University POLITEHNICA of Bucharest

Faculty of Chemical Engineering and Biotechnologies

Department of General Chemistry

DOCTORAL THESIS – ABSTRACT

Electrochemical behaviour of dental alloys based on Ni, Cr, Co, Mo and rare elements

Doctoral Supervisor:

Prof. Dr. Ioana DEMETRESCU

PhD student:

Florentina Gina IONAȘCU

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CUPRINS

INTRODUCTION

THE IMPORTANCE AND MOTIVATION OF CHOOSING THE THEME

The thesis aims to describe the study of the contribution and novelties brought to the field of dentistry.

In recent years, new procedures and technologies have been introduced, which, complemented by the advent of advanced materials, have helped to introduce new methodologies, aiming at the production of new dental prostheses and restorations. The combination of advanced technology, both in digital techniques and computer integrated automated manufacturing systems, has led to a leap forward in dentistry under the name of ,,Digital Dentistry", taking into account key factors such as: surface finish quality, marginal accuracy, mechanical properties, corrosion resistance, ion release behaviour and, of course, biocompatibility.

The research carried out over time with the help of methods and experiments on alloys, aims to create new high-performance medical devices, and minimize the occurrence of risks of any kind.

Based on the studies and experimental results obtained, the front thesis considers the on-the-fly adaptation of the research and use trends, foreseen within the challenges launched by the EU requirements, regarding medical devices made from alloys that can lead to a possible toxicological risk. In this context, in addition to the experiments on classical NiCr and CoCr type alloys, the mechanical microstructure properties and anticorrosive qualities of a new CoCrNbMoZr alloy compared to the commercial CoCrMo based alloy were studied.

During the investigations carried out on the new alloy, which includes rare elements in different percentages, having a very high degree of biocompatibility, it was found that they can increase the level of safe use and correspond to recent regulations. The thesis includes another aspect of the alternative strategies to achieve this desired, namely, the coating of the new alloy, which maintains the original content of the research proposed for the realization of the thesis. The results obtained and published fall within the current trends of the transition period for the use of biomaterials with Cr, Co, Ni, etc., in medical devices that find full motivation and utility.

B. EXPERIMENTAL PART AND PERSONAL CONTRIBUTIONS

The beginning of the ongoing century which expanded and deepened nanotechnology and its materials also brought a new development for biomaterials including dental biomaterials Even if some of the metallic dental materials are those known from the last century, their processing and exploitation method bears the stamp of certain technologies us who fight for performance and safety.

The work is balanced, built both as a way of organizing the literature part and as a presentation, including two chapters reviewing the existing literature on the field and another 5 chapters of original experimental research. The final conclusions and a rich bibliography with carefully selected titles and including your own contributions complete the thesis, which also mentions separately at the end a list of works with related citations.

Regarding the detailed content and organization of the material in the work, the following comments are worth noting.

In total, the thesis has nine chapters, two of which include the literature part and seven represent the original contributions. The first two chapters from the experimental part, respectively chapters 3 and 4, are dedicated to materials and work methods, very briefly reviewing the composition of the alloys of the working electrolytes, the synthesis of the coatings made and their electrochemical and surface characterization procedures. The following three basic chapters for the experimental part, chapters 5, 6 and 7 introduce the main investigated aspects, respectively the dependence of the behaviour of NiCr and CoCr alloys on temperature in chapter 5 and recent aspects of biomaterials approach in the light of EU directives regarding toxicological risk (Regulation (EU) 2017/745) in chapters 6 and 7. Chapter six addresses a combined strategy to improve the performance of dental alloys using a new CoCrNbMoZr alloy and an anodic oxidation coating. The chapter characterized by a multitude of data that includes the morphological and structural characterization of the deposited anodic layer and a comprehensive electrochemical characterization (open circuit potential determinations, potentiodynamic polarization and electrochemical impedance studies) is succinct and well organized ending with a series of partial conclusions. The seventh chapter is entitled Electrodeposition of polypyrrole on different CoCr alloys from ionic liquids with the simultaneous incorporation of indomethacin, it presents complexity both at the level of polymer deposition from ionic liquids coupled with the simultaneous incorporation of the drug and at the level of characterization of the deposited layer. And this chapter ends with a series of partial conclusions which, combined with those existing at the end of the other chapters, represent chapter eight.

Based on the data from the chapters with experimental data, the PhD student published 3 papers in ISI rated journals with a cumulative impact factor of 9,138 as well as a paper published in the ISI indexed volume of Bull. Sci. UPB Series B. These articles, as well as the citations they obtained in a relatively short time, are an example of many original elements that the present thesis proposes and which are detailed in chapter 9 and mentioned in the following:

 Testing the studied alloys in natural saliva collected from patients in compliance with ethical requirements.

 Identifying the compositions of some new alloys, namely the CoCrNbMoZr alloy, as well as combining the use of this alloy with surface modification methods to reduce the risk of toxicity by increasing corrosion resistance, respectively reducing the amount of released ions. The surface modification used the anodic oxidation process.

 Simultaneous electrodeposition of polypyrrole and incorporation of a drug on the commonly used commercial CoCr alloys respectively Wirobond and Hearenium. The incorporated drug was indomethacin and the release kinetics was established by selecting the existing models in the specialized literature.

CHAPTER VIII. FINAL CONCLUSIONS

For the first time, the behaviour of two commercial NiCr-based dental alloys, Niadur and I-Bond, was investigated in natural saliva using potentiodynamic polarization and electrochemical impedance spectroscopy tests.

Based on experimental data, it was determined that the corrosion rate in natural human saliva is higher than in artificial Ericsson-type saliva. Kinetic parameters calculated using two methods: Tafel slope extrapolation and polarization resistance, reconfirm that natural saliva collected from male patients is a more corrosive medium than other natural saliva.

It was also found that an increase in the temperature of the artificial saliva leads to a decrease in the polarization resistance for both NiCr-based alloys, indicating an increase in the corrosion rate. The EIS tests confirmed the data obtained from the potentiodynamic polarization tests.

The electrochemical results indicate an increase in the corrosion rate of each biomaterial studied in Fusayama–Meyer artificial saliva with increasing temperature. SEM together with EDS measurements revealed the same behaviour; temperature favours the occurrence of corrosion phenomena, due to which the oxide films on the surface of the metallic biomaterial tend to break after the temperature of 310 K. The ICP-MS results show that with the increase in temperature, the amounts of ions released from both dental alloys increase, by also, remaining in the order of several tens of ppm, in perfect accordance with the results obtained by the electrochemical studies.

A coating on a new CoCrNbMoZr dental alloy using an anodic oxidation procedure was discussed in this paper. A comparison was made between an unanodized alloy sample and three anodized samples of the same alloy at three potentials of 1 V, 1.05 V and 1.1 V. We demonstrated that the anodizing procedure is an easy and inexpensive way to obtain surfaces with superior anticorrosive properties.

From the SEM determinations we established the morphology of the samples and from the XRD analysis the oxides existing in the protective layer were identified.

For all three samples, from anodized alloys, the percentage of oxygen that appeared in the EDX spectrum was greater than 32 at.%.

The presence of Cr2O3 and MoO3 in the passive film resulted in a significant resistance to the transfer of metal ions through the passive film. The contact angle showed that anodization conferred a decrease in the hydrophilic character of the anodized sample at 1.05 V, while anodization at 1 V and 1.1 V caused an increase in surface hydrophilicity.

From the electrochemical studies, we observed that all three types of coatings formed on the anodized samples studied protected the alloy from corrosion in Ericsson-type artificial saliva. For all three types of anodized samples, lower corrosion current density values were obtained compared to the non-anodized alloy. The best anti-corrosion properties were obtained for sample S3, anodized at 1.05 V. Corrosion resistance as a function of anodizing potential is the result of the combined effect of different surface characteristics. The high corrosion resistance in the

Ericsson-type saliva of the oxidized samples was revealed in the experimentally quantified results of the electrochemical measurements and was due to the presence of a mixture of all the oxides identified in the XRD experiments (Cr_2O_3, MoO_3, CoO, NbO).

The simultaneous incorporation of indomethacin during the electrosynthesis of polypyrrole from choline chloride-based ionic liquids was achieved for the first time on various commercial CoCr alloys. Compared to aqueous electrolytes, this type of electrolyte allows greater solubility for indomethacin.

SEM micrographs of PPy and PPy-Indo coatings revealed a granular surface morphology and no insoluble precipitate of drug molecules. By adding Indo to PPy, the cluster size increases from 200 nm to 500 nm, the surface of the alloys being uniformly covered by the PPy-Indo film. The presence of indomethacin in the polypyrrole layer was confirmed by the recorded FTIR spectra.

The enhancement of the hydrophilic characteristics when the studied CoCr alloys were coated with PPy or PPy-Indo was determined by measuring the contact angle.

Also, coating the studied commercial CoCr alloys with polymer films or drug-incorporated polymer films led to improved anticorrosive properties of the samples in Tani-Zuchi artificial saliva.

Indomethacin release tests showed that the PPy-Indo coatings can release the drug for periods longer than 460 h on the Hera alloy substrate. In the case of the drug-doped polymer layer electrosynthesized on the WBC alloy, half of the amount of drug incorporated into the polymer layer is released in about 40 h. The maximum released amount was determined to be about 99.8%, indicating that the drug layers polypyrrole functioned as an efficient reservoir for indomethacin. A non-Fickian behaviour was established as a mechanism for the release profiles of indomethacin from the polymer layer.

CHAPTER IX. ORIGINALITY ELEMENTS

The elements of originality and innovative contributions introduced by this paper are identified in the second part of the doctoral thesis as follows:

a. The concept of testing and assessment of CoCr and NiCr alloys considering the EU regulatory framework, classification, and toxicological risks (Regulation (EU) 2017/745 of the European Parliament and of the Council of 5 April 2017 on Medical Devices) according to which biomaterials used in medical devices containing Co, Cr and Ni nominated as elements of allergenic and toxicological risk were to have limitations of use after May 2020. Even if the pandemic offered a grace period until 2025 the trend of using alternative strategies which the thesis promoted is an innovative element of the works developed within the present thesis.

b. As a result of the concept of identifying and promoting alternative strategies for the use of alloys above, the thesis identified both new alloy compositions, namely the CoCrNbMoZr alloy, and the combination of the use of this alloy with surface modification procedures to reduce the risk of toxicity by increasing corrosion resistance, respectively reducing the amount of released ions. Anodic oxidation was used as a surface modification method to obtain synergistic results in reducing the risk of use.

c. Considering the wide use of these alloys in the dental field where temperature variations are also frequent and over a wider range of temperatures than in the case of other metallic biomaterials used in restorations, the electrochemical behavior of NiCr and CoCr alloys in different saliva was investigated artificial ones whose composition was made in the laboratory.

d. Testing the investigated alloys in the natural saliva collected from patients in compliance with the requirements represented another element of novelty.

e. Obtaining protective coating layers by electrochemical deposition from ionic liquids gained original character in the front work by simultaneous electrodeposition of polypyrrole and incorporation of a drug. The support alloys were selected from the commonly used commercial CoCr alloys Wirobond C and Hearenium CE respectively. The embedded drug was indomethacin and its release kinetics was also followed.

ANNEXES

A1. LIST OF PUBLICATIONS

Published ISI articles

1. Florentina Golgovici, Florentina Gina Ionașcu, "Electrochemical behavior of NiCr based alloys in human and artificial saliva", University Politehnica of Bucharest Scientific Bulletin Series B - Chemistry and Materials Science, ISSN 1454-2331, 79 (4), 157-166, 2017, WOS: 000424134600015.
2. Florentina Golgovici, Mariana Prodana, Florentina Gina Ionașcu, Ioana Demetrescu, "A comparative electrochemical and morphological investigation on the behavior of NiCr and CoCr dental alloys at various temperatures ", Metals, 2021, 11(2), pp. 1–14, Article number 256, DOI: 10.3390/met11020256, WOS: 00062278780000, Impact Factor 2021: 2,695.
3. Florentina Gina Ionașcu, Mariana Prodana, Florentina Golgovici, Ioana Demetrescu, " Combined Strategy to Improve the Performance of Dental Alloys Using a New CoCrNbMoZr Alloy with Mn and Si Coated via an Anodic Oxidation Procedure", Metals 2021, 11(7), Article Number 1017, DOI:10.3390/met11071017,WOS: 000676238700001, Impact Factor 2021: 2,695.
4. Florentina Golgovici, Florentina Gina Ionașcu, Mariana Prodana, Ioana Demetrescu, "Simultaneously Embedding Indomethacin and Electrodeposition of Polypyrrole on Various CoCr Alloys from Ionic Liquids ", *Materials 2022,* 15(13), Article Number 4714, doi: 10.3390/ma15134714, WOS: 000825596800001, Impact Factor 2021: 3,748.

Total Impact Factor: 9,138

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