INVESTIGAÇÃO EXPERIMENTAL E TEÓRICA DAS PROPRIEDADES DE CORROSÃO DO AÇO X13 NO ÁCIDO ACÉTICO A 20 E 80 °C

EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE CORROSION PROPERTIES OF STEEL X13 IN THE ACETIC ACID AT 20 AND 80 °C

ЭКСПЕРИМЕНТАЛЬНОЕ И ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ КОРРОЗИОННЫХ СВОЙСТВ СТАЛИ X13 В УКСУСНОЙ КИСЛОТЕ ПРИ 20 И 80 °C

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RESUMO

As curvas de polarização de aço inoxidável X13 em uma solução de 5% NaCl + 0.5% CH₃COOH + CH₃COONa + CO₂ (P_{CO₂} = 0.1 MPa) em pH 3 e 4 e temperaturas 20 e 80 °C foram obtidas pelo método potencioestático. As características eletroquímicas de corrosão do aço nesses ambientes foram medidas. Os potenciais - diagramas de pH do aço do sistema X13 - CH₃COOH - CO₂ - H₂O foram construídos e o comportamento de corrosão do aço foi determinado usando estes diagramas. A passivação do aço pode prosseguir devido à formação de camada de fase de cromita de ferro (FeCr₂O₄) e de policamada de oxalato de ferro (FeC₂O₄).

Palavras-chave Aço inoxidável X13, ambientes de ácido acético, curvas de polarização, diagrama de potencial - pH.

ABSTRACT

Polarisation curves of stainless steel X13 in a 5% NaCl + 0.5% CH₃COOH + CH₃COONa + CO₂ (P_{CO₂} = 0.1 MPa) solution at pH 3 and 4 and temperatures 20 and 80 °C were obtained by the potentiostatic method. The corrosion-electrochemical characteristics of the steel in these environments were measured. The potential – pH diagrams of system steel X13 – CH₃COOH – CO₂ – H₂O were constructed and the corrosion behaviour of the steel was determined using these diagrams. The passivation of the steel may proceed due to the formation of iron chromite (FeCr₂O₄) phase layer and of iron oxalate (FeC₂O₄) polylayer.

Keywords: Stainless steel X13, acetic acid environments, polarisation curves, potential – pH diagram.

АННОТАЦИЯ

Потенциостатическим методом получены поляризационные кривые нержавеющей стали X13 в растворе 5% NaCl + 0,5% CH₃COOH + CH₃COONa + CO₂ (P_{CO₂} = 0,1 МПа) при pH 3 и 4 и температурах 20 и 80 °C. Измерены коррозионно-электрохимические характеристики стали в этих средах. Построены диаграммы потенциал – pH системы сталь X13 – CH₃COOH – CO₂ – H₂O и с помощью этих диаграмм определено коррозионное поведение стали. Пассивация стали может происходить из-за образования фазового слоя хромита железа (FeCr₂O₄) и полислоя оксалата железа (FeC₂O₄).

Ключевые слова: Нержавеющая сталь X13, уксуснокислая среда, поляризационные кривые, диаграмма потенциал – pH.

INTRODUCTION

Acetic acid is widely used in various branches of industry, and the study of corrosion of the metallic equipment in the acetic media is an important task (Davis, 2000; Schweitzer, 2006). Numerous studies on the corrosion of various metals and alloys in the acetic media were conducted in the past years (Malakhova *et al.*, 1995; Nickel Institute, 2016; Onuchukwu and Oppong-Boachie, 1986; Thirumalaikumar and Jegannathan, 2011; Hassan and Fahmy, 2008; Rafiquee *et al.*, 2007; Ansari and Quraishi, 2011; Allahkaram *et al.*, 2011; Veloz and González, 2002; Amri *et al.*, 2008; Tétreault *et al.*, 1998; Rocca *et al.*, 2004; Turnbull *et al.*, 2003; Lou and Singh, 2010; Singer *et al.*, 2011). This study aims the investigation of the corrosion properties of the stainless steel X13.

Steel X13 is an instrumental stainless steel produced in accordance with the Russian State Standard GOST 5632–72. It is designed for usage in weakly aggressive environments. This steel grade is analogous to such steel grades as UNS S42000 (USA), ASTM 420–SS2303 (EU), SUS420J1 (Japan) or 2Cr13 (China) (Database of Steel and Alloy, 2016). The average composition of steel X13 is presented in Table 1.

MATERIALS AND METHODS

Sample preparation

The cylindrical samples made of steel X13, 9.5 mm in diameter and 5 mm in height with the small hole in the cylinder base for binding current-conductible parts were used. The working surface of the samples was approximately equal to 2.7 cm². Before the polarisation tests the

samples were polished and degreased in acetone.

Reagents of CO₂ analytical quality were used. Analytical balance with maximum uncertainty of ±0.0001 g was used for taking weights. pH-meter with maximum uncertainty of ±0.01 pH unit was used to control solution pH. The solutions for polarisation measurements were prepared in accordance with NACE/ASTM TM0169 G0031 12A Standard Guide for Laboratory Immersion Corrosion Testing of Metals: 1 L of the solution containing (by weight) 5 % NaCl and 0.5 % CH₃COOH was saturated by CO₂ at P_{CO₂} = 0.1 MPa, after that 100 ml of the 100 g/mL Na₂CO₃ solution was added, and then pH was adjusted to the necessary value by adding hydrochloric acid.

Polarisation measurements

The polarisation measurements were performed in the potentiodynamic mode using the potentiostat Gamry Series G750 in the standard three-electrode thermostated cell. A saturated calomel electrode was used as the reference electrode. The temperature of the solution was maintained at 20 ± 2 °C or 80 ± 2 °C. IR drop was minimised by using and accurately positioning the Luggine capillary.

The potential of dissolution of steel X13 was preliminary determined. For this the potential on steel was measured without external polarisation during at least one hour, taking E_{corr} as the potential at the end of exposure with the condition that potential change in the last 30 minutes was no more than ±30 mV. After that the sample was cathodically polarized at the potential of –1.1 V (SHE) for 10 minutes and potentiodynamic curve was registered with

potential sweep rate of 0.1 mV/s. The experiment was repeated until three polarisation curves compatible with each other were obtained for each solution. The potential with respect to the standard hydrogen electrode was calculated taking into account the temperature dependency of the potential of a saturated calomel electrode.

Construction of potential – pH diagrams

The method of plotting the potential – pH diagrams of multielement systems and the application of these diagrams to the thermodynamic study of the corrosion processes is described in detail elsewhere (Thompson *et al.* 2011).

RESULTS AND DISCUSSION

The polarisation curves

The polarisation curves of steel X13 in a solution containing 5% NaCl + 0.5% CH₃COOH + CH₃COONa + CO₂ at 20 °C are presented in Figure 1, and at 80 °C – in Figure 2.

From the anodic branches of polarisation curves the following quantities were determined: passivation potential (E_p), pitting formation potential (E_{pit}), the size of the passivity region ($\Delta E = E_{pit} - E_p$), the pitting resistance index ($\Delta E_{pit} = E_{pit} - E_{corr}$) (Freiman *et al.* 1986), the Tafel slope of the active corrosion region of the curve (b_a) and the corrosion rate in the passive state (i_p). The results are presented in Table 2.

The experimental data show that at elevated temperature both the passivity region size and the pitting resistance index substantially decrease, which indicates lesser stability of metal and higher probability of pitting formation at higher temperatures. Lowering pH of the test media from 4 to 3 also causes the narrowing of the passivity region size and the increase of the corrosion rate. A very high value of the corrosion rate in the passivity state region at 20 °C and pH 3 indicates the change of the passivation mechanism.

The visual inspection of the samples after electrochemical tests is presented in Figure 3. Pittings are present on all samples, and moreover, the number of local corrosion damage nuclei is significantly larger at pH 3. The surface

of the samples tested at pH 4 is generally brilliant and for the samples tested at pH 3 it becomes dull. It shows that whereas at pH 4 the test media inflicts only local damage to the surface of the steel, at pH 3 the anodic dissolution occurs not only in pittings but also over the entire surface.

Thermodynamic evaluation of the corrosion properties of steel

The steel X13 has the crystal structure of ferrite (a Fe-based solid solution with body centered cubic lattice). The thermodynamic description of this solid solution was performed using the quasi-regular solution model (Chen, 1988) using the data from Kaufman and Nesor (1973). The calculated thermodynamic activities of iron and chromium in the steel are the following: at 20 °C $a_{Fe(bcc)} \approx 0.99$ and $a_{Cr(bcc)} \approx 114.3$; and at 80 °C $a_{Fe(bcc)} \approx 0.99$ and $a_{Cr(bcc)} \approx 31.1$. The activities of chromium exceed unity, which is proved by the phase diagram of Fe – Cr system (Kaufman and Nesor, 1973) and indicates that at low temperatures steel X13 is metastable.

The basic chemical and electrochemical equilibria of the steel X13 in acetic media along with the temperature dependencies of the Gibbs free energies of reactions are listed in Table 3. Since the studied temperature interval is relatively narrow, the temperature dependencies of the Gibbs free energies are approximated as linear functions of temperature. The parameters of temperature relationships were calculated from the data of Tyurin (1999), Lee (1981), Belyaev *et al.* (1984) and Saltykov *et al.* (2004).

The duration of single electrochemical test was ~4 hours, from which 1.5 hours was the duration of corrosion potential measurements and 2.5 hours was the duration of polarisation curve registration. It was estimated from the corrosion rate values listed in Table 2 that the average content of iron and chromium in a solution after four-hour exposure has the order-of-magnitude of 10⁻⁴ mol/L. The potential – pH diagram of steel X13 – CH₃COOH (~0,1 mol/L) – CO₂ (~ 10⁻⁴ mol/L) – H₂O system at 20 °C, P=1 bar (air) and the activities of iron and chromium ions in solution ~10⁻⁴ mol/L is presented in Figure 4, and at 80 °C – in Figure 5. Thermodynamic calculations show that at pH 3 and 4 and potentials from –0.6V to +0.3 V (SHE) the passivation of steel is determined by the

formation of iron chromite (FeCr_2O_4) or iron oxalate (FeC_2O_4) on its surface. At pH 4 iron chromite forms a protective layer on the steel surface both at ambient and elevated temperatures, whereas at pH 3 the situation is different. At 80 °C FeCr_2O_4 remains thermodynamically stable, but at 20 °C it decomposes and the protective layer consists from iron oxalate. Thermodynamic calculations explain the unusually high value of the corrosion rate at pH 3 and 20 °C in Table 2. The protective effect of iron chromite is very well known (Reformatskaya *et al.*, 2004), and it is significantly stronger than that of iron oxalate (Saltykov *et al.*, 2004). At lower pH, however, the strength and the protective function of the iron chromite layer decreases, and the iron oxalate layer is not able to fully resist the destructive influence of the aggressive components of the environment, and the steel is affected by overall corrosion. In these conditions rising the temperature can shift the border of thermodynamic stability of iron chromite and slow down the dissolution of steel.

CONCLUSIONS

1. The corrosion-electrochemical behaviour of steel X13 in a solution containing by weight 5% NaCl + 0.5% CH_3COOH + CH_3COONa + CO_2 ($P_{\text{CO}_2} = 0,1$ MPa) at pH 3 and 4 and temperatures 20 and 80 °C was studied by the potentiodynamic method. The values of the potentials of corrosion (E_{corr}), passivation (E_p) and pitting formation (E_{pit}) as well as corrosion rate in the passive state (i_p) were determined. The anomaly in the temperature dependency of the corrosion rate at pH 3 was revealed.

2. The thermodynamic evaluation of the corrosion properties of steel X13 in a solution containing by weight 5% NaCl + 0.5% CH_3COOH + CH_3COONa + CO_2 ($P_{\text{CO}_2} = 0,1$ MPa) at pH 3 and 4 and temperatures 20 and 80 °C was performed. The potential – pH diagrams of steel X13 – CH_3COOH (~0,1 mol/L) – CO_2 (~ 10^{-4} mol/L) – H_2O were plotted.

3. It is shown that the passivation of steel X13 in the studied range of pH and temperatures can be provided by the formation of the iron chromite or iron oxalate layers on its surface.

4. The changing of the nature of the protective layer at pH 3 from FeC_2O_4 at 20 °C to FeCr_2O_4 at 80 °C lowers the corrosion rate 3 times. The increase of temperature of the environment can be used for retaining the passivation state of the steel in acetic environments

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Table 1. The average chemical composition of steel X13

Composition of the element, weight %												
C	Si	Mn	P	S	Cr	Ni	Cu	Mo	Al	Ti	V	W
0.15	0.41	0.35	0.010	0.002	12.5	0.16	0.07	0.007	0.016	0.001	0.021	0.001

Table 2. The corrosion-electrochemical characteristics of steel X13 in a 5% NaCl + 0,5% CH₃COOH + CH₃COONa + CO₂ solution

Conditions	E _{corr} , mV	E _p , mV	E _{pit} , mV	ΔE, mV	ΔE _{pit} , mV	b _a	i _p , mA/cm ² (mm/year)
t = 20 °C, pH 4	-345	-260	-30	230	315	0.072	0.005 (0.04)
t = 20 °C, pH 3	-360	-210	-30	180	330	0.135	0.111 (0.86)
t = 80 °C, pH 4	-380	-315	-240	75	140	0.060	0.018 (0.14)
t = 80 °C, pH 3	-390	-330	-295	35	95	0.035	0.046 (0.36)

Table 3. The Gibbs free energies of the basic chemical and electrochemical reactions in Fe – Cr – CH₃COOH – CO₂ system

No of line at Figs. 4 and 5	Electrode reaction	Δ _r G _T ^o = f(T), J/mol
a	2H ⁺ + 2e = H ₂	0
b	O ₂ + 4H ⁺ + 4e = 2H ₂ O	-571620 + 326.5 T
1	Cr ²⁺ + 2e = Cr (bcc, ferrite)	206230 – 100.9 T
2	Fe ²⁺ + 2e = Fe (bcc, ferrite)	87930 – 10.0 T
3	Cr ³⁺ + e = Cr ²⁺	108010 – 230.5 T
4	Fe ³⁺ + e = Fe ²⁺	-21330 – 178.1 T
5	Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e = 2Cr ³⁺ + 7H ₂ O	-987830 + 731.2 T
6	FeO ₄ ²⁻ + 8H ⁺ + 3e = Fe ³⁺ + 4H ₂ O	-710120 + 246.0 T
7	Cr ₂ O ₃ + 6H ⁺ + 6e = 2Cr(bcc) + 3H ₂ O	426190 – 301.5 T
8	FeCr ₂ O ₄ + 2H ⁺ + 2e = Fe(bcc) + Cr ₂ O ₃ + H ₂ O	102760 – 74.2 T
9	Fe ₃ O ₄ + 8H ⁺ + 8e = 3Fe(bcc) + 4H ₂ O	179450 – 382.0 T
10	Cr ₂ O ₃ + 6H ⁺ + 2e = 2Cr ²⁺ + 3H ₂ O	14110 – 99.8 T
11	FeCr ₂ O ₄ + 8H ⁺ + 4e = Fe(bcc) + Cr ²⁺ + 4H ₂ O	140030 – 251.0 T
12	FeCr ₂ O ₄ + 8H ⁺ + 2e = Fe ²⁺ + Cr ²⁺ + 4H ₂ O	8040 – 93.0 T
13	FeCr ₂ O ₄ + 8H ⁺ = Fe ²⁺ + 2Cr ³⁺ + 4H ₂ O	195810 – 372.7 T
14	Fe ₃ O ₄ + 8H ⁺ + 2e = 3Fe ²⁺ + 4H ₂ O	-211330 + 92.0 T
15	3Fe ₂ O ₃ + 2H ⁺ + 2e = 2Fe ₃ O ₄ + H ₂ O	87550 – 142.3 T
16	Fe ₂ O ₃ + 6H ⁺ + 2e = 2Fe ²⁺ + 3H ₂ O	-180070 + 144.8 T
17	Fe ₂ O ₃ + 4Cr ³⁺ + 5H ₂ O + 2e = 2FeCr ₂ O ₄ + 10H ⁺	357550 – 876.1 T
18	2Cr ₂ O ₃ + Fe ₂ O ₃ + 2H ⁺ + 2e = 2FeCr ₂ O ₄ + H ₂ O	-83080 – 153.8 T
19	2CrO ₂ + 2H ⁺ + 2e = Cr ₂ O ₃ + H ₂ O	-101640 – 96.7 T
20	CrO ₄ ²⁻ + 4H ⁺ + 2e = CrO ₂ + 2H ₂ O	-277260 – 125.1 T
21	Cr ₂ O ₃ + 6H ⁺ = 2Cr ³⁺ + 3H ₂ O	-201760 + 361.1 T
22	CrO ₂ + 4H ⁺ + e = Cr ³⁺ + 2H ₂ O	-151710 + 132.5 T
23	Fe ₂ O ₃ + 6H ⁺ = 2Fe ³⁺ + 3H ₂ O	-99340 + 370.1 T
24	Cr ₂ O ₇ ²⁻ + 6H ⁺ + 4e = 2CrO ₂ + 3H ₂ O	-494760 – 169.7 T
25	Cr ₂ O ₇ ²⁻ + H ₂ O = 2CrO ₄ ²⁻ + 2H ⁺	30 + 273.3 T
26	2FeO ₄ ²⁻ + 10H ⁺ + 6e = Fe ₂ O ₃ + 5H ₂ O	-1122400 – 546.2 T
27	2CrO ₂ ⁻ + 6H ⁺ = Cr ₂ O ₃ + 3H ₂ O	-215640 – 26.3 T
28	CrO ₄ ²⁻ + 4H ⁺ + 3e = CrO ₂ ⁻ + 2H ₂ O	-232340 – 138.5 T

29	$4\text{CrO}_2^- + \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e} = 2\text{FeCr}_2\text{O}_4 + 3\text{H}_2\text{O}$	-511230 – 216.3 T
30	$\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{e} = 3\text{HFeO}_2^- + \text{H}^+$	409090 – 194.9 T
31	$\text{HFeO}_2^- + 3\text{H}^+ + 2\text{e} = \text{Fe}(\alpha) + 4\text{H}_2\text{O}$	-34880 + 202.2 T
32	$\text{FeCr}_2\text{O}_4 + 2\text{e} = 2\text{CrO}_2^- + \text{Fe}(\text{bcc})$	317350 – 445.0 T
33	$\text{CrO}_2^- + 4\text{H}^+ + 3\text{e} = \text{Cr}(\alpha) + 2\text{H}_2\text{O}$	69510 + 180.0 T
34	$\text{FeCO}_3 + \text{H}^+ + 2\text{e} = \text{Fe}(\alpha) + \text{HCO}_3^-$	94950 – 26.8 T
35	$\text{Fe}^{2+} + \text{H}_2\text{CO}_3 = \text{FeCO}_3 + 2\text{H}^+$	19840 + 114.2 T
36	$\text{Fe}_3\text{O}_4 + 3\text{HCO}_3^- + 5\text{H}^+ + 2\text{e} = 3\text{FeCO}_3 + 4\text{H}_2\text{O}$	-148700 – 141.8 T
37	$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	14640 + 148.6 T
38	$\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$	7740 + 97.4 T
39	$\text{CH}_3\text{COOH} = \text{CH}_3\text{COO}^- + \text{H}^+$	-420 + 92.5 T
40	$\text{C}_2\text{O}_4^{2-} + 7\text{H}^+ + 6\text{e} = \text{CH}_3\text{COO}^- + 2\text{H}_2\text{O}$	113340 – 183.3 T
41	$\text{FeC}_2\text{O}_4 + 2\text{e} = \text{Fe}(\text{bcc}) + \text{C}_2\text{O}_4^{2-}$	-58380 + 646.4 T
42	$\text{Fe}_3\text{O}_4 + 3\text{C}_2\text{O}_4^{2-} + 8\text{H}^+ + 2\text{e} = 3\text{FeC}_2\text{O}_4 + 4\text{H}_2\text{O}$	-217180 – 345.5 T
43	$\text{FeC}_2\text{O}_4 + 7\text{H}^+ + 8\text{e} = \text{Fe}(\text{bcc}) + \text{CH}_3\text{COO}^- + 2\text{H}_2\text{O}$	73890 + 411.7 T
44	$\text{FeC}_2\text{O}_4 + 8\text{H}^+ + 6\text{e} = \text{Fe}^{2+} + \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	-106320 + 607.8 T
45	$\text{Fe}_2\text{O}_3 + \text{C}_2\text{O}_4^{2-} + 6\text{H}^+ + 4\text{e} = \text{FeC}_2\text{O}_4 + 3\text{H}_2\text{O}$	-122650 – 193.1 T
46	$\text{Fe}^{3+} + \text{H}_2\text{C}_2\text{O}_4 + \text{e} = \text{FeC}_2\text{O}_4 + 2\text{H}^+$	-7160 – 305.5 T
47	$\text{HC}_2\text{O}_4^- = \text{C}_2\text{O}_4^{2-} + \text{H}^+$	-6570 + 35.4 T
48	$\text{H}_2\text{C}_2\text{O}_4 = \text{HC}_2\text{O}_4^- + \text{H}^+$	-3140 + 35.4 T

Figure 1. The polarisation curves of steel X13 in a solution containing 5% NaCl + 0.5% CH₃COOH + CH₃COONa + CO₂ at 20 °C.

Figure 2. The polarisation curves of steel X13 in a solution containing 5% NaCl + 0.5% CH₃COOH + CH₃COONa + CO₂ at 80 °C.

Figure 3. The view of the samples of X13 steel after electrochemical test in various conditions: a – 20 °C, pH 4; b – 80 °C, pH 4; c – 20 °C, pH 3; d – 80 °C, pH 3.

Figure 4. The potential – pH diagram of steel X13 – CH₃COOH (~0,1 mol/L) – CO₂ (~ 10⁻⁴ mol/L) – H₂O system at 20 °C, P=1 bar (air) and the activities of iron and chromium ions ~10⁻⁴ mol/L (unhydrated form of the oxides).

Figure 5. The potential – pH diagram of steel X13 – CH₃COOH (~0,1 mol/L) – CO₂ (~ 10⁻⁴ mol/L) – H₂O system at 80 °C, P=1 bar (air) and the activities of iron and chromium ions ~10⁻⁴ mol/L (unhydrated form of the oxides).