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SURFACE COMPOSITION OF THE Co-Cr BASED ALLOYS AFTER DIFFERENT LAB DENTURE TREATMENTS USING AUGER ELECTRON SPECTROSCOPY

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Метою даної роботи є аналіз хімічного складу поверхні сплаву на основі Co-Cr після декількох технологічних процедур, прийнятих у стоматологічній практиці за допомогою оже-електронної спектроскопії (ОЕС). Цей аналіз проводили після відливання зразків сплавів піддавали наступним послідовним обробкам: розрізанням на алмазному колесі, електроіскровим різанням і шліфуванням, електрополірування, витримки в штучній слині 2 дні після електрополірування

Ключові слова: обробка поверхні, стоматологічні сплави на основі Co-Cr, оже-електронна спектроскопія, штучна слина

1. Introduction

Co-Cr based dental alloys currently gain wide attractiveness for dental restorations such as customized abutments, crown and bridge in the anterior and posterior region, telescope and conical crowns, screw-retained restorations and for fabrication the substrate of the metal-ceramic restorations. With time, Co-Cr alloys entered in another fields of usage, such as orthopedic implant material for body joints and fracture fixation applications as well [1, 2]. The wide popularity of such alloys is explained by a superior combination of the useful properties, such as fracture toughness, strength, excellent wear resistances, good bond with ceramics and the quality/price ratio [3, 4]. These alloys are also characterized by excellent corrosion resistance [5, 6]. The bulk microstructure of Co-Cr alloys is well documented. These alloys generally have a two phase structure consisting of a γ phase with a face-centered cubic structure and martensitic ϵ phase with a hexagonal close packed structure. Molybdenum is often also present in their chemical composition, to exploit its strengthening effect by solid solution hardening [7, 8].

2. Literature review

However, the use of Co-Cr-based alloys is associated with a significant disadvantage associated with the possibility of positively charged ions, their constituent metals, being released into the surrounding saliva and the appearance of negative charge ions on the dentures surface. In some cases these processes cause galvanisms, toxic-allergic reactions and other pathological reactions resulting in manifestations of the clinical symptocomplex intolerance metal alloys in the oral cavity [2]. Therefore, the clinical and laboratory assessment of intolerance to the metal prostheses, as well as the use of new methods of diagnosis, prevention and treatment of this pathology are the urgent tasks of modern dentistry.

It is known that in the development of electrochemical interactions between metals that take place in electrolytes, electrode factors play a leading role, the main of which is the structural, physical and chemical state of the electrode surface. Their chemical and electrochemical activities in the oral cavity, in particular, the return of metal ions to saliva, discoloration, roughness, formation of the oxide layers, passivation kinetics, depend on the state the of metal dentures surface. Physical

and chemical properties of the metal surface, for example, adhesion and fatigue strength, wear resistance, corrosion behavior, significantly depend on the technological treatments used in dental practice. It should also be noted that the finishing surface treatment determines the quality of the metallic inclusions biocompatibility and the similarity of their contamination by microorganisms.

The complexity of understanding the nature of physical, chemical, mechanical, and biological processes involving material surface is due to the fact that atoms and molecules of the uppermost surface layer and several underlying layers are initially involved in these processes. It is the structural and chemical state of the thinnest surface area with a length of several nanometers that determines the mechanism and kinetics of the surface processes noted above. Therefore, application of the traditional in the orthopedic practice of the visual, macro- and microscopic methods for diagnosing the surface state does not fit to modern requirements. It is necessary to use new surface-sensitive methods of the analysis, allowing to obtain information about the metal surface state at the atomic-molecular level. Currently the metal surface can be analyzed by different surface sensitive spectroscopic methods. The choice of the measurement technology is influenced by the nature of the material and surface finishing treatment. Such analytical methods, for example, are widely used in the development of the materials for in mechanical engineering, electronics and heterogeneous catalysis [9, 10]. These include AES, X-ray Photoelectron Spectroscopy (XPS), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), Scanning Electronic Microscopy (SEM) with energy dispersive X-ray analysis (EDX). Methods are commonly used for surface chemical analysis: AES, XPS and EDX. The highest sensitivity for superficial layers is pertinent to the AES method. The average depth of the analysis for the AES measurement is approximately 1-2 nm. In addition, this method allows to obtain the depth distribution of the elements over the near-surface region. The experience in the recent years indicates the successful application of these methods in dentistry and the implantation of metal structures into a living organism [11, 12].

3. The aim and objectives of the study

The aim of this work was to analysis of the dental Co-Cr-based alloy surface chemical composition after

several technological procedures adopted in the dental practice and exposure in artificial saliva using AES.

To accomplish the aim, the following objectives have been set:

1. To prepare samples of the dental Co-Cr-based alloy with required of the chemical and phase composition of the alloy bulk.

2. To treatment samples using the following procedures adopted in the dental practice after casting: cutting on by the diamond wheel, electric-spark cutting and grinding, electropolishing, exposure in artificial saliva.

3. To obtain quantitative information on the concentration depth distributions of the chemical elements in the near-surface region using AES.

4. Analysis of changes in the chemical and phase composition of the treated samples taking into account the thermodynamics laws.

4. Material and methods

The bulk chemical composition of the Co-Cr-based alloy as determined by X-ray Fluorescence Spectroscopy, is represented in the Table 1. Samples of 3 mm thickness and 15 mm diameter were produced by conventional casting technique. After casting (treatment 1), the alloy samples were subjected to the following sequential treatments: cutting on by the diamond wheel (treatment 2), electric-spark cutting and grinding (treatment 3), electropolishing (treatment 4) and exposure in artificial saliva after electropolishing during 2 days (treatment 5). These treatments types are typical in dental technology. Exposure to artificial saliva was of interest as a model process widely used in laboratory experiments. Fusayama artificial saliva solution [21] with pH of 5.5 at 37°C constant temperature was used.

Table 1

The chemical composition of the Co-Cr-based alloy surface samples after various processing methods according to AES

Chemical elements	Composition, at. %					
	Bulk	Surface				
		Treatments				
		1	2	3	4	5
Co	58,1	–	17,0	8,6	7,9	19,6
Cr	31,2	4,0	18,9	12,6	30,2	5,8
Ni	3,9	–	2,6	1,8	1,0	2,3
Mo	2,9	–	1,4	1,7	1,2	1,1
Ti	<0,002	–	1,0	1,1	1,1	1,3
Ca	–	–	1,6	–	–	–
K	–	–	–	–	–	0,9
Si	1,3	–	19,0	1,8	–	–
C	–	89,1	16,1	27,3	32,3	10,6
O	–	6,9	11,3	21,9	22,7	38,9
N	–	–	11,0	4,0	–	–
S	–	–	–	19,1	3,5	19,5

The experiments were performed using a JAMP-10S Auger spectrometer (Japan, JEOL). The Auger electrons energy of the alloy components and impurity atoms was measured using a cylindrical mirror-type energy analyzer with an energy resolution of $\Delta E/E=0.5\%$. The chemical elements quantitative analysis (in at. %) was carried out in accordance with the atlas of standard Auger spectra and the elemental sensitivity coefficients [15]. Auger electrons that escape into vacuum carry information from a depth of 0.4–1 nm, depending on their kinetic energy. When applied to the material surface impurities AES can detect about 0.02 monolayer coating. The absolute sensitivity of the method is 0.1 at. % and the relative sensitivity is $10^{-3}\%$. To obtain information on the chemical elements distribution within the surface area (up to $\sim 1\ \mu\text{m}$), depth concentration profiles are constructed. For this purpose, the Auger electrons spectra are continuously recorded as the atomic layers are removed by etching with Ar^+ ions. In the present work, depth

profiles were obtained as a result of ion sputtering the sample surface by Ar^+ ions with an energy of 0.6 keV and ion current of $2 \cdot 10^{-6}\ \text{A}$ having an ion beam diameter of 3 mm.

5. Results

To obtain more complete information of the samples surface chemical composition, the Auger electrons spectra were recorded in the range of 0–1000 eV. For example Fig. 1 shows typical Auger spectra recorded for two states of the sample surface. Auger spectrum 1 corresponds to the initial state of a sample placed in a vacuum chamber of an Auger spectrometer after electropolishing. Auger spectrum 2 characterizes of the same sample surface after etching by argon ions to a depth of $\sim 100\ \text{nm}$. A quantitative analysis of the both spectra allows to establish, firstly, the presence of the main alloy components (Co, Cr, Ni) and impurity atoms (Mo, K, Ti, S, O, C, Si), secondly, a significant changes in the intensity of all peaks recorded for deeper surface layers.

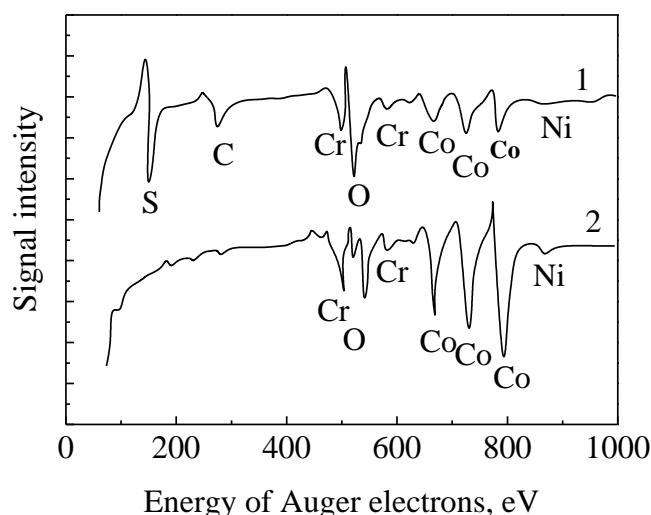


Fig. 1. Overview of the Auger electrons energy spectrum: 1-initial state; 2-after ion sputtering with 60 s.

The results of the surface atomic concentration for all surface treatment are represented in the Table. For comparison, the same Table contains information about the atomic composition of the alloy bulk. Detailed scrutiny of the obtained results reveals two groups of the chemical elements that are presented in the thinnest surface layer (up to ~ 1 nm): elements that are in the bulk of the alloy as its main components (Co, Cr, Ni) or technological impurities (Mo, Ti, Si), and elements which presence are due to the interaction of the samples surface with the environment (C, O, K, N, S). As a result of this interaction, the surface of the all samples is “polluted” with carbon and oxygen. The highest concentration of carbon (89.1 at. %) was found on the surface of the casting sample (treatment 1), and the lowest (10.6 at. %) is registered after exposure to the artificial saliva (treatment 5). At the same time, in the first case the smallest amount of oxygen (6.9 at. %) is set, and in the second – the maximum one (38.9 at. %). The feature characteristic of the surface chemical state after all types of its processing is a decrease in the concentration of the main components of the alloy (Co, Cr, Ni

and Mo) as compared with their content in the bulk alloy. The lowest amount of Co (7.9 at. %) was determined after electrolytic etching (treatment 4), and Cr (5.8 at. %) after exposure in the artificial saliva (treatment 5). The Cr content (30.2 at. %) close to the bulk composition was found only for the electropolished surface. As can be seen from the Table, the concentration of other introduced impurities (Ca, K, N, S) varies significantly depending on the method of the surface treatment. It has to be noted in particular, an extremely high concentration of sulfur (S) after grinding (treatment 3) and exposure in artificial saliva. The highest N content is pertinent to the sample after mechanical cutting (treatment 2).

To obtain quantitative information on the concentration depth distributions of the chemical elements in the near-surface region, layer-by-layer profiles were constructed using the method by ion etching as described above. As an example, Fig. 2 represents such profiles for the sample that was exposure to the artificial saliva. Depth profiles have similar qualitative characteristics for other types of treatments (2, 3, 4).

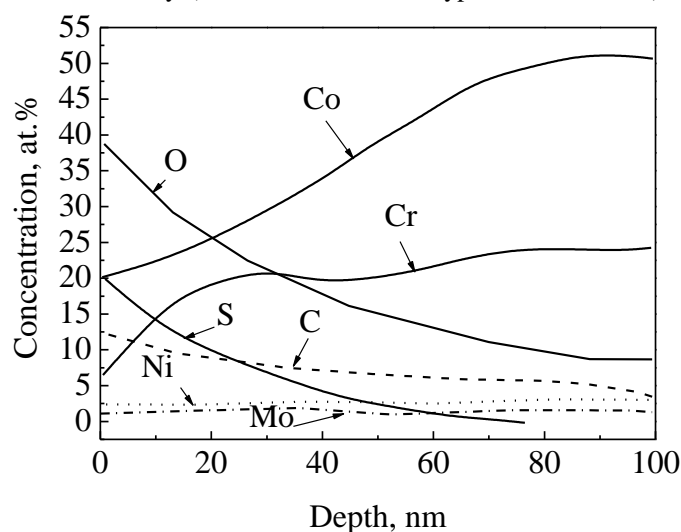


Fig. 2. Depth profiling of the chemical elements

6. Discussion

In all cases, three characteristic regions of the layer-by-layer distribution of all elements can be distinguished:

- 1) region closest to the free surface is relatively sharp in composition;
- 2) transition region characterized by a smooth course of concentration curves;
- 3) concentration yield region is practically at a stable level as the distance from the free surface to a depth of ~ 100 nm is reached.

For the first of these areas, there is typically a strong decrease in the amount of introduced surface impurities C, O, S and a significant increase in the concentration of Co, Cr, Ni and Mo. These results indicate that the appearance of these impurities is a consequence of the interaction of the sample surface with the environment. As a result of this interaction, the formation of oxides, carbides, nitrides, sulfides and silicides, as well as more complex compounds with the participation of adsorbed water and hydrocarbons is possible. The formation of the surface compounds is governed by the thermodynamics laws, the most important factor of which is the free surface energy. In parallel with the processes of the surface chemical compounds formation, the effects of the selective dissolution of the alloy components are possible when they are aged in an active chemical solution, to which artificial saliva can also be attributed. As can be seen from the Table, there is a selective enrichment of the samples surface with Cr after electropolishing, while, after exposure to artificial saliva, Co has the highest concentration.

It is known that Cr, Ni and Co are characterized by high affinity to oxygen and their oxides have high values of the enthalpy formation [22] as well. The following surface compounds can be formed: Cr_2O_3 (–756 kJ/mol), NiO (–487 kJ/mol) and Co_3O_4 (–428 kJ/mol). At the same time, only Cr atoms possess high affinity to carbon. Therefore, it is most likely that the carbon detected by the AES method belongs to carbide Cr_{23}C_6 (–591 kJ/mol). Cr also has a fairly

high affinity for nitrogen, which can lead to the formation of the Cr_2N nitride (–130.2 kJ/mol) surface particles. The probability of the nitrides formation in the case of Co and Ni is low. The high S content after treatments 3 and 4 may indicate the possible formation of the sulfides Ni_3S_2 , Co_4S_4 .

7. Conclusions

1. The samples of the Co-Cr-based alloy of the following bulk composition (at. %) was prepared: Co-58,1; Cr-31,2; Ni-3,9; Mo-2,9; Si-1,3; Ti-<0,002. After annealing these alloys have a two phase structure consisting of a γ phase with a face-centered cubic structure and an martensitic ϵ phase with a hexagonal close packed structure.

2. After conventional casting technique (treatment 1) the alloy samples were subjected to the following sequential treatments: cutting on by the diamond wheel (treatment 2), electric-spark cutting and grinding (treatment 3), electropolishing (treatment 4) and exposure in artificial saliva after electropolishing during 2 days (treatment 5).

3. To chemical elements distribution within the surface area (up to ~ 1 μm) and the depth concentration profiles after surface treatments are constructed using Auger Electron Spectroscopy.

4. Based on the obtained results and the thermodynamics laws, it can be assumed that a significant decrease in the surface concentration of the Co-Cr-based alloy main components as a result of using various methods for treating of the samples surface is due to the formation of the various chemical compounds that were captured from the environment. This may also explain the concentration gradient of all elements that is observed within the depth of the near-surface region. It is important to emphasize that such changes may cause a significant impact on the structure of the technological oxide coatings, on the dental structures corrosive behavior, and therefore on their biocompatibility and various pathological manifestations

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ХЕМОМЕТРИЧНІ МЕТОДИ ДОСЛІДЖЕННЯ БІОЛОГІЧНОЇ АКТИВНОСТІ ПОХІДНИХ ХІНОЛІНУ

© **О. А. Бражко, М. П. Завгородній, Є. О. Карпун, О.О. Бражко, Я. І. Романенко, А. М. Богдан**

Важливою характеристикою хімічних сполук є їх біологічна активність, оскільки її наявність може стати основою для використання речовини в терапевтичних цілях, або, навпаки, обмежити можливість його практичного застосування внаслідок прояву побічних і токсичних ефектів. Комп'ютерна оцінка спектра біологічної активності дає можливість визначити найбільш перспективні напрямки для тестування фармакологічної дії конкретних речовин і відсіяти потенційно небезпечні молекули на ранніх стадіях досліджень. Опис структури молекул органічного з'єднання реалізовано в PASS за допомогою дескрипторів атомних околиць (Multilevel Neighborhoods of Atoms)

Ключові слова: "структура-активність", спектр біологічної активності, прогнозування, PASS, передбачувальна здатність, QSAR

1. Вступ

В даний час близько 80 млн. різних хімічних сполук є для тестування у вигляді вже синтезованих зразків. В реєстраційній системі Chemical Abstracts Service міститься інформація про 138 млн. органічних і неорганічних речовин, описаних в літературі з початку XIX століття. In silico згенеровано сотні мільйонів структурних формул органічних молекул разом з вихідними реагентами і реакціями синтезу і понад 166 млрд. структурних формул, повністю покривають хімічний простір, що включає до 17 атомів С, N, O, S і галогенів [1].

Поява вільно-доступних програм дала змогу отримувати інформацію про структуру та біологічну активність хімічних сполук, створювати необхідні передумови для розвитку методів дизайну ліків, заснованих на структурі лігандів і прогнозувати профілі біологічної активності для нових речовин.

Серед похідних хіноліну існує значна кількість біологічно активних сполук широкого спектру дії, які можуть стати основою для нових біорегуляторів [2, 3]. Для вибору таких сполук вивчається спектр їх біологічної активності, рівень потенційної токсичності, визначається їх фармакодинаміка, чим пояснюється практична доцільність використання методів хемоінформатики.

Нижче розглянуто хемометричні методи аналізу біологічної активності хімічних сполук, в PASS методі аналізу залежностей "структура-активність" та QSAR аналізу за допомогою розробленого нового програмного засобу QuS [4].

2. Літературний огляд

Традиційно при моделюванні властивостей хімічних сполук використовують методи квантової хімії, молекулярного моделювання та хімічної ін-