that the predominant species is the TiO₂, as could be seen from fig.1, where the photo emission spectrum of Ti6Al4V electrode in Ringer 2 is presented.

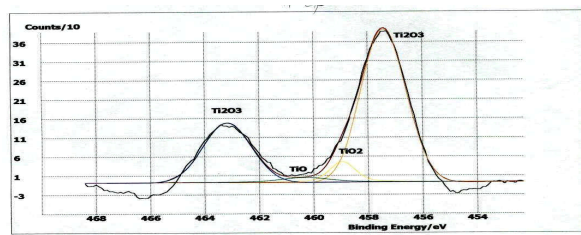


Fig 1. X- ray photoelectron emission spectrum of Ti6Al4V electrode in Ringer 2

The evaluation of the spectra was based on the peak parameters, according to literature data .[3]

The TiO₂ formation is evidenced place at 458.94 eV bonding energy. It is to point out that no vanadium oxide was put in evidence, and the presence of aluminum is due to Al³⁺. A value of 71.2 denotes the oxide formation at the external surface of the electrode. All the titanium oxides are in the internal part of the surface in the vicinity of the metal and are responsible for the high corrosion resistance .

In spite of the very good properties, these passivating alloys can generate metal ions, which diffuse through the passive oxide films. First of all the titanium ion release was put in the evidence for the studied electrodes and the evolution of the titanium quantity is presented in fig 2 together with the regression equation of the process.

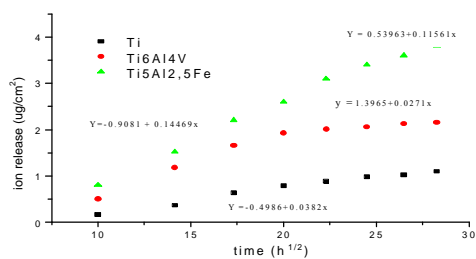


Fig.2. The evolution of titanium ion release in Ringer 2 solution

The initial event during the immersion of titanium in bioliquids is the hydrolysis of the oxide and the establishing of surface-solution equilibrium. Therefore, the passive dissolution is determined by the hydrolysis in the first step. The second step is the transport of dissolution products to the bulk electrolyte. This is a molecular diffusion rate-determining step. The dissolution products released are either neutral species like $\text{Ti}(\text{OH})_2$ or hydroxocomplex such as $\text{TiO}(\text{OH})_2$ [4].

It can be shown why Ti in Ringer 2 solution provides a less susceptibility to corrosion in comparison with Ringer 1 solution [3], probably due to $(\text{H}_2\text{PO}_4)^-$ adsorption. In this case, repassivation is the fast step, in the presence of phosphate ions being adsorbed at metal-oxide interfaces. Phosphate adsorption is also supported by spectral data, according to the following arguments :

- characteristic phosphate band (350cm^{-1} and 1077cm^{-1} for bonded phosphate) appears in the IR spectrum of the reaction product on the electrode surface, and in the same time a decrease of 3400cm^{-1} absorption band related to the OH of hydrogen bonding is observed. At 590 and 470cm^{-1} respectively the existence of Me-OH bond is observed. The $(\text{H}_2\text{PO}_4)^-$ and $(\text{HPO}_4)^-$ adsorption is probably due to a complex formation [4] according to the reaction (1) and (2) respectively:

$$\text{TiO}(\text{OH})_2 + 2 (\text{H}_2\text{PO}_4)^-(\text{aq}) \rightarrow \text{TiO}(\text{H}_2\text{PO}_4)_2 + 2 (\text{OH})^- \quad (1)$$

$$\text{TiO}(\text{OH})_2 + \text{aq} \rightarrow \text{TiO}(\text{HPO}_4) + 2 (\text{OH})^- \quad (2)$$

Antioxidant effect of Ringer 2 solution is confirmed by chemiluminescence data (fig.3) where the chemiluminescent signal evolution after various immersion time of a titanium electrode is presented.

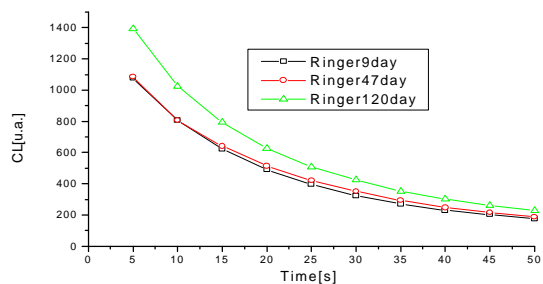


Fig 3. Evolution of chemiluminescent signal in Ringer 2 solution

A change in the solution behavior could be seen, probably related to the passive stratum penetration. In fact, this is an argument for short life radicals consumption (reactive species of oxygen) during complex formation.

CONCLUSION: Chemiluminescence, infrared, photoelectron X-ray, and atomic absorption spectroscopy are valuable arguments for a better understanding of Ti behaviour in body fluids.

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