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RESEARCH ARTICLE

The Study of Ni-Cr, Co-Cr Dental Alloys and Ceramics Chemical Indifference using ZrO_2-HfO_2-Y_2O_3 System *in Vitro*

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ABSTRACT:
The purpose of this study was to find out the electrical-chemical behavior of *Ni-Cr*, *Co-Cr* alloys and ceramics using the ZrO_2-HFO_2-Y_2O_3 system in vitro. The study was conducted using the System *NH* (Germany) and Starbond *CoS* (Germany) prefabricated alloys, previous processing-free; and the Nacera Pearl (Germany) ceramics using the ZrO_2-HFO_2-Y_2O_3 system, represented with frames manufactured in a dental technical laboratory, without subsequent veneering. There were two identical samples, each of them put in the electrical-chemical cell with 3% *NaCl* water solution, its temperature equal to 37°C. The potentials were evaluated using the potentiostat which defined the data of both samples in the cell. The experiment lasted for 5 days. The obtained results were recorded each hour throughout the working day. The parameters (values, positive or negative charge) of electrical-chemical potential on both identical samples from the System *NH* alloy have been changing intermittently. We have concluded that under certain conditions there may appear electrical current between the samples obtained from the same alloy, located in the same medium, unaffected by any external factors (heat, mechanical influence, etc.). The up-to-date methods of measuring the potentials and currents between the metallic dental prostheses may reflect the electrical balance by the photo, at the certain moment, so they are characterized by sufficiently high margin of error to be used while deciding on the certain alloy.

KEYWORDS: Galvanic corrosion, dental alloy, in vitro corrosion.

INTRODUCTION:

Relevance of the study:

When choosing the material for clinical practice, we often ask about its biological indifference and the negative effect it may express toward the certain patient. Most dentists care not only about their clinical reputation, but health of their patients as well, and they have also been concerned with the issue. Almost all fields of stomatology engage dental metal alloys: in orthodontic and orthopedic treatment with fixed or removable prostheses as well as during rehabilitation of patients with implants.

Background:

For the last 10 years we have been studying problems related to negative effect of metal dental prosthetic components onto the bodies of their users. During this period the authors and dentists of the O. Bohomolets National Medical University Stomatological Center Clinics have examined hundreds of patients with characteristic complaints and peculiar for the metal dental prostheses negative clinical manifestations. We have studied vitro behavioral mechanisms of modern metal alloys and ceramics with the ZrO_2-HFO_2-Y_2O_3 system under conditions which were close to the real ones. The prostheses, fabricated from the low-quality alloys or produced with technological errors, haven't been considered by this study.

The aim of the study:

The aim of the study was to realize why homogenous alloys, which, according to the researchers,[1-3] were the most widely used due to their biological indifference, may cause allergic responses, exacerbation of chronic oral inflammations and other negative manifestations.

LITERATURE REVIEW:

Even the *Ti* material, used for fabrication of the fixed dental prostheses and implants, considered to as the best sample material, in many cases received critical reviews of its users[4-7]. While studying the specialized literature dedicated to the issue and analyzing the experience of managing the problem, we analyzed numerous publications, where the authors described and commented on their studies of the oral metal dental prostheses destruction within the oral cavity. The authors noted the prostheses negative effects for the human body as follows:

The main causes of corrosion on the dental prosthesis:

Heterogenity of alloys (production of galvanic current):

If we put some metal dental prostheses from heterogeneous alloys in the oral fluid, then, according to the electrochemistry laws, there will appear electrical potential difference between some prostheses. This difference produces galvanic current which destroys the alloys. Then corrosion affects the metal dental prosthesis. The released products negatively affect both oral cavity and the human body, triggering the chain of responses[8-14].

Effect executed by bacteria on their metabolites:

The storage conditions of the fabricated prosthesis are of primary importance regarding the subsequent negative manifestations[15-17]. The scientists have studied the effect executed by bacteria on their metabolites, correcting the corrosive environment around dental alloys, including **oxygen concentration, salinity, and acidity**, all of which influence the corrosion behavior of the alloys,[18-20] **changes in *pH* and temperature** related to food or beverage intake, and the action of different **medications**[21,22].

Wear effect (masticatory forces + salivary environment):

Modern studies highlight the synergistic interaction between wear and corrosion, which occurs when masticatory forces combine with the salivary environment of the oral cavity[4,23,24]. The study of Craig L.[23] focused on the Wear and Corrosion Interactions at the Titanium/Zirconia Interface, highlights the synergistic interaction between wear and corrosion, which occurs when masticatory forces combine with the salivary environment of the oral cavity. Overall, the zirconia groups outperformed the titanium groups. In fact, the titanium groups generated 5 to 6 times more wear to the implant alloys as compared with the zirconia counterparts. The best performing group was *Zr/Ti*, and the worst performing group was *Ti/Ti*[23].

Genotoxic effects → allergic and inflammatory manifestations:

According to some researchers, dental alloy components may induce genotoxic effects[25-27] and lead to allergic and inflammatory manifestations[28]. Though, it is considered that the homogenous alloy constructions don't induce galvanic currents and they are more favorable due to the biological indifference. This has been proved by numerous metal and alloy corrosion studies in vitro, the corrosion usually studied by placing the galvanic matches from various metals or alloys in artificial saliva (nutritive environment or a serum) under temperature of 37° *C*, with different *pH*[29-32].

The solution of the problem:

The solution of the problem seemed to be evident: all metal dental prostheses should be fabricated from the same alloy, strictly according to the technology on all stages of fabrication. The classical electrochemistry states that no potential difference may be observed between the same alloys or metals, placed in the same medium, under the t_{const}, consequently, the electrical current won't be observed there as well as the corrosion. But the problem turned out to be more complicated than this.

V. A. Kistyakovskiy experiment:

In early 20th century, a D.I. Mendeleev's disciple, an outstanding chemist, professor Vladymyr Aleksandrovych Kistyakovskiy made a unique experiment. He placed two copper electrodes in the container with potassium cyanide and connected a galvanometer to it. The scientist noticed that when he inclined the construction to different sides, the galvanometer showed different electric potential meanings. He called this device the "breathing electrode". In 1909 in London at the 7th Congress of Applied Chemists V.A. Kistyakovskiy demonstrated this equipment and received great appraisal from his colleagues (Fig. 1, 2).

Fig. 1: Professor V.A. Kistyakovskiy

Fig. 2: Container with electrodes:

1 – core electrode; 2 – gauze electrode; 3 – electrolyte:

Explanation of the potential difference due to oxygen absorption:

The processes occurring are very difficult for understanding, being still insufficiently studied. The "Ukrainian chemical journal"[8] and the "Junior Technician" magazine[33], published articles with explanation of the potential difference appearing in electrical-chemical medium due to oxygen absorption or superficial absorption of oxygen atoms by the metal core. The numerous studies of the respected scientists, dedicated to the dental alloy's biological compatibility, confirm this statement.

Explanation of titanium degradation caused by saliva:

The authors[5,10,23], concluding their studies, state that saliva, acting as a weak electrolyte, has been documented in vitro to contribute to electrochemical degradation of titanium at physiological *pH* levels. Titanium is a passive metal well known for biocompatibility, primarily due to the oxide layer that spontaneously forms on its surface. When this passive film is disrupted, the underlying raw metal becomes exposed and susceptible to corrosion. This process typically occurs in cycles: the oxide layer is damaged and removed, corrosive attack occurs, and the surface recovers, reforming a new protective passivation layer. Micromotion from masticatory activity is a contributing factor, causing repeated destruction and removal of surface oxides. Repeated damage at the implant interface from the combined effects of wear and corrosion may ultimately lead to component misfit, titanium fatigue, and potentially implant failure. The released metal ions/debris (*Ti* and *Ti* alloys) from the degradation process have been documented to cause local inflammation and titanium tattoos in adjacent tissues. These mechanical and biologic processes affect prosthesis longevity and potentially compromise the patient's esthetic result.[23]

The task of the study:

What exactly may happen in the oral cavity and the adjacent organs to the stomatological alloys which are multicomponent? We have set up the following task: to study the electrical-chemical behavior of various dental alloys and ceramics using the ZrO_2-HFO_2-Y_2O_3 system *in vitro*.

MATERIALS AND METHODS:

Materials:

The following three samples have been selected for the study:

- Alloy System *NH* (Germany), used for manufacturing of the metal-ceramic frames, consisting of the components such as: *Ni* − 58.4%, *Cr* − 26.9%, *Mo* − 12.9%, *Si* − 1.6%, others − <0,1% (prefabricated without special preparation 1).
- Alloy Starbond *CoS* (Germany), used for manufacturing of the metal-ceramic frames, consisting of the components such as *Co* − 59%, *Cr* − 25%, *W* − 9.5%, *Mo* − 3.5% (prefabricated without special preparation).
- Nacera Pearl (Germany) ceramics using the ZrO_2-HFO_2-Y_2O_3 system (as the frames fabricated in a dental technical laboratory without subsequent veneering).

Instrumentation:

The study has been conducted using the potentiostat "ПИ 50-1" ("*PI* 50-1") (Fig. 3) and electrical-chemical cell "ЯСЭ-1" ("*YASE*-1") (Fig. 4).

Fig. 3: Potentiostat "ПИ 50-1"("*PI* 50-1")

Fig. 4: Electrical-chemical cell "ЯСЭ-1" ("*YASE*-1")

Method:
Two identical samples containing alloys and ceramics were placed in the electrical-chemical cell of the "ЯСЭ-1" ("YASE-1") with 3% *NaCl* water solution, and held there under fixed temperature 37°*C*. The samples in the electrical-chemical cell didn't contact directly. The distance between the samples in the *NaCl* solution made up 30mm. The potentials were measured using the potentiostat "ПИ 50-1" ("PI 50-1"), which fixed characteristics on each of the samples in the cell. The trial lasted for 5 days for each sample pair. The obtained results of the potential difference were daily evaluated and registered in the registry book. The equipment was switched off at night, no evaluations conducted at this time. The container with the physiological solution imitation and the studied samples in it didn't move and the solution wasn't mixed up.

RESULTS:
According to the evaluated parameters, there were made approximate time potential changes in time schemes, with the first derivative of these potential changes to be defined (Tab. 1−3).

Table 1: Measurement of the continuous stationary potential changes of the System *NH* samples (Germany)

Day	**Onset time**	$\gamma^{stationary}(V)$	**Day**	**Onset time**	$\gamma^{stationary}(V)$
I	9^{35}	-0. 165	III	9^{00}	+ 0.048
	10^{30}	- 0. 175		10^{00}	- 0.222
	11^{30}	- 0. 138		11^{00}	- 0.335
	12^{40}	- 0. 105		12^{00}	- 0.440
	13^{30}	- 0. 094		13^{00}	- 0.524
	14^{30}	- 0. 080		14^{00}	- 0.596
	15^{20}	- 0. 072		15^{00}	- 0.677
	16^{30}	- 0. 068		16^{00}	- 0.731
II	9^{00}	+ 0.264	IV	8^{15}	+ 0.127
	10^{00}	+ 0.068		9^{15}	- 0.279
	11^{00}	- 0. 045		10^{15}	- 0.485
	12^{00}	- 0. 14		13^{35}	- 0.812
	13^{00}	- 0. 264			
	14^{00}	- 0. 315			
	15^{00}	- 0. 394			

After completing the experiment, the operation surface of both samples was unchanged.

Table 2: Measurement of the continuous stationary potential changes of the Starbond *CoS* (Germany).

Day	**Onset time**	$\gamma^{stationary}(V)$	**Day**	**Onset time**	$\gamma^{stationary}(V)$
I	10^{30}	- 0, 365	**III**	11^{00}	+ 0,080
	11^{30}	- 0.368		12^{00}	+ 0.006
	12^{30}	- 0.416		13^{00}	+ 0.005
	13^{30}	- 0.443		14^{00}	+ 0.008
	14^{30}	- 0.423		15^{00}	+ 0.011
	15^{30}	- 0.439		16^{00}	+ 0.015
II	8^{00}	+ 0.041	**IV**	9^{00}	+ 0.022
	9^{20}	+ 0.045		10^{20}	+ 0.042
	10^{00}	- 0.033		11^{00}	+ 0.022
	11^{10}	- 0.035		12^{00}	+ 0.019
	12^{40}	- 0.033		13^{00}	+ 0.020
	13^{40}	- 0.030		14^{00}	+ 0.019
	15^{00}	- 0.024			

During evaluation of the stationary potential of the Starbond alloys sample, with the potential difference equal to 80 *mV*, the circuit was made using the external micro ampermeter with standard internal resistance 1 *kOhm*, the external circuit received the current of approximately 0.22 μA. Stationary potential abruptly declined, which evidences that the used by the external micro ampermeter power which is taken away during evaluation from the micro source as the *NaCl* dental samples solution, abruptly affects the process. No conclusions may be drawn as well as the subsequent analysis, basing on the established current of 0.22 μA. The same samples during the onset of the potential measurement showed separate gas bubbles.

Table 3: Measurement of the continuous stationary potential changes of the Nacera Pearl (Germany).

Day	**Onset time**	$\gamma^{stationary}(V)$	**Day**	**Onset time**	$\gamma^{stationary}(V)$
I	9^{00}	- 0.430	**III**	8^{15}	- 0.445
	10^{00}	- 0.503		9^{00}	- 0.504
	11^{00}	- 0.501		10^{40}	- 0.521
	12^{00}	- 0.430		11^{10}	- 0.521
	13^{00}	- 0.528		12^{00}	- 0.518
	14^{00}	- 0.640		13^{00}	- 0.525
	15^{00}	- 0.830		14^{00}	- 0.525
II	8^{00}	- 0.532			
	9^{00}	- 0.503			
	10^{00}	- 0.540			
	11^{00}	- 0.524			
	12^{00}	- 0.523			
	13^{00}	- 0.537			
	14^{00}	- 0.533			

DISCUSSION OF THE RESULTS:
The evaluation showed that the electrical chemical potential of two identical samples, e.g. the System *NH* alloy, intermittently changed its figures and the value sign. So, electrical current may be induced between the same alloy samples which are positioned in the same medium, unaffected by the external factors (heat, mechanical influence, etc.). The first derivative of the potential parameters, **depending on time**, shows that the general potential background of the certain sample is distinctly affected by the potential value sign alteration, which **occurs with certain periodicity**. Such changes are more vividly manifested in the Nacera Pearl.

So, the up-to-date potential measurement methods applied for certain metal dental prostheses as well as measurement of current between them doesn't count for alterations on the metal prostheses in time potentials (consequently, changes of the currents), which, according to the studies, **intermittently alter their parameters**. If we base only on the results of the single (conducted during the short time period, required for measurement) evaluation of potentials and currents, then the decision on the use of a certain alloy for the dental metal prosthesis fabrication may be characterized with a relatively high margin of error.

CONCLUSIONS:

- The up-do-date methods of estimation of the current and potentials between the metal dental prostheses may just reflect on the electrical balance at the certain moment, so they are characterized with quite high margin of error, when it's necessary to decide on applying the certain alloy.
- The conducted studies provided for defining the characteristics and the charge sign of potentials during the certain time period, in the solution which reminds the oral cavity solution by its chemical composition.
- The obtained data show that even placing the metal dental prostheses, fabricated from the same alloys, doesn't provide for absolute electrical chemical indifference.
- We suppose it necessary to compose the tables of the metal dental prostheses alloys potential change periodicity according to the *pH*.

The author hopes that the results and conclusions of this study will be checked and supported by other independent researchers.

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