Surface modification of Co-Cr-Mo alloys by electron-beam treatment

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Abstract. We present a study on the possibility of modifying the structure and properties of Co-Cr-Mo alloys by using the electron-beam surface modification technique. The technological parameters were optimized in order to obtain the highest cooling rate without melting the surface. The samples were characterized in terms of their phase composition and microstructure by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The surface roughness was evaluated by atomic force microscopy (AFM). The corrosion properties were investigated by electrochemical tests. It was found that the treatment process leads to a transition in the phase composition, from ε + γ to a single-phase γ structure. The electron-beam surface modification process causes an increase in the surface roughness and a significant improvement of the corrosion resistance.

1. Introduction

Currently, the Co-Cr-Mo alloy is an attractive material for applications in the modern medicine due to its biocompatibility and suitable mechanical properties and is widely used for manufacturing of joint replacements [1-3]. However, the biological corrosion leads to a release of metallic ions, which in turn leads to adverse reactions and failure of the implant [4]. Since the surface of the material is exposed during the implant’s service, the discussed limitations can be overcome by an appropriate technology of surface treatment.

Recently, surface treatment of materials by high-energy fluxes (e.g., laser or electron beams) has become a common approach to improving the surface properties of materials due to the possibility of controlling precisely the input energy, the very short process time necessary, etc. The mechanism behind the electron-beam technologies is the transformation of the electrons’ kinetic energy into heat bringing about a specific heat distribution from the surface to the bulk. The heating and cooling rates are quite high, which leads to changes in the phase and chemical composition, the surface topography, the microstructure, etc. [5-8]. Wei et al. [9] have investigated the possibilities of optimizing the
hardness and tribological performance of a Co-Cr-Mo implant alloy by means of laser interference lithography; the results demonstrated a significant enhancement in the discussed properties.

However, the improvement of the surface properties of Co-Cr-Mo alloys by means of electron-beam treatment (EBT) has not yet been extensively studied. Furthermore, analyses of the EBT process effect on the surface topography and corrosion properties of Co-Cr-Mo-based alloys are currently lacking in the scientific literature. The study reported here aims to reveal the influence of electron-beam surface treatment of Co-Cr-Mo-based alloy on the material’s surface topography and corrosion resistance. These properties are of major importance for the practical application of such implants; the results are expected to add knowledge to and extend the understanding of the processes of manufacturing modern implant materials.

2. Experimental

The Co-Cr-Mo alloy used had a chemical composition of 25.5 wt % Cr, 0.2 wt % Mn, 4.3 wt % Fe, 59.9 wt % Co, 1.0 wt % Ni, 4.7 wt % Mo, 0.6 wt % W and 3.8 wt % other elements. The surfaces of specimens with dimensions of 20×20 mm and a thickness of 4 mm were electron-beam treated by Leybold Heraeus (EWS 300/15-60) electron-beam equipment using a continuous electron-beam scanning. The technological parameters were as follows: accelerating voltage 52 kV, electron-beam current 25 mA, electron-beam scanning frequency 1 kHz, speed of specimen motion 40 mm/sec; electron-beam diameter 0.5 mm, linear electron-beam trajectory. These technological parameters were optimized in order to obtain a treated zone without the formation of a melt pool. However, partial melting of some parts of the surface of the sample probably takes place during the scanning electron-beam treatment process. The temperature was evaluated at about 1200 °C by using a numerical model published in works [10, 11].

The samples were characterized by X-ray diffraction (XRD) with CuKα (1.54 Å) radiation. The experiments were carried out in a symmetrical Bragg-Brentano (B-B) mode at a 20 scale within the range from 20° to 100° with a step of 0.03° and a counting time of 5 s per step.

The samples were further studied by means of a LYRA 3 XMU scanning electron microscope (SEM, Tescan), equipped with an EDX detector (Quantax 200, Brucker), which integrates a true standardless analysis with P/B ZAF corrections (Z is the atomic number correction factor; A, the X-ray absorption correction factor; F, the fluorescence correction factor). During the experiments, back-scattered electrons were used.

The surface topography of the specimens was studied by atomic force microscopy (AFM). The force constant was 43 N/m and the radius of the silicon nitride tip was 10 nm. The experiments were performed in a non-contact mode.

The experiments on determining the corrosion properties of the samples were conducted in an electrochemical cell with a platinum counter electrode and a saturated Ag/AgCl reference electrode. Both electrodes together with the working one with a 0.2-cm² exposed area were immersed in 80 ml of naturally aerated artificial saliva solution (Fusayama) containing KCl (0.4 g/l), NaCl (0.4 g/l), CaCl₂·2H₂O (0.795 g/l), NaH₂PO₄·2H₂O (0.690 g/l), Na₂S·9H₂O (0.005 g/l), CH₃N₂O (1 g/l) with pH 5 (decreased with 1 N HCl) at 37±0.05 °C. After OPC carried out for 30 min, potentiodynamic polarization curves were recorded by sweeping the potential starting at a cathodic potential of about 250 mV below the OPC up to +2000 mV vs. Ag/AgCl at a scan rate of 1 mV s⁻¹ using a potentiostat 263A (EG&G Princeton Applied Research) coupled to a PC by a controller. The corrosion parameters, Ecorr (corrosion potential) and Icorr (corrosion current density) were obtained from the polarization curves by using the Tafel extrapolation method. The polarization resistance, Rp, was determined from the Stern-Geary equation.

3. Results and discussion

Fig. 1 presents the XRD results. The diffraction pattern in Fig. 1 (a) pertains to the initial Co-Cr-Mo alloy, while Fig. 1 (b)) is the diffractogram of the electron-beam modified specimen. The pattern of the untreated sample exhibits some peaks of ε-Co and, in addition, there is one diffraction maximum at
about 2θ of 44.45° belonging to γ-Co. It should be noted that the ε-Co phase has a hexagonal closed-packed (hcp) crystal lattice which is stable at room temperature and transforms to γ at 900 °C. The latter phase has a face-centered cubic (fcc) structure. The phase transition fcc-to-hcp during the alloy manufacturing usually occurs slowly and some traces of the metastable at room temperature fcc phase remain [12, 13]. During the electron-beam surface treatment of the Co-Cr-Mo alloy, (Fig. 1 (b)), a phase transition takes place to the fcc-γ phase. During the EBT process, the surface of the sample is heated up to a certain temperature, where the gamma phase is stable. As already mentioned, the transformation fcc-to-hcp is too slow and cannot occur during the following rapid cooling process. It should be noted that the results obtained by the XRD analysis are in agreement with those published in Ref. [9] where a surface modification of Co-Cr-Mo implant alloy by laser interference lithography has been studied.

![Figure 1. X-ray diffraction pattern of the Co-Cr-Mo alloys a) untreated; b) electron-beam treated.](image)

Figure 2 presents a scanning electron microscopy (SEM) image of the untreated Co-Cr-Mo sample (Fig. 2 (a)). The chemical composition of the alloy was studied by EDX and the results are shown in Fig. 2 (b) and Table 1. One can see the biphasic ε+γ microstructure of the discussed specimen. The main phase is ε surrounded by the line-like regions of γ phase. The SEM results are in agreement with those of the XRD analysis pointing to a presence of the discussed bimodal structure.

![Figure 2. a) SEM image of the untreated Co-Cr-Mo sample, and b) the corresponding EDX spectrum.](image)

Figure 3 presents a SEM micrograph of the treated Co-Cr-Mo sample (Fig. 3 (a)). The results of the EDX study of this sample’s chemical composition are shown in Fig. 3 (b) and Table 1. After the EBT, the microstructure becomes a single-phase structure and no traces of the second phase can be seen. These results match those of the XRD experiments, where a single γ-Co phase was registered.
Therefore, the phase transformation from $\varepsilon$-Co + $\gamma$-Co to $\gamma$-Co after the electron-beam surface modification of the Co-Cr-Mo alloy observed by the XRD experiments is confirmed by the SEM analysis. The EDX measurements, presented in Figs. 2 (b) and 3 (b), were conducted in order to evaluate the influence of the electron-beam surface modification on the chemical composition of the Co-Cr-Mo alloys; the results are summarized in Table 1. It is evident that the surface treatment leads to an increase in the amount of Cr and a decrease in the content of Co attributed to the evaporation of cobalt due to its lower melting temperature.

![Figure 3](image1.png)

**Figure 3.** a) SEM image of the treated Co-Cr-Mo sample, and b) the corresponding EDX spectrum.

|                  | Cr  | Mn  | Fe  | Co  | Ni  | Mo  | W   | Other |
|------------------|-----|-----|-----|-----|-----|-----|-----|-------|
| Untreated alloy  | 22.2| 0.3 | 4.5 | 59.6| 1.6 | 5.1 | 1.0 | 5.7   |
| Treated alloy    | 34.3| 1.5 | 3.4 | 49.1| 1.1 | 3.1 | 3.6 | 3.9   |

**Table 1.** Chemical composition of the Co-Cr-Mo alloy with and without electron-beam surface modification

Fig. 4 shows three-dimensional AFM images of the specimens’ surface topography. It is obvious that the EBT process strongly affects the surface topography.

![Figure 4](image2.png)

**Figure 4.** Three dimensional AFM images of a) untreated Co-Cr-Mo alloy; b) electron-beam treated Co-Cr-Mo alloy.

The surface roughness was quantitatively evaluated by mean of the roughness parameter $S_a$, which is given by

$$S_a = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |z(x_k, y_l) - \mu|$$

(1)

In (1), $M$ and $N$ are the numbers of measured points along the $x$ and $y$ axes; $z$ is the height of each measured point with coordinates $x_k$ and $y_l$; $\mu$ is the mean height. The results obtained for the parameter $S_a$ are 14.59 nm for the untreated alloy and 69.99 nm for the EBT Co-Cr-Mo alloy. Thus, the electron-beam surface modification leads to an about fivefold increase in the surface roughness, which can be due to the evaporation of a small amount of the treated material during the EBT and the subsequent
condensation of the vapors. According to the authors of [14], the vapors condensation can form protrusions thus increasing the surface roughness. It should be noted that the increase observed in the surface roughness after the EBT is associated with an increase in the contact surface area, which enhances the cell adhesion and supports the cell growth. Furthermore, according to the authors of [15, 16], such nano-rough surface architecture is less susceptible to being colonized by bacterial cells in comparison with the conventionally manufactured surfaces.

Fig. 5 shows experimental polarization curves of untreated and EBT Co-Cr-Mo alloy in artificial saliva (pH 5) at 37±0.05 °C. The results demonstrate a decrease in the corrosion current density and an increase in the corrosion potential values pointing to a significant improvement in the corrosion resistance of the treated sample compared with the untreated alloy. It is known that lower values of the corrosion current density correspond to a lower corrosion rate. At the same time, the increase in the $E_{corr}$ indicates a better corrosion resistance of the tested material [17-19]. The change in the relative chemical elements content at the surface of an alloy alters the oxide resistance and, therefore, the corrosion rate. According to Dobrzanski and Reimann [20], the Cr concentration plays a major role in the corrosion behavior, the higher chromium content corresponding to a better performance.

**Figure 5.** Potentiodynamic polarization curves of initial and treated samples in artificial saliva (pH 5) at 37±0.05 °C.

### 4. Conclusions

The results obtained in the present study show the possibility of modifying the structure and properties of Co-Cr-Mo alloys by means of electron-beam surface treatment. The treatment leads to a phase transformation, from main $\varepsilon$ phase and a small amount of $\gamma$ phase, to a single-phase $\gamma$ structure due to the fast cooling rate. The depth of the treated zone is about 250 μm. It is also shown that the use of electron-beam surface modification results in an about fivefold increase in the surface roughness corresponding to an increase in the contact surface area. Furthermore, the results of the electrochemical experiments demonstrate a significant improvement in the corrosion resistance following the electron-beam surface modification of the Co-Cr-Mo alloy.

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**References**

[1] Al Jabbari Y 2014 *J. Adv. Prosthodont.* **6** 138–145
[2] Vendittoli P, Amzica T, Roy A, Lusignan D, Girard J and Lavigne M 2011 *J. Arthroplasty.* **26** 282–288
[3] Niinomi M 2002 *Metall. Mater. Trans. A* **33** 477–486
[4] Abu-Amer Y, Darwech I and Clohisy J 2007 *Arthritis Res. Ther.* **9** S6
[5] Weglowski M, Blacha S and Phillips A 2016 Vacuum 130 72-92
[6] Ormanova M, Petrov P and Kovacheva D 2017 Vacuum 135 7-12
[7] Petrov P, Dechev D, Ivanov N, Hikov T, Valkov S, Nikolova M, Yankov E, Parshorov S, Bezdushnyi R and Andreeva A 2018 Vacuum 154 264-271
[8] Nevskii S, Sarychev V, Konovalov S, Granovskii A and Gromov V 2020 Metals 10 1399
[9] Wei X, Li W, Liang B, Li B, Zhang J, Zhang L and Wang Z 2016 Tribology International 97 212-217
[10] Angelov V, Ormanova M, Kaisheva D, Lazarova R, Dimitrova R and Petrov P 2019 Nucl. Instr. Meth. Phys. Res. Sec. B 440 88–94
[11] Ormanova M, Angelov V and Petrov P 2016 J. Phys. Conf. Ser. 700 012033
[12] Mani A, Salinas-Rodriguez A and Lopez H 2011 Mater. Sci. Eng. A 528 3037–3043
[13] Wei D, Koizumi Y, Takashima T, Nagasako M and Chiba A, 2018 Mater. Res. Lett. 6 93-99
[14] Zhang K, Zou J, Grosdidier T, Gey N, Weber S, Yang D and Dong C 2007 J. Vac. Sci. Technol. 25 (1) 28–36
[15] Curto B, Brunella M, Giordano C, Pedeferri M, Valtulina V, Visai L and Cigada A 2005 Int. J. Artif. Organs 28 (7) 718–730
[16] Pokrowiecki R, Szaraniec B, Chlopek J and Zaleska M 2014 Eng. Biomater. 124 2–10
[17] Liu C, Zhou Z and Li K 2017 Electrochimica Acta 241 331-340
[18] Jin W, Wu G, Feng H, Wang W, Zhang X and Chu P 2015 Corros. Sci. 94 142–155
[19] Zhang T, Deng Q, Liu B, Wu B, Jing F, Leng Y and Huang N 2015 Surf. Coat. Technol. 273 12–19
[20] Dobrzański L and Reimann L 2011 J. Achieve. Mater. Manuf. Eng. 49 193–199