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Corrosion behavior of austenitic stainless steels in road salt solutions

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Abstract

Stainless steels are widely used for various automotive components. Some of them (e.g., parts of the exhaust system) are exposed to the external environment. In winter conditions, they are affected by chloride containing road salt solutions, which can lead to the local corrosion of these stainless steel parts. The presented paper is focused on the pitting corrosion resistance of two austenitic stainless steels (AISI 304 and AISI 316L) in 5 wt% and 10 wt% road salt solutions. The evaluation and comparison are based on the potentiodynamic polarization test method carried out at the temperature of 20 ± 2°C. The pitting potentials were determined from the polarization curves. Local corrosion damage of exposed surfaces caused by potentiodynamic polarization in the used solutions was observed by optical microscope. Experimental results confirmed a worse pitting corrosion resistance case, especially for AISI 304 stainless steel in 10 wt% road salt solution.

Introduction

The automotive and transportation sectors are increasingly using stainless steels to reduce weight, improve aesthetics, increase safety, and minimize costs. Their suitable mechanical properties – i.e., the excellent formability, strength, high corrosion resistance, and fatigue resistance – make them potentially very suitable as construction materials (Jessen, 2011; Oravcová et al., 2018; Oršulová et al., 2018; Lipinsky, 2019; Wiaderek, 2021). These stainless steels features are ideal for bumpers, car frames (crash resistance), exhaust system components, fuel tanks, or chassis. Many "small" components such as tubes, springs, clamps, and flanges that support the vehicle, connect the parts, and form the structure of the vehicle are also made of stainless steel (Santacreu et al., 2006).

One of the main reasons for the use of stainless steels as passivating alloys is their high corrosion resistance in common oxidation environments. In fact, however, they are subjected to some local corrosion forms in halide (mainly chloride) solutions (Szklarska-Smialowska, 2005; Liptáková, 2009; Rustandi et al., 2016). Therefore, care must be taken to select the appropriate stainless-steel type and/or surface treatment, especially for the components exposed to the external environment affected by a chemical road treatment in winter conditions (Kadry, 2008). Road salt solutions created by the snow melting, which contain the chloride anions, are the major cause of motor vehicles corrosion (Kadry, 2008, Kelly et al., 2010).

For winter road maintenance in Europe, NaCl-based de-frosting spreading material is the most widely recommended. Its advantages are high availability, low cost, ease of use, and storage (Kelly et al., 2010). However, it is not effective in extremely cold conditions (since it can only be used for the temperature range –1 to 15°C) and poses significant environmental risks associated with soil, surface, and groundwater contaminations because it can contain harmful elements such as lead, cadmium, chromium, aluminum, and manganese (Helmenstine, 2020). Concentration of the aggressive anions is one of the most important external factors affecting the resistance of stainless steels to the pitting corrosion (Yi et al., 2013; Rustandi et al., 2016; Xie et al., 2017). According to the authors (Szklarska-Smialowska, 2005; Ibrahim, Abd El Rehim & Hamza, 2009; Zatkalíková & Markovičová, 2019), a raise of the aggressive anions concentration brings a decrease of the pitting potential and, therefore, a deterioration of the resistance to the pitting.

The objective of this paper is to assess and compare the resistance of two austenitic stainless steels (AISI 304 and AISI 316L) to the pitting corrosion in 5 wt% and 10 wt% road salt solutions. The evaluation is based on the linear potentiodynamic polarization test method performed at the temperature of 20 ± 2°C. Local corrosion damage of the exposed surfaces caused by potentiodynamic polarization in the used solutions was observed by optical microscope.

Experimental

AISI 304 and AISI 316L austenitic stainless steels, with the chemical compositions given in Table 1, were used for the experiments. They were purchased in sheets (1000×2000 mm) of 1.5 mm thickness. Their production processes were based on continuous casting in electric arc furnace. Then, they were annealed (AISI 304 at 1040–1100°C and AISI 316L at 1050°C). The IIB surface finish (smooth and matte metallic glossy surface) was realized by pickling after slightly smoothing rolling (www.italinox.sk).

Microstructures of the tested steels (Figure 1) are polyhedral in shape and composed of austenitic grains with numerous twins created by annealing or by rolling.

The rectangular specimens 15×40 mm were used for the potentiodynamic polarization. The surface of the specimens was not mechanically, or chemically, treated only degreased with ethanol. The potentiodynamic polarization was carried out in 5 wt% and 10 wt% road salt solutions at the temperature of 20 ± 2°C. The used road salt contained 98 wt% NaCl (produced in Poland, Kopalnia Soli "KŁODAWA" S.A.). The test was performed in the conventional three-electrode cell system with a calomel reference

Table 1. Chemical composition of the AISI 304 and AISI 316L stainless steels (wt%)

Steel	Cr	Ni	Mo	Mn	N	C	Si	P	S	Fe
AISI 304	18	8.01	–	1.4	0.075	0.027	0.38	0.031	0.0037	Balance
AISI 316L	16.79	10.14	2.03	0.82	0.05	0.02	0.31	0.03	0.001	

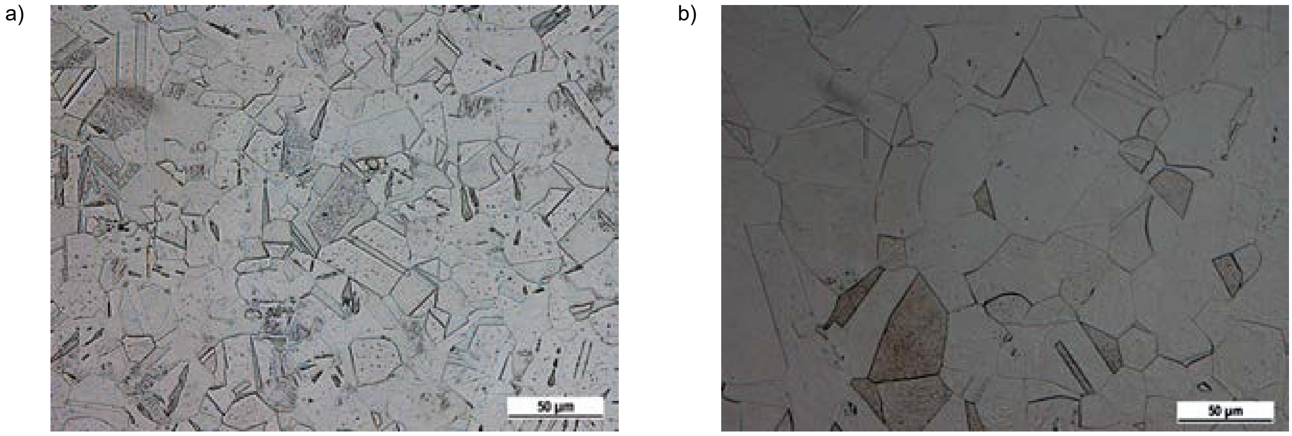

Figure 1. Microstructures in longitudinal sections: a) AISI 304 (glycerine + HNO_3 + HCl etch) and b) AISI 316L (Kallings 2 etch)

electrode (SCE) and a platinum auxiliary electrode (Pt), using a BioLogic corrosion measuring system with a PGZ 100 measuring unit. The time for potential stabilization between the specimen and the electrolyte was set at 10 minutes, the exposed area of a specimen was 1 cm^2 (Kucharikova et al., 2018, Štrbák et al., 2022). The potentiodynamic polarization curves were recorded at the sweep rate of 1 mV/s, a potential scan range was applied between –0.3 and 0.8 V vs. the open circuit potential (OCP). For both AISI 304 and AISI 316L specimens in both solutions, at least three experiment repeats were carried out and the representative curves were selected.

Results and discussion

The potentiodynamic polarization curves for AISI 304 and AISI 316L in 5 wt% and 10 wt% road salt solutions are shown in Figures 2 and 3, respectively. All the curves are typical for passivating metals, anodic passive branches point to the anodic dissolution rate control by the passive current density.

Values of the corrosion potentials, E_{corr}, and the pitting potentials, E_p, are determined directly from the curves (Tafel extrapolation was not applicable); they are listed in Table 2. These electrochemical parameters were used for the assessment and comparison of the thermodynamic stability, and the resistance to the pitting of both steels in both solutions. E_p is the potential at which aggressive anions penetrating through the disturbed sites of the passive layer reach the fresh metal and the phase of stable pit-growth begins. E_p is determined as the potential of a sudden permanent increase in current density on the polarization curve. The higher E_p value means a larger resistance to the pitting solutions (Szklarska-Smialowska, 2005; Liptáková, 2009).

As can be seen from the polarization curves (Figures 2 and 3) and from the E_p values (Table 2), the concentration of the aggressive chloride anions affected the resistance of both stainless steels to the pitting. The negative Cl$^-$ concentration effect was significantly stronger for AISI 304 stainless steel (E_p decreased from 0.189 V vs. SCE to 0.080 V vs. SCE). The marked dependence of the Cl$^-$ concentration on resistance of austenitic stainless steels to the pitting (expressed by the E_p decrease) was also observed by the authors (Ibrahim, Abd El Rehim & Hamza, 2009; Zatkalíková & Markovičová, 2019). The authors (Ibrahim, Abd El Rehim & Hamza, 2009) also recorded a more pronounced E_p decrease for AISI 304 than for AISI 316 stainless steel. The deterioration of the corrosion resistance at high Cl$^-$ concentrations could be related to the intensive penetration of chloride anions through the weakened localities of the passive film, and to the consequential pitting corrosion initiation (Park, Matsch & Böhmi, 2002).

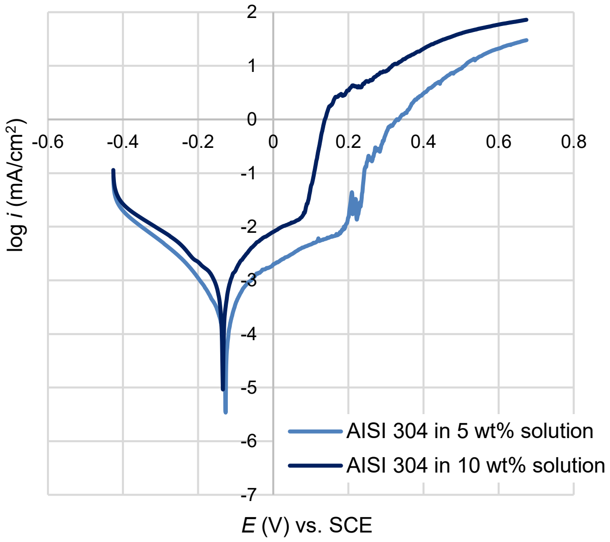

Figure 2. Potentiodymamic polarization curves for AISI 304 stainless steel

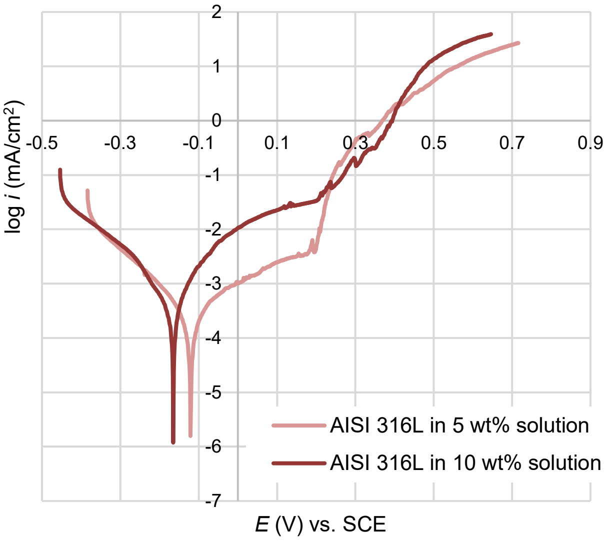

Figure 3. Potentiodymamic polarization curves for AISI 316L stainless steel

Table 2. Values of potentiodynamic polarization parameters of the tested stainless steels

Stainless steel	Solution	Corrosion potential, E_{corr} (V vs. SCE)	Pitting potential, E_p (V vs. SCE)
AISI 304	5 wt%	–0.127	0.189
	10 wt%	–0.134	0.080
AISI 316L	5 wt%	–0.121	0.210
	10 wt%	–0.165	0.202

An increase of chloride concentration caused not only a decrease in the E_p values, but it also led to a less stable passive state with higher passive current density. Figures 4 and 5 present details of the polarization curves in the narrow potential ranges close to the pitting potentials. It is clearly visible that, for both steels, the passive current density is significantly higher in 10 wt% road salt solution than in the 5 wt% one.

According to the obtained experiment results, AISI 316L stainless steel showed higher resistance to the pitting compared to the AISI 304 stainless steel. This difference, probably related to the molybdenum content, is reflected in more than the twice higher E_p value of the AISI 316L steel in 10 wt% solution (0.202 V vs. SCE) compared to the AISI 304 steel (0.080 V vs. SCE). The effect of molybdenum on the E_p values increase of austenitic stainless steels, was also documented by the authors (Szewczyk-Nykiel, 2015; Ha et al., 2018). According to the authors (Upadhyay et al., 2020), the molybdenum concentration raise decreases the pit initiation rate and the pit growth in austenitic stainless steels.

Differences between both tested materials in their resistance to the pitting in both solutions are also notable in Figure 6. In spite of the pitting corrosion

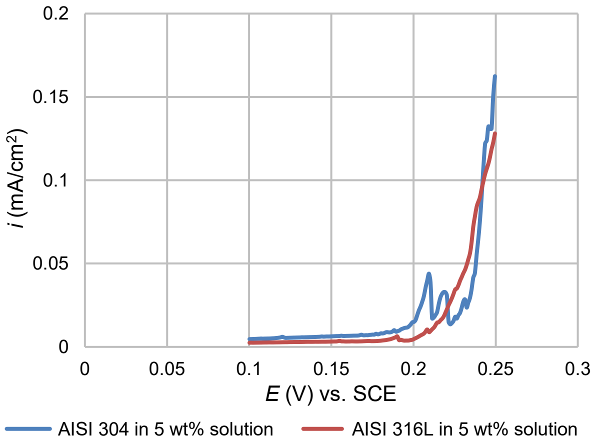

Figure 4. Details of the potentiodynamic polarization curves in linear axes. A comparison of passive current densities close to the E_p potentials in the 5 wt% solution

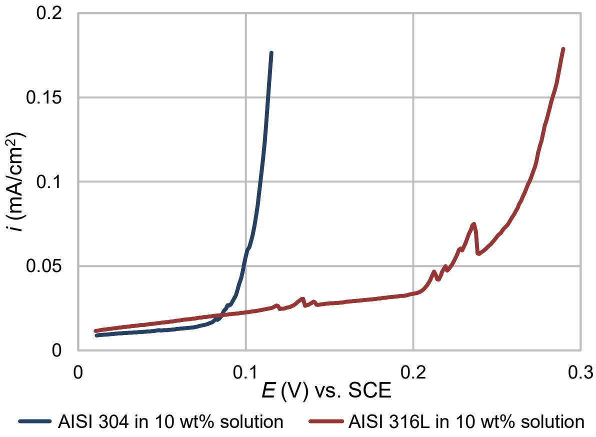

Figure 5. Details of the potentiodynamic polarization curves in linear axes. A comparison of passive current densities close to the E_p potentials in the 10 wt% solution

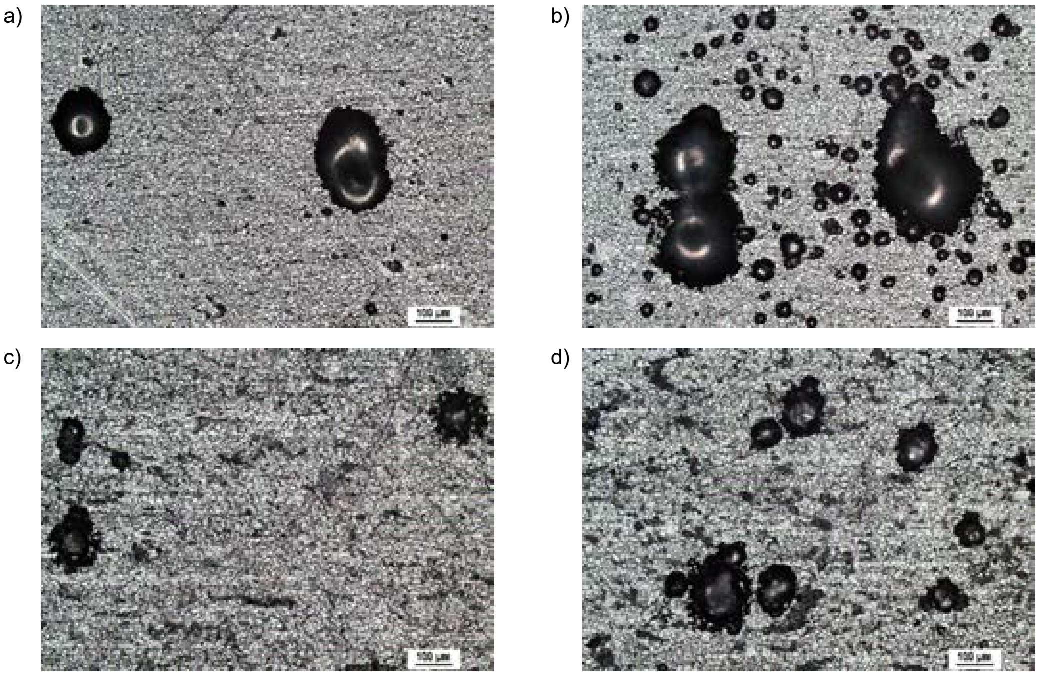

Figure 6. Local corrosion damage of the tested surfaces caused by potentiodynamic polarization in road salt solutions, observed by optical microscope: a) AISI 304 in 5 wt% solution, b) AISI 304 in 10 wt% solution, c) AISI 316L in 5 wt% solution, and d) AISI 316L in 10 wt% solution

not being natural, but evoked by anodic potentiodynamic polarization, it is obvious that corrosion damage of the AISI 304 surface is more extensive, namely in the 10 wt% solution.

Conclusions

On the basis of the performed potentiodynamic polarization tests in 5 wt% and 10 wt% road salt solutions, it can be concluded that:

- The chloride concentration increase caused a decrease in the pitting potential values (Table 2) and an increase in the passive current densities (Figures 4 and 5) of both stainless steels. The negative Cl^- concentration effect was significantly stronger for AISI 304 stainless steel (E_p decreased from 0.189 V vs. SCE to 0.080 V vs. SCE).
- AISI 316L stainless steel showed a higher resistance to the pitting corrosion compared to the AISI 304 stainless steel. This was mainly reflected by the more than twice higher pitting potential value in 10 wt% solution (0.202 V vs. SCE) compared to the AISI 304 steel (0.080 V vs. SCE), and by the slighter pitting corrosion damage of the surface evoked by the potentiodynamic polarization.

Changing the chloride concentration in road salt solutions, especially in combination with varying temperatures (Park, Matsch & Böhmi, 2002; Zatkalíková & Markovičová, 2019), can cause dangerous local corrosion of stainless-steel automotive components. Therefore, it is important to minimize their exposure to these environments. In addition, molybdenum-containing steels should be preferred in the manufacture of road salts exposed automotive components.

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