

# Chemical passivation as a method of improving the electrochemical corrosion resistance of Co-Cr-based dental alloy

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*Purpose:* The purpose of the study was to evaluate corrosion resistance of Wirobond C® alloy after chemical passivation treatment. *Methods:* The alloy surface undergone chemical passivation treatment in four different media. Corrosion studies were carried out by means of electrochemical methods in saline solution. Corrosion effects were determined using SEM. *Results:* The greatest increase in the alloy polarization resistance was observed for passive layer produced in Na<sub>2</sub>SO<sub>4</sub> solution with graphite. The same layer caused the highest increase in corrosion current. Generally speaking, the alloy passivation in Na<sub>2</sub>SO<sub>4</sub> solution with graphite caused a substantial improvement of the corrosion resistance. The sample after passivation in Na<sub>2</sub>SO<sub>4</sub> solution without graphite, contrary to others, lost its protective properties along with successive anodic polarization cycles. The alloy passivation in Na<sub>3</sub>PO<sub>4</sub> solution with graphite was the only one that caused a decrease in the alloy corrosion properties. The SEM studies of all samples after chemical passivation revealed no pit corrosion – in contrast to the sample without any modification. *Conclusions:* Every successive polarization cycle in anodic direction of pure Wirobond C® alloy enhances corrosion resistance shifting corrosion potential in the positive direction and decreasing corrosion current value. The chemical passivation in solutions with low pH values decreases susceptibility to electrochemical corrosion of Co-Cr dental alloy. The best protection against corrosion was obtained after chemical passivation of Wirobond C® in Na<sub>2</sub>SO<sub>4</sub> solution with graphite. Passivation with Na<sub>2</sub>SO<sub>4</sub> in solution of high pH does not cause an increase in corrosion resistance of WIROBOND C. Passivation process increases alloy resistance to pit corrosion.

*Key words:* corrosion resistance, dental alloys, electrochemical test, chemical passivation

## 1. Introduction

Metal alloys, commonly applied in dental prosthodontics, i.e., austenitic steel, Co-Cr alloys and titanium alloys exhibit lower corrosion resistance and induce stronger biological response in comparison to the alloys with high precious metal content. Studies aiming at the alloy surface protection against influence of aggressive environments have been carried out for years. In the case of medical application,

these studies are connected with biological property enhancement [10], [14], [30].

The improvement in passive properties of metal surface in human body environment is the next method, that should improve corrosion resistance of the so called non-noble metal alloys [1], [8], [11], [21], [22], [25], [26], [28]. Passivity is the state in which corrosivity is considerably decreased. This is a result of protective layer formation on the alloy surface. Alloys covered by such layers exhibit higher electrochemical potential than in an active state. Beside self-passivation specific for some

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metals and alloys, passivity can be gained by means of chemical interactions with adequate passivator or with electrochemical passivation [4], [24], [29], [33]. Passive layers should exhibit low ionic conduction, low solubility, high abrasion resistance and adhesion.

Biocompatibility of Co-Cr-Mo alloys is connected with high corrosion resistance, which results from intrinsic passive layer formation on the alloy surface [15]–[19]. Unfortunately, these alloys were often found to release ions in human body environment [3], [6], [7]. It could be possibly caused by passive layer solubility as a result of metal ion diffusion through the layer, pulping in transpassivation conditions or local damage of passive layer as a result of local corrosion, or mechanical damage. There is little literature on electrochemical properties, chemical composition or modifications of passive layers on Co-Cr-Mo alloys. The passivation of acid resistant steels and titanium alloys applied in medicine has been intensively investigated [5], [12]. Most of the previous studies on Co-Cr-Mo alloys concentrate on abrasion resistance evaluation of these alloys and on depassivation processes in the test on mechanical superficial scratch of surface alloys [9], [20], [27], [31], [32].

The aim of the study was to evaluate the influence of chemical passivation treatment of Co-Cr alloy surface on corrosion resistance.

## 2. Materials and methods

The samples made of Co-Cr alloy (Wirobond C<sup>®</sup>, Bego, Bremen, Germany) were casted by means of a rotary method. The chemical composition of Wirobond C<sup>®</sup> is shown in Table 1.

Table 1. The chemical composition of Wirobond C<sup>®</sup>

Wirobond C	Co [%]	Cr [%]	Mo [%]	W [%]	Si, Fe, Ce [%]
	61	26	6	5	<2

Alloy samples in the shape of a cylinder (11 mm in diameter and 5 mm in height) were fabricated as follows: Frontal surfaces were mechanically polished using water with abrasive paper ranged from 80 to 2000 grain. Next, samples were polished with polishing paste. Every sample was washed, degreased and dried with compressed air.

The following reagents were used during passivation process of Wirobond C<sup>®</sup> samples:

– Solution of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O (pH = 7);

(a passivating solution of 25 grams per liter Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O).

- Solution of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O (pH = 7) + graphite.
- Solution of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O (pH = 12) + graphite;
- Solution of NaNO<sub>3</sub> + Cr(III) + Co(II) (pH = 1.89); (a passivating solution of 7 grams per liter NaNO<sub>3</sub>·12H<sub>2</sub>O + 15 grams of Co<sub>2</sub>N<sub>3</sub> \* 6 H<sub>2</sub>O + 13 grams CrCl<sub>3</sub> \* H<sub>2</sub>O to which nitric acid was added to adjust the pH to pH 1.89).

Sodium salts were selected to achieve non-aggressive oxyanions that promote the formation of a uniform passive layer on the alloy surface, but does not chemically react with the alloy surface. By using the graphite rod we achieved galvanic passivation: passivation with the macroscopic separation of the anodic and cathodic processes.

Passivation process was carried out by 24-hour immersion in a reagent at the temperature of 20 °C. Next, the corrosion resistance study was performed and the results were collected with the control sample (without modification).

For each sample the following measurements by means of AUTOLAB electrochemical study set were performed:

- polarization resistance Rp, curvature points distant from corrosion potential up to 30 mV were approximated. The polarization resistance was calculated from linear dependence of current intensity from potential in this range.
- potentiodynamic study: corrosion potential value and corrosion current value were obtained upon approximation of function in the cathodic and anodic range in the area close to linear dependence of current intensity from potential (in the distance not smaller than 20 mV from potential value, for which the current intensity exhibits minimal value – Tafel's range).

Each sample undergone three polarization cycles.

Samples were initially degreased in ethanol and mounted successively in a vessel filled with 0.9% aqueous solution of NaCl in the manner that the submerged surface amounted to 1.73 cm<sup>2</sup>. A platinum strip above the sample served as a counter electrode. The reference electrode was a saturated calomel electrode with electrolytic bridge terminated with a Luggin capillary. The anodic polarization was carried out for all samples about 120 min after submersion. Measurements were taken with the speed of 1mV/s. All potential values were calculated for the saturated calomel electrode ( $E^0 = 0.241$  V vs. SHE).

The surface condition of all samples after corrosion study was evaluated in the scanning microscope Hitachi S-3000N.

### 3. Results

The dependence of current intensity from potential for three successive anodic polarization cycles (in the potential range from  $-400$  to  $-100$  mV) performed on the sample without passivation is shown in Fig. 1.

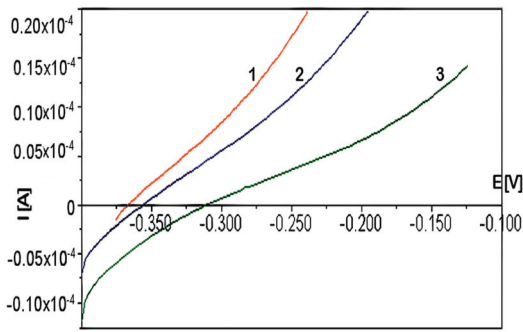


Fig. 1. Dependence  $I = f(E)$  for unmodified sample. 1 – first polarization series, 2 – second polarization series, 3 – third polarization series

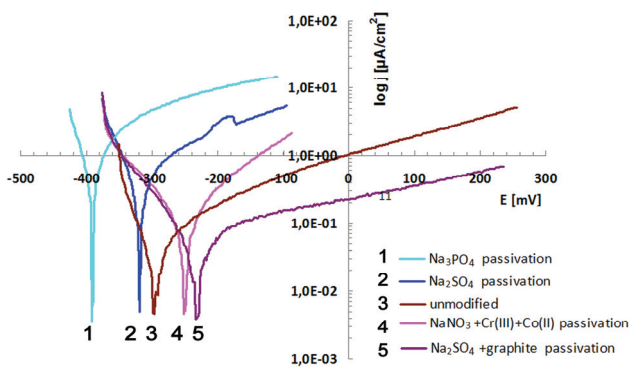


Fig. 2. Polarization curves for passivated samples of Wirobond C<sup>®</sup> alloy and the unmodified

Figure 2 presents cumulative polarization curves for all underground evaluation. Table 2 shows the values of the corrosion current ( $I_{cor}$ ) and corrosion

potential ( $E_{cor}$ ) calculated after extrapolation linear ranges of polarization curvatures in the range of Tafel curvatures, for three polarization cycles performed successively on each sample. After that, the influence of successive anodic polarization cycles on polarization resistance was calculated (for each one of the samples) using both linear polarization method and the above-mentioned Tafel's method. Results of these calculations are presented in Fig. 3a and 3b.

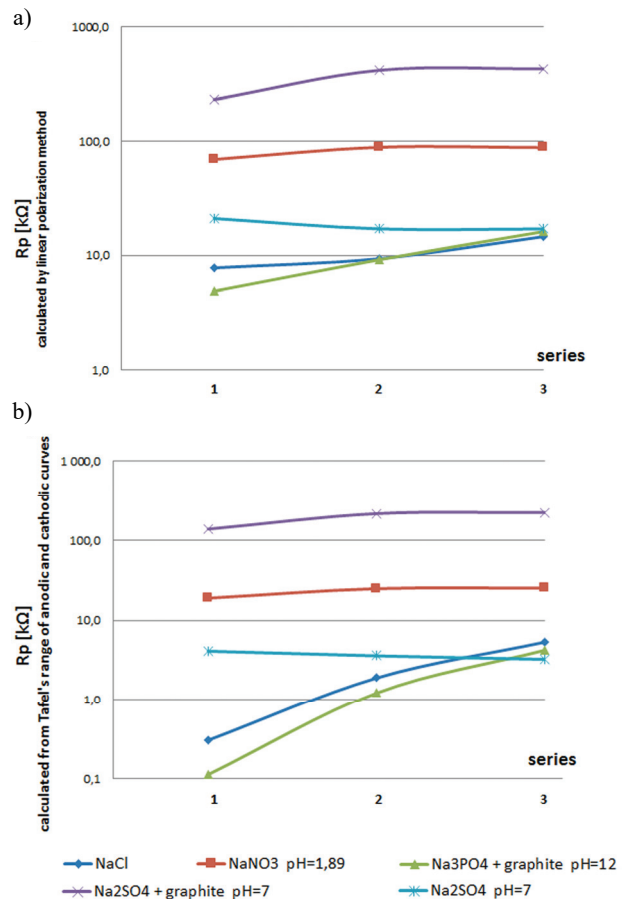


Fig. 3. The influence of consecutive polarization series on the polarization resistance  $R_p$ : a) the linear polarization method; b) the extrapolation of linear polarization curves in Tafel's range

Table 2. Values of corrosion current ( $I_{cor}$ ), corrosion potential ( $E_{cor}$ ) for all passivated and unmodified samples of Wirobond C<sup>®</sup> alloy

Passivation type	Corrosion Current $I_{cor}$ [ $\mu$ A]			Corrosion Potential $E_{cor}$ [mV]		
	Series I	Series II	Series III	Series I	Series II	Series III
Unmodified	1.590	1.740	1.670	-367	-356	-310
Na <sub>3</sub> PO <sub>4</sub> +graphite	1.147	1.866	1.724	-372	-391	-395
Na <sub>2</sub> SO <sub>4</sub>	0.695	0.940	0.862	-319	-330	-329
NaNO <sub>3</sub>	0.272	0.205	0.211	-261	-254	-254
Na <sub>2</sub> SO <sub>4</sub> +graphite	0.119	0.101	0.104	-230	-223	-222

## 4. Discussion

Wirobond C<sup>®</sup> alloy exhibited considerable corrosion resistance, which manifested as a wide passive range and low corrosion current resulting from also the polarisation resistance is reasonably high and the corrosion potential properly high. This observation was confirmed by corrosion study. Each subsequent anodic polarization cycle enhanced anticorrosive properties of Wirobond C, which was expressed by the shift of corrosion potential to the positive direction – thanks to progressing self-passivation of alloy (Fig. 1, Table 2).

In the literature, methods used to increase corrosion resistance by means of surface modification of Co-Cr alloys mainly refer to electrochemical passivation with potential in passive range [13], [23], [28] and are thought to improve in electrochemical corrosion resistance.

It is worth underlining that in the present study on the surface modification by means of chemical and galvanic passivation in salt solutions as alternative to typical passivating medium such as nitric acid was applied [2], [28]. The creation and evaluation of this passivation method has not been presented in the literature, yet. Result analysis of Wirobond C alloy surface modification with potentiodynamic method (Fig. 2) shows that the polarization curves for chemical passivation in Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub> and NaNO<sub>3</sub> solutions represented higher current values in anodic range than the control sample. However, the passivation in Na<sub>2</sub>SO<sub>4</sub> solution with graphite resulted in the decrease of current values in anodic range. Moreover, the passivation in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> solutions resulted in the shift of polarisation curves to positive values. Other passivation method caused unfavourable decrease in corrosion potential.

Parameters defining material corrosion properties that were determined with the extrapolation of linear polarization curves in Tafel's range, i.e., corrosion potential ( $E_{cor}$ ), polarization resistance ( $R_p$ ), corrosion current ( $I_{cor}$ ) (the latest additionally verified with linear polarization method) (Tab. 2, Fig. 3a, b), clearly indicated the increasing corrosion resistance of Wirobond C alloy after chemical passivation in Na<sub>2</sub>SO<sub>4</sub> solution with graphite and NaNO<sub>3</sub> solutions. Both corrosion potential ( $E_{cor}$ ) and polarization resistance ( $R_p$ ) increased after passivation with concurrent decrease in corrosion current ( $I_{cor}$ ). It was confirmed by the increase in  $E_{cor}$  and  $R_p$  and the decrease in  $I_{cor}$  with each polarisation cycle. The opposite effect was observed for alloys after modification in Na<sub>2</sub>SO<sub>4</sub> solution and particularly in Na<sub>3</sub>PO<sub>4</sub> solution.

The best electrochemical corrosion resistance in the environment of 0.9% NaCl solution exhibited the alloy passivated in Na<sub>2</sub>SO<sub>4</sub> solution with graphite. Corrosion current ( $I_{cor} = 0,119 \mu\text{A}$ ) (for the 3rd cycle:  $0,104 \mu\text{A}$ ) was three-fold lower than for pure Wirobond C. The corrosion potential was shifted in the positive direction: from value of  $-367 \text{ mV}$  for alloy without passivation to value of  $-230 \text{ mV}$ , and polarization resistance ( $R_p$ ) increased of two orders of magnitude. Anticorrosion parameters of alloy after passivation in NaNO<sub>3</sub> solutions were slightly worse than for the above-mentioned modification, although still higher than for pure self-passivating Wirobond C alloy. In this case, the corrosive current decreased upto the value of  $0.272 \mu\text{A}$  in comparison to  $I_{cor} = 1,590 \mu\text{A}$  for pure Wirobond C. The corrosion potential ( $E_{cor}$ ) increased by over  $100 \text{ mV}$  and polarization resistance ( $R_p$ ) was several times higher than for pure alloy.

The alloy passivation in Na<sub>3</sub>PO<sub>4</sub> solution with graphite was the only one that caused a decrease in the alloy corrosion properties. This could result from the high pH of the solution ( $\text{pH} = 12$ ). The sample after passivation in Na<sub>2</sub>SO<sub>4</sub> solution without graphite (in contrast to others) lost its protective properties together with successive anodic polarization cycles.

In the present study only 24-hour chemical passivation was observed. It can be expected, that the increase in corrosion resistance with chemical passivation by means of different passivators can be optimised by the proper choice of time, temperature and medium of passivation.

The surface conditions of all samples after corrosion study are shown in the Figs. 4 and 5. The SEM studies of all samples after chemical passivation revealed no pit corrosion – in contrast to the sample

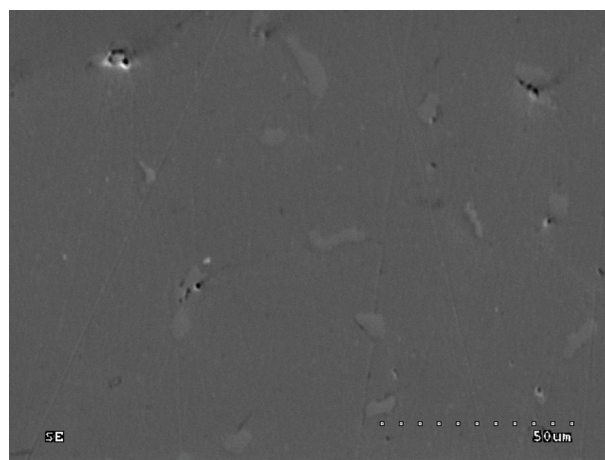


Fig. 4. SEM-SE micrograph of unmodified Wirobond C<sup>®</sup> surface. Pit corrosion can be observed



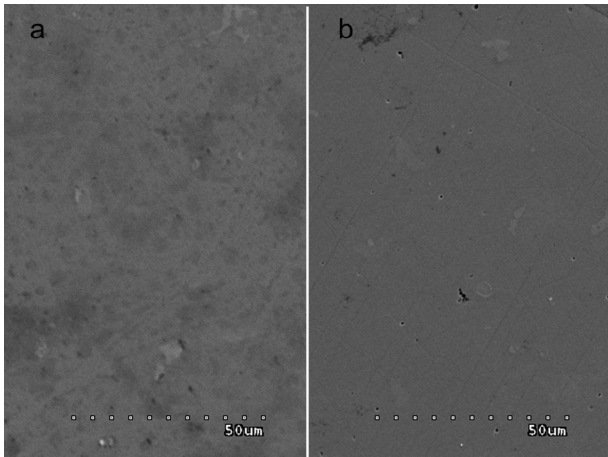


Fig. 5. SEM-SE micrograph: a)  $\text{Na}_2\text{SO}_4$  passivated Wirobond C<sup>®</sup> surface; b)  $\text{Na}_2\text{SO}_4 + \text{C}$  passivated Wirobond C<sup>®</sup> surface. No pit corrosion can be observed

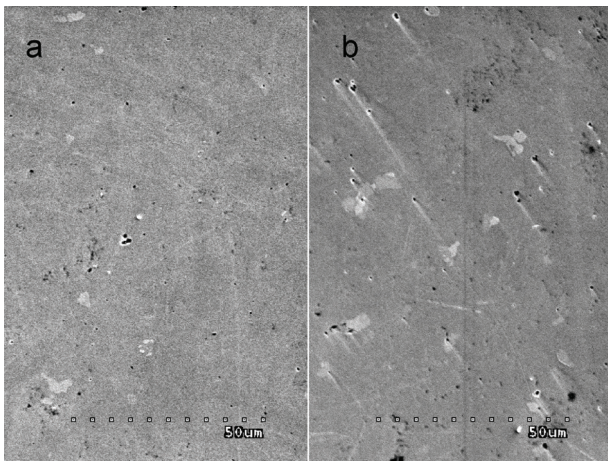


Fig. 6. SEM-SE micrograph: a)  $\text{NaNO}_3$  passivated Wirobond C<sup>®</sup> surface; b)  $\text{Na}_3\text{PO}_4 + \text{C}$  passivated Wirobond C<sup>®</sup> surface. The defects left on the sample as a result of carbide loss can be observed

without any modification (Fig. 4). The passive layers show no signs of cracking. The defects left on the sample as a result carbide loss during sample polishing could be seen only on the surface modified by means of  $\text{Na}_3\text{PO}_4$  with graphite (Fig. 6b). Few casting pores were detected on samples shown on Figs. 4, 6a, and 6b. The quality enhancement of castings through elimination of pores would, in all probability, have a positive influence on the corrosion resistance.

## 5. Conclusions

The general conclusion from this study is that passivation enhances corrosion resistance. More specifically, it can be stated that:

1. Every successive (out of three) polarization cycle in anodic direction of pure Wirobond C<sup>®</sup> alloy enhances corrosion resistance shifting corrosion potential in the positive direction and decreasing corrosion current value.
2. The chemical passivation in solutions with low pH values decreases susceptibility to electrochemical corrosion of Co-Cr dental alloy.
3. The best protection against corrosion was obtained after chemical passivation of Wirobond C<sup>®</sup> in  $\text{Na}_2\text{SO}_4$  solution in the presence of graphite. This passivation process caused an increase in corrosion potential value by more than 130mV in relation to alloy without surface modification.
4. Passivation with sodium phosphate in a solution of high pH causes an decrease in corrosion resistance of Wirobond C<sup>®</sup> alloy.
5. Passivation with  $\text{Na}_2\text{SO}_4$  solution do not enhance electrochemical corrosion resistance of alloy.
6. Passivation process increases alloy resistance to pit corrosion.

## References

- [1] AMATO L.E., LOPEZ D.A., GALLIANO P.G., CERE S.M., *Electrochemical characterization of sol-gel hybrid coatings in cobalt-based alloys for orthopedic implants*, Mater Lett., 2005, 59, 2026–2031.
- [2] ASTM F-86 Standard Practice for Surface Preparation and Marking for Surgical Implants.
- [3] CHANG J.-CH., OSHID Y., GREGORY R.L., ANDRES C.J., BARCO T.M., BROWN D.T., *Electrochemical study on microbiology-related corrosion of metallic dental materials*, Bio-Med. Mater Eng., 2003, 13, 281–295.
- [4] CHENG X., MA H., CHEN SH., NIU L., LEI SH., YU R., YAO Z., *Electrochemical behavior of chromium in acid solutions with  $\text{H}_2\text{S}$* , Corros. Sci., 1999, 41, 773–788.
- [5] DE NARDO L., ALTOMARE L., DEL CURTO B., CIGADA A., DRAGHI L., *Electrochemical surface modifications of titanium and titanium alloys for biomedical applications*, Titanium and titanium alloys for biomedical applications, Woodhead Publishing Limited, (2012), 106–142.
- [6] ESCHLER P.Y., RECLARU L., LUTHY H., BLATTER A., LARUE C., SUSZ C., BOSCH J., *Corrosion Testing of Cobalt-Chromium Dental Alloys doped with Precious Metals*, Eur. Cells Mater., 2005, 9, 64–65.
- [7] GERSTORFER J.G., SAUER K.H., PASSLER K., *Ion release from Ni-Cr-Mo and Co-Cr-Mo casting alloys*, Int. J. Prosthodont., 1991, 4, 152–158.
- [8] GŁOGOŃKA D., NOCULAK A., PUCIŃSKA J., JOPEK W., PODBIELSKA H., LANGNER M., PRZYBYŁO M., *Analysis of metal surfaces coated with europium-doped titanium dioxide by laser induced breakdown spectroscopy*, Acta of Bio-engineering and Biomechanics, 2015, Vol. 17, No. 3, 33–40.
- [9] GUO F., DONG G., DONG L., *High temperature passive film on the surface of Co-Cr-Mo alloy and its tribological properties*, Applied Surface Science, 2014, 314, 777–785.

- [10] KEDICI S.P., ABBASAKSU A., ALIKILI M., ARSLAN C., BAYRAMOG G., GOKDEMIR K., *Corrosion behavior of dental metals and alloys in different media*, J. Oral. Rehabil., 1998, 25, 800–808.
- [11] KHELFAOUI Y., KERKAR M., BALI A., DALARD F., *Electrochemical characterization of a PVD film of titanium on AISI 316L stainless steel*, Surf. Coat. Tech., 2006, 200, 4523–4529.
- [12] KIEL-JAMROZIK M., SZEWCZENKO J., BASIAGA M., NOWIŃSKA K., *Technological capabilities of surface layers formation on implant made of Ti-6Al-4V ELI alloy*, Acta of Bioengineering and Biomechanics, 2015, Vol. 17, No. 1, 31–37.
- [13] KOCIJAN A., MILOSEV I., PIHLAR B., *Cobalt-based alloys for orthopaedic applications studied by electrochemical and XPS analysis*, Journal of Materials Science: Materials in Medicine, 2004, 15, 643–650.
- [14] MANARANCHE C., HORNBERGER H., *A proposal for the classification of dental alloys according to their resistance to corrosion*, Dent. Mater., 2007, 23, 1428–1437.
- [15] *Metallic biomaterials: types and advanced applications, New functional biomaterials for medicine and healthcare*, Woodhead Publishing Limited, 2014, 121–148.
- [16] METIKOS-HUKOVIC M., BABIC R., *Passivation and corrosion behaviours of cobalt and cobalt–chromium–molybdenum alloy*, Corros. Sci., 2007, 49, 3570–3579.
- [17] MILOSEV I., STREHLOW H.H., *The composition of the surface passive film formed on CoCrMo alloy in simulated physiological solution*, Electrochim. Acta, 2003, 48, 2767–2774.
- [18] MILOSEV I., *The effect of biomolecules on the behaviour of CoCrMo alloy in various simulated physiological solutions*, Electrochimica Acta, 2012, 78, 259–273.
- [19] NAGAI A., TSUTSUMI Y., SUZUKI Y., KATAYAMA K., HANAWA T., YAMASHITA K., *Characterization of air-formed surface oxide film on a Co–Ni–Cr–Mo alloy (MP35N) and its change in Hanks solution*, Applied Surface Science, 2012, 258, 5490–5498.
- [20] NASCIMENTO M.L., MUELLER W.-D., CARVALHO A.C., TOMAS H., *Electrochemical characterization of cobalt-based alloys using the mini-cell system*, Dent. Mater., 2007, 23, 369–373.
- [21] NOURI A., WEN C., *Introduction to surface coating and modification for metallic biomaterials*, Surface Coating and Modification of Metallic Biomaterials, Elsevier Ltd., 2015, 1–60.
- [22] ORDINE A., ACHETE C.A., MATTOS O.R., *Magnetron sputtered SiC coatings as corrosion protection barriers for steels*, Surf. Coat Tech., 2000, 133–134, 583–588.
- [23] REIMANN L., *Electrochemical characteristics of a cobalt alloy with a protective passive layer*, Proof-Reading Service.com, 2016.
- [24] RIES L.A.S., DA CUNHA BELO M., FERREIRA M.G.S., MULLER I.L., *Chemical composition and electronic structure of passive films formed on Alloy 600 in acidic solution*, Corros. Sci., 2008, 50, 676–686.
- [25] RIVIERE J.P., DELAFOND J., MISAELIDES P., *Corrosion protection of an AISI 321 stainless steel by SiC coatings*, Surf. Coat. Tech., 1998, 100–101, 243–246.
- [26] SANTAVIRTA S., TAKAGI M., NORDSLETTEN L., ANTTILA A., LAPPALAINEN R., KONTTINEN Y.T., *Biocompatibility of silicon carbide in colony formation test in vitro. A promising new ceramic THR implant coating material*, Arch. Orthop. Trauma Surg., 1998, 118, 89–91.
- [27] SCHMALZ G., GARHAMMER P., *Biological interactions of dental cast alloys with oral tissues*, Dent. Mater., 2002, 18, 396–406.
- [28] SINGH R., DAHOTRE NARENDRA B., *Corrosion degradation and prevention by surface modification of biometallic materials*, J. Mater Sci: Mater Med., 2007, 18, 725–751.
- [29] VAFAEIAN S., FATTAH-ALHOSSEINI A., KESHAVARZ M.K., MAZAHERI Y., *The influence of cyclic voltammetry passivation on the electrochemical behaviour of fine and coarse-grained AISI 430 ferritic stainless steel in an alkaline solution*, Journal of Alloys and Compounds, 2016, 677.
- [30] WATAHA J.C., *Biocompatibility of dental casting alloys: A review*, J. Prosth. Dent., 2000, 83, 223–234.
- [31] WILLIAMS D.F., *Biocompatibility of Clinical Implant Materials*, Vol. I, CRC Press, Boca Raton, FL, 1981.
- [32] YAN Y., NEVILLE A., DOWSON D., *Biotribocorrosion of CoCrMo orthopaedic implant materials – Assessing the formation and effect of the biofilm*, Tribol. Int., 2007, 40, 1492–1499.
- [33] ZHANG Y.S., ZHU X.M., LIU M., CHE R.X., *Effects of anodic passivation on the constitution, stability and resistance to corrosion of passive film formed on an Fe-24Mn-4Al-5Cr alloy*, Appl. Surf. Sci., 2004, 222, 89–101.