



STABILITY OF NiCr DENTAL ALLOY AFTER 15 YEARS OF SERVICE

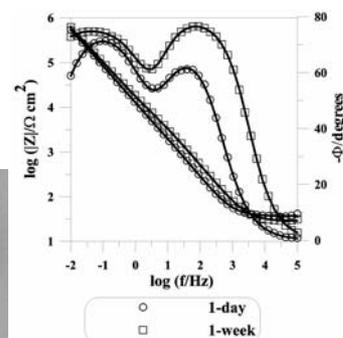
Georgiana BOLAT,^a Carmen PADURARU,^a Sorin Claudiu IACOB STRUGARU,^b
Corneliu MUNTEANU^b and Daniel MARECI^{a,*}

^a“Gheorghe Asachi” Technical University of Iași, Faculty of Chemical Engineering and Environmental Protection,
73 Prof. dr. doc. D. Mangeron Blvd., 700050, Iași, Roumania

^b“Gheorghe Asachi” Technical University of Iași, Faculty of Mechanical Engineering, 61-63 Prof. dr. doc. D. Mangeron Blvd.,
700050, Iași, Roumania

Received October 17, 2013

The European Directive imposes a ban on any objects which exceed a rate of nickel release of $0.2 \mu\text{g}/\text{cm}^2$ week (2004/96/EC: “Piercing in the human Body”). When exposed to artificial saliva and acidified artificial saliva NiCr dental alloy (VeraSoft, Allba Dent, USA) remained inside a patient for almost 15 years without visible indications of localized corrosion. The passivation of sample occurred spontaneously at open circuit potential. The electrochemical properties of the spontaneously passivated dental alloys at open circuit potential were studied by electrochemical impedance spectroscopy (EIS). The release of 4 cations (Ni, Cr, Mn and Cu) was studied by extraction tests in artificial saliva and acidified artificial saliva. In the present case the NiCr dental alloy was not aggravated sufficiently after 15 years of service and is considered quite remarkable for dental application.



INTRODUCTION

Ni-based and Co-based alloys have become widely used in the prosthetic dentistry and were introduced as a possible replacement for the much more expensive precious dental metal alloys due to the increasing cost of gold throughout the 1980s.¹⁻³

These materials are currently used for crowns, bridge casting and denture brasses.^{4, 5} Doubts remain as to the biocompatibility of Ni-based alloys since nickel is the most allergenic of all metallic elements.⁶

Through the allergic properties of the metal ions of Ni-based alloys should be considered carefully, these alloys still remain very popular for dental use.

However, for objects containing nickel intended for permanent contact with skin, the European Directive 2004/96/EC “Piercing in the human Body” was issued which limits the rate of nickel release of $0.2 \mu\text{g}/\text{cm}^2$ week.

There is a wide variety of commercially available Ni-based alloys on European Union (EU) markets. Recently, Reclaru et al. reported that, on a study of 8 Ni-based alloys, the biological tests did not show any cytotoxic effect on Hela and L929 cells or any change in TNF-alpha expression in monocytic cells.⁷

Recent works reported that Ni-based dental alloys showed evidence of localized corrosion.^{4, 8-10} Therefore it would be surprising if VeraSoft dental bridge were recovered without any significant

* Corresponding author: danmareci@yahoo.com

signs of localized corrosion. For elucidating this remarkable corrosion resistance, the VeraSoft dental bridge after clinical use was teased in vitro, by electrochemical and surface analysis techniques, and the concentration of the dissolved metallic ions in the solution was measured by means of atomic adsorption spectrometry.

MATERIALS AND METHODS

Materials

The NiCr old bridge (VeraSoft dental alloy) fabricated at the Alba Dent Inc., USA, was removed after being in oral cavity for about 15 years. The condition of the bridge was remarkably good (Fig. 1).

The bridge was examined under a scanning electron microscope (SEM). Elemental analysis was performed by an energy dispersive X-ray (EDX)

attachment on the SEM. To perform this Quanta 200 3D scanning electron microscope, was used.

The SEM micrographs of VeraSoft dental bridge after 15 years of service with EDX spectra are shown in Fig. 2. Small discrete pits are observed for this dental alloy after remove from oral cavity as shown by the arrows in Fig. 2A. The EDX spectrum (Fig. 2B) illustrates the Ni, Cr, Mn, and Cu presence on the VeraSoft dental alloy surfaces.

Electrochemical measurements

The electrochemical measurements were performed in Fusayama artificial saliva.⁴ The pH was lowered, by adding lactic acid and was fixed arbitrarily at 3.1. This acid was chosen in order to obtain conditions that were as close as possible to clinical reality because acid is naturally released by bacteria in oral cavity.¹¹



Fig. 1 – The removed VeraSoft dental bridge.

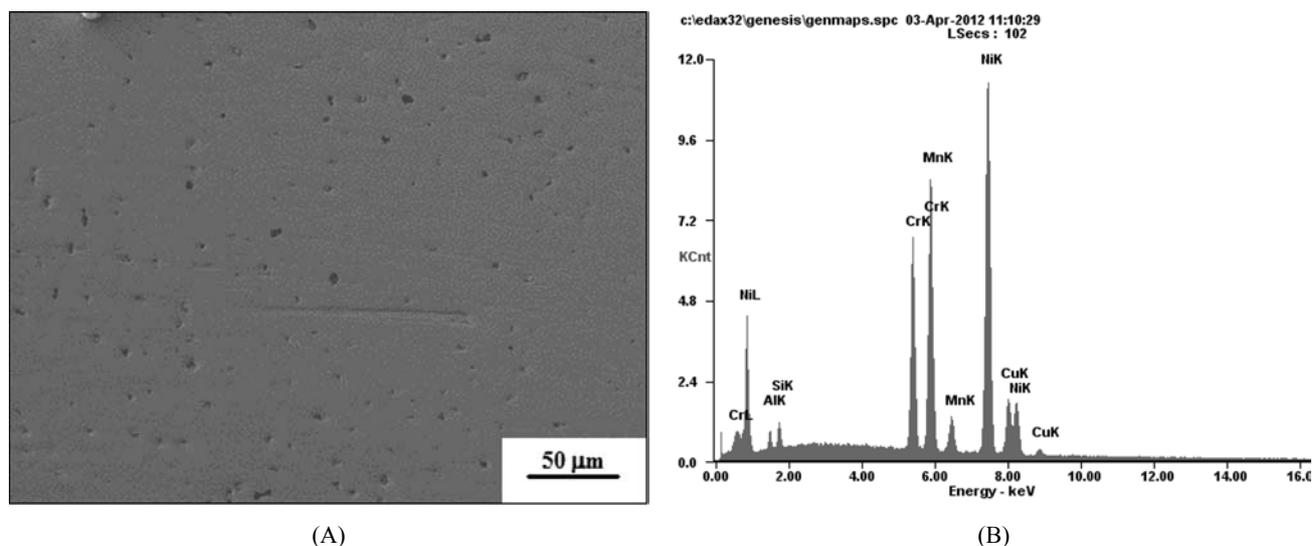


Fig. 2 – (A) SEM image and (B) EDX spectrum of the VeraSoft dental alloy after 15 years of service.

Electrochemical measurements were carried out in aerated solution at 37 °C using a PARSTAT 4000 potentiostat (Princeton Applied Research, USA) controlled by a personal computer and specific software (VersaStudio[®], PAR, USA).

A glass corrosion flow cell kit (C145/170, Radiometer, France) with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the electrochemical measurements. The C145/170 is fitted with a PCTFE sample holder and a freely adjustable Luggin capillary. All potentials referred to in this article are with respect to SCE.

Measurement of linear potentiodynamic polarization curves (LPC) was initiated after different time exposure to the test acidified artificial saliva. The tests were conducted by scanning the potential at 1 mV s⁻¹ between 200 mV negative of open circuit potential to 450 mV. Using VersaStat[®] software, the linear potentiodynamic polarization curves were plotted, and the corresponding values for the zero current density (ZCP), the corrosion current density (j_{corr}) and the passivation current densities (j_{pass}) were determined.

Electrochemical impedance spectroscopy (EIS) measurements were also performed in this study. The alternating current impedance spectra for VeraSoft dental alloy was obtained with a scan frequency ranging from 100 kHz to 10 mHz with an amplitude of 10 mV. The EIS spectra were obtained at different times after the electrode was immersed in the acidified artificial saliva. The EIS experimental data were analysed in terms of equivalent circuits (EC) using ZSimpWin software version 3.22.

All electrochemical tests were repeated three times to ensure reproducibility of the measurements.

Release of cations

The concentrations of the metallic ions released into solution were determined by atomic absorption spectrometry (Buck Scientific, Model 210 VGB). The extraction of the VeraSoft dental alloy was performed in two different media, artificial saliva (pH = 5.6) and acidified artificial saliva (pH = 3.1), and 4 chemical elements (Ni, Cr, Mn and Cu) were quantified in the extraction solution by AAS. The samples were first cleaned in ethanol p.a., under ultrasound and placed in the high density polyethylene (HDPE). The ratio of the release solution volume/total sample surface was equal to one. All HDPE bottles were placed at 37 ± 1 °C.

Every day the HDPE bottles were agitated in order to homogenize the solution. The concentrations of released metal ions in solutions were determined after 1 week of specimens' immersion. The calibration curves were created with six points obtained by increasing concentrations of standard.

RESULTS AND DISCUSSIONS

Electrochemical characterization

Fig. 3 shows typical linear potentiodynamic polarization (LPP) curves for VeraSoft dental alloy plotted in a semi-logarithmic presentation traced between 200 mV negative of open circuit potential to 450 mV with 1 mV/s potential sweep rate. This polarization value was chosen to account for the eventual development of positive potentials (up to +300 mV) in the oral cavity.^{12, 13}

They were recorded after 1-day and 1-week immersion in acidified artificial saliva at 37 °C. Average zero corrosion potential (ZCP), corrosion current density (j_{corr}), passive current density (j_{pass}) and breakdown potential (E_{bd}) values determined from the polarization curves are listed in Table 2 for the NiCr dental material tested.

Independent of immersion time, VeraSoft dental alloy exhibited a distinctive active-passive transition in the polarization curves following the Tafel region, but they entered directly into a stable passive regime. Fig. 3 clearly proves that VeraSoft dental alloy immersed 1-week in acidified artificial saliva had a better corrosion resistance than the same alloy immersed 1-day in the same corrosion medium. The linear polarization curves of VeraSoft dental alloy showed a shift of ZCP to more positive value with immersion time. The corrosion current density (j_{corr}) and passive current density (j_{pass}) decrease in time because of the surface passivation by covering probable with an oxide layer. The susceptibility of an alloy to localized corrosion in a given environment can be characterized in terms of the breakdown potential (E_{bd}) relative to the corresponding zero corrosion potential value (ZCP). The potential range comprised between the open circuit potential and E_{bp} represents the passivity zone, where corrosion is small or even insignificant. Thus, the difference $E_{\text{bd}} - \text{ZCP}$ can be adopted as a measure of the passive range of the material.^{14, 15} Table 1 lists the values of breakdown potential (E_{bd}) together with values calculated for $E_{\text{bd}} - \text{ZCP}$. The passive zone of VeraSoft dental alloy is very large; extends up 800 mV.

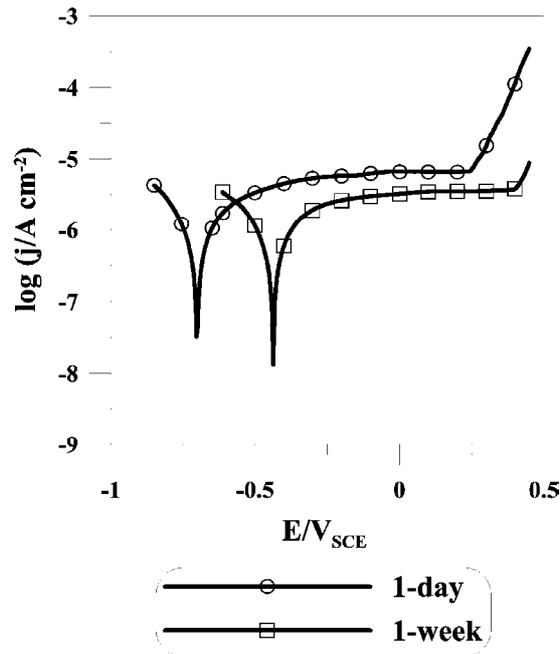


Fig. 3 – Linear potentiodynamic polarization curves of the VeraSoft dental alloy for different exposure times in acidified artificial saliva at 37 °C. Scan rate: 1 mV s⁻¹.

Table 1

The mean and standard deviation values of parameters measured and calculated of VeraSoft dental alloy after different time immersion in acidified artificial saliva at open circuit potential

Immersion time	ZCP (mV)	j_{corr} (nA/cm ²)	j_{pass} (μA/cm ²)	E_{bd} (mV)	$E_{bd} - ZCP$ (mV)
1-day	-701±19	940±30	6.6±0.3	245±3	945±11
1-week	-448±15	410±15	3.2±0.2	415±5	865±15

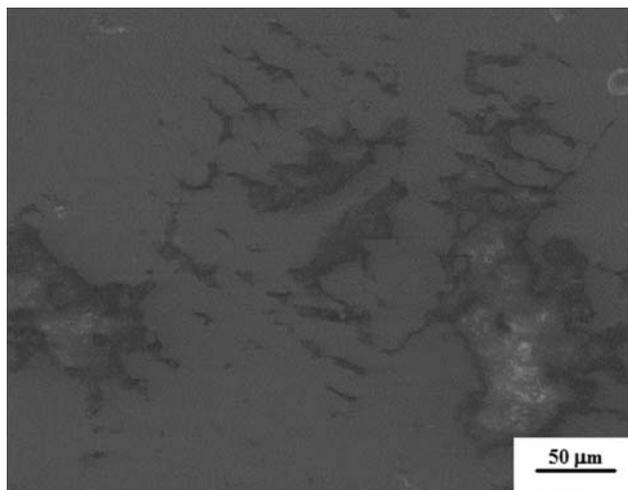


Fig. 4 – The surface morphology of VeraSoft dental alloy after the LPP measurements at 450 mV.

The SEM surface morphology observation of the VeraSoft dental alloy after the LPP measurements at 450 mV in acidified artificial saliva, as shown in Fig. 4, demonstrates that remarked localized corrosion has already occurred.

From Fig. 2B it can be observed that the VeraSoft surface after 15 years of service in oral cavity exhibited discrete pit, through without the presence of notable localized pitting corrosion. Although it appears that there was an initial small

degree of pitting, this did not develop into large pits because the dental alloy doesn't expose of +0.45 V in oral cavity.

Fig. 5 depicts the Bode impedance plots for VeraSoft dental alloy under open circuit potential conditions for different exposure times in acidified artificial saliva at 37 °C.

In this case, the Bode-phase plots show two relaxation constants, i.e., two peaks are observed in the Bode-phase plots. They can be satisfactorily fitted with the equivalent circuit (EC) shown in Fig. 6. The EC is characterized by two parallel combination term (RQ) in series with the resistance of the solution (R_{sol}). The two RQ elements can be attributed to charge transfer and separation processes at the alloy/oxide layer

interface ($R_{ct}Q_{ct}$) and to the oxide layer formed on the surface ($R_{ox}Q_{ox}$).

The high quality of the fitting is readily seen from the good match between the measured and the fitted spectra, which are presented as solid lines together with experimental data on the Bode plots in Fig. 5. Table 2 shows the impedance parameters obtained for VeraSoft dental alloy maintained different time periods in acidified artificial saliva at open circuit potential.

Large values of R_{ox} , at open circuit potential (order $10^5 \Omega \text{ cm}^2$) were obtained confirming the formation of a passive oxide layer with good corrosion protection ability. As the time immersion increased, R_{ox} increased (from $0.4 \text{ M}\Omega \text{ cm}^2$ to $0.7 \text{ M}\Omega \text{ cm}^2$) and Q_{ox} decreased. These results seem to correspond to a slight thickening of the oxide layer.

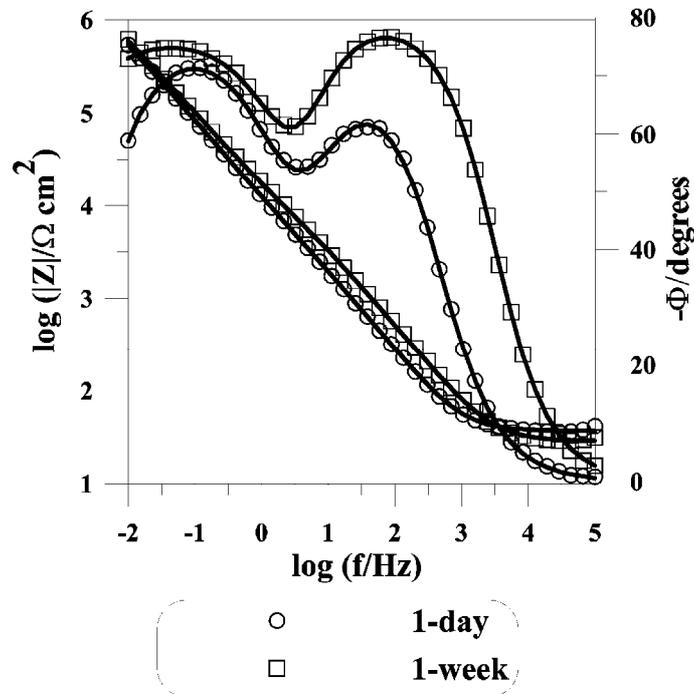


Fig. 5 – Measured (discrete points) and fitted (solid lines) Bode impedance spectra for: VeraSoft dental alloy maintained different time periods in aerated acidified artificial saliva at open circuit potential at 37 °C.

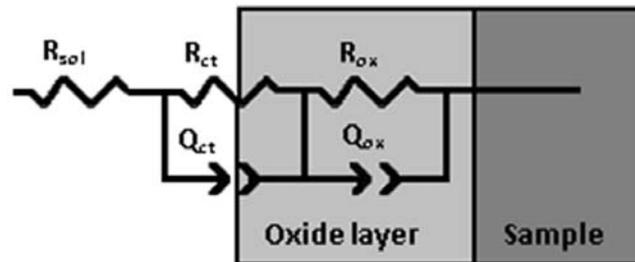


Fig. 6 – Proposed equivalent circuit for VeraSoft dental alloy maintained in aerated acidified artificial saliva at open circuit potential at 37 °C.

Table 2

Impedance parameters of VeraSoft dental alloy after different time immersion in acidified artificial saliva at open circuit potential

Immersion time	$10^5 Q_{ct}$ ($S\ cm^{-2}\ s^n$)	n_{ct}	R_{ct} ($k\Omega\ cm^2$)	$10^5 Q_{ox}$ ($S\ cm^{-2}\ s^n$)	n_{ox}	R_{ox} ($M\Omega\ cm^2$)
1-day	3.5	0.85	6.4	1.4	0.81	0.4
1-week	2.6	0.87	8.7	1.1	0.85	0.7

Table 3

Quantities of metal ions dissolved during 1 week of immersion of VeraSoft dental alloy in artificial saliva (pH = 5.6) and acidified artificial saliva (pH = 3.1)

Quantity of released VeraSoft dental alloy (ng/cm ² week)	Ni	Cr	Mn	Cu
Artificial saliva (pH = 5.6)	120	15	10	5
Acidified artificial saliva (pH = 3.1)	250	25	65	25

Nickel, chromium, molybdenum and manganese concentration in artificial saliva

The results obtained in static immersion test are listed in Table 3. The quantities of released metal ions detected in artificial saliva with different pH, are expressed in $\mu\text{g/L}$. Given that the ratio of volume of extraction solution/surface of the sample is equal to one, the same results may be expressed in $\text{ng}/(\text{cm}^2\ \text{week})$.¹⁶

Generally, the dissolution of the metal ions is dependent on the alloy itself and the chemical composition, pH, temperature, etc. of the solution. It was generally observed that the released quantities of metal ions were greater in the acidified artificial saliva than in the artificial saliva. This is probable related to the pH of the environment. Almost two time higher concentrations of Ni are obtained in the acidified artificial saliva than in the artificial saliva. Also, the quantities of Cr, Mn and Cu are higher in the acidified artificial saliva than in the artificial saliva.

However, Goldhaber¹⁷ indicates that the risk assessment in high intakes essential elements results in a toxicology spectrum and low intakes result in nutritional deficiencies.

CONCLUSIONS

VeraSoft dental bridge from NiCr based alloy remained inside a patient's oral cavity for almost 15 years without visible indications of localized corrosion. This aspect was considered quite remarkable, because the NiCr based dental alloys with low chromium (around 14 wt.%) content is considered susceptible for localized corrosion. In the present case the VeraSoft dental bridge presents a sufficiently passive zone (around 800 mV) to prevent localized corrosion. By decreasing the pH of artificial saliva, the quantity of the metal ions released from the VeraSoft dental alloy

increase, but remains in reasonable limits for use in dental applications.

Acknowledgements: This work was supported by a grant of the Roumanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0218.

REFERENCES

1. K.F. Leinfelder, *J. Am. Dent. Assoc.*, **1997**, *128*(1), 37-45.
2. D. Mareci, M. Romas, A. Cailean and D. Sutiman, *Rev. Roum. Chim.*, **2011**, *56*(7), 697-704.
3. M. Romas, D. Mareci, S. Curteanu and D. Sutiman, *Rev. Roum. Chim.*, **2013**, *58*(1), 11-17.
4. D. Mareci, R. Chelariu, S. Iacoban, C. Munteanu, G. Bolat and D. Sutiman, *J. Mater. Eng. Perform.*, **2012**, *21*(7), 1431-1439.
5. M. Sharma, A.V. Ramesh Kumar, N. Singh, N. Adya and B. Saluja, *J. Mater. Eng. Perform.*, **2008**, *17*(5), 695-701.
6. H.F. Hildebrand, C. Veron and P. Martin, *Biomaterials*, **1989**, *10*(8), 545-548.
7. L. Reclaru, R.E. Unger, C.J. Kirkpatrick, C. Susz, P.-Y. Eschler, M.-H. Zuercher, I. Antoniac and H. Luthy, *Mater. Sci. Eng. C*, **2012**, *32*(6), 1452-1460.
8. V.S. Saji and H.C. Choe, *Bull. Mater. Sci.*, **2010**, *33*(4), 463-468.
9. D. Mareci, Gh. Nemtoi, N. Aelenei and C. Bocanu, *Eur. Cells Mater.*, **2005**, *10*, 1-7.
10. D. Mareci, D. Sutiman, A. Cailean and J.C. Mirza Rosca, *EEMJ*, **2009**, *8*(3), 397-407.
11. M.R. Grimsdottir and A. Hensten-Pettersen, *Scand. J. Dent. Res.*, **1996**, *101*(4), 229-231.
12. G.J. Ewers and E.H. Greener, *J. Oral Rehab.*, **1985**, *12*(6), 469-476.
13. M.A. Ameer, E. Khamis and M. Al-Motlaq, *Corros. Sci.*, **2004**, *46*(11), 2825-2836.
14. J.R. Scully and R.G. Kelly, *Methods for determining aqueous corrosion reaction rates* in Cramer S.D., Covino B.S. Jr, editors. ASM Handbook, 13A Materials Park, OH: ASM International, 2003.
15. G.S. Frankel, *Pitting corrosion* in: Cramer S D, Covino B S Jr, editors. ASM Handbook, 13A. Materials Park, OH: ASM International, 2003.
16. L. Reclaru, R. Ziegenhagen, P.-Y. Eschler, A. Blatter and J. Lemaitre, *Acta Biomater.*, **2006**, *2*(4), 433-444.
17. S.B. Goldhaber, *Regul. Toxicol. Pharmacol.*, **2003**, *38*(2), 232-242.

