

THE ELECTROCHEMICAL BEHAVIOUR OF VARIOUS NON-PRECIOUS NI AND CO BASED ALLOYS IN ARTIFICIAL SALIVA

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Abstract

Five non-precious Ni-Co based alloys were analyzed with respect to their corrosion behaviour. The correlation between the amount of the elements Cr, Mo, V and the corrosion behaviour, expressed by the PREN (pitting resistance equivalent number) index in the case of the allied steels, was extended for Ni-Cr and Co-Cr dental alloys characterisation. Open circuit potential, corrosion current densities, as a measure of the corrosion rate, and main parameters of the corrosion process were evaluated from linear and cyclic polarization curves, for five Ni-Cr or Co-Cr alloys in an Afnor type artificial saliva. The maintenance times of the alloy in the corrosive medium influence the corrosion rate; the corrosion current values decrease with the maintenance time due to their passivation in solution. The microscopic analysis of the alloy surfaces shows that this passivation in solution does not modify the corrosion type. The alloys with $PREN \leq 32.9$ are susceptible of localized corrosion.

Key Words: corrosion potential, corrosion current, potentiodynamic cyclic curves, potentiodynamic linear curves, scanning electron microscopy.

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. In the actual socio-economical conditions, the dental physician should select with discernment the alternatives Ni-Cr-Fe, Ni-Cr-Mo and Co-Cr-Mo containing alloys, existing at the present time in the Romanian market. The selection is made depending on the mechanical and biocompatibility properties but also on the corrosion resistance of the alloy and is dependent on the clinical case. In order to realise certain prostheses the choice of dental alloy is very important, because inadequate material may lead to mechanical, chemical or biological failures that have undesirable consequences in time for the patient's general state of health.

Meyer and collaborators reported in an old study about the electrochemical behaviour of nickel-based casting alloys (useful for surgical implants) that the alloys with high molybdenum and manganese contents definitely show a better resistance to corrosion. The alloys without any molybdenum are unable to resist the artificial saliva and are constantly active and corroding (Meyer *et al.*, 1978).

Reclaru and Meyer (1998) studied the effects of fluorides on titanium and other dental alloys (Co-Cr and stainless steel). If fluoride ions are present, the dental alloys tested undergo a crevice and pitting corrosive process, as soon as the pH drops below 3.5.

Venugopalan and Gaydon (2001), in a review of the corrosion behaviour of surgical implant alloys observe that cobalt alloys do not show the traditional active-passive transition as they were also in a passive state prior to testing. The wrought alloys do not exhibit a hysteresis loop in a potentiodynamic polarization curve as compared to the cast alloys, indicating that they can repair damage to their oxide/passive layer faster/better.

The electrochemical behaviour of a dental alloy in artificial saliva permits the estimation of the behaviour of the material in the oral cavity. The modifications of the dental alloys properties could be determined using rapid electrochemical tests as a qualitative criterion to estimate the corrosion resistance. The electrochemical methods, consisting of open circuit potential measurements and polarisation curve recording, are of particular interest (Pourbaix, 1984). In this work we present the results of a comparison of the corrosion behaviour of various non-precious Ni-Cr and Co-Cr based alloys in artificial saliva.

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Experimental

Materials

Five non-precious dental alloys used in the construction of dental prosthetics were investigated. Their provenance and composition are shown in Table 1.

As corrosion medium an aerated solution of Afnor artificial saliva (Carter-Brugirard AFNOR/NF (French Association of Normalization) 591-141) was used, having the composition: NaCl – 0.7 g/l, KCl – 1.2 g/l, Na₂HPO₄·H₂O – 0.26 g/l, NaHCO₃ – 1.5 g/l, KSCN – 0.33 g/l, urea – 1.35 g/l, and pH = 8 (Grosogogeat *et al.*, 1999).

Methods

The determination of open circuit potential and the cyclic polarisation curves recording were performed with the VOLTALAB-32 electrochemical system, which consists of a potentiostat, a three electrode cell, an electrochemical interface and a PC. Experimental data were acquired and processed with the VoltaMaster 2 software. The saturated calomel electrode (SCE) was used as reference electrode and platinum as a counter electrode.

The working electrode, made from alloy sample was processed into a cylindrical shape and mounted in a Teflon support. Under these conditions the surface exposed to corrosion was a one-dimensional circular area.

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

Linear polarization measurements were performed, in an aerated solution, at potentials near the corrosion potential (E_{corr}) in the potential range ($E_{corr} - 10$) mV to ($E_{corr} + 10$) mV and a potential scan rate of 0.5 mV/s. The polarization resistance (R_p) was calculated as the tangent slope at the electrode potential vs. current density curve, in the E_{corr} point. Subsequently, potentiodynamic cathodic polarization was initiated at E_{corr} and terminated at 200 mV below the E_{corr} value at a rate of 0.5 mV/s in aerated medium. The cathodic Tafel slope (β_c) was calculated as the potential change over one decade (one order of magnitude) decrease in the current density at potentials near the E_{corr} . The anodic Tafel slope (β_a) was determined in a similar way.

A linear polarization method was used to determine when a test electrode was at its steady state. Polarization resistance was used to estimate the general corrosion rate of the metal. Anodic polarization is a test to characterize the corrosion behaviour of a metal and evaluate how effectively a passive film protects a metal from corrosion. Cathodic polarization of metal was used in combination with anodic polarization to determine Tafel constants and to determine the corrosion current density (J_{corr}).

On the basis of these data, the corrosion current density (J_{corr}), which is a measure of the corrosion rate, was calculated with the Stern-Geary equation (Kelly *et al.*, 2003):

$$J_{corr} = \frac{\beta_a \beta_c}{2,3R_p (\beta_a + \beta_c)}$$

Table 1: The composition and source of the studied dental alloys

Alloy	Provenance	Main Components (%)
Wiroloy	Beco - Germany	63.5 Ni 23Cr 9Fe 3Mo 0.5Mn 1Si
VeraSoft	Barth Dental.Lab.- USA	53.6Ni 19.5Mn 14.5Cr 9.5Cu 1.6Al 1.5Si
Vitallium	AlbaDent -USA	63.8Co 28.5Cr 6Mo
WironNT	Beco-Germany	61.4Ni 22.9Cr 8.8Mo 2.5Fe 3.9Nb
NicromalSoft	Rare Metal Inst.-Romania	64.6Ni 17.8Cr 9.8Cu 3.5Mn 1.8Si 1.5Al 0.5Ti 0.5Fe

Three additional corrosion parameters: transpassivation potential (E_{tr}), breakdown potential (E_{br}) and repassivation potential (E_{rep}), were determined from the cyclic potentiodynamic polarization curve, performed at a potential scan rate of 10 mV/s, on the electrode potential range: –35 to +1500 mV.

Results ($n = 4$) were subjected to statistical analysis. After calculation of the dispersion deviation, we calculated the standard deviation (Ceausescu, 1982).

To study the microstructure of the alloys their surface was chemically treated in agreement with standard procedures. The solution used for chemical attack was: 10 ml HNO₃ + 30 ml HCl + 20 ml glycerine (Bane, 1991). The treated surface was examined with an optical microscope of the MC-6 type (Bucharest, Romania).

After the electrochemical treatments, a study of the modifications of the surface of the alloys was performed on a TESLA BS 300 scanning electron microscope and the optical microscope mentioned above.

Results and Discussion

The microstructure was similar for all five alloys; an $\alpha + \beta$ biphasic composition, the studied alloys differed only by the phase morphologies. The VeraSoft, NicromalSoft and Wiroloy alloys showed a granular structure, the grains being oriented in rows, while the Vitallium and Wiron NT alloys showed a dendritic structure (Fig. 1).

The first objective of this study was to estimate the degree of modification of the thermodynamically corrosion tendency by keeping the alloy in artificial saliva solution. For that purpose the open circuit potential was continuously measured for 24 hours. In Table 2 open circuit

Table 2: The open circuit potential values: initial and 24 hours after alloys samples immersion in artificial saliva. Entries are mean (standard deviation), $n = 4$.

Alloy	Open circuit potential, E/SCE (mV)	
	Initial	24 hours after immersion
Wiroloy	-259 (1.08)	-33(0.98)
VeraSoft	-257(1.1)	-251(1.2)
Vitallium	-83(1.14)	-7(1.06)
WironNT	-161(1.04)	-67(1.14)
NicromalSoft	-282(1.2)	-212(1.12)

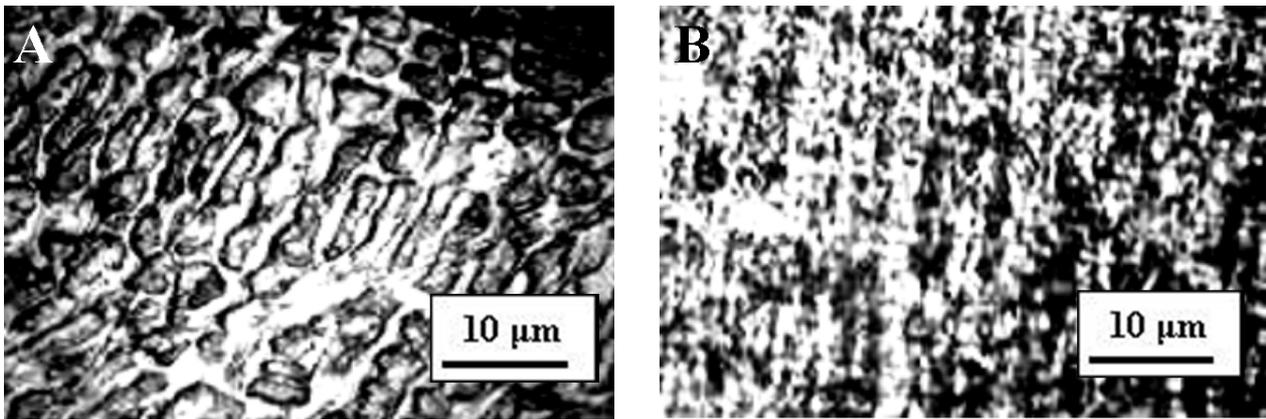


Figure 1: Micrographs of: A) VeraSoft, B) WironNT

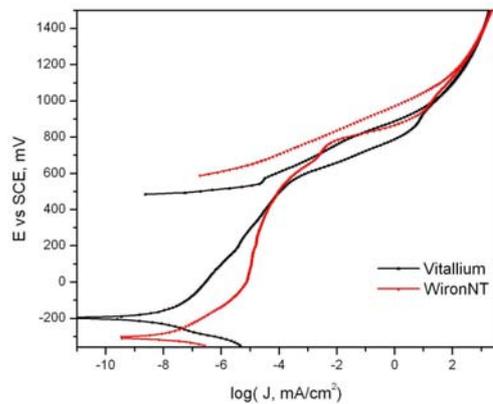


Figure 2: The cyclic polarisation curves for Vitallium and WironNT alloys (fresh surface)

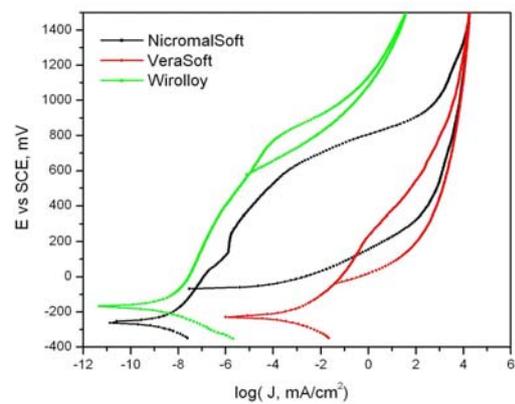


Figure 3: The cyclic polarisation curves for VeraSoft, NicromalSoft and Wirolloy alloys (fresh surface)

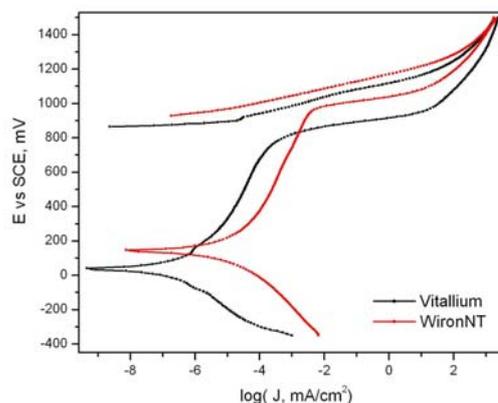


Figure 4: The cyclic polarisation curves for Vitallium and WironNT alloys (7 days after immersion in artificial saliva)

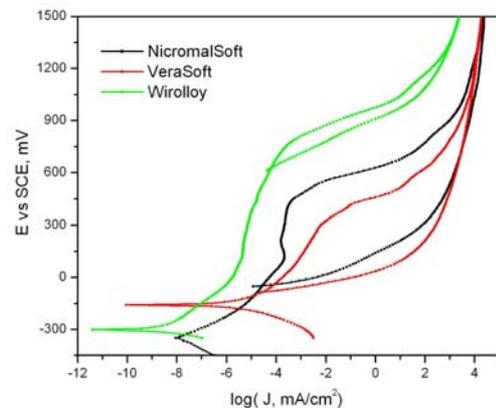


Figure 5: The cyclic polarisation curves for the VeraSoft, NicromalSoft and Wirolloy alloys (7 days after immersion in artificial saliva)

potential values are presented at the initial moment of time and 24 hours after immersion of the alloy in artificial saliva.

The open circuit potential value corresponding to each of the five alloys tested increased in time, leading to the conclusion that the alloys are passivated. In the case of the molybdenum based alloys the passivation process is more intense compared to the other alloys with copper and manganese in their composition. For each alloy, the main parameters of corrosion process were established using the cyclic polarisation curves. Figure 2 shows the cyclic

polarisation curves for the Vitallium and WironNT alloys and Figure 3 shows the cyclic polarisation curves for the VeraSoft, NicromalSoft and Wirolloy alloys, immediately after mechanical polishing of the electrode surface with abrasive SiC paper and washing with double-distilled water. In Figure 4 are presented the cyclic polarisation curves for the Vitallium and WironNT alloys and Figure 5 shows the cyclic polarisation curves for the VeraSoft, NicromalSoft and Wirolloy alloys 7 days after maintaining in an artificial saliva solution.

Table 3: The main parameters of the corrosion process. Entries are mean (standard deviation), n = 4.

Alloys	E_{corr} (mV)	R_p (K Ω cm ²)	J_{corr} (nA/cm ²)	E_{tr} (mV)	E_{br} (mV)	E_{rep} (mV)	ΔE (mV)
Alloys with freshly polished surface							
Vitallium	-197 (1.2)	227 (0.88)	59.7 (1.2)	835 (1.12)	-	-	-
Wiroloy	-305 (1.13)	276 (1.2)	33.6 (0.96)	-	931 (0.96)	693 (0.98)	238 (0.92)
WironNT	-306 (1.1)	138 (1.26)	89.7 (1.3)	960 (1.2)	-	-	-
VeraSoft	-166 (1.2)	5.2 (1.08)	1670 (1.24)	-	450 (1.15)	-36 (1.02)	486 (0.98)
NicromalSoft	-350 (0.96)	28.1 (1.1)	278 (1.08)	-	620 (1.03)	120 (1.1)	500 (1.03)
Alloys maintained for 24 hours in artificial saliva							
Vitallium	-159 (0.92)	209 (1.12)	42.4 (0.8)	835 (1.28)	-	-	-
Wiroloy	-208 (0.88)	274 (1.2)	32.8 (1.22)	-	915 (1.22)	684 (1.13)	231 (1.08)
WironNT	-141 (1.2)	242 (1.32)	46 (1.2)	960 (1.1)	-	-	-
VeraSoft	-190 (1.12)	100.4 (1.12)	79.6 (1.14)	-	500 (0.98)	-36 (1.2)	536 (1.14)
NicromalSoft	-290 (1.24)	11.2 (1.14)	320 (1.04)	-	720 (0.97)	110 (1.16)	610 (0.97)
Alloys maintained for 7 days in artificial saliva							
Vitallium	42 (1.22)	215 (1.2)	41 (1.02)	890 (0.92)	-	-	-
Wiroloy	-166 (1.08)	320 (1.08)	30.8 (1.2)	-	960 (1.13)	830 (0.97)	130 (0.99)
WironNT	147 (1.3)	210 (0.96)	45.2 (1.08)	1010 (1.1)	-	-	-
VeraSoft	-229 (1.26)	7.72 (0.88)	7050 (1.07)	-	280 (1.2)	12 (1.18)	268 (0.96)
NicromalSoft	-262 (1.06)	45 (0.89)	780 (1.15)	-	800 (0.98)	130 (1.12)	670 (1.1)

E_{corr} – corrosion potential, R_p – polarisation resistance, J_{corr} – density of corrosion current, E_{tr} – transpassivation potential, E_{br} – breakdown potential, E_{rep} – repassivation potential, $\Delta E = E_{\text{br}} - E_{\text{rep}}$.

In Table 3 are present the corrosion process parameters corresponding to the five alloys studied with various surface treatments: freshly polished surface, maintained for 24 hours and for 7 days, respectively, in artificial saliva.

Analysing the data contained in Table 3 one finds that at the initial moment of immersion in artificial saliva, all of the five alloys shows relatively high negative values of corrosion potential. Corrosion current densities have values in the order of 10^{-9} A, the highest value being recorded in the case of the VeraSoft alloy (approximately 10 to 100 times higher than the other four alloys).

The cyclic polarisation curves from Figures 2 and 3 show that a clear distinction exists between the electrochemical behaviour of the alloys tested. Thus the cyclic polarisation curves for VeraSoft, NicromalSoft and Wiroloy alloy are typical curves of pitting corrosion. One can observe that these materials do not exhibit the traditional active-passive transitions, they pass in a passive state immediately after immersion in solution. VeraSoft alloy presents the highest susceptibility to this type of corrosion because E_{br} has a low value and the repassivation

potential value is close to E_{corr} .

The Wiroloy alloy shows a reduced susceptibility to pitting corrosion indicated by a high value of E_{br} and the quick repassivation of the surface (ΔE has a low value). The alloys Vitallium and WironNT exhibit high values of transpassivation potential, over 800 mV.

24 hours after maintenance of the alloys in artificial saliva, the corrosion potential values increase with the exception of VeraSoft alloy. The alloys are passivating and the corrosion currents values decrease in case of the other four alloys. A slight increase of the corrosion current was recorded for the NicromalSoft alloy. Though E_{br} of the NicromalSoft and VeraSoft alloys had slightly increased values, the susceptibility to the pitting corrosion is still high as pointed out by the low values of repassivation potentials (ΔE has a high value).

The cyclic polarisation curves of Vitallium and WironNT alloys maintained for 24 hours in the corrosion environment indicate a generalized corrosion process. These alloys have transpassivation potentials over 800 mV in the medium tested.

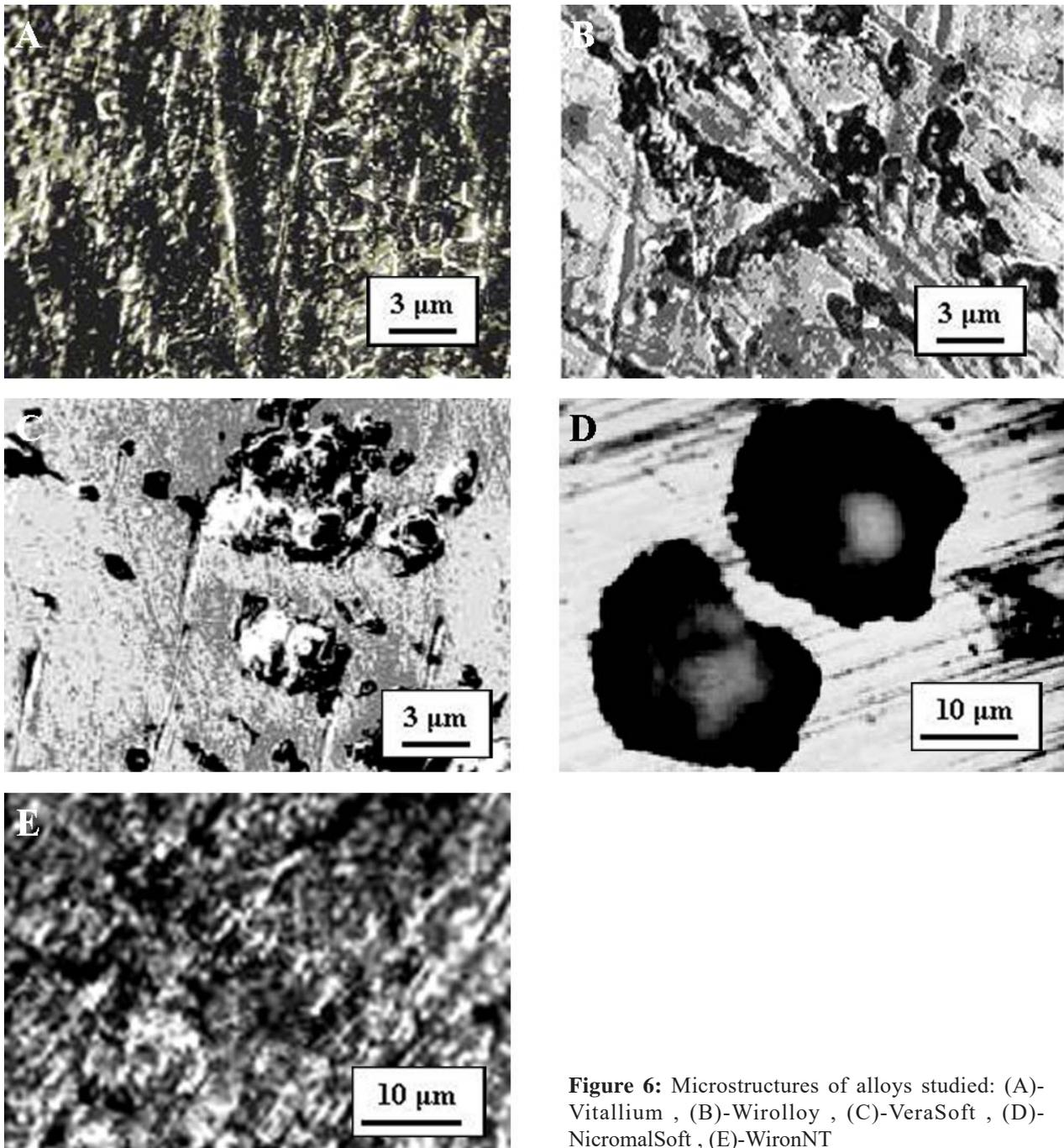


Figure 6: Microstructures of alloys studied: (A)- Vitallium , (B)-Wiroloy , (C)-VeraSoft , (D)- NicromalSoft , (E)-WironNT

7 days after immersion in artificial saliva one finds an increase of corrosion potential values, which achieve positive limits in case of Vitallium and WironNT alloys. The corrosion currents corresponding to Vitallium, WironNT and Wiroloy alloys remain approximately the same as those recorded 24 hours after immersion. Only in the case of VeraSoft and NicromalSoft alloys the value of corrosion currents increases significantly. Moreover, 7 days after maintenance of the alloys in artificial saliva the type of corrosion is not changed.

All materials went directly into a stable passive behaviour from the “Tafel region” without exhibiting a traditional active-passive transition.

The Vitallium and WironNT alloys do not exhibit a breakdown potential or pitting potential in the range of potentials tested indicating that their passive/oxide layer

is very integral and protective, thus preventing corrosion.

The value of E_{br} in case of VeraSoft alloy decreases in time, thus the pitting corrosion susceptibility is increased. The repassivation and E_{br} potential values increase for Wiroloy alloy, proving that the pitting corrosion susceptibility decreases.

The microscopic analysis confirms a different behavior of Vitallium and WironNT alloys in comparison with the other three alloys characterized by pitting corrosion. Figure 6 shows the microstructures of Vitallium, Wiroloy, VeraSoft, NicromalSoft and WironNT alloys after corrosion.

The analysis of Figure 6 indicates the appearance of corrosion points at the surface of VeraSoft, NicromalSoft, Wiroloy, alloys and the development of a generalised corrosion process in case of Vitallium and WironNT alloys.

It is known that Mo and Cr represent alloy components having a decisive contribution during the passivation processes. Thus their presence in the alloy composition determines the increase in pitting corrosion resistance.

The pitting corrosion resistance for steel could be evaluated by the value of numerical equivalent of the pitting resistance (PREN), (DIN 13912, 1996):

$$\text{PREN} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W})$$

Over the nickel and cobalt surface (99.9% purity) a pitting corrosion was developed. For that reason, the alloying with elements that permit the formation of a passive layer is necessary. The PREN index could be extended to this type of alloys. The use of the PREN index should be accompanied by another method of corrosion study (in this case SEM). For the alloys studied the PREN index values are:

$$\text{PREN}=51.94 \text{ (WironNT)}>$$

$$\text{PREN}=48.3 \text{ (Vitallium)}>$$

$$\text{PREN}=32.9 \text{ (Wiroloy)}>$$

$$\text{PREN}=17.8 \text{ (NicomalSoft)}>$$

$$\text{PREN}=14.5 \text{ (VeraSoft)}.$$

Most susceptible to the pitting corrosion is the VeraSoft alloy, a fact confirmed by the electrochemical behaviour and the microscopic analysis.

Conclusion

Saliva in the human oral cavity is generally considered to be an aerated environment. Linear and cyclic polarization 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, Wiroloy and Wiron NT alloys shows a strong corrosion resistance. All the alloys translated directly into a stable passive region, exhibiting the traditional active-passive transition.

Over the surfaces of the Vitallium and WironNT alloys a uniform corrosion appears, while in case of the VeraSoft, NicomalSoft and Wiroloy alloys surface a pitting corrosion is developed.

The chromium and molybdenum contents play a significant role in corrosion resistance: alloys with high chromium and molybdenum content exhibit a much wider passivation range and a better resistance to pitting corrosion.

An increased resistance to the pitting corrosion can be obtained by alloying with molybdenum and chromium to obtain a PREN value higher than 32.9.

The alloys Vitallium, WironNT, Wiroloy and NicomalSoft are in the optimum corrosion resistant conditions and are acceptable to be used as dental materials. The VeraSoft alloy, which presented a breakdown potential

between +280 mV (7 days after immersion in artificial saliva) and +500 mV (24 hours after immersion in artificial saliva) is marginal.

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Discussion with Reviewers

Reviewer I: The pitting resistance equivalent is applicable for homogeneous ferritic or austenitic stainless steels. Is the application for nickel and cobalt based alloys so straight forward?

Authors: $\text{PREN} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + x(\text{N})$. Depending on the value of x, PREN is applicable for ferritic, austenitic or duplex stainless steels. Over the nickel and cobalt surface (99.9% purity) a pitting corrosion was developed. For that reason, the alloying with elements that permit the formation of a passive layer is necessary and the PREN index could be extended to this type of alloys. The use of PREN index should be accompanied with another method of corrosion study (in this case SEM). (U. Bahr, E. Liehr, M. Poppinga and R. Strietzel in the paper: Venerable non-precious alloys for LFC materials use PREN index for the gold core2 alloys (the composition is: 63.5Co 21 Cr 6.5 Mn 4.5 Ga 2.5 Al 2 Au). The same relation was used in case of Ni-Cr-Mo alloys in the paper:

J. Charles, J.P. Audouard, M. Verneau, *Metallic Answers for F.G.D. Systems (Paper 480) in Corrosion '98*, San Diego: National Association of Corrosion Engineers.

Reviewer I: As reported in the paper, localized corrosion occurred on the alloys VeraSoft (14% Cr), NicromalSoft (18% Cr) and Wirloy (23% Cr). This contradicts greatly the discussion, where it is stated that the alloys become more corrosion resistant with increasing PREN. What is the influence of the different microstructure of the alloys on the corrosion behaviour reported?

Authors: The PREN index reflects only the influence of Cr and Mo content on the pitting corrosion intensity. The microstructure is similar for all five alloys; an a + b biphasic composition, the studied alloys differing only by the phase morphologies. The VeraSoft, NicromalSoft and Wirloy alloys show a granular structure, the grains being oriented in rows, while the Vitallium and Wiron NT alloys show a dendritic structure.

Reviewer I: Dental alloys may be exposed to different environmental conditions: alloy / bone (crevice situation), alloy / gingiva (loose crevice), alloy to saliva (open). What is the relevance of the results with respect to a crevice corrosion situation?

Authors: Saliva in the human oral cavity is generally considered to be an aerated environment. Linear and cyclic polarization 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. Even the oxidation reaction is not modified, the possibility of the increasing of the reaction rate exists.

Reviewer I: What are the implications for the patient when such high corrosion currents are measured and metal ions go into solutions?

Authors: In the studied alloys nickel is the main

component, its percentage in the dental materials being between 55 and 65. The utilization of this chemical element in dental alloys is due to the fact that its properties satisfy the essential needs of dental replacements: corrosion resistance, strong, thin and cheap. The alloy with chromium and cobalt provides the mechanical properties accepted by dentistry. It was demonstrated that nickel dissolves from dental devices into natural saliva, the dissolution rate being accelerated if beryllium is present in the alloy. On the other hand, nickel is recognized as the most carcinogenic metal on earth. Thus alloys producing nickel ions generate cancer because these ions can be absorbed readily across the cell membrane.

In the other direction, nickel has the ability to bind to oxygen, nitrogen, and sulfur from bio-compounds, replacing the usual catalysts (magnesium and calcium), which are essential in many metabolic activities. Moreover, nickel is considered as a metal that can create reproductive toxicity, create chromosomal aberrations, is immunosuppressive, etc. Nevertheless, twenty years ago about 85% of the dental crowns were made from nickel based alloys, while in the last decade we are still faced with over 50% of the crowns being nickel.

Reviewer II: Is there a clear correlation between the shape of the corrosion curves and the appearance of the microscopic pits found on the surface?

Authors: The cyclic polarization curves, which present a hysteresis loop, are characteristic for pitting corrosion. If $\Delta E = E_{br} - E_{rep}$ has a high value the alloy is susceptible to the pitting corrosion. One considers that if the hysteresis loop area is high, the alloy is susceptible to the pitting corrosion.

Reviewer II: What do you think influences the size and shape (not the amount of corrosion) of the corrosion pits?

Authors: The pit size is influenced by many factors such as: type of alloy impurities, composition of the corrosion medium, pH, but essentially by the current density, which depends on electrode over-potential.