

ELECTROCHEMICAL AND SPONTANEOUS PASSIVATION OF THE CoCr ALLOY AS CORROSION PROTECTION

Łukasz Reimann¹

¹Silesian University of Technology, Institute of Materials Engineering and Biomaterials, Gliwice Poland

Abstract:

The aim of this work was to compare the level of protection of spontaneous and electrochemical passivation of the CoCr alloy against corrosion in environment simulating the conditions prevailing in the mouth.

Passivation layer was obtained as spontaneous in air at 23 °C for 1 and 24 hours and by electrochemical method by polarization at potentials 0 and 100 mV for 1 and 24 hours. The corrosion resistance tests was realized by potentiodynamic method in Fusayamya saliva solution.

Based on realized research it was concluded that electrochemical passivation better protects material from corrosion than passivation in air; extending the electrochemical passivation time results in greater corrosion resistance and higher passivation potential and longer time was related to formation of a thicker protective layer on the material's surface.

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1. INTRODUCTION

The cobalt based alloys next to precious metal alloys or high noble alloys, are one of the groups used in dental prosthetics, because of their very good mechanical properties and good prices, compared to other alloys groups. They find frequent use in manufacturing of dentures, though they are characterized by the worse corrosion resistance, compared to precious metal alloys [1].

There are many methods for improving the corrosion resistance of CoCr alloys. In work [2] on the application of treatment by nitriding, as a method to improve the corrosion resistance of alloys used as tools in dentistry, authors obtained positive results and created a protective TiN layer on the surface. In addition, there was no need for creation of a corrosion protective layer. In another work [3], 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. To improve the corrosion resistance of CoCr alloys, other authors

[4, 5] 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 [5], the authors did not recognize the 10% reduction of chromium in the concentration that has a critical influence on corrosion resistance, as mentioned in [6]. In study [7] it was found that a heat treatment processes also effects corrosion resistance, and it was noted that the 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 [8].

The aim of this work was to compare the level of protection of spontaneous and electrochemical passivation of the CoCr alloy against corrosion in environment simulating the conditions prevailing in the mouth.

2. METHODOLOGY

Samples casted from one of cobalt based alloys, applied in dental prosthetics, whose chemical composition is presented in tab. 1, were used in this research. All the samples were ground with SiC paper and polished, and, before each test, they were degreased and washed in acetone. The environment center for the tests was an artificial saliva solution prepared on the basis of Fusayamya (tab. 2) at room temperature.

The corrosion resistance research was conducted by a potentiodynamic method on the Potentio-stat-Galvanostat ATLAS 0531 according to EN ISO 17475:2008 [9] standard. Three electrodes were used in this research: a working electrode (the sample), the reference electrode Ag/AgCl and platinum auxiliary electrode (fig. 1).

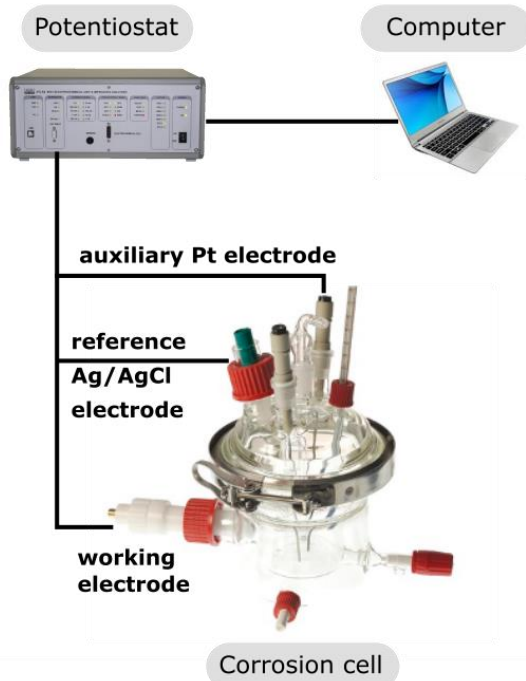


Fig. 1. Passivation of tested material

At the beginning, the corrosion resistance test for a sample after the casting was realized by using the potentiodynamic method. After this research, it was possible to define in what potential range was the studied alloy the passivation stage. Experiments 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 related to electrochemical corrosion resistance, the Tafel extrapolation method was used.

The passivation layer was obtained by the following two methods:

- spontaneous passivation in air at 23 °C for 1 and 24 hours;
- electro-chemical passivation by polarization at potentials 0 and 100 mV for 1 and 24 hours. The potentiostat, with Ag/AgCl reference electrode and platinum rod as auxiliary electrode, was applied.

Table 1. Chemical composition of tested alloy

Elements	[wt. %]
Cr	25
Mo	7
W	5
Si	1,5
Mn, N	< 1
Co	balance

Table 2. Composition of an artificial saliva

Elements	Content
NaCl	0.4 g/l
KCl	0.4 g/l
NaH ₂ PO ₄ • 2H ₂ O	0.69 g/l
CaCl ₂ • 2H ₂ O	0.79 g/l
Na ₂ S • 9H ₂ O	0.005 g/l
Urea	1.0 g/l
Distilled water	1 l

The next step was to realize the test of corrosion resistance for samples with obtained passive layer also by using the potentiodynamic method.

3. RESULTS

Based on the conducted examinations for casted sample, it was stated that the passivation range for studied alloy is between 0 and 650 mV, what was showed on fig. 2.

The samples were passivated firstly and curves were registered for both potentials of 0 and 100 mV (fig. 3). They indicated, that after about 100 s, a compact protective layer was formed on the surface, which was the protection against the further digestion of samples. Then the tests were done with open circuit potential for all samples (fig. 4), whose value, after spontaneous passivation was about -270 mV and did not depend on the

time left in air. For samples after passivation for 1 h the potential was in the range from -180 to -160 mV. When the passivation time was prolonged to 24 h, the potential increased from about 0 V (passivation in 0 V) to 100 mV (passivation in 100 mV).

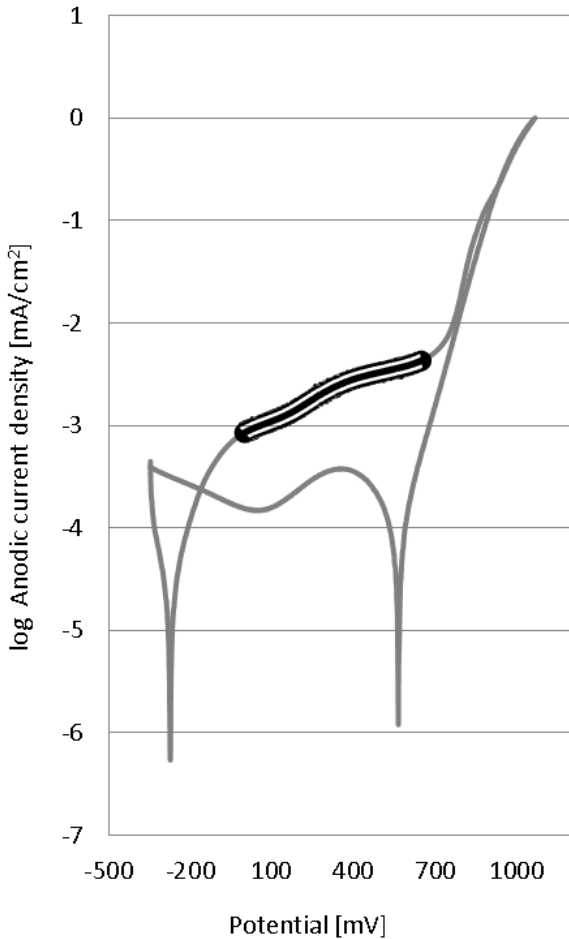


Fig. 2. Electrochemical research of cast alloy

Based on the registered anodic polarization curves (fig. 5) and performed Tafel analysis, the characteristic corrosive parameters were determined shown in tab. 3.

4. DISCUSSION

The CoCrMoW alloy, used in this study, is applied on the dentures as a metallic substrate on which is then finally fired porcelain, as an aesthetic ceramic layer. Although metal part is covered by the ceramic layer, it will still have contact with the environment in the oral cavity; thus the selected alloy should have good resistance to corrosion.

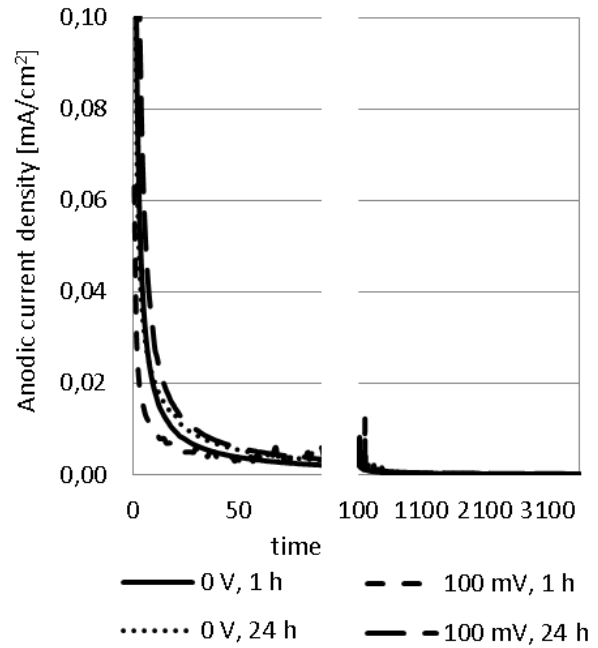


Fig. 3. Passivation of tested material

Table 3. Electrochemical parameters after corrosion tests

Sample	E _{cor} [mV]	i _{cor} [μA/cm ²]	R _p [kOhm*cm ²]
air 1 h	-275	0.85	220
air 24 h	-278	0.92	233
0 V 1 h	-261	0.01	254
0 V 24 h	-96	0.01	310
100 mV 1 h	-246	0.01	275
100 mV 24 h	2	0.005	844

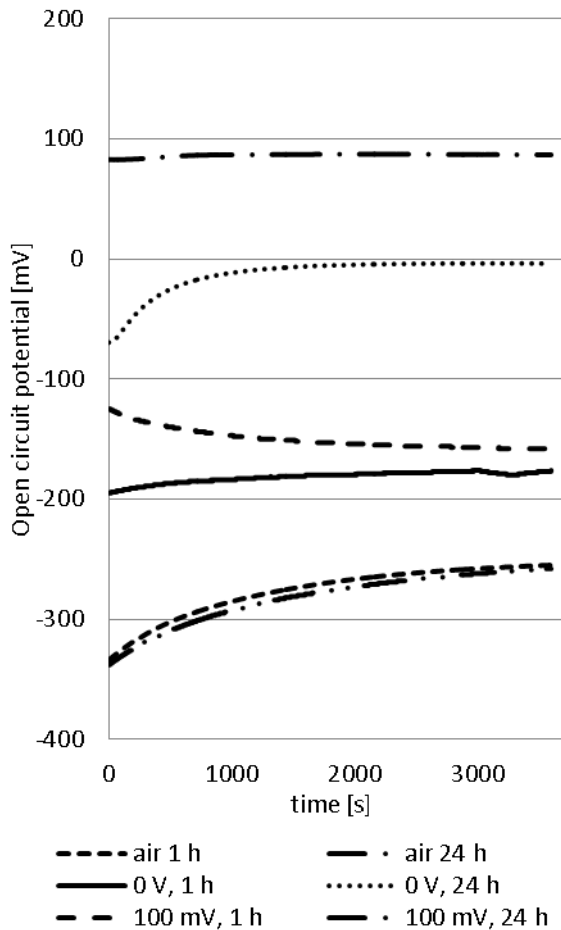


Fig. 4. Open circuit potential after spontaneous and electrochemical passivation

The aim of this study was the creation of a durable and compact passive layer on the CoCrMoW alloy, which would limit 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 literature [10-12], passive films are mainly composed of chromium oxides, although with passivation in air Mo appears in the formed passive layer, as well.

Spontaneous passivation in the air did not seem to be beneficial to the corrosion resistance, comparing to electrochemical method, for which the value of corrosion current is about 100 times lower. Using the higher potential for passivation for 1 h does not significantly improve the corrosion resistance, while prolonged passivation time, from 1 to 24 h, increased the corrosion potential by up to two orders of magnitude from -246 mV for sample at 100 mV, 1 h to 2 mV for sample at 100 mV, 24 h.

The higher corrosion resistance of samples, after the electrochemical passivation, compared to self-passivated samples, is due to the polarization resistance, which for passivation of material for 1

h, 0 and 100 mV was higher for about 10÷18 %, and after 24 h of passivation it was higher for 33 % with passivation at 0 V, to 260 % for passivation at 100 mV. Authors in work [10] presented that the increase of the passivation potential and increase of its duration cause an increase of the passive layer thickness what results in better corrosion resistance of material.

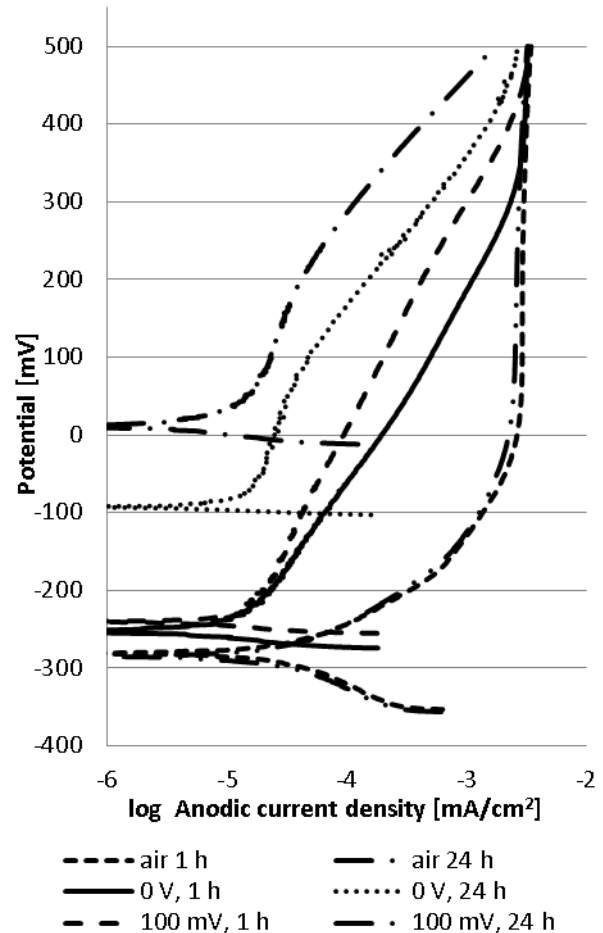


Fig. 5. Anodic polarization curves after corrosion research

5. CONCLUSIONS

The realized research on comparison of corrosion resistance of the CoCrMoW alloy after passivation by the two methods allowed reaching the following conclusions:

- electrochemical passivation better protects material from corrosion than passivation in air what was proven by about 88 times lower corrosion current and for about 2 times higher value of polarization resistance;
- extending the electrochemical passivation time results in greater corrosion resistance of researched material;

- increase in corrosion resistance with an increase in value of the passivation potential and prolongation the time was related to formation of a thicker protective layer on the material's surface.

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