

Corrosion behavior of nitrogen stainless steel in Ringer's solution

G.P. Ilieva¹, M.H. Loukaycheva^{2*}, B.R. Tzaneva², L.T. Gekova³ and L.B. Fachikov¹

¹University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd, 1756 Sofia, Bulgaria

²Technical University- Sofia, 8 Kliment Ohridski Blvd, 1756 Sofia, Bulgaria

³Institute of Metal Science, Equipment and Technologies "Acad. A.Balevski" with Hydro-aerodynamics Centre - BAS, 67 Shipchenski prohod Str., 1574 Sofia, Bulgaria

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The implant materials used in medicine are made from different materials and the principle requirement to each material used is its biocompatibility. This work reports preliminary results regarding assessment of high nitrogen stainless steel (HNS) Cr18Mn12N as an implant material replacing of the common Ni containing stainless steels which are toxic. Short - time (for 1 h) and long - time (for up to 220 h) open circuit potential measurements were performed as well as potentiodynamic and potentiostatic studies in Ringer's solution at 37°C. The effect of the preliminary treatment was also considered. After the potentiostatic tests optical and scanning electron microscopies were used to determine the character of the corrosion attack. The surface of the samples was examined and by EDX analysis in order to find out the corrosion products content. Based on the obtained results it can be concluded that the HNS steel exhibits better corrosion resistance in Ringer's solution.

Key words: stainless steel, HNS, nitrogen, Ringer solution, potentiodynamic polarization, potentiostatic polarization

INTRODUCTION

Orthopedic implants use various biocompatible materials [1, 2] which have to be corrosion resistant to body fluids since the release of metallic ions could provoke their degradation and undesired reactions in the human body. Stainless steels, Co, Ti, Ta, Mg and its alloys, for instance, are widely used [3, 4] as materials of implants in surgical operations. Therefore, electrochemical tests of new materials suggested as implants should be performed in controlled media simulating human body fluids prior to final implementations.

The use of austenitic stainless steels as surgical implants is due to its relatively low value in comparison with the other biocompatible materials. The classic austenitic stainless steels exhibit good mechanical and corrosion properties but its Ni content provokes toxicity in the human body [5]. To avoid this problem high nitrogen stainless steels (HNS) such as 314L [6] have been developed to replace Ni-containing materials for implants. The interest about the corrosion resistance of HNS as implant material is provoked by the fact that stems

made of Orthinox (high nitrogen stainless steel but still containing nickel), for instance, occupies 70 % of the hip prostheses market in the UK [7], and it is necessary to be replaced by non-toxic materials.

This work reports preliminary results regarding assessment of high nitrogen nickel free stainless steel Cr18Mn12N as an implant material for replacing the common Ni containing stainless steel Cr18Ni9.

EXPERIMENTAL

Two austenitic stainless steels: the conventional Cr18Ni9 and the new HNS Cr18Mn12N (for chemical content see Table 1) were investigated in Ringer's solution containing (in g/l): 6.8 NaCl, 0.2 CaCl₂, 0.4 KCl, 0.2048 MgSO₄·7H₂O, 0.143 NaH₂PO₄·H₂O, 2.2 NaHCO₃ and 1.0 C₆H₁₂O₆, with pH 7.25 [8]. All tests were carried out in a conventional three electrodes cell in open air conditions at 37°C with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All potentials were reported with respect to the SCE. Three electrochemical methods were used: (i) Cyclic potentiodynamic polarization method (scan rates 0.16, 1.0 and 5.0 mV s⁻¹), (ii) Open circuit potential (OCP) - time measurement (up to 1 or 240 hours) and (iii) Potentiostatic method.

To whom all correspondence should be sent:
E-mail: loukaycheva@tu-sofia.bg

The electrochemical results were obtained with a Galvanostat/potentiostat (Princeton Applied Research Model 263) and computer software Power Suite.

After the anodic polarization for 20 minutes at potential 100 mV more positive than the pitting potential obtained potentiodynamically, the topography and chemical content of the surface layers were studied by optical microscope, SEM and EDX analysis. Bruker GmbH, primary energy 30 keV and detector type XFlash 5010 were used.

RESULTS AND DISCUSSION

OCP - time measurements: Two types of OCP - time measurements were performed: *short-time* (for 1 h) and *long-time* (for up to 220 h) tests. During the short-time measurements the OCP - time dependencies indicate that both steels are in passive state since the potentials shift in positive direction. The initial potential values are in range of -0.35 V and after 1 hour reach about -0.2 V (SCE) for both steels. The small difference between the open circuit potentials of both steels specimens could be attributed to dissimilarities in their surface states, i.e. presence of non-metallic inclusions, scratches, crevices, etc., associated with the steel surface morphology and content. However, the measured potentials for both steels are quite close and correspond to the steels surface passivation.

After 1 hour stay of samples in the experimental solution the potentials of both steels do not reach constant values. For this reason the tests were extended up to 220 h. The obtained results provide information about the steel surface state in conditions close to the real encountered in practice.

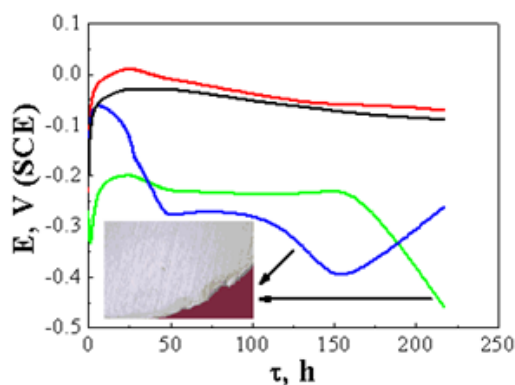


Fig. 1. Long OCP - time measurements for Cr18Mn12N steel in Ringer's solution, for 220h, 37°C

During the long-time experiments performed only for the HNS (Fig. 1) two types of behaviors were observed. The first ones show that the potential slightly shifts in negative direction after one initial ennoblement and attains almost stable value of about -0.05 V(SCE). This slight potential

shift in negative direction could be associated with partial dissolution of non-metallic inclusions or of the metallic surface around them.

The second type dependencies are characterized by sharp decrease in the potential due to crevice corrosion development (between the steel sample and the insulation) which was proved by optical microscopy after the experiments.

Potentiodynamic studies: Regarding the European [9] and American [10] standards for local corrosion investigations it is accepted the experiments to be carried out with scan rate 0.16 mV s^{-1} . However, in the corrosion investigations it is common to use significantly higher scan rate and to perform a large number of repetitions because of the random nature of the pits nucleation. Thus, in the most of the scientific works the potentiodynamic investigations were performed with scan rate 1.0 mV s^{-1} and even with 5 to 10 mV s^{-1} [11].

In order to check if the scan rate effects on the corrosion parameters of investigated steels in Ringer's solution tree different scan rates were chosen: 0.16 , 1.0 and 5.0 mV s^{-1} . In addition, the effect of different preliminary treatments of the steel surface was considered, too. The potentiodynamic studies revealed that both, the scan rates and the preliminary treatment of the samples affect significantly the obtained electrochemical parameters such as: corrosion potential (E_{corr}), pitting potential (E_{pit}), repassivation potential (E_{rp}), passive current density (j_{pass}), etc.

Influence of the scan rate: The increase of the scan rate (Fig. 2) induces increase in corrosion (j_{corr}) and passive (j_{pass}) current density for both steels. The corrosion current densities of Cr18Mn12N and Cr18Ni9 steels change from 0.32 to $6.36 \mu\text{A cm}^{-2}$ and 0.29 to $4.26 \mu\text{A cm}^{-2}$ respectively with the scan rate increase. The obtained values for passive current densities are 0.50 to $16.18 \mu\text{A cm}^{-2}$ for nitrogen steel and 0.69 to $19.00 \mu\text{A cm}^{-2}$ for the nickel bearing steel. The effect of the scan rate on the E_{corr} , E_{pit} and E_{rp} is not so considerable for both steels.

The scan rate effects on the electrochemical parameters of both steels revealing that the passive film formation and recovery if it is broken take place slowly. For the investigated steels the passive film formation and its quality are in a great importance. The hold of the steels at potentials in the passive area at scan rate 0.16 mV s^{-1} allows formation of thick passive film. The increase in the film thickness results in reduced current densities when the scan rate is decreased. Moreover, at slow

scan rates the pits on the surface of both steels try to repassivate and this is more pronounced for the Cr18Mn12N steel samples.

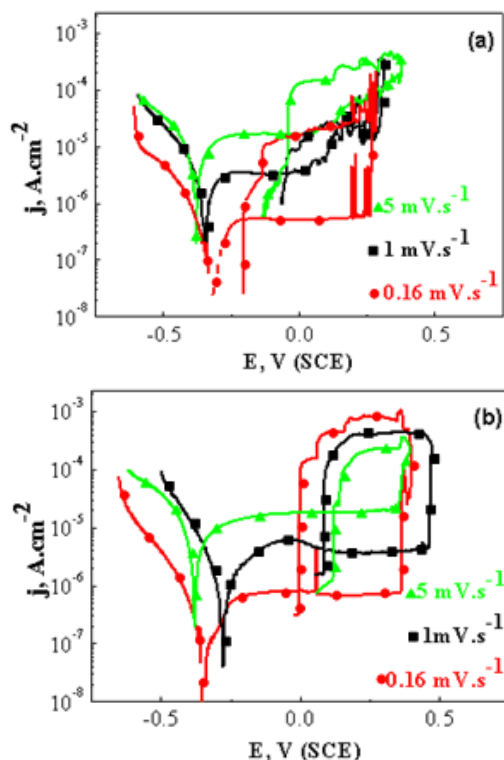


Fig. 2. Potentiodynamic dependencies for (a) Cr18Mn12N and (b) Cr18Ni9 steels obtained with 0.16, 1.0 and 5.0 mV s^{-1} , 37°C.

Effect of the preliminary treatment: With a view to investigate the effect of the initial surface state on the electrochemical parameters of the investigated steels, four different type of dependencies according to preliminary treatments were obtained (Fig. 3): (i) dependencies obtained immediately after the grinding and degreasing of specimens starting from potential by 0.25 V more negative than the OCP, (ii) after grinding, degreasing and cathodic treatment for 5 min at -0.7 V (SCE), (iii) after grinding, degreasing and 1 hour stay in solution and (iv) after grinding, degreasing and 120 hours stay in Ringer's solution.

Contrary, of the scan rate, the preliminary treatment affects mainly the E_{corr} , E_{pit} and E_{rp} , but does not change significantly j_{corr} and j_{pass} .

The preliminary cathodic treatment at negative potential (-0.7 V (SCE)) leads to dissolution of the passive film formed on the steel surface (at air) prior to the immersion in the corrosive solution. Alternatively, the preliminary stay of steels in corrosive media leads to natural formations of passive layers and this is manifested by lower corrosion current densities and ennoblement of the corrosion potential.

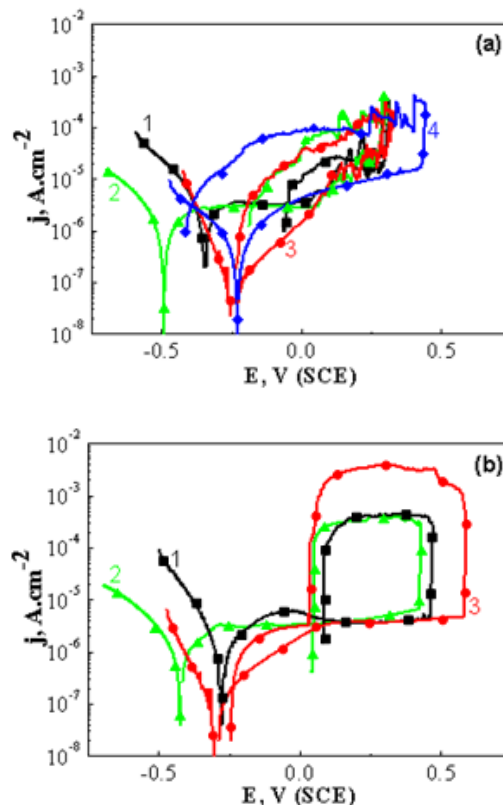


Fig. 3. Potentiodynamic dependencies for (a) Cr18Mn12N and (b) Cr18Ni9 steels obtained after different preliminary treatment, 1.0 mV s^{-1} , 37°C.

(1) ■ scan in positive direction from -0.25 V in regards to OCP (2) ● cathodic treatment for 5 min. at -0.7 V(SCE) and subsequent scan in positive direction (3) ▲ after 1 hour in solution and scan in positive direction from -0.25 V in regards to OCP (4) ◆ after 120 hours in solution (only for HNS steel) and scan in positive direction from -0.25 V in regards to OCP.

The preliminary stay of nitrogen bearing steel in the work solution, irrespective how long it is (1 or even 200 hours), leads to steady increase in j_{pass} , without clearly expressed plateau. This behavior could be result of the difference in the structure of naturally formed passive layer compared to the structure of the layer formed under polarization. The longer stay in the Ringer's solution prior the potentiodynamic study shifts E_{corr} and E_{pit} in positive direction and wide the passive area, but on the other hand the re-passivation of appeared pits during the scan in opposite direction is impossible.

For the nickel containing steel the passive area also expands for longer preliminary stays in the corrosive solutions. In this case, the appeared pits repassivate during the scan in negative direction and E_{rp} is not affected by the time of preliminary stay.

Potentiostatic studies: The potentiodynamic studies described above showed significant effect

of scan rate on the values of the characteristic potentials. The last could be avoided by obtaining dependencies current vs. time at applied potential. In this way the series of dependencies at applied potentials from 0.05 to 0.4 V (SCE) were developed. This range of potentials was determined from potentiodynamic tests and it includes potentials lower and greater than E_{pitt} obtained potentiodynamically. The potentiostatic curves (Fig. 4) allow both E_{pitt} and the incubation time (t_i) to be determined. At the beginning of each experiment the current goes down reaching a minimum value. If it remains stable in time at this value this indicates that the steel surface is in passive state. If, in opposite the current suddenly grows up this is an indication of pits nucleation. The incubation time is defined by range between the experiment start-up and the onset of the abrupt current rise, which physically corresponds to the time necessary for passive film to be destroyed at the applied potential.

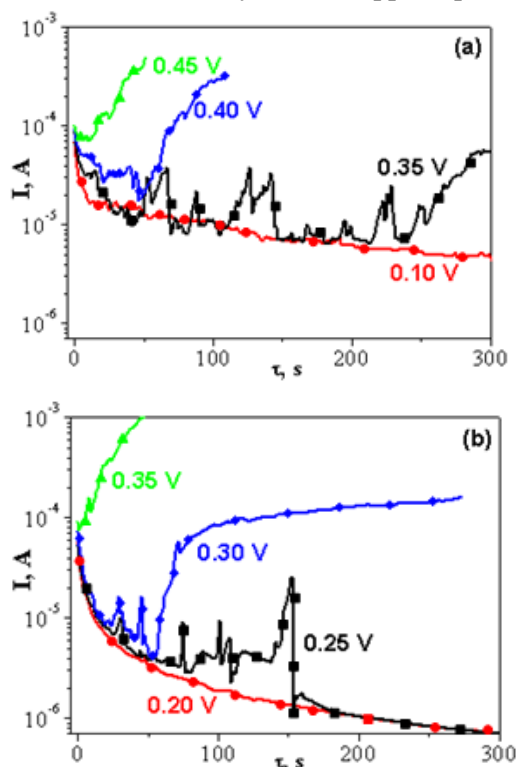


Fig. 4. Potentiostatic dependencies (the applied potentials are presented against SCE) for (a) Cr18Mn12N and (b) Cr18Ni9 steels, 37°C.

The plots in Fig. 5 show that for the Cr18Mn12N steel the pitting potential is $E_{\text{pitt}} = 0.35$ V (SCE) (Fig. 4a) while for the Cr18Ni9 sample it is $E_{\text{pitt}} = 0.30$ V (SCE) (Fig. 4b). These values vary from the values obtained potentiodynamically, as the E_{pitt} of Ni-bearing steel is significantly more negative than the same obtained by potentiodynamic method. The numerous fluctuations in the current vs. time dependence of

nitrogen steel at 0.35 V(SCE) correspond to the formation of metastable pits, which completely re-passivate and stop to develop.

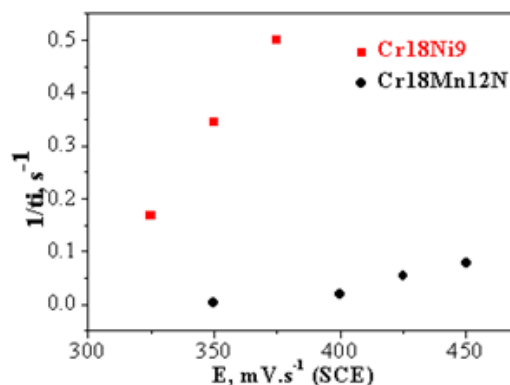


Fig. 5. Pits nucleation rate as a function of the applied potential.

For the applied potentials at which the pits do not appear, the established stationary current for nickel bearing steel is lower than those of nitrogen steel at the same applied potential. This lower value, to some extent, indicates denser and thicker as well as more stable protective layers [12, 13].

Alternatively, the incubation time required for the destruction of Cr18Mn12N steel passive layer is ten times longer than the same for Ni containing steel. For example, at applied potential of 0.35 V (SCE) the incubation time for the nickel steel is about 2.91 s, while for the nitrogen steel it is about 255 s. Therefore, it could be decided that the value of the established stationary current is not adequate for evaluation of the passive layer stability.

The inverse of the incubation time ($1/t_i$) known as *the pit nucleation rate* [13] exhibits almost linear behavior (see Fig. 5) as a function of applied potential. It is obvious that the pits on the high nitrogen steel occur with a lesser speed, which increases slightly with the rise of applied potential. The pits nucleation rate for the chromium-nickel steel is significantly higher and increases linearly with the shift of applied potential in positive direction by step of 25 mV.

Optical microscopy and SEM: In order to establish the type, size and shape of the pits appeared on the surfaces of both investigated steels after the potentiostatic experiments at applied potential by 100 mV more positive than E_{pitt} , the samples were observed by optical and scanning electron microscopy. The images for both steels are presented on Fig. 6.

The optical microscopy after the potentiostatic experiments indicate numerous pits on Cr18Ni9 steel surfaces which are larger in contrast to these on the surface of the Cr18Mn12N samples. These observations confirm the results from potentiostatic

method where the Cr18Ni9 steel has higher pits nucleation rate and shorter incubation time. The pits on nickel bearing steel are in bigger size, more numerous and deeper.

The pits at the nitrogen steel surface are with fine lace cover into which residues of salt products can be observed. The pits are in spherical shape and could be divided formally in two groups: small pits with diameters in the rage 50-60 μm and large pits with diameters of about 200-250 μm .

The pits on the nickel steel surface are also in spherical shape, but in contrast to the nitrogen steel

ones they are larger (with 200-1000 μm in diameter), the pit covers are partially dissolved and with greater degree of cracking.

EDX analysis: EDX analyses of the steels surfaces were performed for surface after 20 minutes stay in Ringer's solution at applied potential more positive than the E_{pitt} . The value of the potential chosen in order to ensure development of the pits at about 10^{-4} A cm^{-2} anodic current density.

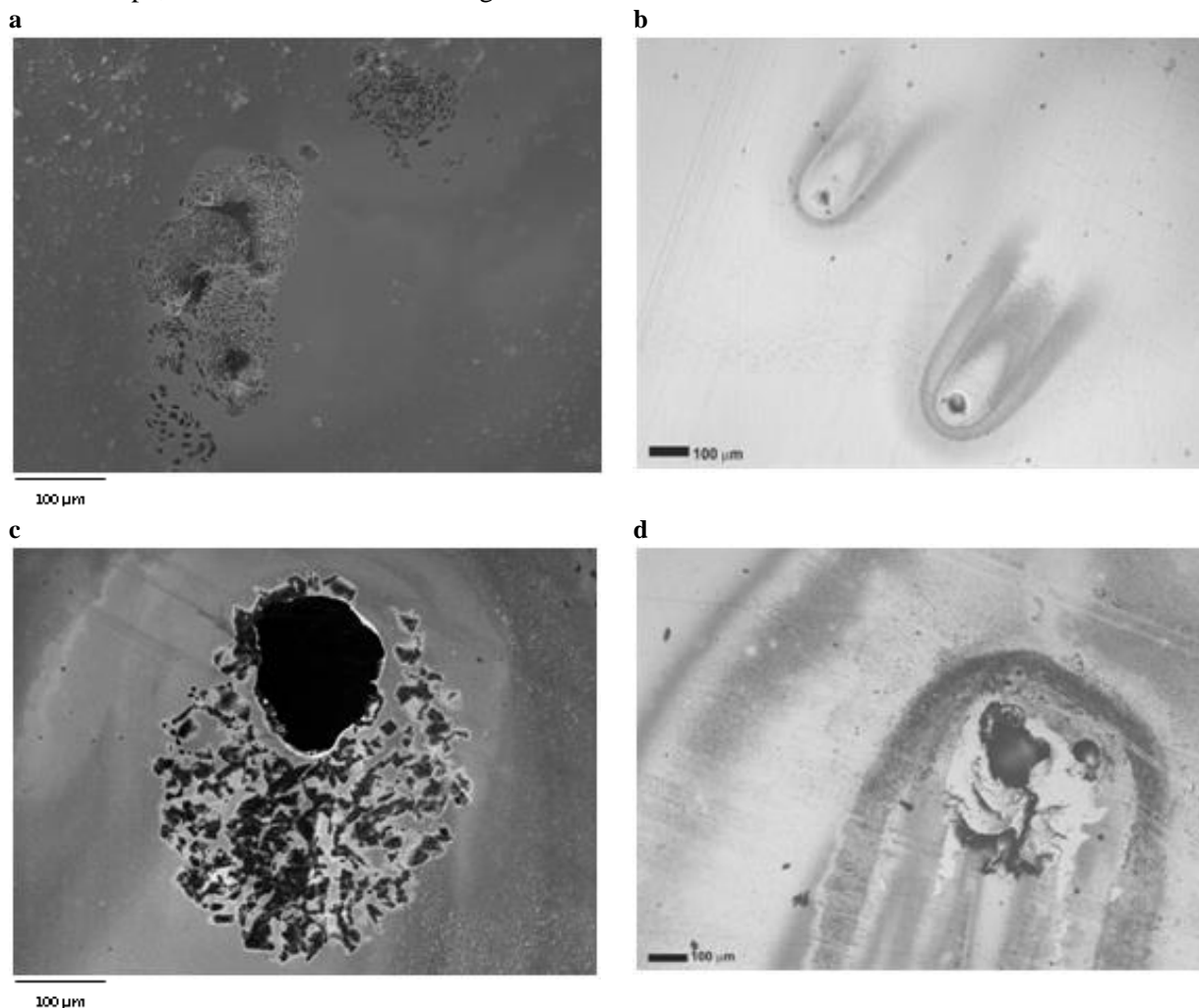


Fig. 6. SEM and optical images of (a, b) Cr18Mn12N and (c, d) Cr18Ni9 steels after potentiostatic polarization

Table 1. The chemical composition (wt.-% and at. %) of the tested stainless steels.

Steel		Cr	Ni	Mn	C	N	Si	P	S
Cr18Mn12N	wt.%	16.50	0.05	12.00	0.04	0.61	0.36	0.011	0.023
	at.%	17.07	0.05	11.74	0.16	2.37	0.70	0.02	0.005
Cr18Ni9	wt.%	17.49	9.37	1.29	0.05	-	0.52	0.022	0.009
	at.%	18.74	8.85	1.23	0.23	-	1.03	0.04	0.016

Table 2. Chemical content of the surface after the potentiostatic corrosion tests, at. %

Elements	Fe	Cr	Mn	Ni	O	C	Si	P	S	Cl	Ca
Cr18Mn12N	24.20	9.08	3.53	-	56.14	4.21	0.63	1.46	0.47	0.17	0.13
Cr18Ni9	37.49	10.24	-	5.24	37.50	6.16	1.00	1.13	0.63	0.30	0.13

The results reveal that in the passive layer of Cr18Mn12N steel the following elements are included (in descending content): Fe, O, Cr, N, Mn and C. For the Cr18Ni9 steel the passive layer consist from Fe, O, Cr and Ni. Therefore, it can be assumed that the passive films on both steels are built mainly from iron and chromium oxides. The high nitrogen content in Cr18Mn12N steel could be result of N enrichment under the passive layer as it is previously described in the literature [14].

The analysis of the surface after the potentiostatic corrosion tests (Table 2) shows that the surface layers consist of oxides of the main alloying elements. Besides, small quantities of C, P, Cl, and Ca are registered. These are result of corrosion solution salts inclusion in the passive layer. It worth noting that the Cl content in Cr18Mn12N corrosion products is relatively low which can be related to formations of nitrates form complexes with iron chlorides and hydroxychlorides which finally hinder the pitting processes [6]. This explanation was proved by Fu et al. [15] and Misawa and Tanabe [16] who demonstrated that the iron dissolution can be reduced by increase in the nitrogen content which actually facilitates the passivation process. The Raman spectroscopy studies [16] revealed that the nitrogen and the oxygen ions in the passive layer form nitrate ions which are incorporated into the oxide layer and suppress the action of the hydrated chloride ions resulting in increased pitting corrosion resistance.

CONCLUSIONS

The corrosion behavior of the high nitrogen steel Cr18Mn12N compared to the nickel steel Cr18Ni9 in Ringer's solution was studied by electrochemical and physical methods in order to evaluate preliminarily the possibility of using Cr18Mn12N for implants in the human body. The study allows to claim the following results, among them:

1. The open circuit potentials of both examined steels in the corrosive media are in the passive states and very close as values.

2. The extended in time stay of the samples in the corrosive solution prior to the electrochemical tests improves the passive films formation.

3. The potentiodynamic and potentiostatic results reveal that the nitrogen steel passes through the stage of metastable pits formation which need more time to pass into active dissolution state. For the nickel steel the pits nucleate faster in shorter incubation time and are larger in size.

Finally, it could be outlined that the HNS steel exhibits better corrosion resistance in Ringer's solution, but additional studies in various media stimulating human body fluids should be carried out.

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КОРОЗИОННО ПОВЕДЕНИЕ НА N-СЪДЪРЖАЩИ НЕРЪЖДАЕМИ СТОМАНИ В РАЗТВОР Ringer

Г. П. Илиева¹, М. Х. Лукайчева^{2*}, Б. Р. Цанева², Л. Ц. Жекова³ и Л. Б. Фачиков¹

¹Химикотехнологичен и металургичен университет, бул. Кл. Охридски 8, 1756 София, България

²Технически университет- София, бул. Кл. Охридски 8, 1756 София, България

³Институт по металознание, съоръжения и технологии "Акад. А. Балевски" с Център по хидроаеродинамика при БАН, ул. Шипченски проход 67, 1574 София, България

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(Резюме)

Материалите за изработване на импланти използвани в медицината са изработени от различни метали и сплави като основното изискване към всеки от тях е биосъвместимостта. Настоящата работа представя предварителни резултати касаещи приложимостта на високоазотната стомана Cr18Mn12N като материал за изработване на импланти заместващ Ni-съдържащите стомани, които са токсични. За целта са проведени краткосрочни (в продължение на 1 час) и дългосрочни (до 220 часа) измервания на потенциала на отворена верига, както и потенциодинамични и потенциостатични изследвания в разтвор Ringer при 37°C. Разгледано е и влиянието на предварителната подготовка на повърхността. След потенциостатичните измервания с цел определяне на характера на корозионната атака са използвани оптична и сканираща електронна микроскопия. Повърхността на образците е изследвана и посредством Енергийно-дисперсивна спектроскопия с цел определяне на състава на корозионните продукти. На базата на получените резултати може да се заключи, че високоазотната стомана показва по-добра корозионна устойчивост в разтвор Ringer.