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SOME TYPICAL CYCLIC VOLTAMOGRAMS OBTAINED FOR DENTAL ALLOYS IN SIMULATED HUMAN BODY FLUIDS

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ABSTRACT. The existence of various classes of implant materials and metallic alloys used in dentistry, as well as the complex compositions of natural or simulated human body fluids, make possible to appear a very contrasting and complicated chemical and electrochemical behaviour. Among the experimental methods for studying the corrosion performances in simulated human body fluids, the potentiodynamic tests take up a special place, being very rapid and providing many informations about the electrochemical processes involved.

A few cyclic voltamograms are presented and discussed, analyzing the main processes which characterize the electrochemical behaviour of the studied materials in various solutions, as: passivation by anodic oxidation (titanium and titanium alloys in acidic media and in Ringer type solutions), "pitting" type corrosion (Cu-Al-Fe and Ni-Cr-Fe alloys in artificial saliva), secondary anodic processes as insoluble salt formation (Cu-Al-Fe alloy in a complex sulfuric medium and allied titanium in Ringer solution).

KEY WORDS: titanium alloys, gaudent, cyclic voltamograms, corrosion, pitting corrosion

INTRODUCTION

The corrosion of metals and metallic alloys in aqueous environments of body fluids is one of the major processes that cause problems when these materials are used as implants in the human body [1]. The corrosion resistance of various metal alloys is evaluated usually by such techniques as immersion tests or vapor contact tests, which nevertheless are subjective and time consuming. On the other hand, as a guide for optimum corrosion resistance, American Dental Association prescribes some composition limits of alloy [2], but it has been demonstrated that composition limits are not always a guarantee of satisfactory corrosion resistance [3].

Because corrosion in an aqueous medium of the sort provided by body fluids is an electrochemical process [1], [4], many electrochemical methods can be used for characterizing the corrosion processes, these being very quick tests for screening of alloys from the corrosion stand point. The electrochemical measurements include zero-current tests (open circuit potential-time curves), impedance tests, potentiostatic tests, linear polarization curves and cyclic polarization curves. By far, the most common electrochemical test for corrosion resistance is cyclic polarization, where the working electrode, realized on the basis of the studied alloy, is polarized in a positive direction (potential increases) until localized or generalized corrosion initiates, as indicated by a large increase of the corrosion current, followed by a cathodic polarization (a polarization in a negative direction) until a pre-established potential, when the current have a negative value. These potential curves evidences many electrochemical processes which are involved in the corrosion or passivation of metallic alloys.

This paper presents a few typical cyclic voltamograms, evidencing different electrochemical processes characteristic for metallic biomaterials.

EXPERIMENTAL

The corrosion behaviour of the investigated alloys was studied by cyclic polarization curves obtained on a VoltaLab 32 electrochemical system (Radiometer Copenhagen) consisting from a potentiostat, an electrochemical interface and a computer equipped with the acquisition and processing data software Voltamaster 2. The three-electrode electrochemical cell used was equipped with a thermostatic system and a stirring and bubbling of inert gas system. Working cylinder electrodes were mounted in a teflon support to enable the connecting to rotating electrode of electrochemical system. A 0.02 cm^2 cross-area of working electrode was used. Each specimen was polished with SiC paper down up 2500 grit specification, washed in distilled water, degreased with acetone, washed and maintained in double-distilled water until the immersion of specimen within the electrochemical cell. A saturated calomel electrode (SCE) was used as a reference and a platinum electrode as a counter. The electrolytes were maintained at 36.5 ^{o}C throughout the tests. In some tests the electrolytes were de-aerated with pure nitrogen gas at a flow rate of 150 cm^3/min for 60 min before and 15 min after the immersion of the work electrodes.

From a test to another the testing conditions were modified, namely: potential range, scan rate of potential (dE/dt), resolution time t_r and corrosion medium.

The compositions of the used electrolytes are presenten in Table 1.

Table 1

The compositions of the corrosion media

Nr.	Electrolyte	Composition
1	SALIVA 1 (Fusayama [5]) pH = 6.18	NaCl - 0.400 g/L, KCl - 0.400 g/L, $NaH_2PO_4.H_2O$ - 0.690 g/L, $Na_2S_{.}$ $9H_2O$ - 0.005 g/L, Urea - 1.000 g/L, $CaCl_2.2H_2O$ - 0.795 g/L
2	SALIVA 2 (Rondelli, [6]) pH = 7.75	KCl - 1.47 g/L, $NaHCO_3$ - 1.25 g/L, KSCN - 0.52 g/L, $KH_2PO_4.H_2O$ - 0.19 g/L
3	RINGER 1 PH = 6.3	NaCl /8.6 g/l , KCl - 0.3 g/l , $CaCl_2$- 0.33 g/l H_2O , HCl 0.1N – 1mL
4	RINGER 2 [7] pH = 7.3	NaCl /8.6 g/l , KCl - 0.3 g/l , $CaCl_2$- 0.33 g/l H_2O , HCl 0.1N – 1mL
5	ACIDIC SOLUTION 3 pH = 2.64	Lactic acid - 4.5 g/l, NaCl - 2.9 g/l
6	ACIDIC SOLUTION 4 pH = 1.35	H_2SO_4 /- 9.8 g/l , NaCl - 4.3 g/l
7	HCl, 1N	37.5 gHCl/l
8	H_2SO_4, 1N	49 g H_2SO_4/l

The studied alloys have the composition presented in Table 2.

Table 2

The compositions of the studied alloys

Nr.crt.	ALLOY	MAIN COMPOSITION
1	GAUDENT S	Cu-82.0 %, Al-9.97 %, Ni – 4.35 %, Fe – 1.32 %, Mn – 2.04 %
2	Ti6Al4V	Ti – 90 %, Al – 6%, V – 4 %
3	Ti5Al2.5Fe	Ti – 92.5 %, Al – 5%, Fe –2.5 %
4	V – ALLOY	Ni-72%, Cr-20%, Fe-6%
5	N - ALLOY	Ni-63%, Cr-25%, Mo-10%
6	C - ALLOY	Co-65%, Cr-29%, Mo-6%
7	VITTALIUM 2000	Co-63.8%, Cr-28.5%, Mo-6%

RESULTS AND DISCUSSION

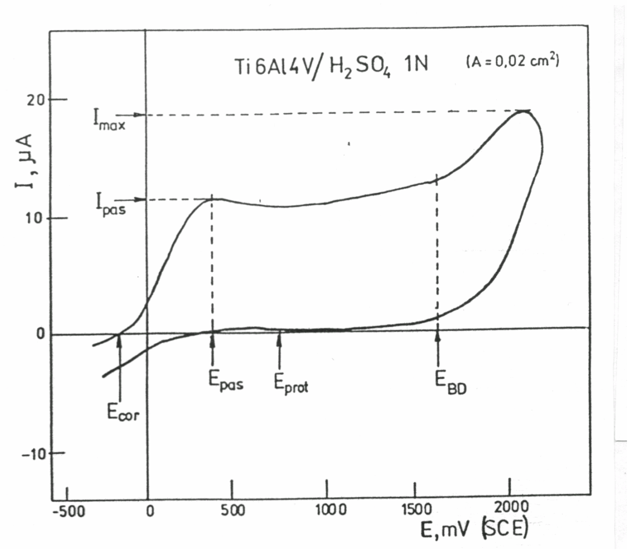


Fig. 1. Cyclic voltamogram for Ti6Al4V alloy 1N H_2SO_4 at 36.5^0C, dE/dt=20 mV/s, t_r=0.8s

In Fig 1 is presented the cyclic voltamogram for Ti6Al4V alloy in 1N sulfuric acid. This curve is characteristic for materials which in an adequate medium presents an anodic oxidation process, in this case Ti → Ti^{4+} and the formed TiO_2 is a protecting film which prevent the corrosion. This process takes place in the potential domain E_{pass} – E_{BD} and is characterized by the passivation current, I_{pass}. At potentials higher than E_{BD} the anodic corrosion or oxygen formation take place.

When the reverse branch of the voltamogram passes by zero current value, E = E_{prot}, one considers that the respective material is protected against corrosion.

Fig.2 presents, comparatively, the cyclic votamograms for Ti6Al4V alloy in acid media (1N H_2SO_4), in weak acid and weak basic simulated human fluids on Ringer type. These point out that, as different on the electrochemical behavior in sulfuric acid, in more complex media other anodic processes, as salt formation and deposition on the metal surface disturb the passivation process. Moreover, in these media the degradation processes are more pronounced, as indicate by fact that the corrosion current at potentials higher than break down potential is much more than that for pure acid medium.

Cyclic voltamograms for Ti5Al2.5Fe in sulfuric acid and in Ringer solutions emphasize a similar behavior (Fig 3 and 4). In sulfuric acid the oxidation/ passivation process is non-disturbed and the formed TiO_2 film is stable, while in Ringer solutions the disturbing processes is more pronounced than those found in the case of Ti6Al4V alloy. This is due to the Fe from alloy composition.

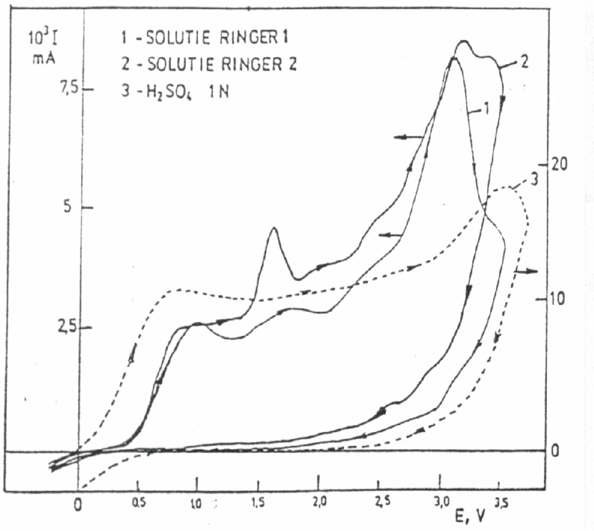
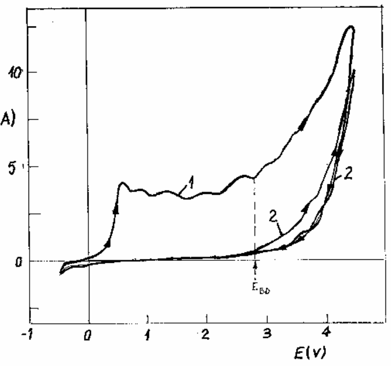


Fig. 2. Cyclic voltamogram for Ti6Al4V in H_2SO_4 and Ringer solutions at 36.5^{0}C, dE/dt=20 mV/s



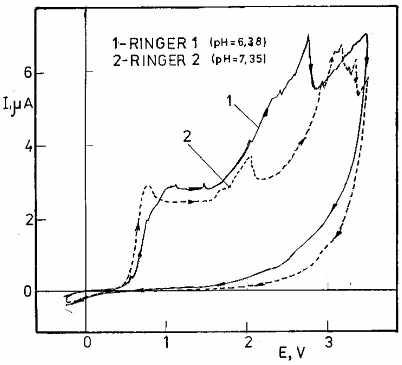


Fig 3. Cyclic voltamograms for Ti5Al2.5Fe In H_2SO_4 1N **–** (1) **–** fresh cleaned surface (2)- electrochemical passived surface

Fig. 4. Cyclic voltamograms for Ti5Al2.5Fe in Ringer solutions(1) ; pH =6.38; (2) **-** Ringer 2 soluttion; pH = 7.35

The anodic passivation process is not present in the case of the alloys without titanium as in the case of the non-noble Ni-Cr or Co-Cr alloys.

In Fig. 5 are presented some cyclic voltamograms obtained for V-alloy (Ni-Cr-Fe) obtained in deaerated SALIVA 2 (Rondelli) working with, fresh surface, old surface or cathodic polarized surfaces of the studied electrode:

- curve 1 - fresh surface;
- curves 2 and 3 - old surface (after first and second cyclic polarization
- curve 4 - registered after 10 s cathodic polarization at –500 mV;

- curve 5 – registered after 30 s cathodic polarization at –500 mV;
- curve 6 - registered after 120 s of cathodic polarization at –500 mV.

As can be seen these curves point out a "pitting" corrosion, irrespective of metal surface preparing. This behaviour is due only to presence of the iron in the alloy.

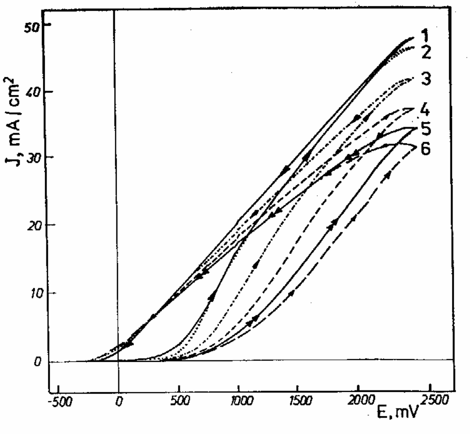


Fig. 5. Cyclic potentiodynamic curves for V-alloy in SALIVA 2, at 36.5 ^{o}C; dE/dt=50 mV/s t_r = 0.8 s

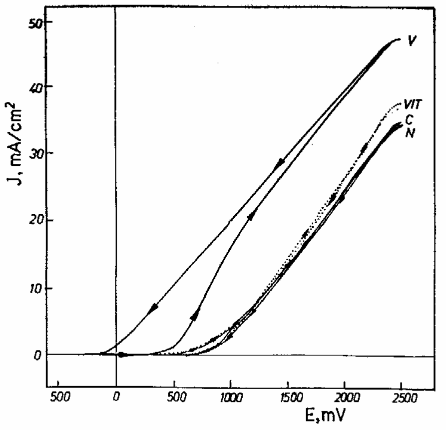


Fig. 6. Cyclic potentiodynamic curves for non-noble alloys in SALIVA 2, at 36.5 ^{o}C dE/dt=50 mV/s , t_r = 0.8 s

The cyclic potentiodynamic curves for the other three non-noble dental alloys (N, C and Vitallium 2000), by comparison with those obtained in same condition for V-alloy, are presented in Fig. 6. While the Ni-Cr-Fe alloy exhibit a typical curve for pitting corrosion, appearing at a relative little electrode potential, the alloys without iron in composition exhibit a generalized corrosion, taking place at a much more potential, the same for the three samples. This generalized corrosion is due perhaps to the oxidizing dissolution of Cr. Relative high values of the break down potential can be associated wit the presence of molybdenum in alloy, this element playing a distinctive role for the passivation rate decrease and provide an efficient resistance to pitting (quite different from the Fe-containing alloys).

The behavior of the Gaudent alloy in various corrosion media are presented in Fig. 7, 8.

It can be seen the essential role of the corrosion medium. Thus, in Fusayama 's solution (SALIVA 1) the alloy exhibit a pitting type corrosion, with a relative large potential domain of repassivation. In Rondelli solution (SALIVA 2) also a pitting corrosion is prresent, but the repassivation interval is considerable reduced; the break down potential and the repassivation potential coincides [8]

In the saline organic solution (acidic solution 3) the current densities are two time higher than those obtained in the other two solutions and no pitting corrosion is observed. In this case a typical dissolution process being perhaps the most probable process, but a hysterezis loop appears.

In sulfuric acid solution (acidic solution 4) the cyclic voltamogram is quite complexe, indicating a very complicated corrosion process, where the dissolution of CuO or Cu_2O fim is accompanied by formation of some insoluble saline deposits or soluble salts.

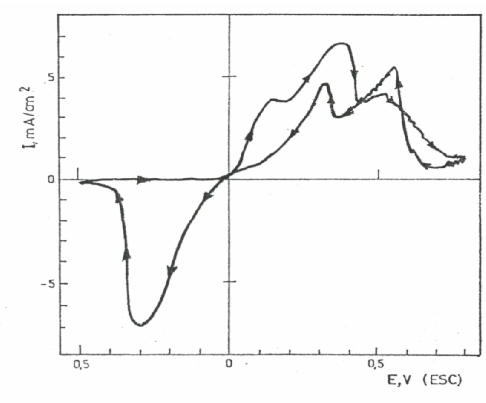


Fig. 7. Cyclic voltamograms for Gaudent S in SALIVA 1, SALIVA 2 and acidic solution 3 dE/dt = 50 mV/s, t_r = 0.8 s

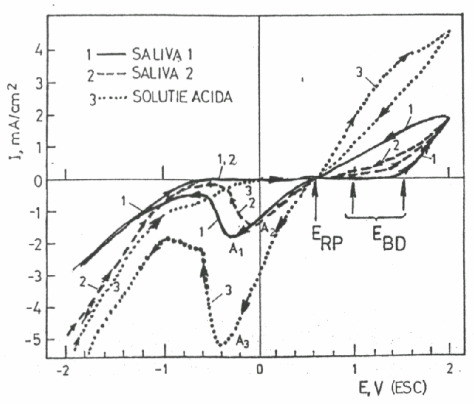


Fig. 8. Cyclic voltamogran for Gaudent S in acidic solution 4 ; dE/dt = 50 mV/s t_r = 0.8 s

In all solutions, the cyclic polarization curves for Gaudent S alloy exhibit a pronounced cathodic peak associated with any electro-reduction processes of the corrosion products [9].

CONCLUSIONS

The cyclic polarization curves have very different shapes depending on nature and composition of the studied alloy, on composition of the corrosion media, on pH, and so on.

Cyclic polarisation curves offer many informations concerning the passivation/corrosion processes taking place in various alloy/corrosion media systems under action of an electrode potential.

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