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SUSCEPTIBILITY OF Cr – Ni – Mo STAINLESS STEEL TO PITTING IN RELATION TO TEMPERATURE

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ABSTRACT: The effect of temperature is important external factor of inclination of stainless steels to pitting. It is held to be very complicated problem connected with many factors (composition of electrolyte, character of metal, experimental conditions). This paper deals with the corrosion behavior of AISI 316Ti stainless steel in temperature range 22 - 80 °C in aggressive chloride environments (3 and 5% $FeCl_3$ solutions). The corrosion resistance of tested steel is evaluated on the base of results of the exposition immersion tests (visual and microscopic observation of failed surfaces, mass losses of specimens) and the cyclic potentiodynamic tests.
KEYWORDS: pitting corrosion, temperature, cyclic potentiodynamic test, immersion test, pitting potential

INTRODUCTION

Temperature is a factor that strongly affects both thermodynamics and kinetics of pitting corrosion. Numerous studies on the effect of temperature on pitting have been carried out. Most of them deal with the temperature in range 20 – 100°C [1, 2].

In regard to the fact, that the majority of chemical and electrochemical reactions proceed more rapidly at higher temperatures it was anticipated that the rate of pitting would increase with increasing temperature according to the Arrhenius equation [1]. Semino et al. [3] indicate its validity only for very narrow temperature range. In many cases, the proportionality between the pitting rate and reciprocal absolute temperature is absent, even in narrow temperature range.

Most of authors consider influence of temperature on pitting corrosion by the change of electrochemical characteristics (pitting potential E_p and repassivation potential E_r) with temperature [1].

Szklarska-Smialowska [4] found that for Cr a Cr–Ni stainless steel in 3% NaCl solution a linear relationship exist between the E_p and the temperature (an increase in temperature by 10 °C caused a decrease in E_p by 30 mV). The similar shift of E_p was later marked by other authors too [5]. For Cr–Ni–Mo stainless steel the dependence of E_p on temperature is different. The decrease of E_p stops above 70 °C and E_p keeps the same value to 100 °C [4].

Bond [6] studied the influence of Mo in steels (18% Cr + 0 – 5% Mo) on the E_p in different temperatures. A temperature increase from 1 °C to 70 °C caused the strong decrease of E_p (in 1 M NaCl solution). The author also noticed that the most positive E_p was reached by 3.5% Mo content at all studied temperatures.

Numerous authors use the critical pitting temperature (CPT) as a criterion for susceptibility to pitting. The authors [7] locate the CPT as the temperature of strong discontinuous decrease of E_p. According to Newman and his colleagues [5, 8] this discontinuity in E_p can be interpreted in terms of competition between the salt film and oxide formation within a pit. Bellow CPT, the oxide passivation occurs preferentially and stable pits growth is therefore prevented [5, 8].

Presented paper is focused on the effect of the temperature on the corrosion resistance of AISI 316Ti stainless steel. It is Cr–Ni–Mo stainless austenitic steel stabilized by Ti, considered to be the steel with the high corrosion resistance. In spite of it, this steel often underlies local corrosion, namely pitting, in the strong operating conditions (chemical composition - namely Cl-, Br-, ClO-, temperature, mechanical loading) [2, 9, 10, 11]. The experiments are carried out at the temperatures 22 – 80 °C in aggressive chloride environments. Evaluation of the corrosion resistance is based on the results of exposition immersion tests (visual and microscopic observation of failed surfaces, corrosion rates calculated from the mass losses of specimens) and on the results of the cyclic potentiodynamic tests.

EXPERIMENTAL MATERIAL

AISI 316Ti stainless steel with the chemical composition shown in Table 1 was used as an experimental material. It was bought in ITALINOX company, and its treatment (marked as 2B) was based on annealing and pickling after smoothing rolling [12].

Microstructure of the original material was observed on the optical metallographic microscope Neophot 32 in transversal and longitudinal cut (Figure 1).

Table 1. Chemical composition of the steel AISI 316Ti

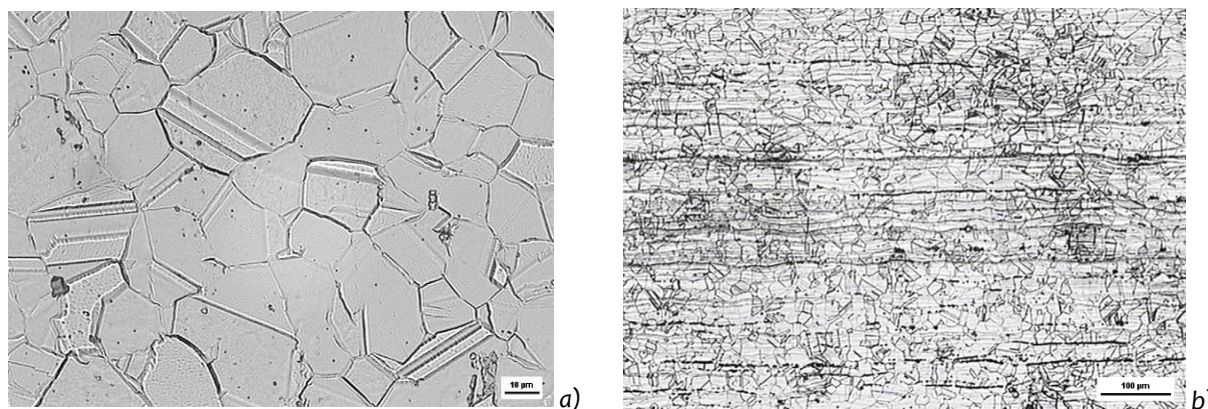| Content of element [wt.%]	Cr	Ni	Mo	Mn	N	Ti	C	Si	P	S	Fe
	16.5	10.6	2.12	1.69	0.012	0.41	0.04	0.43	0.026	0.002	balance

Figure 1 Microstructure of the steel AISI 316Ti, etch. 10ml HNO₃, 30ml HCl, 30ml glycerine, a) detail of austenitic grains in transversal cut, b) general view, longitudinal cut

Microstructure is created by polyedric austenitic grains with observable twins (fig. 1 a), which could be created by annealing or by rolling. Strong lines visible in longitudinal cut (fig. 1 b) arose by the rolling during the technologic process.

COURSE OF EXPERIMENTS

IMMERSION TESTS:

The specimen's shape was rectangular with one nominal dimension for simplification of the exposed area definition (30mm x 80mm x 1,5mm). The surface of the specimens was not treated (neither mechanically nor chemically) but the edges of ones were grinded by abrasive paper grain 600. The grease from the tested specimens was removed by diethyl ether, then they were weighted out (Mettler Toledo XS 205, accuracy ± 0.000 01g).

Immersion tests (ASTM G 48) were carried out in 3% and 5% $FeCl_3$ solutions (Cl⁻ concentration 0.5682 $mol.dm^{-3}$ and 0.9624 $mol.dm^{-3}$) at the temperatures 22 ± 0.5, 30, 40, 50, 60, 70 and 80°C [13]. The duration of the tests was 24 hours. The group of three parallel specimens was observed for each combination of conditions (temperature, Cl⁻ concentration). After 24 hour exposure the specimens were carefully brushed, washed by de-mineralized water, freely dried up and weighted out again.

ELECTROCHEMICAL TESTS:

The specimens of rectangular shape with dimensions 10mm x 10mm x 1,5mm degreased by diethyl ether were used for the electrochemical test. The cyclic potentiodynamic tests (ASTM G 61) were carried out in the same solutions at the same temperatures as immersion tests [13]. The steady time of the free potential was 5 minutes, operating speed of the sample was 1000 rpm, start potential -200 mV, reversal potential +900 mV, finish potential -200 mV and shift rate of the potential was 10 mV. s^{-1}.

RESULTS AND DISCUSSION OF EXPERIMENTS

24 hours immersion of specimens in both aggressive Cl⁻ solutions caused the pitting failures in the temperature range 22 – 80°C. The size, the shape and the density of pits were strongly affected by temperature and chloride concentration of exposition solutions. Edges of specimens were noticeably damaged at the temperatures 22 – 40°C. This fact points to the different corrosion behavior of edges (different capillarity, higher surface roughness) in comparison with specimen area.

In both $FeCl_3$ solutions the density of pits increases with the temperature (Figure 2, Table 2). The strongest change in the appearance of pitted surfaces is related to the temperature range 40 – 50°C.

Tab.2 Evaluation of density and size of pits by standard ČSN ISO 11463

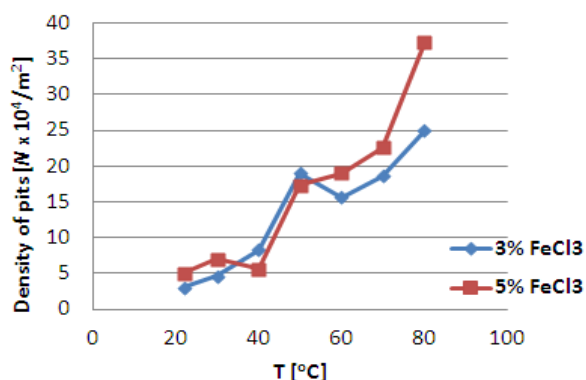| Temperature [°C]	3 % FeCl₃		5 % FeCl₃	
	Density of pits (A)	Size of pits (B)	Density of pits (A)	Size of pits (B)
22	A2 – A3	B1	A3	B1 – B2
30	A2 – A3	B1	A3 – A4	B1 – B2
40	A3 – A4	B1	A3 – A4	B2
50	A4 – A5	B1	A4 – A5	B1
60	A4 – A5	B1	A4 – A5	B1 – B2
70	A4 – A5	B1	A4 – A5	B1 – B2
80	A4 – A5	B1	A4 – A5	B1 – B2

Figure 2. Average density of pitting
in dependence on the temperature

The changes of pit profiles are the sharpest in 5% FeCl$_3$ solution (Figure 3). The pits become narrower and deeper with the rise of the temperature.

The top view indicates decreasing of the size of pits with temperature in both Cl$^-$ solutions. The largest pits arose at 30 °C (Figure 4).

Average corrosion rates (g.m^{-2}.h^{-1}) calculated from mass losses during the immersion tests in dependence on the temperature are shown in Figure 5. The course of corrosion rates can not be generally considered to be the essential factor of evaluation of pitting corrosion. However, it helps to make conception about probable changes in controlling processes of the pitting corrosion kinetics. In 3% FeCl$_3$ solution the highest average corrosion rate was reached at 30 °C (Figure 5a). This result was confirmed by additional immersion tests at 25 a 35 °C (Figure 5b).
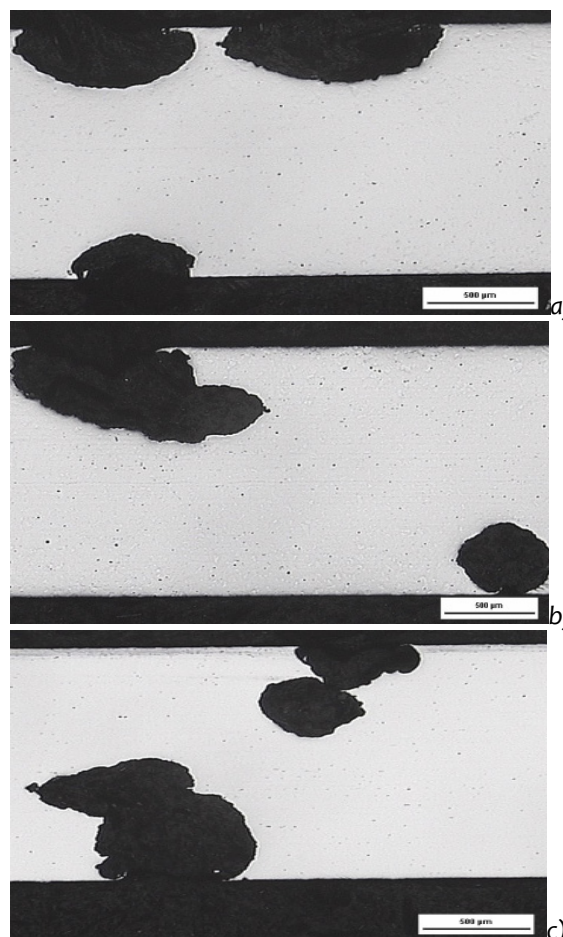

Figure 3. Changes of pit profiles in 5% FeCl$_3$ in dependence of temperature a) 30°C, b) 50°C , c) 80°C (optical metallographic microscope)
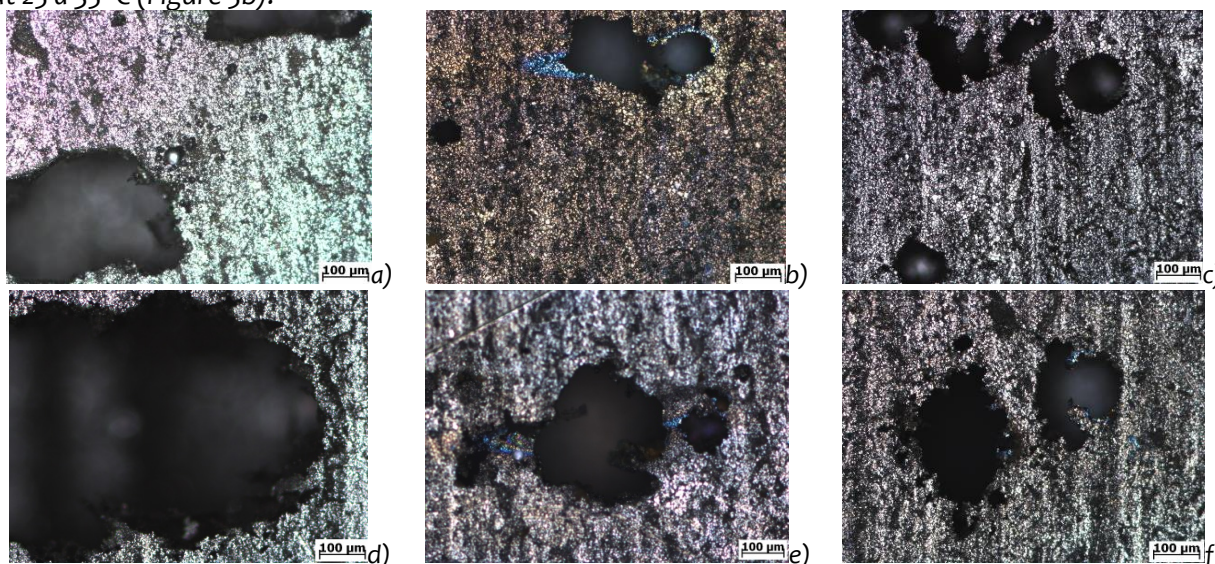

Fig.4 Size and shape of pits after 24-hours immersion test, observed microscopically: a) 30 °C, b) 50 °C, c) 80 °C in 3 % FeCl$_3$; d) 30 °C, e) 50 °C, f) 80 °C in 5 % FeCl$_3$

The highest corrosion rates were globally marked in 5% FeCl$_3$. The rapid rise of corrosion rates in temperature ranges 22 – 30 °C and 40 – 50 °C was also confirmed in additional immersion tests at 25, 35, 45 and 55 °C (Figure 5c). Clear jumps of corrosion rates may point to the change in controlling process of the pitting corrosion kinetics. In order to find an indicator of this change it is recommended [14, 15] to use Arrhenius equation in logarithmic form

$$log\, v_{corr} = A' - \frac{k}{T} \qquad (1)$$

where: v_{corr} – corrosion rate, A´- constant, T – absolute temperature, k – slope of a straight line. According to authors [14, 15] it is possible to determine the type of controlling process by the value of k. If k is about 0.9 it means diffusion controlling of corrosion process, k of combined controlled processes is usually about 3.2. The highest value of k (cca 6.9) is typical for chemically controlled processes. In regard to non-linear dependence of corrosion rates on temperature (Figure 5) in range 22 – 80°C, k values were determined only for linear parts of curves with strong increase of corrosion rates (Table 3).

Tab. 3. Values of slope k calculated from (1)

Temperature range [°C]	k	
	3% FeCl₃	5% FeCl₃
22 -25	2.26	0.89
25 - 30	2.45	1.32
40 - 45		0.80
45 - 50		2.39
60 - 70	0.94	
70 - 80		0.40

Values of slope k point to possible conversions between combined and diffusion controlling of pitting corrosion process in mentioned conditions. Especially strong conversion from diffusion to combined controlling is observed in temperature range 40 – 50 °C in 5 % $FeCl_3$ solution (Table 3).

The pitting potential E_p is the main electrochemical characteristic of the pitting corrosion resistance obtained from cyclic potentiodynamic curves (ASTM G 61). It can be located as the potential of the strong rising of current density on the curve of direct measurement. This potential is not equilibrium but rather it describes the state of the pitting corrosion. The shift of E_p to more positive values on the polarization curve means the rise of stability to pitting [3, 5, 11].

a)

b)

c)

Figure 5. Dependence of average corrosion rates on temperature: a) comparison for 3 and 5% $FeCl_3$ solutions; b), c) more detailed graphs for 3 and 5% $FeCl_3$ solutions

Because of lucidity, Figures 8 and 9 do not show the cyclic potentiodynamic curves for all temperatures but only for the lowest and the highest temperature. Other curves would be situated in the space between the lowest and the highest curve. Because of the shape of the curves, E_p could be located only for the specimens at 22°C (5 % $FeCl_3$) and at 22, 30, 40°C (3 % $FeCl_3$). E_p values decrease with temperature and with the concentration of chlorides (Figure 10).
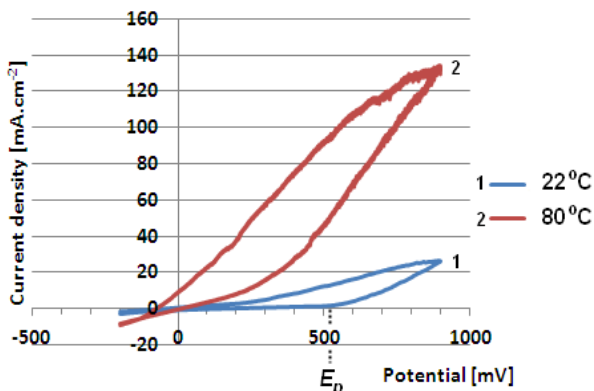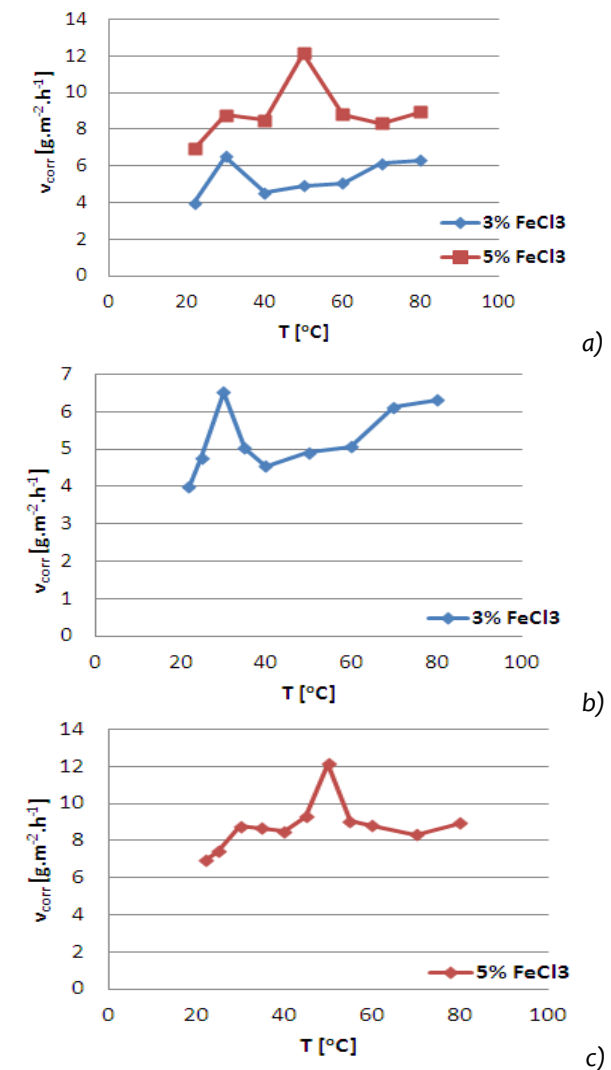
Figure 8. Cyclic potentiodynamic curves with marked value of E_p for curve 1; 3 % $FeCl_3$ solution
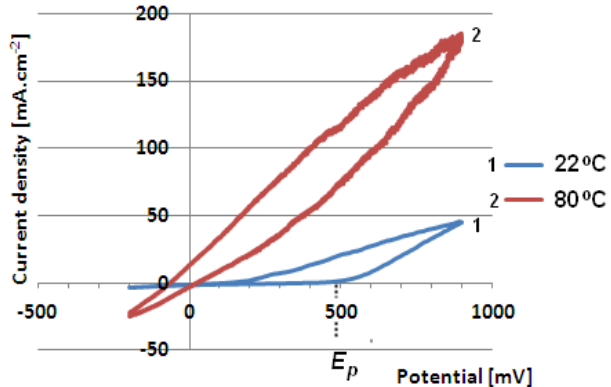
Figure 9. Cyclic potentiodynamic curves with marked value of E_p for curve 1; 5 % $FeCl_3$ solution

At higher temperatures a surface passive film was probably broken at the start potential. It became evident by increase of current density immediately after overreaching of its zero value. Therefore in these cases it was not possible to determine the pitting potential E_p and the pitting corrosion resistance was considered from the shape of cyclic potentiodynamic curves (Figure 8, 9; curves for 80°C). According to the sharpness of the curve of direct measurement after overreaching of the zero current density value the thermodynamic stability decreases with the rise of temperature in both FeCl$_3$ solutions.
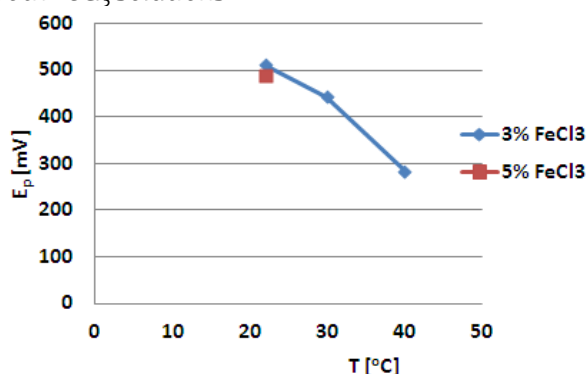

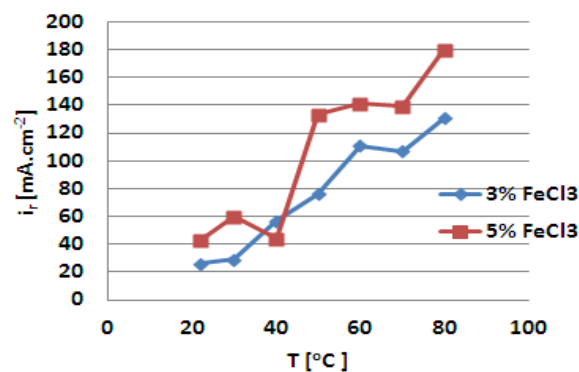Figure 10. Dependence of pitting potential E_p on temperature

Figure 11. Dependence of approximate current density at the potential of reverse i_r on the temperature

Figure 11 illustrates dependence of approximate current density at the potential of reverse (i_r) on the temperature. The influence of experimental conditions on reached i_r values is evident. However it is supposed that all data used for formation of curves have the same error and therefore it is possible to compare and to follow changes in the pitting corrosion kinetics.

The sharpest increase of i_r observed in temperature range 40 – 50 °C in 5 % FeCl$_3$ solution points to changes of corrosion kinetics. It corresponds to mentioned change of appearance of pitted surfaces, to the strong increase of corrosion rates calculated from mass loses and also to the possibility of conversion of the controlling process of corrosion kinetics.

CONCLUSIONS

Corrosion resistance of AISI 316Ti is strongly affected by temperature changes in the range 22 – 80°C. Intensity of corrosion attack increases with the rise of Cl⁻ concentration.

Gentle changes of temperature and Cl⁻ concentration cause strong differences in character of local failure. The appearance of pitted surfaces changes with the rise of the temperature (a density of pitting increases, a size of pits decreases). The strongest change in appearance is observed between 40 and 50 °C.

The changes of pit profiles are the sharpest in 5 % FeCl$_3$ solution. The pits become narrower and deeper with the rise of the temperature.

The course of average corrosion rates points to the sharp changes in kinetics of pitting corrosion process in dependence of temperature in both solutions. Conversion from diffusion to combined controlling is supposed in temperature range 40 – 50°C in 5 % FeCl$_3$ solution.

According to the shape of cyclic potentiodynamic curves the thermodynamic stability of tested material decreases with the temperature in both FeCl$_3$ solutions. Decrease of the thermodynamic stability in 3 % FeCl$_3$ solution in range 22 – 40 °C is also shown by decrease of the values of the pitting potential E_p.

The strong increase of current density at the potential of reverse (i_r) in range 40 – 50 °C (5 % FeCl$_3$) solution points to changes of corrosion kinetics and also corresponds to change of appearance of pitted surfaces, to the strong increase of corrosion rates and to the possibility of conversion of the controlling process of the corrosion kinetics.

The electrochemical characteristics obtained by cyclic potentiodynamic test are not sufficient for independent objective examination of susceptibility to pitting in dependence on temperature. It is appropriate to combine them with exposition tests with different corrosion mechanism.

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