Corrosion resistance of electropolished AISI 304 stainless steel in dependence of temperature

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Abstract. AISI 304 is Cr-Ni austenitic stainless steel currently used for numerous applications that require high corrosion resistance. Due to the passive surface film this steel is resistant against a uniform corrosion, but halides present in environment can evoke local pitting. Electropolishing is recommended to obtain the high quality passive film and to increase the pitting corrosion resistance. This paper is focused on the assessment of the effect of elevated temperature (50 °C) on the resistance of AISI 304 electropolished surface to pitting corrosion in acidified 1 M chloride solution. Evaluation is based on the results of electrochemical cyclic potentiodynamic polarization tests (determination and comparison of pitting potentials $E_p$) and on the microscopic observation of specimen surfaces attacked by pitting during performed testing procedure.

1. Introduction
AISI 304 is the most widely used Cr-Ni austenitic stainless steel. It is recommended for a wide variety of applications that require high corrosion resistance, good formability and weldability. Common uses for this stainless steel type are found in such areas as food industry (e.g. cooking appliances, stoves, refrigerators, milk processing, wine-making, storage tanks), petrochemical, chemical and nuclear industry, dyeing industry, architecture and medicine. Other areas of use include chemical containers, heat exchangers, mining equipment, and marine nuts, bolts and screws, filtration systems.

Due to the passive surface film the stainless steels are resistant to the uniform corrosion in oxidation environments [1-4]. However, a presence of aggressive substances in environment can evoke local breakdown of protective film and consequently destructive and dangerous local corrosion, namely pitting [1, 2, 4-5].

There are a lot of various factors that influence the resistance of stainless steels to pitting. In addition to internal factors (chemical composition, surface treatment which affects the quality of passive surface film) important role is played by the environmental conditions (temperature, pH, concentration of aggressive ions) [1, 2, 5-7]. Temperature is a factor that strongly affects both thermodynamics and kinetics of pitting corrosion [1, 2, 7]. 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]. The authors [1, 2, 5-7] consider influence of temperature on pitting corrosion by the change of electrochemical characteristics – decrease of the pitting potential $E_p$ and the repassivation potential $E_r$ with temperature.
Many authors, e.g. [8-11] have documented an effect of surface characteristics on the pitting corrosion resistance of austenitic stainless steels. To obtain a high quality passive film which results in smooth material surface, various polishing techniques are commonly used. Traditional mechanical polishing usually causes deformed layer and residual stresses on the treated surface [10]. Electropolishing as a surface finishing process of electrochemical anodic dissolution which enhances high surface brightness (mirror finish) without residual surface tensions appears as a better alternative. A particular layer from the metal’s surface is removed and a high quality passive, chromium enriched oxide film is created [11]. According to the authors [12, 13], the increase of Cr/Fe ratio is caused by selective dissolution leading to the formation of a passive layer during the electropolishing process. Improved corrosion resistance and reduced bacterial attachment are other benefits of electropolished surfaces important for various industrial and medical applications of these materials [10].

This paper is focused on the pitting corrosion resistance of AISI 304 in acidified 1 M chloride solution. Resistance of three surface types (“as received”, electropolished and ground + electropolished) is studied at compared at two temperatures (22 ± 3 °C, 50 °C). Evaluation of the corrosion resistance is based on the results of electrochemical cyclic potentiodynamic polarization tests and on the microscopic observation of specimen surfaces attacked by pitting during performed testing procedure.

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. Its heat treatment was based on cold rolling, homogenization annealing (1040 – 1100 °C) and pickling after slightly smoothing rolling. The IIB surface finish means smooth and matte metallic glossy surface of the “as received steel” [14].

| Cr  | Ni  | Mo | Mn  | N  | C  | Si  | P   | S   | Fe  |
|-----|-----|----|-----|----|----|-----|-----|-----|-----|
| 18  | 8.01| -  | 1.40| 0.075| 0.027| 0.38 | 0.031| 0.0037| balance |

Microstructure of experimental material (figure 1) is polyedric, 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.

Figure 1. Microstructure of AISI 304 stainless steel, cross section (glycerine + HNO₃ + HCl etch.).
3. Experimental procedure

Three types of studied steel surfaces were used for cyclic potentiodynamic tests (figure 2):

1. “as received” surface (AR), i.e. without additional mechanical /chemical treatment;
2. electropolished surface (EP);
3. ground (1200 mesh) and consequently electropolished surface (G+EP).

Electropolishing was performed in $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ electrolyte under the conditions listed in table 2 [15, 16]. During electropolishing process the specimen was immersed into electrolyte and connected to the positive pole of the power source as an anode. A cathode was of the same material as the anode [16].

![Figure 2. Types of steel surfaces used for potentiodynamic tests.](image)

1M chloride acidified solution was used as the corrosion environment for electrochemical cyclic potentiodynamic test. This solution was represented by $0.9\text{M NaCl} + 0.1\text{M HCl}$ (pH = 1.1, specific conductivity 98 mS.cm$^{-1}$, redox potential 0.509 V). The used solution was chosen because of its similar aggressiveness and the same chloride concentration as the FeCl$_3$ solution used for the ASTM G48 standard method for the pitting corrosion resistance testing [2, 4].

Cyclic potentiodynamic polarization tests (ASTM G61) were carried out in a three electrode cell of corrosion measuring system (VoltaLab 10 with VSP unit). Potentiodynamic polarization curves were obtained by the EC-LAB SOFT software. Potential between the sample and the electrolyte has been settled for 10 minutes before the polarization. Scan range was -0.3V – 0.9 V vs the open circuit potential and the scan rate was 1 mV/s, the limit current was 0.15A. The surface of working electrode AISI 304 of 1 cm$^2$ area was rinsed with ethanol before measurement. The saturated calomel electrode (SCE) was applied as the reference electrode and platinum foil as a counter electrode. Experiments were carried out at ambient temperatures of 22 ± 3 °C and 50 °C. At least five experiment repeats were carried out for all specimens.

Surfaces of working electrode AISI 304 were observed by the optical microscope (Zeis Axio Imager A1m) after potentiodynamic measurements.

| Component | Content (wt. %) | Temperature (°C) | Current density (A.cm$^{-2}$) | Time (s) |
|-----------|----------------|------------------|-----------------------------|----------|
| $\text{H}_3\text{PO}_4$ | 64 | 40 | 0.8 | 420 |
| $\text{H}_2\text{SO}_4$ | 13 | | | |
| $\text{H}_2\text{O}$ | 23 | | | |

4. Experiment results and discussion

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 [1, 2, 5].

Cyclic potentiodynamic curves of the tested steel in experimental solution at 22 ± 3 °C are presented in figure 3. All three curves have a typical loop shape which points to the breakdown of passive film in the given conditions. According to the common comparison of the curves, the AR surface reflected the most narrow passivity region. The important part of the curves that approximates the interface between the passive state and the active one is enlarged and shown in figure 4 (the location of the respective pitting potentials $E_p$ is indicated by arrows). As can be seen in figure 4, electropolished surfaces have a higher thermodynamic stability and a lower passive state current density than AR one. Fluctuations in the passive current density of AR curve indicate a significantly less stable passive state. Similar differences in passive current density between unpolished and electropolished surfaces describe also authors [11].

The curves of tested steel in experimental solution at 50 °C are shown in figure 5. At this temperature AR curve 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. Therefore it was not possible to determine the pitting potential $E_p$ (missing AR curve in figure 6). According to figure 6, there is the strong difference between stability of passive state of EP and G+EP surface. The detail of EP curve shows a slight gradual increase of the passive current density and it points to less stable passive state in comparison with G + EP surface.

The comparisons of the curves (figure 4 and figure 6) and the $E_p$ values (figure 7) point to quality differences between EP and G+EP surfaces. The grinding followed by electropolishing enabled to obtain more resistant oxidic passive layer. This result is consistent with authors [17] who found the key role of grinding prior to the electropolishing in defining the final surface roughness of AISI 304 stainless steel.

![Figure 3. Cyclic potentiodynamic curves of AISI 304 stainless steel in 0.9M NaCl + 0.1M HCl solution, 22 ± 3 °C (AR – as received surface, EP – electropolished surface, G + EP - ground + electropolished surface).](image-url)
Figure 4. Detail of the cyclic potentiodynamic curves of AISI 304 stainless steel in 0.9M NaCl + 0.1M HCl solution, 22 ± 3 °C (interval 0.0 – 0.25 V; $E_p$ location is indicated by arrows).

According to the comparison of the pitting potentials in figure 7, elevated temperature is the essential external factor that radically decreases the $E_p$ potential even after electropolishing. High quality and chromium enriched passive layer did not prevent adsorption and consequent penetration chloride anions. The passive film was broken at low $E_p$ values and the local pitting corrosion has started.

Figure 5. Cyclic potentiodynamic curves of AISI 304 stainless steel in 0.9M NaCl + 0.1M HCl solution, 50 °C (AR – as received surface, EP – electropolished surface, G + EP - ground + electropolished surface).

The setting of the cyclic potentiodynamic test conditions with a sufficiently high limit current (0.15 A) allowed the pitting corrosion progress manifested by well observed pitting. Figures 8 and 9 show pitted surfaces after performed potentiodynamic tests. At the both temperatures AR surface is covered by numerous pits which are smaller than those on the electropolished surfaces. A worse quality of the passive film could cause its breakdown by chloride anions in many places. It led to the formation of the high number of small pits which size was affected by temperature (figures 8a, 9a; 8b, 9b).
higher temperature = higher number and smaller size of pits). EP and G+EP surfaces are similar with a smaller number of oval/oblong pits. Chloride anions penetrated through a higher quality passive layer in fewer places, resulting in a smaller number of larger pits (figures 8b, c; 9b, c).

**Figure 6.** Detail of the cyclic potentiodynamic curves of AISI 304 stainless steel in 0.9M NaCl + 0.1M HCl solution, 50 °C (interval -0.05 – 0.09 V; $E_p$ location is indicated by arrows).

**Figure 7.** Comparison of the pitting potentials ($E_p$) at the temperatures 22 ± 3 and 50 °C in dependence on the surface treatment.
5. Conclusion
Based on the results of performed experiments can be concluded:

- The pitting corrosion resistance (expressed by the pitting potentials $E_p$) of all tested AISI 304 stainless steel surfaces was negatively affected by elevated temperature (50 °C). The most striking negative effect was recorded on “as received surface”.

- According to $E_p$ values at both temperatures the ground and electropolished (G + EP) surface showed the most quality passive film and the highest corrosion resistance. However it should be noted that strong $E_p$ decrease at 50 °C points to not sufficient protection against the pitting corrosion in aggressive chloride environment.

In accordance with the results obtained the use of tested steel with the “as received surface” in aggressive chloride environments is not recommended. The ground and consequently electropolished surface seems to be the best alternative. In spite of it caution should be recommended when used in aggressive chloride environments at increased or varying temperatures.

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