

THE ELECTROCHEMICAL BEHAVIOUR OF SOME UNNOBLE ALLOYS IN FUSAYAMA ARTIFICIAL SALIVA

Daniel Mircea Sutiman¹, Daniel Mareci¹, Teodor Mircea Nechita¹, Ioan Iordache²,
Julia Claudia Mirza Rosca³

¹*Technical University “Gh. Asachi” of Iasi, Faculty of Chemical Engineering,
D. Mangeron 71 A, Iasi-700050, Romania*

²*S.C. OLTCHIM S.A. – Research Center, Str. Uzinei 1, Ramnicu Valcea -240050, Romania*

³*Las Palmas de Gran Canaria University, Department of Mechanical Engineering, 35017, Spain
sutiman@ch.tuiasi.ro*

Two non-precious Ni based alloys (Wiroloy and VeraSoft) and one Co based alloy (Vitallium) were investigated in this study. Based on the cyclic and linear polarization curves of the three commercial alloys maintained in artificial saliva, the type and the intensity of the corrosion process can be established by means of the corrosion current values. The corrosion current values decrease after the alloys were kept in the corrosive medium, due to their passivation. The microscopic analysis of the alloys surfaces shows that the corrosion type is not modified. The alloys Vitallium and Wiroloy are in the optimum corrosion resistant condition and are acceptable to be used as dental materials. The VeraSoft alloy presented a pitting potential between +450 mV (with fresh polished surface) and +500 mV (24 hours after immersion in artificial saliva) and is considered marginal.

Key words: unnable alloys; Fusayama artificial saliva; corrosion current; passivation; pitting corrosion

ЕЛЕКТРОХЕМИСКО ОДНЕСУВАЊЕ НА НЕКОИ НЕБЛАГОРОДНИ ЛЕГУРИ ВО FUSAYAMA ВЕШТАЧКА ПЛУНКА

Испитувани се корозивните карактеристики на две неблагородни легури, врз основа на Ni (Wiroloy и VeraSoft) и една врз основа на Co (Vitallium). Врз основа на испитувањата со помош на циклична и линеарна поларизација се добиени вредностите на корозивните струи на трите наведени комерцијални легури во вештачка плунка и е одреден типот и интензитетот на корозивниот процес. Утврдено е дека по изложување на легурите во корозивниот медиум вредноста на корозивната струја (брзина на корозија) се намалува како резултат на нивната пасивизација. Микроскопските испитувања на површините на легурите не укажуваат на промени во типот на корозијата (пасивна), па според тоа легурите Vitallium и Wiroloy имаат оптимална корозивна отпорност и можат да се користат како материјали во стоматологijата. Легурата VeraSoft поради појавата на точкеста (pitting) корозија, по 24-часовно изложување во корозивен медиум, не се препорачува за наведената цел.

Клучни зборови: неблагородни легури; Fusayama-вештачка плунка; корозивна струја; пасивизација; точкеста корозија

INTRODUCTION

The non-precious alloys react easily with the biochemical medium from the oral cavity due to their complex composition, and are especially degraded by electrochemical corrosion. The most commonly used base metal alloys in dentistry are nickel-chromium alloys. These materials are cur-

rently used for crowns, bridges casting, and denture bases. New Ni-free austenitic stainless steels with high Cr, Mo and Nb content have been developed and are exhibiting excellent mechanical and tribological properties [1]. The titanium alloys, which have small modulus (comparable with those of the bone), and excellent corrosion properties [2, 3] do not possess good tribological properties. The

most important factors that affect the choice of dental metallic material are the capacity of the body acceptability for the alloy, or so-called biocompatibility.

Since the corrosion products of dental alloys are metal ions which may be the reason for allergies and some other diseases, the electrochemical behaviour of non-precious alloys such as Ni-Cr alloys has been the subject of a number of prior investigations [4–7].

Meyer *et al.* [8], reported in a study of the electrochemical behaviour of nickel-based casting alloys useful for surgical implants that these alloys with high molybdenum and manganese contents show a definitely better resistance to corrosion. The alloys without any molybdenum were unable to resist in the artificial saliva and they were constantly active and corroding.

Although there have been several reports on the repeated use of precious metals and evaluation of their physical and mechanical properties, there were few reports on the evaluation of the corrosion resistance of non-precious alloys after their repeated use [9].

Utilization of Ni in dental alloys is beneficial because its properties satisfy the essential requirements of dental replacements: corrosion resistance, strong, thin, and cheap material. Only the alloys with chromium and cobalt provide the mechanical properties accepted by dentistry. It was demonstrated that nickel dissolves from dental devices into the saliva, the dissolution rate being accelerated by beryllium, if present in the alloy. On the other hand, nickel is recognized as the most carcinogenic metal on Earth. Thus alloys producing nickel ions can cause cancer because these ions can be absorbed readily across the cell membranes [10]. In some cases the utilization of low concentration of Cr, up to 11 %, is enough for delaying the release, due to the formation of a stable passive layer which covers the alloys surface. Increasing the Cr concentration above 11 % increases the corrosion protection but also increases the melting point of the alloy [11]. Addition of nickel improves the protection of the alloy from corrosion in neutral and weakly oxidized media and improves the ductile and formalization properties [12].

EXPERIMENTAL

Three non-precious dental alloys used in dental prosthetics construction were investigated. Their composition is shown in Table 1.

Table 1

The chemical composition of the dental alloys

| Alloy | Main components (%) |
|-----------|--|
| Wirrolloy | 63.5 Ni 23Cr 9Fe 3Mo 0.5Mn 1Si |
| VeraSoft | 53.6Ni 19.5Mn 14.5Cr 9.5Cu 1.6Al 1.5Si |
| Vitalium | 63.8Co 28.5Cr 6Mo |

The Vitalium and VeraSoft alloys were obtained from AalbaDent, USA, and the Wirrolloy alloy from Beco, Germany. The electrolyte used as corrosion medium was a solution of the aerated artificial saliva (Fusayama) that is composed of: NaCl – 0.4 g/l, KCl – 0.4 g/l, Na₂HPO₄·H₂O – 0.069 g/l, Na₂S·9H₂O – 0.005 g/l, CaCl₂·2H₂O – 0.795 g/l, urea – 1.0 g/l, pH = 6.2. All chemicals were of p.a. purity.

The electrochemical measurements were made with an assembly of three electrodes: a working electrode, a platinum counter-electrode, and a reference electrode of saturated calomel (SCE). The working electrode, made from alloy sample was processed into a cylindrical shape and mounted in a Teflon support. In these conditions the surface exposed to corrosion was a one-dimensional circular surface. The surface area of the working electrode was 0.385 cm².

Before experimental determinations the samples were mechanically polished using abrasive SiC paper with up to a granulation number of 2500 mesh. Then they were washed with water, degreased with ethyl alcohol, and preserved in double-distilled water.

The measurement system was managed by an electrochemical system VOLTALAB-32, which consists of a potentiostat, an electrochemical interface, and a PC. Experimental data were acquired and processed with the VoltaMaster 2 software. Determination of open circuit potential and the cyclic polarization curves recording were performed with a saturated calomel electrode (SCE) and a platinum grit as a counter electrode.

The corrosion process was characterized by several electrochemical parameters:

– The open circuit potential (E_{OC}), recorded for 24 h with the sample immersed in an aerated electrolyte.

– The polarization resistance (R_p), calculated from traces of the polarization curve at ± 10 mV vs. E_{OC} .

– The Tafel slopes (b_a and b_c) and the corrosion current (I_{corr}) using the Stern-Geary [13] equation:

$$I_{corr} = \frac{b_a b_c}{2.3R_p(b_a + b_c)}$$

The Tafel slopes were calculated from plots of the polarization curves at ± 150 mV vs. E_{OC} . The scanning rate was 0.5 mV/s.

– The cyclic potentiodynamic polarization curve (-350 mV...+1500 mV...-350 mV), recorded with a scanning rate of 10 mV/s.

All tests were repeated twice. After the electrochemical treatment, the analysis of the alloys surface was performed with a scanning electron microscope TESLA BS 300 and an optical microscope MC6.

RESULTS AND DISCUSSIONS

Metals immersed in an electrolytic environment generate an electric potential that change with time and stabilises to a stationary value after a period of immersion. As in the case of any surface phenomenon, this potential may vary with time because changes in the nature of the surface of the electrode occur (oxidation, formation of the passive layer or immunity). The alloys with the most active (negative) potentials will generally undergo more significant corrosion, while the other alloys (with more positive potential values) will generally suffer less attack. The open circuit potential is used as criteria for the corrosion behaviour. This approach is qualitative and remains insufficient for a complete analysis.

Figure 1 shows the curves of the open circuit potentials versus time for the three alloys.

Following the immersion, an abrupt open circuit potential displacement towards positive potentials, for Vitallium and Wirolloy alloys, was noticed in Figure 1 during a period of 2 hours. After two hours in the case of the Vitallium alloy, its potential increase from -389 to -77 mV, and for Wirolloy alloy from -345 to -125 mV. Afterwards, the open circuit potential for Vitallium and Wirolloy alloys slowly increase, suggesting the growth of a film onto the metallic surface. The open circuit potential for Vera Soft, initially decrease reaching an approximate constant value at the active-passive transition zone. This phenome-

non is probably characteristic of corrosion of the sample before formation of a passive layer.

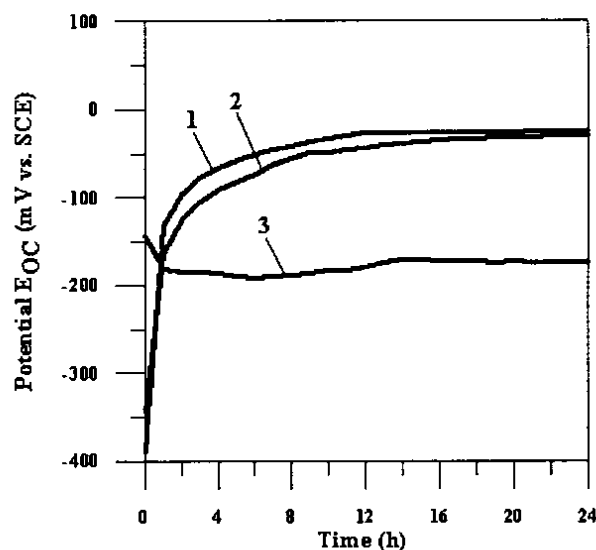


Fig. 1. Variation of open circuit potential with time for three dental alloys in artificial saliva: 1– Vitallium alloy, 2 – Wirolloy alloy, and 3 – VeraSoft alloy

The open circuit potential of the all the alloys are summarized in Table 2.

The highest E_{OC} was found for the Vitallium alloy, followed by the Wirolloy alloy, and the VeraSoft alloy.

Table 2

The open circuit potential values: initial and after 24 hours since alloys samples immersion in artificial saliva

| Alloy | Open circuit potential, E_{OC} (mV vs. SCE) | |
|-----------|---|----------------|
| | Initial | After 24 hours |
| Wirolloy | -345 | -30 |
| VeraSoft | -142 | -174 |
| Vitallium | -389 | -25 |

Figure 2 shows the cyclic polarization curves for the Vitallium, Figure 3 shows the cyclic polarization curves for the VeraSoft, and Figure 4 shows the cyclic polarization curves for the Wirolloy alloy, having the surface mechanically polished with abrasive SiC paper, and after 24 hours in an artificial saliva solution. The cyclic polarization curves show the best behaviour for Vitallium and Wirolloy alloys. This behavior will be explained by the values of the parameters detailed in Table 3.

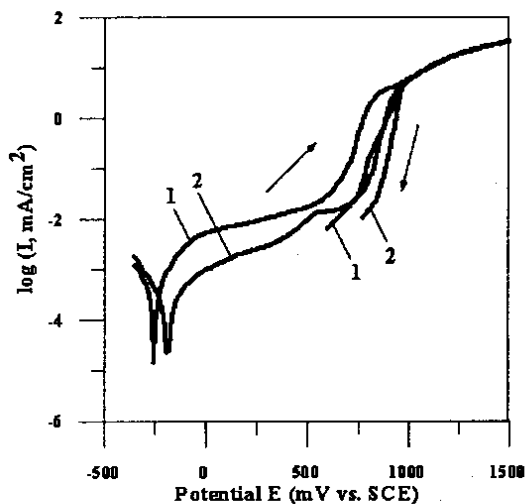


Fig. 2. The cyclic polarization curves for the Vitallium alloy: 1 – with fresh polished surface, 2 – after 24 hours of immersion in artificial saliva

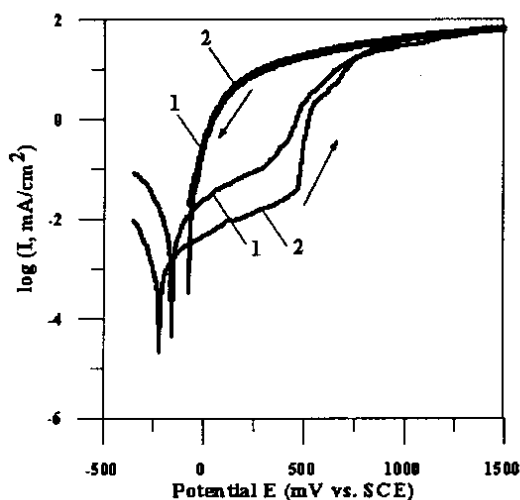


Fig. 3. The cyclic polarization curves for the VeraSoft alloy: 1 – with fresh polished surface, 2 – after 24 hours of immersion in artificial saliva

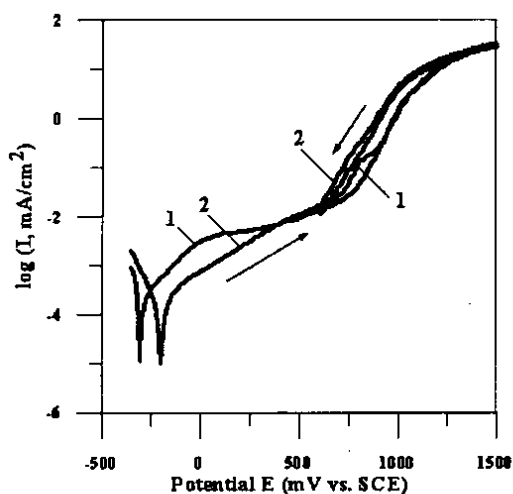


Fig. 4. The cyclic polarization curves for the Wiroloy alloy: 1 – with fresh polished surface, 2 – after 24 hours of immersion in artificial saliva

In Table 3 presented are the corrosion process parameters corresponding to the three alloys studied with various surface treatments: fresh polished surface and the alloy surface maintained for 24 hours.

The polarization resistance (R_p) was determined by the tangent of the polarization curve (± 10 mV vs. E_{OC} SCE) at $I = 0$. The R_p is representative of the degree of protection of the passivation layer of the alloy surface. As the value of R_p increases, the alloys will resist better to corrosion. All the results are shown in Table 3. The best behaviour for the alloys with fresh polished surface is revealed by Vitallium and Wiroloy, with R_p values of $227 \cdot 10^3 \Omega \text{ cm}^2$ and $107 \cdot 10^3 \Omega \text{ cm}^2$, respectively. The Tafel slopes (b_a and b_c) were determined by fitting of a theoretical polarization curve to the experimental polarisation curve plotted in a range of ± 150 mV vs. E_{OC} . The corrosion current (I_{corr}) is representative of the degree of degradation of the alloy. An alloy with a tendency toward passivation will have a value of b_a greater than b_c , whereas an alloy that corrodes will have a b_a less than b_c [14].

Table 3 shows the evaluated values of b_a , b_c and I_{corr} calculated using the Stern-Geary equation.

Figure 5 shows in linear representation the part of the polarization curve for all the three alloys with fresh polished surface in artificial saliva, in the scale of anodic currents between 0 and $500 \mu\text{A}/\text{cm}^2$. This helps to visualize the pitting and transpassivation potential and another electrochemical parameters, which characterize the corrosion behaviour of the alloys.

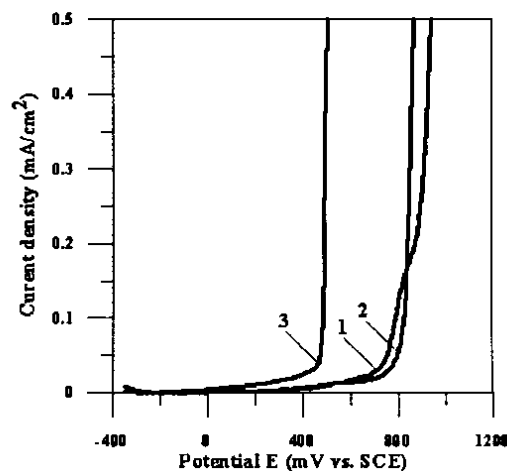


Fig. 5. Potentiodynamic polarization curves presented on linear axes in order to reveal the transpassivation and pitting potential for the: 1 – Vitallium alloy, 2 – Wiroloy alloy, and 3 – VeraSoft alloy (with fresh polished surface in artificial saliva)

The pitting and transpassivation potentials are the potentials at which the anodic current strongly increases. The potential range situated between the zero current potential ($E_{(I=0)}$) and the transpassivation potential or the pitting potential represents the immunity zone in which the corrosion is weak or insignificant.

Table 3 presents the values of the pitting potential, repassivation potential, and transpassivation potential.

Analysis of the data contained in Table 3 reveals that at initial moment of immersion in artificial saliva, all three alloys show relatively high negative values of zero corrosion potential (ZCP).

The high values of b_a compared with the values of b_c for all four alloys indicate an anodic control in the corrosion process. The control implies the existence of a passive layer on the material surface.

Corrosion currents have values of nA order, the highest value being recorded for the VeraSoft alloy.

From the cyclic polarization curves, a typical pitting corrosion is evidenced for the Wirolloy and VeraSoft alloys (they have clockwise loops). In cyclic polarization curve the repassivation (protection) potential E_{rep} is noted where the reverse scan intersects the forward scan. The E_{rep} is defined as the potential below which pre-existing corrosion pits will passivate and cease to grow under the particular cyclic polarization conditions.

For the VeraSoft dental material the repassivation potential is still very small and near ZCP; therefore the susceptibility degree of pitting corrosion is high.

A hypothesis explaining the physical significance of E_{rep} is proposed as follows: On the forward scan of the cyclic polarization curve, an oxide layer grows on the VeraSoft alloy.

At higher (more noble) potentials, above the pitting potential (E_{pit}), localized micro-cracking of the oxide layer occurs resulting in the underlying alloy being exposed to corrosive medium leading to the formation of pits. There is thus a rapid rise in the current density at potentials nobler than the pitting potential. When the scan is reversed at the vertex potential, the pits developed during the forward scan begin to repassivate as the potential decreases. In the case of VeraSoft, the repassivation process is slow, the current will decrease at a slower rate as a function of potential (and time), resulting in a lower repassivation potential value. In the case of Wirolloy, the repassivation process is fast, the current will decrease at a faster rate as a function of potential. The Wirolloy alloy shows a reduced susceptibility to the pitting corrosion due to the high value of E_{pit} and to the quick repassivation of the surface (ΔE has a low value).

The alloy Vitallium exhibits high value of transpassivation potential, over 700 mV. The cyclic polarization curve is typical for a uniform corrosion.

Table 3

The main parameters of the corrosion process

| Alloys | ZCP (mV) | R_p ($\Omega \text{ cm}^2$) | b_c (mV/div) | b_a (mV/div) | I_{corr} (nA/cm ²) | E_{tr} (mV) | E_{pit} (mV) | E_{rep} (mV) | ΔE (mV) |
|---|-------------|------------------------------------|-------------------|-------------------|-------------------------------------|------------------|-------------------|-------------------|--------------------|
| The alloys with fresh polished surface | | | | | | | | | |
| Vitallium | -253 | $227 \cdot 10^3$ | 90 | 170 | 113 | 710 | - | - | - |
| Wirolloy | -305 | $107 \cdot 10^3$ | 100 | 160 | 250 | - | 750 | 680 | 70 |
| VeraSoft | -188 | $20 \cdot 10^3$ | 115 | 150 | 1413 | - | 450 | -35 | 4865 |
| The alloys maintained for 24 hours in artificial saliva | | | | | | | | | |
| Vitallium | -182 | $310 \cdot 10^3$ | 120 | 180 | 101 | 820 | - | - | - |
| Wirolloy | -208 | $274 \cdot 10^3$ | 110 | 165 | 105 | - | 830 | 750 | 80 |
| VeraSoft | -41 | $101 \cdot 10^3$ | 115 | 165 | 291 | - | 500 | -35 | 535 |

ZCP = $E_{(I=0)}$ – zero corrosion potential; R_p – polarization resistance; b_c and b_a – Tafel slopes; I_{corr} – density of corrosion current; E_{tr} – transpassivation potential; E_{pit} – pitting potential; E_{rep} – repassivation potential; $\Delta E = E_{pit} - E_{rep}$

After the alloys immersion for 24 hours in artificial saliva, the ZCP values increase for Vitallium and Wiroloy over time, but decrease for the VeraSoft alloy. This behaviour is in agreement with the variation of open circuit in time. Twenty-four hours after the alloys immersion in artificial saliva, the polarization resistance increases, and the corrosion decreases, but the type of corrosion (pitting) is not changed. Although E_{pit} of VeraSoft alloy has slightly increased value, the susceptibility to the pitting corrosion is still high due to the low values of repassivation potentials (ΔE has a high value).

The cyclic polarization curve of Vitallium alloy with the surface maintained for 24 hours in the corrosion environment corresponds to a generalized corrosion process. These alloys present transpassivation potentials over 800 mV. The Vitallium does not exhibit a pitting potential in the range of potential tested indicating that its passive/oxide

layer is very compact and protective, preventing corrosion.

The repassivation potential, E_{rep} , and pitting potential, E_{pit} , values increase for Wiroloy alloy, proving that the pitting corrosion susceptibility decrease.

All materials passed directly into a stable passive behaviour from the "Tafel region" without exhibiting a traditional active-passive transition.

The microscopic analysis of the samples surface confirms a different behaviour of Vitallium alloy in comparison with the other two alloys characterized by pitting corrosion. Figure 6 shows the microstructures of Vitallium, VeraSoft, and Wiroloy alloys after corrosion.

The analysis of Figure 6 indicates the appearance of corrosion points at the surface of VeraSoft and Wiroloy alloys and the development of a generalized corrosion process in case of Vitallium alloy.

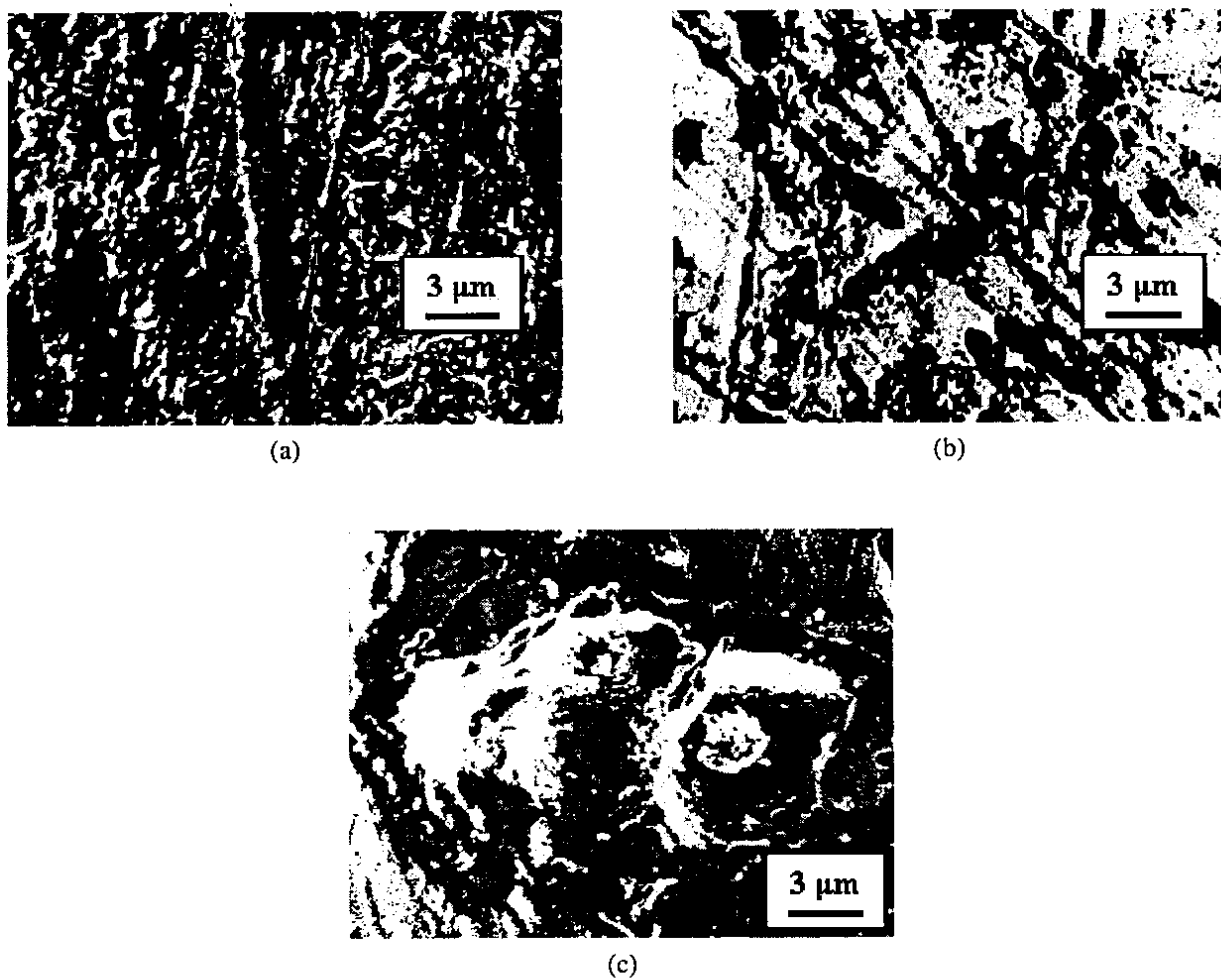


Fig. 6. Microstructures of alloys studied:
(a) – Vitallium, (b) – Wiroloy, (c) – VeraSoft.

CONCLUSIONS

Saliva in the human oral cavity is generally considered to be an aerated environment. Linear and cyclic polarizations were conducted in an aerated medium in this study. However, a deaerated environment will only affect the reduction reaction, not the oxidation reaction. In addition, certain areas in the oral cavity, such as the subgingival region, and areas under the plaque, are in a deaerated condition.

The Vitallium and Wiroloy alloys show a strong corrosion resistance.

All the alloys passed directly into a stable passive region, without exhibiting the traditional active-passive transition.

Over the surface of the Vitallium alloy a uniform corrosion appears, while in case of the Vera-Soft and Wiroloy alloys surface a pitting corrosion is developed.

The alloys Vitallium and Wiroloy are in the optimum corrosion resistant condition and are acceptable to be used as dental materials. The Vera-Soft alloy that presented a pitting potential between +450 mV (with fresh polished surface) and +500 mV (24 hours after immersion in artificial saliva) is considered to be marginal.

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