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J. AUGUSTYN-PIENIĄŻEK*, A. ŁUKASZCZYK**, R. ZAPAŁA**

MICROSTRUCTURE AND CORROSION RESISTANCE CHARACTERISTICS OF Cr-Co-Mo ALLOYS DESIGNED FOR PROSTHETIC MATERIALS

CHARAKTERYSTYKA MIKROSTRUKTURY I ODPORNOŚCI KOROZYJNEJ STOPÓW Cr-Co-Mo PRZEZNACZONYCH NA MATERIAŁY PROTETYCZNE

The work presents the results of microscopic tests of two alloys: Co-Cr-Mo and Co-Cr-W-Mo, together with a quantitative local analysis of the chemical composition, with the use of an electron microprobe X-ray analyzer EDS. Corrosion resistance tests were also performed on the alloys, in the artificial saliva environment. The microstructure of the examined alloys was of the dendrite type. An eutectic consisting of alloy carbides and a cobalt austenite was observed in the interdendritic spaces. The dendritic matrix was a solid solution of chromium, molybdenum and carbon in cobalt (γCo), and the precipitates present in the interdendritic spaces were rich with Cr and Mo – in the case of Co-Cr-Mo – and with W and Mo – in the case of Co-Cr-W-Mo. The analyzed materials exhibited a similar progress of polarization curves. The obtained currentless potential values and the wide passivation area of those alloys made it possible to conclude their high corrosion resistance in the examined environment.

Keywords: dental alloys, cobalt matrix alloys, corrosion resistance

W pracy przedstawiono wyniki badań mikroskopowych dwóch stopów: Co-Cr-Mo i Co-Cr-W-Mo wraz z ilościową analizą punktową składu chemicznego przy wykorzystaniu mikroanalizatora rentgenowskiego EDS. W ramach pracy wykonano również badania odporności korozyjnej stopów w środowisku sztucznej śliny. Mikrostruktura badanych stopów miała budowę dendrytyczną. W przestrzeniach międzydendrytycznych występowała eutektyka składająca się z węglików stopowych i austenitu kobaltowego. Osnowę dendrytyczną stanowił roztwór stały chromu, molibdenu i węgla w kobalcie (γCo), zaś wydzielenia występujące w obszarach międzydendrytycznych były bogate w Cr i Mo – w przypadku stopu Co-Cr-Mo oraz W i Mo – w przypadku stopu Co-Cr-W-Mo. Analizowane materiały wykazywały zbliżone przebiegi krzywych polaryzacji. Z otrzymanych wartości potencjału bezprądowego oraz na podstawie szerokiego obszaru pasywacji tych stopów można wnioskować o ich wysokiej odporności korozyjnej w badanym środowisku.

1. Introduction

The oral cavity can be treated as a peculiar example of an ecosystem, and the alloys applied in dental prosthetics are faced with very high requirements. The material should be selected in such a way so that it allows for an interaction between the human body and the implant. The basic criteria which have to be met by a material used in dental prosthetics are biocompatibility and a set of required mechanical and physical properties.

The basic characteristics of skeletal prosthesis materials used in stomatology are biotolerance in the environment of body tissues and fluids and a high pitting and crevice corrosion resistance. Also important is the stability of the set of particular physico-mechanical properties (high strength, adequate ductility, hardness and abrasion resistance), as well as a homogeneity of the chemical composition [1÷3].

The common metal alloys used by prosthetics dentists in substructures, crowns and permanent and removable prostheses were developed in the 1930s and became an alternative for the costly gold alloys. In that period, two types of common metal alloys were introduced: nickel-chromium and cobalt-chromium. Those alloys mainly provided a lower mass of the prosthetic filling (a lower specific gravity of the alloy), better mechanical properties and a lower price than that of the precious metals. The cobalt-chromium alloys belong to the group of common metal alloys. They are used in the construction of skeletal prostheses, crowns and bridges for ceramic material facing, retention beams and ready-made implant pillars.

The cobalt-chromium alloys are applied not only because of their low price but also their good corrosion resistance. These alloys possess high elasticity and hardness, which hinders their mechanical treatment. However, they do not contain elements harmful for the human body, such as nickel or beryllium [2÷5].

Most of the industrial cobalt alloys originate from the ternary Co-Cr-Mo and Co-Cr-W alloys. The wolfram and/or

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* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND
** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING, 23 REYMONTA STR., 30-059 CRACOW, POLAND

molybdenum additions determine their mechanical properties and corrosion resistance, and their microstructure is dependent on the type of technology and the processing conditions [4, 6, 7].

Co-Cr-Mo alloys are the most useful for the construction of non-permanent prosthetic elements, due to their mechanical properties, corrosion resistance and surface finish. The wolfram containing alloys are designed to be joined with ceramics. Their asset is a higher resistance to the dimension changes at the temperature of ceramic burning.

A higher content of W than Mo or its total replacement by Mo, together with the elimination of carbon, significantly improves the ductility in cobalt matrix alloys, expressed by higher values of elongation A and contraction Z [5].

Many properties of cobalt alloys are determined by the crystallographic structure of the metal and the introduced alloy elements. The cobalt based alloys applied in stomatology are low-carbon alloys. The carbon addition, although low in the amount, has a very significant effect on the mechanical properties, especially the plasticity. A higher carbon content – within 0.3÷1.0% – determines a high strength. During the heat treatment, the presence of carbide-forming alloy additions with a significant content of carbon causes the formation of carbides of a complex $M_{23}C_6$ – type structure, distributed along the grain boundaries and in the interdendritic areas. The chromium content of these alloys determines their high corrosion resistance. The molybdenum influences the matrix reinforcement and the grain refining. The basic element which undergoes segregation is chromium. Its high content in the alloy (within the range of 19-35%) makes the $M_{23}C_6$ – and M_3C_2 – type carbides dominant. Compared to chromium, molybdenum exhibits a lower tendency for segregation. The change of its concentration varies between 4% in the dendrites and 6% in the interdendritic areas [2, 4, 6, 8÷12].

The aim of the research was to characterize the microstructure and corrosion resistance of the Co-Cr-Mo and Co-Cr-W-Mo alloys applied in dental prosthetics. The work included an observation of the microstructure with the use of light and scanning microscopy. Additionally, the chemical composition analysis was performed on selected areas, with the application of an EDS analyzer. Corrosion resistance tests were also carried out in the artificial saliva environment.

2. Material and test methodology

The following casting alloys were used in the research:

- Co-Cr-Mo (by Vaskut Kohászati KFT)
- Co-Cr-W-Mo (by Mesa di Sala Giacomo & c. s.n.c).

The dimensions of the test samples were: *d* =8,5 mm, h=12 mm. The chemical composition of the tested alloys are presented in Table 1.

The metallographic tests were performed on mechanically cut-out samples, which were next ground and polished with the use of $^1/_4$ μm diamond paste. The prepared surfaces of the samples were etched with a reagent consisting of 3 parts of HCl and 1 part of HNO_3. The observation of the microstructure of the test samples involved the application of a light microscope MeF2 by Reichert.

TABLE 1

Chemical composition of tested alloys

Alloy	Chemical composition, % wt								
	Cr	Mo	W	Mn	Fe	Nb	Si	C	Co
Co-Cr-Mo	26.89	2.51	0.02	0.66	1.3	0.73	1.5	0.25	reszta
Co-Cr-W-Mo	19.75	6.03	7.02	0.49	0.41	0.02	0.04	0.15	reszta

What is more, the prepared samples underwent a chemical composition test of the phases existing on the structure of the examined materials. The analysis was performed with the use of a scanning electron microscope HITACHI S-3500N, equipped with an electron microprobe X-ray analyzer EDS by Noran.

The electron microscope tests were conducted with the accelerating voltage of 15 kV. The chemical composition analysis was performed with the use of the point-by-point method in the matrix and the eutectic precipitates.

The electrochemical measurements aimed at an assessment of the corrosion resistance of the examined alloys with the cobalt matrix, on the basis of the currentless potential and the polarization measurements.

Before the measurement, the tested electrodes of the Co-Cr-Mo and Co-Cr-W-Mo alloys were prepared by means of grinding the electrodes' surfaces with abrasive paper, gradation 1200. The electrode in the shape of a cylinder was immersed in a teflon holder. After the electrode had been fixed in the teflon holder, it was defatted with an organic solvent. The corrosive environement was artificial saliva of the chemical composition given in Table 2. The tests were carried out at 37°C (for the best possible simulation of the working conditions of the examined alloys – the human body temperature). The polarization tests were carried out within the potential range of 1500-1250 mV, with four rates of potential changes: 1, 3, 5 and 10 V/min. The measurements of the polarization curves were performed in a tri-electrode vessel, in which the working electrode was represented by the examined alloys and the reference electrode was a chlorosilver electrode. The values of the potential were recalculated into the hydrogen standard (SHE), with the consideration of the temperature coefficients. The surface of the test-prepared alloys equaled 0.13 cm^2. The measurements were carried out with the use of a potentiostat PGZ301 VoltaLab.

TABLE 2

Composition of artificial saliva (ISO 10271:2001 – Dental metallic materials - Corrosion test methods)

Component	Quantity [g/l]
NaCl	0.400
KCl	0.400
$CaCl_2 \cdot H_2O$	0.795
$NaH_2PO_4 \cdot H_2O$	0.780
$Na_2S \cdot H_2O$	0.005
urea	1.000

3. Test results

Figures 1 and 2 present exemplary microstructures of the tested cobalt-chromium materials. The performed tests showed that the analyzed materials characterized in a dendritic structure, typical of casting alloys. The Co-Cr-Mo alloy has a microstructure consisting of an austenite matrix, that is a solution of solid cobalt and chromium in the core dendritic structure.

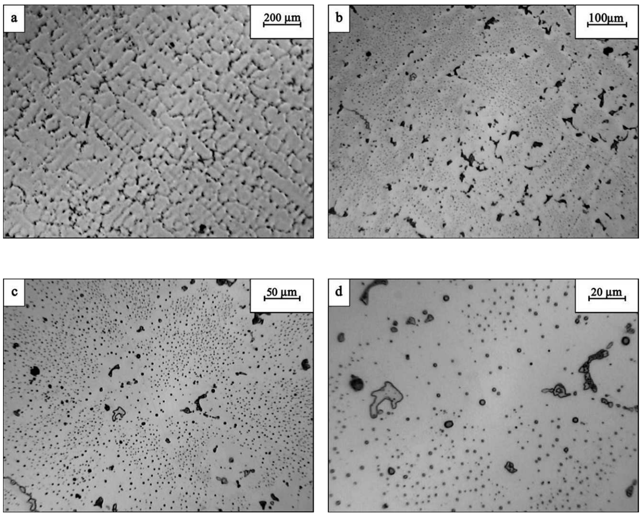

Fig. 1. Microstructure of Co-Cr-Mo alloy

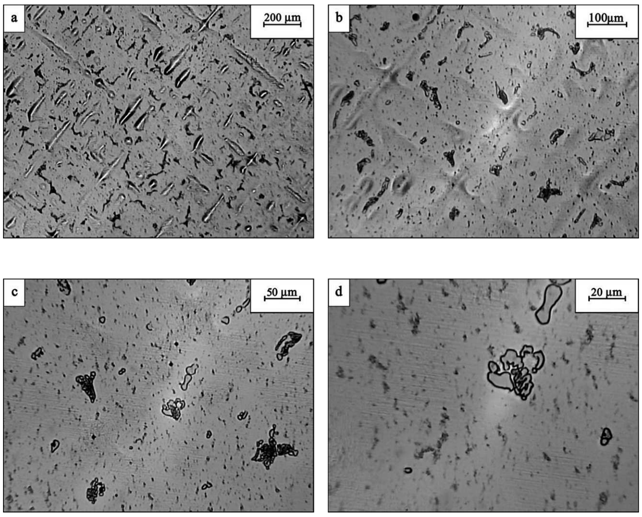

Fig. 2. Microstructure of Co-Cr-W-Mo alloy

Within the crystallites, one can observe dendritic microsegregations and in those areas, the $M_{23}C_6$ – type carbides are present. The created carbides exhibit a tendency to precipitate at the grain boundaries and in the interdendritic areas. The observed microstructure corresponds to the literature description for Co-Cr-Mo alloys [3, 5, 6, 9÷12].

3.1. Chemical composition microanalysis

The chemical composition tests of the precipitates occurring in the examined samples made it possible to determine the contents of such elements as Co, Mo, Cr, W and Mn. The chemical composition tests analyses were performed on both the matrix and the eutectic precipitates revealed during the etching of the tested material.

Figure 3 presents the microscope image of the Co-Cr-Mo alloy with marked areas of a local microanalysis of the chemical composition, as well as the spectrograms of the induced X-radiation. The results of the quantitative analysis of the marked areas are included in Table 3.

As it can be seen, the matrix of the tested material has a higher content of Co and Cr in comparison with the eutectic precipitates, in which Mo, Nb and Si are in higher amounts.

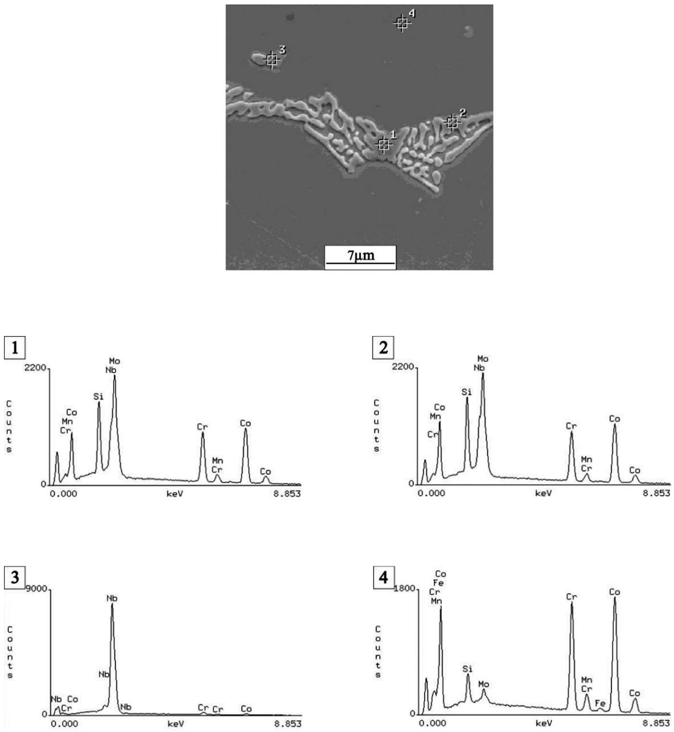

Fig. 3. SEM image of Co-Cr-Mo alloy and EDS spectrogram of areas shown in SEM image

TABLE 3

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

Area	Chemical composition, %wt						
	Si	Mo	Cr	Mn	Fe	Co	Nb
1	6.56±0,20	21.05±0,62	17.64±0,57	0.88±0,31	0.30±0,28	41.70±1.26	11.86±0.75
2	6.40±0.19	21.07±0.95	17.35±0.55	0.70±0.30	0.36±0.27	42.65±1.24	11.47±0.56
3	-	-	3.14±0.26	-	-	3.00±0.83	93.86±1.15
4	2.32±0.16	2.29±0.27	28.25±0.63	0.93±0.33	1.49±0.30	64.71±1.44	-

The image of the Co-Cr-W-Mo alloy microstructures together with the X-ray spectograms is presented in Figure 4. The results of the quantitative analysis of the chemical composition are included in Table 4. The microanalysis showed that the matrix of Co-Cr-W-Mo alloy was rich in cobalt and chromium, whereas the eutectic contained higher values of W and Mo.

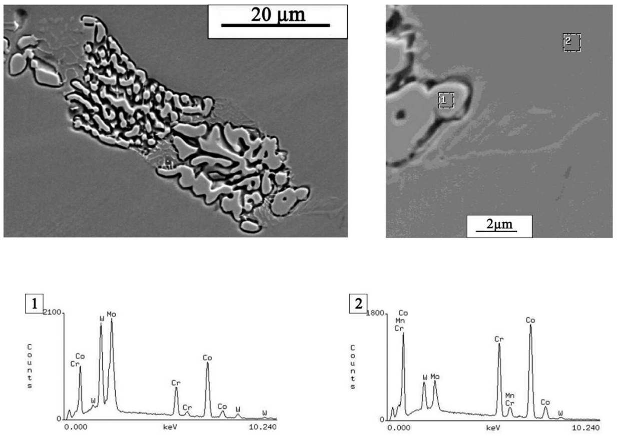

Fig. 4. SEM image of Co-Cr-W-Mo alloy and EDS spectrograms of areas shown in SEM image

TABLE 4
Chemical composition of the precipitates observed in Co-Cr-W-Mo alloy

Area	Chemical composition, %wt				
	Mo	Cr	Mn	Co	W
1	21.96±0,91	11.57±0,54	0.24±0,31	44.42±1.33	21.81±2.56
2	7.15±0.51	21.40±0.57	0.59±0.30	61.72±1.40	9.14±3.60

3.2. Currentless potential measurement

The open circuit potential (corrosion potential) of the metal changes is the function of time. Figure 5 presents the value change of the potential of the tested alloys in time. For the Co-Cr-W-Mo alloy, the corrosion potential value significantly increases, beginning from the potential of about -170 mV up to the value of 20 mV, in the time of 2400 s, and next its value rises slightly in the following 1100 s up to 48 mV, with the tendency for a minor increase. The potential value of the Co-Cr-Mo alloy is almost constant and varies from 0 mV to 32 mV after the time of 3600 s.

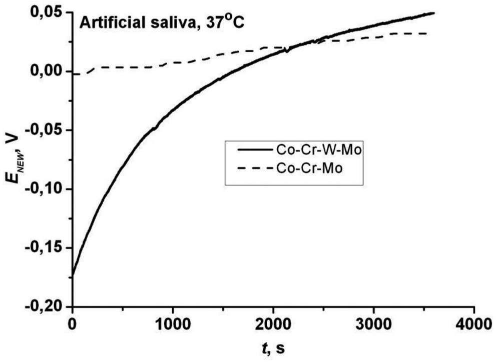

Fig. 5. Evolution of open circuit potential of tested alloys

3.3. Polarization tests

The polarization tests for the Co-Cr-W-Mo and Co-Cr-Mo alloys provided voltamperometric curves are shown in Figure 6. The tested materials characterize in a similar progress of the obtained curves for different rates of the potential changes: 1, 3, 5 and 10 V/min. Figure 6 compares the progress of the curves with the potential change rate of 3 V/min.

The progress of the curves is characteristic for materials of a very high corrosion resistance. The tested alloys characterize in a wide passive region (-770÷880 mV) of a very low current density (about 0.5 mA/cm^2). In the consideration of the Co-Cr alloys, once should note the chromium content (29.84% Cr, 17.64% Cr). The chromium content of >18% [13] assures passivation of the alloy's surface and protects it from corrosion. Additionally, the passivizing factor in the examined alloys is the molybdenum (2.53%Mo, 4.87%Mo), which significantly increases their corrosion resistance [14]. A number of tests performed on the corrosion resistance of the Co-Cr-Mo alloys points to the fact that the content of the protective film which forms at the surface of the alloys is dominated by the presence of Cr_2O_3 with a minor addition of cobalt and molybdenum oxides [15].

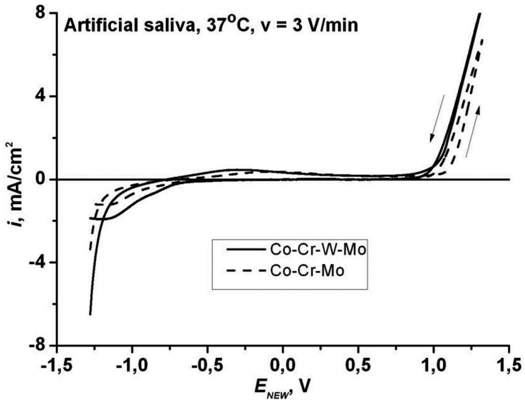

Fig. 6. Polarization curves of alloys

4. Conclusions

The basic properties which should be possessed by metals and their alloys applied, among others, in skeletal prostheses in stomatology are the following: biotolerance (they should not dissolve in the saliva and body fluids present in the oral cavity); a high corrosion resistance (they should not oxidize); a stability of the set of particular physical an mechanical characteristics and a homogeneity of the chemical composition. Also required is the provision of particular and permanent esthetic properties as well as taste and smell organoleptic properties.

As a result of the performed tests, Giacchi et al. [11] observed structure defects in the Co-Cr-Mo alloys, such as porosity and crystalline structure tendency, which are one of the most important structural determinants of casting brittleness. They also include dendritic segregations and carbide precipitates localized at the crystallite boundaries.

On the basis of the performed tests, it was stated that the analyzed alloys characterized in a dendritic structure typical of casting alloys. The characterized alloys, in the cast state, had an austenite structure. The matrix was a solid solution of chromium, molybdenum and carbon in cobalt of the γCo structure (the chromium and molybdenum contents are selected in such a way so as the alloy matrix can be a γCo solution of an A1 structure) with the present precipitates rich in Cr and Mo (Co-Cr-Mo) and in W and Mo (Co-Cr-W-Mo). In the eutectic areas, $M_{23}C_6$-type carbide precipitates were present. Carbide precipitates increase the strength parameters, but they can also cause a tendency for corrosion. In the interdendritic areas, a σ phase rich in Cr and Mo can also be present.

Corrosion is one of the main problems in the application of metals as biomaterials. The chemical compositions of stomatological alloys with a cobalt matrix were selected in such a way so as to guarantee good corrosion resistance and biocompatibility.

The electrochemical corrosion of Co-Cr alloys is significantly dependent on the content of chromium and molybdenum, which largely contribute to alloy passivation. The grain size does not remain uninfluential to the corrosion of cobalt alloys [3, 16÷17]. Dockal's test results [cited after [3]] prove that a coarse-crystalline cast has a lower corrosion resistance than a fine-crystalline one.

The presence of a foreign matter in the human body in the form of a prosthesis activates defensive reactions and stimulates mechanisms whose aim is its elimination, which resultantly leads to its degradation. When a foreign substance is detected by the immunological system, the body begins the production of proteins (antibodies) of a strong oxidizing effect. The presently applied stomatological materials acquire their required corrosion resistance by creating a layer of oxides on their surface, which are the inhibitors of the corrosion processes [1].

The wet and warm oral cavity is an ideal environment for corrosion. Within it we can observe chemical and electrochemical reactions between the prosthetic filling and the surrounding saliva and tissue fluids. In such an environment, the alloy faces numerous corrosion factors, such as: the presence of oxygen dissolved in the body fluids or the differences in the electrochemical potentials leading to the creation of local corrosion cells.

Co-Cr alloys can be implanted directly into the bone for an extended period of time and will not cause a detrimental reaction. This beneficial property is connected with the alloy's low solubility and electrogalvanic reaction. The material is inert and does not cause an inflammatory reaction [3].

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