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Corrosion Resistance and Microstructure of Recasting Cobalt Alloys Used in Dental Prosthetics

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Abstract

The work presents the results of the studies of Co-Cr-Mo casting alloys used in the production of frame casts of removable dentures, crowns and bridges in dental prosthetics. The studies were performed on four Co-Cr-Mo alloys of different contents of Mo, W and other additives. Electrochemical tests were performed, which aimed at examining the corrosion resistance of the alloys and observing the alloy structure after chronoamperometric tests with the potential in the area of the occurrence of the passive layer breakpoint. The alloy microstructure images after chronoamperometric tests show the presence of non-uniformly distributed general corrosion. Moreover, a project of cobalt alloy casting was elaborated using a ceramic mold casting. Additionally, analysis of the obtained microstructure was performed. The microstructure of the examined alloys was of the dendrite type. This microstructure was chemically inhomogeneous and consisted of an austenitic matrix formed by a solid cobalt solution and chromium in the core dendritic structure.

Keywords: Investment casting technology, Ceramic moulds, Stomatology, Cobalt alloys, Corrosion resistance

1. Introduction

The tissues found in the oral cavity are subjected to constant changes in the chemical environment, due to the different chemical composition of food and drink. To complement human denture, the resulting loss of teeth in the mouth, are used supplement in the form of prostheses, implants or crowns. They are often made of metals and alloys with very high chemical resistance in saliva solution and other physiological solution enable their use in large-scale dental prosthetics [1]. Very important role, play mechanical properties: tensile strength,

ductility, fatigue life, fretting fatigue life, wear properties and Young's modulus. Cobalt-chromium alloys (Co-Cr) have a better corrosion resistance compared to alloys contain nickel. Therefore, they are used to cast of moving dental prosthesis. Most alloys Co-Cr additionally includes molybdenum (Co-Cr-Mo) and tungsten (Co-Cr-W) [2-3].

Co-Cr alloys with alloying elements have a good resistance to oxidation treatment and corrosion. They are classified as non-toxic and safe to human body, but only with passive layer on the surface. Cobalt alloys are good resistance to pitting corrosion and fatigue crack. Cobalt alloys are low-carbon alloys. High resistance

to creep metal and strength is associated with low-carbon content under 1%. Thermal treatment of cobalt alloys content carbon over 1% promotes the formation of carbide precipitates $M_{23}C_6$. Carbide precipitates $M_{23}C_6$ are located, i.e. $Cr_{23}C_6$ and MC type distributed in the characteristic dendritic bands [4].

Cobalt alloy with chromium is formed by a chemically homogeneous solution. The presence of tungsten and molybdenum provide a much stronger reinforcement of the alloy and formed of intermetallic Co_3M phase. Additionally, the electrochemical corrosion of Co-Cr alloys is significantly dependent on the content of molybdenum, which largely contribute to alloy passivation. Manganese and silicon added to cobalt alloys improve castability [5-9].

Ceramic mold casting is a widely used casting technique of dental elements in which a pattern is usually made of wax. The main advantages of ceramic molds are excellent surface finish and close dimensional tolerances. The production of ceramic forms part of the process, which consists of several stages following one another. Scheme of preparing the ceramic casting mold used in dental prosthetics is presented in Fig. 1.

At the beginning the wax model is created, often with complex shapes. Then, multi-component slurries is prepared. It contains in its composition of refractory filler and binder system. The next step is to dip the wax model in multi-component slurries and application of a coarse-grained refractory stucco. From formed ceramic mold wax is melted, used high pressure in autoclave and empty space remains in ceramic mould.

Pouring the ceramic mould with liquid metal or alloy is performed for dried. Properties of a liquid moulding sand have a significant influence on the morphology of the formed ceramic moulds. Then, the ceramic layer is destroyed and the gating system is removed. The surface of the casting is cleaned mechanically and chemically. The time required for the first castings varies from 8 to 16 weeks [10-12].

The aim of the work was to characterize corrosion resistance and changes in the microstructure after corrosion destruction processes of recasting Co-Cr-Mo alloys as metal materials assigned for dental prosthetics elements.

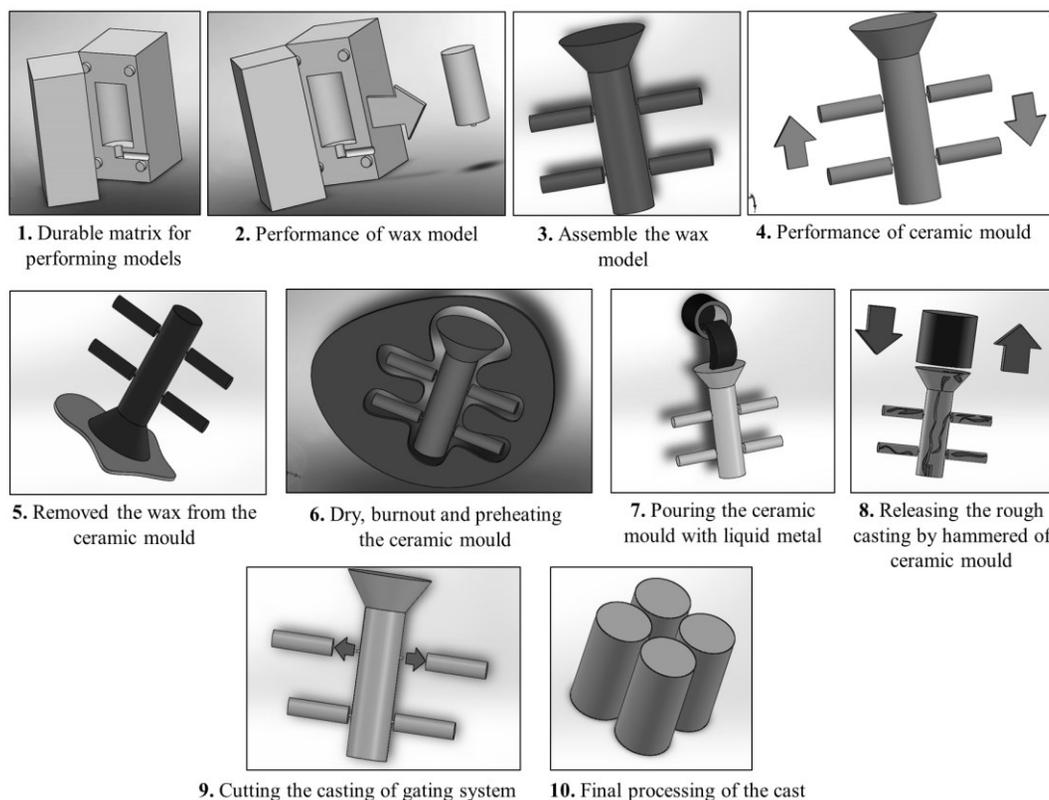


Fig. 1. Scheme of preparing the ceramic casting mold used in dental prosthetics (A. Krzykała)

2. Materials and methods

2.1. Ceramic mold casting

Samples for measurements were prepared in the following way: by ceramic mold casting. The wax patterns were produced

with the shape cylinder. From wax cylinders were created a model system. On degreased wax patterns phosphate, ceramic moulding sand were deposited. Multilayer mould was dried in an autoclave (4 atm.) for a period of 20 min and was annealed in oven. Heating ceramic mold was carried out with isothermal stops (Table 1).

Table 1.
Parameters of preparing the casting mold

Isothermal stops	Temperature, °C	Time, min	Effect
1	250	20	The evaporation of the wax and water from the casting ring
2	600	20	Transformation of the silica took place
3	950	20	The state of the liquid alloys

Casting process was conducted with the use of the Vulcan 3-550 furnace. After casting, the samples were cooled in air. The following stage of the work was removing the refractory as well as mechanical sand blasting with the Ecoblast Kombi machine, granularity 200µm, pressure 0.6 MPa. The final stage included mechanical removal runner.

2.2. Microstructure

The following casting alloys were used in the research: Co-Cr-Mo: Colado CC, Heraenium P, Remanium 2001 and Wironit LA. Chemical compositions of the tested alloys is presented in Table 2.

Table 2.
The chemical compositions of the tested alloys, % wt

Commercial name	Co	Cr	Mo	W	Si	Mn	Ga
Wironit LA	63,5	29,0	5,0		1,2		
Remanium 2001	63,0	23,0	7,3	4,3	1,6		
Colado CC	59,0	25,5	5,5	5,0			3,2
Heraenium P	59,0	25,0	4,0	10	1,0	0,8	

The test samples were mechanical treatment, which consisted of two consecutive processes:

- mechanical grinding with abrasive papers, granulation 120-1200,
- mechanical polishing including the final stages of sample preparation.

The initial polishing involved the use of diamond paste, with the preliminary gradation of 1µm, whereas, during the final polishing, the gradation of ¼ µm was applied. The grinding and polishing processes were performed with the use of a polishing-grinding machine by Struers. In order to reveal the microstructure of the examined materials, the samples underwent chemical etching with the application of the following etching reagents: 1 part of HNO₃ + 3 parts of HCl and 3 parts of HNO₃ + 1 part of HF + 1 part of glycerol.

The test samples were observed with the use of the LEICA DM 4000 optical microscope.

2.3. Electrochemical studies

The aim of the electrochemical measurements was an analysis of the corrosion behaviour of tested alloys. The surface of the electrochemical test-prepared alloys equaled 0,2 cm². Before the electrochemical studies, specimens of the Co-Cr-Mo alloys were polished with the use of abrasive papers made of silicon carbide (SiC) with the granularity of up to 4000. The corrosive environment was artificial saliva (pH = 7,4). The tests were carried out at 37°C. The composition of the artificial saliva is given in Table 3.

Table 3.
Chemical composition of artificial saliva [13]

Component	Quantity [g/l]
NaCl	0,7
KCl	1,2
KH ₂ PO ₄	0,2
NaHCO ₃	1,5
Na ₂ HPO ₄ x 2H ₂ O	0,33
KSCN	0,33

There were used following electrochemical techniques: open circuit potential, the polarization measurements with a potential scan rate of 1mV/s and chronoamperometry at constant potential equaled +0,8V.

The electrochemical studies of the samples were carried out using a potentiostat Autolab PGSTAT302N. The measurements were performed using a classical three-electrode cell, where the working electrode was a Co-Cr-Mo alloys. Potentials were measured vs. Ag/AgCl in 3 mol/l KCl and the counter electrode was made of platinum wire.

3. Results and discussions

The performed microscopic observations made it possible to reveal the microstructure of the examined Co-Cr-Mo alloys. The test materials were observed with the magnifications of 200x and 1000x, by means of an optical microscopy (Fig. 2 a,b,c,d).

The examinations with the use of an optical microscopy showed that the analyzed primary structure of the tested alloys, after crystallization, has a dendritic microstructure characteristic for cast materials.

This microstructure is chemically homogeneous and consists of an austenitic matrix formed by a solid cobalt solution and chromium in the core dendritic structure. According to the literature data [6, 8, 14-17], in the interdendritic spaces, carbide precipitates M₂₃C₆ are located, i.e. Cr₂₃C₆ distributed in the characteristic dendritic bands. These carbides constitute the main source of the material's reinforcement.

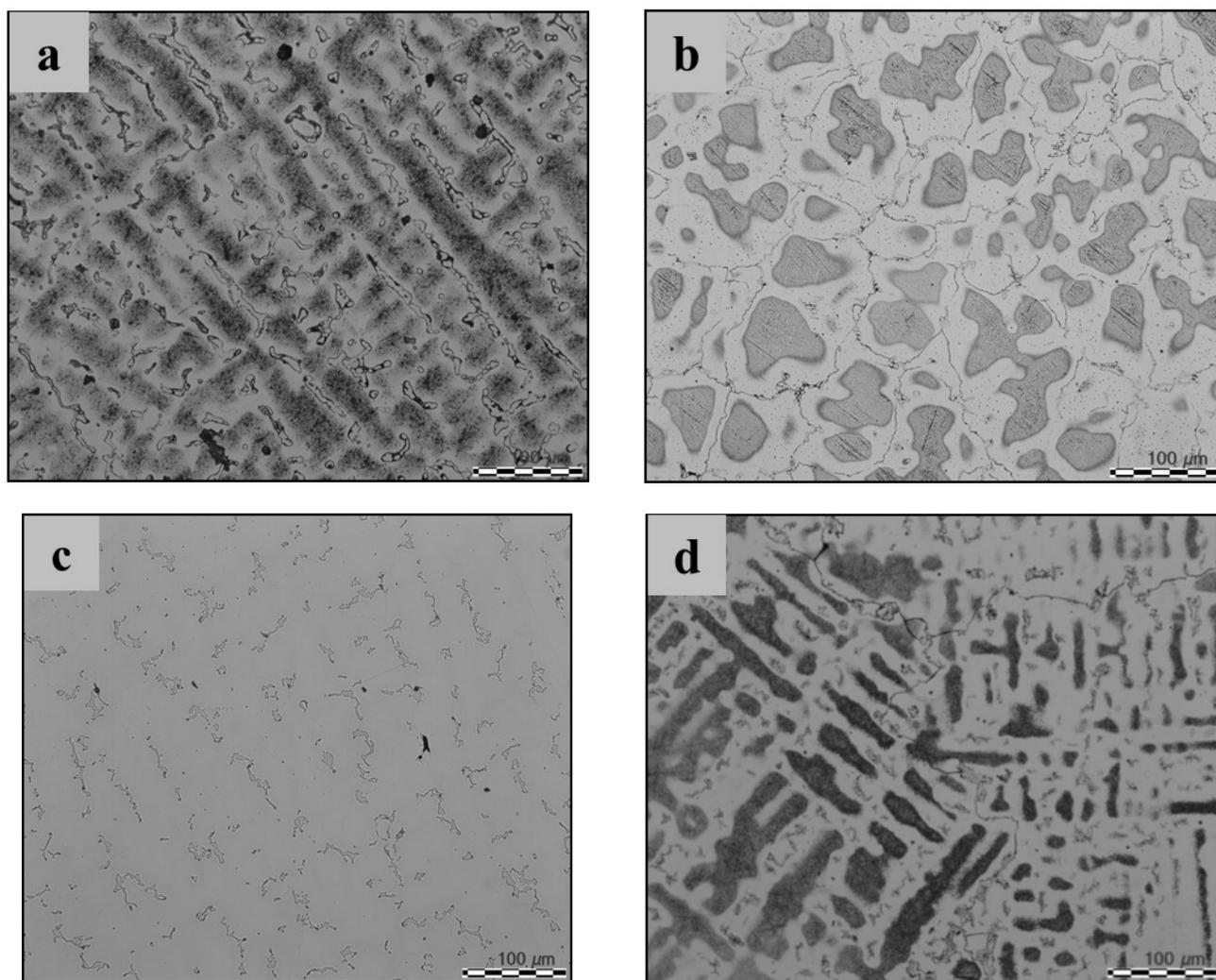


Fig. 2. Microstructure of investigated alloys: a) Colado CC, b) Heraenium P, c) Remanium 2001, d) Wironit LA

For each tested alloy, the open circuit potential as a function of time in the examined solution was determined. Stationary corrosion potential (Fig.3) decreased for each alloy and reached a stable value after about 1h 40 minutes (6000s). The potential value for all of investigated alloys was similar and equalled about -0,50V.

Figure 4 shows the voltamperometric curves running in the anodic direction as well as the voltamperometric curves running in the cathodic direction. The potential in the anodic direction equalled: -0,42 V for alloys Colado CC and Remanium 2001; -0,47 V for alloy Wironit LA; and -0,32 V for alloy Heraenium P. In the cathodic direction, the potential value equalled respectively: -0,51 V for alloys Colado CC and Wironit LA; -0,33 V for Remanium 2001 alloy; and +0,13 V for Heraenium P alloy. In such cases, the corrosion rate can be defined by the limiting current density which passes through the passivating film, thus becoming a measure of the film protective performance [18].

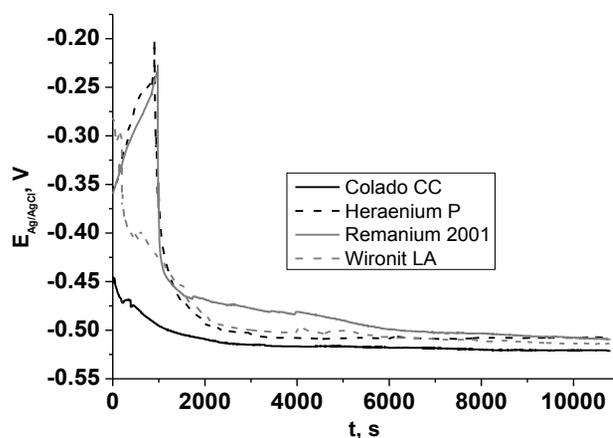


Fig. 3. Evolution of open circuit potential vs time of tested cobalt alloys in artificial saliva, temp. 37°C

The passivation area of Heraenium P alloy within the range of about $-1 \div +0,6$ V, comparable to the other alloys, as well as the shift of the anodic-cathodic potential towards positive values ($-0,32$ V) and the lowest values of the current density in the passive area ($\sim 0,7$ mA/cm²), point to the best corrosion resistance of the considered material. A slightly higher current density values in the passive area were recorded for alloy Colado CC. Remanium 2001 and Wironit LA alloys characterized in a similar course of the polarization curves and the highest current density value equaling about 1 mA/cm². The cobalt compounds are largely responsible for the passive state of those alloys [19-21]. Above the potential of about 0,65 V for Colado CC 0,90V for Heraenium P, 0,81V for Remanium 2001 and 0,80V for Wironit LA we can see a clear increase of the current density values for all the examined alloys, what is corresponding to breakdown of the passive layer and the initiation of corrosion processes of the alloys.

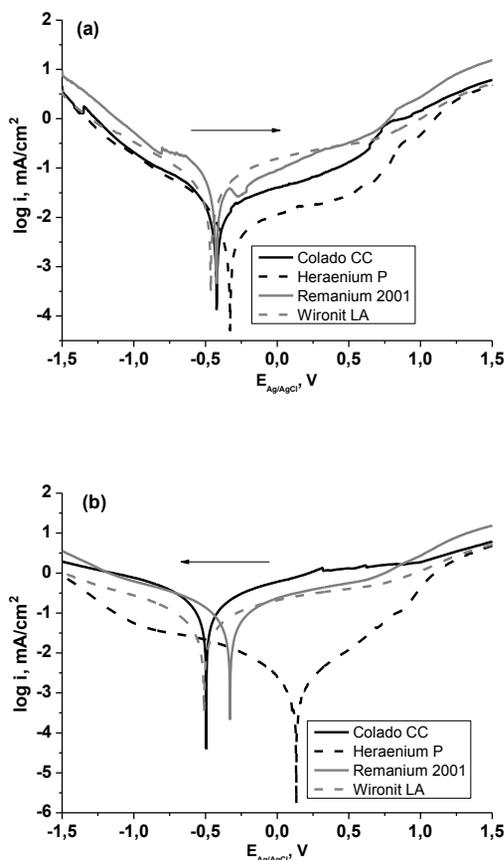


Fig. 4. Polarization curves of Co-Cr-Mo alloys in artificial saliva (a) anodic, and (b) cathodic direction

Figure 5 presents the results of the chronoamperometric polarization tests with the constant potential of $+0,8$ V vs. Ag/AgCl for all the alloys. The potential value set for the chronoamperometric polarization tests was selected based on the results of the polarization curve examinations. With this potential value, we observe a breakdown of the passive layer and the initiation of corrosion processes of the investigated materials.

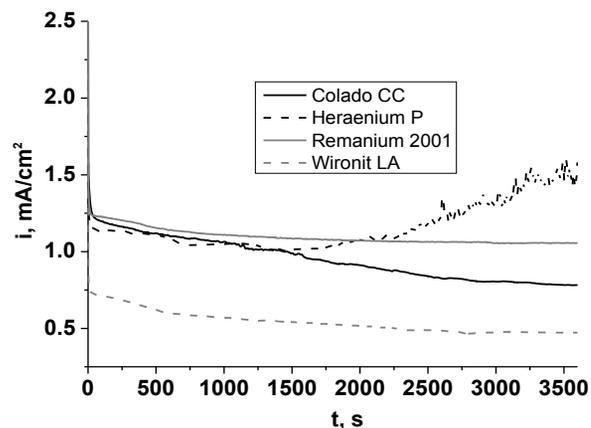


Fig. 5. Chronoamperometry measurement performed for Co-Cr alloys at a constant potential ($E_{Ag/AgCl} = +0,8$ V)

Figure 6 shows the surface of alloy Wironit LA after chronoamperometric tests. All the alloys characterized in the presence of non-uniformly distributed general corrosion in the area of the passive layer breakdown.

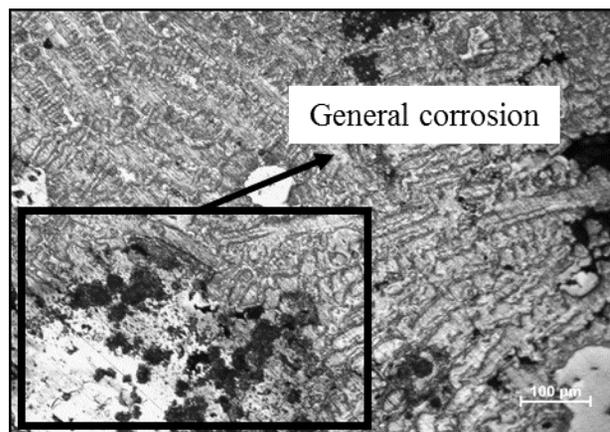


Fig. 6. Microstructure of Wironit LA alloy after chronoamperometry measurement at $+0,8$ V

3. Conclusions

- 1) All the examined casting alloys characterize in a good corrosion resistance in the solution of artificial saliva.
- 2) Alloy Heraenium P exhibited the best corrosion resistance as compared to the remaining alloys.
- 3) Based on the alloys' chemical composition analysis, we can conclude that high tungsten content significantly improved the corrosion resistance of alloy Heraenium P.
- 4) All four alloys: Colado CC, Remanium 2001, Heraenium P, Wironit LA, after chronoamperometric tests with the constant potential of $+0,8$ V, exhibited the presence of non-uniformly distributed general corrosion.

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References

- [1] Khamis, E. & Seddik, M. (1995). Corrosion evolution of recasting non – precious dental allays. *International Dental Journal*. 45(3), 209-17.
- [2] Biomedical materials: Laboratory of materials science. Lodz University of Technology, Faculty of Mechanical Engineering, Institute of Materials Science and Engineering. Retrieved May 15, 2016, form <http://iim.p.lodz.pl/media/materialy/mat-kier-MiBM-AiR-PiP/Trans/Cwiczenie%2013.pdf> (in Polish).
- [3] Górny, Z. (2008). Foundry cobalt alloys. Structure, properties, melting and casting. *Foundry Review (Przegląd Odlewnictwa)*. 58(7-8), 420-430. (in Polish).
- [4] Giachci, J.V., Morando, C.N., Fornaro, O. & Palacio, H.A. (2011). Microstructural characterization of as - cast biocompatible Co-Cr-Mo alloys. *Materials Characterization*. 62(1), 53-61.
- [5] Augustyn-Pieniążek, J. & Wilkosz, K. (2013). Structural defects of metallic prosthetic dental. *Modern Dental Technician (Nowoczesny Technik Dentystyczny)*. 2, 30-36 (in Polish).
- [6] Hajduga, M., Kosiba A. (2004). Analysis of typical casting defects of metallic prostheses. *Research Journals of the Faculty of Applied Mechanics. Silesian University of Technology*. 24, 99-104 (in Polish).
- [7] Surowska, B., Beer, K., Borowicz, J. & Veremchuk, J. (2011). Effect of the casting technology on the quality of a stomatological cobalt alloy. *Progress of Science and Technology (Postęp Nauki i Techniki)*. 11, 81-88. (in Polish).
- [8] Craig, R.G., Powers, J.M. & Wataha, J.C. (2008). *Dental Materials*. Wrocław. Elsevier Urban & Partner.
- [9] Polak, A. (2005). The theoretical basis and practical guidance in the field of foundry. *Nowoczesny Technik Dentystyczny*. 2, 28-36. (in Polish).
- [10] Gawroński, J., Szajnar, J., Stawarz, M., Wojarski, T. (2013). *Artistic Casting*. Gliwice. Silesian University of Technology (in Polish).
- [11] Lewandowski, J. (1997). *Materials for molds*. Krakow. Akapit (in Polish).
- [12] Yuan, C. & Jones, S. (2003). Investigation of fibre modified ceramic moulds for investment casting. *Journal of the European Ceramic Society*. 23, 399-407.
- [13] PN – EN ISO 10993 – 15, Biological evaluation of medical devices – Vol. 15; Identification and quantification of degradation products identified metals and alloys 2005 (in Polish).
- [14] Augustyn-Pieniążek, J., Łukaszczyk, A., Szczurek, A. & Sowińska, K. (2014). Structure and properties of dental cobalt alloys used to perform framed dentures. *Materials Engineering*. 34(2), 116-120. (in Polish).
- [15] Yamanaka, K., Mori, M. & Chiba, A. (2014). Effects of carbon concentration on microstructure and mechanical properties of as cast nickiel – free Co-28Cr-9W-based dental alloys. *Materials Science and Engineering C*. 40, 127-134.
- [16] Podrez-Radziszewska, M., Haimann, K., Dudziński, W. & Morawska-Sołtysik, M. (2010). Characteristic of intermetallic phases in cast dental CoCrMo alloy. *Archives of Foundry Engineering*. 10(3), 51-56.
- [17] Giacci, J.V., Morando, C.N., Fomaro, O. & Palacio, H.A. (2011). Microstructural characterization of as-cast biocompatible Co-Cr-Mo alloys. *Materials Characterization*. 62, 53÷61.
- [18] Mc Cafferty, E. & Hubler, G.K. (1978). Electrochemical behavior of palladium-implanted titanium. *Journal of the Electrochemical Society*. 125(11), 1892-1893.
- [19] Metikos-Huković, M., Pilić, Z., Babić, R. & Omanović, D. (2006). Influence of alloying elements on the corrosion stability of CoCrMo implant alloy in Hank's solution. *Acta Biomaterialia*. 2(6), 693-700.
- [20] Augustyn-Pieniążek, J., Łukaszczyk, A. & Zapala, R. (2013). Microstructure and corrosion resistance characteristics of Co-Cr-Mo alloys designed for prosthetic materials; *Archives of Metallurgy and Materials*. 58(4), 1281-1285.
- [21] Loch, J., Łukaszczyk, A., Augustyn-Pieniążek, J. & Krawiec, H. (2015). Electrochemical behaviour of Co-Cr and Ni-Cr dental Alloy. *Solid State Phenomena*. 227, 451-454.