

Study of Electrochemical Behavior of Some Dental Alloys

ALICE ARINA CIOCAN PENDEFUNDA¹, CONSTANTA MOCANU^{2,*}, DORIANA AGOP FORNA¹, CRISTINA IORDACHE¹, ELENA LUCA¹, GABRIELA IFTENI¹, CONSUELA NORINA FORNA¹

¹Grigore T.Popa University of Medicine and Pharmacy Iasi, Faculty of Dental Medicine, 16 Universitatii Str., 700115, Iasi, Romania

²Apollonia University, Faculty of Dental Medicine, Endodontics Department, 2 Muzicii Str., 700399, Iasi, Romania

The purpose of the study is to investigate the electrochemical behavior of two dental alloys: palladium alloy (Palidor) and Ni-Cr alloy (Verasoft) in three types of artificial saliva. Determination of corrosion potential and recording of linear and cyclic polarization curves were performed with PGP201 potentiostat (VoltaLab 21-Radelkis Copenhagen). In order to study the modifications produced on the surface of the electrodes, a complex optical microscope MC 1 research type (IOR, Romania) was used, adapted to a digital camera, which was connected to a computer for the digital acquisition of images. Two metal alloys based on Ag-Pd and Ni-Cr were used for the experiments. The materials used came from different types of dental restorations removed from the oral cavity of the patients after a 5-15 years period. As corrosion environments, three artificial saliva were used: Fusayama, Afnor and Rondelli. The Pd-Ag dental alloy exhibits a very good corrosion resistance and the treatment in the Afnor saliva does not affect the surface of the alloy. Electrochemical behavior in Fusayama-Meyer's saliva of the alloy surface results in a series of spots representing deposits of insoluble salts resulting from the oxidation process, while in the Rondelli saliva there is a series of small corrosion points on the alloy surface. The behavior of the Verasoft alloy in the Afnor and Rondelli saliva is similar; In both solutions, the potential breakthroughs are very close, but in Fusayama-Meyer's saliva, the potential for initiation of corrosion points is very low (206 mV), a potential that can be encountered in the oral cavity. All metals and metal alloys, even the noble and semi-precious ones, are susceptible to corrosion, forming compounds with properties different from those of the metal or base alloy, which change their surface condition. Metallic dental restorations are permanently affected by the factors of the oral environment (physical-mechanical, chemical and biological), being subjected to a continuous process of degradation.

Keywords: dental alloys, corrosion, artificial saliva

Electrochemical methods for the study of the behavior of metals and dental alloys in various environments allow for quick information on: the thermodynamic corrosion probability of a metal immersed in a fluid, the instant corrosion rate (corrosion speed at simple metal immersion in the medium corrosion), the type of corrosion (generalized or localized) and its intensity, as well as the influence factors of corrosion [1,2]. Another method of characterizing corrosion processes is cyclic potentiometry [1-4]. In this method the polarization curves are plotted, successively for the first increasing and then decreasing values of the work electrode potential, recording the current in the circuit. Both the corrosion potential and the instantaneous corrosion current characterize the metal corrosion in a given equilibrium environment when the metal is immersed in the medium [4,5]. When the metal is polarized, positively or negatively, by applying a potential different from the potential of corrosion (the equilibrium potential) in the system, oxidation or reduction reactions may occur on both the metal surface and the electrolyte [4]. Additional details on processes that occur in the system can be obtained from the analysis of cyclic polarization curves. In order to obtain them, the potential of the electrode formed with the alloy to be studied is increased at a constant rate in a positive sense to a pre-set value, after which it is scaled backwards (to negative values up to the initial value or to another value) [4,5]. Throughout the duration of the potential sweep the current passing through the solution between the working electrode and an auxiliary platinum electrode is measured,

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dental alloys: palladium based alloy (Palidor) and Ni-Cr alloy (Verasoft).

Experimental part

Material and method

Experimental measurements

Determination of corrosion potential and recording of linear and cyclic polarization curves were performed with PGP201 potentiostat (VoltaLab 21) Radelkis Copenhagen). A glass cell with a useful volume of 50-150 mL was used for measurements. A reference electrolyte of a capillary electrode with Luggin capillary was used, and a platinum electrode was used as an auxiliary electrode (measuring electrode). For the study of the modifications produced on the surface of the electrodes, a complex optical microscope of type MC 1 (IOR, Romania) (fig. 1) was used,



Fig. 1. MC 1 research microscope

*email: constanta_mocanu@yahoo.com

which allows the observation in transmitted light, in reflected light, in polarized light, in fluorescent light, in dark field and phase contrast, to which a LOGITECH CLICKSMART 510 digital camera has been adapted, which has been connected to a computer for digital image acquisition.

Provided with several interchangeable lenses, with various reflected image increments of 133, 266 and 500 times, sufficient to highlight the superficial aspects observed.

Dental materials used

Two metal alloys were used for studies, the compositions of which are presented in table 1. The materials used came from different types of dental restorations removed from the oral cavity of the patients after a 5-15 year operation (fig. 2).

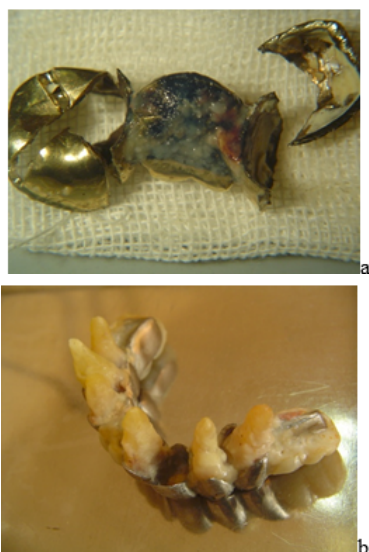


Fig. 2 Removable prosthetic restorations from patient oral cavity used for sample preparation

Table 1
COMPOSITION OF DENTAL ALLOYS USED

ALLOY	Composition	Density (g/cm ³)
PALIAG	Ag-58.5%, Pd-27.4%, Cu10.5%, Au-2%, Zn-1.5%, Ir-0.1%	11.1
VERASOFT	Ni-53.6%, Mn-19.50%, Cr- 14.5%, Cu-9.5%, Al-1.6%, Si-1.5%	7.7

Corrosion environment	Composition	pH
Saliva Afnor [5]	NaCl-0.7 g/L, KCl-1.2 g/L, Na ₂ HPO ₄ ·H ₂ O- 0.26 g/L, NaHCO ₃ -1.5 g/L, KSCN-0.33 g/L, uree -1.35 g/L)	6.78
Saliva Fusayama[5]	NaCl - 0,40; KCl - 0,40; NaH ₂ PO ₄ ·H ₂ O - 0,69; uree - 1,00; Na ₂ S·9H ₂ O - 0,005; CaCl ₂ - 0,79	6.24
Saliva Rondelli [5]	KCl-1.470 g/L, NaHCO ₃ -1.250 g/L, KSCN- 0.520 g/L, KH ₂ PO ₄ ·H ₂ O-0.190 g/L	7.52

As corrosion environments, three artificial saliva were used, the composition and pH of which are shown in table 2.

Electrodes preparation

The electrodes used in electrochemical corrosion measurements were made from dental materials recovered from the oral cavity of some patients. The electrodes have been made so that the surface exposed to the corrosion medium was flat, without edges or corners. After being embedded in epoxy resin, the surface with the metallic sample was polished flat on SiC abrasive paper, with various granulations, until a glossy surface was obtained (mirror type). Before the measurements, the electrodes were ground again on very fine abrasive paper (sand 1500, 2000 and 2500), degreased and ultrasonically cleaned in acetone, ethyl alcohol and distilled water.

In the present study, the cyclic polarization curves (cyclic voltamograms) were recorded on the potential range between (-1000) mV and (+1000) mV with a potential sweep rate of 10 mV / s. Starting from a sufficiently high negative potential in order to reduce all ionic or molecular species in the solution and possibly on the surface of the alloy, the electrochemical process is performed on a *clean* surface. The maximum anode limit (+ 1000 mV) is chosen by about 400 to 500 mV higher than galvanic potentials that can normally occur in the oral cavity, in order to *catch* any potential processes that may occur accidentally. The velocity variation of the work electrode potential was relatively high in order to obtain sufficient current intensities

Results and discussions

The behavior of the Paliag alloy in artificial saliva

Potential-dynamic cyclic polarization curves obtained for Paliag in the artificial saliva with which it was worked are shown in figure 3.

From the diagram it can be seen that the Paliag dental alloy exhibits very good corrosion resistance, the peak current recorded on the anodic branch of the polarization curve in the Fusayama-Meyer saliva does not indicate alloy

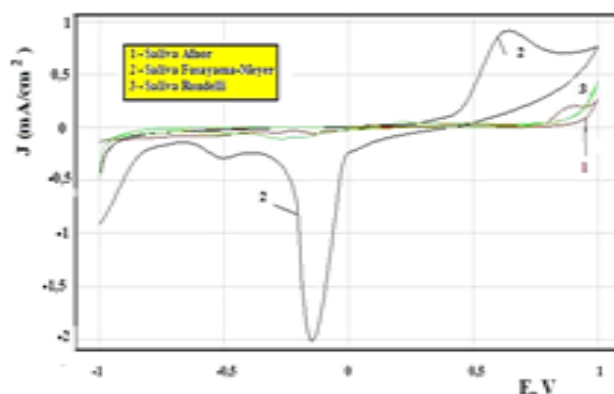


Fig. 3. Cyclic voltamograms for Paliag alloy in artificial saliva

Table 2
COMPOSITION AND pH OF THE CORROSION ENVIRONMENTS USED

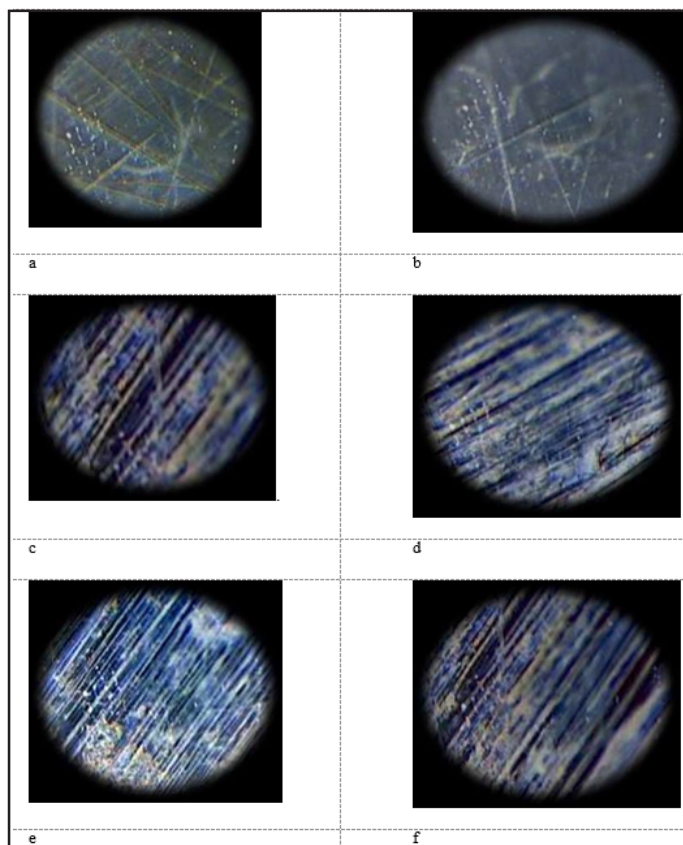


Fig. 4. Paliag alloy surface appearance (x500) - initially, (b) - in Afnor saliva, (c) - after treatment with Fusayama-Meyer saliva, (d) idem after removing of salts with filter paper (e) - after treatment with Rondelli saliva (e) idem after removing of salts with filter paper (f)

corrosion but is due to the oxidation of a species from the solution under the catalytic action of alloy palladium.

The peak on the cathodic branch (the turning curve) indicates the process of reduction of the oxidized species in the anodic process. Probably the species that undergoes this oxidation/reduction process is sodium sulphide. As can be seen from figure 4, these processes in solution do not essentially affect the surface of the alloy.

Thus, the following can be mentioned:

-The treatment in Afhor's saliva does not affect the surface of the alloy, neither in terms of corrosion nor by deposition of oxidation products from the solution (fig. 4 b);

-Following the electrochemical treatment of Fusayama-Meyer saliva on the surface of the alloy, a series of stains appear to represent deposits of insoluble salts resulting from the oxidation process (fig. 4 c) and which are easily removed by simply wiping off with filter paper (fig. 4 d). Such spots have also been reported in the case of restorations and ganato-prosthetic devices in Paliag, in the oral cavity.

-Following the electrochemical treatment of Rondelli saliva on the surface of the alloy, small oval corrosion points are formed which are no longer removed by wiping with filter paper (figs. 4 e and f).

However, since the recorded current density in this saliva is very small (fig. 3), it seems that this is not electrochemical corrosion, but rather it is possible to admit a chemical corrosion through the interaction of silver and copper alloy with Sulphonium ammonium and, respectively, with sodium bicarbonate in the slightly alkaline medium.

The behavior of VERASOFT alloy in artificial saliva

Verasoft alloy is part of the category of non-precious metal alloys with an appreciable content of nickel, manganese and chromium but also contains about 10% copper. Nickel and copper are recognized as metals in alloys that can induce point corrosion (2). This can also be

seen from the cyclic polarization curves presented in figure 5.

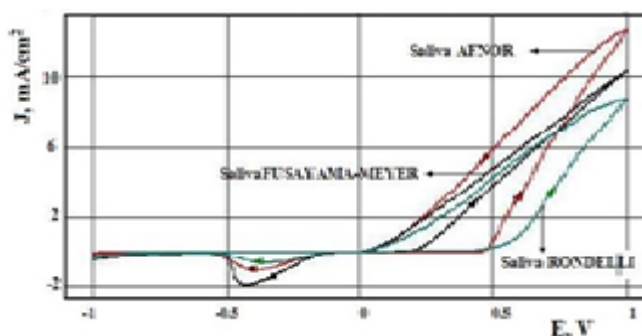


Fig. 5. Cyclic polarization curves for VERASOFT dental alloy in artificial saliva

The value the points of the corrosion process in points are presented in table 3.

The analysis of the polarization curves in figure 5 and the data in table 3 allow for the following results:

- The behavior of the Verasoft alloy in the Afnor and Rondelli saliva is similar; in both solutions, the potential breakthroughs are very close. The initiation of corrosion points in both salivas takes place at lower potentials (470 and 485 mV respectively), marking a greater vulnerability of Verasoft to point corrosion. In both solutions, the hysteresis loop surface is large, indicating a slow re-passivation of corrosion points formed in the 500-1000 mV potential range.

-Here too, the behavior of the Verasoft alloy is quite different in the Fusayama-Meyer saliva than in the other two salivas; the potential at which initiation of corrosion points takes place is almost half (206 mV), a potential that can also be met in the oral cavity. Moreover, after the initiation of the corrosion points they increase in proportion to the electrode potential (the linear portion of the anode branch in the range 200 mV ... 1000 mV), but the growth rate is lower than the other two salivas. The surface of the

SALIVA	E_{str} (mV)	E_{RP} (mV)	ΔE (mV)	Observations
AFNOR	470	-4	474	Average, distinct corrosion points
FUSAYAMA-MEYER	206	-76	282	Relatively small Corrosion points
RONDELLI	485	-70	555	Moderate corrosion points and salt deposits

Table 3
POINT CORROSION PARAMETERS FOR VERASOFT IN ARTIFICIAL SALIVA

hysteresis loop is small and probably the number and dimensions of the corrosion points are also small.

In all three solutions the potential for re-passivation is negative between -4 and -76 mV (ESC); at lower potentials of these values, the occurrence of corrosion points does not take place. The formation of corrosion points on the surface of the electrochemically treated alloys is also confirmed by the photomicrographs of the alloy surface after treatment in AFNOR saliva (fig. 6).

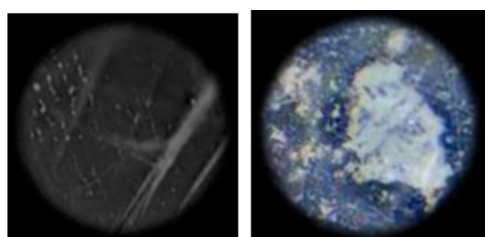


Fig. 6. Surface of VERASOFT alloy before and after electrochemical treatment in AFNOR saliva (x500)

In Afnor saliva, intense corrosion, with well-developed corrosion points can be noted, but also a large number of early-stage corrosion points that can grow over time and uniform corrosion on the entire surface of the alloy can occur.

As shown in figure 7, the Fusayama-Meyer's saliva is much less aggressive for the VERASOFT alloy than the other two salivas. In this case the number of corrosion points is small and their growth has not yet taken place under the conditions of electrochemical treatment applied.

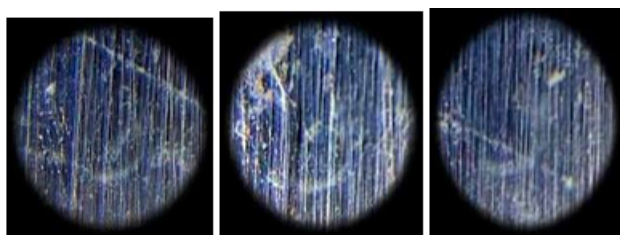


Fig.7. Microscopy of the VERASOFT sample surface after electrochemical treatment in FUSAYAMA-MEYERsaliva (x500)

In figure 8 it is possible to notice the appearance of well developed corrosion points on the surface of the alloy. In addition, these points are covered with saline deposits, probably resulting in the corrosion process. Removing these salts can be done easily by simply removing them with a filter paper. The appearance of the surface after wiping on filter paper is shown in figure 9.

It is noted that by simply wiping off the filter paper the deposits of salts are removed and the corrosion points appear visible and deep. Saliva Rondelli seems to be an aggressive agent much more powerful than saliva Fusayama-Meyer.

Materials used in dental restorations can be influenced by the oral environment through alterations that can lead to surface changes and irreversible macroscopic deformities (corrosion) [6,7, 18-20]. In the case of minimal errors during the treatment steps with such materials, the

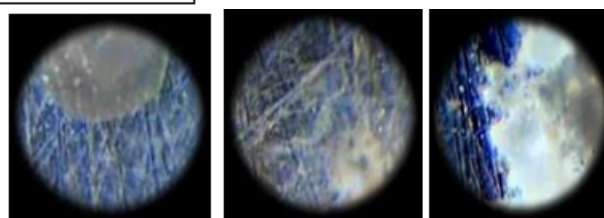


Fig. 8. VERASOFT Sample Surface Appearance After Electrochemical treatment in RONDELLI saliva (x500)

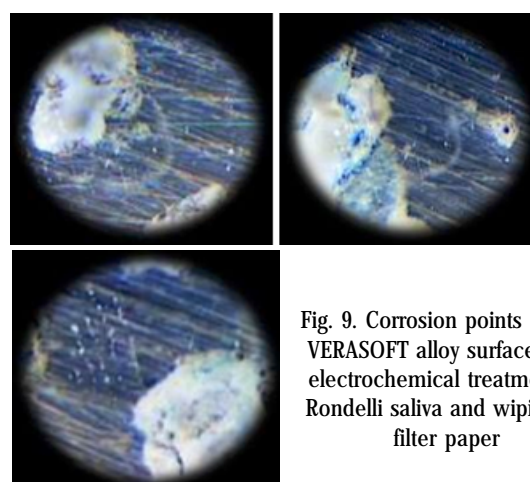


Fig. 9. Corrosion points on the VERASOFT alloy surface after electrochemical treatment in Rondelli saliva and wiping on filter paper

resulting restorations will present major shortcomings immediately or after a short period of time in the oral cavity [8, 21-23].

Due to the electrolytic corrosion phenomenon to which metal alloys are subjected in the oral environment, metal ions result in local and general toxic and local staining and allergies, especially in chromium and nickel ions [6]. Semi precious alloys, are based on Ag and Pd, metals that give homogeneous solid solutions, where palladium (over 20%). protects the alloy against corrosive agents, the noble metal alloy protects the Ag from the alloy against the sulphurising agents in the oral environment and the alloy silver forms the texture, lowers the fusion point and increases the fluidity of the alloy [7]. The corrosion resistance of the alloy in the mouth is good but inferior to gold alloys, and inappropriate machining predisposes to alloy quality altering and corrosion in the oral environment [9]. Non-ferrous or stainless alloys are based on common metals or non-metallic metals (Fe, Cr, C, Co, Ni, Mo, Cu, Zn) [10]. Despite remarkable progress, dental practice is still confronted with issues of susceptibility to contamination, porosity, shrinkage, lack of adhesion, resulting from incorrect use of these materials, with adverse consequences in time for both restorations and of periodontal tissues [11,12]. All dental materials (especially mono-components) have a certain solubility in saliva. Metallic alloys, by their structure, surface appearance, chemical properties (corrosion resistance) may have pathogenic influences on neighbouring gingival tissues by acting through various mechanisms [11,12]. With low solubility and increased corrosion resistance, Co-Cr alloys

have noble alloy characteristics [6,8]. Changes resulting from technological processes in the structure or surface aspect of materials adversely affect the mechanical resistance of the restorations [12]. The oral fluid is an excellent electrolyte capable of effecting ion exchange on metal surfaces and generating galvanic microcircuits favouring electrochemical corrosion.

Regarding the mechanical and corrosion resistance of dental restoration as well as the obtaining and maintenance of an acceptable surface condition, an important role also lies in the technological process in which casting and final processing have a well-defined role [13]. The chemical and electrochemical corrosion phenomena are greatly reduced by casting the prosthetic parts in a monolith system, eliminating the susceptible areas [13,14]. The primary structure of a metal alloy, and not even its composition, changes during the casting and processing processes, which implies a rigorous technique to homogenize and order the crystalline structures of the alloy so as to bring it close to its primary structure [5,8]. An important sign of corrosion attack is often present, through chromatic changes (brown or reddish spots), both in the case of precious and semi-precious alloys, or common alloys on lateral surfaces in the gingival region [14,15]. An examination of the restored metal restorations from the oral cavity, after variable wearing times, sometimes reveals a brown-black coloration in both palliag, gold, or pallidor, but with a higher intensity on Al-Cu-Ni alloys at which is also a brown - black deposit [15]. All metals and metal alloys, even the precious and semi-precious ones, are susceptible to corrosion, forming with the environmental agents compounds with properties different from those of the parent metal or alloy, which modifies the surface condition [8,12,15]. Corrosion can occur in the form of pitting, the corrosion process, on the one hand reducing the section thickness of the restoration, on the other hand, generates internal stresses during mechanical stresses constituting the initial stage of fatigue cracks. Studies show that most metal works, irrespective of their alloy, lose their metallic gloss and matt out. Poor and incomplete mechanical polishing, especially in hard-to-reach areas, leaves pores and rivets capable of favoring retention, with the production of sulphurous chemical compounds [16,17]. Enzymatic processes in the oral cavity and especially in the bacterial plaque lead to the production of sulphurous, sulphurous, sulphonated, chlorine-containing metabolites, favoring the chemical and electrochemical corrosion attack on metallic dental alloys [17].

Conclusions

Under their influence there are structural changes and especially of the surface condition, mainly in the poorly aerated and self-cleaning areas.

In spite of the remarkable progress, dental practice continues to face problems of contamination susceptibility, porosity, contraction, lack of adhesion, resulting from incorrect use of these materials, with adverse consequences in time both on restorations and on periodontal tissues.

In the oral environment, dental materials are subjected to a continuous process of degradation due to physico-chemical attacks but also due to the mechanical pressures exerted on them.

The mechanical stress may be intermittent or permanent.

Both phenomena contribute to the aging phenomenon of the material.

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