Computer Applications in Electrical Engineering
Vol. 13 *2015*

The effects of conductivity and pH of saliva on electrochemical potentials of metallic dental materials

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The paper presents results of the study on electrochemical potentials of metallic dental materials. Seven alloys, amalgam and chromium-nickel steel were examined as well as the effect of the solution conductivity ranging from 12.5 μS/cm to 2.01 mS/cm and solution pH within the range of 5.5 to 11.2 on electrochemical potentials of the materials. Amalgam presented with the lowest changes of the standard potential due to changing conductivity and pH of the solution within experiment conditions. Moreover, increase of pH value caused decrease of electrochemical potential of all examined materials, apart from amalgam. It was proved that electromotive force of galvanic cells formed by some of the examined materials and amalgam are often higher than 200 mV. Statistica software was used for mathematical analysis of the results.

KEYWORDS: metallic dental materials, electrochemical potential, galvanic cells, oral galvanism, conductivity, pH

1. Introduction

Metals and alloys have been widely used in medicine as biomaterials providing the proper mechanical strength, rigidity, elasticity and biocompatibility. They are essential for repairing or replacement of bones and joints in orthopedic surgery. In dentistry metals and alloys are used for restorations, fixed and removable dentures, orthodontic appliances, splints and implants [2, 7, 12, 14]. One of the fundamental conditions of these materials is their safety to human body. Thus, they should not show any toxicity to human tissues [4, 5, 13]. Generally metallic dental materials are biologically well-tolerated, unless they produce corrosion products that are harmful to the person. Corrosion is a process in which metal is destroyed by chemical or electrochemical reaction. It results in partial or complete dissolution, deterioration, and weakness of the material. Corrosion causes disintegration of metals and limits durability of the material [1, 3, 9, 11, 12].

Although the alloys used in dentistry should be resistant to corrosion, the conditions existing in oral cavity favor some unwanted electrochemical phenomena [1, 3, 9, 11]. The materials form a system of electrodes, in which one of the electrodes is the introduced metallic material and the other is the mucous membrane of oral cavity [11]. The considered system is, at least partially, immersed in saliva being an electrolyte that includes carbonates, phosphates, potassium thiocyanate and chlorides. Values of electrochemical potentials of metallic materials introduced to the patient's oral cavity are different from the potential of mucous membrane of the oral cavity. In consequence, a galvanic cell is created and, if more metallic materials are introduced to the oral cavity, many galvanic cells are formed [1, 3, 9, 11]. Electromotive force of these cells induces electric currents flowing in the oral cavity, the values and paths of which permanently vary, e.g. in result of the changes in oral cavity shape (due to chewing, speaking and facial expressions), consumption of meals and beverages that change the electrochemical environment. Values of the flowing currents depend on the values of the electromotive forces of the cells created and on the resistances of the flux paths. This may cause destruction of the metallic material and may give rise to various diseases and unpleasant feelings, the diagnostics and treatment of which is very difficult [6, 8, 15, 16].

The experience of acute "galvanic shock" is familiar to patients when new amalgam filling contacts old metallic restorations or aluminum utensils. Besides release of elements from the alloy due to galvanic corrosion may cause adverse biological effects such as cytotoxicity, allergy, or mutagenesis [16]. Local side effects such as gingivitis and periodontitis, where observed, when a large amount of metal ions was released [13]. Elements such as nickel, chromium, cobalt, and aluminum have been reported to cause an allergic reaction in sensitive patients [8, 13, 15].

As was already pointed out, the value of current intensity has a decisive influence on the results of the current flowing in human organism. It is mainly determined by electromotive force of the generated galvanic cell, equal to the difference of electrochemical potentials of the cell electrodes. Therefore, the metallic dental materials should be properly selected to equalize values of electrochemical potentials of these materials, under the conditions existing in the oral cavity. However, these conditions are variable, changing in time, determined by saliva composition, its conductivity and pH. Therefore, the choice of appropriate material or a set of dental materials is difficult. Taking into account the data determining the electrochemical potentials of the dental materials and the effect of oral cavity conditions on their variation, the risk of the patient's unpleasant feeling and disease symptoms may be reduced.

The paper is aimed at supplementing the data [11] on electrochemical potentials of selected dental materials and determining the effect of saliva conductivity and pH on the values of these potentials.

2. Description of the considered samples, the equipment used and the research methods

The electrochemical potentials of the following materials used for construction of cast partial dentures, crowns, bridges, restorations and orthodontic appliances have been investigated (in parentheses are reported the per cent weight contents of the elements of the materials):

1) Wironit Extrahard, (Co 63.0; Cr 30.0; Mo 5.0; Si; Mn; C < 2),
2) Wiron® 99 (Ni; Cr 22.5; Mo 9.5: Nb 1; Si 1; Fe 0.5; Ce 0.5; Cmax 0.02),
3) Gialloy PA (Co 61.6; Cr 30.1; Mo 5.5: C 0.6: Si 1.0, Fe 0.6: Mn 0.6),
4) Remanium GM 380+ (Co 64.6; Cr 29; Mo 4.5; less than<1% Si; Mn; N; C),
5) Gialloy CB/H (Co 60.0; Cr 24.7, W 9.0; Nb 2.0; V 2.0; Mo 1.1, Si 1.0; Fe 0.2),
6) Remanium 2000+ (Co 58.0; Cr 22.6; Mo 9.1; W 5.1; Si 1.3),
7) Gialloy CB/N (Ni 61.5; Cr 25.9; Mo 11.1, Si 1.5),
8) Ruby Cap amalgam (Ag 45; Sn 30.5; Cu 24; Zn 0.5),
9) Co-axial Dentaflex wire, chromium-nickel steel.

The samples of the examined materials (the items (1) to (8)) had the cylindrical shape of 8 mm diameter and 15 mm length. In one of the bases of these cylindrical samples, made of the materials numbers from (1) to (7) a hole was drilled, that was threaded and, afterwards a cooper wire of 1 mm^2 cross-section and about 100 mm length was fixed with the help of an M3 screw. The place of the wire and sample joint as well the wire surface was electrically insulated from the solutions, in which the samples were investigated, by covering them with an Epidian 5 epoxy resin. At the same time, a non insulated wire end of several millimeters was left, in order to allow electric connection of the sample with the voltmeter terminal. Similar approach was used in case of the amalgam specimen (8), however, the amalgam was shaped in a gypsum mould, while the copper wire connection caused setting of the amalgam. On the other hand, the specimen (9) made of Dentaflex wire was prepared by tight winding, coil by coil, of the wire on a polyethylene rod of 7 mm diameter.

Before measuring of electrochemical potential the specimens were polished to perfect mirror finish, washed in the final phase in ethyl alcohol and water and, afterwards, passivated in aerated aqueous solution of NaCl of the conductivity 1.5 mS/cm, pH = 6.09, and temperature 37°C.

Electrochemical potentials were measured with respect to the reference electrode, namely a saturated calomel electrode manufactured by the Production Plant of Physicochemical Equipment Elements HYDROMET in Gliwice. The potential of the electrode measured with reference to the potential of normal hydrogen electrode (NHE) amounts to +244.4 mV in temperature 25°C and +236.7 mV in temperature 37°C.

The potential difference between the potential of the analyzed sample and the reference electrode was measured with a BM805 digital multimeter from Brymen Company. Internal resistance of the voltmeter system of this instrument amounts to 1000 MΩ, with voltage measurement accuracy ±0.3% of the measured value.

The measured values of potential difference between the analyzed samples and the reference electrode were then converted with respect to the potential of the normal hydrogen electrode.

The pH indexes of the solutions were measured with the digital pH-meter of N517 type, from MERA-ELWRO, while conductivity of the solutions was measured with the CC-411 conductometer from ELMETRON.

In order to investigate the effect of various conditions existing in oral cavity on the values of electrochemical potentials of the considered materials the potentials were measured in artificial saliva, the properties of which (i.e. conductivity and pH) were subjected to changes. The artificial saliva was imitated by distilled water with NaCl and phosphates addition. NaCl increased the conductivity, while phosphates caused pH growth. The measurements were carried out under the temperature of the solutions equal to 37°C.

Mathematical analysis of the investigation results was carried out with the help of the Statistica computer program [10]. The χ^2 test allowed to find that at the threshold level of the 0.05 test there is no reason for rejecting the hypothesis of compliance of the reiterated measurements of electrode potentials of the considered materials with normal distribution. Therefore, the arithmetic average of the measured values is considered as a representative value of the electrochemical potential, with the standard deviation being assumed to be the measure of the dispersion.

The following procedure was adopted during the measurements: the tested specimen and the reference electrode were located in a solution of definite parameters, prepared in advance (conductivity, pH, and temperature 37°C), imitating the saliva. After one hour the specimen potential to the reference electrode was measured seven times, with one minute intervals between each measurement.

In order to avoid anomalies of the measurement results the highest and the lowest values were rejected from each of the seven measurements series. Three independent measurement series were repeated under equal conditions. Hence, the potential values specified in the paper are arithmetic average values taken from fifteen measurements obtained in three independent measurement series.

3. The measurement results and discussion

The results of the effect of the solution conductivity on the electrochemical potential value of the tested materials are summarized in Table 1. The solutions, in which the material potentials have been measured had pH = 6.8 (average pH of human saliva).

Table 1. Arithmetic averages and standard deviations of the electrochemical potential values of the tested materials (E_{NHE}±s), converted with reference to the potential of normal hydrogen electrode, measured in the solutions imitating the human saliva of pH = 6.8, and conductivity: 12.5 µS/cm, 315 µS/cm, 640 µS/cm, 1.09 mS/cm, 1.32 mS/cm and 2.01 mS/cm

Material type	Arithmetic averages and standard deviation of the electrochemical potential values of the tested materials, converted with reference to the potential of normal hydrogen electrode (E_{NHE}±s) in mV, measured in the solutions imitating the human saliva of pH = 6.8 and conductivity:					
	12.5 µS/cm	315 µS/cm	640 µS/cm	1.09 mS/cm	1.32 mS/cm	2.01 mS/cm
1	150.9 ± 13.4	149.7 ± 5.8	137.9 ± 4.6	130.9 ± 7.5	141.2 ± 13.4	132.5 ± 4.1
2	136.6 ± 4.8	136.2 ± 3.6	124.7 ± 3.0	80.2 ± 5.8	65.8 ± 4.7	57.5 ± 5.1
3	164.1 ± 9.1	140.5 ± 3.7	153.2 ± 3.8	114.2 ± 4.4	79.7 ± 7.4	53.6 ± 5.8
4	137.9 ± 4.8	111.3 ± 3.0	109.7 ± 9.1	122.5 ±10.2	77.8 ± 4.4	49.4 ± 5.1
5	194.7 ± 6.2	154.7 ± 9.1	117.9 ± 5.0	104.7 ± 6.0	77.8 ± 4.8	77.0 ±9.1
6	99.2 ± 5.6	62.7 ± 9.0	48.4 ± 5.5	51.1 ± 6.4	22.4 ± 4.2	34.6 ± 4.2
7	158.5 ± 4.7	160.4 ± 6.4	155.0 ± 6.8	129.2 ± 6.8	50.5 ± 6.8	72.1 ± 4.1
8	− 98.3 ± 4.2	−115.6 ± 3.6	−121.2 ± 2.5	−123.6 ± 4.2	−121.8 ± 2.1	−124.3 ± 1.8
9	199.9 ± 4.8	174.6 ± 5.0	171.2 ± 4.3	155.0 ± 3.4	159.7 ± 4.6	159.6 ± 3.8

The measurement results specified in Table 1 are presented in Fig. 1 in the form of dependence of the electrochemical potential value of the material on the solution conductivity.

The Table 1 and Figure 1 show that the lowest change in the electrochemical potential caused by the solution conductivity varying in the range of the experiment was observed for the alloy (1). In case of the wire of chromium-nickel steel (9) and amalgam (8) the changes were slightly higher. On the other hand, the increase in solution conductivity was conducive to significant changes

– reduction of electrochemical potentials of the alloys from (2) to (7). Values of these potentials dropped down to about 0.3 – 0.5 of the values measured for the smallest solution conductivity.

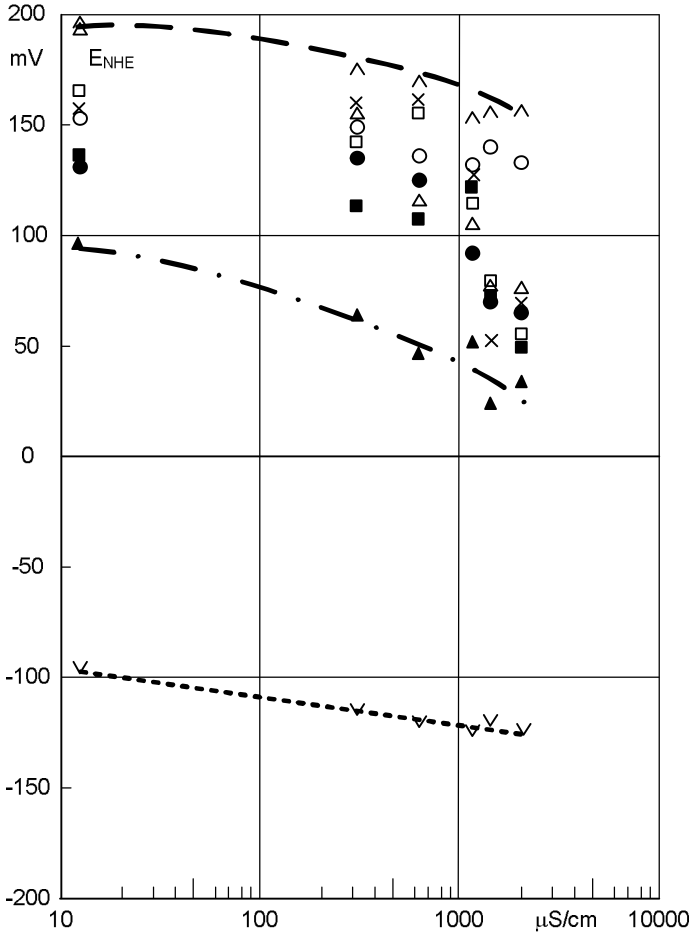

Fig. 1. Dependence of the electrochemical potential value of the tested materials, converted with reference to normal hydrogen electrode, on conductivity of the solution of pH = 6.8; the graphical symbols of the measurement points of the material: 1 – ○, 2 – ●, 3 – □, 4 – ■, 5 – Δ, 6 – ▲, 7 – x , 8 – V, 9 – Λ

Moreover, the Table 1 and Fig. 1 demonstrate that all the materials, except for the amalgam (8), have positive potential values (with respect to the potential of normal hydrogen electrode). Therefore, the electromotive forces of the electrochemical cells arising with amalgam by the other materials are the highest. Values of these forces, equal to the potential difference of the materials giving rise to the cell, often significantly exceed the level of 200 mV. Such an electrochemical cell is created in oral cavity if these two materials are used simultaneously.

Investigation of the effect of solution pH on the value of electrochemical potential of materials are presented in Table 2. The tests were carried out for constant conductivity of the solution, equal to 1.5 mS/cm.

Table 2. Arithmetic averages and standard deviation of the electrochemical potential values of the tested materials (E_{NHE}±s), converted with reference to the potential of normal hydrogen electrode, measured in the solutions imitating the human saliva of the conductivity equal to 1.5 mS/cm, with pH: 5.5; 6.0; 7.3; 8.3 and 11.2

Material type	Arithmetic averages and standard deviation of the electrochemical potential values of the tested materials, converted with reference to the potential of normal hydrogen electrode (E_{NHE}±s) in mV, measured in the solutions of the conductivity 1.5 mS/cm, with pH:				
	5.6	6.0	7.3	8.3	11.2
1	152.9 ± 3.8	146.6 ± 6.2	109.0 ± 7.9	107.0 ± 1.5	− 8.9 ± 8.0
2	47.7 ± 8.9	37.3 ± 7.8	48.1 ± 5.3	64.2 ± 3.8	− 61.8 ± 3.5
3	101.3 ± 9.1	96.6 ± 3.7	88.0 ± 3.5	82.79 ± 2.4	− 84.1 ± 3.2
4	85.1 ± 4.0	81.7 ± 3.9	73.5 ± 6.2	26.9 ± 8.3	− 31.5 ± 4.1
5	118.7 ± 5.1	109.0 ± 7.6	31.6 ± 10.9	21.1 ± 4.3	− 26.2 ± 5.9
6	78.8 ± 8.8	15.2 ± 3.2	−2.6 ± 6.8	− 4.1 ± 4.4	− 36.5 ± 4.7
7	88.7 ± 2.9	63.6 ± 3.8	47.7 ± 1.9	− 8.1 ± 2.3	− 90.3 ± 1.8
8	− 134.5 ± 2.5	− 135.3 ± 2.6	− 118.0 ± 3.3	− 118.3 ± 2.1	− 134.3 ± 3.9
9	135.7 ± 4.7	151.1 ± 3.2	144.9 ± 3.8	132.9 ± 3.1	68.1 ± 3.2

The measurement results specified in Table 2 are presented in Fig. 2 in the form of dependence of the electrochemical potential value of the material on the solution pH, distinguished by the conductivity of 1.5 mS/cm.

The Table 2 and Figure 2 show that the increase in pH of the solution, within the experiment range, caused reduction of electrochemical potential of the materials, except for amalgam (8) distinguished by the lowest potential change, equal about to 10%.

Since the pH value of saliva or beverage that might occur in oral cavity usually falls within the range from 5.6 to 8.3, the highest potential variations caused by pH change in this range arise in case of the alloys (5) and (7) and amount about to 100 mV, while in case of the alloy (6) about 80 mV.

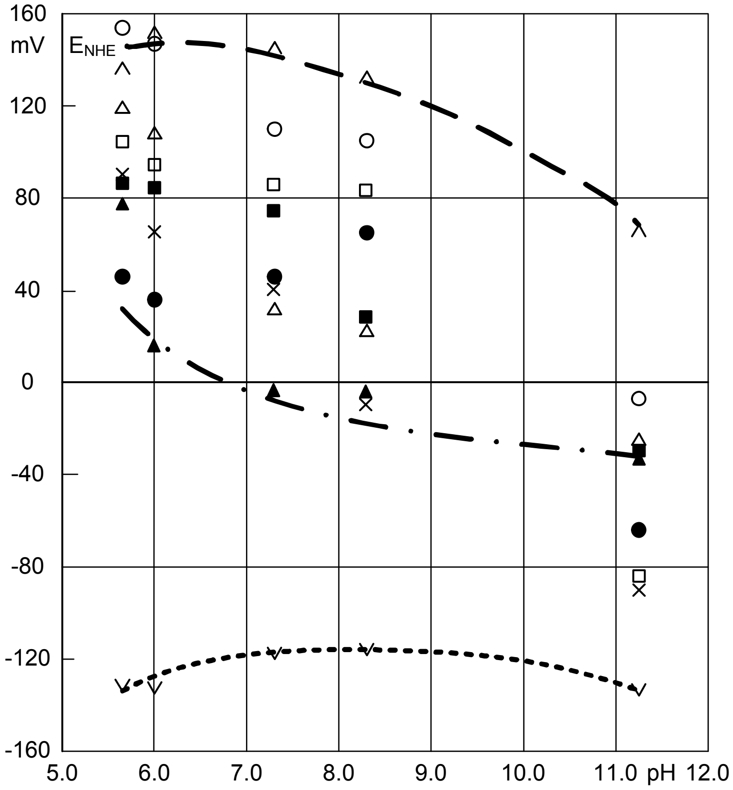

Fig. 2. Dependence of the electrochemical potential value of the tested materials, converted with reference to normal hydrogen electrode, on pH value of the solution having the conductivity of 1.5 mS/cm ; the graphical symbols of the measurement points of the material: 1 – ○, 2 – ●, 3 – □, 4 – ■, 5 – Δ, 6 – ▲, 7 – x , 8 – ∨, 9 – ∧

The Tables 1 and 2 show that the electrochemical cell of the highest electromotive force developed based on the two considered materials (except for amalgam (8) giving the cells of the highest electromotive force) is created of the materials (6) and (9).

4. Conclusions

The present paper provides the following conclusions important for a dentist, dental technician, and patient's health:

1. Among the considered materials the lowest variation of electrochemical potential, caused by the changes of conductivity and pH value within the range used in the experiment, occurs in case of amalgam (8). Moreover, amalgam (8), unlike the other considered materials, is characterized by

negative potential value to the normal hydrogen electrode within the whole experiment range.

2. Values of electromotive force of the electrochemical cells created by some of the considered materials with amalgam (8) often exceed 200 mV.
3. The lowest potential change (about 10%) caused by variation of the solution conductivity, within the range from 12.5 μS/cm to 2.01 mS/cm, is observed for the alloy (1 – Wironit Extrahard). Slightly higher change occurs in case of the wire made of chromium-nickel steel (9) and amalgam (8). On the other hand, in case of the other alloys the increase in the solution conductivity caused significant reduction of their electrochemical potential (down to about 0.3 – 0.5 of the value measured for the lowest solution conductivity).
4. Increase in the solution pH within the experiment range is conductive to reduction of electrochemical potential of all the tested materials, except for amalgam (8) that showed only small change of the potential (about 10%) caused by pH variation.
5. Large differences in electrochemical potential values of metallic dental materials indicate the need of proper choice of the materials introduced to patient's oral cavity.

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(Received: 7. 10. 2015, revised: 21. 12. 2015)