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BIOCOMPATIBILITY AND SENSITIZATION TO NICKEL RELATED CORROSION PROCESS OF Ni – Cr DENTAL METAL ALLOYS

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A high interest of today dentistry is focussed to improve fix or mobile dental prostheses. For this purpose a large variety of metal alloys is used, making thus difficult to evaluate their technical, biological and clinical properties. A large number of dental allergies, including responses to nickel containing dental alloys, like type IV hypersensitivity reactions, mediated by T-lymphocytes, were reported. Also, nickel containing dental alloys can undergo corrosion with release of metal ions. The present study presents the results concerning the electrochemical behaviour and corrosion of two commercial dental Ni – Cr alloys such as: Vera soft (from AlbaDent Company) and Wirocer plus (from Bego Dental Company). The investigation was performed using a medium of Fusayama-Meyer artificial saliva. Based on the polarization curves and electrochemical impedance spectroscopy (EIS) it was established the type and the intensity of the corrosion process by means of the corrosion currents value.The passivation of all the samples occurred spontaneously at the open circuit potential. The corrosion current values decrease after the alloys maintenance in the corrosive medium due their passivation. The corrosion currents decrease with the increase of the immersion time. The metal alloy of Wirocer plus is in an optimum corrosion resistant condition. The Vera Soft alloy sample presents a deep breakdown potential (about 250 mV). With an advantage of dendritic structure after casting process (producing a better surface quality), the Wirocer plus alloy presents a better electrochemical behaviour and biocompatibility than Vera Soft alloy.

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1. Introduction

Metallic materials play an essential role in the repair or replacement of the lost or damaged dental structure. These materials are currently used for crowns, bridges casting and denture bases. Ni based alloys are commonly used as the substructure of metallic-ceramic crown. Ni based alloys offer the advantage of an increased modulus of elasticity that allows thinner alloy sections to be used and consequently less tooth destruction during the crown preparation. They have the advantage of preserving a larger tooth part (teeth, instead of bridges). The preserving of a larger number of teeth for the life time, is the goal of today dentistry. Chromium is the main alloying element in Ni-based alloys and is added to promote the formation of a stable passive oxide layer highly resistant to corrosion [1].

A good evaluation of the corrosion process is connected with a complete investigation of the metal alloy biocompatibility [2]. A higher interest is noticed in non-noble alloys (Ni, Cr, Co, Ti), to avoid expensive costs and limited resources of noble alloys. The chemical nature of the

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metal alloy determines the composition of the superficial films with strong influence to corrosion behaviour in saliva [3, 4].

The electrochemical study of the dental alloy in artificial saliva permits the evaluation for alloy property modification in the oral cavity, using rapid electrochemical tests as qualitative criteria to estimate the corrosion resistance [5, 6]. Corrosion manifestations on dental alloys could exhibit biological, functional and aesthetic effects, the biological effects having the greatest significance. The oral environment is particularly favourable for the biodegradation of metals due to its ionic, thermal, microbiological and enzymatic properties and one can presume that the patient is always exposed to a certain quantity of corrosion products. If these products are not biocompatible, the organism may be injured due the metal toxicity and the allergy risk. Therefore, the ultimate goal must be to use only those alloys with minimal metal ion release. The release of metal ions depends upon the corrosion rate of the alloy and the solubility of the corrosion products [7, 8].

Nickel containing dental alloys can undergo corrosion with release of metal ions. The metal ions released from Ni -Cr dental casting alloys interfere with cellular metabolism [9]. Ni is known as an allergen specimen, but there is no evidence that patients are at a significant risk to develop sensitivity on the contact with nickel containing dental restoration works. Hypersensitivity reactions to nickel are only likely to occur with a prior sensitization from non-dental contacts and, indeed, these are rare (some cases were reported) [10]. The majority of dental allergies, including responses to nickel containing dental alloys, comprise type IV hypersensitivity reactions, cell mediated by T-lymphocytes.

Though the allergic properties of the metal ions of Ni - Cr based dental alloys should be considered carefully, these alloys still remain very popular for dental use motivating the interest of the present study.

2. Materials and methods

The following materials, respecting the commercial names with their chemical compositions, used in the present study, are shown in Table 1.

We emphasize that there are two categories of Ni – Cr dental alloys: (i) 55 % Ni and 15 %, Cr (ii) 65 % Ni and 25 % Cr and with no grain refiners added (Mo, Nb). The investigated materials are representative for the categories of Ni – Cr dental alloys.

All alloy samples were cast and subjected to heat treatment before beginning the electrochemical investigations [11, 12]. Results from EDX samples investigation, are depicted in Table 1. The average values were obtained for main specimens (carbon being neglected), on five points of samples surface.

Table 1. Composition of Ni – Cr alloy samples after casting process. EDX results.

Specimen / Sample	Ni	Cr	Mn	Al	Si	Mo	Fe
Vera soft	53.6	14.5	19.5	1.6	1.6	---	0.7
Wirocer plus	65.2	22.5	1.6	0.9	1.1	9.5	1.6

The test sample specimens were shaped as discs with a thickness of 0.7 mm and a diameter of 25 mm, obtained by centrifugal cast (time 10 – 15 seconds, in conditions of 39.03 g acceleration) according to the manufacturing process. The active surface was metal - graphically prepared by means of fine-grained abrasive paper. At the end, the surface was polished with diamond paste with 1 μm grains, cleaned for impurities by ultrasound and finally washed [13, 14]. Samples manufacturing process was performed at the Dental Laboratory of Medicine University 'Carol Davila', Bucharest, Faculty of Dentistry.

The surface samples of Ni – Cr alloys were investigated with an electron microscope (SEM). It was used an electron microscope, model FEI Inspect S 50. Also a surface screening was performed for samples with bacteria deposits and for those plated with ceramic. The investigation reveals the importance of the metal surface quality and influences of secondary thermal cycles caused by aesthetic plating process.

For electrochemistry studies, it was used an electrolyte medium Fusayama-Meyer artificial saliva prepared as a solution with the following composition (g/L): 0.4 NaCl, 0.4 KCl, 0.8 $CaCl_2$, 0.69 NaH_2PO_4, 0.005 Na_2S*9H_2O, 1 urea and pH 5.9. During electrochemical experiments, the alloy samples were immersed in the electrolyte medium.

An electrochemical equipment Voltalab PGZ 301 it was used which is an electrochemical workstation provided with an Impedance Analyzer [15]. The protocol for the applied electrochemical method was as follows: the time evolution of the Open Circuit Potential (EOC), Potentiodynamic Polarization Curves (PPC) and Electrochemical Impedance Spectroscopy (EIS), carried out with data acquisition software. There cell is containing the working electrode (Vera Soft, Wirocer plus metal alloy samples), where the counter electrode was a circular Pt sieve and the reference electrode was a Saturated Calomel Electrode (SCE). The electrolyte was permanently stirred by an electromagnetic stirrer. All the experiments were carried out at the temperature of 37.0 ^{0}C ± 0.1^{0}C (i.e., the human body temperature).

3. Results and discussion

3.1. Microstructure characterisation

The microstructure of the Ni-Cr-based alloys samples before corrosion process is depicted in micrographs presented in Fig. 1. The surface of Wirocer plus cast alloy showed dendrite microstructure and a rippled structure between the matrix and particle phases. The Vera Soft alloy has a complex two-phase structure, grains with interdendritics particles in larger size.

Regarding the EDX spectra we noticed a non homogenous aspect for Vera Soft sample, with differences of up to7 % and even higher for some major specimens as Ni, Cr or Fe for different points compared with 1 % in difference for Wirocer plus.

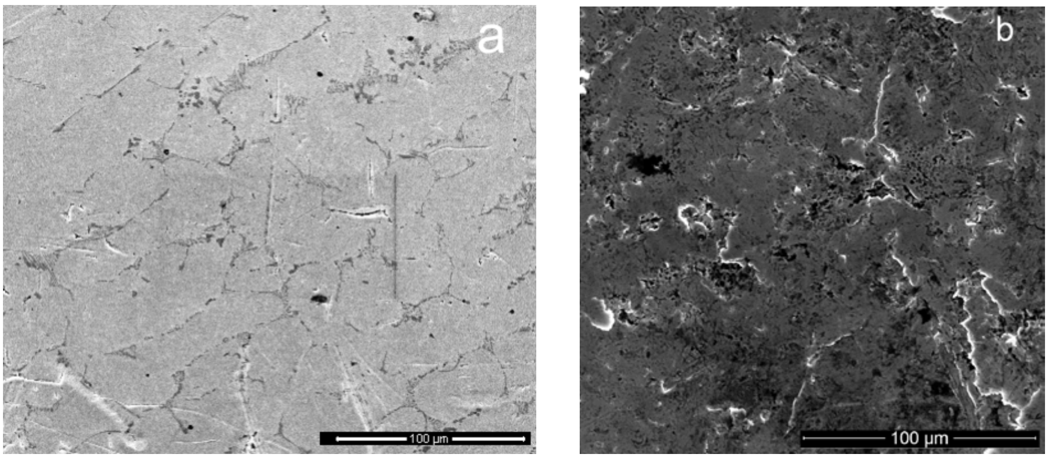

Fig. 1. Ni – Cr alloy cast samples. SEM micrographs: a) Wirocer plus, b) Vera Soft.

3.2. Electrochemical Measurements

When an alloy is placed into the oral environment, an electrochemical interaction (corrosion) between alloy and environment is taking place. The effect of this interaction may be manifested as: release of soluble metallic ions into the oral environment, formation of corrosion products on the alloy surface and combination of both. The phenomena are very complex and may act as a uniform attack, pitting and crevice corrosion and galvanic corrosion as well. An important aspect is the ageing process of restored dental structures that is improved by the corrosion process. It is difficult to perform an evaluation of this process.

These effects, depending on the altered alloy surface and/or the nature of released metallic ions, may cause adverse biological reactions such as allergy [16]. For a specific environment, corrosion depends on the structure and composition of the alloy. The alloys of the present study have different compositions and microstructure. For the oral biotope, the temperature widely fluctuates because of ingestion of hot or cold food and beverage. Furthermore, different areas of oral biotope are exhibited different temperatures. Nevertheless, it can be reasonably approximated in experimental settings for a value of 37 ^{0}C, that is, over the environmental temperature of 25 ^{0}C [17].

Open Circuit Potential (EOC method)

The metals immersed in an electrolytic environment generate an electric potential which stabilises to a stationary value after a period of time.

In Fig. 2 are presented the curves of the open circuit potentials versus time for the Ni – Cr alloys in the electrolyte solution. After 1 hour of immersion, we notice the EOC displacement towards positive potentials as it is shown in Fig. 2. The increase is related to the thickness of the oxide film, this improving its corrosion protection ability.

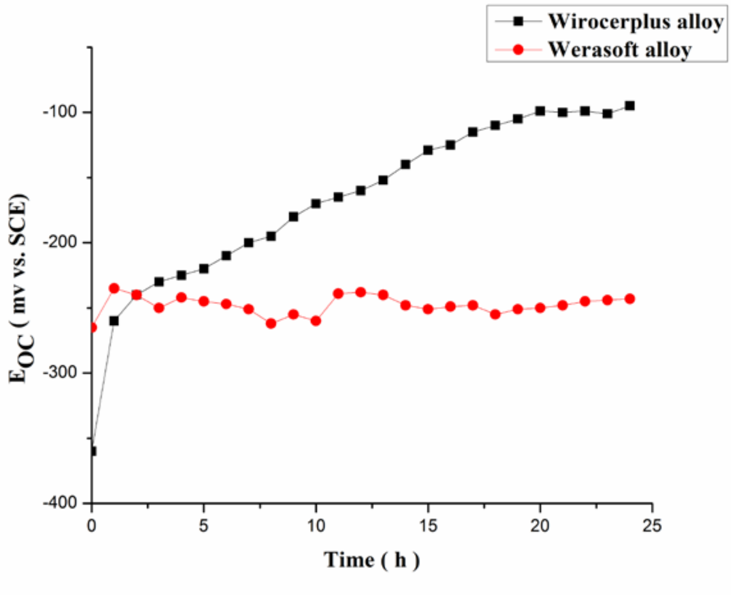

Fig. 2. Open Circuit Potential (E_{OC}) vs. time, for Ni -Cr alloy samples.

We noticed for Wirocer plus investigated sample, no potential drops associated with surface activation during 24 hours exposure electrolyte solution. This kind of behaviour suggests that the air-formed native oxide is thermodynamically resistant at chemical dissolution in electrolyte solutions. The disruptions noted for the curve of Vera Soft alloy are difficult to interpret, but they came from surface phenomenon such as depassivation-passivation in the system caused by non homogenous composition revealed by EDX sample surface investigation. The open circuit potential results, in the case of both alloys are summarized in Table **2**. The highest EOC was found for Wirocer plus.

Table 2. The Open Circuit Potential values, for samples immersed in artificial saliva solution.

Sample	E_{OC} (mV)		
	0 hours	1 hour	24 hours
Vera Soft	-245 ± 15	-218 ± 15	-234 ± 5
Wirocer plus	-292 ± 15	-228 ± 15	-96 ± 15

Potentiodynamic Polarization (PPC method)

Plots in a logarithmic scale for values between -600 mV and +1200 mV of SCE, for the current density of the two Ni-Cr based alloys after 24 hours maintaining in the artificial saliva solution, are displayed in Fig. 3. Standard techniques were used to extract zero current potential (ZCP) and corrosion current (i_{corr}) values from the potentiodynamic polarization plots.

The two Tafel slopes intercept at the point of the coordinates (ZCP, i_{corr}). In both cases, the ZCP values are smaller than those corresponding to EOC (Table 2). The variation is probably due to depassivation phenomena on the surface during cathodic scanning. The corrosion currents for sample alloys are of the same order of magnitude (nA/cm^2), as presented Fig. 3**.** Potentiodynamic polarisation curves of Ni-Cr based alloy, tested after 24 hours of maintaining in artificial saliva solution, plotted on logarithmic axes are depicted in Fig. 3.

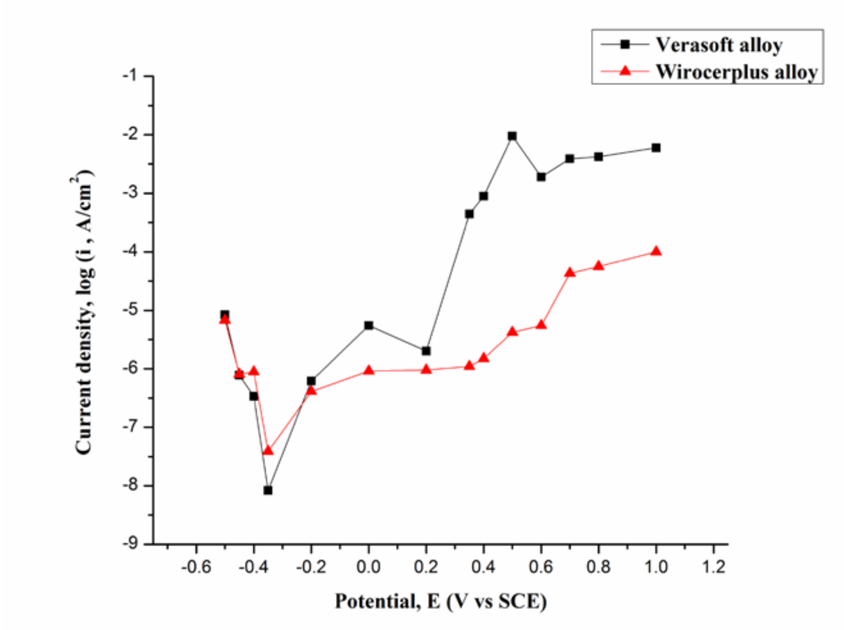

Fig. 3. Potentiodynamic polarisation curves (PPC) of Ni -Cr alloy samples, on logarithmic axes. Results after 24 hours of samples maintaining in artificial saliva solution.

According to Fig. 3, the polarisation curve is placed into a „better behaviour" for Wirocer plus Ni – Cr sample, where in the anodic area (from 300 to 600 mV) there are anodic currents of μA order. For Vera Soft sample the „worst behaviour" is noticed, with anodic currents of mA order in the same anodic area from 300 to 600 mV. Both samples translated directly into a stable passive behaviour from the "Tafel region" without exhibiting a traditional active-passive transition [18].

In the same conditions (after 24 hours of maintaining in artificial saliva solution), a linear plot of polarisation curves is depicted (Fig. 4). For anodic currents, the scale values were chosen in the interval 0 – 500 μA/cm^2.

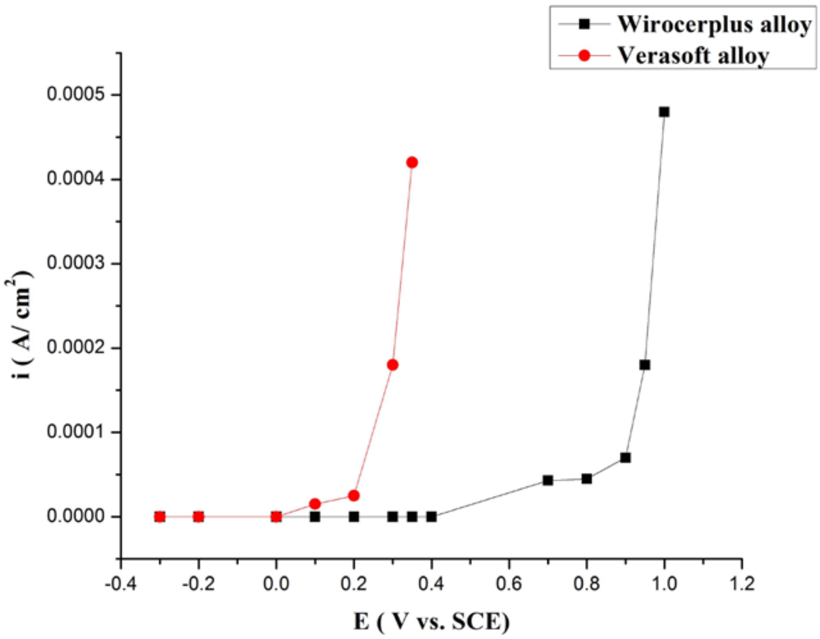

Fig. 4. Potentiodynamic polarisation curves (PPC) of Ni -Cr alloy samples, on linear axes. Results after 24 hours of samples maintaining in artificial saliva solution.

This presentation help to reveal the values of the breakdown potential, E_{bd}, an important electrochemical parameter, which characterises the corrosion process of Ni-Cr alloys. The potential values from the interval ZCP and E_{bd} represent the passivity area, with an insignificant corrosion. We notice that E_{bd} value for Vera Soft Ni - Cr alloy is very low, approximately 180 mV. For Wirocer plus, the E_{bd} value is higher: 900 - 1000 mV.

A low Cr and Mo content of the Ni - Cr alloys is causing a high corrosion rate and susceptibility to an improved bacteria deposits [18]. We conclude that the presence of larger passive range for the Wirocer plus sample with respect to the Vera Soft sample was ascribed mainly to a higher percentage of Cr and Mo, for the chemical composition of specimens.

An important parameter (also, an easy evaluation) for Ni-Cr-Mo-Fe alloys, is the relative effectiveness of Cr and Mo content on pitting or crevice corrosion usually that can be considered equivalent with pitting resistance equivalent (PRE). It can be calculated with the empirical equation [19]:

PRE = % Cr + 3.3 % Mo

A PRE value above 38, is supposed to provide good resistance to pitting corrosion in a Cl^- containing solution, as is the case of artificial saliva [19]. The Ni-Cr-Mo casting alloy is pitting resistant in artificial saliva when the PRE value increases up to approximately 49 [19]. For the investigated alloys, according to the PRE equation, the PRE value for the pitting-resistant of Wirocerplus alloy is 53.85. The other Ni – Cr alloy, is high susceptible to pitting corrosion, has the PRE value of 14.5 (no Mo containing).

A complementary and sophisticated study of electrochemical impedance spectroscopy (EIS) was performed to investigate the corrosion resistance of Ni-Cr based alloys. There was evaluated corrosion current intensity (i_{corr}), polarisation resistance (R_p) and Tafel slopes according Stern – Geary equation [20].

The corrosion currents obtained from the Stern-Geary equation for the Ni-Cr based alloys maintained for 24 hours in the artificial saliva are in agreement with the polarization data.

Nickel is a known allergen. Allergic responses are mediated through the immune system. The majority of dental allergies, including responses to nickel containing dental alloys, comprise the type IV hypersensitivity reactions mediated by T-lymphocytes [21- 23]. The mechanisms of high allergy frequency to nickel are not known, but probably has a genetic origin [24, 25]. In addition, the tendency of nickel containing alloys to release relatively large amounts of nickel ions probably contributes to their allerginicity. Nickel ions are documented mutagens in humans, but there is no evidence that nickel ions cause intraoral any carcinogenesis [26]. Galvanic current or release of ions (caused by corrosion process) could account for many types of dyscrasias, such as lichenoid lesions, ulcers, leukoplakia, cancer and kidney disorder, although research has failed to find any correlation between dissimilar metals and tissue irritation.

3.3 Surface characterisation after corrosion process

Important is to know and evaluate the capability of metal dental alloys to devolop bacteria deposits, motivating the present study. Microorganisms and their by-products can affect metal alloys in different ways: certain species can absorb and metabolize metal from alloys, leading to corrosion. Another way is that of normal metabolic by-products of some microbial species altering the environmental conditions, thus making them more conductive to corrosion by increasing the local acidity levels [27, 28].

A SEM of the same samples surface after corrosion investigation was performed (24 hours time exposure), samples being exposed, in the mean time, to action of *Streptococcus mutans* bacteria from ATCC 700610 (American Type Culture Collection), representative for the oral biotope.

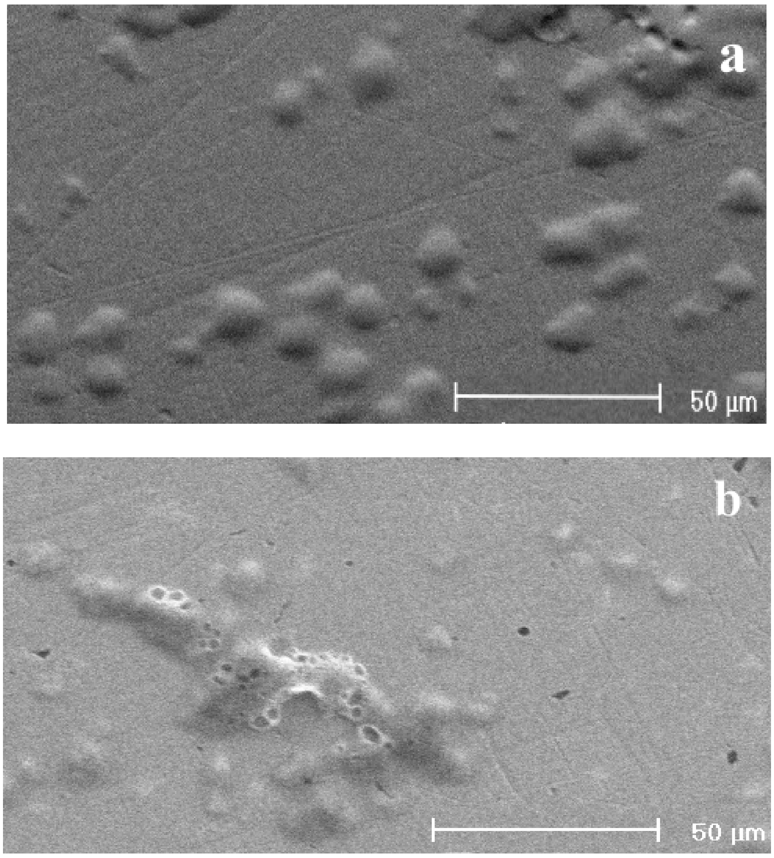

Fig. 5. Bacteria deposits and corrosion on Ni -Cr alloy surface samples. SEM micrographs: a) Vera Soft, b) Wirocer plus.

As is presented in Fig. 5 b, we noticed an improved development of bacteria colony on Vera Soft sample, the improved corrosion activity represented by pitting process. Dark dots, upper right corner, are observed. The existing surface defects as result of the casting process (Fig. 1 b), are improving the process. A better and not affected surface it was observed for Wirocerplus Ni – Cr sample, confirming the electrochemical results (Fig.5 a).

An important aspect is that the most of the situations, the cast metal alloy samples suffer a second thermal procedure at high temperature (approximately $1,200^0$ C) for plating with an aesthetic veneer (ceramic most) in order for metal oxidation and ceramic bonding [27, 28]. The alloy surface is affected about the thermal process and presents at the interface (bonding area) the crevice corrosion and an improved bacteria deposits Fig. 6.

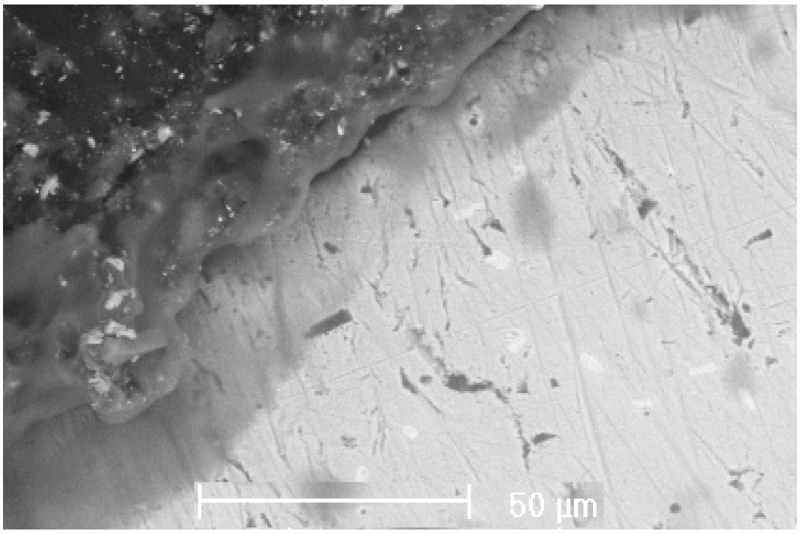

Fig. 6. Crevice corrosion of Ni - Cr alloy samples. SEM micrograph of plated area from a dental metal ceramic restoration work.

4. Conclusions

In the present study, the electrochemical behaviour for two Ni-Cr based alloys was evaluated by electrochemical techniques. Nickel containing dental alloys can undergo corrosion with release of metal ions.

Very low corrosion current densities, typical for passive materials, were obtained for the two tested samples. For Vera Soft alloy, a deep and dangerous breakdown potential was recorded. A uniform corrosion appears onto the surface of the Wirocer plus alloy, while in case of Vera Soft alloy surface, a pitting corrosion is developed. The Cr and Mo contents play a significant role in the corrosion resistance: Wirocerplus alloy with high Cr and Mo content exhibit a much wider passivation range and a better resistance to pitting corrosion. For the investigated samples, the polarization resistance is increasing with the immersion time, due to the surface passivation. The Wirocer plus Ni - Cr alloy with an improved quality surface microstructure shows the best electrochemical behaviour in artificial saliva solution and a less Ni ions release process.

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