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CORROSION RESISTANCE OF Co-Cr-Mo ALLOY USED IN DENTISTRY

ODPORNOŚĆ KOROZYJNA STOPU Co-Cr-Mo WYKORZYSTYWANEGO W STOMATOLOGII

The presented paper studies the effect of the casting technology on the corrosion resistance of Co-Cr-Mo alloy. The investigations were conducted on a commercial alloy with the brand name ARGELOY N.P SPECIAL (Co-Cr-Mo) produced by Argen as well as the same alloy melted and cast by the lost wax casting method performed by a dental technician. The corrosion behavior of the dental alloys in an artificial saliva was studied with the use of the following electrochemical techniques: open circuit potential and voltammetry. After the electrochemical tests, studies of the surface of the examined alloys were performed by means of a scanning electron microscope with an X-ray microanalyzer. The results of the electrochemical studies show that the dependence of the corrosion resistance on the microstructure associated with the recasting process is marginal. The results of the electrochemical studies of the considered alloy clearly point to their good corrosion resistance in the discussed environment.

Keywords: cobalt alloys, corrosion resistance, method of wasted wax, microstructure

Zbadano wpływ technologii odlewania na odporność korozyjną stopu Co-Cr-Mo. Badaniom poddano stop komercyjny o nazwie handlowej ARGELOY N.P SPECIAL (Co-Cr-Mo) firmy Argen oraz ten sam stop przetopiony i odlany przez technika dentystycznego metodą traconego wosku. Zachowanie korozyjne badanego stopu w środowisku sztucznej śliny zostało zbadane przy użyciu technik elektrochemicznych: pomiaru potencjału bezprądowego, woltamperometrii cyklicznej.

Po przeprowadzeniu badań elektrochemicznych wykonano badania powierzchni badanego stopu przy pomocy elektronowego mikroskopu skaningowego z mikroanalizatorem rentgenowskim. Wyniki badań elektrochemicznych wskazują, że na odporność korozyjną oraz mikrostrukturę stopu proces powtórnego odlania wpływa jedynie w niewielkim stopniu. Wyniki badań elektrochemicznych rozpatrywanego stopu wskazują jednoznacznie na ich dobrą odporność korozyjną w rozpatrywanym środowisku.

1. Introduction

Cobalt-chromium alloys have been used as a dental and orthopaedic implant material owing to their excellent strength, hardness, toughness and adequate corrosion resistance [1÷5]. Strengthening of alloys is obtained through combination of solid-solution hardening by the addition of carbon, chromium, molybdenum, tungsten or nickel to the pure cobalt matrix [6, 7]. Biocompatibility of cobalt alloys is based on the spontaneous formation of a passivating oxide film [8, 9]. In regard to the individual effects of the elements forming cobalt alloys, niobium and titanium are considered as inert. Cobalt, chromium, nickel and molybdenum belong to the group of the microelements which participate in the metabolic process. Despite the potential for a harmful activity of the particular elements constituting biomaterials, Co-Cr-Mo alloys characterize in a low toxicity because of their passivity in the organism.

The passive layer lowers the amount of metal ions coming through to the tissues, and so, a systemic toxic activity of cobalt frame dentures is rarely observed [8, 10].

S. Saji Viswanathan et al. proved that the type of the applied casting technique (centrifugal casting method and high frequency furnace smelting) has a marginal effect on the test results for the microstructure of Co-Cr-Mo alloys [10].

On the other hand, a significant problem is the lack of possibility of multiple alloy melting, due to the significant drop in the properties of these materials, which prevents their optimal use. There are also reports on their corrosion resistance being decreased as a result of their multiple casting [11, 12]. The casting method (mostly lost wax casting) is used to produce crowns, bridges, clamps and entire frame dentures. The technology of cast production is difficult and depends on many factors. The cast quality largely depends on the quality and cost of the production. For a high-quality cast, each stage of the process should be stabilized [13].

The purpose of this work was to show the important results regarding the electrochemical behavior and the structural morphology of Co-Cr-Mo alloy used in stomatology, which were remelted and re-cast.

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2. Material and test methodology

The material assigned for the tests was a Co-Cr-Mo alloy, which is used to cast frame dentures, clamp dentures as well as those mounted by means of bolts, latches and locks. One of the test samples was a commercial Co-Cr-Mo alloy named ARGELOY N.P. SPECIAL in the form of factory-prepared rolls, 9 mm in diameter and 12 mm high. Next, the examined alloy was remelted and cast by a dental technician by means of the lost wax casting method. The casting moulds were prepared from a silicon mass. The samples after casting were cleaned of the refractory mass and next underwent a vapour blasting treatment by means of corundum with the plasticity of 50 μm. The cast samples were produced in the form of bars, 5 mm in diameter and 15 mm high. The chemical compositions of the tested alloy are presented in Table 1. The physico-chemical and mechanical properties of the Co-Cr-Mo alloy certified by the producer are compiled in Table 2.

TABLE 1

Chemical composition of tested alloy Co-Cr -Mo

Brand name	Alloy	Chemical composition, % weight					
		Cr	Mo	Si	Mn	C	Co
ARGELOY N.P SPECIAL	Co-Cr-Mo	31.5	5	2	max 1	max 1	rest

TABLE 2

Physical properties of alloy Co-Cr-Mo according to producer

Mechanical properties		Physical properties	
Yield pointRe$_{0,2}$ [MPa]	450	Density [g/cm^3]	8,8
Young's modulus [GPa]	160	Expansion coefficient thermal	14,3÷14,8
Hardness [HV10]	280	Melting point [°C]	1240÷1350
Extending A$_5$ [%]	9	Soaking heat [°C]	870
		Temperature of pouring out [°C]	1480

The surface of the electrochemical test-prepared alloy equaled 0,5 cm^2. Before the measurement, specimens of the Co-Cr alloy were polished with the use of abrasive papers made of silicon carbide (SiC) with the granularity of up to 4000.

The chemical composition of artificial saliva solution includes: NaCl: *0,400 g/l*, KCl: *0,400 g/l*, CaCl$_2$· H$_2$O: *0,795 g/l*, NaH$_2$PO$_4$· H$_2$O: *0,780 g/l*, Na$_2$S· H$_2$O: *0,005g/l*, urea: *1,000g/l* [14]. The tests were carried out at 37 °C. The polarization tests were carried out within the potential range of -1,5÷1,5 V, with rate of potential changes equal 1 mV/s. The measurements of the polarization curves were performed in a three-electrode system, where the auxiliary electrode was a platinum gauze, the working electrode was represented by the examined alloys and the reference electrode was a Ag/AgCl in 3M KCl. The measurements were carried out with the use of a potentiostat VoltaLab PGZ301.

In order to determine the microstructure, metallographic specimens of the cross sections were prepared, which underwent chemical etching with the use of reagents consisting of 3 parts of HNO$_3$+ 1 part of HF + 1 part of glycerol. The microstructure observations were performed with the use of a light microscope LEICA DM 4000.

The microanalysis of the chemical composition of the corrosion-tested samples was performed by means of a scanning electron microscope HITACHI S-3500N, equipped with an EDS analyzer by Noran. The analysis was conducted by the point-by-point method on the surface of the examined alloy. The results of the analysis are presented in the form of characteristic X-ray spectra; also, the element contents were determined. What is more, X-ray structural tests were performed with the use of a diffractometer D500 by Siemens with monochromatic radiation of the copper-target tube $\lambda_{K\alpha}$ = 1,54Å. The measurement conditions were: angle step $\Delta 2\theta$ =0,02°, calculation time τ =5÷10 s. The angle measuring range was 2θ = 30÷100°.

3. Analysis of the microstructure

The performed microscopic observations made it possible to determine the microstructure of the examined Co-Cr-Mo commercial alloy as well as the one after casting by means of the lost wax casting method. The test samples were observed with the magnifications of: 100x, 200x and 500x. Exemplary microstructure images are shown in the photographs below (Fig. 1).
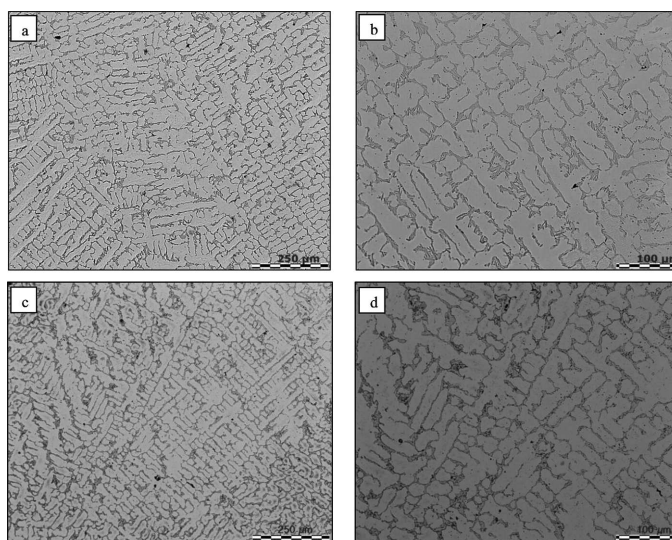

Fig. 1. Microstructure of Co-Cr-Mo alloy; a÷b **commercial** alloy, c÷d **recast** alloy

The microstructure of the examined cobalt-chromium-molybdenum alloy was dendritic – typical for cast materials. The examined material characterized in a chemically non-uniform microstructure consisting of an austenitic matrix of a cobalt and chromium solid solution in a core dendritic structure. According to the literature data [13, 15÷17], the dendritic areas are constituted by a eutectic consisting of M$_{23}$C$_6$ type carbides and a cobalt austenite.

4. X-ray phase qualitative analysis

The X-ray diffraction analysis was conducted in order to identify the phases present in the examined materials, and its results are presented in Fig. 2.
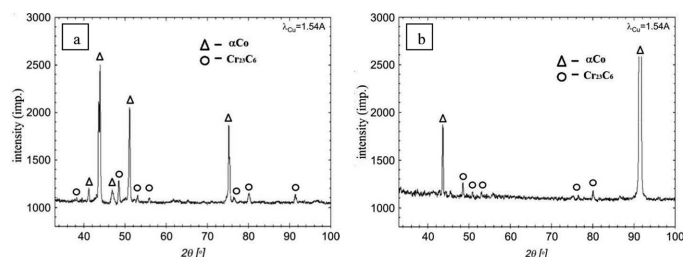

Fig. 2. X-ray diffraction of the phase qualitative analysis of alloy Co-Cr-Mo, a) **commercial** alloy, b) **recast** alloy

The performed qualitative analysis for the Co-Cr-Mo alloy demonstrated the presence of a αCo phase and $Cr_{23}C_6$ carbides. In the sample of the alloy in the production delivery state (commercial alloy), the content of the $Cr_{23}C_6$ type carbides is higher than that in the recasted alloy.

5. Electrochemical tests results

5.1. Open Circuit Potential

The open circuit potential of the alloys changes in the function of time. Figure 3 presents the change in the potential value of the examined alloys in time. The potential value was measured for the period of 24h. The value of the potential of the commercial alloy is much higher than in the case of the alloy re-cast by the dental technician. The potential value of the industrial alloy at the beginning of the measurement equaled -0,040 V and it changed in time, constantly increasing its value till the moment when it reached about 0,004 V after approximately 77160 s. The potential of the re-cast alloy equaled -0,280 V at the beginning of the measurement. After about 9440 s, it reached -0,210 V and then it slightly varied in time, till the moment when it reached approximately -0,180 V after 84880 s. The obtained test results clearly demonstrate that the commercial alloy exhibits a significantly higher corrosion resistance than the recast alloy.
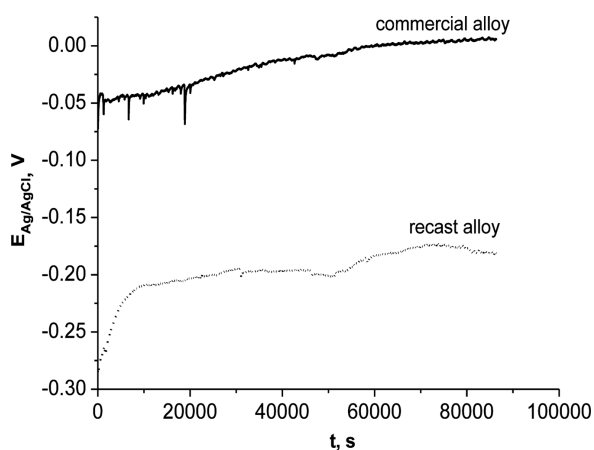

Fig. 3. Evolution of open circuit potential of tested samples

5.2. Polarization and SEM/EDS analysis

As a result of the polarization tests, we obtained polarization curves presented in Figure 4. The examined materials characterize in similar courses of the obtained curves for the rate of the potential change equaling 1 mV/s.
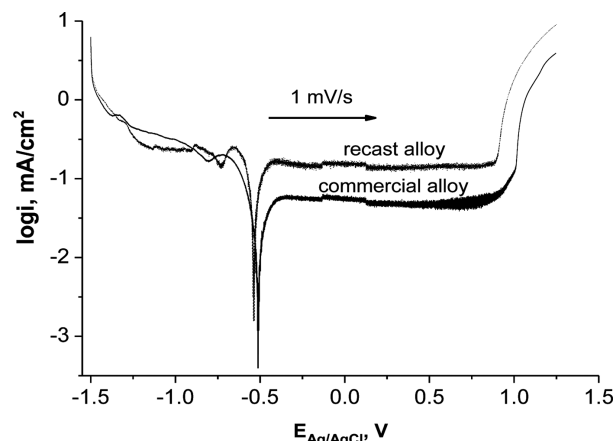

Fig. 4. Polarization curves of tested samples

The polarization curves made for the tested samples confirm the results of the open circuit potential tests, which demonstrate that the commercial alloy characterizes in a higher corrosion resistance that the one recasted by the technician. For the commercial alloy, both the cathode and anode currents were slightly lower than those for the cast alloy. For the latter, the equilibrium potential equals about -0,537 V. A slightly higher value – about -0,508 V – was registered in the case of the commercial alloy. Potentials lower than this value are connected with the cathodic process, and higher potentials – with the anodic one.

On both obtained curves, in the area of the anodic process, we can observe a very wide plateau range (-0,337÷0,868 V), which, for the commercial alloy, is minimally longer than in the case of the cast alloy, and it is in the potential range of: -0,375÷0,878 V.

On both obtained curves, no peaks of anodic dissolution are observed. The passivity of those alloys is largely accounted for by the cobalt compounds Co(II) causing the formation of a non-soluble layer of compounds on the surface of the examined alloy. The literature suggests that they are probably CoO, $CoCO_3$ and $Co(OH)_2$ compounds. The passivation is accounted for by the oxygen forms on the surface of the examined sample, leading to the formation of a passive layer of chromium Cr(III), most often in the form of the Cr_2O_3 or CrOOH oxide. The transpassive region for both tested alloys begins with the value of about 0,870 V vs Ag/AgCl, connected with the intense oxidation of cobalt Co(III) to Co(IV) and for pH >8 of the formation of ions of CrO_4^{2-} [18, 19].

The surfaces of the alloys after the potentiodynamic polarization experiment were examined using SEM to identify the sites of corrosion attack (Fig. 5). There is thick corrosion product layer on the investigated alloy. Such a layer is visible to the naked eye.
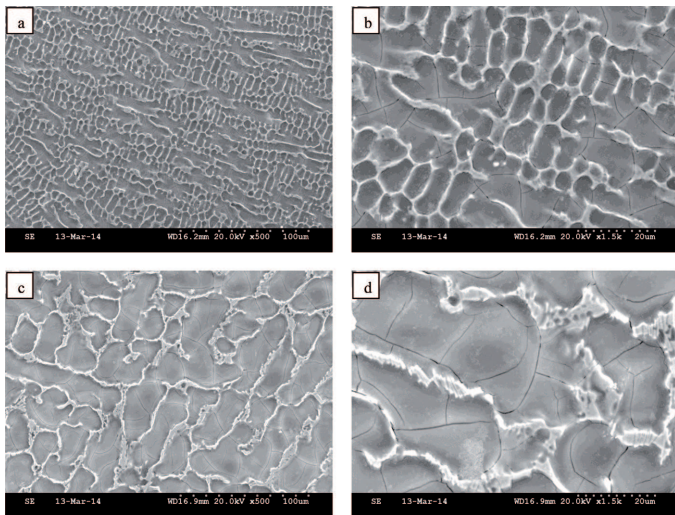
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Fig. 5. SEM images of Co-Cr-Mo alloy after polarization test; alloy; a÷b **commercial** alloy, c÷d **recast** alloy

EDS line analysis of the corroded areas indicates severe depletion of cobalt from the matrix on both samples. The surface of both investigated samples (Fig. 6, Fig. 7) reveal two-phase of structure. EDS analysis shows that the chemical compositions of the dendrite and matrix regions are different.

In the matrix of the commercial alloy, we can see that together with the increase of the chromium content (Fig. 6, points 1, 2), the Mo and Si contents also significantly increase (over twice). The increasing values of Mo and Si work as additional factors passivizing the alloy. According to the conducted EDS studies, the dendritic areas pointed (Fig. 6, points 1, 2) indicated to a large drop in the content of Co (from about 38 to about 43%). The chromium content did not undergo any significant changes; yet, a clear decrease of the content of Mo was observed – from 5% weight on the surface before the alloy polarization to about 2,5% weight after the performed experiment.
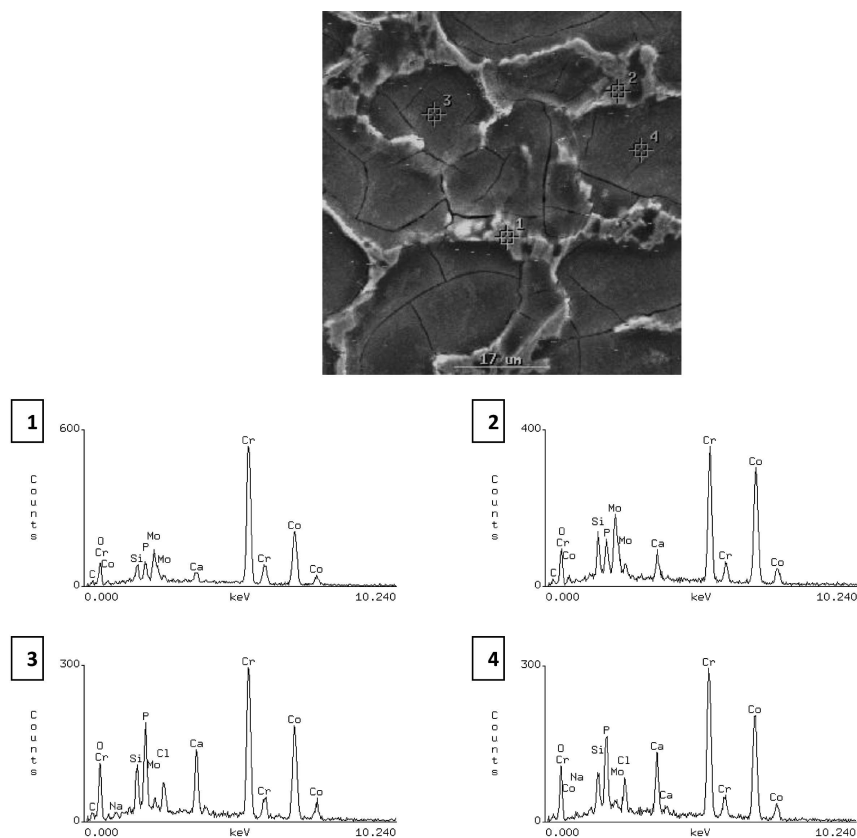
Chemical composition microanalysis
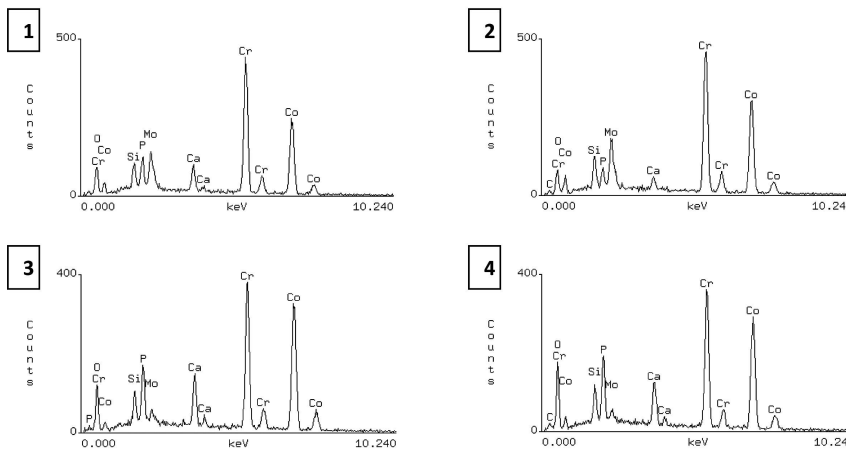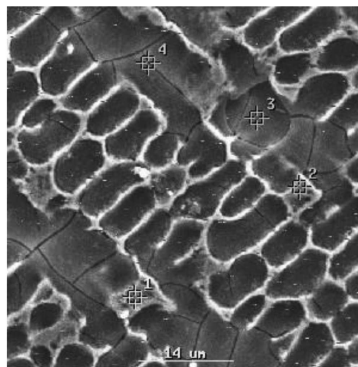
Chemical composition of the precipitates observed in Co-Cr-Mo alloy

Area	Chemical composition, % weight					
	Ca	P	Si	Mo	Co	Cr
1	4.06±0.60	3.32±0,34	3.25±0.31	10.95±1.09	38.95±1.54	39.47±2.40
2	1.81±0.47	1.62±0.27	3.54±0.28	12.69±0.99	43.60±2.28	36.74±1.37
3	5.88±0.36	5.63±0.36	2.53±0.29	2.66±0.79	52.31±2.51	30.98±1.35
4	6.42±0.66	6.62±0.40	3.77±0.34	2.61±0.84	48.06±2.59	32.52±1.46

Fig. 6. SEM image of Co-Cr-Mo **commercial** alloy and EDS spectrogram of areas shown in SEM image

Chemical composition of the precipitates observed in Co-Cr-Mo alloy

Area	Chemical composition, % weight					
	Ca	P	Si	Mo	Co	Cr
1	1.74±0.26	2.39±0,28	2.28±0.26	9.51±0.95	35.42±1.64	48.66±1.61
2	2.95±0.56	3.00±0.33	3.75±0.31	14.53±1.14	46.93±2.46	28.83±1.35
3	7.46±0.46	8.39±0.82	4.46±0.39	2.95±0.96	40.74±2.00	36.00±1.70
4	6.98±0.44	7.81±0.75	3.97±0.36	3.43±0.96	42.37±2.73	35.62±1.69

Fig. 7. SEM image of Co-Cr-Mo **recast** alloy and EDS spectrogram of areas shown in SEM image

In the recast alloy, the chromium content did not change, regardless of the area of analysis. After the performed polarization studies, we observed an increase of the Cr content up to about 49% weight in the dendritic area (Fig. 7, measuring point 1). In both analyzed Co-Cr-Mo alloys, we can observe a significant increase of the Mo content in the dendritic areas (Fig. 6 and 7, measuring points 1 and 2). The molybdenum significantly contributes to the alloy's passivation. Additionally, on the surface of the alloy after casting and polarization studies, we can see that the Si distribution in the alloy is quite uniform. What is more, the layer of the corrosion products was enriched with this element (from 2% weight to about 3,5% weight).

6. Conclusions

On the basis of the obtained results, we can state that the re-casting of alloy ARGELOY N.P. SPECIAL did not significantly affect the microstructure of the examined material, which was dendritic in character. The microstructure of the cobalt-chromium alloy in the state as-cast was non-uniform and consisted of an austenitic matrix formed by a solid cobalt-chromium solution in a dendritic structure. The per-

formed qualitative analysis for the Co-Cr-Mo alloy demonstrated the presence of a αCo phase and $Cr_{23}C_6$ carbides. In the sample of the alloy in the production delivery state (commercial alloy), the content of the $Cr_{23}C_6$ type carbides is higher than that in the recasted alloy.

The measurements of the open circuit potential suggest that the recast alloy characterized in a lower corrosion resistance than the commercial alloy. The values of the corrosion potentials of the examined materials correspond to the passivity read from the polarization curves for those alloys. The progress of the curves is characteristic for materials of a very high corrosion resistance. The tested alloys characterize in a wide passive region.

The obtained results of the scanning electron microscope tests and the EDS analysis performed after the polarization tests point to the fact that chemical compositions of the obtained corrosion products differ from each other depending on the analyzed alloy. In the matrix of the commercial alloy, together with the increase of the chromium content, Mo and Si significantly increase as well.

In the re-cast alloy, after the polarization tests, we observed an increase in the Cr content up to about 49% wt. in the dendritic area. In both analyzed Co-Cr-Mo alloys, we

observe a clear increase of the Mo content in the dendritic areas. Despite some differences in the construction of a corrosion products layer of tested materials, it should be underlined that segregation of the molybdenum and silicon contributes significantly for passivation of analyzed materials.

Acknowledgements

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