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The effect of heat treatment on the microstructure and properties of the corrosion resistance of the prosthetic alloy Wironit ExtraHart (Co-Cr-Mo)

Wpływ obróbki cieplnej na mikrostrukturę i odporność korozyjną protetycznego stopu Wironit ExtraHart (Co-Cr-Mo)

Abstract

The presented study performs an analysis of the effect of thermal treatment on the microstructure and corrosion resistance of the commercial prosthetic alloy Wironit ExtraHart (Co-Cr-Mo). Experiments of thermal treatment, homogenization, oversaturation as well as oversaturation with ageing of the alloys were carried out. Metallographic tests, hardness measurements, EDS analyses and electrochemical investigations were performed. For the examined samples, the corrosion potential (OCP) and polarization curve (LSV) were determined, based on which the corrosion properties in the simulated solution of artificial saliva were established. The results of the obtained tests made it possible to evaluate the effect of the performed thermal treatment on the changes in the properties (hardness) as well as the microstructure and corrosion resistance of the examined alloy Co-Cr-Mo.

Keywords: Co-Cr-Mo alloys, heat treatment, dendritic microstructure, corrosion resistance

Streszczenie

W pracy dokonano analizy wpływu obróbki cieplnej na mikrostrukturę i odporność korozyjną komercyjnego stopu protetycznego Wironit ExtraHart (Co-Cr-Mo). Przeprowadzono eksperyment obróbki cieplnej stopów, wyżarzania ujednorodniającego, przesycania i przesycaenia ze starzeniem. Wykonano badania metalograficzne, analizę EDS oraz badania elektrochemiczne. Dla badanych próbek wyznaczono potencjał korozyjny (OCP) oraz krzywą polaryzacji (LSV), na podstawie których określono właściwości korozyjne w symulowanym roztworze sztucznej śliny. Wyniki otrzymanych badań pozwoliły stwierdzić wpływ przeprowadzonej obróbki cieplnej na zmiany własności (twardość) i mikrostrukturę oraz odporność korozyjną badanego stopu Co-Cr-Mo.

Słowa kluczowe: stopy Co-Cr-Mo, obróbka cieplna, mikrostruktura dendrytyczna, odporność korozyjna

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1. Introduction

Co-Cr-Mo alloys, belonging to the group of biomaterials, are extensively applied in prosthetics and stomatology, owing to their desired mechanical properties, high corrosion resistance and good biotolerance in the environment of tissues and body fluids [1]. The microstructure and properties of Co-Cr-Mo alloys are largely dependent on the technique of their production [2]. Prosthetic elements are usually produced through casting [1, 3] due to the complexity of the shapes and the necessity of adjusting the element to the anatomy of the patient. Such a manner of production, however, can lead to insufficient mechanical properties caused by porosity, chemical heterogeneity or the presence of a carbide phase in the interdendritic zones, which, ultimately, can lead to rapid damage of the cast element [4]. In the case of alloys based on cobalt, thermal treatment is applied in order to improve their mechanical properties by changing the volume fraction of the present phases, thus creating a more homogenous structure with improved mechanical properties. This makes it possible to obtain carbides with the proper dispersion and size and in consequence also good plasticity and high mechanical properties of the alloy [5]. In the study of Minciun [6], the alloy Co-Cr-Mo, having been subjected to homogenization at 1100°C for 5 hours, was characterized by an oblong system of dendritic arms with interdendritic precipitations. Also, a fine carbide agglomeration was observed. In their study, Clemow and Daniell [7] subjected three types of Co-Cr-Mo alloys to the procedure of oversaturation. The samples were annealed in an electric resistance furnace in a protective atmosphere of argon at temperatures of 1165, 1210, 1230, 1250 and 1270°C for the time of: 30 minutes and 1, 2, 4, 8, 16, 32 and 64 hours, and after the required time had passed, they were oversaturated in water. At the lowest temperature from which the alloy was oversaturated, 1165°C, even after 64 hours of annealing, the carbides did not dissolve, while further precipitating around the primary carbides was observed. Based on the diffraction tests, it was established that a partial transformation of the primary carbides type $M_{23}C_6$ w M_6C had taken place [7]. Oversaturation from the temperature of 1210°C, with short annealing times, caused rapid carbide dissolution, while with the longer annealing times, the carbide dissolution rate decreased. Despite this, the oversaturation of the alloys after 64-hour annealing at 1210°C led to a homogeneous microstructure of the alloys. This effect was attributed to the carbides $M_{23}C_6$ dissolving during the first hour, while the carbides M_6C , more stable at a higher temperature, dissolved more slowly [7]. In the case of oversaturation at 1230°C, the transformation of carbide $M_{23}C_6$ into M_6C took place within 15 minutes for each of the three examined Co-Cr-Mo alloys. Also, a different mechanism of carbide dissolution in the alloys where the carbides dissolved faster was observed. It was established that the process of carbide dissolution at 1230°C was controlled by a diffusion of the metallic alloy elements in the matrix [7]. Tests performed at 1250 and 1270°C showed a varying rate of carbide dissolution, which

was related to the macrosegregation of the alloy elements. The authors of the study [7] proved the existence of a range of reactions occurring during the thermal treatment consisting in oversaturation of alloy Co-Cr-Mo. In particular, it was noticed that the temperature range in which carbide dissolution takes place at the rate controlled by diffusion is very narrow (1210–1230°C) and depends on the composition of the alloy.

2. Description of research object

The tests were performed on a commercial cobalt-based alloy (Co-Cr-Mo) with the commercial name Wironit ExtraHart by BEGO USA [8]. The alloy is obtained through casting by the lost wax method. It is a stomatological alloy, which does not contain nickel and is assigned for prosthetic restorations, especially partial prostheses. The chemical composition of the examined alloy Wironit ExtraHart is given in Table 1. The content of C in the alloys up to 0.35%. The dimensions of the test specimens were the following: diameter 7.5 mm, height 15 mm.

Table 1. Chemical composition of Wironit ExtraHart (Co-Cr-Mo) [8]

Element content [% mass]				
Co	Cr	Mo	Si	Mn
63.0	30.0	5.0	1.0	1.0

3. Research methodology

Co-Cr-Mo (Wironit ExtraHart) alloy samples as-cast (ACM) underwent the following processes: homogenization at 1150°C for 2 hours (denotation H), homogenization followed by oversaturation (1150°C/2 h + 1200°C/2 h/H₂O) (denotation H + S) and homogenization followed by oversaturation and ageing (1150°C/2 h + 1200°C/2 h/ H₂O + 850°C/1 h/air) (denotation H + S + A). The thermal treatment was performed in a laboratory pipe furnace in the atmosphere of nitrogen. The thermally treated alloy was subjected to microscopic observations. The samples were etched electrolytically, the voltage was 3–4 V, the chemical composition of the applied electrolyte was: 60 cm³ HCl, 15 cm³ HNO₃, 15 cm³ CH₃COOH and 15 cm³ distilled water. The microstructural observations of the prepared microsections were made with the use of a light microscope and a scanning electron microscope with an analyzing adapter. For each sample, 5 hardness measurements were made (Vickers method); the loading force operating on the indenter was 10 kG. The electrochemical tests were performed in a simulated solution of artificial saliva with a free oxygen access, at the temperature of 37°C. The chemical composition of the artificial

saliva was as follows: 0.7 g NaCl, 1.2 g KCl, 0.2 g KH_2PO_4 , 1.5 g NaHCO_3 , 0.26 g Na_2HPO_4 , 0.33 g KSCN per 1 litre of H_2O [9]. The tests were carried out in a three-electrode system: the working electrode – the examined alloy, the measuring electrode – Ag/AgCl in 3 M KCl and a platinum reference electrode. For the examined samples, the corrosion potential (OCP) and the polarization curve (LSV) were determined, based on which the corrosion properties were established.

4. Research results

The performed microscopic tests aimed at revealing the microstructure of the examined alloy Co-Cr-Mo after the successive thermal treatment operations. The obtained microstructure images are shown in Figure 1.

The microstructure of the samples as-cast alloy – Wironit ExtraHart (Co-Cr-Mo) characterized in a dendritic structure typical of casting alloys (Fig. 1a). Based on the literature data [10–13], we know that in casting cobalt alloys, the structure is homogeneous. The primary structure of cobalt-based alloys, after crystallization under conditions typical of prosthetic alloys, consists of very large crystals of the matrix, which is constituted by a solution of chromium, molybdenum and carbon. It can be inferred from the observations of the microstructure of alloy Co-Cr-Mo subjected to homogenization (H) (Fig. 1b) that the dendritic arms are long and similarly oriented, and so we can conclude that a partial reduction of segregation took place. Alloy Co-Cr-Mo after homogenization and oversaturation (H + SS) (Fig. 1c) characterizes in expanded grain, and alloy homogenization is visible. In the alloy's matrix, no dendritic systems are observed. In the analysis of the microstructure of alloy Co-Cr-Mo (Fig. 1d) subjected to homogenization followed by oversaturation and ageing (H + SS + A), we can observe grains which are smaller at the surface and bigger towards the inside of the material. Inside the grains, there are voids left after uniformly distributed dispersive precipitations. The precipitations are also present at the grain boundaries. On the basis of the research performed by Clemow and Daniell [7], we can presume that these are undissolved carbide precipitations, both of the M_{23}C_6 and M_6C type. The literature reports [14] that chromium carbide precipitations type M_{23}C_6 are a result of ageing of the alloy. The results of the EDS analysis have been presented in the form of X-ray spectra, which made it possible to examine the chemical composition of the tested micro-area of the alloy subjected to thermal treatment. The test results have been shown in Figures 2–4.

The homogenization process caused a partial homogenization of the chemical composition of the tested sample; however, it can still include precipitations with a higher content of chromium. We can presume that the annealing time (2 h) was insufficient to obtain a total homogenization of the alloy (Fig. 2).

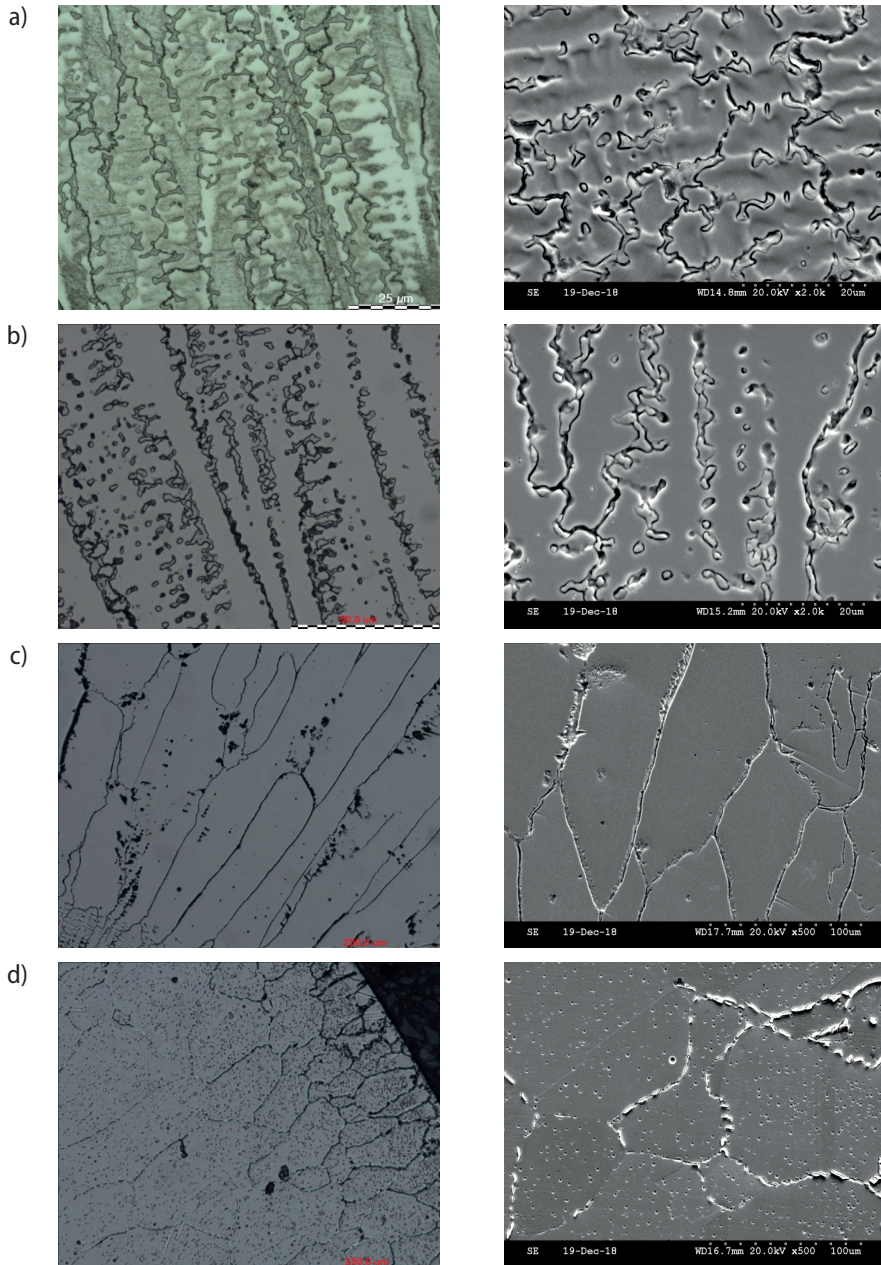


Fig. 1. Microstructures of the Co-Cr-Mo Wironit ExtraHart alloy (photos from the left – light microscopy, photos from the right – SEM): a) samples as-cast (ACM); b) homogenization (H); c) homogenization and oversaturation (H + S); d) homogenization followed by oversaturation and ageing (H + S + A)

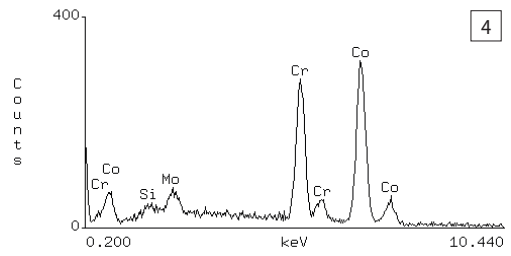
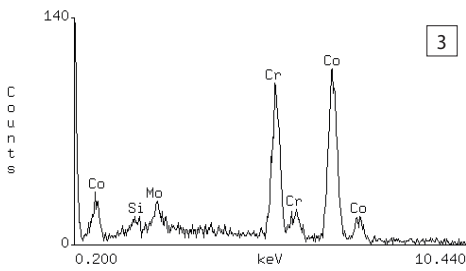
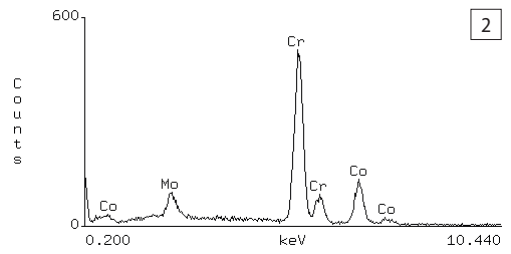
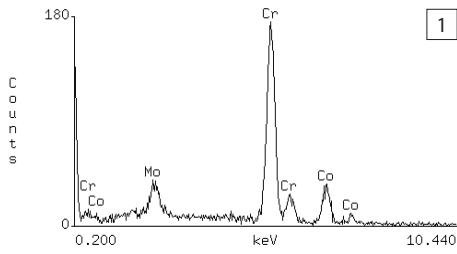
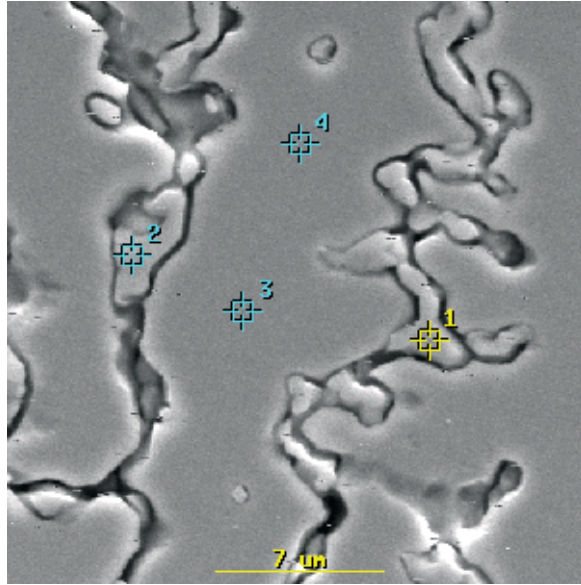


Fig. 2. SEM image of Co-Cr-Mo (Wironit ExtraHart) alloy sample subjected to the process homogenization (H)

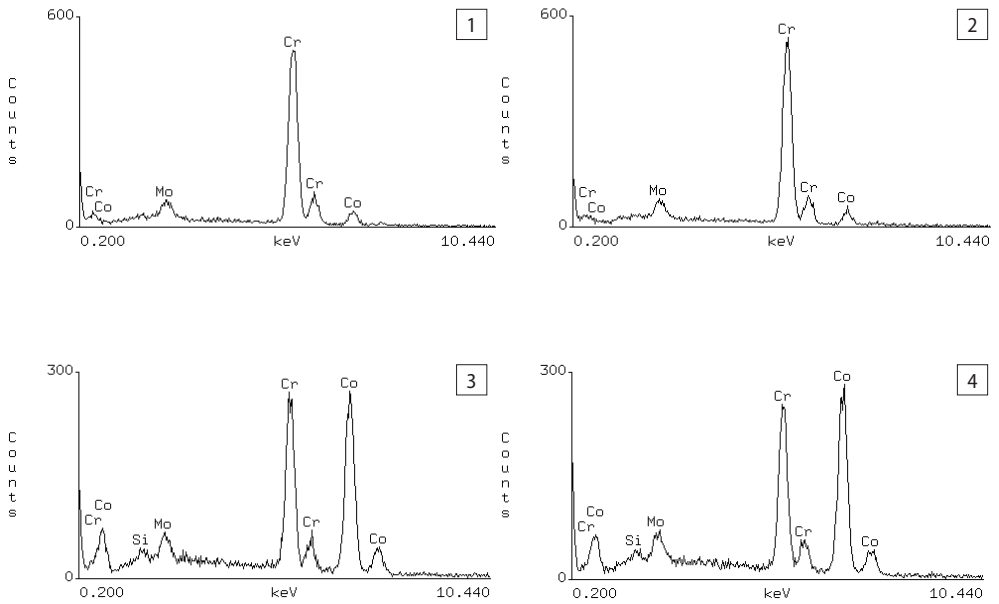
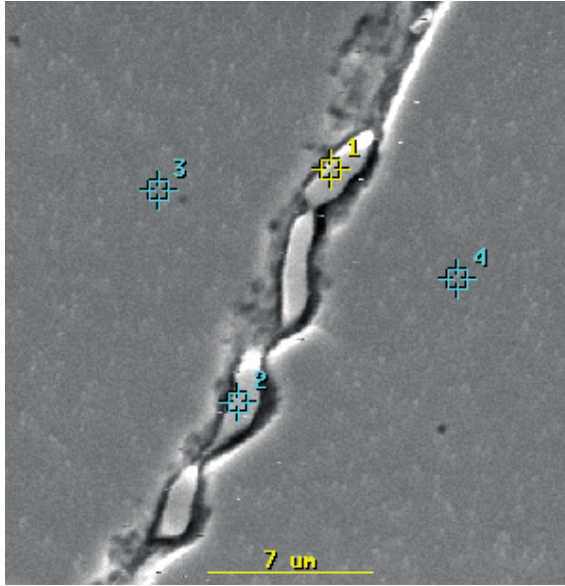


Fig. 3. SEM image of Co-Cr-Mo (Wironit ExtraHart) alloy sample subjected to the processes homogenization and oversaturation (H + S)

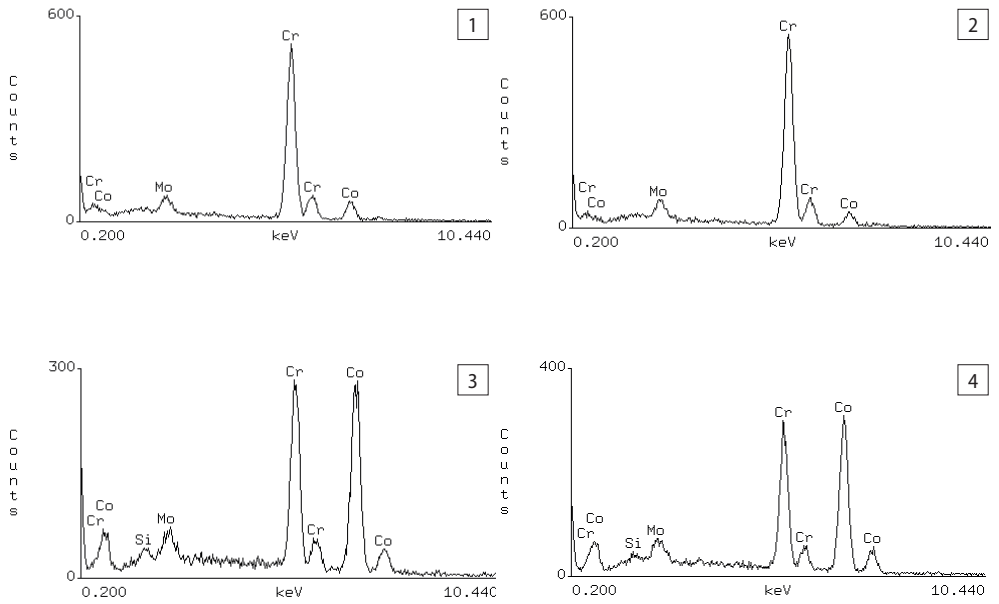
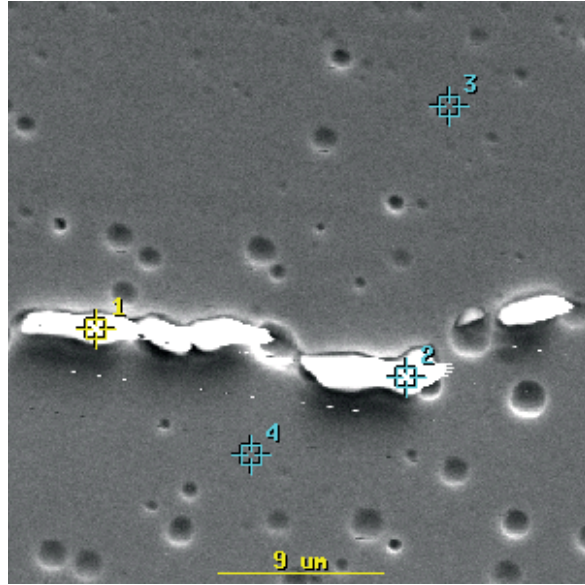


Fig. 4. SEM image of Co-Cr-Mo (Wironit ExtraHart) alloy sample subjected to the processes homogenization followed by oversaturation and ageing (H + S + A)

The EDS analysis of the microareas of Co-Cr-Mo alloy samples subjected to H + S shows the presence of small irregular precipitations at the grain boundaries with a high content of chromium. Based on the literature data [15], we can state that they are probably not fully dissolved chromium carbides, which proves a partial oversaturation of the alloy. The analysis of the precipitations present at the grain boundaries in the samples of alloy Co-Cr-Mo subjected to H + S + A (Fig. 4) also showed the presence of irregular precipitations at the grain boundaries, characterized by a high chromium content. According to the literature data [14, 15], these can be chromium carbides type $M_{23}C_6$.

The results of the performed hardness measurements (Tab. 2) show a higher hardness of the cast alloy Wironit ExtraHart (ACM) (504 HV10) compared to the hardness declared by the producer (385 HV10) [8].

Table 2. Results of measurements of hardness of the alloy in the as-cast Co-Cr-Mo Wironit ExtraHart and after heat treatment

Test samples Co-Cr-Mo	\bar{x} HV10	(S_x)
Samples as-cast (ACM)	385	5
Homogenization (H) (1150°C/2 h)	389	17
Homogenization and oversaturation (H + S) (1150°C/2 h + 1200°C/2 h/H ₂ O)	347	6
Homogenization followed by oversaturation and ageing (H + S + A) (1150°C/2 h + 1200°C/2 h/ H ₂ O + 850°C/1 h/air)	411	14

It should be pointed out that the applied thermal treatment caused a drop of hardness for the examined alloy Co-Cr-Mo. Among the examined samples of alloy Wironit ExtraHart subjected to thermal treatment, the highest mean hardness is exhibited by sample H + SS + A, for which the mean hardness equals 411 HV10, whereas the lowest hardness was demonstrated by sample H + S with the mean hardness of 347 HV10. The high hardness of the sample of the alloy subjected to homogenization followed by oversaturation and ageing may result from the presence of hard secondary carbide precipitations in its structure, formed during the ageing process, which significantly strengthen the alloy. In turn, the low value of the hardness of the alloy after oversaturation probably results from a part of the carbides being dissolved in the solution [7]. The obtained hardness results are comparable to the results of tests presented by Dobbs and Robertson [10].

For each sample after thermal treatment, as well as for the sample of the cast alloy Co-Cr-Mo Wironit ExtraHart, the non-current stationary potential was determined in the function of time (OCP) in the examined solution. Figure 5 shows the change in the corrosion potential in time.

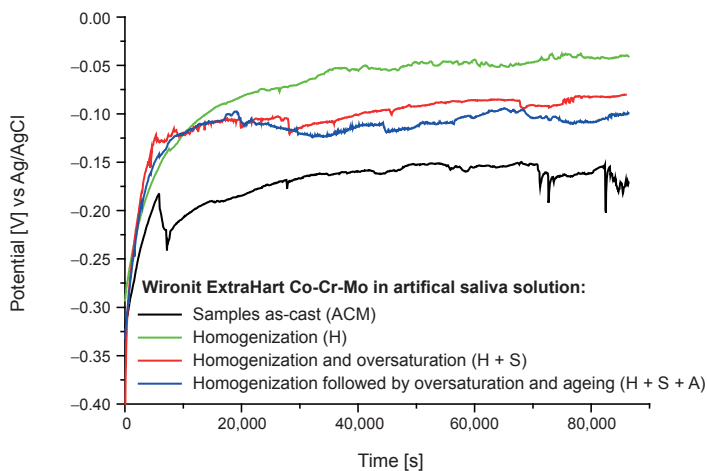


Fig. 5. Evolution of the corrosion potential vs. time determined for samples of Co-Cr-Mo Wironit ExtraHart alloy cast and after heat treatments

The stationary potential for each of the examined samples increased with time; slight fluctuations of its level aiming at reaching stability could be observed. This means that passivation of the sample took place in the simulated artificial saliva solution. The highest potential level was recorded for the sample subjected to homogenization (H), in the case of which the longest time of its growth was also observed (about 11 h), after which the value began to stabilize and equalled about -50 mV vs. Ag/AgCl (Fig. 5). The remaining samples demonstrated lower corrosion potential values, with slight fluctuations. The potential of the sample after homogenization and oversaturation (H + S) began to stabilize after about 8 hours, whereas the sample of the alloy subjected to H + S + A, in the process of reaching stability, exhibited the highest fluctuations of the potential, oscillating in the vicinity of -120 mV vs. Ag/AgCl. The lowest stationary potential was demonstrated by the sample of alloy Co-Cr-Mo as-cast (ACM), whose potential, similarly to the remaining samples, initially, rapidly increased, while after about 2 hours, a rapid drop could be observed, after which it began to increase again and eventually stabilized. It can be inferred from the determined stationary potentials that subjecting a sample of alloy Co-Cr-Mo Wironit ExtraHart to each of the performed thermal treatments causes an increase of the stationary potential, which means that thermal treatment increases the corrosion resistance of the alloy. For a more accurate determination of the corrosion properties of the examined commercial alloy and the samples after thermal treatment, polarization curves were made (LSV) in a solution of artificial saliva. The obtained current density values were recalculated into the surface area of the sample equaling 1 cm^2 (Fig. 6).

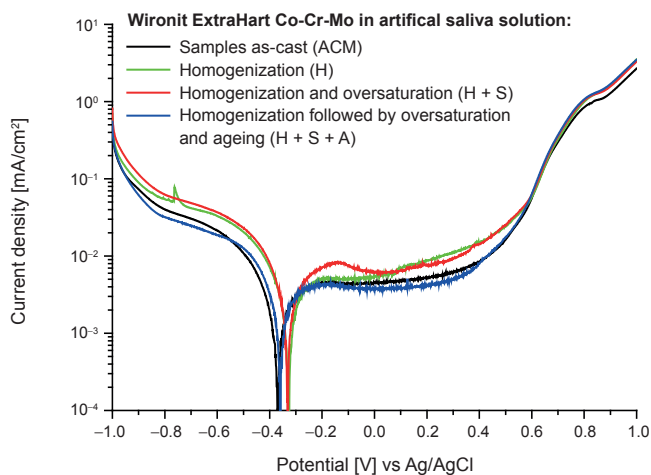


Fig. 6. Polarization curves were obtained for samples of Co-Cr-Mo Wironit ExtraHart alloy cast and after heat treatments

Figure 6 shows the polarization curves which look similar in character for all the examined samples. The scope of the potential in which the passive state is reached is rather narrow, i.e. about -0.2 do 0.4 V vs. Ag/AgCl. In the case of the obtained polarization curves, the lowest anodic current densities, and thus the highest corrosion resistance, were obtained for the alloy subjected to oversaturation and ageing. Very similar values were recorded for the commercial alloy (about $3.8 \mu\text{A}/\text{cm}^2$). The remaining samples reached slightly higher anodic current values in the passive scope. With the potential of about 0.6 V vs. Ag/AgCl, in each sample, the transpassive region starts and a rapid increase of anodic current is visible. This is connected with the change of the oxidation degree of the compounds being part of the passive layer. With low potential values, chromium oxide and hydroxide (III) are formed, whose value increases together with the potential. With higher potential values corresponding to the transpassive region on the polarization curve, chromium oxide (IV) is also formed [16]. The literature [17] reports that with the potential higher than 0.7 V, in the transpassive region, cobalt dissolution takes place. The passive layer formed on the surface of alloys Co-Cr-Mo consists mainly of oxide Cr_2O_3 with a small share of cobalt and molybdenum oxides. Its presence affects the corrosion rate, owing to the limited cathodic and anodic reactions. It is so because it constitutes a barrier for the transport of anions and cations to the surface of the metal. The studies performed by Vidal and Muñoz [18] state that, in simulated biological solutions, the passive behavior of Co-Cr-Mo alloys is caused by the formation of an oxide layer with a high Cr content (containing up to 90% Cr oxides, mainly as Cr (III) and a lower amount as $\text{Cr}(\text{OH})_3$), which is confirmed by the

research carried out by Hodgson [19]. Based on the performed corrosion tests, we are unable to accurately establish whether the thermal treatment performed on the commercial alloy Co-Cr-Mo Wironit ExtraHart improves the corrosion properties of the examined samples, which was shown by the obtained polarization curves. The performed thermal treatment of alloy Co-Cr-Mo does not worsen the passivation properties of the alloy.

The corrosion resistance determined, based on the stationary potential for the samples after the thermal treatment, is higher than for the sample of the alloy as-cast.

5. Conclusions

1. The highest hardness (411 HV10) of Co-Cr-Mo alloy was observed for the sample after homogenization followed by oversaturation and ageing (H + S + A).
2. The higher hardness after the alloy's ageing is a result of the presence of uniformly distributed, dispersive hard secondary carbide precipitations in its microstructure, formed during the ageing process, which significantly strengthen the alloy.
3. The microscopic observations made it possible to establish that, as a result of homogenization, the Co-Cr-Mo alloy samples had a dendritic structure, and after oversaturation as well as oversaturation plus ageing, the grain expanded, while on the internal side of the grain boundaries, precipitations of a carbide phase were present.
4. The EDS analysis made it possible to establish the presence of precipitation with a high chromium content at the grain boundaries, both in the case of the oversaturated alloy and of the oversaturated and aged one. According to the literature data, these are chromium carbides type $M_{23}C_6$.
5. The stationary potential for each of the examined samples increased with the prolongation of time, which means that passivation of the samples took place in the simulated solution of artificial saliva. The highest potential level was recorded for the sample subjected to homogenization annealing, in the case of which the longest time of its growth was also observed (about 11 h), after which the value began to stabilize and equalled about -50 mV vs. Ag/AgCl.
6. It can be concluded that the thermal treatment of alloy Co-Cr-Mo performed does not worsen the passivation properties of the alloy. It seems true that the corrosion resistance determined based on the stationary potential of the samples after thermal treatment is higher than for the alloy as-cast.

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