

CORROSION OF HIGH NITROGEN STAINLESS STEEL IN SODIUM ORTHOPHOSPHATE SOLUTIONS

Mladenka Loukaycheva^{1,2}, Boriana Tzaneva², Ludmil Fachikov¹

¹University of Chemical Technology and Metallurgy,
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: fachikov@uctm.edu

²Technical University
8 Kl. Ohridski, 1756 Sofia, Bulgaria

Received 02 September 2013

Accepted 06 January 2014

ABSTRACT

The corrosion behavior of Cr18Mn12N (0.61% N) and Cr18Ni9 steels in water solutions of sodium orthophosphates (NaH_2PO_4 , Na_2HPO_4 u Na_3PO_4) - 0.1 M, with sodium chloride addition (0.5M) have been investigated by potentiostatic and galvanostatic methods.-

Galvanostatic results reveal that both steels exhibit almost identical behaviors. The increase in the current density does not affect the value of the stationary potentials reached after 1 hour of polarization. In solutions of NaH_2PO_4 and Na_2HPO_4 both steels develop pitting corrosion. In Na_3PO_4 with added chloride, the steels show passive behavior at the applied current densities; there are indications of pitting occurrence on the chrome-nickel steel surface that subsequently repassivate.

The potentiostatic dependencies provide a basis to determine the values of the pitting formation potentials, E_{pit} and the incubation time, t_i of the pitting nucleation. The recorded E_{pit} for the nitrogen steel have more negative values than those obtained with the classical stainless steel. However, the nickel free steel demonstrates 5-10 times lower speed of pitting nucleation and growth compared to Cr18Ni9. In Na_3PO_4 solutions in presence of NaCl, the Cr18Mn12N steel shows better corrosion resistance – more positive E_{pit} and longer incubation time.

Keywords: corrosion, pitting, high nitrogen steels, incubation time, polarization.

INTRODUCTION

Orthophosphates are commonly used as inhibitors in various aqueous media as they form protective film on the metal surfaces. Yo Zuo et al. [1] compared the inhibiting action of several types of anions with regard to nucleation and growth of pitting on austenitic stainless steel in 0.1 M NaCl solution and found that it decreases in the order $\text{PO}_4^{3-} > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$. The authors claim that the number of active sites on the steel surface decreases due to the competitive adsorption of the anions mentioned with Cl^- . Moreover, the results obtained indicate that PO_4^{3-} - ions not only delay the development of metastable pits but also support its repassivation. Most often the reference studies on the influence of phosphate ions upon corrosion of stainless steels are carried out in

neutral media at low concentration of phosphates [1-7].

Herein we investigated the behavior of chrome-manganese-nitrogen steel Cr18Mn12N and conventional chrome-nickel steel Cr18Ni9 in 0.1 M water solutions of three types of orthophosphates, i.e. NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 , with addition of 0.5M NaCl, using galvanostatic and potentiostatic polarization electrochemical methods.

EXPERIMENTAL

The chemical composition of the examined steels Cr18Mn12N and Cr18Ni9 is shown in Table 1. The specimens are disks shaped with working area 0.5 cm². The rest surface is isolated with polymeric reactoplast “Duracryl”. The preparation of samples includes sub-

Table 1. Chemical composition of steels Cr18Mn12N and Cr18Ni9.

| | Cr, % | Ni, % | Mn, % | C, % | N, % | Si, % | P, % | S, % |
|-----------|-------|-------|-------|------|------|-------|-------|-------|
| Cr18Mn12N | 16.50 | 0.05 | 12.00 | 0.04 | 0.61 | 0.36 | 0.011 | 0.023 |
| Cr18Ni9 | 17.49 | 9.37 | 1.29 | 0.05 | - | 0.52 | 0.022 | 0.009 |

sequent grinding of the working surface using grinding papers No 220, 400, 600 and 800, washing in running and distilled water, and degreasing with alcohol-ether mixture. The stay of samples on air before their exposure to model media is minimized in order to prevent the surfaces from forming films.

The experiments are carried out in mono-, di- and tri-substituted sodium orthophosphates (NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4) with concentration 0.1M in presence of chloride ions (0.5M). The values of pH for the corresponding phosphates are 4.2, 8.3 and 11.0. The examinations were performed at room temperature in open three-electrode cell with platinum counter-electrode, and reference saturated calomel electrode.

The electrochemical tests are carried out using potentiostat-galvanostat PAR 263 and the control of polarization, as well as the recording and processing of the experimental data are made using computer software PowerSuite. The galvanostatic anode polarization is accomplished applying current densities 10, 20 and 40 $\mu\text{A}\cdot\text{cm}^{-2}$ and the variation of potential of the working electrode is recorded for 1 hour. The potentiostatic experiments are carried out applying constant potentials in the range -0.2 to 0.6 V (SCE) at 0.2 V increments. The current transient at each applied potential is recorded for a period of 60 min.

RESULTS AND DISCUSSION

Galvanostatic method

The chronopotentiometric dependencies obtained for steels Cr18Mn12N and Cr18Ni9 in 0.1M solutions of phosphates with added 0.5M NaCl are shown in Fig. 1. The breakdown potentials E_{pit} and that of steady development of pitting E_{st} are determined from the chronopotentiometric curves. The pitting potential is defined as the first potential at which a deviation in negative direction is observed [9], and at steady development of pitting the potential remains comparatively constant in time [8]. It is also visible from the course of curves that the pitting potentials depend

on the value of the charging anodic current: with its increase, the potentials and the speed of formation of passive film increase in both steels examined for all solutions tested.

The dependencies shown in Fig. 1a show that the chrome-manganese-nitrogen steel has higher resistance in $\text{Na}_3\text{PO}_4 + \text{NaCl}$ solution. According to the curves obtained, the steel remains in passive state that is disturbed at a very high anode polarization when it passes into trans-passive state. In both, the acid and neutral phosphate solutions there are oscillations of potential visible on the curves, which indicate for development of pitting corrosion on the surface of steel Cr18Mn12N. Based on the number of the fluctuations of potential registered and its inclination to stationing with time, we can conclude that the number of occurring pitting in the neutral phosphate is larger than that in the acidic one, however they repassivate more easily and their steady growth occurs later.

Unlike the chrome-manganese-nitrogen steel, according to the course of curves for chrome-nickel steel taken (Fig. 1b), occurrence of metastable pits is also observed in the alkaline electrolyte that repassivate later on. Considering the frequency of fluctuations of potential in both the acidic and alkaline electrolytes, we can claim that the number of nucleated pits on the chrome-nickel steel is lower but the potential for their steady growth is reached sooner compared to chrome-manganese-nitrogen steel.

It follows from the dependencies of E_{pit} and E_{st} on the anode current density presented in Fig. 2 that both characteristic potentials remain relatively constant regardless of the value of polarization applied. However a tendency to ennoble their values is observed for the chrome-manganese-nitrogen steel during increase of anode current density.

Compared to the conventional chrome-nickel steel, more positive values for E_{pit} and more negative ones for E_{st} are obtained for chrome-manganese-nitrogen steel. These results are evidence for the higher resistance of chrome-manganese-nitrogen steel against formation of

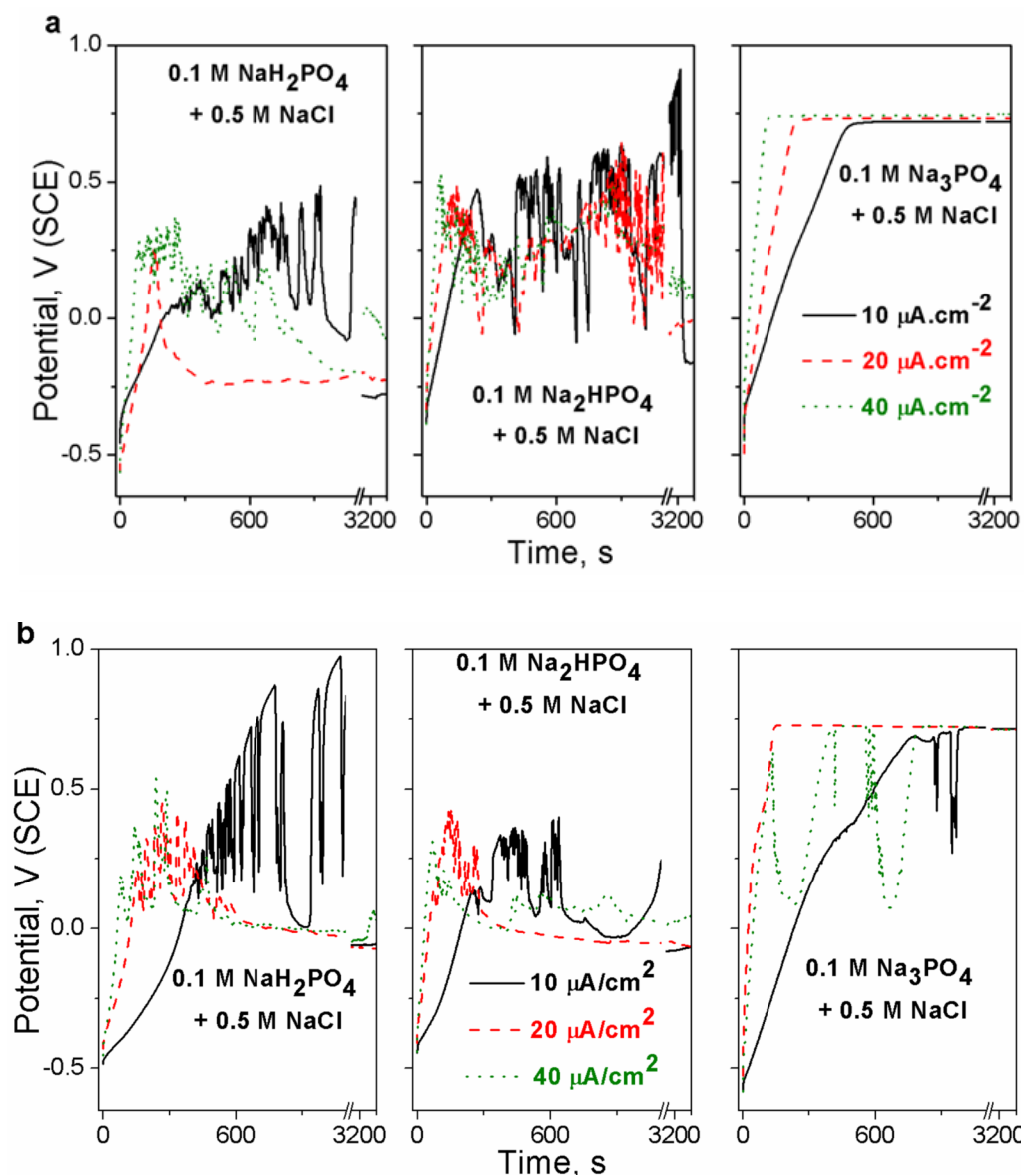


Fig. 1. Variation of electrode potential during anode polarization of specimens: a) Cr18Mn12N and b) Cr18Ni9.

pitting in phosphate solutions with acidic and neutral character but for existing of larger active sites on the steel Cr18Mn12N surface. A more positive pitting potential in nitrogen containing steel is also observed during the investigations described in [10].

Potentiostatic method

The current/time dependencies are taken at constant potentials in the range from -0.2 to +0.6V(SCE). Using this method, the pitting formation potential is determined, as well as the incubation time and the speed of pitting nucleation. The behavior of steels in each of

the chloride ions containing solutions examined can be divided in two groups depending on whether they remain in passive state or there are pitting occurring on their surface.

At potentials more negative than E_{pit} when occurrence of pitting is not observed, initially the current density rapidly decreases due to formation of passive layer and its thickening and/or densification [11-14]. Within a short time the current value settles at a certain lowest stationary value i_{ss} (Fig. 3) that correspond to the current needed to maintain the passive film at the particular conditions. The value of the stationary current is the

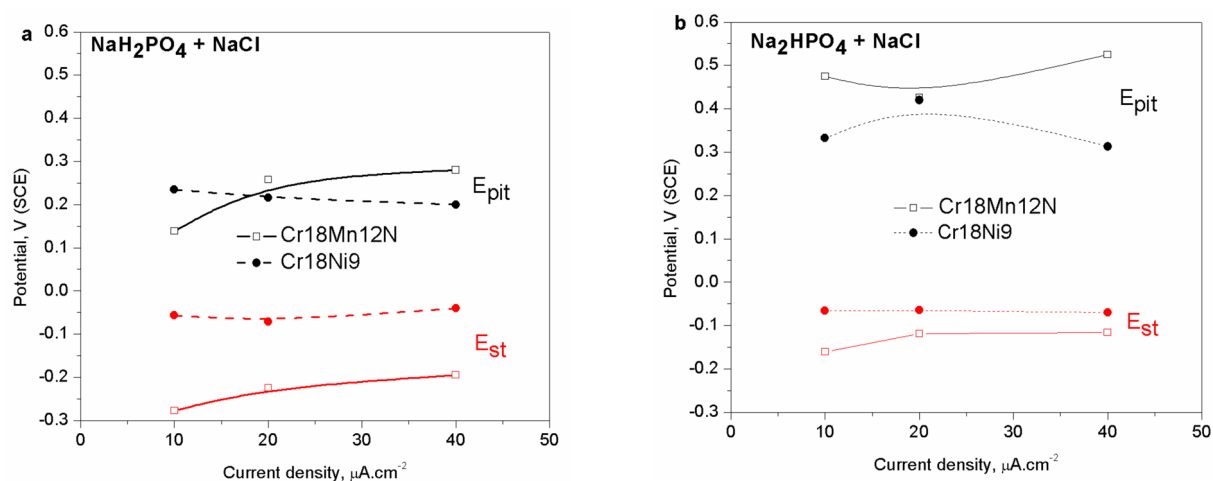


Fig. 2. Influence of the current density applied on E_{pit} and E_{st} : a) 0.1 M NaH_2PO_4 + 0.5 M NaCl and b) 0.1 M Na_2HPO_4 + 0.5 M NaCl.

measure for the protective properties of the passive layer. It is believed that the lower the value of i_{ss} is, the larger is the thickness of the passive film that affects directly the breakdown mechanism, the incubation time and the speed of repassivation of the film [15].

Upon comparison of the stationary current densities presented in Fig. 3 it is visible that in neutral and alkaline solutions the passive layer on the chromium-manganese-nitrogen steel has better protective properties than that on the nickel-chromium one.

Similar results showing lower values of the passive current for high-nitrogen nickel-free steels in comparison with chrome-nickel steels are found by

Alvarez et al. [16] in 3.5% NaCl + 1 M HCl (pH 1), which the authors associate with the amount of nitrogen dissolved in austenite. They believe that the presence of nitrogen results in increased pH of the medium due to transformation of NH_3 into NH_4OH . Yao Fu et al. [10] also come to the conclusion that the addition of nitrogen to austenitic steels improves the protective properties of their passive films in solutions of 0.5 M H_2SO_4 + 0.5 M NaCl. Heon-Young Ha et al. [13] have carried out XPS and Mott-Schottky analyses of the passive films of a series of steels with various contents of nitrogen and carbon, i.e. Fe-18Cr-10Mn-(0.39-0.69)N-(0-0.38)C, in 1 M NaCl and borate-phosphate buffer solution. The

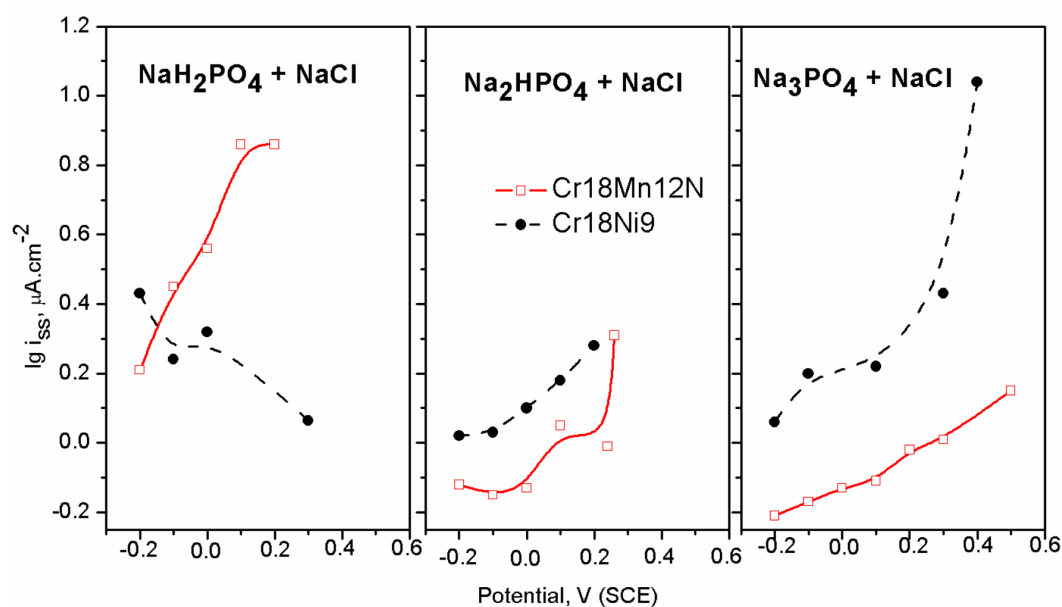


Fig. 3. Variation of stationary current density depending on the potential applied.

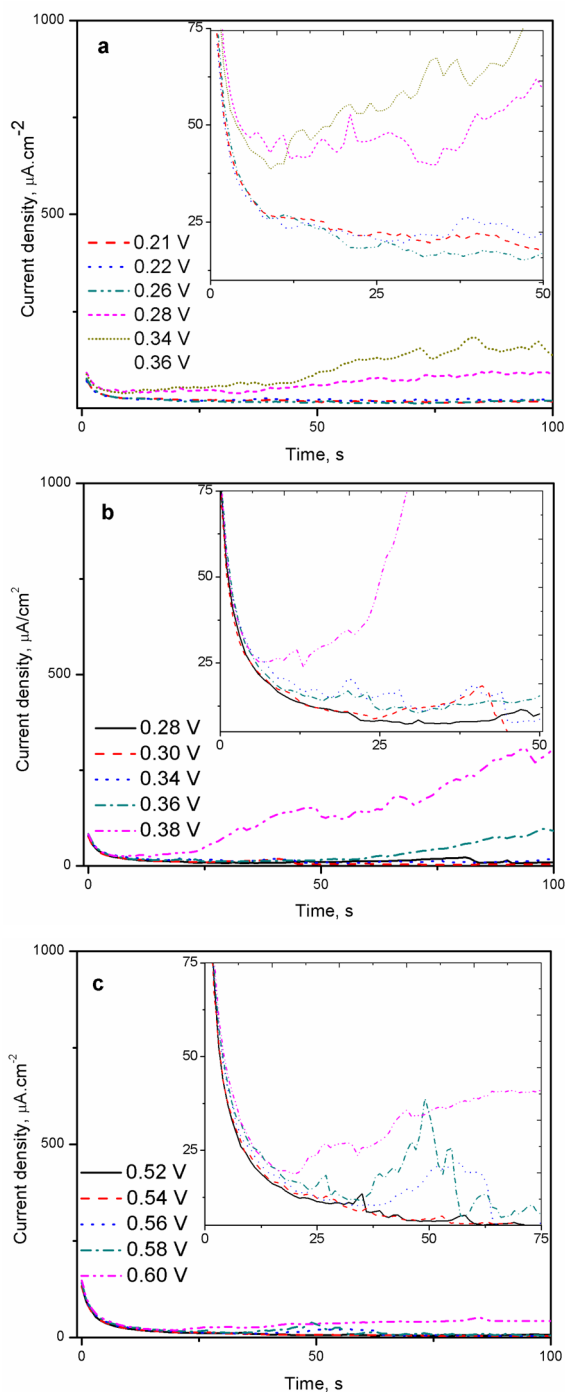


Fig. 4. Chronoamperometric dependencies of steel Cr18Mn12N: a) 0.1 M NaH_2PO_4 + 0.5 M NaCl; b) 0.1 M Na_2HPO_4 + 0.5 M NaCl; c) 0.1 M Na_3PO_4 + 0.5 M NaCl (all applied potentials are vs. SCE).

compositions are similar to the composition of steel we examined and it is found that both the thickness and the concentration of Cr in the passive layer increases with the increase of N and C, thus improving its protective properties without changing its basic structure – Fe_2O_3 .

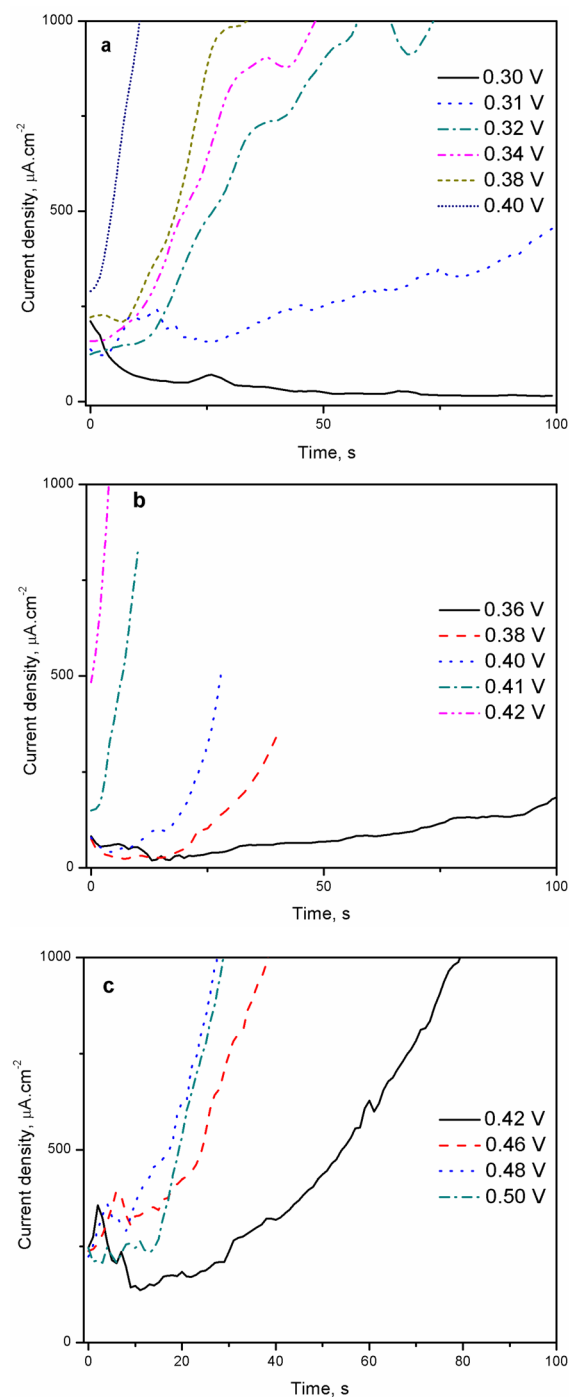


Fig. 5. Chronoamperometric dependencies of steel Cr18Ni9: a) 0.1 M NaH_2PO_4 + 0.5 M NaCl; b) 0.1 M Na_2HPO_4 + 0.5 M NaCl; c) 0.1 M Na_3PO_4 + 0.5 M NaCl (all applied potentials are vs. SCE).

At potentials more positive than pitting potential (Fig. 4 and 5), the current density initially decreases until a certain value and then begins increasing. The increase of current is evidence for damages of the passive layer and appearance of active sites, i.e. pitting.

The registered minimum of current in the curves is associated with the so called «incubation time» (t_i). This is the time necessary for the appearance of the first pitting on the passivated metal surface when the critical conditions for its development are achieved [17]. Upon reaching t_i , the dominating anode process is nucleation and growth of pitting and the current density indicates for the susceptibility of the passive film to breakdown [18, 19, 20]. It is seen from the dependencies taken in the three phosphate media with addition of 0.5M NaCl (Figs. 4 and 5) that the incubation time and the current value upon elapsing of incubation time (corresponding to the ascending part of curves) depend on the polarization applied. With the shift of potential in positive direction, the incubation time decreases while the current density increases indicating for increasing speed of pitting corrosion. That tendency is more clearly pronounced in the nickel-containing steel showing a higher predisposition of the passive film to breakdown in all three solutions. It is also seen from Figs. 4 and 5 that in acid and neutral electrolyte, the pits on steel Cr18Mn12N occur at more negative potentials compared to steel Cr18Ni9 but the incubation time is longer in the first case. Furthermore, the chrome-manganese-nitrogen steel exhibits a smaller susceptibility to pitting nucleation in the alkaline electrolyte which is evidenced by the more positive potential and the longer incubation time until pitting initiation.

The chronoamperometric dependencies can provide additional information about the repassivation processes of the particular occurring pitting. Thus for example, when the current abruptly jumps and then falls to its initial value before the peak, the pitting is considered completely repassivated and it does not develop more. However, if the current falls to a value higher than the initial one, the pitting that caused the particular peak is considered partially repassivated, i.e. a portion of its surface remains active [21].

Accounting for the intensity and the shape of current fluctuations (Figs. 4 and 5), we can conclude that the nitrogen alloyed steel goes through a pronounced field of potentials, which induce nucleation of metastable pits. In steel Cr18Ni9 the stage of nucleation of metastable pits is either entirely absent, or is hardly distinguishable. Judging from the increased sections of the dependencies obtained for steel Cr18Mn12N, one can say that in acidic, neutral or alkaline phosphate

solution at potentials below 0.34, 0.38 and 0.6 V (SCE) respectively, the pits appeared are metastable and there is not sustainable development of pitting corrosion.

The potentials for occurrence of both metastable (E_{mpit}) and stable (E_{pit}) pits on the two steels are potentiostatically determined in the three phosphate solutions containing chlorine ions and are presented in Table 2. It is visible from the values revealed that in the nitrogen-containing steel the passive film begins distorting at more negative potentials; since the nucleated pits are metastable for development of real pitting corrosion, i.e. growth of stable pitting however, it is necessary to achieve potentials that are approximately equal or even more positive than the pitting potentials for chrome-nickel steel.

The reciprocal value of the incubation time $1/t_i$ is assumed to be the speed of pitting nucleation [11, 17]. It is shown in Fig. 6 that the speed of pitting nucleation ($1/t_i$) increases with the increase of potential. This tendency is more pronounced for steel Cr18Ni9.

The above-described substantial differences in the behavior of the two steels during anode polarization could largely be attributed to the high, i.e. over equilibrium, content of nitrogen in the chrome-manganese steel. There are a number of reference studies describing the influence of nitrogen on the passive state and its breakdown. However, there are still some discrepancies in the interpretations. Some authors prove that the addition of nitrogen to ferrous alloys influences positively the stage of pitting nucleation by extending the incubation time [22, 23]. **These results are related to improving the stability of the passive layer, as well as to creating favorable micro-chemical changes at the interface electrolyte / passive film / metal.** Other studies [24] however show that the key role of nitrogen is to support the repassivation processes but that nitrogen does not affect the initial

Table 2. Metastable pitting and stable pitting potentials of Cr18Mn12N and Cr18Ni9.

| | V (SCE) | Cr18Mn12N | Cr18Ni9 |
|----------------------------------|------------|-----------|---------|
| NaH ₂ PO ₄ | E_{mpit} | 0.21 | 0.31 |
| | E_{pit} | 0.34 | 0.32 |
| Na ₂ HPO ₄ | E_{mpit} | 0.28 | 0.36 |
| | E_{pit} | 0.36 | 0.38 |
| Na ₃ PO ₄ | E_{mpit} | 0.52 | - |
| | E_{pit} | 0.60 | 0.42 |

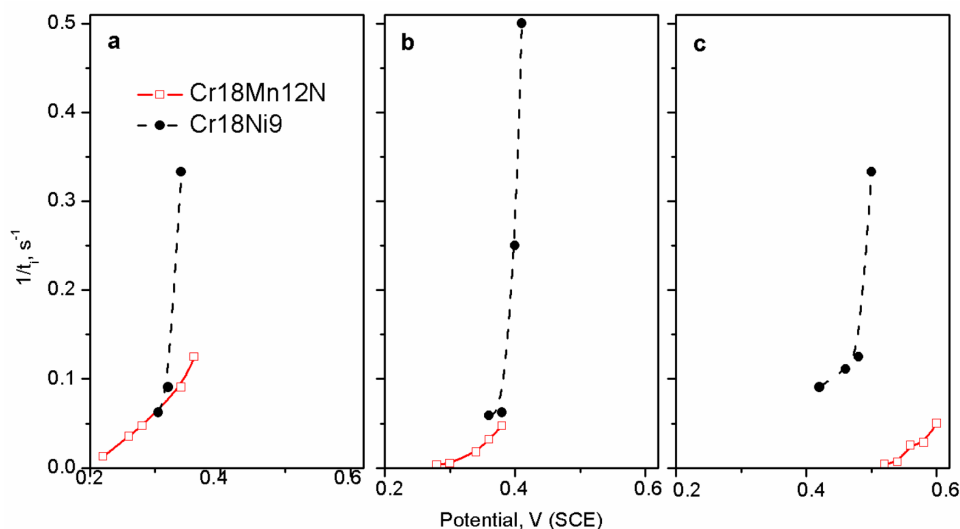


Fig. 6. Rate of pitting nucleation depending on the applied potential: a) 0.1 M NaH_2PO_4 + 0.5 M NaCl; b) 0.1 M Na_2HPO_4 + 0.5 M NaCl; c) 0.1 M Na_3PO_4 + 0.5 M NaCl.

stage of formation of pitting. According to Newman [25], the influence of N on the resistance to pitting corrosion can be divided into three groups, namely: (1) increase of pH in the emerging pitting due to dissolution of nitrogen; (2) enrichment of the passivated surface with nitrogen; and (3) enrichment of the active sections with nitrogen. According to Clayton et al. [26], the NH_4^+ ions released during the anode dissolution react with the anions in the electrolyte to form a saline layer inside the pitting that can serve as a temporary barrier between the metal and the solution. On the same lines Newman and Ajjawi [27] have shown that the nitrate inhibition of stainless steels in chloride solutions includes formation of a saline film.

The results presented in the recent study support the assertion claimed by some authors [23, 25] that the nucleation of pitting itself is not quite affected by the content of nitrogen in the steel but that nitrogen prevents the steady growth of pitting by facilitating their repassivation.

CONCLUSIONS

The following main conclusions can be drawn from the comparative study on corrosion behavior of steels Cr18Mn12N and Cr18Ni9 in aqueous solutions of sodium orthophosphates with addition of sodium chloride using potentiostatic and galvanostatic methods:

- In neutral- Na_2HPO_4 and alkaline- Na_3PO_4 solutions the passive layer on chrome-manganese-

nitrogen steel exhibits better protective properties than that on chrome-nickel steel.

- The passive film in steel Cr18Mn12N is destroyed at more negative potentials but the forming pits are metastable and rapidly repassivate. The actual beginning of pitting corrosion (pitting stable growth) is reached at potentials that are approximately equal to, or even more positive, than the corresponding potentials of pitting formation in chrome-nickel steel.

REFERENCES

1. Yo Zuo, Haitao Wang, Jingmao Zhao, Jinping Xiong, The effects of some anions on metastable pitting of 316L stainless steel, *Corros. Sci.*, 44, 2002, 13-24.
2. J. Schreifels, P. Labine, R. Gailey, S. Goewert, M. O'Brien, S. Jost, An Auger depth profile study of corrosion-inhibiting films formed under cooling water conditions, *Corrosion*, 45, 1989, 420-428.
3. S.A.M. Refaey, S.S. Abd El-Rehim, F. Taha, M.B. Saleh, R.A. Ahmed, Inhibition of chloride localized corrosion of mild steel by PO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} , and NO_2^- anions, *App. Surface Sci.*, 158, 2000, 190-196.
4. M. Reffass, R. Sabot, M. Jeannin, C. Berziou, Ph. Refait, Effects of phosphate species on localised corrosion of steel in NaHCO_3 + NaCl electrolytes, *Electrochim. Acta*, 54, 2009, 4389-4396.
5. Yuming Tang, Xuhui Zhao, Jianpeng Mao, Yu Zuo, The electrochemical characteristics of pitting for two

- steels in phosphate buffer solution with chloride, *Mater. Chem. and Phys.*, 116, 2009, 484-488.
6. M. Lakatos-Varsányi, F. Falkenberg, I. Olefjord, The influence of phosphate on repassivation of 304 stainless steel in neutral chloride solution, *Electrochim. Acta*, 43, 1998, 187-197.
 7. M. Urretabizkaya, C.D. Pallotta, N. De Cristofaro, R.C. Salvarezza, A.J. Arvia, Changes in the composition of the passive layer and pitting corrosion of stainless steel in phosphate-borate buffer containing chloride ions, *Electrochim. Acta*, 33, 1988, 1645-1651.
 8. S. Frangini, N. De Cristofaro, Analysis of the galvanostatic polarization method for determining reliable pitting potentials on stainless steels in crevice-free conditions, *Corros. Sci.*, 45, 2003, 2769-2786.
 9. I.L. Rozenfeld, Corrosion and protection of metals, *Metallurgy*, 1969 (И.Л. Розенфельд, Коррозия и защита металлов, изд. Металлургия, 1969).
 10. Yao Fu, Xinqiang Wu, En-Hou Han, Wei Ke, Ke Yang, Zhouhua Jiang, Effects of nitrogen on the passivation of nickel-free high nitrogen and manganese stainless steels in acidic chloride solutions, *Electrochim. Acta*, 54, 2009, 4005-4014.
 11. M.A. Amin, S.S. Abd El Rehim, Essam E.F. El Sherbini, AC and DC studies of the pitting corrosion of Al in perchlorate solutions, *Electrochim. Acta*, 51, 2006, 4754-4764.
 12. M. Kumagai, S.-T. Myung, S. Kuwata, R. Asaishi, Y. Katada, H. Yashiro, Application of Ni-free high nitrogen stainless steel for bipolar plates of proton exchange membrane fuel cells, *Electrochim. Acta*, 54, 2009, 1127-1133.
 13. Heon-Young Ha, Tae-Ho Lee, Chang-Seok Oh, Sung-Joon Kim, Effects of combined addition of carbon and nitrogen on pitting corrosion behavior of Fe-18Cr-10Mn alloys, *Scripta Mater.*, 61, 2009, 121-124.
 14. D.E. Williams, J. Stewart, P.H. Balkwill, The nucleation, growth and stability of micropits in stainless steel, *Corros. Sci.*, 36, 1994, 1213-1235.
 15. J. Kruger, Effect of the nature of the passive film on Fe and Fe-Cr alloys on breakdown - a brief review, *Proceedings of the Symposium on Critical Factors in Localized Corrosion*, 1st Symp. From the 180th Meeting of The Electrochemical Society, Phoenix, USA, Oct. 13-17, 1991, ECS Proceedings, Vol. 92-9, 184-199.
 16. K. Alvarez, S.-K. Hyun, H. Tsuchiya, S. Fujimoto, H. Nakajima, Corrosion behaviour of Lotus-type porous high nitrogen nickel-free stainless steels, *Corros. Sci.*, 50, 2008, 183-193.
 17. M.B. Ives, Guo Ruijin, S.C. Srivastava, On the origin of pitting induction time, 10th Int. Cong. on Metallic Corros., 7-11 November 1987, Madras, India, 14.23, 3235.
 18. G. Latha, S. Rajeswari, Versatility of superaustenitic stainless steels in marine applications, *JMEPEG*, 5, 1996, 577-582.
 19. M. Sumita, T. Hanawa, S.H. Teoh, Development of nitrogen-containing nickel-free austenitic stainless steels for metallic biomaterials - review, *Mater. Sci. and Engineering C*, 24, 2004, 753-760.
 20. J. Menzel, W. Kirschner, G. Stein, High nitrogen containing Ni-free austenitic steels for medical application, *ISI International*, 36, 1996, 893-900.
 21. G.T. Burstein, P.C. Pistorius, S.P. Mattin, The nucleation and growth of corrosion pits on stainless steel, *Corros. Sci.*, 35, 1993, 57-62.
 22. F.M. Bayoumi, W.A. Ghanem, Effect of nitrogen on the corrosion behavior of austenitic stainless steel in chloride solutions, *Mater. Lett.*, 59, 2005, 3311-3314.
 23. U. Kamachi Mudali, B. Reynders, M. Stratmann, Localised corrosion behaviour of Fe-N model alloys, *Corros. Sci.*, 41, 1999, 179-189.
 24. R.F.A. Jargelius-Pettersson, Electrochemical investigation of the influence of nitrogen alloying on pitting corrosion of austenitic stainless steels, *Corros. Sci.*, 41, 1999, 1639-1664.
 25. R.C. Newman, T. Shahrabi, The effect of alloyed nitrogen or dissolved nitrate ions on the anodic behaviour of austenitic stainless steel in hydrochloric acid, *Corros. Sci.*, 27, 1987, 827-838.
 26. C.R. Clayton, L. Rosenzweig, M. Oversluizen, Y.C. Lu, The influence of nitrogen on the passivity of 18-8 (0.24%N) stainless steels, *Surfaces, Inhibition and Passivation*, Eds McCafferty and R.J. Brodd, Electrochemical Society, Pennington NJ, 1986, 323.
 27. R.C. Newman, M.A.A. Ajjawi, A micro-electrode study of the nitrate effect on pitting of stainless steels, *Corros. Sci.*, 26, 1986, 1057-1063.