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# ASPECTS OF METALLIC BIOMATERIALS DEGRADATION IN VARIOUS SIMULATED BIOLOGICAL FLUIDS

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**INTRODUCTION:** Corrosion [1-2] of implant materials is an important aspect of biocompatibility and only the noblest metals (gold and platinum group metals) or the most passive (titanium or chromium) metals have corrosion rates within apparently acceptable levels.

The metallic biomaterials behaviour in bioliquids is a function of many parameters, related to surface preparation and environment specific composition, including the special influence of the chlorine or fluoride anion, [2] or the effect of organic compounds [3].Taking into account such parameters this paper is an assessment of the behaviour of a range of implant materials,including titanium and titanium alloys and stainless steels

**EXPERIMENTAL PART:** Specimens were made from Ti, Ti6Al4V and Ti 6Al2,5Fe and stainless steels ($V_4AS$,$V_2AS$)

*Table 1 Composition of the studied metallic biomaterials*

| Biomaterials | % Wt. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Fe | V | C | O | Cr | Ni | Mo | N | Ti |
| Ti | 0.005 | 0.095 | - | 0.04 | 0.056 | | | | 0.045 | rest |
| Ti-5Al-4V | 4.88 | 0.021 | 3.72 | 0.048 | 0.175 | | | | 0.0153 | rest |
| Ti-6Al-4Fe | 6.12 | 3.87 | - | 0.18 | 0.26 | | | | 0.035 | rest |
| Stainless Steel$V_4AS$, | | rest | | 0.03 | | 16.5-18 | 10.5-13 | 2-2.5 | | - |
| Stainless Steel $V_2AS$ | | rest | | 0.03 | | | 9-11 | - | | 0.05 |
| Stainless Steel DIN 14571 | - | rest | | 0.08 | | | 10.5-13.5 | 2-3 | | 0.4 |

All metallic biomaterials were used as cylindrical electrodes. The experiments were performed in Hank, Ringer 1, Ringer 2 solutions with and without lactic acid, artificial saliva. The temperature measurements was 37°C, the usual temperature of the human body. The surface was prepared in 2 different ways [5]. The treatment A was the usual cleaning, , including chemically polished in 3% HF+20%$HNO_3$, and the procedure B was a more carefully one, including ultrasonic treatment.

Composition of the bioliquids are :

Ringer 1: NaCl 8,6 g/l, $CaCl_2$ 0,33 g/l, KCl 0,3 g/l; pH=7

Ringer 2: NaCl 0.3 g/l, KCl 0.37 g/l, NaHCO3 2.44 g/l, MgCl $_2$.6H $_2$0.203 g/l, $MgSO_4.7H_2O$ 0.123 g/l,

$Na_2HPO_4 12H_2O$ 0.07 g/l and $NaH_2PO_4$.H $_2$0.069 g/l. The pH is 7.4.

Hank: NaCl 8g/l, $CaCl_2$ 0,14 g/l, KCl 0,4 g/l, $MgCl_2.6H_2O$ 0,1 g/l, $Na_2HPO_4.2H_2O$ 0,06 g/l; $KH_2PO_4$ 0,06 g/l, $MgSO_4.7H_2O$ 0,06 g/l si glucoza 1g/l

Artificial saliva: KCl 1,5g/l; $NaHCO_3$ 1,5 g/l; $NaH_2PO_4$ 0,5g/l KSCN 0,5g/l ; lactic acid 0,9g/l

The experiments were performed using following techniques:

Open circuit potential measurement: In open circuit experiments curves potential versus time for a short, medium and long time were obtained and simultaneousely the dependence pH-time was recorded.

Linear polarisation test and cyclic polarisation voltametry using VoltaLab21 with VOLTAMASTER electrochemistry software as a procedure of corrosion rate evaluation.(Stern Geary- method )

Cyclic polarisation experiments were performed using PAR 179 with computer interface

Atomic absorption spectrophotometer determinations for ions release identification

Surface analysis type atomic force microscopy with image analysis program for roughness evaluation

A MedCalc program devoted to medical applications was the instrument for the statistical treatment.

**RESULTS AND DISCUSSIONS:** Variations of open circuit potentials reveal, for all studied implant materials, that these potentials are active at the beginning and tend to a constant level, denoting passive, protective, very stable films for long term exposure, therefore, the implant materials present a long-term stability.In all simulated body solutions, the open circuit

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potentials of the studied materials were more electronegative for the initial period of about 12 exposure days, then and after various period of exposure days ( depending of the material ) became nobler.These values fluctuated from more electronegative value in the order $V_4$AS,$V_2$AS, Ti-6Al-4Fe, Ti-5Al-4V and Ti. This trend is the same in all bioliquids as an argument of the idea that alloying is not a corrosion prevention requirement, titanium being more stable than its alloys.Monitoring of open circuit potential and the use of a statistical treatment program allows to obtain the scatter diagrams. The help of such diagrams is important for the computing of the regression equation and the prognosis of the potential evolution for longer time than the experimental one.

The corrosion rates were obtained by linear polarisation. From table 1, it results that all tested implant materials present a good resistance for the 8000 hours period, confirming their very good stability.for Ti and Ti alloys in body fluds, as well as the good stability for stainless steels in the same conditions.

*Table 2 Corrosion rates (mm/yr) of all studied implant materials in bioliquids surface treatment (A )*

| Biomaterial | Corrosion rates (mm/yr) | | | | | |
|---|---|---|---|---|---|---|
| | Ringer 1 | Ringer 2 | Hank | Lactic acid 10% | Ringer 1 +lactic acid 10% | Ringer 2 +lactic acid 10% |
| Ti | 0,0079 | 0,0001 | 0,00035 | 0,048 | | 0,0000013 |
| Ti-5Al-4V | 0,0114 | 0,000096 | 0,000095 | 0,1470 | | |
| Ti-6Al-4Fe | 0,024 | 0,00783 | O,0174 | 0.0 156 | | |
| $V_4$AS | 0,352 | 0,289 | 0,304 | - | 0,284 | 0,312 |
| $V_2$AS | 0,387 | 0,295 | 0,324 | - | 0,329 | 0,315 |
| 316L | 0,221 | 0,176 | 0,195 | - | 0,198 | 0,218 |

According to these corrosion rates the amount of ion release is small in all cases, but being a contamination, the monitoring is an important aspect of the degradation and was performed in all cases. As an example in fig.1 evolution of ion releas eand regression equations are presented

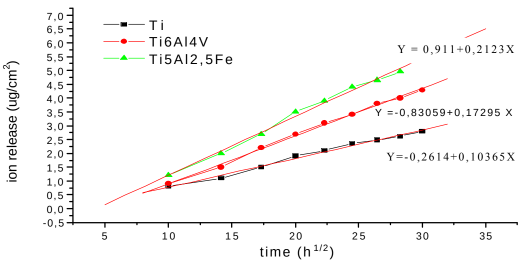


*Fig 1. Ion release in Ringer 1.*

Polarisation curves and cyclic voltamogrames of titanium and Ti-5Al-4V, Ti-6Al-4Fe alloys obtained after various exposure periods [ ] show that all biomaterials are self passivated and the corrosion process is under anodic control. The passive films formed on the surface ary stable.

Ti- alloy with iron and stainless steel voltammogrames has revealed pitting attack at a pitting initiation potential around 3 V; the hysteresis curve indicates that the cease pitting potential is in all cases around +1.75 V, a very noble potential which can not be reached in the biological liquids. Therefore, there is no risk of pitting attack for this alloy in extra-cellular fluids. In table 3 a measure of susceptibility to local corrosion the difference between breakdown potential ($E_{br}$ )and the protection potential ($E_{pr}$) are presented for studied implant materials.

*Table 3. Parameters from cyclic anodic polarization (surface treatment A)*

| Biomaterial | $E_{br} - E_{pr}$ ( mV) | | | | | |
|---|---|---|---|---|---|---|
| | Ringer 1 | Ringer 2 | Hank | Saliva | Ringer 1 +lactic acid | Ringer 2 +lactic acid |
| Ti | - | - | - | 130 | - | - |
| Ti-5Al-4V | 2654 | 800 | - | 415 | 100 | 100 |
| Ti-6Al 4Fe | 2694 | 1000 | 1900 | - | 1520 | 700 |
| $V_2$AS | 384 | 332 | 370 | - | 358 | 340 |
| $V_4$AS | 250 | 217 | 352 | 360 | 225 | 308 |
| 316 L | 232 | 154 | 202 | 373 | 256 | 195 |

Regarding the surface treatment influence to the corrosion susceptibility, as an example, a Ti-6Al-4Fe electrode sample treated in the way A is compared with a similar electrode treated in the way B, when all the other conditions are similar. As a result, AFM analysis indicates a 281.4006 nm average roughness, which is correlated with a 1000mV value ($E_{br}$ - $E_{pr}$ ) for Ti-6Al-4Fe electrodes alloy treated with. 3% HF+20%$HNO_3$. In the case of second sample of Ti-6Al-4Fe electrode, treated in the way B, no breakdown was registered and the average roughness has lower values (194.71 nm ).

**CONCLUSIONS:** In vitro, all tested materials present low corrosion rates which attest their good (stainless steel ) and very good stability ( Ti and Ti alloys), and this stability is related to environment, and surface treatment and properties.

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