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Influence of temperature on corrosion resistance of austenitic stainless steel in cl$^-$ containing solutions

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Abstract

Temperature is considered a complicated external factor of the susceptibility of stainless steels to the pitting. This paper deals with the corrosion behaviour 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 exposure immersion tests and cyclic potentiodynamic tests. According to the obtained results the resistance of AISI 316Ti to the pitting is markedly 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 significant differences in character of local damage. 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 50ºC.

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1. Introduction

The passive surface film makes the stainless steel resistant to the uniform corrosion in oxidation environments (Jambor et al., 2018; Lipinsky, 2019; Oravcová et al., 2018; Oršulová et al., 2018; Szklarska-Smialowska, 2005). However, a presence of halides can evoke local breakdown of the protective film and, consequently, dangerous and destructive pitting corrosion (Szklarska-Smialowska, 2005; Liptáková, 2009; Zatkalíková et al., 2019).

Temperature is one of the important external factors of the corrosion resistance of stainless steels (Park et al., 2002; Trépanier et al., 2004). Taking into account 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 (Szklarska–Smialowska, 2005). However, its validity was indicated only for very narrow temperature range. In many cases, the proportionality between the pitting rate and reciprocal absolute temperature is absent. Most authors consider the influence of temperature on pitting corrosion as the change of electrochemical characteristics (pitting potential E_p and repassivation potential E_r) with temperature (Laycock et al., 1998; Szklarska–Smialowska, 2005, Zatkalíková et al., 2019). The critical pitting temperature (CPT) is generally used as a criterion for susceptibility to the pitting. The authors (Laycock et al., 1998; Moayed et al., 2006) locate the CPT as the temperature of strong discontinuous decrease of $E_{p.}$

The presented paper focuses on the effect of the temperature on the corrosion resistance of AISI 316Ti stainless steel (Cr–Ni–Mo stainless austenitic steel stabilized by Ti) considered the alloy with the high corrosion resistance. In spite of this, such steel often suffers from the pitting corrosion in strong operating conditions (chemical composition - namely Cl$^-$, Br$^-$, ClO$^-$, temperature, mechanical loading), (Szklarska-Smialowska, 2005; Liptáková, 2009). The experiments are carried out at the temperatures 22-80°C in aggressive chloride environments (3 and 5% $FeCl_3$ solutions). The 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.

2. Experimental

AISI 316Ti stainless steel with the chemical composition shown in Table 1 was used as the experimental material.

Table 1. Chemical composition of the AISI 316Ti steel (wt. %)

Cr	Ni	Mo	Mn	N	Ti
16.5	10.6	2.12	1.69	0.012	0.41
C	**Si**	**P**	**S**	**Fe** balance	
0.04	0.43	0.026	0.002		

The specimen's shape for immersion tests was rectangular (30mm x 80mm x 1,5mm). The surface of the specimens was not treated (either mechanically or chemically) but the edges were ground by the abrasive paper grain 600. The grease was removed by diethyl ether, then the specimens were weighted out (accuracy ± 0.000 01g). Immersion tests (ASTM G48) were carried out in 3% and 5% $FeCl_3$ solutions at the temperatures 22 ± 0.5, 30, 40, 50, 60, 70 and 80ºC (Baboian, 1995). 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 brushed, washed by demineralized water, freely dried up and weighted out again.

The specimens for electrochemical tests were of rectangular shape with dimensions 10mm x 10mm x 1,5mm. The cyclic potentiodynamic tests (ASTM G 61) were carried out in the same solutions at the same temperatures as immersion tests (Baboian, 1995). 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 10mV/s.

3. Results and discussion

24 hours immersion of specimens in both aggressive Cl^- solutions at the temperatures 22–80°C caused the pitting corrosion damage. The size, the shape and the density of pits were strongly affected by the temperature and the chloride concentration. 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 the specimen area.

In both $FeCl_3$ solutions the density of pits increases with the temperature (Figure 1,). The strongest change in the appearance of pitted surfaces is related to the temperature range 40 - 50°C.

The changes of pit profiles are the most significant in 5% $FeCl_3$ solution (Figure 2). The pits become narrower and deeper with the temperature increase.

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 4. The course of corrosion rates cannot be, generally, considered the essential factor of an evaluation of the pitting corrosion; however, it helps to make a conception about probable changes in controlling processes of the pitting corrosion kinetics.

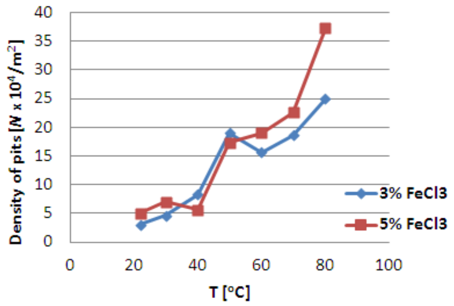

Fig. 1. Average density of pitting in dependence on the temperature

The top view indicates decreasing of the size of pits with temperature in both Cl^- solutions. The largest pits arose at 30 ºC (Figure 3).

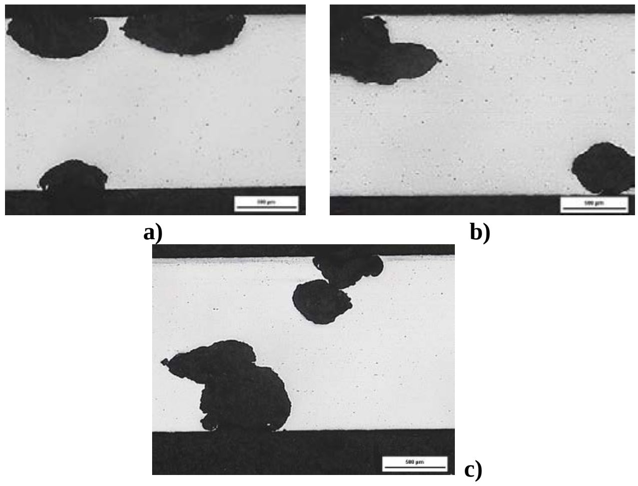

Fig. 2. Pit profiles in 5% $FeCl_3$ in dependence on temperature: a) 30°C, b) 50°C , c) 80°C

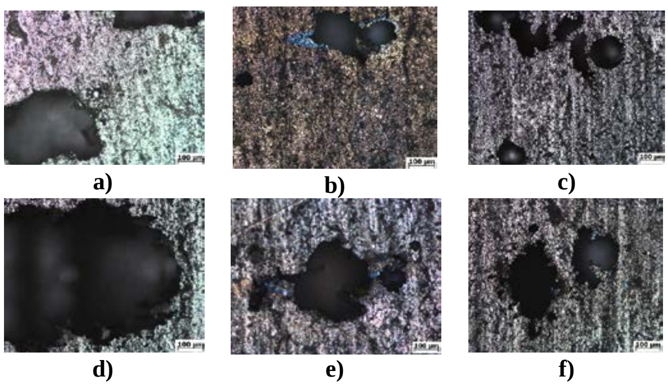

Fig. 3. Size and shape of pits after 24-hours immersion test: a) 30 ºC, b) 50 ºC, c) 80 ºC in 3 % $FeCl_3$; d) 30 ºC, e) 50 ºC, f) 80 ºC in 5 % $FeCl_3$

In 3% $FeCl_3$ solution the highest average corrosion rate was reached at 30 °C (Figure 4). This result was confirmed by additional immersion tests at 25 a 35 ºC (Figure 5).

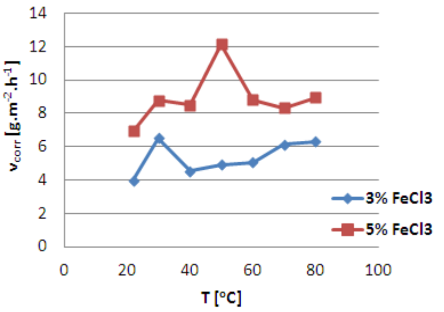

Fig. 4. Dependence of average corrosion rates on temperature: comparison for 3 and 5% $FeCl_3$ solutions

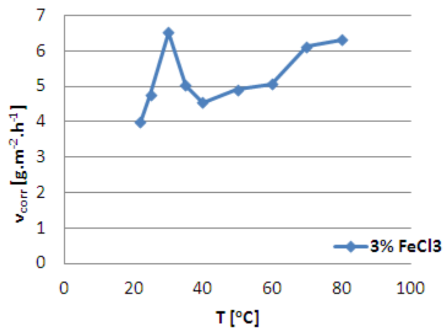

Fig. 5. Dependence of average corrosion rates on temperature: more detailed graph for 3% $FeCl_3$ solution

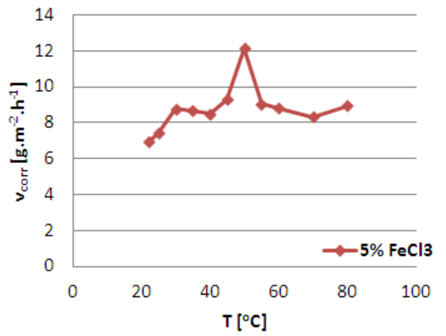

Fig. 6. Dependence of average corrosion rates on temperature: more detailed graph for 5% $FeCl_3$ solution

The highest corrosion rates were globally marked in 5% $FeCl_3$ (Figure 4). The rapid rise of corrosion rates in temperature ranges 22 – 30 ºC and 40 – 50 ºC was also confirmed in additional immersion tests at 25, 35, 45 and 55 ºC (Figure 6). A definite increase of corrosion rates may point to the change in controlling process of the pitting corrosion kinetics (Liptáková, 2009).

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 increase of current density on the curve of the 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 (Szklarska–Smialowska, 2005; Liptáková, 2009). For clarity, Figures 7 and 8 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. Due to 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.

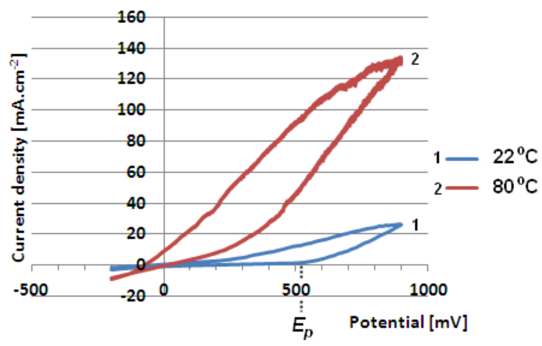

Fig. 7. Cyclic potentiodynamic curves in 3 % $FeCl_3$ solution with marked E_p value for curve 1

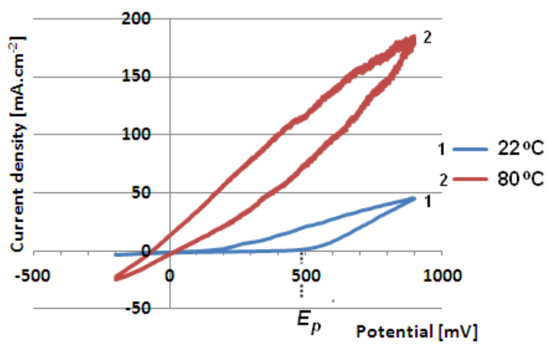

Fig. 8. Cyclic potentiodynamic curves in 5 % $FeCl_3$ solution with marked E_p value for curve 1

At higher temperatures, the surface passive film was probably broken at the start potential. It became evident by the current density increase right after the 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 7, 8; curves for 80°C). According to the curve of direct measurement slope, after overreaching of the zero current density value the thermodynamic stability decreases with the temperature increase in both $FeCl_3$ solutions.

Figure 9 shows dependence of approximate current density at the potential of reverse (i_r) on the temperature. The reached i_r values could be affected by experimental conditions. However, it can be assumed that all data used for the construction 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 – 50ºC 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.

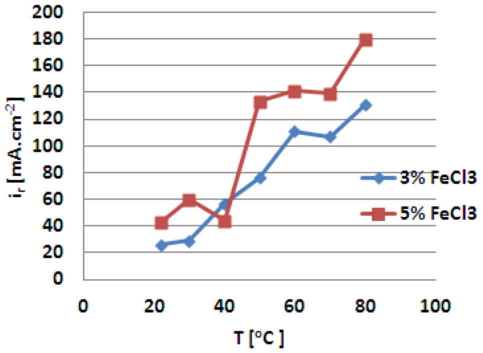

Fig. 9. Approximate current densities at the reverse potential depending on the temperature

4. Summary and conclusion

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

The appearance of pitted surfaces changes with the temperature rise (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 increase of average corrosion rates points to the sharp changes in pitting corrosion kinetics depending on temperature in both solutions.

According to the shape of cyclic potentiodynamic curves the thermodynamic stability of tested material decreases with the temperature in both $FeCl_3$ solutions..

The strong increase of the current density at the potential of reverse (i_r) in range 40–50 °C in 5% $FeCl_3$ solution points to changes of the corrosion kinetics and also corresponds to the 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.

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Reference

Baboian, R., 1995. *Corrosion Test and Standards: Aplication and Interpretation, ASTM Manual Series*, PA 19103, Philadelphia, USA.

Jambor, M., Nový, F., Bokůvka, O., Trško, L., Oravcová, M., 2018. *Influence of structure sensitising of the AISI 316Ti austenitic stainless steel on the ultra-high cycle fatigue properties*, MATEC Web of Conferences, 157, 05011.

Laycock, N.J., Moayed, M.H., Newman, R.C., 1998. *Metastable Pitting and the Critical Pitting Temperature*, J. Electrochem. Soc. 145, 2622-2628.

Lipinsky, T., 2019. *Corrosion of the 1.4362 duplex stainless steel in a nitric acid environment at 333 K*, Acta Physica Polonica A, 135, 2, 203-206.

Liptáková, T., 2009. *Bodová korózia nehrdzavejúcich ocelí* (*Pitting corrosion of stainless steels*), EDIS – Žilinská univerzita, Žilina.

Moayed, M.H., Newman, R.C., 2006. *Evolution of Current Transients and Morphology of Metastable and Stable Pitting on Stainless Steel near the Critical Pitting Temperature*, Corros. Sci., 48, 4, 1004-1018.

Oravcova, M., Palcek, P., Chalupova, M., Uhricik, M., 2018. *Temperature dependent measurement of internal damping of austenitic stainless steels*, MATEC Web of Conferences, 157, 07008.

Oršulová, T., Palček, P., Roszak, M., Uhríčik, M., Kúdelčík, J., 2018. *Change of magnetic properties in austenitic stainless steels due to plastic deformation*, Procedia Structural integrity, 13, 1689-1694.

Park, J.O., Matsch, S., Böhmi, H., 2002. *Effects of temperature and chloride concentration on pit initiation and early pit growth of stainless steel*, J. Electrochem. Soc., 149, 2, B34-B39.

Szklarska-Smialowska, Z., 2005. *Pitting and crevice corrosion*, Nace, Houston.

Trépanier, Ch., Pelton, A.R., 2004. *Effect of temperature and pH on the corrosion resistance of passivated nitinol and stainless steel*. Proceedings of the International Conference on Shape memory and superelastic technologies October 3-7, Baden-Baden Germany.

Zatkalíková, V., Markovičová, L. 2019. *Corrosion resistance of electropolished AISI 304 stainless steel in dependence of temperature*, IOP Conference Series-Materials Science and Engineering, 465, UNSP 012011.

温度对含Cl溶液中奥氏体不锈钢耐蚀性的影响

關鍵詞

点腐蚀，温度，循环电势测试，浸没测试，点电位

摘要

温度被认为是不锈钢对点蚀敏感性的复杂外部因素。本文讨论了AISI 316Ti不锈钢在腐蚀性氯化物环境（3和5%FeCl3溶液）中在22-80° C的温度范围内的腐蚀行为。根据暴露浸泡试验和循环电位-动力试验的结果评估被测钢的耐腐蚀性。根据获得的结果，AISI 316Ti的抗点蚀性能受到22 - 80° C范围内温度变化的显着影响。随着Cl-浓度的增加，腐蚀侵蚀的强度也增加。温度和Cl-浓度的细微变化会导致局部损坏的性质发生明显差异。点蚀表面的出现随温度的升高而变化（点蚀密度增加，点蚀尺寸减小）。在40至50° C之间观察到外观的最大变化。