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Ł. REIMANN*,#

ELECTROCHEMICAL CHARACTERISTICS OF A COBALT ALLOY WITH A PROTECTIVE PASSIVE LAYER

The aim of this study was to assess the quality of the passive layer formed on the surface of a CoCr alloy used on dentures to see the effect on resistance to pitting corrosion and electrochemical parameters. Studies were performed using on potentiodynamic tests and electrochemical impedance spectroscopy. The passive layer was formed spontaneously and by electrochemical method on samples after casting and after simulation porcelain firing on metal. Samples of the passivation electrochemical characterized by the improvement in corrosion resistance. Prolonging the passivation time from one to 24 hours and increasing the potential value from 0 to 200 mV improved the quality of the passive layer and all characteristics of electrochemical parameters.

1. Introduction

Materials used for dental prostheses must comply with a number of requirements related to the place of their implantation in the human mouth. These include biocompatibility in the environment of tissues and liquids present in the stomatognathic system [1], biotolerance [2], a lack of adverse reactions in tissues such as an allergy to the alloy's components, no inflammation, a non-toxic condition, especially for the patient but also persons that would have to work with the material, and not being mutagenic or carcinogenic [3-6]. Furthermore, the material intended to be used on restorations should be characterized by the durability of aesthetic qualities and desirable organoleptic properties (taste and fragrance). It must also not create a product related nuisance due to its presence in the oral cavity [4].

Cobalt based alloys are used in dental prosthetics due to very good mechanical properties and good prices, compared to precious metal alloys or high nobel alloys. They find frequent use in the manufacture of dentures, though they are characterized by inferior corrosion resistance, compared to a precious metal alloy [7].

In the literature, you can find many papers on methods for improving the corrosion resistance of CoCr alloys. In work [8] a cobalt alloy was subjected to nitriding and oxidation operations in different conditions, which contributed to increasing the corrosion potential but advantageously influenced the corrosion's current value. Also, there was not the creation of a corrosion protective layer. Another work [9on the application of treatment by nitriding as a method to improve the corrosion resistance of alloys used as tools in dentistry obtained positive results and created a protective TiN layer on the surface. To improve the corrosion resistance of CoCr alloys, other authors [10, 11] doped them with precious metals: gold, platinum and palladium. Based on their research results, it can be stated that adding gold or platinum to the CoCr alloy has a positive effect on corrosion resistance while the addition of palladium causes a deterioration of corrosion resistance although, in the work [11] the authors did not recognize the 10% reduction of chromium in the concentration that has a critical influence on corrosion resistance as mentioned in [12]. In the studies [13] it was found that a heat treatment processes also effects corrosion resistance, and it was noted that CoCr alloy annealing homogenizes the structure and reduces the hardness, resulting in a reduction of corrosion resistance. An important aspect is also good technology practice and adjusting an alloy's melting temperature because overheating of the material may also reduce its resistance to corrosion [14].

Cobalt chrome alloys used in dentures belong to a group of materials, which might spontaneously overlap with a passive layer. Although there is such a passive layer an alloy still might release a slow diffusion of ions into tissues [15]. Therefore, it is very to properly constitute the passive layer on an alloy's surface.

The aim of this study was to assess the quality of the passive layer formed on the surface of a CoCr alloy used on dentures with regard electrochemical conditions and the time of creation and to see the formation effect on resistance to pitting corrosion based on potentiodynamic tests and electrochemical impedance spectroscopy.

2. Material and test methodology

The experimental material was a CoCrMo alloy used to produce the dental prostheses with the chemical composition as shown in Table 1. Samples were prepared in a centrifugal casting device in the form of flat tablets with dimensions of 10x10 mm and a thickness of 1 mm. Then, part of the samples were subjected to a heat treatment simulating the dental

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* SILESIAN UNIVERSITY OF TECHNOLOGY, INSTITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS, FACULTY OF MECHANICAL ENGINEERING, , 18A KONARSKIEGO STR., 44-100 GLIWICE, POLAND

Corresponding author: lukasz.reimann@polsl.pl

porcelain firing on a metal substrate (PFM) in three stages. Conditions for the heat treatment are shown in Table 2. All samples were ground with SiC paper and polished, and, before each test, they were degreased and washed in acetone. Samples after casting without heat treatment (PFM) were marked "C" and after firing as "HT".

TABLE 1

Chemical composition of alloy used in studies

Element	Co	Cr	Mo	W	Si	Mn, N
Concentration	61	25	7	5	1,5	< 1

TABLE 2

Conditions of the porcelain firing on metal (PFM)

Stage	Start temperature	Heat speed	Temperature	Annealing time
	°C	°C/min	°C	min
I	500	80	950	1
II		55	930	
III		55	920	

TABLE 3

Composition of an artificial saliva

Element	Content
NaCl	0,4 g/l
KCl	0,4 g/l
$NaH_2PO_4 \cdot 2H_2O$	0,69 g/l
$CaCl_2 \cdot 2H_2O$	0,79 g/l
$Na_2S \cdot 9H_2O$	0,005 g/l
Urea	1,0 g/l
Distilled water	1 l

Electrochemical studies of samples were made on the potentiostat using two methods: potentiodynamic and electrochemical impedance spectroscopy (EIS).

The studies involved three electrodes: a working electrode, a reference Ag / AgCl electrode and a platinum electrode in the form of a wire. The environment centre for the tests was an artificial saliva solution prepared on the basis of Fusayamya at room temperature. The potentiodynamic tests were divided into two stages. In the first stage, an open circuit potential (E_{ocp}) under electroless conditions was determined for 1 h; in the second stage, curves of anodic polarization with a change in potential by 1 mV/s from the initial potential (E_{ocp} - 100 mV) were recorded until reaching the potential or current. Then, the polarity was reversed and the curve to the initial value of the potential was recorded. In order to determine the characteristic parameters relating to electrochemical corrosion resistance, the Tafel extrapolation method was used.

The second test method, EIS, was chosen because of the opportunity to study the characteristics and resistance of the passive layer. The tests were based on a study of responses to the measuring system within the free potential and given frequency, in the form of a current pulse with an amplitude decreased by the resistance of the sample and phase-shifted relative to the excitation pulse. The frequency range used in the test changed from 100 kHz to 10 mHz. The results of impedance were shown as Nyquist graphs (curve of the real and imaginary part of the impedance f(Re(Z)) = -Im(Z)) and as Bode graphs (two curves showed the influence of the frequency from impedance f(log(f)) = log(Z) and from phase f(log(f)) = log(φ)). In order to match the electrical equivalent circuit for the obtained impedance spectra, the experimental curves were compared with the curves generated by a computer model. The electrical equivalent circuit with the constant phase element (CPE) was chosen. For resistive elements, one had the resistance of the material surface layer, and the second represented the electrical resistance of the electrolyte. The smallest possible number of elements was used to build the circuit.

Then, the samples were passivated for one and 24 hours in air and electrochemically in the same water solution, which was used for the corrosion tests at potentials 0, 100 and 200 mV. Electrochemical potentiodynamic and EIS studies were performed for the obtained samples. After corrosion tests samples were observed microscopically in order to evaluate the surface destruction using a light microscope in the magnification range 200 to 500x.

3. Results

First, potentiodynamic curves for the material after casting without firing and after the heat treatment were

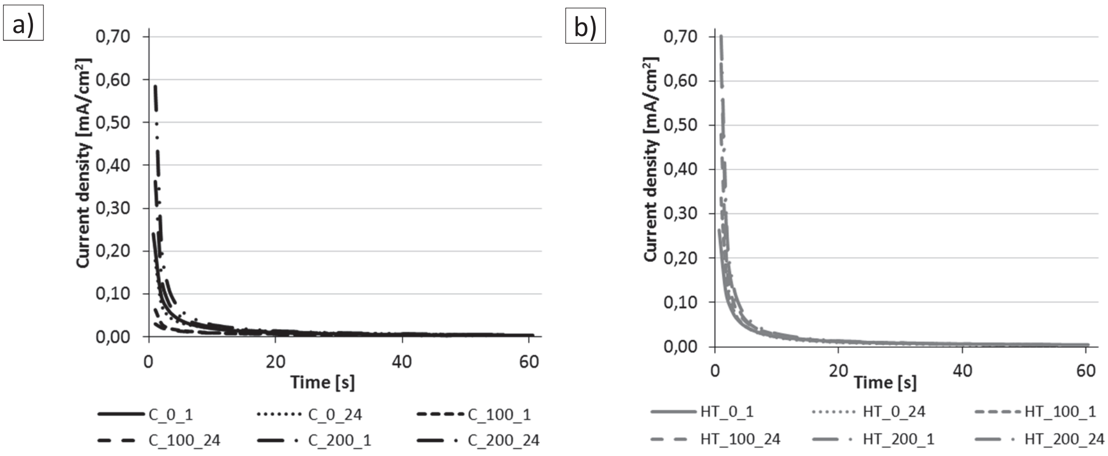
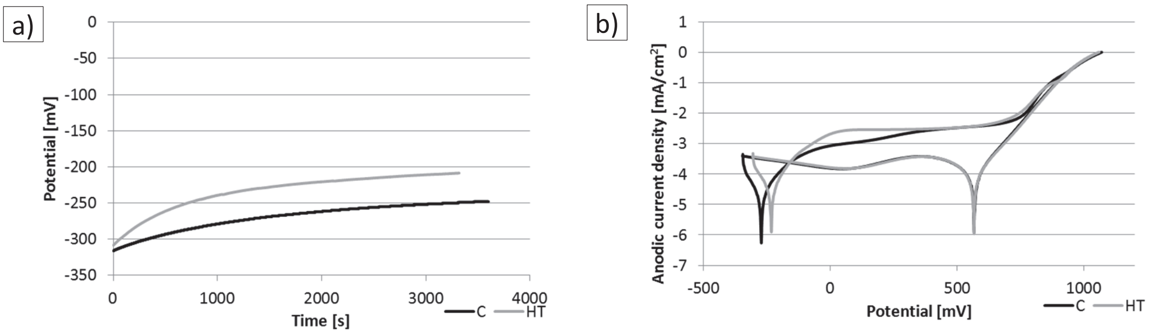


Fig. 1. Potentiostatic curves recorded for passivation tested materials: a) samples after casting, b) samples after firing



Sample	E_{ocp} [mV]	R_p [kOhm*cm²]	E_{cor} [mV]	i_{cor} [µA/cm²]	Eb [mV]	Ere [mV]	r [g/m2*year]
C	-248	495	-264	0,55	916	935	1,81
HT	-209	262	-227	0,60	917	903	1,95

Fig. 2. The corrosion testing results for material after casting and after heat treatment: a) open circuit potential, b) anodic polarization curves

recorded. This simulated the firing of porcelain in metal-ceramic dental prostheses. The characteristic values of corrosion for the two materials were very similar to each other. The free potential (Eocp), corrosion potential (Ecor), breakdown (Eb) of the passive layer and repassivation potential (Ere) varied only from 1 to 40 mV. Next, samples were examined by EIS, during which the impedance spectrums presented as a replacement circuit with the associated electrical components Rs, R1 and CPE were determined. The best matched electrical circuit for the obtained results is shown in Fig. 3.

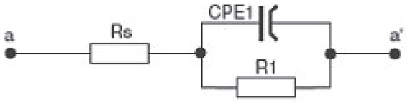
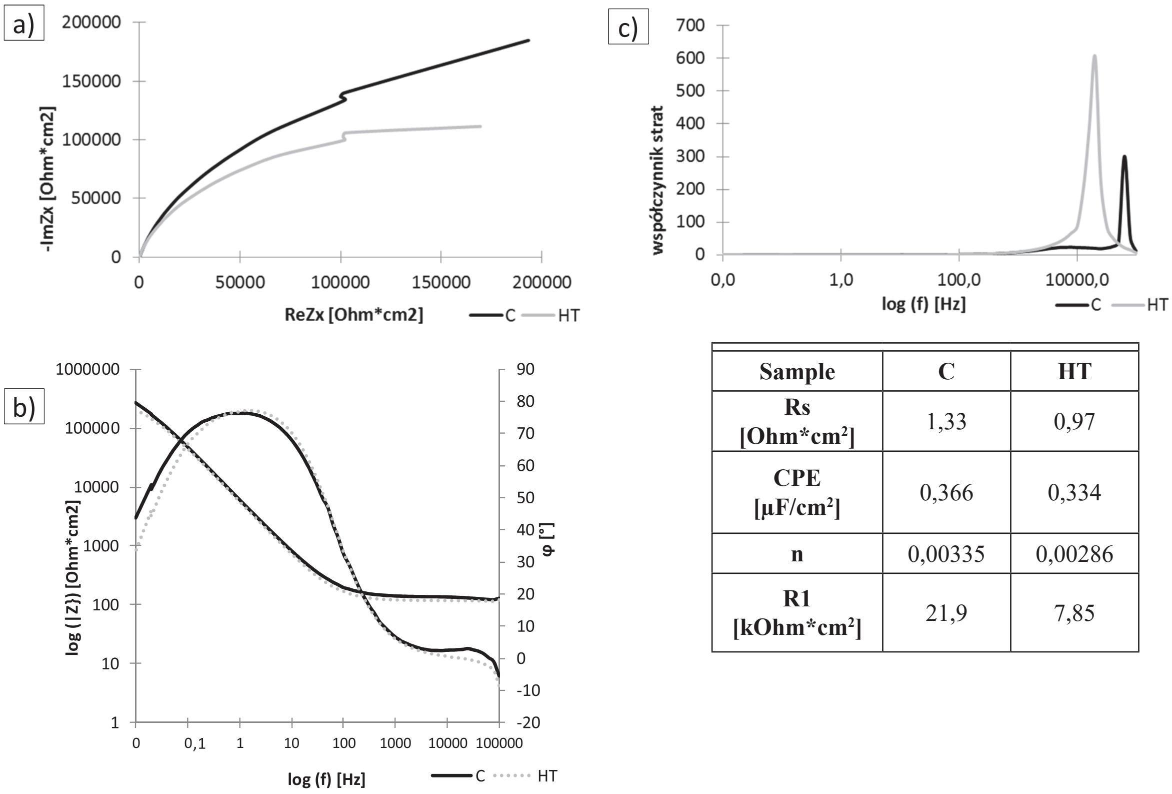


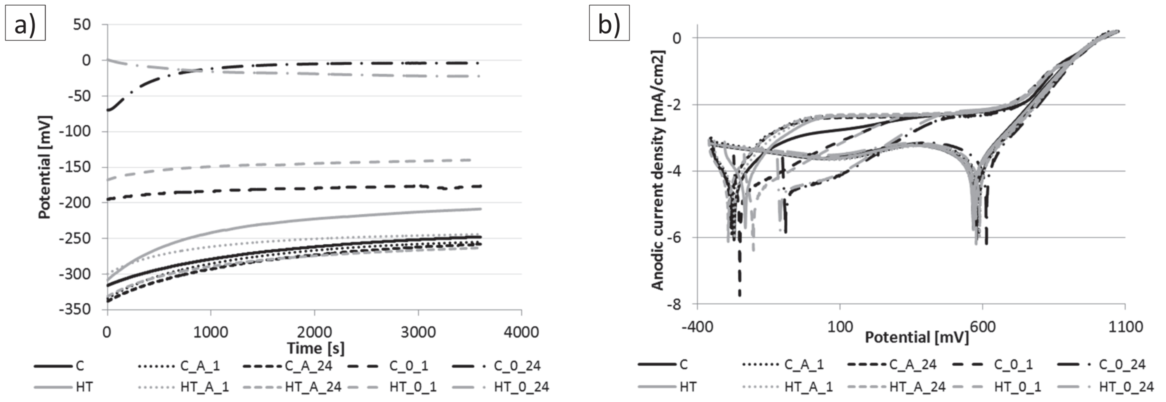
Fig. 3. Equivalent circuit representing the impedance spectrums tested materials

Based on the recorded results presented in the form of a Nyquist plots (Fig. 4a), Bode plots (Fig. 4b) and a dissipation factor (Fig. 4c), it was found that the material after heat



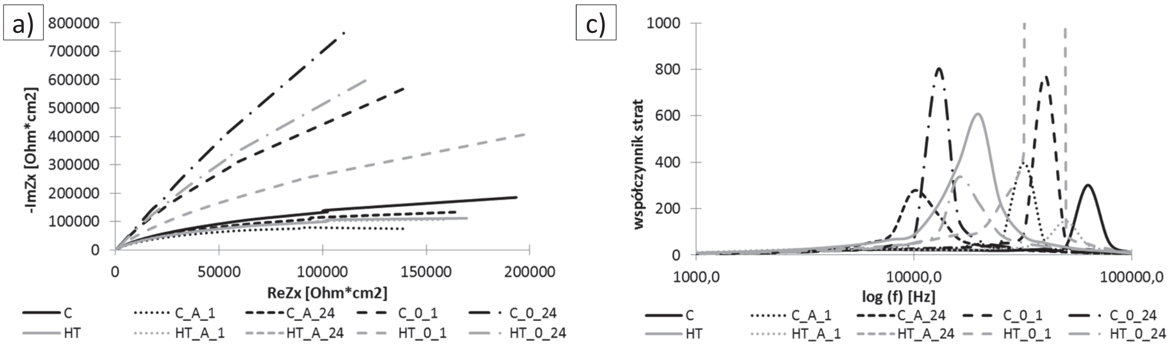
Sample	C	HT
Rs **[Ohm*cm²]**	1,33	0,97
CPE **[µF/cm²]**	0,366	0,334
n	0,00335	0,00286
R1 **[kOhm*cm²]**	21,9	7,85

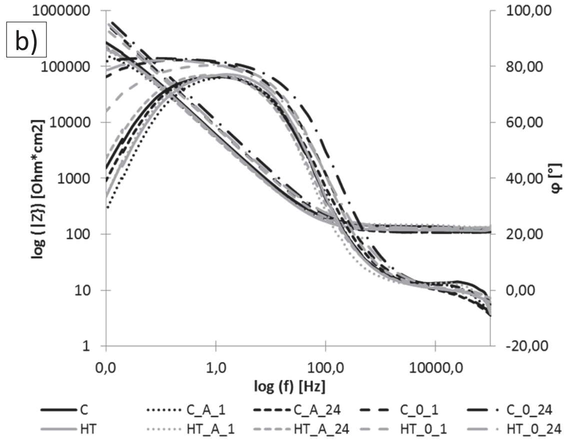
Fig. 4. The impedance spectrum for material after casting (E_{ocp} = -274 mV) and after heat treatment (E_{ocp} = -260 mV): a) Nyquist representation, b) Bode representation, c) dissipation factor



Sample	E_{ocp} [mV]	R_p [kOhm*cm^2]	E_{cor} [mV]	i_{cor} [µA/cm^2]	E_b [mV]	E_{re} [mV]	r [g/m^2*year]
C	-248	495	-264	0,55	916	935	1,81
C_A_1	-255	220	-275	0,85	921	916	2,77
C_A_24	-258	233	-278	0,92	920	919	3,01
C_0_1	-176	354	-261	0,01	916	904	0,05
C_0_24	-4	210	-96	0,01	927	939	0,04
HT	-209	262	-227	0,60	917	903	1,95
HT_A_1	-244	233	-262	0,92	920	913	3,02
HT_A_24	-263	207	-281	1,19	917	919	3,88
HT_0_1	-140	525	-218	0,01	920	914	0,05
HT_0_24	-22	217	-114	0,01	921	910	0,04

Fig. 5. The corrosion testing results for material after passivation on air and after electrochemical passivation at 0 V: a) open circuit potential, b) anodic polarization curves





Sample	Rs [Ohm*cm^2]	CPE [µF/cm^2]	n	R1 [kOhm*cm^2]
C	1,33	0,366	0,00335	21,9
C_A_1	1,09	0,424	0,00333	6,34
C_A_24	1,06	0,394	0,00321	13,7
C_0_1	1,26	0,232	0,00302	8470
C_0_24	0,93	0,145	0,00232	2,1E+21
HT	0,97	0,334	0,00286	7,85
HT_A_1	1,15	0,349	0,00296	7,82
HT_A_24	0,95	0,315	0,00250	17,6
HT_0_1	0,68	0,137	0,00165	93,7
HT_0_24	1,58	0,256	0,00350	1,5E+19

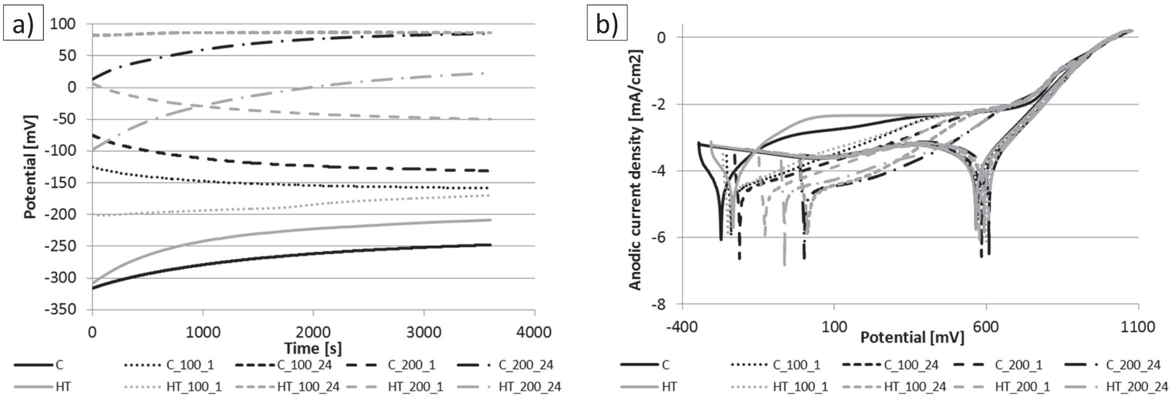
Fig. 6. The impedance spectrum for material after passivation on air and after electrochemical passivation at 0 V: a) Nyquist representation, b) Bode representation, c) dissipation factor

treatment was characterized by worse anticorrosion properties than the sample after casting as evidenced by the less exponential shape of the Nyquist impedance spectrums graph and the lower resistance value (R1). For both samples based on the Bode plots and values of the coefficient n for element CPE near 0, their resistive nature was concluded.

Then, a potentiodynamic test for samples passivated for 1 or 24 hours in the air and electrochemically at potential 0 V was performed. Whether leaving the sample in air for 1 or 24 hours, in both cases after casting and after PFM, there was no effect on the improvement of corrosion resistance. There was even an increase in weight loss of about 50–60% compared to non-passivated samples. For materials passivated by the electrochemical method, in each case after one and 24 hours, there was a clear improvement in corrosion resistance. When analysing particular parameters, there was increased open circuit potential and corrosion potential, while the corrosion current's value decreased by an order of magnitude, and the corrosion rate decreased from about 2 to 0.05 g/m^2*year. This same effect of passivation was found for the material after casting and after PFM(Fig. 5). Elongating the passivation time from one to 24 hours at potential 0 V caused an increase in the corrosion potential of the two materials by an average of 100 mV.

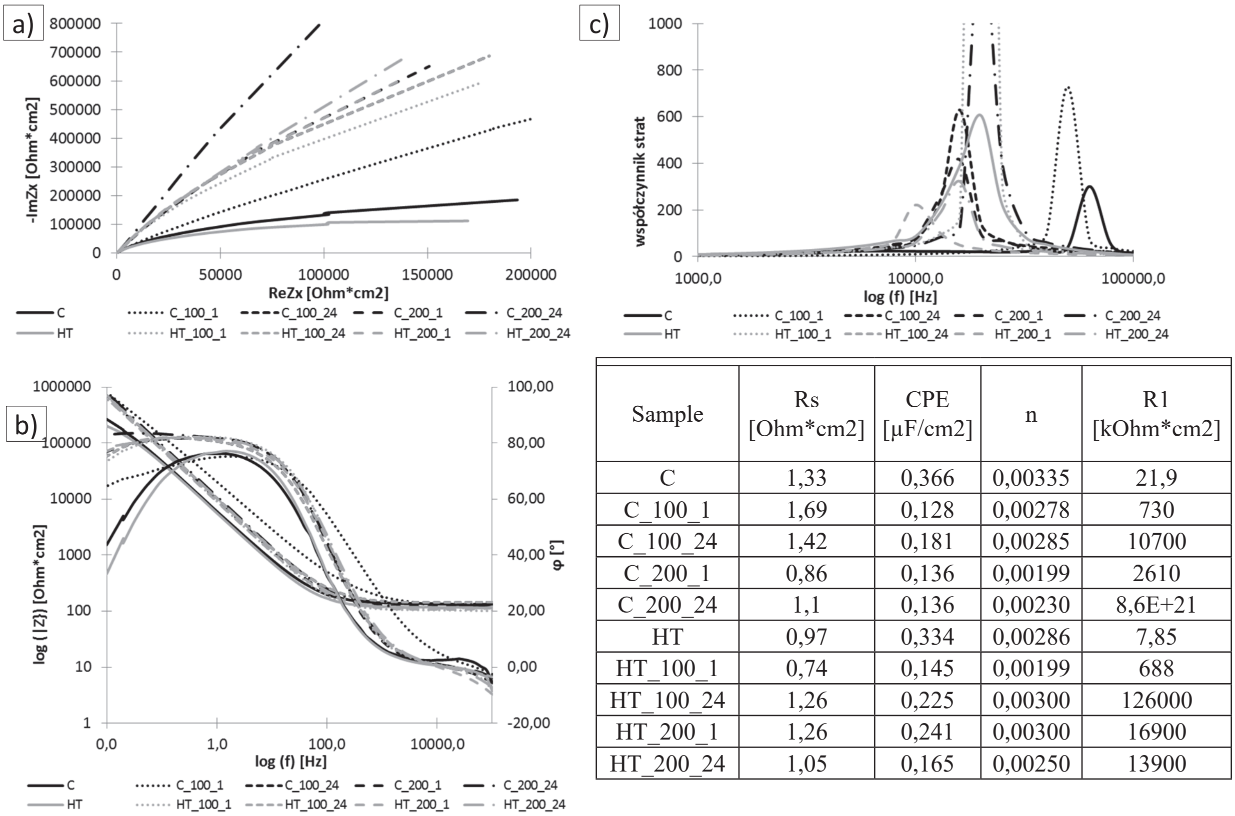
The effect of surface passivation of the alloy on its electrical characteristic was also presented by impedance spectra at the Nyquist and Bode plots (Fig. 6). The obtained results showed that the passivation in the air did not produce beneficial changes in resistance to corrosion damage of the surface, and, from analysing the Nyquist spectrum (Fig. 6a), it can be concluded that the corrosion rate of these samples increased. Spectrum analysis shown on the Bode diagram (Fig. 6b) demonstrates that the materials with a passive surface exhibit resistance as evidenced by the shape of the curve of the impedance in the low frequency range and the CPE coefficient n close to 0.

In the last series of samples, materials passivated with higher potential values 100 and 200 mV were compared as before for 1 and 24 hours (Fig. 7). Analysing obtained results, it was found that increasing the passivation time from one to 24 hours resulted in the creation of a better quality surface film, as evidenced by an increased value of polarization resistance from one even to three times for the sample after passivation at 100 mV. Comparing the open circuit potential values (Fig. 7a), it was found that an increase in the potential from 100 to 200 mV resulted in an increase in the Eocp value of about 17% for the sample after casting and about 70% for the PFM sample. A similar pattern of increasing the value of the above-identified potential values was found in the comparison of samples passivated by increasing the potential from 100 to 200 mV and by prolonging the passivation time from one to 24 hours. Analysis of the impedance spectra for materials with a deposited passive layer at a potential of 100 and 200 mV for one and 24 hours revealed that they were characterised by typical resistance as evidenced by the element CPE coefficient n CPE close to 0 and the curve shapes shown on the Bode diagram (Fig. 8b). On the bases of Nyquist impedance spectrum (Fig. 8a) curves and their angle of slope to the ordinate axis, it can be concluded that the use of surface passivation, both at potentials of 100 mV and 200 mV, significantly influenced the reduction of the wear rate of the corrosion of tested alloy. Prolonging the passivation time from one to 24 hours also affected the quality of the obtained surface



Sample	E_{ocp} [mV]	R_p [kOhm*cm^2]	E_{cor} [mV]	i_{cor} [µA/cm^2]	E_b [mV]	E_{re} [mV]	r [g/m^2*year]
C	-248	495	-264	0,55	916	935	1,81
C_100_1	-158	275	-246	0,01	918	908	0,05
C_100_24	87	844	2	0,005	914	965	0,02
C_200_1	-131	282	-218	0,01	925	919	0,05
C_200_24	85	372	-4	0,008	922	920	0,03
HT	-209	262	-227	0,60	917	903	1,95
HT_100_1	-170	258	-257	0,02	922	927	0,05
HT_100_24	87	734	2	0,01	914	967	0,02
HT_200_1	-50	387	-136	0,01	922	918	0,04
HT_200_24	23	242	-68	0,01	924	909	0,04

Fig. 7. The corrosion testing results for material after passivation at 100 and 200 mV: a) open circuit potential, b) anodic polarization curves



Sample	Rs [Ohm*cm2]	CPE [μF/cm2]	n	R1 [kOhm*cm2]
C	1,33	0,366	0,00335	21,9
C_100_1	1,69	0,128	0,00278	730
C_100_24	1,42	0,181	0,00285	10700
C_200_1	0,86	0,136	0,00199	2610
C_200_24	1,1	0,136	0,00230	8,6E+21
HT	0,97	0,334	0,00286	7,85
HT_100_1	0,74	0,145	0,00199	688
HT_100_24	1,26	0,225	0,00300	126000
HT_200_1	1,26	0,241	0,00300	16900
HT_200_24	1,05	0,165	0,00250	13900

Fig. 8. The impedance spectrum for material after passivation at 100 and 200 mV: a) Nyquist representation, b) Bode representation, c) dissipation factor

film profitably. The most profitable anticorrosive properties of the analysed combination were found for the sample after 24 h of passivation at a potential of 200 mV.

A very low dissipation factor for the tested materials over a wide range of frequencies up to 10 kHz proves their good dielectric properties (Fig. 4c, 6c, 8c).

The performed microscopic observation of samples after the electrochemical tests confirmed the corrosion destruction and, in some cases, grain boundaries and the typical dendritic structure for cobalt casting alloys were evident (Fig. 9).

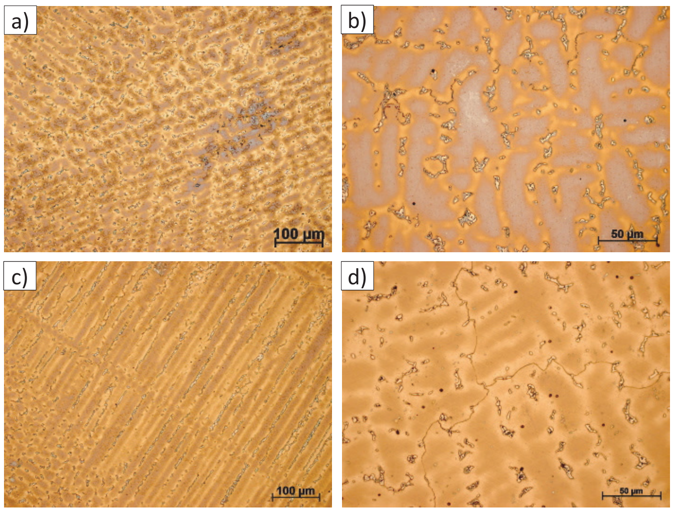


Fig. 9. Examples of corrosion damage the surface of the tested materials: a) after casting without PFM, b) sample C_200_1, c) sample after PFM, d) sample HT_100_24

4. Discussion

When determining the properties of a material to be used on a selected product, one must use the most accurate possible approximation of the state in which it will be applied. In the case of cobalt alloys used for complex metal-ceramic dentures, it seems necessary to perform a heat treatment in accordance with the terms of the firing of dental porcelain after casting and before examining the material. Similarly here [16,17], the authors simulated porcelain firing for metal treatment. In this study, it was found that the electrochemical corrosive properties of the material after casting were different than those of the material after simulated PFM. A disadvantage for the later was found. The material after heat treatment was even slightly characterized by worse corrosion resistance than the material after casting, as evidenced by an almost 50% lower polarization resistance (Fig. 2) and a higher corrosion rate (the smaller angle of slope of the Nyquist spectrum impedance curves (Fig. 4a)). Differences in the corrosion rate of the material after casting and the material after PFM can be observed on the most graphs presented in this work. Similar results [18-20] with lower resistance values and a smaller slope angle on Nyquist plots for samples after PFM were obtained in this work. The reduction in corrosion resistance, lower Rp after firing, may be due to changes in the structure occurring under the influence of the firing process [18]. According to other studies of similar issues [21], the corrosion resistance of a cobalt alloy does not change significantly when comparing the results before and after firing porcelain to the metal substructure, although in analysis of selected results it can be stated that here are meaningful changes in the corrosion current from 50 to 100%. The investigation confirms an increase of the corrosion current for PFM samples of about 10 to 30% (Fig. 5), but these differences occur in the case of samples without depositing the passive layer and after passivation in air. For samples passivated electrochemically, differences in the corrosion current value of the material after casting and after heat treatment are not significant (Fig. 7).

Obtaining the test alloy surface of passive film is one of the methods to improve the biocompatibility of materials used for dentures. The aim of this study was the creation of a durable and compact surface CoCrMo alloy passive layer, which limits the diffusion of metal ions into the tissues in the body. The layers were formed by spontaneous passivation in the air and electrochemically. According to the literature [22-24], passive films are mainly composed of Cr oxides, although, with passivation, an air-formed passive layer also appears Mo .

Spontaneous passivation in the air did not seem to be beneficial to the corrosion resistance of the test material. Polarization resistance relative to the sample after casting and after PFM decreased by 17 to 50%, and the corrosion current increased from 60 to 75%. Other electrochemical properties, such as the open circuit potential and the corrosion potential, also were worse. The results of EIS showed a lower resistance for surface film R1, and the smaller angle of the curve (Fig. 6a) finally confirmed the negative impact of natural self-passivation in the air on the corrosion resistance of the CoCrMo alloy.

The use of different conditions of electrochemical passivation was to compare the effectiveness of formed layers in protection against corrosion. Increasing the passivation potential values from 0 to 100 and 200 mV and increasing the processing time from one to 24 hours increased the thickness of the constituted surface film [22]. Increasing the passivation potential values, both at the one and 24-hour process, had a positive influence on the free potential value (Fig. 10) and the corrosion potential of the material. Similarly, a prolonged passivation time had a positive effect on the mentioned potential values.

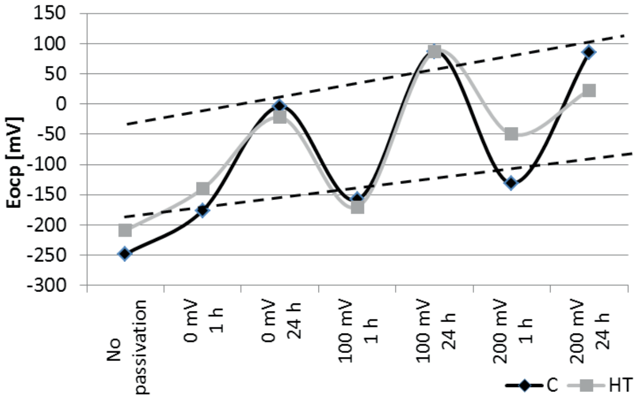


Fig. 10. Influence of electrochemical passivation conditions to free potential of investigated materials

After formation of the passive layer by the electrochemical method, all the characteristic electrochemical parameters improved their values. The largest difference in the polarization resistance measured in the potentiodynamic tests was recorded for the layer prepared at 100 mV by 24 hours for the material after casting and after PFM. The corrosion current value for all samples with the obtained passive film decreased to about 0.01 μA/cm^2. In addition, the loss of material through the use of passive layers was reduced by two orders of magnitude from 1.81–1.95 to 0.04 g/m^2*year. The formed passive layer did not affect the value of breakdown and repassivation potentials of any tested samples, and the breakdown potential value was in the range of 914 to 925 mV. The repassivation potential was in the range of 903 to 967 mV. Results of EIS research confirmed the positive effect of passivating the surface on the characteristic electrochemical parameters. The value of element R1, defined as the resistance of the layer between the electrolyte and the test material (resistance of the passive layer) after the electrochemical formation, increased by several orders of magnitude, from 22 Ohms*cm^2 for the sample after casting to 126 MV*cm^2 for the sample passivated at 100 mV over 24 hours. Similar results were found for the sample after PFM.

Analysis of impedance spectra presented as a Nyquist curve and increased angle slope of curves to the axis of the real impedance value for samples with a passive layer formed by the electrochemical method, leads to the conclusion that the electrochemical passivation process reduced the corrosion rate of the material, compared to the samples without a passive film, and, when a higher potential of passivation and longer process were used, the destruction rate decreased even further, a factor related to the thickness of the formed layer [22].

The shape of impedance spectra curves shown in the Bode plots increased for samples with a passive layer formed electrochemically. A frequency range comprising low frequencies in which the phase angle reaches values close to 90° and in which there is a characteristic linear part of the graph at intermediate frequency values provides a compact formed passive layer. For samples without a passive layer, a shift angle close to the value of 90° occurs only for a short distance curve while extending the passivation and increasing the passivation potential result in a noticeable extension of that section. The largest length was recorded for samples passivated over 24 hours at 200 mV (Fig. 8b). An observed reduction of the phase angle for the material without the passive film or a layer formed in natural way in air to about 30° provides a lower quality of the existing layer [20,25].

The curve showing the relation log|Z| = f(log(f)) at high frequencies looks like a straight line. It is constant in combination with the value of the phase angle, which is approximately 0°. This leads to the conclusion that the passive layer formed on the test material has a typical resistive characteristic.

As a development and complement to the performed tests, in the next step, it will be worth it to carry out research about the ion release of alloys with the obtained passive layers.

5. Conclusions

The realized analysis and electrochemical tests of the CoCrMo alloy after formation on the surface of the passive layer allow the following conclusions:

- The material after PFM heat treatment was characterized by worse electrochemical properties than the material after casting, particularly as regards corrosion resistance;
- Natural alloy passivation in air, independent of the time of activity, 1 or 24 hours, adversely affected the corrosion resistance, and all the characteristic electrochemical parameters were aggravated, in comparison to the material after casting and after PFM;
- Electrochemical passivation of the material allowed formation of a compact passive layer characterized by high resistance with advantageous electrochemical properties in the research environment;
- Prolonging the passivation time from one to 24 hours and increasing the potential value from 0 to 200 mV improved the quality of the passive layer and all characteristics of electrochemical parameters.

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