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Corrosion resistance of Cr-Ni-Mo steel after sterilization process

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ABSTRACT

Purpose: The aim of the work was to evaluate how the process of high pressure steam sterilization influences the pitting corrosion resistance of Cr-Ni-Mo steel used for implants production.

Design/methodology/approach: Surfaces of samples were prepared by electrolytic polishing and chemical passivation. Samples were sterilized in steam with the use of different parameters of temperature, pressure and time. Corrosion resistance investigations were carried out with the use of potentiodynamic method. The test were realized in solution simulating human blood environment (artificial plasma) at the temperature of 37±1ºC and pH = 7.2. Parameters describing the corrosion resistance have been determined on the basis of analysis of anodic polarization curves.

Findings: High pressure steam sterilization process improves all parameters relating to pitting corrosion resistance of Cr-Ni-Mo implantation steel that is: corrosion potential Ecorr, breakdown potential Eb, polarization resistance Rp, corrosion current density icorr and corrosion rate. The increase of sterilization time for constant parameters of temperature and pressure of steam was the important factor which improved significantly the corrosion resistance of tested samples.

Research limitations/implications: Further investigations of chemical composition of the layers formed during sterilization process are planed.

Originality/value: The obtained results show the advantageous influence of passivation and high pressure steam sterilization on the pitting corrosion resistance of Cr-Ni-Mo steel in solution simulating human blood environment (artificial plasma).

Keywords: Corrosion; Biomaterials; Steam sterilization

PROPERTIES

1. Introduction

Biomaterials which are used for implants production have to fulfill many quality requirements. Biotolerance in contact with tissues and physiological liquids is one of the main criteria. A good corrosion resistance of a biomaterial close connected with biotolerance limits the adverse effects on implant-tissue interface.

Cr-Ni-Mo austenitic steels, however commonly used in production of implants for orthopedic and maxillo-facial surgery, as well as for different kinds of stents (for interventional cardiology) are the biomaterials of a lowest corrosion resistance among the metallic biomaterials. Therefore the investigations referring to implants quality which is formed in surface treatment processes, modifying physicochemical properties of its surface, are of great importance. The worked out methods of electrochemical treatment and chemical passivation [1-9] as well as deposition of carbon coating in rf PACVD [10-14] process guarantee good corrosion resistance, good biotolerance and limit the development of disadvantageous toxic and allergic reactions.

Quality of medical devices and effectiveness of therapeutic process in which they are used depends also on the efficiency of sterilization process. The purpose of this process is to eliminate or

destroy all forms of microorganisms in their vegetative as well as spore forms, so that the implants can be safety used in clinical application. In the most often used methods of sterilization the bactericidal properties of high pressure steam, ethylene oxide and ionizing radiation are applied.

The purpose of investigations presented in the paper was evaluation whether and how the parameters of sterilization process influence the corrosion resistance of specimens made of Cr-Ni-Mo implantation steel.

2. Materials and methods

The investigations were carried out on the samples made of Cr-Ni-Mo steel [15] in a bar form of diameter d = 6 mm. The samples were polished by electrochemical method to ensure the required roughness of the surface ($R_a \leq 0{,}16\mu m$) and finally chemical passivation in 40% HNO_3 was performed [9]. Next the process of steam sterilization with the use of different parameters of temperature, pressure and time was carried out – Table 1.

Table 1.
Parameters of high steam sterilization process

Sterilization program	Temperature T, °C	Pressure p, bar	Time t, min.
P1	134	2,1	4
P2	121	1,1	20
P3	134	2,1	12
P4	121	1,1	30

In order to evaluate the influence of the sterilization process on the physicochemical properties of the steel surface, the corrosion resistance investigations with the use of potentiodynamic method were carried out [16]. The pitting corrosion tests were realized by recording of anodic polarization curves. The VoltaLab® PGP 201 system of Radiometer firm for electrochemical tests was applied. The recording of anodic polarization curves was carried out from potential value $E = E_{corr} - 100$ mV with polarization in direction of positive values and with the potential changes rate equal to 1mV/s. When the current density has achieved the value equal to $1mA/cm^2$ the direction of polarization was changed and the returned curve has recorded. On the basis of the obtained curves the breakdown potentials E_b, polarization resistance R_p, corrosion current density i_{corr} and corrosion rate have been determined.

Table 2.
An artificial plasma composition acc.to [17]

Chemical compound	Mass concentration %/H_2O
NaCl	6,8
$CaCl_2$	0,2
KCl	0,4
$MgSO_4$	0,1
$NaHCO_3$	2,2
Na_2HPO_4	0,126
NaH_2PO_4	0,026

The investigations have been carried out for the samples of a polished and passivated surface – before and after sterilization process, in the electrolyte simulating human blood environment (artificial plasma) at the temperature 37±1°C and pH = 7,2 – Table 2.

3. Results

The first stage of research was the investigation of corrosion resistance of the samples of electrolitycaly polished surface and electrolitycaly polished + passivated surface but not subjected to sterilization process. The values of corrosion potentials for samples of electrolitycaly polished surface were in the range of $E_{corr} = +19 \div +26$ mV. The chemical passivation process caused the increase of corrosion potential to the values $E_{corr} = +58 \div +62$ mV. The run of anodic polarization curves for electrolitycaly polished and electrolitycaly polished + passivated surfaces has been presented on Fig.1 and the values referring to corrosion resistance parameters in Table 3.

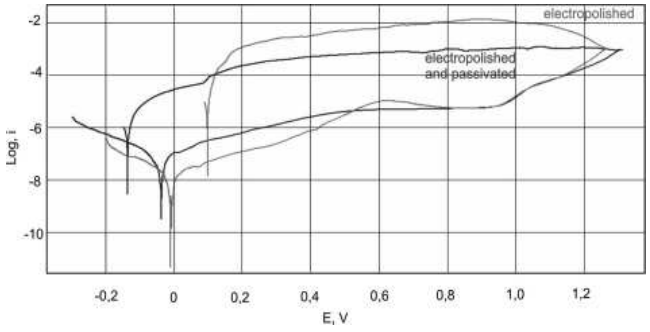

Fig. 1. Anodic polarization curves recorded for samples of Cr-Ni-Mo steel of different way of surface preparing and not subjected to sterilization process

Chemical passivation of the specimens' surfaces influenced also increasing of the breakdown potentials of about 30mV. The significant decrease of both the corrosion current density i_{corr} from the range of $63{,}2 \div 72{,}8$ to $3{,}1 \div 4{,}2$ nA/cm^2 and the corrosion rate from 271 nm/year to 36 nm/year have also been stated. The three times increase of polarization resistance R_p has been observed.

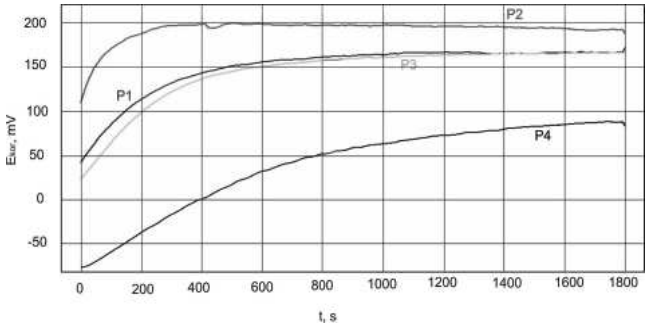

Fig. 2. The course of corrosion potential changes for samples of Cr-Ni-Mo steel after sterilization process according to programs P1, P2, P3 and P4 in time function

Table 3.
Results of pitting corrosion resistance investigations

Method of surface preparing		Corrosion potential E_{corr}, mV	Breakdown potential E_b, mV	Corrosion current density i_{corr}, nA/cm^2	Polarization resistance R_p, kΩcm	Corrosion rate, nm/year
Electrolytic polishing	Not sterilized	+19 ÷ +26	+1170 ÷ +1190	63,2 ÷ 72,8	96,5 ÷ 98,2	271
Electrolytic polishing +Passivation		+58 ÷ +62	+1190 ÷ +1210	3,1 ÷ 4,2	352,9 ÷ 384,2	36
Electrolytic polishing +Passivation	Sterilized P1	+173 ÷ +178	+1227 ÷ +1230	2,8 ÷ 3,1	450,2 ÷ 524,2	37
Electrolytic polishing +Passivation	Sterilized P2	+192 ÷ +202	+1238 ÷ +1245	1,7 ÷ 3,8	288,7 ÷ 296,3	27
Electrolytic polishing +Passivation	Sterilized P3	+176 ÷ +184	+1235 ÷ +1255	0,6 ÷ 0,8	610,2 ÷ 616,2	28
Electrolytic polishing +Passivation	Sterilized P4	+99 ÷ +102	+1255 ÷ +1265	0,4 ÷ 0,5	681,4 ÷ 696,3	31

In a result of the first stage investigations the further ones were conducted only for the passivated samples. The next stage of research was determination of corrosion resistance of passivated and sterilized samples. Different values of temperature and pressure of steam as well as the time of sterilization have been applied – Table 1.

At first the results of corrosion resistance investigations of samples sterilized in temperature 134°C – program P1 and 121°C – program P2 were compared. Meaningful increase of corrosion potential values E_{corr}, average of about +150 mV independently to temperature of process has been observed – Fig. 2, Table 3.

Sterilization process has also caused the increase of breakdown potentials of about 40 mV – Fig. 3, Table 3. The values of corrosion current density were established on the similar level for P1 and P2 programs (i_{corr} = 1,7 ÷ 3,1 nA/cm^2) and were slightly lower comparing to unsterilized samples.

When the higher temperature of sterilization (134 °C) was used the meaningful increase of polarization resistance up to value R_p = 450,2 ÷ 524,2 kΩcm has been observed. Corrosion rate described in nm/year has not been changed – Table 3.

In further tests the time of sterilization was extended without any changes in temperature and pressure of steam. The anodic polarizations curves recorded after polarization for P3 and P4 program are shown on Fig. 4. Extending the time from 4 to 12 min, when temperature 134°C and pressure 2,1 bar were used, influenced advantageously the physicochemical properties of steel and caused the decrease of corrosion current density to the value i_{corr} = 0,6 ÷ 0,8 nA/cm^2. Also a further shift of breakdown potential of about 20 mV in direction of its positive values has been observed - Table 3. The longer time of sterilization didn't cause significant differences in corrosion potentials values – Fig. 2, Table 3.

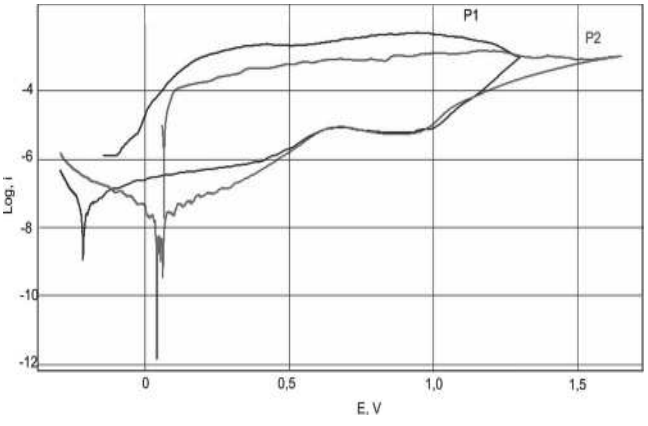

Fig. 3. Anodic polarization curves recorded for samples of Cr-Ni-Mo steel of electrolyticaly polished + passivated surface after sterilization in steam according to P1 and P2

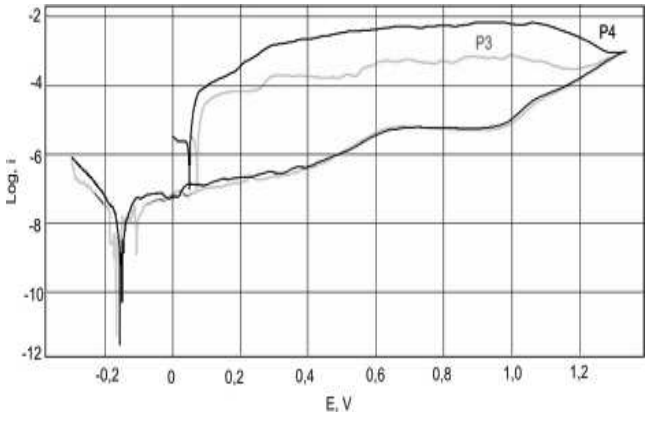

Fig. 4. Anodic polarization curves recorded for samples of Cr-Ni-Mo steel of electrolyticaly polished + passivated surface after sterilization in steam according to P3 and P4

The similar tendency of changes of parameters describing the pitting corrosion resistance has been noted for samples sterilized at temperature 121 °C, pressure 1,1 bar and in time prolonged from 20 to 30 min (P4).

The course of establishing of the corrosion potential shows Fig. 2 and anodic polarization curves for the samples sterilized according to program P4 have been presented on Fig. 4.

The increase of sterilization time comparing to P2 caused the decrease of corrosion current density from values i_{corr} = 1,7 ÷ 3,8 nA/cm^2 to i_{corr} = 0,4 ÷ 0,5 nA/cm^2. A considerable increase of polarization resistance from values R_p = 288,7 ÷ 296,3 kΩcm to R_p = 681,4 ÷ 696,3 kΩcm has been recorded although the corrosion rate was on a similar level – Table 3.

4. Conclusions

The worked out investigations of Cr-Ni-Mo steel have showed that passivation and sterilization process realized with the use of steam in pressure improved the corrosion resistance of the tested samples. Analysis of the results which describe the changes of all parameters relating to pitting corrosion resistance has shown the favorable interaction of steam sterilization process. It has been stated that for all sterilized samples independently of the used parameters (temperature, pressure and time of acting of steam), the corrosion potentials E_{corr} were shifted in the direction of higher positive values - Table 3. A similar tendency of changes has been observed for all the recorded values of breakdown potentials E_b which have achieved the values higher of about 50 mV for all samples subjected to the sterilization process. The advantageous influence of high pressure steam treatment was also expressed in decrease of current corrosion density i_{corr} values and in increasing of polarization resistance R_p of all samples. The analysis of particular influence of sterilization parameters has shown the most significant effect of the time of acting of steam. It should be pointed out that increasing the time of sterilization for constant parameters of temperature and pressure of steam was the factor which improved all parameters describing the corrosion resistance of specimens of Cr-Ni-Mo steel.

It can be stated that sterilization process of Cr-Ni-Mo steel, conducted in purpose to ensure the proper procedure related to quality requirements of implants made of this steel and to their safety use, contributes to the favorable changes which influence the improvement of corrosion resistance of this kind of biomaterial. The investigations of oxide layers formed on the surface of steel during oxidation process in high pressure steam are being planned, in order to explain the changes of chemical and stoichiometric composition of the constituted chemical compounds.

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