ABSTRACT

The general and pitting corrosion of austenitic Cr23N1.2 steel in 3.5% NaCl solutions have been investigated. The open circuit potential, the cyclic potentiodynamic and the galvanostatic methods have been employed in order to investigate the effect of pH (1-12) on the passivity and the tendency to pitting corrosion. Optical microscopy has been used to detect the surface sites for pit formation and the growth of pit nuclei. The results obtained for chromium–nitrogen steel have been compared with these for austenitic 304 stainless steel. The results from the galvanostatic method confirm these, received by potentiodynamic method that in the region of pH 2-10, the character of the environment has not an important influence on the protective properties of the passive layers formed in 3.5% NaCl solutions. In spite the similar electrochemical results, a considerable difference in the pit shape and the pit initiation sides is established.

Keywords: corrosion resistance; pitting; high nitrogen stainless steel; pH; sodium chloride; galvanostatic; cyclic potentiodynamic polarisation

INTRODUCTION

Corrosion resistance of the stainless steels generally depends on the stability of the passive layers, formed on their surface. Regarding this, one of the most important parameters is the hydrogen index of the environment (pH). It is well known, that pH affects directly the cathodic processes of hydrogen and oxygen depolarisation. pH has strong influence also on the kinetics of the anodic processes through solubility of the corrosion products and theirs protective properties. In general, in both neutral and alkaline environments, the stainless steel passive layers are stable, because of the incorporation of hydroxide groups in their composition. Lowering the pH value favours the dissolution of the passive film and hence makes worse its protective properties [1]. According to Rozenfeld [2], the dependence of the corrosion potential on pH for the steel Cr18Ni10Ti in 0.1M NaCl is expressed as follows:

$$ E = a + b \log \text{pH}, $$

where $a=0.40$ and $b = 0.03$ are experimentally obtained constants. Other authors have found that a critical value of pH exists, under which the corrosion rate sharply increases. Thus, for the steel Cr18Ni9, the critical pH value is 1.5 [3]; for chromium and chromium-nitrogen steels it is about pH 3 [4].

The stability of the passive state of the stainless steel depends also on the presence of aggressive ions in the environment, such as chloride ions. In this case under anodic polarisation above a critical potential value, defined as pitting potential ($E_{pit}$), a local breakdown of the protective layers occurs and pitting corrosion takes place. The free corrosion potential of the metal can be shifted in positive anodic direction not only by external polarisation, but also by oxidizing agents in the environment like oxygen, whose potential depends on pH. The pitting potential is not neither thermodynamically, nor kinetically defined value. It depends on both, the
electrochemical heterogeneity of the surface and the processes of formation and repassivation of pits nuclei. Therefore, the determination of the pitting corrosion resistance of steels can be done only on the base of the experimental results. According to some authors, pH of the environment in the region 3-9 does not have considerable influence on the potentials of pitting and repassivation of stainless steels [5-8].

The presented paper describes a part of the study, related to assessment of the stability of nickel-free high nitrogen stainless steel Cr23N1.2 against general and pitting corrosion in chloride environments with pH 1-12. The results are compared to these for conventional austenitic chromium-nickel stainless steel Cr18Ni9 (AISI 304 SS).

EXPERIMENTAL

Two types of austenitic stainless steels have been investigated in this work: high nitrogen chromium steel Cr23N1.2 (22.35 % Cr, 1.23 % N, 1.10 % Mn, 0.04 % C, 0.36 % Si, balance Fe) and conventional steel Cr18Ni9 (17.49 % Cr, 9.37 % Ni, 1.29 % Mn, 0.05 % C, 0.52 % Si, balance Fe). The experimental specimens were disk shaped with a working area of 0.5 cm$^2$. The preliminary treatment of the specimens included subsequently polishing by abrasive paper 220, 400 to a 600 grit finishing, rinsing with water and drying. Just before the start of the experiment the specimens were polished to an 800 grit finish, followed by rinsing with distilled water and degreasing with an alcohol-ether mixture.

The solutions used were 3.5 wt. % NaCl (corresponding to 0.6 M chloride ions) with adding of HCl or NaOH for pH adjusting in the region 1 - 12. Concentrated solution of NaCl was added in order to achieve total concentration of the chloride ions 0.6 M. The test solutions were prepared using analytical grade reagents and distilled water. The electrochemical tests were performed under open air conditions at room temperature (20 ± 2 °C).

Three electrochemical techniques were used in the corrosion measurements. Open circuit potential (OCP)-time dependence was recorded in the test solutions for an hour at room temperature. Just after OCP record the specimen surface was anodically galvanostatic charged under current density 60 μA cm$^{-2}$ and the potential change with time was recorded. Cyclic potentiodynamic polarisation measurements were performed with potential scan rate 1mV s$^{-1}$, starting from the potential of -0.7 V vs. SCE, at which the specimen was kept for 5 min, followed by anodic polarisation (in positive potential direction). After passing through the passive state and the current density exceed $10^{-4}$ A cm$^{-2}$, polarisation in the reverse (negative potential direction) was carried out down to the point where the curve intersected the anodic one.

The electrochemical measurements were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The measurements were performed using PAR 263 potentiostat-galvanostat and Power Suite corrosion measurement and analysis software. After the polarisation tests the specimens were rinsed with distilled water, dried in air and the surfaces were investigated with an optical microscope.

RESULTS AND DISCUSSION

Open circuit potential

Fig. 1 presents OCP variation with time for the steels Cr23N1.2 and Cr18Ni9 in 3.5% NaCl solutions (pH 1 – 12). The initial part of the curves manifests the considerable differences in the behaviour of the two steels. The dependences OCP-time for chrome-nitrogen steel (Fig.1) begin with sharp shift of the potential in positive direction. Starting from about -0.2 ± -0.4 V vs. SCE the OCP in some seconds reach to about 0.1±0.3
V vs. SCE. This shows extremely high rate of formation of passive film with low conductivity. After a short time the potential shifted towards less noble direction. On the curves OCP-time fluctuations exist, which fade in 30 min and the potential reaches a stationary value of about – 0.25 V vs. SCE. The described results for chrome-nitrogen steel clearly show that in contact with 3.5 % NaCl solutions with pH 1 to 10 the steel surface is charged positively and reaches a critical potential value, where local processes of dissolution starts. The OCP fluctuations probably result from a strongly exhibited and variable in time electrochemical inhomogeneity of the surface.

In solution with pH 12 for the steel Cr23N1.2 only a smooth and stable increase of the potential is seen. Such kind of dependence is characteristic of the chromium-nickel steel in solutions with all studied pH values, which shows a good stability of the protective layers. Despite the start course of the curve OCP-time, the stationary value of the OCP for both steels in the most test solutions is close.

**Cyclic potentiodynamic polarization method**

The results presented in Fig. 2 are typical cyclic polarisation curves for Cr23N1.2 and Cr18Ni9 steels obtained in 3.5 % NaCl at room temperature and pH in the range 1-12. Corrosion parameters determined from the potentiodynamic curves as corrosion potential ($E_{corr}$), corrosion current density, as well as pitting potential ($E_{p}$) and repassivation potential ($E_{rp}$) are shown on Figs. 3 and 4.

According to the summarized results three different

Fig. 3. Influence of pH on corrosion potential (round symbols), pitting potential (rhomboid symbols) and repassivation potential (triangular symbols) of Cr23N1.2 (black symbols and solid lines) and Cr18Ni9 (blank symbols and dotted lines) stainless steels in 3.5% NaCl, 20°C.

Fig. 4. Influence of pH on corrosion current density of steels Cr23N1.2 (black symbols and solid lines) and Cr18Ni9 (blank symbols and dotted lines) in 3.5 % NaCl.

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Fig. 2. Cyclic polarisation curves of steels Cr23N1.2 and Cr18Ni9 in 3.5% NaCl; pH=1÷12; 20°C.
behaviour types of the steels can be separated: (i) Active state in strongly acidic solutions; (ii) State of spontaneous passivity and its breakdown at anodic polarisation by the pitting corrosion and (iii) Stable passive state and its transformation to transpassivity under anodic polarisation.

(i) In solutions with pH 1-2 for Cr23N1.2 and pH 1 for Cr18Ni9, the steels are in active state, characterized with high corrosion current density and active-passive transition under anodic polarisation. For the chromium-nitrogen steel the corrosion potential is about -0.6 V vs. SCE and the critical current density is reaching $3.6 \times 10^{-3}$ A cm$^{-2}$ (Fig. 4). The more negative values of $E_{\text{corr}}$ and $E_{\text{pit}}$ as well as higher corrosion current for Cr23N1.2 steel indicate its lower corrosion resistance compared with the chromium-nickel steel in acidic chloride solution. Similar results, showing sharply decreasing in corrosion stability of the chromium-nitrogen steel at pH lower than 3 are received from H.-Y. Ha et al. [4].

(ii) The analysis of obtained results shows, that at pH value above 2 for the chromium-nitrogen steel and above 1 for the chromium-nickel steel, the pH of the chloride solution has not a considerable influence on the corrosion behaviour of the steels. In this pH region, the austenitic steels are in passive state, the width of the passive region is about 0.6-0.7 V. In the region of pH 4-8 the steel Cr23N1.2 has better corrosion stability to general and pitting corrosion as compared to the chromium-nickel steel.

The anodic polarisation above the pitting potential leads to a sharp current increase as a result of development of pits. Fig. 3 shows that $E_{\text{pit}}$ of the chromium-nitrogen steel is increased only with 0.08 V when increasing the pH from 2 to 10. The relatively feeble influence of pH on this characteristic potential shows a stability of the passive film, probably due to the high content of chrome and especially of nitrogen in this steel. The pitting potential for the chromium-nickel steel is considerably more sensitive to the increase of pH and it grows with 0.25 V in the pH region 2-10. The $E_{\text{pit}}$ values for Cr18Ni9 become more positive as compared to these for the chromium-nitrogen steel in alkaline media with pH 8-10. This behaviour is due to the presence of nickel in the steel composition, which has good corrosion stability in neutral and alkaline media [9].

Widespread opinion exists in the literature, that the increase of the chromium content in the stainless steels composition favours the passivation process [2, 9]. Similar positive influence has also been established for nitrogen and some mechanisms have been proposed for this phenomenon [10]. The results, obtained in this paper, however, does not support the expectations for a better repassivation ability of the chromium-nitrogen steel compared with the chromium-nickel steel. On the contrary, despite the high chromium and nitrogen content in the studied steel Cr23N1.2, its potentials of repassivation are more negative with about 0.2 V at low values of pH and with about 0.35 V in alkaline media compared with the same potential for the Cr18Ni9. It is also unusual that the $E_{\text{pit}}$ decreases with the rising of solution pH for the chromium-nitrogen steel.

These results show that the positive effect of the nitrogen and chromium on the processes of restoring of the passive state is not sufficiently strong. More probably, the rupture in the passive films, formed on the chromium-nitrogen steel, occurs on the places, where their repassivation is very difficult. Such places are, for example, the grain boundaries (if the accumulation of the non-metallic inclusions exists).

(iii) In solutions with pH 12, under anodic polarisation the samples of austenitic stainless steels acquired a passive state, with breakdown at the transpassivity potential – about 0.63 V vs. SCE.

Galvanostatic method

This method gives the possibility for determination of the minimal positive potential, at which the surface activation begins (pitting potential, $E_{\text{pit}}$). According to this method, the sample is anodically charged at constant current and the change of the potential with time is recorded. If the steel is susceptible to pitting corrosion, characteristic fluctuations of the potential appear on the curve, related to the repair/breakdown events. Through the magnitude and the width of the peaks, a conclusion about the transient surface state can be made [11-13]. For example, as wider are the peaks in the lower part (at more negative potentials), as stable is the pit growth. After certain time the potential fluctuations fade and it is possible totally to disappear; the potential decreases and reaches a stationary value $E_{\text{stat}}$, which shows stable pits growth [11, 13]. As the values of the $E_{\text{pit}}$ are usually close to these of the repassivation potential, determined potentiodynamically, some authors define this stationary value as potential of repassivation [14].
Fig. 5 shows typical chrono-potentiometric curves received for steels Cr23N1.2 and Cr18Ni9 in 3.5% NaCl solutions (pH 1-12) at applied current density of 60 μA cm\(^{-2}\). This current density was determined as the most proper according to the literature [11, 14] and the experimental data, following the method of Rosenfeld and Danilov [11]. According to the results from the potentiodynamic method, the passive current density for both steels is in the range 2-20 μA cm\(^{-2}\) in all studied model solutions. Hence, the chosen current density for anodic polarisation 60 μA cm\(^{-2}\) on one hand, is sufficiently high, in order to promote the pit formation in the studied pH region of 3.5% NaCl solutions and on the other hand it is low and has not an important influence on the values of the characteristic potentials, determined from the curves [14].

The fluctuations of the potential, observed on the galvanostatic dependencies, indicate a rupture of the passive layer, and their very small magnitude and width of the peaks are indications for the development and fast repassivation of metastable pits. After about 20-30 min the fluctuations are calming down, which is an indication for the stable pit growth. The values of the \(E_p\) does not depend on the solution pH. For the steel Cr23N1.2 in solutions with pH 2-10, the potential does not achieve stationary value after an hour anodic polarisation. Only for the steel Cr23Ni12 in the solution with pH 12 the dependence potential-time has not a maximum and after about two minutes achieves the highest stationary value of about 0.68 V vs. SCE. This behaviour is characteristic for the state of stable passivity, the potential deviation from the start linear growing is due to the establishing of transpassive potential [15]. This form of the curve for the chromium-nitrogen steel shows that at pH 12, the formation of pits does not take place on the passive surface. At the same pH the potential of Cr18Ni9 shifts to the values of the transpassive state, but after reaching it, sharply decreases with about 0.7 V vs. SCE to the values of \(E_{\text{st}}\) characteristic for lower pH.

In contrast with the curves of chromium-nitrogen steel, these for the chromium-nickel steel show fluctuations in the region of the maximum, which can be related to difficulties in the passive film rupture in the beginning and trend toward its restoring. The fluctuations in the curve during the lowering of the potential are few but are wider and with bigger intensity which show formation of small number but larger pits compared with these, formed on the chromium-nitrogen steel.

The effect of pH on the values of \(E_{\text{pit}}\) and \(E_{\text{st}}\) determined chronopotentiometrically, is presented in the Fig. 6. The values of \(E_{\text{pit}}\) for both steels are close and stay in the region 0.34 \(\pm\) 0.42 V vs. SCE. At pH 1, \(E_{\text{pit}}\) decreases with about 0.36 V compared with the value at pH 2, which shows sharp decrease in the protective properties of the passive film on the surfaces of both steels. The values of \(E_{\text{pit}}\) determined galvanostatically, for both steels are close to these, determined through cyclic potentiodynamic method. Thus, the results from the galvanostatic method confirm these, received by potentiodynamic method that in the region of pH 2-10, the character of the environment has not an important influence on the protective properties of the passive
layers, formed in 3.5% NaCl solutions.

**Microscopic observations**

With an aim of determination of the character and dimensions of the corrosion damages, after each polarisation test the surface of the samples was investigated in detail at magnifications 50x, 200x and 500x. The samples, subjected to anodic polarisation in 3.5%NaCl solutions with pH 1-10, are affected by pitting corrosion. The main differences in the corrosion attack of the steels Cr23N1.2 and Cr18Ni9, for all solution conditions, are the shape and location of the surface defecteds. The pits, formed on the chromium-nitrogen steel, are predominately with irregular shape, situated along the grain boundaries (Figs. 7a and 7b). The pits on this steel are open and uniformly distributed by size. In a solution with pH 1, chromium-nitrogen surface is affected also by corrosion dissolution, leading to manifestation of the structure (Fig. 7a). Increasing the pH of the solution from 1 up to 10, results in lowering of the number but increases the size of the larger pits respectively from about 0.03 to 0.06 mm. In all model solutions the pits on the chromium-nitrogen steel are an open type.

In the 3.5% NaCl solution with the lowest pH, the surface of the steel Cr18Ni9 is not affected from general corrosion, but the number and dimensions of the pits is several times greater than those on the chromium-nitrogen steel. At pH 1 on the surface of Cr18Ni9, the average number is 20-30 macropits/cm², which are subsurface, with irregular shape and depth about and over 0.15 mm. The micropits number is also considerable. With pH raising from 2 to 8 an important change in the shape and in the number of pit nucleus is not observed. In contrast to the pits on the steel Cr23N1.2 in the same pH range, the pits on the chromium-nickel steel are separated by shape and type. Enormous number of shallow open micropits (about and over 50-60 micropits/cm²) with pit hole less than 0.010 mm and few macropits (up to 8-10 macropits/cm²), hidden under lacy cover (Fig. 8) are registered. Despite the small pit mouth, the macropits reach considerable dimensions and penetrate into the steel to the depth of over 0.12 mm. At pH 10 the pits number on the chromium-nickel steel decreases to 3-4 macropits/cm², but some of them have a diameter about 0.25 mm (Fig. 8b).

In solutions with pH 12 some discrepancies between the results from the two polarisation methods are registered. According to the potentiodynamic dependencies, the pitting corrosion at this pH value does not appear, while the results from the galvanostatic method shows definitely a local break in the passive layer for the steel.

![Fig. 6. Influence of pH on $E_{pit}$ (round symbols) and $E_{st}$ (triangular symbols) of steels Cr23N1.2 (solid lines) and Cr18Ni9 (dotted lines) in 3.5% NaCl, 20 °C.](image)

![Fig. 7. Pits on Cr23N1.2 after polarisation test in 3.5% NaCl, pH 1 (a) and pH 6 (b).](image)
Cr18Ni9. The microscopic observations of the chromium-nickel steel surface after the galvanostatic test at pH 12 show well-defined single pits with dimension about 0.06 mm, which are not observed after the potentiodynamic tests. Most probably the cited differences are due to the difference between the two electrochemical methods. In the cyclic potentiodynamic method the anodic polarisation is growing up gradually until the pitting potential, the passive layer on the steel has already thickness and structure, different from those, formed at the open circuit potential. During the galvanostatic method, the fast polarisation with relatively high anodic current is applied and maintained on the natural passive layer for longer time. The high positive potential, reached in this case, gives an opportunity to the created local ruptures to grow in short time and turn into big and stable pits. Despite the high pH value, in the galvanostatic conditions the repassivation process is straitened because of the large size and closed type of the pits, which facilitates the growth of acidity in the pit solution.

CONCLUSIONS

The susceptibility to general and pitting corrosion of the chromium-nitrogen steel Cr23N1.2 in 3.5% NaCl solution with pH 1 and 2 is lower as compared to this one of the chromium-nickel steel Cr18Ni9. At pH value above 2, the pH of the chloride solution has not a considerable influence on corrosion behaviour of the steels. In 3.5% NaCl solutions with pH 1-10, the anodic polarisation leads to development of pits, which are different not only in shape, but also in depth of penetration. The pits on the chromium-nitrogen steel Cr23N1.2 are of open type, with irregular shape and they are formed mainly on the grain boundaries. In contrast, the pits on the steel Cr18Ni9 are of closed type and penetrate in bigger depth as compared to these of the steel Cr23N1.2. The possibility for formation of lacy cover depends in great extent on the steel composition and the sensibility of the repassivation potential on the pH changes.

Acknowledgements

Special thanks are due to Assoc. Prof. Dr. L. Fachikov, Head of the Department of Electrochemical production and Anticorrosion Protection, University of Chemical Technology and Metallurgy, for discussion of the present results.

REFERENCES

6. Y. M. Liou, S. Y. Chiu, C. L. Lee, H. C. Shih,


