Influence of Fe and Al addition on corrosion resistance of CoCrMoW alloy

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ABSTRACT

Purpose: The aim of this study was to evaluate the influence of alloying additions iron or aluminium on corrosion resistance in artificial saliva solution of a dental cobalt alloy Remanium 2000+ after casting.

Design/methodology/approach: Pitting corrosion resistance was evaluated on the basis of anodic polarization curves obtained during electrochemical potentiodynamic polarization tests, which was also performed for samples after one and twelve hours of passivation. Corrosion potential, repassivation potential and corrosion current were picked as an assessment criteria.

Findings: Results obtained in the test showed that both alloying additions have a slight influence on the pitting corrosion resistance of the tested alloy. Nevertheless, comparing iron and aluminium additions, corrosion parameters values were better for samples admixed with aluminium. On the basis of microscopic observations it was stated, that tested alloys have the structure with noticeable dendritic segregation.

Research limitations/implications: The research was carried out on samples, not on final elements. Tests were carried out in in vitro conditions.

Practical implications: Scientific research of cobalt alloys, as materials used for dentures, allows to specify the influence of alloying additions on material properties. It is always important to determine the nature of the impact of a specific element.

Originality/value: The aim of the paper is to improve corrosion resistance of Co based alloy by modification of the original chemical composition.

Keywords: Biomaterials; Corrosion; Cobalt alloys; Potentiodynamic study; Passivation

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PROPERTIES

1. Introduction

A biomaterial is any substance, not being a medication, which can at any time be used to replace, fully or partially, a tissue or organ, or to repossess their functions. There are following types of biomaterials: metallic, ceramic, polymer, carbon and composite materials. Amongst them, metal alloys are ones most frequently used in dentistry (Tab. 1). The use of metallic materials for biomedical implants connects with their direct contact with the internal environment of the organism and different body fluids. Such conditions further corrosion, consequently leading to the falloff of mechanical properties of the alloy. This is the reason why it is so important for a biomaterial to be not only biocompatible but also highly resistant to corrosion. Cobalt-based alloys belong to this kind of materials, marked by good pitting and crevice corrosion resistance and additionally having the ability of passivation and repassivation in physiological solutions, what allows them to be used as long-term implants. In order to enhance their properties, cobalt alloys are usually admixed with chromium, molybdenum and nickel [1].

Table 1.
Groups of alloys used in dentistry [2,3]

Group		Major elements	Basic applications
Amalgam	mercury-based	Hg, Ag, Sn, Pd, Cu, In	fillings
Precious metals	gold-based	Au, Ag, Cu, In, Pd, Pt, Zn	restorations, solders
	silver-based	Ag, Pd	restorations, solders
	palladium-based	Pd, Ag, Ga, Cu	restorations
Non-precious metals	cobalt-based	Co, Cr, Mo, Fe, C, Si, Mn	restorations, implants
	nickel-based	Ni, Mo, Fe, C, Be, Mn	restorations, orthodontic appliances
	iron-based	Fe, C, Ni, Cr	orthodontic appliances , implants
	titanium-based	Ti, O, N, C, Fe, H	implants

The main factor that determines the structure of the alloy is the manufacturing process. Currently used cobalt alloys can be divided into three basic groups [4-9]:
- cast alloys,
- plastic forming alloys,
- alloys manufactured by powder metallurgy.

In comparison to other metal alloys used in dentistry, cobalt alloys exhibit slightly worse properties when it comes to electrochemical tests. Their breakdown potential can be even 150 mV lower than that of gold or palladium based alloys. Nevertheless, their corrosion resistance is sufficient for them to be used in medicine. Additionally, they have good mechanical and tribological properties and are much cheaper comparing to other alloys, what decides of their common use [2,10-12].

2. Materials and methods

2.1. Materials

Experiments were carried out on a non-precious, cobalt-based commercial alloy Remanium 2000+ (Dentaurum), used in prosthodontia for crowns, bridgeworks and full cast partials. The alloy, which chemical composition is given in Table 2, has been admixed respectively with aluminium or iron. Melting point of the alloy comes to 1415°C.

Table 2.
Basic chemical composition of tested alloy

Element	Mass content, %
Co	61
Cr	25
Mo	7
W	5
Si	1.5
other (Mn, N)	< 1

Samples for the tests were manufactured using centrifugal casting technology on the Fornax T machine (Bego). The mould was produced by investment casting. Casting mould preparation methodology included:
- preparation of disc-shaped wax models and runners,
- model fixing to the sprue and covering it with Aurofilm fluid (Bego), in order to gain better wettability of wax models by investment material,

- covering interior of the mould with a special liner to ensure better expandability of investment material (Fig. 1),
- preparation of investment material: for 400 g WiroFine powder, 80 ml 70% solution of BegoSol K,
- manual mixing of the pulp for 15 seconds and mixing in a vacuum mixing unit for 60 seconds afterwards,
- filling the mould with the use of prosthetic vibrator,
- removal of casting cone after 10 minutes,
- placing the mould in the furnace heated up to 950°C for 30 minutes.
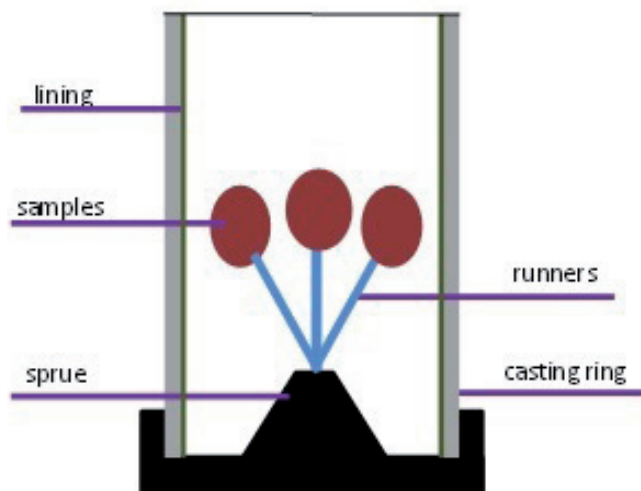
a)
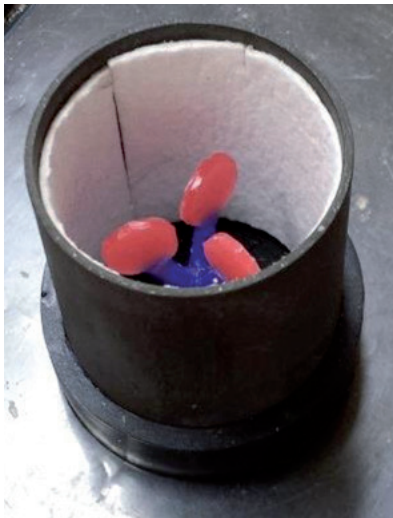
b)

Fig. 1. Casting mould: a) wax model inside casting ring with lining, b) pictorial diagram

Metal charge (cobalt alloy admixed with about 1% of iron powder) was induction molten and casted. The process was repeated for the second mould, however the metal charge this time consisted of a cobalt alloy admixed with about 0.5% of aluminium (purity 99.9 %).

Moulds were left to cool after casting. Then samples were cut off runners and sandblasted. In the next stage samples were sanded on SiC sandpapers with the grain size respectively 220, 500, 800 and 1200 μm. Each sample has been polished for 2 minutes with the use of diamond polish 9 μm, immediately before the corrosion resistance test.

2.2. Research methodology

Pitting corrosion resistance of casted samples was evaluated on the basis of anodic polarization curves obtained during electrochemical potentiodynamic polarization tests. All measurements were proceeded at room temperature in the corroding medium of artificial saliva solution, with chemical composition proposed by Fusayama (Tab. 3).

Table 3.
Chemical composition of artificial saliva solution by Fusayama [13]

Element	Content
distilled water	1 l
Na_2S	0.005 g
NaCl	0.4 g
KCl	0.4 g
$NaH_2PO_4{\cdot}H_2O$	0.69 g
$CaCl_2{\cdot}H_2O$	0.79 g
urea	1 g

Corrosion resistance tests were proceeded using ATLAS 0531 potentiostat (Atlas Sollich), connected to the computer with installed AtlasCorr05 software, enabling to control the parameters of the process and to record the results of the test. Three-electrode electrochemical cell (Fig. 2), consisting of following electrodes, was used for tests:

- working electrode – tested cobalt alloy sample with the area of approximately 0.5 cm^2,
- reference electrode – chloroargentic electrode placed inside luggin's capillary,
- platinum counter electrode.

Fig. 2. Electrochemical test stand which consists of a potentiostat and an electrochemical cell

The distance between working electrode and reference electrode was approximate twice the value of the diameter of working electrode. If the distance is too short it can cause shielding of sample surface, when it is too long it can cause mistakes in potential values readings [13,14].

Corrosion resistance test included:

- open circuit potential determination in electroless conditions during one hour,
- recording of anodic polarization curves for potential changing with the scan rate of 1 mV/s. The initial

potential had the value of an open circuit potential reduced by 100 mV. Original and return curves were recorded,

- 0 mV potential sample passivation for one and twelve hours.

Additionally the structure of the alloy was evaluated in microscopic examination using optical microscope Leica MEF4A (with AxioVision computer software). Confocal microscope (Zeiss LSM 5 EXCITER) was used for topography analysis. To affirm the presence of aluminium and iron in the alloy, chemical composition analysis of microsites of specimens was conducted using EDS spectroscopy in SEM microscope (Zeiss Supra 35). Structure observations and topography analysis were conducted after corrosion tests.

3. Results and discussion

The first step was to confirm that Al and Fe additives can be found in casted samples. EDS technique was used for this purpose. EDS analysis confirmed aluminium and iron content in examined samples (Figs. 3, 4). Microscopic observations revealed dendritic structure in both tested alloys (Fig. 5). Topography analysis showed, that average height difference before and after the corrosion test was 9.7 µm and 27.7 µm for Al and Fe additions respectively (Fig. 6).
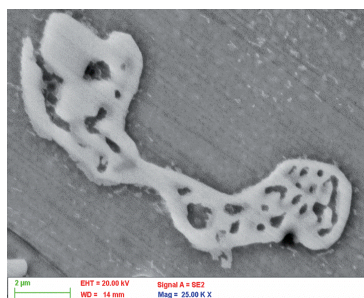
Element	Wt%	At%
CK	02.62	09.99
OK	08.88	25.41
AlK	04.04	06.85
WM	15.21	03.79
MoL	05.94	02.83
CrK	18.32	16.13
FeK	01.35	01.11
CoK	43.63	33.89
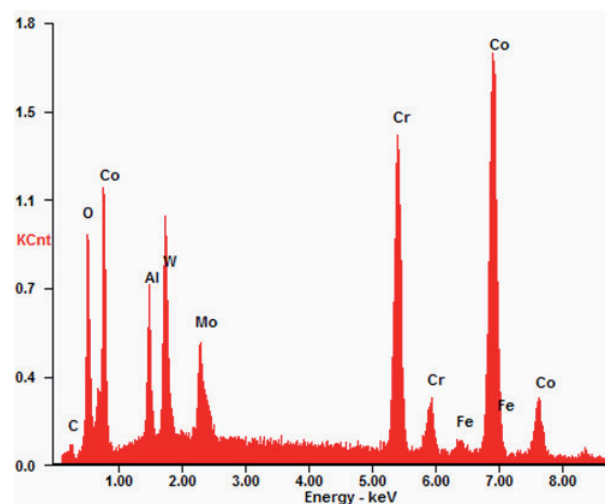
Fig. 3. Chemical composition analysis of microsite of the specimen admixed with Al

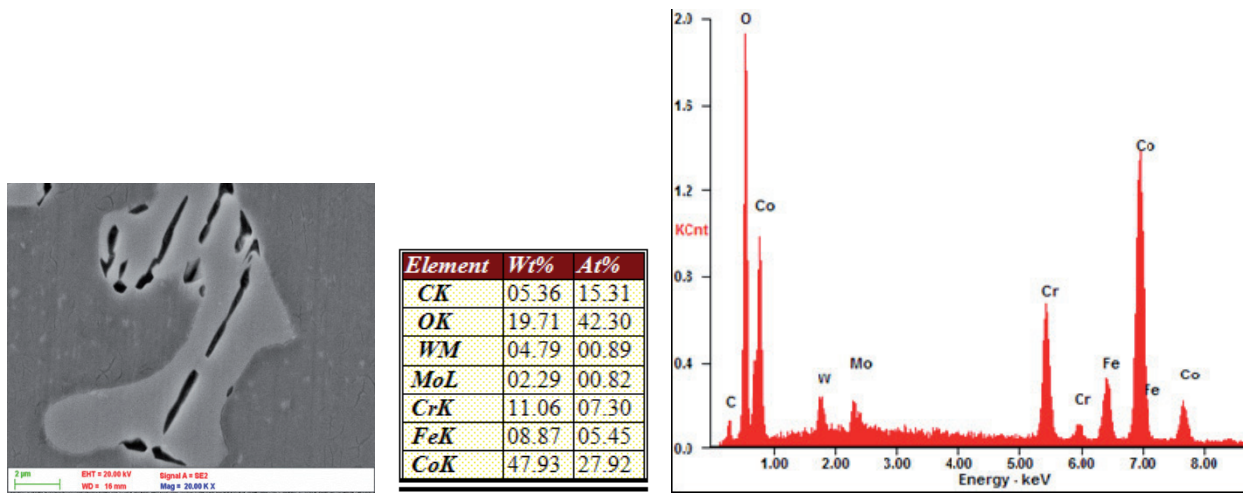| Element	Wt%	At%
CK	05.36	15.31
OK	19.71	42.30
WM	04.79	00.89
MoL	02.29	00.82
CrK	11.06	07.30
FeK	08.87	05.45
CoK	47.93	27.92

Fig. 4. Chemical composition analysis of microsite of the specimen admixed with Fe
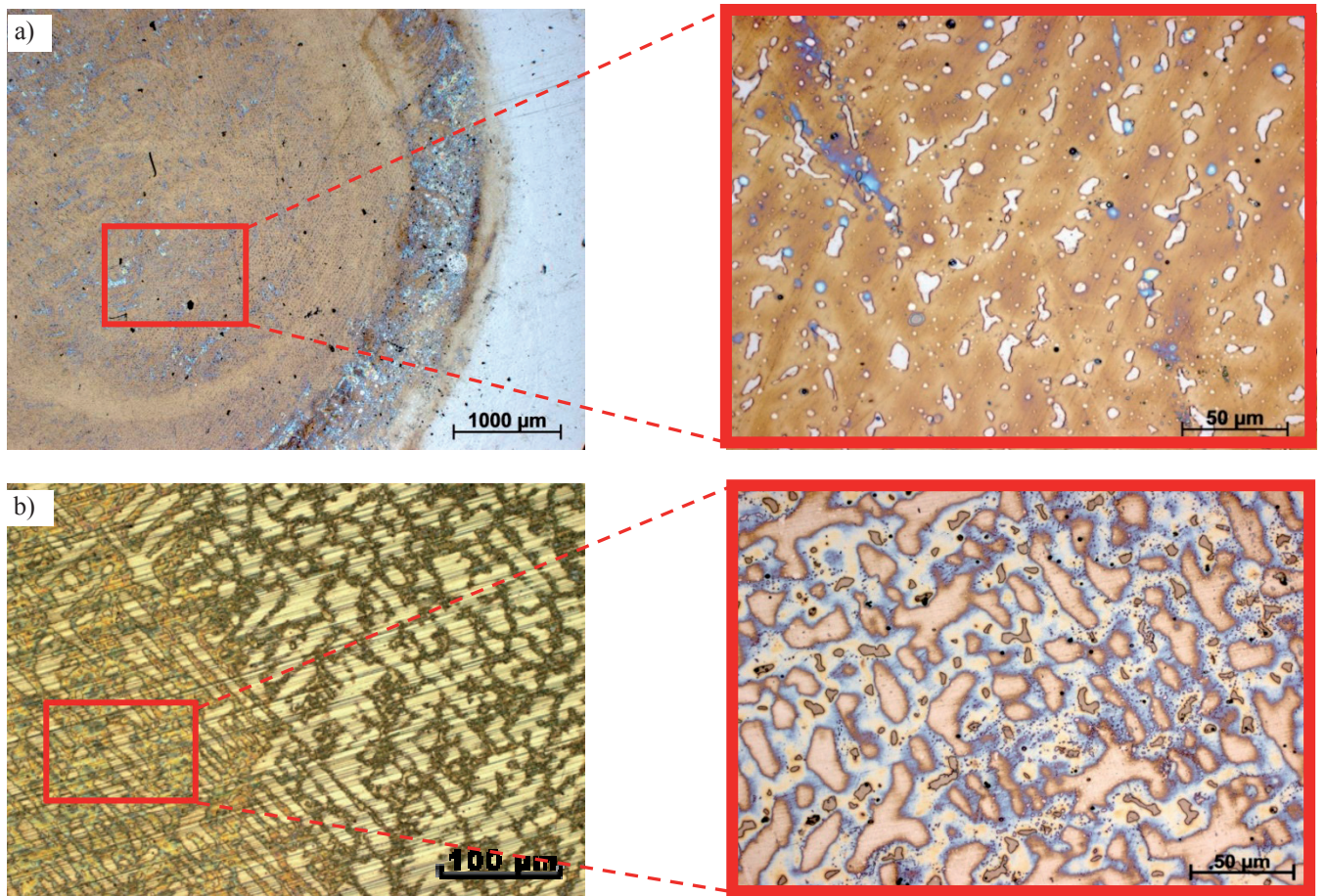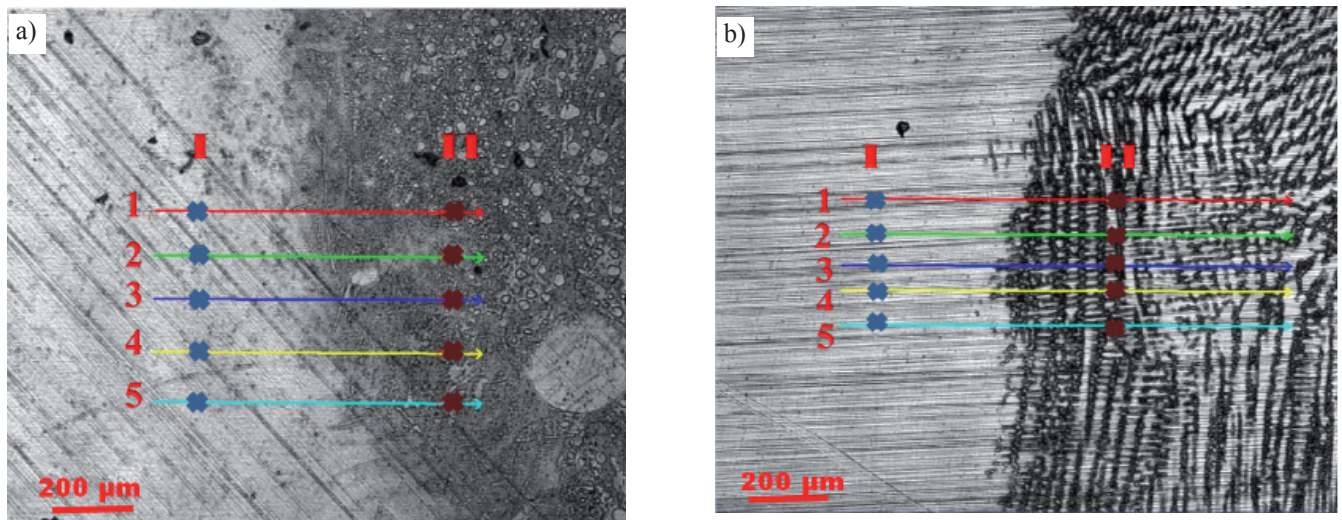

Fig. 5. Structure of tested alloy enriched with alloying additions after corrosion tests; dendritic crystals visible: a) Al addition, b) Fe addition

Al	Marker I	Marker II	Difference
1	43.5 μm	33.3 μm	10.3 μm
2	43.5 μm	31.5 μm	12.0 μm
3	34.9 μm	27.5 μm	7.4 μm
4	43.1 μm	32.3 μm	10.8 μm
5	35.9 μm	27.9 μm	8.0 μm

Fe	Marker I	Marker II	Difference
1	31.7 μm	0.0 μm	31.7 μm
2	31.7 μm	0.0 μm	31.7 μm
3	31.7 μm	0.0 μm	31.7 μm
4	22.0 μm	0.0 μm	22.0 μm
5	21.3 μm	0.0 μm	21.3 μm

Fig. 6. Topography comparison of material surfaces after corrosion test, with the height difference markers flagged and values given in tables: a) alloy with Al, b) alloy with Fe

Table 4.
Corrosion parameters values obtained during the test

Sample	Polarization resistance, kOhm*cm^2	Repassivation potential, mV	Corrosion potential, mV	Breakdown potential, mV	Corrosion current, μA/cm^2
Remanium 2000+	160	986	-279	1002	0.687
Al	454	922	-277	894	0.593
Al 1h	595	918	-236	896	0.014
Al 12h	341	898	-54	901	0.0092
Fe	139	850	-192	972	0.631
Fe 1h	33	884	-63	963	0.845
Fe 12h	1200	841	-105	965	0.0065

On the basis of electrochemical tests it was stated, that repassivation potential values are significantly higher for samples admixed with Al (898-929 mV), than for samples with Fe (830-884 mV). However, comparing to the original alloy, repassivation potential for samples with alloying additions was lower, which means that defects already existing on the surface caused a faster development of the pits. Breakdown potential for samples admixed with iron had the value of about 970 mV and was higher than the one of the alloy with Al addition, for which it averaged 900 mV.
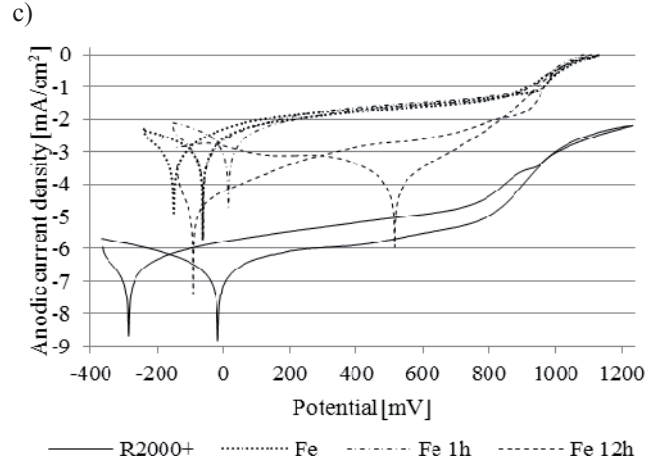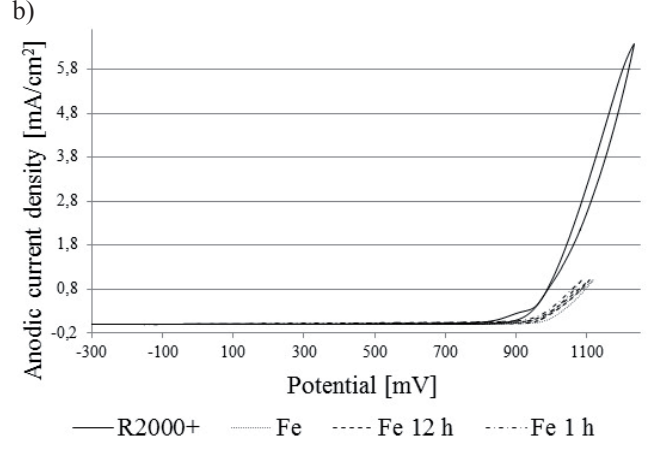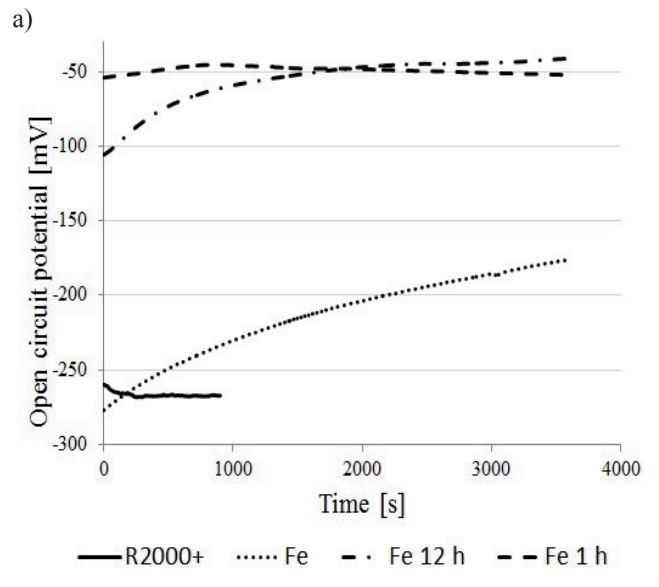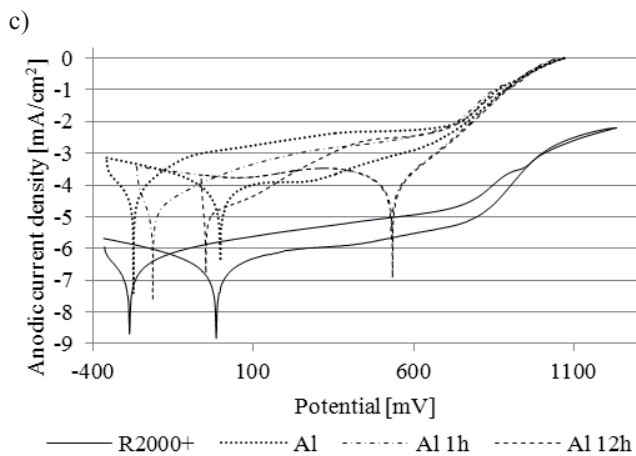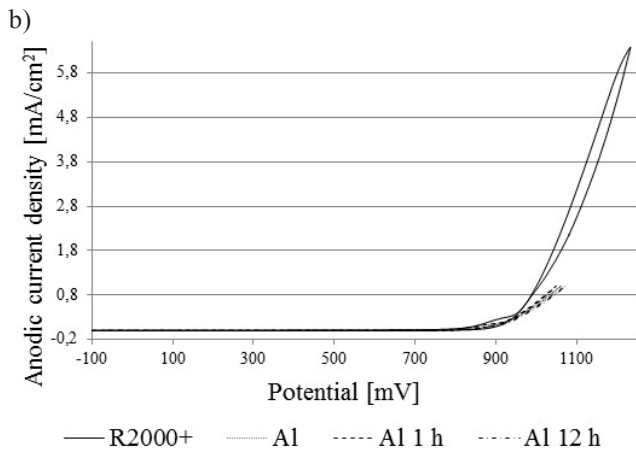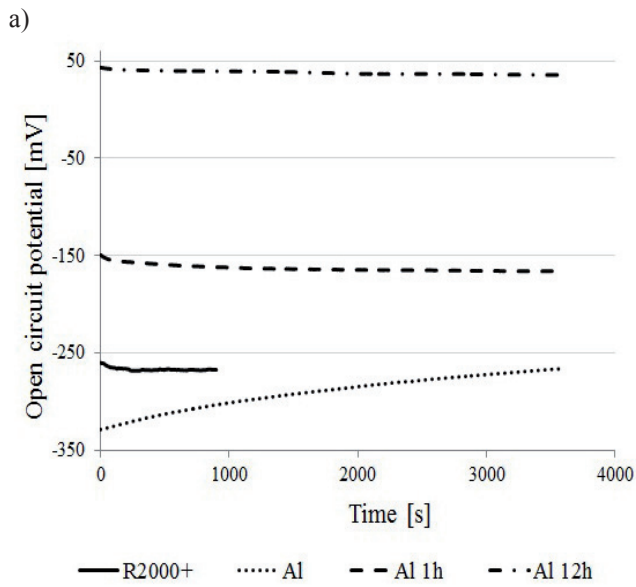
Fig. 7. Electrochemical research of CoCrMoW alloy with Al added: a) open circuit curves, b), c) potentiodynamic curves

Fig. 8. Electrochemical research of CoCrMoW alloy with Fe added: a) open circuit curves, b), c) potentiodynamic curves

Both of this values are slightly lower than that of a pure alloy. It is assumed that breakdown potential values over 600 mV indicate optimal corrosion properties. Al addition caused the increment of corrosion potential only after passivation while Fe addition caused it to increase for all specimens. At the same time corrosion potential reached the highest values for passivated samples, for which it increased by 80%. Corrosion current was lower for admixed samples in comparison with the original alloy and reached the minimum values for specimens passivated for 12 hours [16].

A lot of studies concerning corrosion resistance for different alloying additions can be found in literature. As an example, CoCrMo alloy admixed with precious metals (Au, Pt, Ru) showed a decline of corrosion parameters values in relation to the pure alloy. Breakdown potential for some samples decreased even by 700 mV, reaching the value of -250 mV. In contrast, in the case where molybdenum was substituted with titanium, the corrosion resistance of the alloy was improved and breakdown potential values reached even 1150 mV (with the average value of 1000 mV for all tested samples) [17, 18].

Results of electrochemical tests can vary even with the slightest change of parameters in which they are conducted or surface preparation method. For that reason it is not recommended to compare results obtained in different tests. It is also very difficult to precisely determine correlations between corrosion processes for different materials [2,10,19]. Results of corrosion parameters obtained during the test are presented in Table 4 and Figures 7, 8.

4. Conclusions

On the basis of conducted examinations, it was stated that the shape of polarisation curves suggests, that tested samples undergo local pitting corrosion in electrolyte used for the test.

The inclination of rectilinear segments of anodic curves and sudden increment of current density prove a fast development of pits. Return curve, visible on the diagram, is closing the hysteresis loop what proves the occurrence of repassivation process – formation of secondary protective layer. All tested materials show resistance to formation and expansion of pits up to 840 mV, what confirms their good corrosion resistance in artificial saliva solution.

Aluminium and iron additions did not show any significant influence on anticorrosion properties. Examined alloys were characterized by breakdown potential above 890 mV, what allows to qualify them as corrosion resistant materials. Over 30% increment of corrosion potential has

been reported due to Fe addition to chemical composition of the alloy. At the same time Al and Fe additions caused the decrement of corrosion current by averagely 10%. Corrosion resistance improvement for specimens enriched with alloying additions was obtained after passivation of samples surface. Passivation caused the corrosion potential value to increase by over 80 % simultaneously bringing the corrosion current down even by two orders of magnitude.

Both tested alloys are characterized by typical for this kind of materials, dendritic structure.

References

[1] M. Jurczyk, J. Jakubowicz, Bionanomaterials, Poznan University of Technology Publishing, Poznan, 2008 (in Polish).

[2] D. Upadhyay, M.A. Panchal, R.S. Dubey, V.K. Srivastava, Corrosion of alloys used in dentistry: A review, Materials Science and Engineering A 432 (2006) 1-11.

[3] H. Zohdi, M. Emami, H.R. Shahverdi, Galvanic corrosion behavior of dental alloys, in: Environmental and industrial corrosion – practical and theoretical aspects, B. Valdez (ed.), Intech, 2012.

[4] Ł. Reimann, L.A. Dobrzański, B. Nieradka, M. Kusy, R. Riedlmajer, Influence the heat treatment of two base metal alloys used on dental prosthesis on corrosion resistance, Journal of Achievements in Materials and Manufacturing Engineering 57/2 (2013) 83-90.

[5] J. Marciniak, M. Kaczmarek, A. Ziębowicz, Biomaterials in Dentistry, Silesian University of Technology Publishing, Gliwice, 2008 (in Polish).

[6] J. Łaskawiec, R. Michalik, Theoretical and application aspects of implants, Silesian University of Technology Publishing, Gliwice, 2002 (in Polish).

[7] B. Stodolnik, Material and Biological Studies of Biomedical Cobalt Alloys Endocast and Endocast SL, Proceedings of the Seminar "Mechanics in Medicine 6", Rzeszów, 2002 (in Polish).

[8] W. Walke, Z. Paszenda, A. Ziębowicz, Corrosion behaviour of Co-Cr-W-Ni alloy, Achieves of Materials Science and Engineering 28/5 (2007) 293-296.

[9] M. Król, L.A. Dobrzański, Ł. Reimann, I. Czaja, Surface quality in selective laser melting of metal powders, Archives of Materials Science and Engineering 60/2 (2013) 87-92.

[10] R.R. Al-Hity, H.F. Kappert, S. Viennot, F. Dalard, B. Grosgogeat, Corrosion resistance measurements of dental alloys, are they correlated?, Dental Materials 23 (2007) 679-687.

[11] Ł. Reimann, L.A. Dobrzański, Influence of the casting temperature on dental Co-base alloys properties, Achieves of Materials Science and Engineering 60/1 (2013) 5-12.

[12] I. Peter, M. Rosso, A. Toppi, I. Dan, B. Ghiban, Investigation on Cobalt based alloy modified by Titanium for dental applications, Achieves of Materials Science and Engineering 61/2 (2013) 62-68.

[13] L.A. Dobrzański, Ł. Reimann, C. Krawczyk, Effect of age hardening on corrosion resistance and hardness of CoCrMo alloys used in dental engineering, Achieves of Materials Science and Engineering 57/2 (2012) 5-12.

[14] J. Baszkiewicz, M. Kamiński, Basics of metal corrosion, PW Publishing House, Warsaw, 2006 (in Polish).

[15] C.G. Zoski, Handbook of Electrochemistry, Elsevier, Amsterdam, 2007.

[16] L.E. Kay, Cyclic Potentiodynamic Survey of Medical Materials, IPFW, 2010.

[17] L. Reclaru, H. Luthy, P. Eschler, A. Blatter, C. Susz, Corrosion behaviour of cobalt–chromium dental alloys doped with precious metals, Biomaterials 26 (2005) 4358-4365.

[18] T. Matkovic, L. Slokar, P. Matkovi, Structure and properties of biomedical Co-Cr-Ti alloys, Journal of Alloys and Compounds 407 (2006) 294-298.

[19] W. Kajzer, M. Kaczmarek, J. Marciniak, Influence of medium and surface modification on corrosion behaviour of the cobalt alloy, Journal of Achievements in Materials and Manufacturing Engineering 26/2 (2008) 131-134.