Journal
of Achievements in Materials
and Manufacturing Engineering

VOLUME 57
ISSUE 2
April
2013

Influence the heat treatment of two base metal alloys used on dental prosthesis on corrosion resistance

Ł. Reimann [a,*], L.A. Dobrzański [a], B. Nieradka [a], M. Kusy [b], R. Riedlmajer [b]
[a] Division of Materials Processing Technology and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials,
Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Institute of Materials Science, Faculty of Materials Science
and Technology in Trnava, Slovak University of Technology in Bratyslava,
J. Bottu 25, 917 24 Trnava, Slovakia
* Corresponding e-mail address: lukasz.reimann@polsl.pl

Received 22.01.2013; published in revised form 01.04.2013

Properties

ABSTRACT

Purpose: The goal of the study is to try find the influence of the heat treatment on the corrosion resistance of two base cobalt alloys used on dental prosthesis.
Design/methodology/approach: The investigation was choosen two base cobalt alloys: Remanium 2000+ (Dentaurum) and Wirobond LFC (Bego). Corrosion resistance test were carried out at room temperature and use of the Potentiostat IPS AJ PGU system for electrochemical tests. The examination use of water center which simulated artificial saliva environment. The evaluation of pitting corrosion was realized by recording of anodic polarization curves with use the potentiodynamic methods. Structure observation was made after surface preparation by light microscope.
Findings: Research cobalt alloys are characterized by a dendritic crystals in structure. For both cobalt alloys increasing the time of age hardening effect on growth of the corrosion resistance, especially to increase the potential for pitting initiation.
Research limitations/implications: The research was carried out on samples, not on final elements.
Practical implications: The research material is used on dentures, so it must characterize the corrosion resistance. Results of this work make up an information on what heat treatment parameters may be pay attention for two base cobalt alloys: Remanium 2000+ (Dentaurum) and Wirobond LFC (Bego).
Originality/value: The paper presents influence the heat treatment of two base metal alloys used on dental prosthesis on corrosion resistance.
Keywords: Biomaterials; Corrosion resistance; Age hardening; Prosthodontia; Cobalt alloys

Reference to this paper should be given in the following way:
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.

1. Introduction

Biomaterial is a substance, a combination of synthetic or natural substances, which can be used as part or all of the system, replacing a tissue, organ or performing their functions[1].

The main criterion for suitability of biomaterials used for implants is biotolerance. It is connected with the physicochemical properties of the implant surface layer, which should be compatible with the characteristics of the environment of the tissue of the human body [2-4].

Dental prosthetics is the field of dentistry which deals with the replacement of missing teeth and related mouth or jaw structures by bridges, dentures or other replacement devices. Characteristics of functional dentures depend on the biological and technical factors. The main criterion of the biocompatibility is corrosion resistance of biomaterial in the environment of tissues and body fluids. Despite the many advantages of the introduction and spread of the implants in surgical practice has always been associated with the prevention of corrosion and the effects of its occurrence in connection with their operation in the dynamic environment of the human body, which is particularly aggressive to metals [1,3,5-8].

Long-term presence of dental implants in body fluids may contribute to the development of local primary cells as well as of their concentration. Occurring in the oral cavity electromechanical phenomena rarely not contribute to the formation of pathological changes [9,10].

Corrosion usually starts from small changes in the affected area usually occur on folded material, and then proceeds into the depths, destroying the substances most susceptible to corrosion. The corrosion products formed sometimes passive layer that protects against further development of damage, while in other cases there may be another factor causing further corrosion [11,12].

Cathode and anode reactions are the main reactions that occur in the process of corrosion. The cathode reaction causes reduction processes using the electrons generated in the process of anodic oxidation. While the anodic reaction involves the oxidation of the surface of the material to the environment by providing around the implant metal ions, which affect adversely the human body. The appearance of corrosion due to electrochemical processes may be at the time when the balance between the anode and cathode processes. The material is more resistant to corrosion processes of the time they have a higher electrochemical potential [12,13].

Occurrence of corrosion from a clinical point of view, it may cause [13]:

- negative biological reactions leading to the rejection of the implant;
- reducing the time of the work of implant in the body, as a result of reducing the burden of portability required;
- release into the surrounding tissue the corrosion products which is related to possibility of pain.

From the perspective the proper functioning of the implant is to ensure a sufficiently high durability in a body fluid environment [9].

Metal alloys are widely used materials in prosthetic dentistry due to their high durability and good mechanical properties. In dentistry, there are the use both precious alloys and non-precious alloys [14].

Classification of the ANSI-ADA divides the alloys used in dental prosthetics into three groups. The first group consists the highly noble alloys which contain at least 60% of precious metals (Au+Pt+Pd), including at least 40 % of gold. The second group consists of precious alloys which contain at least 25% of the noble metal (while the amount of gold is not specified) and the third group are predominantly alloys and base metals they contain less than 25% of the precious metals [15].

Precious metal alloys containing a major proportion of elements such as [14,16]:

- gold,
- platinum,
- palladium,
- silver (only in the presence of Pd).

In the base metal alloys the matrix can be [14,16]:

- cobalt (with the addition of chromium, molybdenum),
- titanium (pure titanium, alloys with aluminum, vanadium, niobium, tantalum),
- nickel (with the addition of chromium, molybdenum, niobium),
- iron (with the addition of chromium, molybdenum, niobium).

Reaction on the use of the metals alloys may be undesirable for the body. Theirs effects are a source of corrosion products, and released during the corrosion of the metal ions can migrate into the surrounding tissue. Due to the dangerous brought by corrosion of metallic biomaterials cause necessity to realization the corrosion researches [14].

The use of metallic biomaterials for implants create corrosion problems as a result of direct contact with the saliva. The effects of corrosion dental implants is the deterioration mechanical properties of alloys and the possibility of electrochemical reactions. It is also difficult to adapt the implant to the anatomical structures of the substrate, because insufficient metal structure adaptation to the surrounding tissue pressure increases the concentration of both the implant and the bone [16].

Corrosion resistance of biomaterials is usually defined in comparative studies that allow to reveal the mechanisms and consequences of types of corrosion damage. Research of corrosion resistance also allow comparative analysis of different alloys for varying their chemical composition, phase and surface topography [17].

Survey of biomaterials corrosion resistance are often carried out by electrochemical methods that allow for a relatively short time assessment of a number of corrosion phenomena that occur on the surface of the test piece [17].

Heat treatment of alloys are often used for forming the structure and properties. Commonly heat treatment is realized for non-precious alloys, whose main component is cobalt, used on the dentures substrates because of their excellent mechanical properties and their quite good corrosion resistance. After casting alloys are slow cooling in the air with the casting mould, what may influence on their structure through forming a big crystallites. In consequence it have an effect on properties of final products (prosthesis). In order to prevent disadvantageous phenomenon were realized heat treatment, in particular age hardening which allow on structure homogenizing and improve mechanical properties. The ageing can cause significant improvement of the corrosion resistance. It were shown that the age hardening of cobalt-chromium-molybdenum alloys influence on structure, the numbers of carbides release in alloys with carbon additions and also on hardness and wear resistance [18-22].

The aim of that work is to study the influence of the heat treatment of two base metal alloys used on dental prosthesis on corrosion resistance.

2. Materials and methods

2.1. Materials

Materials used to testing were non precious commercial alloys: Remanium 2000+ (Dentaurum) and Wirobond LFC (Bego), base on cobalt used in prosthodontia on crowns, bridgeworks and full cast partial. The composition of cobalt and alloying additions and producer recommended properties are presented in Tables 1, 2.

Table 1.
Chemical composition of testing alloys used in studies

Element	Co	Cr	Mo	W	Si	Mn	N	C
Remanium 2000+	61	25	7	5	1,5	< 1	< 1	-
Wirobond LFC	33	30	5	0	0	Fe: 29		<1

Table 2.
Properties of testing alloys used in studies

Properties	Density	Hardness	$R_{p0.2}$	A_5	E	CTE
	g/cm^3	HV_5	MPa	%	GPa	10^{-6} K^{-1}
Remanium 2000+	8,6	340	700	7	200	14,0
Wirobond LFC	8,2	315	660	11	200	15,9

Materials were delivered as cylinders dimension was about 15 mm high and diameter was about 7.8 mm.

2.2. Specimens and heat treatment

After casting all specimens in accordance with procedure was shown in earlier authors work [18] was realized the heat treatment which comprised of two process: solutioning and ageing. The detail process was shown in Table 3. The solutioning was done in high temperature HT 1800 Furnace with application argon as protective atmosphere and cooling in water. The ageing was performed in Thermolyne 6000 Furnace and slow cooling in air.

Table 3.
Solutioning and ageing parameters for study alloy

Heat treatment operation	Temperature [°C]	Time [h]	Cooling medium
Solutioning	1250	3	Water - 25°C quenching
Ageing	850	4	Air
		8	
		16	
		24	

2.3. Research methodology

The most commonly used in studies of corrosion resistance of metallic biomaterials is the potentiodynamic method, which allows the evaluation of corrosion resistance that occurs in body fluids. In those method, the material is subjected to potentiodynamic cyclic anodic polarization, in order to determine the parameters characterizing the corrosion behavior. The potential of the sample (provided in a suitable electrolyte) varies in a linear manner until it reaches a value exceeding the value of the breakdown potential, then with the same rate of potential change in the opposite direction (the initial value) [12].

Methodology of this research includes a metal electrode polarization at a preselected series of potentials. Research was realized using the potentiostat (Fig. 1) for continuous monitoring of the potential of the test electrode by adjusting the amplifier control current flow between the working electrode and an auxiliary electrode [12].

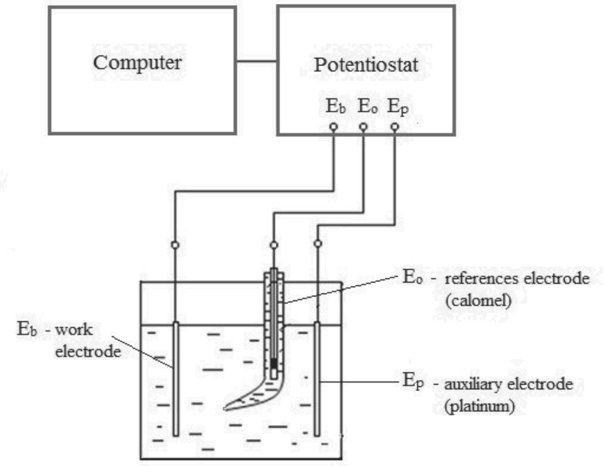

Fig. 1. Scheme of the set to evaluate pitting resistance

During the electrochemical corrosion tests potential is changed with scan rate 2 mV/s, and the current is recorded as a function of potential [12].

The corrosion resistance tests were made in room temperature with use the Potentiostat IPS AJ PGU system for electrochemical tests. The examination were made in water center on composition presented in Table 4. Corrosion resistance tests were carried out accordance with Polish Standard PN-EN ISO 10271:2004 [23]. The standard shows methodology of electrochemical research for dental materials.

For alloys with high corrosion resistance was used platinum as counter electrode, and saturated calomel electrode as a reference electrode - usually coupled with Ługgin's capillary. The range of measurement area was between 0.5 and 1.0 cm^2.

In order to calculate the corrosion current density (i_{cor}), the Stern-Geary equation was used (1). Because it was not possible to evaluate Tafel's b_a and b_k coefficients for each results, corrosion current was estimation using approximated Stern-Geary's equation (2), with assumption that $b_a = b_k = 0.12\ V \cdot dec^{-1}$ [24].

$$i_{cor} = \frac{b_a \cdot b_k}{2{,}3(b_a + b_k)R_p} \tag{1}$$

$$i_{cor} = \frac{0{,}026}{R_p} \tag{2}$$

Where:
b_a - slope coefficient of the anodic Tafel's line
b_k - slope coefficient of the cathodic Tafel's line
R_p - polarisation resistance [Ωcm^2]

Table. 4.
Composition of an artificial saliva by the Fusayama

Element	Content
NaCl	0.4 g/l
KCl	0.4 g/l
$NaH_2PO_4 \cdot H_2O$	0.69 g/l
$CaCl_2 \cdot H_2O$	0.79 g/l
Urea	1.0 g/l
Distilled water	1 l

In the study of electrochemical corrosion was determined: corrosion potential (open circuit potential - E_{ocp}), corrosion current - i_{cor} and pitting potential - E_b.

3. Results and discussion

3.1. Corrosion resistance results

Corrosion current density was determined by analysis of the potentiodynamic polarization curves. The combined polarization curves obtained by asking potential sample from the program in a given direction and set scanning speed are called potentiodynamic curves (Figs. 2, 3). Based on the summary of polarization curves can be evaluated by the progress and rate of the corrosion [25].

Table 5.
Effect of age hardening on electrochemical parameters of testing the Remanium 2000+ cobalt alloys

Samples	Corrosion potential E_{cor} [mV]	Corrosion current density i_{cor} [μA/cm^2]	Breakdown potential E_b [mV]
Solutioning and ageing by 4 hours	-151	0.001	890
Solutioning and ageing by 8 hours	-155	0.0007	827
Solutioning and ageing by 16 hours	-153	0.0006	862
Solutioning and ageing by 24 hours	-131	0.0017	787

Table 6.
Effect of age hardening on electrochemical parameters of testing Wirobond LFC (Bego) cobalt alloys

Samples	Corrosion potential E_{cor} [mV]	Corrosion current density i_{cor} [μA/cm^2]	Breakdown potential E_b [mV]
Solutioning and ageing by 4 hours	-50	0.002	1169
Solutioning and ageing by 8 hours	-154	0.0027	1115
Solutioning and ageing by 16 hours	-96	0.001	1070
Solutioning and ageing by 24 hours	-104	0.0016	1042

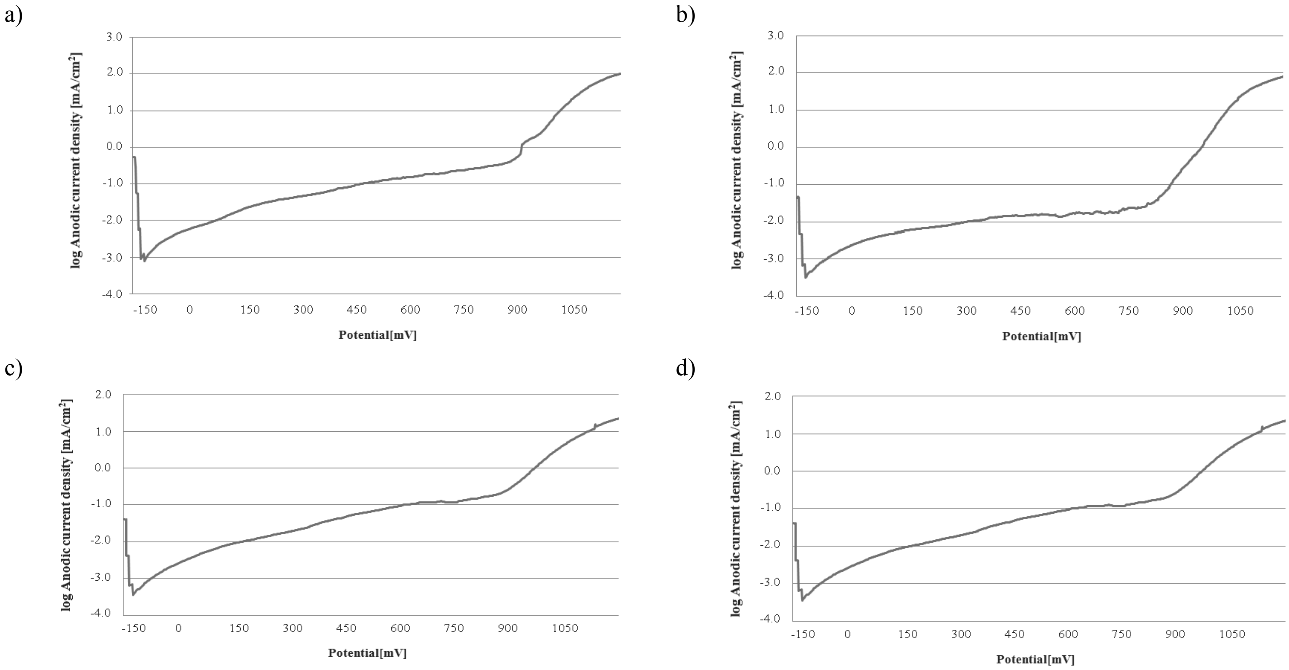

Fig. 2. Potentiodynamic curves of pitting corrosion of Remanium 2000+ (Dentaurum) after different heat treatment conditions: a) solutionized and ageing 4 hours, b) solutionized and ageing 8 hours, c) solutionized and ageing 16 hours, d) solutionized and ageing 24 hours

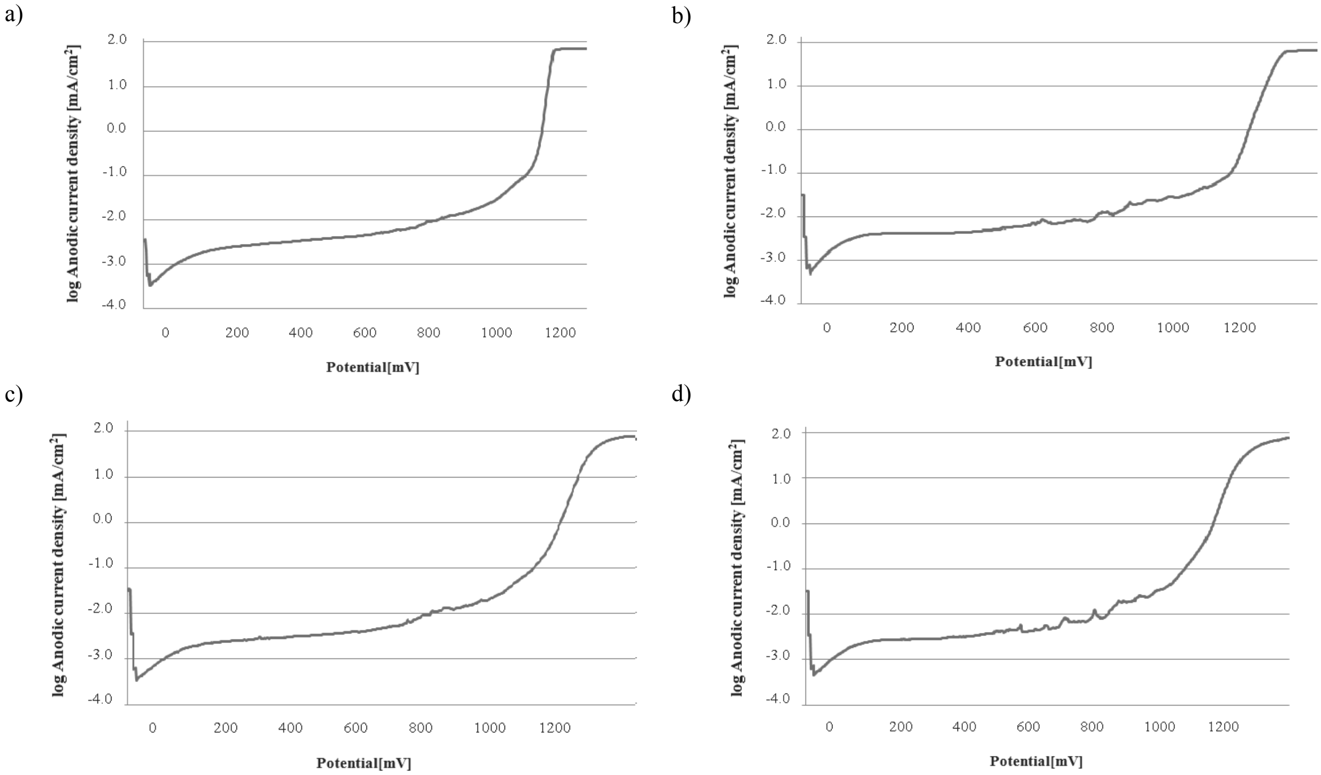

Fig. 3. Potentiodynamic curves of pitting corrosion of Wirobond LFC (Bego) after different heat treatment conditions: a) solutionized and ageing 4 hours, b) solutionized and ageing 8 hours, c) solutionized and ageing 16 hours, d) solutionized and ageing 24 hours

Realized research of pitting corrosion gave an information about electrochemical parameters of cobalt alloys and effect of the age hardening on anticorrosion characteristics (Tables 5, 6). For research was decided that the corrosion current and breakdown potential values were state the corrosion resistance studied materials.

The best corrosion resistance characterized Wirobond LFC alloy after solutioning and ageing by 4 hours, for which breakdown potential amounts to 1169 mV and corrosion current density amounts to 0.002 μA/cm^2. The lowest breakdown potential amounts to 787 mV characterized Remanium 2000+ after solutioning and ageing by 24 hours. Have also been found that increasing, the aging time is result in decrease the breakdown potential both Remanium 2000+ and Wirobond LFC alloys what foster to faster initiate the pits.

3.2. Structure observation

Cobalt alloys in medicine are produced by vacuum metallurgy methods, melted in induction furnaces and casting by the lost wax. Immediately after crystallization in the ceramic mould is obtained of primary structure, which consists of large crystals of the matrix. The matrix is a chemically nonhomogeneous solid solution of chromium, molybdenum and cobalt atoms in the structure of the phase β and carbides type $M_{23}C_6$ distributed along the grain boundaries and in interdendritic spaces (Fig. 5) [26].

The light microscope structures observation of the cobalt alloys for all samples have similar two phases dendritic eutectic microstructure, which is typical for cobalt-base alloy (Figs. 4, 5). Regular construction of dendritic cobalt alloys foundry matrix determines the heterogeneity of distribution of cyclic elements in its composition. During crystallization chromium, carbon, and especially molybdenum gradually enriched interdendritic space and cause nucleation in space of primary carbides as continuous or cell secreted, which are arranged in layers parallel to the branches of dendrites. Continuous change in the share of individual elements induced dendritic segregation and the abrupt change caused by the presence of carbide particles form the total picture of the chemical heterogeneity of the tested alloys.

In the structure (Fig. 5) can be identified as originating from a high temperature casting errors in the form of micropores. In the figures, carbides are $M_{23}C_6$. Occurring in the structure of carbides, are reinforcing phase cobalt alloys. The secondary carbides in the matrix are released, particularly intensively at temperatures of 705-870°C, reducing the alloy plasticity at low temperatures. The controlled degradation of small carbides can be a positive influence on the properties of alloys. Uncontrolled negative dispersion separation and particle size distribution $M_{23}C_6$ lead to a reduction in the plastic properties. Carbides are found only in the second alloy (Wirobond LFC) [26].

Results of metallographic examination by light microscopy performed on the samples after the heat treatment, consisting of solutioning and aging at four different times are shown in Figs. 4-5. The figures shown changes in the structure under the influence of processing done by extending the life of aging 4 by 8 and 16 to 24 hours.

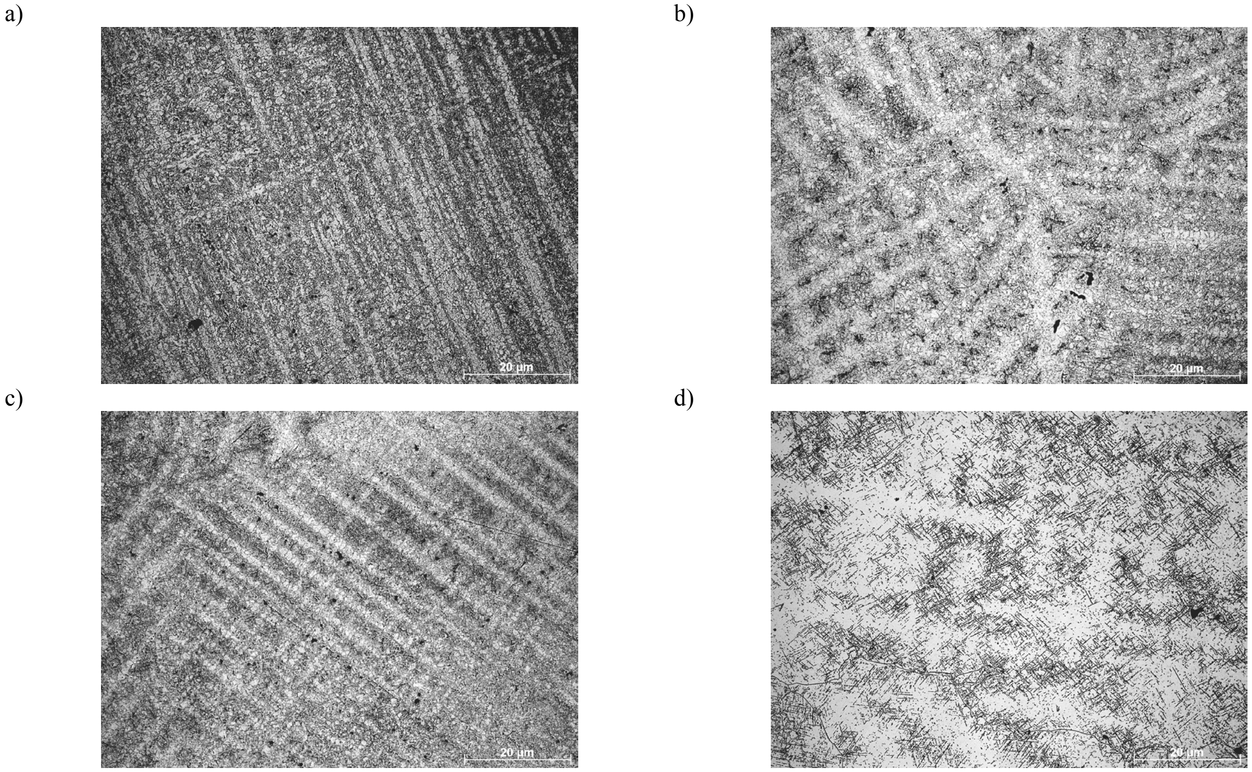

Fig. 4. Structure of research Remanium 2000+ cobalt alloy after ageing by: a) 4 hours, b) 8 hours, c) 16 hours, d) 24 hours.

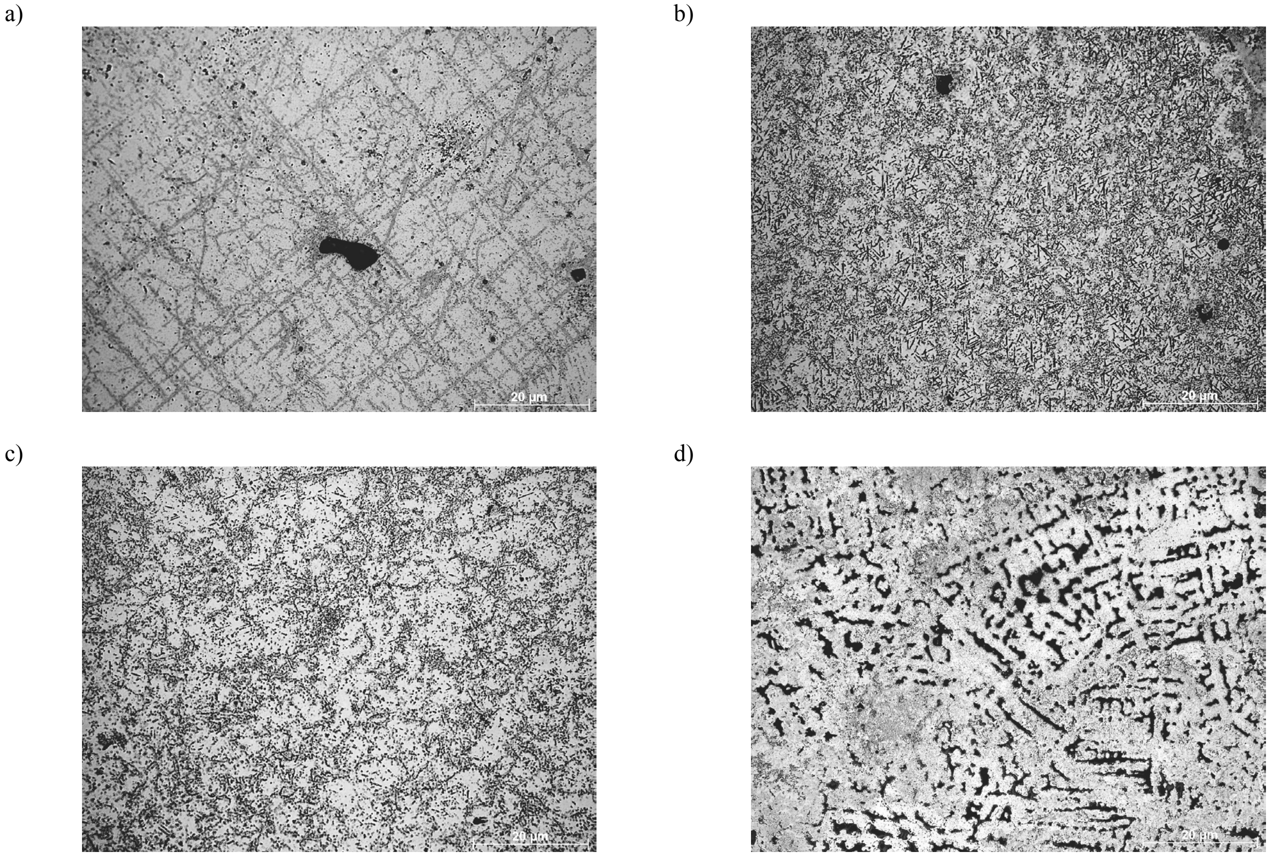

Fig. 5. Structure of research Wirobond LFC (Bego) cobalt alloy after ageing by: a) 4 hours, b) 8 hours, c) 16 hours, d) 24 hours.

4. Conclusions

Realized research has suggested that Wirobond LFC alloy characterized better than Remanium 2000+ anticorrosion protection and the higher values of pitting potential E_b = 937 mV and i_{cor} = 0.002 µA/cm2 was after solutioning and ageing by 4 hours. On the opposite side the worst pitting corrosion protection was characterized Remanium 2000+ alloy after solutioning and ageing by 24 hours: E_b = 727 mV, i_{cor} = 0.0017 µA/cm.

Age hardening has effect on the corrosion resistance especially on the corrosion potential, because if longer ageing time then the potential was decreased.

The microscopic observations show a large number of precipitated $M_{23}C_6$ carbides with high stacking fault energyseparation and plate-type carbides at grain boundaries as a result of aging for more than 4 hours. In addition, the number characterized by faulty arrangement of $M_{23}C_6$ carbides increased with increasing duration of aging, as observed by comparing the figures of the structure. Most of these carbides as discrete contracting separation and dashed lines in the structure of said sample after aging for 24 hours.

The degree of chemical heterogeneity different areas of the crystallites depends on crystallite orientation towards the surface, in the presence of an electrolyte which has an effect on the corrosion resistance of the tested alloys.

Acknowledgements

The presented research was partially funded by the Polish Ministry of Science and Higher Education as a research project No. N N507 438539.

Research was financed partially within the framework of the Scholarship No 51201120 of the International Visegrad Fund realized by Łukasz Reimann, M.Sc., Eng.

References

[1] J. Marciniak, Biomaterials, Silesian University of Technology Library, Gliwice, 2002 (in Polish).
[2] J. Łaskawiec, R. Michalik, Theoretical and applied issues in implants, Silesian University of Technology Library, 2002 (in Polish).
[3] J. Baszkiewicz, M. Kamieński, Corrosion of materials, Publishing House of Warsaw University of Technology, Warsaw, 2006 (in Polish).

[4] A. Ziębowicz, W. Walke, A. Barucha-Kępka, M. Kiel, Corrosion behaviour of metallic biomaterials used as orthodontic wires, Journal of Achievements in Materials and Manufacturing Engineering 27/2 (2008) 151-154.

[5] M. Kiel, A. Krauze, J. Marciniak, Corrosion resistance of metallic implants used in bone surgery, Archives of Materials Science and Engineering 30/2 (2008) 7-80.

[6] M. Kaczmarek, Corrosion resistance of NiTi alloy in simulated body fluids, Archives of Materials Science and Engineering 28/5 (2007) 269-272.

[7] A.D. Dobrzańska-Danikiewicz, J. Żmudzki, Development trends of mucous-borne dentures in the aspect of elastomers applications, Archives of Materials Science and Engineering 55/1 (2012) 5-13.

[8] I. Budak, B. Kosec, M. Sokovic, Application of contemporary engineering techniques and technologies in the field of dental prosthetics, Journal of Achievements in Materials and Manufacturing Engineering 54/2 (2012) 233-241.

[9] B. Walkowiak, Biomedical effect of tissue contact with an implant, Engineering of Biomaterials 7 (2004) 200-205 (in Polish).

[10] M. Hajduga, B. Kalukin, A. Kalukin, Evaluation of the state dental materials after implantation in the human body, Corrosion Protection 4-5 (2009) 166-169 (in Polish).

[11] R. Zuo, Biofilms: strategies for metal corrosion inhibition employing microorganisms, Applied Microbiology and Biotechnology 76 (2007) 1245-1253.

[12] H. Bala, Corrosion of materials - theory and practice, WIPMiFS, Częstochowa, 2002 (in Polish).

[13] M. Nałęcz, Biocybernetics and Biomedical Engineering 2000, Volume 8: medical imaging, Academic Publishing House EXIT, Warsaw, 2003 (in Polish).

[14] L. Klimek, Structure and corrosion resistance of the layers of titanium nitride and carbonitride alloy for dental Wironit, Engineering of Biomaterials 43-44 (2005) 40-43 (in Polish).

[15] R. Craig, J. Powers, J. Watalha, Dental Materials, Medical Publisher, Wrocław, 2010 (in Polish).

[16] J. Marciniak, M. Karczmarek, A. Ziębowicz, Biomaterials in dentistry, Silesian University of Technology Library, Gliwice, 2008 (in Polish).

[17] J. Marciniak, Z. Paszenda, W. Walke, M. Kaczmarek, J. Tyrlik - Held, W. Kajzer, Stents of minimally invasive surgery, Silesian University of Technology Library, Gliwice, 2006 (in Polish).

[18] L.A. Dobrzański, Ł. Reimann, C. Krawczyk, Effect of hardening on corrosion resistance and hardness of CoCrMo alloys used in dental engineering, Archives of Materials Science and Engineering 57/1 (2012) 5-12.

[19] S. Zangeneh, H.R. Lashgari, M. Saghafi, M. Karshenas, Effect of isothermal aging on the microstructural evolution of Co-Cr-Mo-C alloy, Materials Science and Engineering 527/24-25 (2010) 6494-6500.

[20] J.R. Dabrowski, M. Gradzka-Dahlke, The heat treatment of cast cobalt alloys used in dental prostheses, Scientific Papers of Kielce University of Technology, Mechanics 72 (2000) 409-414 (in Polish).

[21] C. Montero-Ocampo, R. Juarez, A. Salinas Rodriguez, Effect of fcc-hcp phase transformation produced by isothermal aging on the corrosion resistance of a Co-27Cr-5Mo-0.05C alloy, Metallurgical and Materials Transactions A 33/7 (2002) 2229-2235.

[22] S. Zangeneh, H.R. Lashgari, A. Roshani, Microstructure and tribological characteristics of aged Co-28Cr-5Mo-0.3C alloy, Materials and Design 37 (2012) 292-303.

[23] Polish Standards PN-EN ISO 10271:2004: Dental metallic materials - Corrosion test methods.

[24] L.A. Dobrzański, Ł. Reimann, Influence of Cr and Co on hardness and corrosion resistance CoCrMo alloys used on dentures, Journal of Achievements in Materials and Manufacturing Engineering 49/2 (2011) 193-199.

[25] L.A. Dobrzański, K. Lukaszkowicz, D. Pakuła, J. Mikuła, Corrosion resistance of multilayer and gradient coatings deposited by PVD and CVD techniques, Archives of Materials Science and Engineering 28/1 (2007) 12-18.

[26] Z. Górny, Cast cobalt alloys, Foundry Institute, Cracow, 2008 (in Polish).