

## Pitting corrosion of stainless steels in chloride solutions

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The electrochemical techniques were used for determining the resistance of stainless steels to pitting corrosion in neutral chloride solutions. Cyclic potentiodynamic polarization measurements were performed to determine the pitting potential values in chloride solutions with different amounts of sulphate or nitrate ions. Critical pitting temperature testing was carried out in the same solutions applying potentiostatic technique. Comparison was made between experimentally determined pitting potential and critical pitting temperature values, in chloride solutions containing different amounts of sulphate or nitrate ions. It was established that nitrates are far more effective than sulphates as inhibitors of stainless steels pitting corrosion in neutral chloride solutions.

*Key words:* stainless steel, corrosion, pitting corrosion, corrosion inhibitors, chlorides, electrochemical methods.

### Introduction

CORROSION of metals is a spontaneous degradation of metals, influenced by corrosive environment. In some cases the corrosion rate is low, though from thermodynamical point of view, the rate of metal dissolution ought to be significantly higher. The state of high corrosion resistance is called passivity.

Stainless steels are Fe based alloys containing at least 12% Cr. They are corrosion resistant because of surface passive film existence, such that separates metal from corrosive environment. Chromium is the most important alloying element for passive film formation. Nickel stabilizes austenite structure, thus improving some mechanical characteristics of stainless steels [1].

Austenitic stainless steel Č4580 (AISI 304) contains cca. 18% Cr and 10% Ni. This steel has a broad application (chemical plants, food industry, articles for everyday use). In some corrosive environments, the breaking down of passive film on this steel takes place and some form of local corrosion occurs: pitting, crevice corrosion, stress corrosion cracking and intergranular corrosion.

Pitting corrosion takes place in two steps: pitting formation and pit growth. Most frequently, pits are formed in the presence of Cl<sup>-</sup> ions on the discontinuities in passive films, as MnS inclusions and grain boundaries [2,3]. The potential present when pits start to grow is called pitting potential,  $E_{pit}$ . It is manifested as a rapid current increase on anodic polarization curve. Pits stop to grow at potentials below protective potential,  $E_{prot}$ . Below the pitting potential pits can be formed and repassivated before they are transformed to stable pits. This stage of pitting corrosion is known as metastable pitting.

Susceptibility of metals to pitting corrosion increases with the temperature rise. Stable pits can not be formed below a certain temperature value, called critical pitting temperature,  $T_{pit}$ . In this temperature range only

transpassive corrosion can occur. Above the critical  $T_{pit}$ , the pitting potential values decrease with temperature increase.

Pitting corrosion resistance of stainless steels is frequently examined applying electrochemical methods. Cyclic potentiodynamic technique is used for determining the pitting potential and protective potential values. The pitting potential (potential when stable growth of pits starts) and protective potential (potential when pit growth stops) are determined from anodic and opposite polarization curves for current density value of  $10 \mu A \cdot cm^{-2}$ .

Critical pitting temperature value (the minimal temperature for stable pits growth) is determined applying potentiostatic technique, using temperature scan. Potential of 700 mV vs. SCE has been found suitable for most stainless steels. The  $T_{pit}$  is defined as the temperature at which the current density exceeds  $100 \mu A \cdot cm^{-2}$  for 60 s.

$E_{pit}$ ,  $E_{prot}$  and  $T_{pit}$  values are determined depending on composition and structure of stainless steels, or composition, pH values and temperature of corrosion environment. Higher values of  $E_{pit}$ ,  $E_{prot}$  and  $T_{pit}$  indicate better pitting corrosion resistance of stainless steels.

Protection of stainless steels against pitting corrosion in chloride solutions can be performed introducing NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, etc. ions in the solutions. These anions reduce adsorption of Cl<sup>-</sup> ions or displace them from metal surface (competitive adsorption) [6, 8, 9]. Also, they may form a more resistive passive film on the metal surface during anodic polarisation [6]. It is necessary to achieve some concentration ratio of these ions and chloride ions to obtain complete pitting corrosion resistance [4]. For example, this ratio is 10 for SO<sub>4</sub><sup>2-</sup>, 7 for CrO<sub>4</sub><sup>2-</sup>, 2 for ClO<sub>4</sub><sup>-</sup> or 0.4 for NO<sub>3</sub><sup>-</sup> ions, for stainless steel 18Cr-10Ni in NaCl solution (0.1 mol dm<sup>-3</sup>).

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## Experiment

Pitting corrosion resistance of stainless steel Č4580 was examined determining pitting potential  $E_{pit}$  and critical pitting temperature  $T_{pit}$ . Values of  $E_{pit}$  are obtained applying cyclic potentiodynamic technique, according to standard ASTM G 61 – 1998 [5]. Polarization curves are recorded using computer assisted electrochemical system for corrosion measurement.

Tests were performed in neutral deaerated NaCl solution ( $0.2 \text{ mol dm}^{-3}$ ), with or without the addition of nitrate or sulphate ions, at  $25^\circ\text{C}$  temperature, applying potential scan rate of  $1 \text{ mV s}^{-1}$ .  $E_{pit}$  and  $E_{prot}$  values are determined from recorded polarization curves for current density of  $10 \mu\text{A cm}^{-2}$ , according to [6].

$T_{pit}$  values are obtained at constant potential (700 mV vs. SCE) according to standard ASTM G 150 – 1999 [7]. Examinations are carried out in NaCl solution ( $0.2 \text{ mol dm}^{-3}$ ) with or without nitrate or sulphate ions. After the electrochemical system was thermostatted at  $0^\circ\text{C}$ , its temperature was gradually increased by the rate of  $1^\circ\text{C min}^{-1}$ . Current changes on the tested specimen (working electrode) were recorded at the same time. The temperature value when current density reaches  $100 \mu\text{A cm}^{-2}$  and remains above this level for minimum 60 s was considered as critical pitting temperature.

Working electrodes of disk shape and  $1.13 \text{ cm}^2$  area were prepared in the following manner: fine ground (SiC paper, 1000 grit), degreasing in ethanol and washing out in distilled water. Tests were performed in electrochemical cell of  $350 \text{ cm}^3$  volume, with separated departments for reference (SCE) and auxiliary electrode (Pt foil).

Working electrodes are made of stainless steel Č4580 with chemical composition given in Table 1.

**Table 1.** Chemical composition of stainless steel Č4580 (in mass %)

Cr	Ni	C	Si max	Mn max	P max	Fe
17,0-19,0	8,5-10,5	< 0,07	1,0	2,0	0,045	remain

Pits formation and their distribution on the electrode surface were examined using stereo-microscope (magnification from x16 to x100), but pit depth measurements were done by optical microscope.

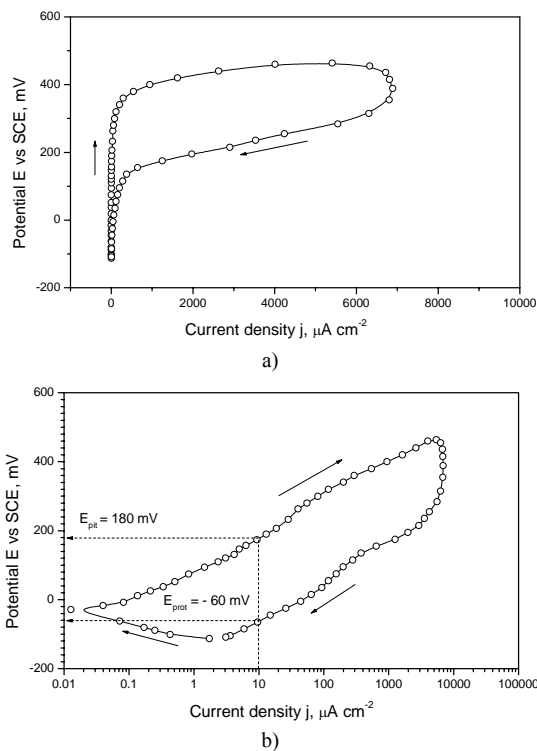
## Results and discussion

Recorded potentiodynamic polarization curves of stainless steel are shown in linear (Fig.1a) and logarithmic form (Fig.1b), where determination of  $E_{pit}$  and  $E_{prot}$  value is presented. Pit formation and their stable growth take place at potentials positive to  $E_{pit}$ . No pit formation takes place in the potential range between  $E_{pit}$  and  $E_{prot}$ , but already existing pits continue to grow. At potentials negative to  $E_{prot}$ , the already formed pits stop growing.

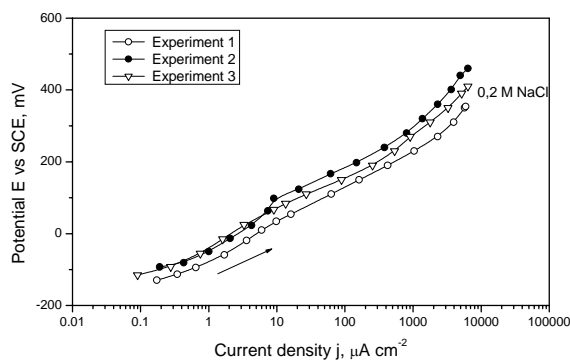
Anodic polarization curves, recorded in repeated tests (under the same experimental conditions) in chloride solution, are presented in Fig.2. Values of  $E_{pit}$ ,  $E_{corr}$  and  $\Delta E$ , obtained from polarization curves in Figures 1 and 2, are presented in Table 2.

The observed scattering of  $E_{pit}$  values is caused by

stochastic nature of pitting corrosion and metastable pit formation. Metastable pit formation takes place at potentials below  $E_{pit}$  and it is most intensive in chloride solution (Fig.3a). This occurrence is less observable in chloride solutions containing sulphate (Fig.3b) or nitrate ions (Fig.3c). Higher current peaks in chloride solutions indicate to an extended periods of pit growth. Metastable pit formation is significantly suppressed in the presence of sulphate or nitrate ions in chloride solutions because competitive adsorption takes place. According to experimental data in Table 2, it can be concluded that  $\Delta E$  values, as well as  $E_{pit}$  values, are indicators of pitting corrosion resistance.



**Figure 1.** Anodic polarization curves of Č4580 in NaCl solution



**Figure 2.** Anodic polarization curves of Č4580 in NaCl solution

**Table 2.**  $E_{corr}$ ,  $E_{pit}$  and  $\Delta E$  values of Č4580 in NaCl solution

Experiment, No.	$E_{corr}$ mV	$E_{pit}$ mV	$\Delta E = E_{pit} - E_{corr}$ mV
1	-150	30	180
2	-100	90	190
3	-120	70	190
4	-30	180	210

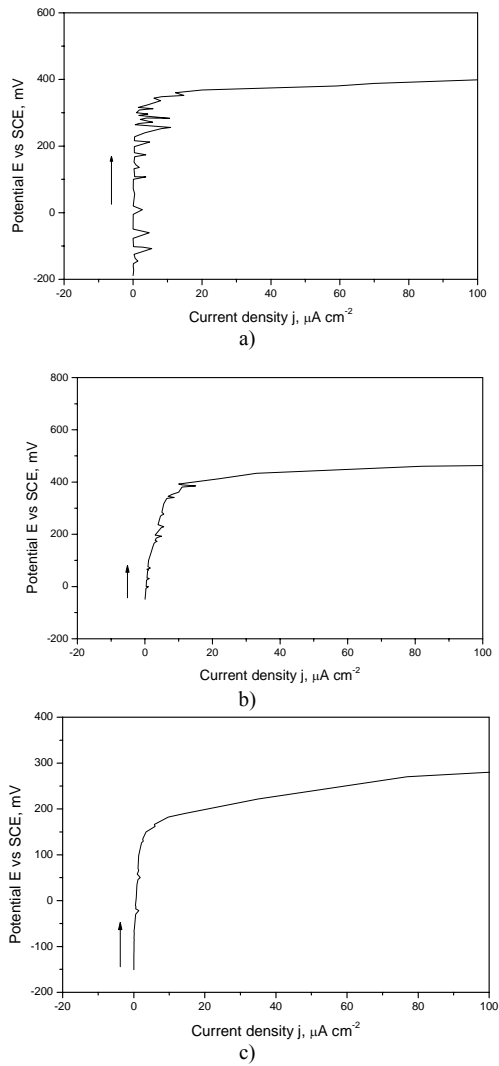


Figure 3. Anodic polarization curves in: a) NaCl, b) NaCl + Na<sub>2</sub>SO<sub>4</sub>, c) NaCl + NaNO<sub>3</sub> solutions

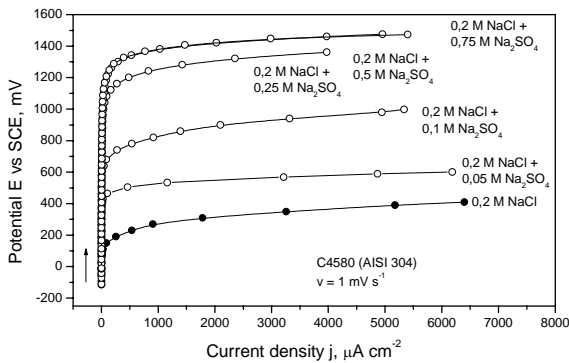


Figure 4. Anodic polarization curves of Č4580 in NaCl solution with different concentrations of sulphate ions.

It can be seen from Fig.4 that the lowest  $E_{pit}$  value is obtained in chloride solution without sulphate ions. As concentration of  $\text{SO}_4^{2-}$  ions increases,  $E_{pit}$  is shifted to positive values which is in fair agreement with competitive adsorption theory of sulphate and chloride ions [6, 8, 9]. Sulphate ions displace chloride ions from metal surface preventing metastable pit formation and shifting  $E_{pit}$  to positive values. It is possible that a more resistant passive film is formed in the presence of  $\text{SO}_4^{2-}$  anions [6], since they contain oxygen atoms.

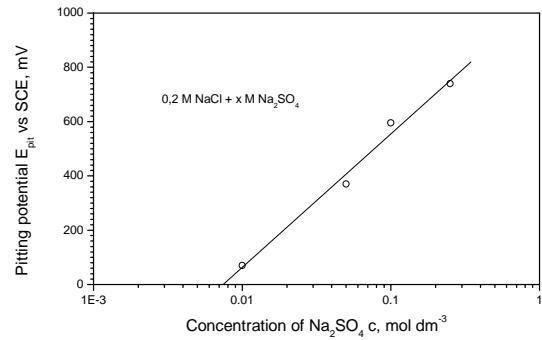


Figure 5. Epit dependence on  $[\text{SO}_4^{2-}]$  in NaCl solution

Linear dependence of  $E_{pit}$  values on  $\log [\text{SO}_4^{2-}]$  ions can be observed from Fig.5. This dependence can be expressed as:

$$E_{pit} = A + B \log [\text{SO}_4^{2-}] \quad (1)$$

A and B are experimental constants.

Pit formation does not take place if the sulphate ions concentration increases above  $0.5 \text{ mol dm}^{-3}$ , until the transpassive range, though the existence of hysteresis between anodic and opposite polarization curve indicates to pitting corrosion (Fig.6). Existence of pits on electrode surface is also established after recording polarization curves (Fig.7). Average pit depth measured by optical microscope was about  $30 \mu\text{m}$ .

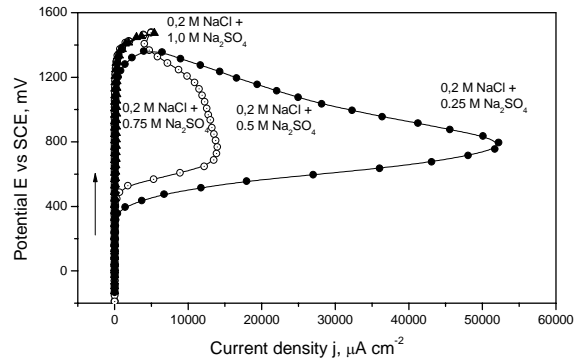
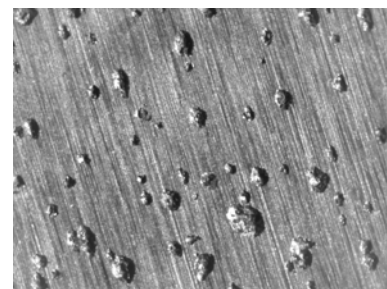
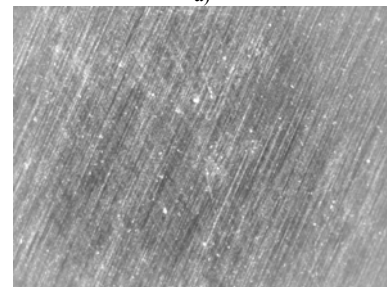


Figure 6. Anodic polarization curves for Č4580 in NaCl + Na<sub>2</sub>SO<sub>4</sub> solutions



a)



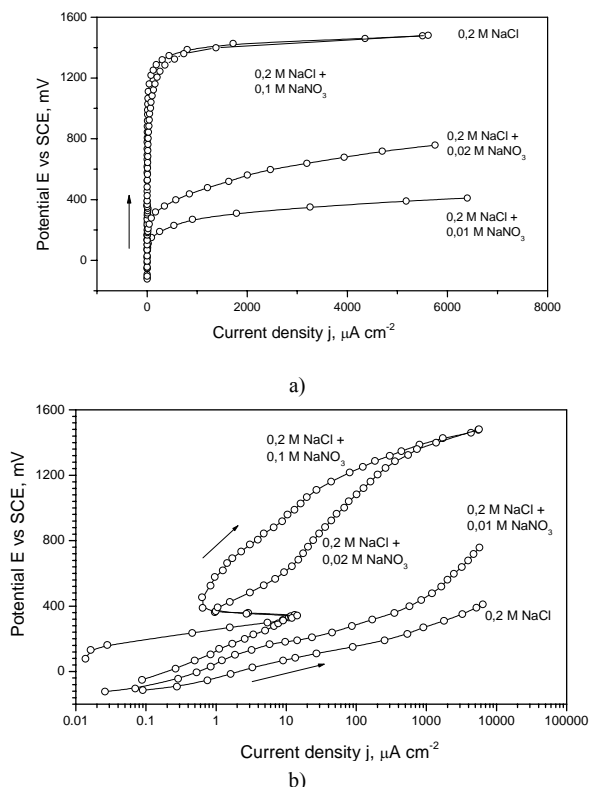
b)

Figure 7. Appearance of electrode surface after examination in NaCl + Na<sub>2</sub>SO<sub>4</sub> solution: a) pitting, b) without pitting. Magnification x 100.

Values of  $E_{pit}$ ,  $E_{corr}$  and  $\Delta E$ , obtained from polarization curves in Figures 4 and 6, are presented in Table 3.

**Table 3.**  $E_{corr}$ ,  $E_{pit}$  and  $\Delta E$  values of Č4580 in NaCl + Na<sub>2</sub>SO<sub>4</sub> solutions

No. of experiment	Na <sub>2</sub> SO <sub>4</sub> , mol dm <sup>-3</sup>	$E_{corr}$ mV	$E_{pit}$ mV	$\Delta E = E_{pit} - E_{corr}$ mV
1	0.05	-50	370	420
2	0.1	-120	600	720
3	0.25	-20	710	730
4	0.5	-150	760	910
5	0.75	-30	820	850
6	1,0	-170	700	870



**Figure 8.** Anodic polarization curves of Č4580 in NaCl solution with different concentrations of nitrate ions

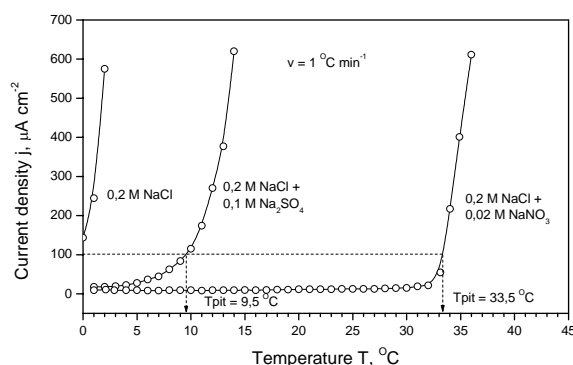
Anodic polarization curves of the examined stainless steel in chloride solution with different amounts of nitrate ions (Fig.8) show that pitting corrosion resistance is lowest in chloride solution without nitrate ions (0.2 mol dm<sup>-3</sup> NaCl). Pitting potential values increase with the rise of NO<sub>3</sub><sup>-</sup> concentration in chloride solution, i.e. pitting corrosion resistance of stainless steel is higher. Transition to practically complete resistance against pits formation occurs when small amounts of nitrate anions (from 0.01 to 0.02 mol dm<sup>-3</sup>) are added to NaCl solution. This is manifested as current peak existence for nitrate ions concentrations higher than 0.02 mol dm<sup>-3</sup>, in potential range from 300 to 350 mV. This current peak precedes the passivation stage.

Values of  $E_{pit}$ ,  $E_{corr}$  and  $\Delta E$ , determined from polarization curves in Fig.8 are presented in Table 4.

**Table 4.**  $E_{corr}$ ,  $E_{pit}$  and  $\Delta E$  values of Č4580 in NaCl + NaNO<sub>3</sub> solutions

No. of experiment	NaNO <sub>3</sub> , mol dm <sup>-3</sup>	$E_{corr}$ mV	$E_{pit}$ mV	$\Delta E = E_{pit} - E_{corr}$ mV
1	0.01	-150	180	330
2	0.02	20	560	540
3	0.10	-60	920	980

Comparison of results presented in Figures 4, 6 and 8 shows that complete pitting corrosion resistance of stainless steel is attained at remarkably lower concentration of nitrate than sulphate ions in chloride solution. Complete pitting corrosion resistance is achieved when chloride solution contains 0.02 mol dm<sup>-3</sup> NaNO<sub>3</sub> or 1.0 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>. It is obvious that NO<sub>3</sub><sup>-</sup> ions are remarkably effective inhibitors of stainless steel pitting corrosion in chloride solution than SO<sub>4</sub><sup>2-</sup> ions, which is in agreement with the references [4, 6]. The affinity of anion adsorption increases as follows: NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, when they are tested individually. However, in the investigated solutions different behavior of inhibiting anions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) is possible. These anions can partially displace Cl<sup>-</sup> ions from electrode surface [6], which can for e.g. be the consequence of lateral effects. Also, inhibiting ions may form a more resistive film on the metal surface.



**Figure 9.** Critical pitting temperature determination for Č4580 in NaCl solution in presence of sulphate or nitrate ions

Determination of critical pitting temperature in chloride solutions with and without sulphates or nitrates is shown in Fig.9. Values of  $T_{pit}$  are higher in the presence of sulphate or nitrate ions. Therefore, pitting corrosion resistance of the examined stainless steel is lower in chloride solutions without sulfate or nitrate ions. It can also be seen that NO<sub>3</sub><sup>-</sup> ions are considerably more efficient as inhibitors of pitting corrosion than SO<sub>4</sub><sup>2-</sup> ions. The damaging influence of temperature increase on pit formation was also observed. For example, the examined stainless steel is almost completely resistant to pitting corrosion in chloride solution (0.2 mol dm<sup>-3</sup>) containing 0.02 mol dm<sup>-3</sup> NaNO<sub>3</sub>, at 25°C. But, pit formation takes place at a temperature of about 33°C, on the same steel in the same solution.

## Conclusion

Performed examination of stainless steel Č4580 pitting corrosion in chloride solution with and without sulphate or nitrate ions indicates that pitting corrosion resistance is lowest in chloride solution (0.2 mol dm<sup>-3</sup> NaCl). Obtained values of  $E_{pit}$  and  $T_{pit}$  were the lowest in this solution.

Pitting corrosion resistance increases with addition of NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions. Nitrate ions are more effective inhibitors of pitting corrosion than sulphate ions, since a considerably lower concentration of nitrate ions is required compared to the concentration of sulphate ions (0.02 mol dm<sup>-3</sup> NaNO<sub>3</sub> and 1.0 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>) to achieve complete pitting corrosion resistance.

Results of the critical pitting temperature determination also show that the pitting corrosion resistance of Č4580 is

lowest in NaCl solution. Values of  $T_{pit}$  increases in the presence of sulphate or nitrate ions. The highest value of  $T_{pit}$  obtained in NaCl + NaNO<sub>3</sub> solutions demonstrates the highest pitting corrosion resistance of the examined stainless steel in this solution.

The applied electrochemical methods i.e. cyclic potentiodynamic technique for pitting potential evaluation and potentiostatic technique for critical pitting temperature determination are suitable for examining the stainless steels pitting corrosion. It is better to represent pitting potential values by a potential range, considering the stochastic nature of the pitting corrosion, but critical pitting temperature values can be determined with high accuracy.

### References

- [1] DAVISON, R.M., BOLD, T. De and JOHNSON, M.J.: *Corrosion of Stainless Steel in Corrosion*, Metal Handbook, Ed. ASM, Ohio, 1997, Vol. 13, 9<sup>th</sup> pp. 546 – 565.
- [2] BOHNI, H.: *Localized Corrosion of Passive Metals*, in Uhlig's Corro-

- sion Handbook, Second Edition, Ed. by R.W. Revie, 2000., pp. 173 – 190.
- [3] PROCTER, R.P.M.: *Effect of Metallurgical Structure on Corrosion in Corrosion*, Ed. by Shreir L.L., Oxford, 2000., pp. 1:36 – 1:54.
- [4] ROZENFELD, I.L.: *Inhibitory korrozii*, Moskva, 1977.
- [5] ASTM G 61–1998: *Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt- Based Alloys*
- [6] ULJANINA, E.A.: *Struktura i korrozija metallov i splavov*, ATLAS, Moskva, 1989.
- [7] ASTM G 150 – 1999: *Electrochemical Critical Pitting Temperature Testing of Stainless Steels*
- [8] UHLIG, H.H. and REVIE, R.W.: *Corrosion and Corrosion Control. An Introduction to Corrosion Science and Engineering*, New York, 1985.
- [9] BURSTEIN, G.B.: *Passivity and Localised Corrosion*, in Corrosion, Ed. by L.L. Shreir, Oxford, 2000., pp. 1:118 – 1:150.

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## Piting korozija nerđajućih čelika u rastvorima hlorida

Za određivanje otpornosti prema piting koroziji nerđajućih čelika u neutralnim hloridnim rastvorima korišćene su različite elektrohemijske metode. Ciklična potenciodinamička polarizaciona merenja su izvedena u cilju dobijanja vrednosti piting potencijala u hloridnim rastvorima koji sadrže različite količine sulfatnih, odnosno nitratnih jona. Primenom potenciostatske metode vršeno je određivanje kritične temperature pitinga u istim rastvorima. Izvršeno je poređenje eksperimentalno dobijenih vrednosti piting potencijala i kritične temperature pitinga u rastvorima hlorida koji sadrže različite količine sulfatnih odnosno nitratnih jona. Utvrđeno je da su nitratni joni znatno efikasniji nego sulfatni joni kao inhibitori korozije nerđajućih čelika u neutralnim hloridnim rastvorima.

*Ključne reči:* nerđajući čelik, korozija, piting korozija, inhibitori korozije, hloridi, elektrohemijske metode.

## Питтинговая коррозия нержавеющей стали в растворах хлоридов

Для определения прочности на питтинговую коррозию нержавеющей стали в нейтральных растворах хлоридов использованы различные электро-химические методы. Циклические потенциодинамические поляризационные измерения проведены со целью получения определённых питтинговых потенциалов в растворах хлоридов, которые содержат различные количества сульфатных, т.е. нитратных ионов. Применением потенциостатского метода сделано и определение критической питтинговой температуры в таких же растворах. Также сделано и сравнение величин питтинговых потенциалов, полученных в экспериментах, и критической питтинговой температуры в растворах хлоридов, которые содержат различные количества сульфатных, т.е. нитратных ионов. Константировано и утверждено, что нитратные ионы в значительной мере более эффективны чем сульфатные ионы в роли ингибиторов коррозии нержавеющей стали в нейтральных растворах хлоридов.

*Ключевые слова:* нержавеющая сталь, коррозия, питтинговая коррозия, ингибиторы коррозии, раствор хлора, электро-химические методы.

## La corrosion pitting des aciers inoxydables dans les solutions de chlorure

Les différentes méthodes électrochimiques ont été utilisées pour déterminer la résistance des aciers inoxydables à la corrosion pitting dans les solutions de chlorures neutres. Les mesures potentiodynamiques cycliques et de polarisation ont été effectuées dans le but d'obtenir les valeurs du potentiel pitting dans les solutions contenant différentes quantités de ions sulfates ou nitrates. La détermination de la température critique du pitting a été réalisée dans les mêmes solutions au moyen de la méthode potentiostatique. On a fait la comparaison entre les valeurs du potentiel pitting obtenues expérimentalement et la température critique du pitting dans les solutions de chlorure qui contiennent différentes quantités de ions sulfates et nitrates. On a pu constater que les ions nitrates sont beaucoup plus efficaces que les ions sulfates comme inhibiteurs de corrosion des aciers inoxydables dans les solutions neutres de chlorure

*Mots clés:* acier inoxydable, corrosion, corrosion pitting, inhibiteurs de corrosion, chlorures, méthodes électrochimiques.