

LOCAL CORROSION OF AISI 304 STAINLESS STEEL IN ACIDIC CHLORIDE SOLUTION

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Abstract: AISI 304 austenitic stainless steel is recommended and used for various applications in industry, architecture and medicine. Presence of halides in environment evokes a possibility of the local corrosion which limits seriously exploitation of this material in aggressive conditions. The presented paper is focused on the pitting corrosion resistance (“as received” steel surface) in 1M chloride solution (pH=1.2) at a common (20 °C) and an elevated (50 °C) ambient temperatures. 24-hours exposure immersion test (ASTM G48) and cyclic potentiodynamic test (ASTM G61) are used as the independent test methods. The exposure immersion test is carried out with cross-rolled and longitudinally rolled specimens and the effect of direction of rolling on the resistance to pitting is studied.

Keywords: austenitic stainless steel, pitting corrosion, exposure test, cyclic potentiodynamic test, direction of rolling

1. INTRODUCTION

AISI 304 is the most common Cr-Ni austenitic stainless steel used in applications that require high corrosion resistance, good formability and weldability. Ordinary uses for this stainless steel type are found in petrochemical, chemical and nuclear industry, food industry, architecture and medicine. Due to the surface passive film, stainless steels are resistant to the uniform corrosion in oxidation environments (Szkłarska-Smialowska, 2005; Liptáková, 2009; Uhrčík et al., 2016; Zatkalíková et al., 2014). However, a presence of halides can evoke local breakdown of the protective film and consequently an initiation of the destructive and dangerous local corrosion, mainly pitting (Szkłarska-Smialowska, 2005; Liptáková, 2009; Zatkalíková et al., 2014).

The resistance of stainless steels to pitting is influenced by various factors. In addition to internal factors (chemical composition, surface treatment which affects the quality of passive film) important role is played by the external factors (temperature, pH, concentration of aggressive ions), (Szkłarska-Smialowska, 2005; Liptáková, 2009; Park et al., 2002; Adeli et al., 2010; Trépanier and Pelton, 2004). The ambient temperature strongly affects both thermodynamics and kinetics of the pitting corrosion

(Szkłarska-Smialowska, 2005; Liptáková, 2009; Trépanier and Pelton, 2004). 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 (Szkłarska-Smialowska, 2005). The authors (Szkłarska-Smialowska, 2005; Liptáková, 2009; Park et al., 2002; Adeli et al., 2010; Trépanier and Pelton, 2004) consider influence of the temperature on pitting corrosion by the change of electrochemical characteristics – decrease of the pitting potential E_p and the repassivation potential E_r with the temperature.

According to various studies, e.g. (Kurc et al., 2010; Oršulová et al., 2018; Ramirez et al., 2013), the corrosion resistance of stainless steels is also negatively influenced by the previous plastic deformation.

The presented paper deals with the pitting corrosion resistance of AISI 304 austenitic stainless steel with unmodified surface (“as received” surface) in low pH (1.2) 1M chloride solution at the temperatures of 20 and 50 °C. The evaluation of the corrosion resistance is based on the results of the exposure immersion test and the cyclic potentiodynamic tests. Exposure immersion test was carried out with cross-rolled and longitudinally rolled specimens and the influence of the rolling direction on the resistance to pitting was evaluated on the bases of visual and microscopic observation of failed surfaces and the corrosion rates calculated from the mass losses.

2. EXPERIMENTAL MATERIAL

The experimental material AISI 304 stainless steel (Table 1) was purchased in sheet (1000 x 2000 mm) of 1.5 mm thickness. The tested steel was processed by continuous casting in electric arc furnace, annealed at 1040 – 1100 °C. The IIB surface finish (smooth and matte metallic glossy surface) was based on pickling after slightly smoothing rolling (www.italinox.sk).

Table 1

Chemical composition of AISI 304 stainless steel

Content of element [wt.%]										
Cr	Ni	Mo	Mn	N	C	Si	P	S	Ti	Fe
18	8.01	-	1.40	0.075	0.027	0.38	0.031	0.0037	-	balance

Microstructure of experimental material (Fig. 1) is polyhedral created by austenitic grains with numerous twins, which could be created by annealing or by rolling. Parallel lines arose by the rolling during the technologic process.

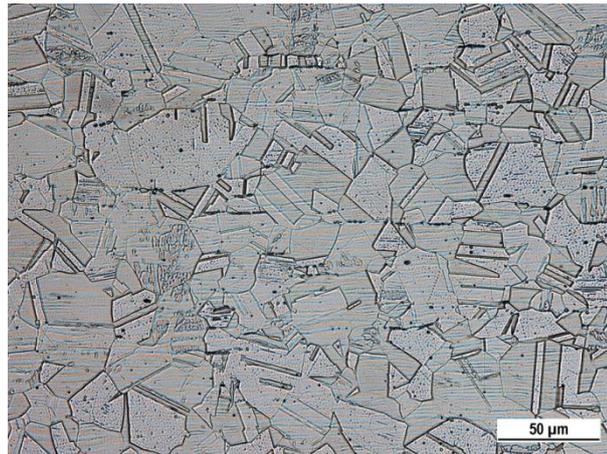


Fig. 1. Microstructure of AISI 304: longitudinal section (HNO₃+HCl+glycerine etch.)

3. EXPERIMENTAL PROCEDURE

1M chloride solution was chosen as the basic corrosion environment for both immersion and cyclic potentiodynamic polarization tests. For the immersion test, the 1M chloride solution was represented by 5 % FeCl₃ (pH=1.2). This aggressive solution is recommended for testing of the pitting corrosion resistance of stainless steels according to ASTM G48 standard method (Liptáková, 2009; Zatkalíková et al., 2014). For the cyclic potentiodynamic test (ASTM G61), the 1M chloride solution was represented by 0.9 M NaCl + 0.1 M HCl (pH=1.2) because of the high aggressiveness of FeCl₃ and the unacceptability for the use in the glass corrosion cell.

Exposure Immersion test (ASTM G48)

The specimen's shape for the immersion test was rectangular with one nominal dimension for the simplification of the exposed area definition (30 mm x 80 mm x 1.5 mm). To consider the effect of rolling direction on the corrosion resistance, two types of specimens have been prepared – the first type with longitudinal direction of the rolling (LR), the second one with the cross direction of the rolling (CR), Fig. 2.

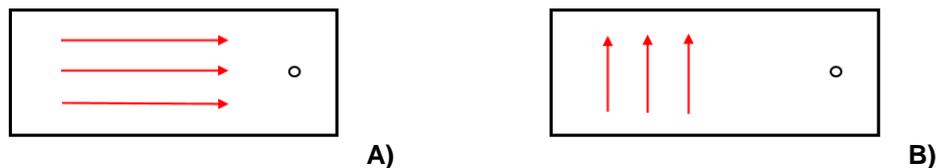


Fig. 2. Two types of specimens for immersion tests: A) with the longitudinal direction of the rolling (LR), B) with the cross direction of the rolling (CR)

The specimen surface was not treated (mechanically or chemically) only the edges were ground by abrasive paper grain 600. The grease was removed by ethanol. The specimens have been weighted out with accuracy $\pm 0.000\ 01$ g (Mettler Toledo XS 205). 24-hours immersion test was carried out at the temperatures 20 and 50 °C. After exposure the specimens were carefully brushed, washed by de-mineralized water and by ethanol, freely dried up and weighted out again.

Specimen surfaces after immersion test were observed by the optical microscope Zeiss Axio Imager. Average corrosion rates ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) were calculated from the mass losses (g) during the immersion test (three parallel specimens were tested for LR and CR types for each temperature, then the average corrosion rates were calculated).

Cyclic potentiodynamic test (ASTM G61)

The test has been carried out in the three electrode cell of the corrosion measuring system VoltaLab 10 with VSP unit. Potentiodynamic polarization curves have been obtained by the EC-LAB SOFT software. The potential between the sample and the electrolyte has been settled for 10 minutes before the polarization. Scan range was -0.3 V – 0.9 V vs the open circuit potential and the scan rate was 1 mV/s. The surface of working electrode AISI 304 of 1 cm² area has not been treated, only rinsed with ethanol before measurement. The saturated calomel electrode (SCE) was applied as the reference electrode and platinum foil as a counter electrode. All experiments have been carried out at the ambient temperatures of 20 and 50 °C. At least three experiment repeats have been carried out for all specimens. This experiment did not enable to take in account the direction of the rolling.

4. EXPERIMENT RESULTS AND DISCUSSION

The tested specimens were attacked by a local corrosion during the immersion tests. To the naked eye the local damage was only visible at the edges of the specimens. It is probably connected with the higher roughness of the edges surface compared to the surface of the specimen area (Table 2), (Hong and Nagumo, 1997).

Table 2

The average roughness parameters measured on the surfaces of the specimen edge and of the specimen area (*Ra* - roughness average, *Rsk* – skewness profile, *Rz* – mean roughness depth)

	<i>Ra</i> [μm]	<i>Rsk</i> [μm]	<i>Rz</i> [μm]
Sample area	0.1	-1.58	1.0
Sample edge	0.7	0.11	3.7

As can be seen (Fig. 3 and Fig. 4), the intensity of the attack strongly increases with the temperature but depends on the direction of the rolling as well. The longitudinally rolled specimens are the most intensively damaged especially on their upper edges. This feature may coincide with the inclusions that are usually located in the lines after rolling. These places with the lower quality of the passive film are probably susceptible to the penetration of the chloride anions and the pitting is initiated (Szkłarska–Smiałowska, 2005; Liptáková, 2009).

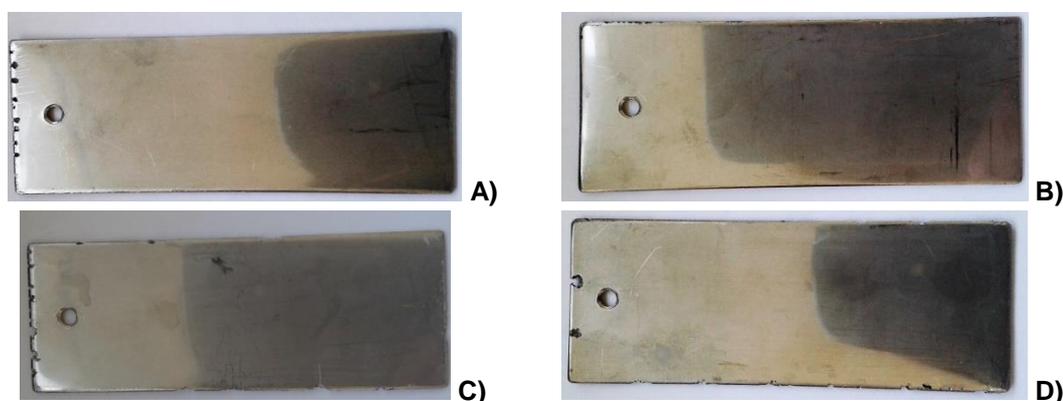


Fig. 3. Specimens after immersion test: A) 20 °C LR, B) 20 °C CR, C) 50 °C LR, D) 50 °C CR

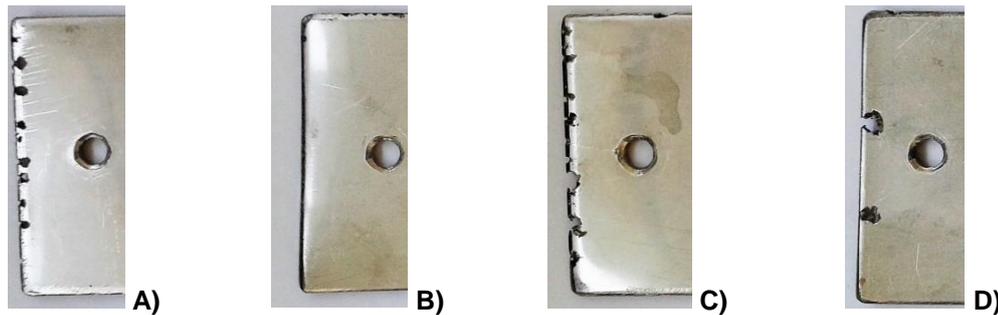


Fig. 4. Details of the upper part of the specimens after immersion test: A) 20 °C LR, B) 20 °C CR, C) 50 °C LR, D) 50 °C CR

The pitting corrosion on the specimen areas became visible by the microscopic observation (Fig. 5). There are no marked differences between character of the pitting dependant on the temperature and the direction of the rolling.

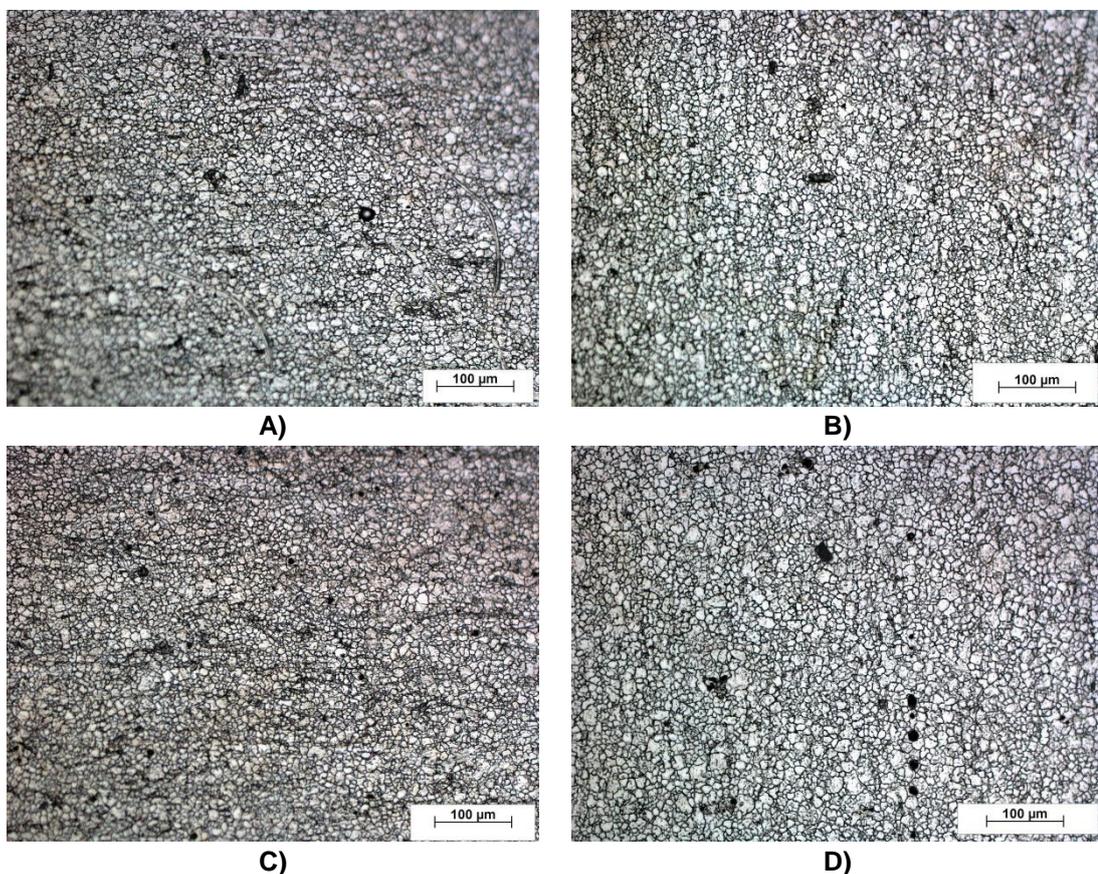


Fig. 5. The pitting corrosion on the specimen areas after immersion test: A) 20 °C LR, B) 20 °C CR, C) 50 °C LR, D) 50 °C CR

The average corrosion rates ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) calculated from the corrosion losses during the immersion test in dependence on the temperature and on the direction of the rolling are shown in Fig. 6. The presented dependence confirms the significant decrease of the corrosion resistance at the elevated temperature and the negative influence of the longitudinal rolling direction on the corrosion resistance as well.

The pitting potential (E_p) is the main electrochemical characteristic determined from a cyclic potentiodynamic polarization curve, that enables an assessment of the resistance to pitting. After the potential reaches this critical value, current density suddenly increases, denoting the breakdown of the passive film and the beginning of stable pit growth. The shift of E_p to more noble value means the higher thermodynamic stability and the rise of resistance to the pitting (Szkłarska-Smialowska, 2005; Liptáková, 2009; Park et al., 2002).

The cyclic potentiodynamic curves of the tested steel in 1M chloride solution at 20 and 50 °C are presented in Fig. 7.

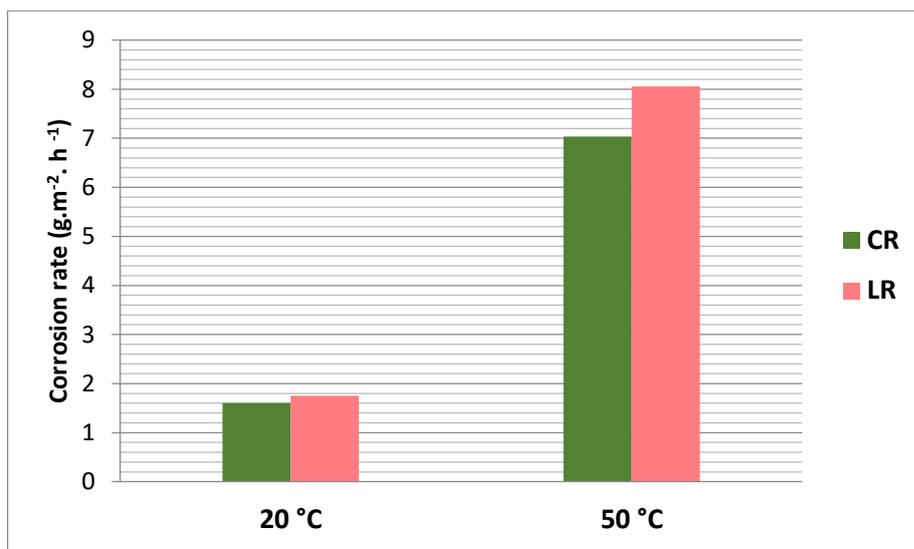


Fig. 6. The average corrosion rates calculated from the corrosion losses

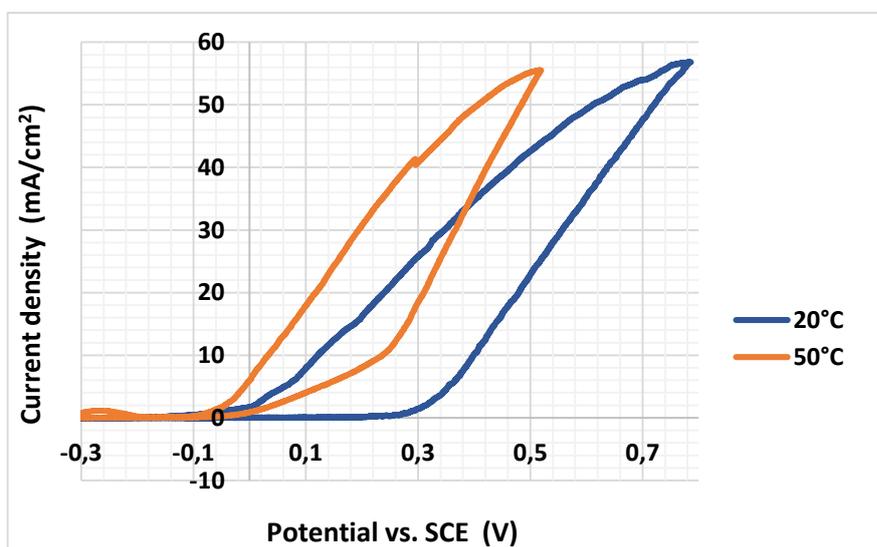


Fig. 7. The cyclic potentiodynamic curves of the tested steel

As can be seen, the curve measured at 50 °C reflects no passivity state, current density increases immediately after overreaching of its zero value. The surface passive film was probably broken just after immersion into experimental solution and therefore the pitting potential could not be determined. The localization of the pitting potential of the other curve (at 20 °C) is obvious from the detail of the curve shown in Fig. 8. the E_p value is around 0.03 V.

The results of the cyclic potentiodynamic test confirmed the significant negative effect of the temperature on the resistance of the tested material to the pitting corrosion.

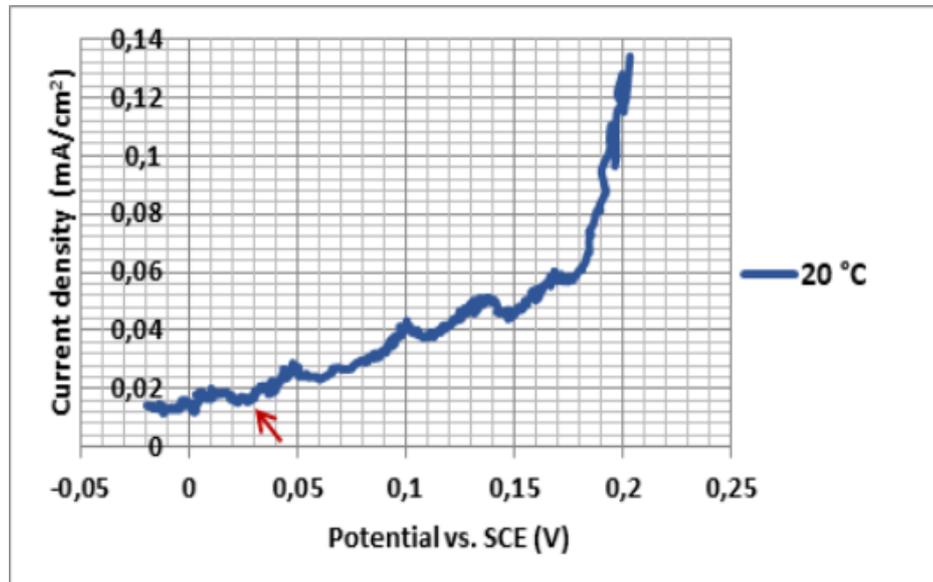


Fig. 8. Detail of the potentiodynamic curve and the localization of the pitting potential

5. CONCLUSION

Based on the results of performed experiments it can be concluded:

- Both independent exposure and cyclic potentiodynamic polarization tests confirmed that the elevated temperature 50 °C significantly decreases (according to the corrosion rates more than four times) the pitting corrosion resistance of AISI 304 stainless steel with the “as received” surface.
- The longitudinally rolled specimens exhibited markedly lower corrosion resistance than the cross-rolled specimens. This phenomenon was stronger at the higher temperature.
- The specimen edges with the higher surface roughness are preferentially attacked by the local corrosion – during the exposure test the upper specimen edges were perforated.

In accordance with the results obtained the use of the tested steel with the “as received” surface in aggressive chloride environments at the increased or varying temperatures is not recommended because of the possibility of the serious local damage including the perforation of the material.

ACKNOWLEDGEMENTS

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