Assessment of Electrochemical Compatibility of Structural Materials of some Dental Products

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Abstract. Orthopedic treatment of tooth anomalies in children and adolescents is provided the longterm use of various metal constructions and devices in the oral cavity – braces, retreaders, locks or rings with struts, wire arches, and so on. They are usually made of corrosion-resistant metals and alloys, most often they are made of stainless chromium-nickel austenitic steels of X18H9T type (import analogue - steel 304), martensitic 08X17 (import analogue - steel 430), nickel-titanium or nickel-molybdenum alloys. The main disadvantage of all metal products is their manifestation of electrochemical properties and participation in electrochemical processes which can flow into the oral cavity and provoke galvanoses, especially for their joint use. In the "in vitro" conditions, according to a specially developed method, investigations of electrode potentials of directly 4 types of very small (2-3 mm)orthodontic products, in recommended for such products environment were carried out: 3 % solution of sodium chloride (pH=6,8), 2 % solution of citric acid (pH=0.5) and 2 % solution of baking soda (pH=8.65). It is found that the considered elements of orthodynamic systems have similar values of electrode potentials in neutral and weakly-alkaline environments and, accordingly, in the absence of other metal inclusions in the oral cavity, can be used jointly without the risk of galvanosis. The most heterogeneous construction is an individual ring with a strut, in which the difference in the values of the potentials between the individual parts in the acidic medium is more than 120 mV, which is a prerequisite for increasing the likelihood of galvanosis. For simultaneous use of other elements, in particular standard doping brackets, the value of EMF can increase up to 160 mV.

1 Introduction

Orthodontic treatment of dental anomalies in children and adolescents involves the long-term use of various metal structures and devices in the oral cavity. Usually they are made of corrosion-resistant metals and alloys, most often of stainless chromium-nickel austenitic steels of type X18H9T (import analogue – steel 304), martensitic steels of type 08X17 (import analogue – steel 430), nickel-titanium and nickel-molybdenum alloys.

The corrosion resistance of such materials in the environment of the oral cavity is very high and is confirmed by many years of medical practice of their use. A common drawback, like all other metals, including and noble, used in dentistry, is manifestation of their electrochemical properties and participation in electrochemical processes that can occur in the oral cavity and cause galvanosis.

Corrosion-electrochemical activity of a metal material is evaluated by the value of the electrochemical potential, which is established at the interface between the surface and the electrolyte (oral fluid). Its values depend on the chemical composition of the metal inclusion, the state of the surface (roughness, the presence of passivating oxide or salt films), internal stresses (compressive or tensile) due to mechanical and thermal factors in the manufacturing process of

dental products. On the other hand, the composition of the oral fluid and its acidity (pH) affect the values of electrode potentials. The values of the potentials and the nature of their change over time allows us to predict corrosion behavior in various conditions, as well as to evaluate the ability of dental alloys to restore a passive state after mechanical depassivation – brushing your teeth.

However, in the practice of dentistry they often operate not with the values of the individual electrochemical potentials inherent in one or another metal inclusion, but with their contact potential difference, because it is the difference in electrochemical potentials that is the root cause of the occurrence of galvanic couples in the oral cavity and, as a consequence, the occurrence of galvanosis. Numerous studies have been devoted to methods for diagnosing, preventing, and treating this phenomenon [1-8].

As a rule, the potential difference of heterogeneous metal inclusions in the oral cavity is determined by direct measurement using a high-resistance potentiometer and two probe electrodes by which touch metal surfaces [2, 3]. The relative disadvantage of this method, first of all, is the impossibility of determining the most active metal inclusion in order to further isolate or replace it. In addition, with such a measurement scheme, the material of the contact electrodes enters saliva and affects the integral value of the electrode potential of the metal inclusion and thereby contributes to the "smoothing" of the potential difference. The mechanical depassivation (scratching) of the surface that occurs at the moment of contact with the probe electrode leads to a surge, i.e. a sharp shift in the value of the electrode potential to the negative region.

These problems are partially solved in methods that provide for individual measurements of the electrode potentials of metal inclusions with respect to the silver/silver chloride reference electrode, which can be placed in the mouth or on the hand [4]. The latter option seems more preferable to us, because it is easier to implement without loss of measurement accuracy [5]. It is much more difficult to ensure a "dry" contact of the probe electrode with a metal inclusion, especially when it comes to the relatively small elements of the bracket systems. In this case, the "wet" contact with wire electrodes (d = 1 mm) can introduce significant distortions into the value of the determined electrochemical potential. The indicated difficulties arising in assessing the electrochemical characteristics of small-sized dental products are easier to overcome in laboratory conditions.

Based on the above, our aim is to study the in vivo electrode potentials of metal products for orthodontic treatment and to evaluate the likelihood of active galvanic processes occurring under their joint use.

2 Methods of Research

Electrode potential studies were performed on real orthodontic products: steel brackets with nickel-titanium clips, retainers (steel 304), individual wire rings with struts (steel X18H9T) and standard brackets (steel 304).

Measurements of potentials were carried out according to a specially developed method, the essence of which is shown in the Fig. 1.

Artificial suede 2 (or other densely porous material) was placed at the bottom of a flat glass vessel 1 and poured with a solution of electrolyte 3 not higher than the thickness of the fabric. A dental product 4 was installed on the surface of the wetted suede, to the outside of which a contact needle electrode 5. A silver/silver chloride reference electrode 6 was inserted through the Luggin capillary 7 into the annular recess of the vessel. In our case, the potentials were measured using the unit of the high-resistance voltmeter 8 of the PI-50-11 potentiostat. For such measurements, you can use any modifications of these devices with an internal resistance of 10^9-10^{10} Ohm.

The developed system allows thin-film wetting of dental products, which approaches the natural conditions of their use in the oral cavity. Another advantage of the scheme is the ease of implementation and the ability to evaluate the potentials of very small (2–3 mm) products, including various sections of their surface by turning over 90^{0} and 180^{0} .



Fig. 1. Schematic diagram of measuring the electrochemical potentials of the bracket system elements

Before measurements, the surface of samples was wiped with a brush with baking soda powder (imitation of brushing your teeth), followed by washing with tap water and drying with filter paper.

As model media used solutions traditionally recommended by medical methods for such studies: 3 % sodium chloride solution (pH=6.8), 2 % citric acid solution (pH=0.5) and 2 % baking soda solution (pH=8.65), which accordingly characterize a neutral, acidic and slightly alkaline environment.

The exposure of the experimental samples in model solutions lasted for 5 minutes. By this time, there was a significant decrease in the rate of change of potential, usually to the positive region, which made it possible, with a small error, to take the achieved potential values as steady-state.

3 Discussion of Results

Because measurements of potential were performed directly on orthodontic products, their values were not averaged but were taken as a range of values that were fixed for three samples of each type of product (see Table 1). This allowed us to estimate the potential difference that may occur between identical elements.

From the analysis of the results it follows that the most significant difference in the values of electrochemical potentials for each group of products is observed depending on the composition of the model medium, and more precisely on its pH-value of acidity. This situation fits into Evans' theory of electrochemical corrosion, according to which the stationary corrosion potential (which is actually the measured electrochemical potential of orthodontic products) in these cases depends on the pH of medium – the lower pH, the more positive the value of potential. That is why it is impossible to compare the corrosion resistance of metal inclusions by the values of potentials measured in media with different pH.

In the process of measuring potentials, it was found that in almost all media after preliminary grinding of the surface with gruel ("brushing your teeth"), "repassivation" occurs within 5 minutes, i. e. restoration of the oxide film, as evidenced by "refinement" – a monotonous shift of the potential values to the positive region. The exception in the form of oscillations of the potential

values – "decontamination" – "ennoblement", was observed in a 3 % sodium chloride solution, and was especially pronounced in design 3 (an individual ring with a strut).

			Range of values, E [V]			
№	Dental products	Material	3 % NaCl	2 % C ₆ H ₈ O ₇	2 % solution (NaHCO ₃)	Visual state of surface
1	Self-adjusting brackets with Ni-Ti clips:	Steel 304, Ni-Ti				
1.1	- face		-0.015 -0.034	-0.060 -0.067	-0.077 -0.107	Brilliant
1.2	– opposite side		-0,035 -0.095	-0.027 -0.033	-0.017 -0.068	Matt
2	Retainers	Steel 304	-0.032 -0.056	0.0370.064	-0.093 -0.105	Brilliant
3	Individual spacer ring:	Steel X18H9T				
3.1	- ring (crown)		-0.015 -0.043	-0.004 -0.037	-0.089 -0.104	Brilliant
3.2	– strut (spring)		-0.078 -0.095	-0.027 -0.088	-0.106 -0.151	Matt
4	Braces of standard alloying:	Steel 304				
4.1	-face		-0.042 -0.065	0.0570.067	-0.112 -0.120	Brilliant
4.2	– opposite side		-0.050 -0,060	0.0670.075	-0.108 -0.117	Brilliant

Table 1. The value of electrode potentials in model environments

Oscillation of potentials in chlorides is associated with the phenomena of short-term destruction of the oxide film (at this moment the potential goes to the side of negative values) and the subsequent reduction of the oxide layer. The aggressive action of Cl-ions that pierce a protective film on metals can ultimately cause pitting or pitting corrosion. Stainless steels are subject to this phenomenon, including those which investigated in this work. The probability and frequency of its occurrence depends on the state of the surface. In particular, a ring with a strut made of X18H9T steel has sharp cut edges, in addition, after stamping; it can be under the action of tensile stresses. All these factors negatively affect the quality of the protective passive film. To the same extent, the above applies to the spacer-spring made of wire material obtained by the broaching method. It should be noted that the electrochemical potential of the strut in all solutions is more negative, which means that it serves as an anode in a galvanic pair with respect to the potential of the ring. In addition, the strut of the ring is an anode in relation to other products (or parts of their surfaces). However, the potential difference that can occur in a neutral solution of sodium chloride or a slightly alkaline environment of baking soda does not exceed 80 mV and, according to the systematization of the manifestations of oral galvanosis developed in studies [6], such difference is permissible with the combined use of different alloys (or products), the likelihood of developing galvanosis is absent.

The most dangerous situation, in terms of the likelihood of an effective galvanic pair, appears only in an acidic environment – a solution of citric acid. The worst option is a combination of standard steel bracets and individual ring strut, resulting in an EMF (electromotive force) of the order of 160 mV is generated. Based on the conclusions of the author [6], with these values, the probability of galvanosis is highest. True, it should be noted that an acidic environment (pH=0.5)

still does not characterize the constant composition of the liquid in the oral cavity, but it should be taken into account as a short-term phenomenon.

Comparison of the values of the electrochemical potentials of orthodontic products in each of the solutions allows us to evaluate the identity of their surface state. Obviously, the most uniform in this sense are the brackets of standard alloy steel – the potential dispersion in them is minimal in all media, both between individual samples and different sides of the surface on each of them. Actually, such a result could be foreseen, since these products are obtained by precision casting with minimal internal stresses and a uniformly shiny surface.

4 Conclusion

The developed technique allows to increase the objectivity of the results of measuring electrochemical potentials directly on dental products, including small-sized ones, as well as to evaluate the electrochemical "heterogeneity" of individual metal structures.

It has been established that the considered (studied) elements of the bracket systems are characterized by close values of electrochemical potentials in neutral and slightly alkaline media, and therefore, in the absence of other metallic inclusions in the oral cavity, they can be used together without the risk of galvanosis.

The most heterogeneous design from the point of view of electrochemical activity is an individual ring with a strut in which the potential difference between the ring and the strut in an acidic medium is more than 120 mV, which serves as a prerequisite for increasing the likelihood of galvanosis. With the simultaneous use of other elements, in particular standard steel alloy bracets, the EMF values can increase up to 160 mV.

The proposed methodology for studying the electrochemical potentials of orthodontic products can be used at the preliminary stage of treatment - assessing the likelihood of developing galvanosis in specific patients if they have metallic inclusions in their mouths.

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