CORROSION BEHAVIOR OF Cr-Ni-Mo STAINLESS STEEL IN CHEMICALLY MODIFIED CHLORIDE SOLUTION

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Abstract: Cr-Ni-Mo stainless steels are susceptible to the pitting in aggressive chloride environments. One of the possible ways for the influence of their corrosion behavior is the use of inhibitors as the chemical modification of the environment. The resistance of AISI 316Ti stainless steel to the pitting with/without the inorganic inhibitor was tested by two independent corrosion tests: 24-hours exposure immersion and potentiodynamic polarization test. Both tests were carried out in 1M chloride acidic solution with/without 0.1M molybdate inhibitor at room temperature. Results of immersion tests were evaluated by the corrosion rates calculated from corrosion losses and by the morphology of the pitting. Potentiodynamic polarization curves were evaluated by the pitting potentials.

Keywords: austenitic stainless steel, pitting corrosion resistance, inorganic inhibitor

1. INTRODUCTION

Cr-Ni-Mo stainless steels are highly resistant to uniform corrosion in oxidation environments due to their passive oxide surface film. Aggressive ions present in environment cause local breakdown of this protective film and the initiation of the pitting corrosion which is very dangerous and it may cause a major failure in industrial applications (Brytan et al., 2016; Jambor et al., 2018; Jessen, 2011; Lipinsky, 2019; Szklarska-Smialovska, 2005). The best way to improve the resistance to the pitting is developing new highly resistant alloys. The major disadvantage of these materials is their high cost compared with conventional stainless steels due to the higher percentage of the alloying elements as well as the complexity of the fabrication process (El Dahan, 1999). The favorable effect of some alloying elements e. g. Cr and Mo can be achieved by their addition into aggressive solution in the form of nonaggressive anions (molybdates MoO_4^{2-}, chromates CrO_4^{2-}) that can be settled on the metal surface, strengthen the passive film and inhibit the pitting corrosion process (El Dahan, 1999). Many authors underline that the corrosion inhibition acts effectively only at the certain non-aggressive/aggressive anions concentration ratio (Ilevbare et al., 2003; Liptáková, 2009; Szklarska-Smialovska, 2005). The authors (Ilevbare et al., 2003) applied 1:10 molybdate/chloride concentration ratio and they documented the positive effect of the

inhibitor on the embryonic stages of pitting corrosion (metastable pitting) and on the value of the pitting potential in acidic chloride solution as well. Several authors (Ebrahimi et al., 2011; El Dahan, 1999; Refaey et al., 2000; Zhuo et al., 2002) added the inhibitors into corrosion solutions in a very broad interval of concentration ratios, and they also bring positive results on their inhibitive effects.

According to many authors, chromans are considered efficient pitting corrosion inhibitors (Ebrahimi et al., 2011; El Dahan, 1999; Ilevbare et al., 2003; Liptáková, 2009; Szklarska-Smialovska, 2005) but they are highly toxic and therefore environment-unfriendly and handling them requires very strict rules. From this point of view molybdates are much more suitable inhibitors for ordinary use (Liptáková, 2009; Szklarska-Smialovska, 2005).

The experimental material AISI 316Ti is Cr-Ni-Mo austenitic stainless steel stabilized by Ti widely used in industrial and biomedical applications (Oravcová et al., 2018; Oršulová et al., 2018; Pardo et al., 2007). The subject of this article is the pitting corrosion behavior of the AISI 316Ti steel in 1 M chloride acidic solution with/without 0.1 M sodium molybdate inhibitor, tested by two independent methods: 24-hours exposure immersion and potentiodynamic polarization test both carried out at the temperature 20 ± 3 °C. Results of immersion tests were evaluated by the corrosion rates calculated from the mass losses and by the morphology of the pitting. Potentiodynamic polarization curves were evaluated by their pitting potentials.

2. MATERIAL AND METHODS

The chemical composition of AISI 316Ti experimental material is listed in Table 1.

Table 1
Chemical composition of experimental material

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

Microstructure (Fig. 1) is created by polyedric austenitic grains with observable twins, probable created by annealing and rolling. Numerous carbides can be observed: cubic shaped (Mo, Ti)C carbides, $(Mo, Cr)_{23}C_6$ carbides (Pardo et al., 2007) localized in the rolling lines.
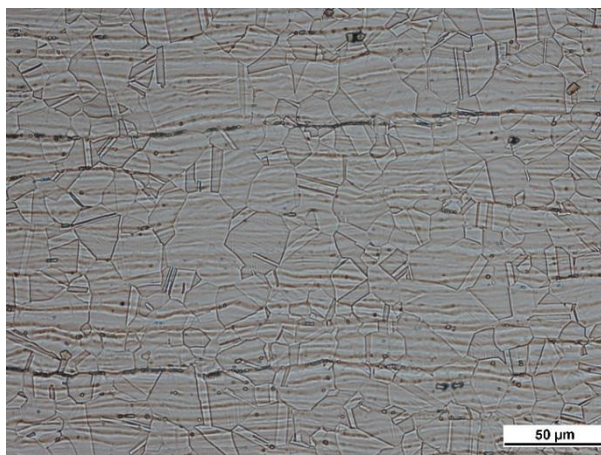

50 µm

Fig. 1. Microstructure of AISI 316Ti stainless steel in longitudinal section (HNO_3 + H_3PO_4 + glycerin etch.)

1M chloride solution was used as the basic corrosion environment for both exposure and potentiodynamic polarization. This solution was represented by 5 wt. % $FeCl_3$ (pH=1.2) for immersion test (according to ASTM G48 standard) and by 0.9M NaCl + 0.1M HCl (pH=1.1) with the same chloride concentration but with lower aggressiveness (due to the lower redox potential) for potentiodynamic polarization ($FeCl_3$ solution is too aggressive for corrosion cell). The basic solution was applied without inhibitor and with 0.1M sodium molybdate (it means 1:10 inhibitive/aggressive anions concentration ratio).

Exposure immersion test

The specimen's shape for immersion test was rectangular (30 mm x 80 mm x 1.5 mm). The surface was not treated (mechanically or chemically) only the edges were grinded by grain 600 abrasive paper. The specimens were rinsed with diethyl ether and weighted out with the accuracy ± 0.000 01 g. The immersion test was 24-hours and it was carried out at 20 ± 3 °C temperature (Baboian, 1995; Liptáková, 2009; Zatkalíková et al., 2020). The group of three parallel specimens was tested for each solution. After exposure the specimens were carefully brushed, washed by de-mineralized water, freely dried up and weighted out again.

Pitted surfaces of specimens were observed by the optical microscope. Average corrosion rates ($g/(m^2.h)$) were calculated from the mass losses during the exposure.

Potentiodynamic polarization

Potentiodynamic polarization was performed in a conventional three-electrode cell system with a calomel reference electrode (SCE) and a platinum auxiliary electrode (Pt) using Voltalab 10 corrosion measuring system. The time for potential stabilization between the specimen and the electrolyte was set to 10 min. The scan range was -0.2 V – 0.7 V vs the open circuit potential and the scan rate was 1 mV/s. The surface of working electrode AISI 316Ti of 1 cm^2 area was not mechanically treated, only rinsed with diethyl ether before measurement. The potentiodynamic polarization curves were obtained by the EC-LAB SOFT software. All experiments were carried out at 20 ± 3 °C temperature (Kuchariková et al., 2018).

3. RESULTS AND DISCUSSION

Regardless of the inhibitor addition, the tested specimens were attacked by the pitting corrosion during the 24-hour exposition in the aggressive solution (Fig. 2). In the both cases (Fig. 2 a), b)) the pits seem to be situated into the lines connected with the rolling and this could be related to the carbides occurring there (Fig. 1) which may affect negatively the local quality of passive film (Pardo et al., 2007). Local corrosion failure is also visible in places with higher surface roughness (edges and holes for hanging of the specimens).

As can be seen in Fig 2 and Fig. 3, the shape and size of the pits depend on the presence of the inhibitor in the corrosive solution. While the typical pits in 1M chloride solution without inhibitor are oblong with dissected margins and markedly bigger, the pits on the specimens immersed in the solution with inhibitor are smaller and rounder shaped (Fig. 3). The cause may be the molybdate ions adsorption on the steel surface that probably prevented the sideways pits growth and this led to the better bounded rounder pits.

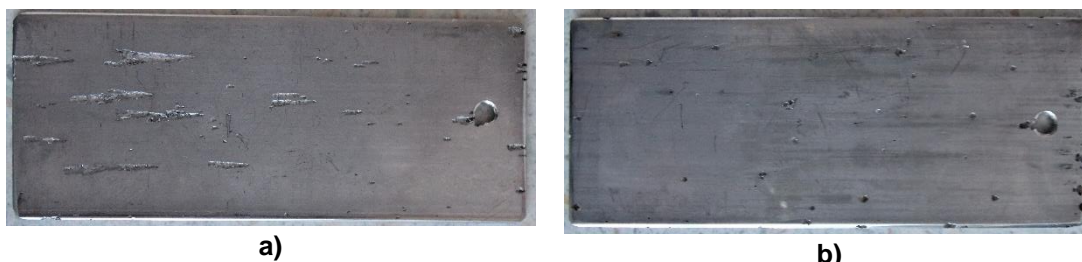**a)**   **b)**

Fig. 2. The specimens after 24-hours exposure immersion test: a) without inhibitor, b) with inhibitor
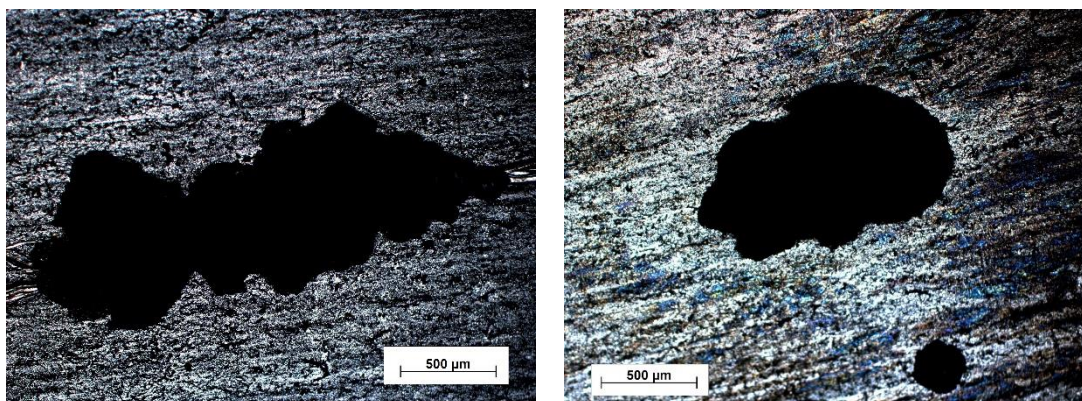

Fig. 3 Typical pit shapes on the specimens surfaces after e 24-hours exposure immersion test: a) without inhibitor, b) with inhibitor

The presence of the molybdate in the solution also had a positive effect on the average corrosion rate calculated from the mass losses, which is significantly lower with molybdate than without it (Table 2). It could be caused be the smaller and probably more shallow pits (Zatkalíková et al., 2020).

Table 2
Values of the average corrosion rates

Presence/absence of molybdate inhibitor	Average corrosion rates v_{corr} (g/(m².h))
Without inhibitor	5.954 ± 0.65 %
With 0.1M inhibitor	3,517 ± 0.71 %

Potentiodynamic polarization curves in the chloride solution within/with the molybdate inhibitor are shown in Fig. 4. The susceptibility to the pitting was evaluated by the pitting potentials E_p that denote the breakdown of the passive surface film and the onset of the stable pit growth. The wider region of the passivity and the higher E_p value points to a higher resistance to the pitting (Liptáková, 2009; Szklarska-Smialovska, 2005; Zatkalíková et al., 2017).

For both curves the E_p values (Table 3) were determined as the potentials of a sudden sharp increase in current density at the anodic polarization. According to the course of the polarization curves (Fig. 4) and E_p values, the molybdate addition to the chloride solution ensured wider passive region and higher resistance of the passive film to the failure and finally better resistance to the pitting corrosion. As in the exposure immersion test, the positive effect of molybdate surface adsorption probably appeared also in this case.
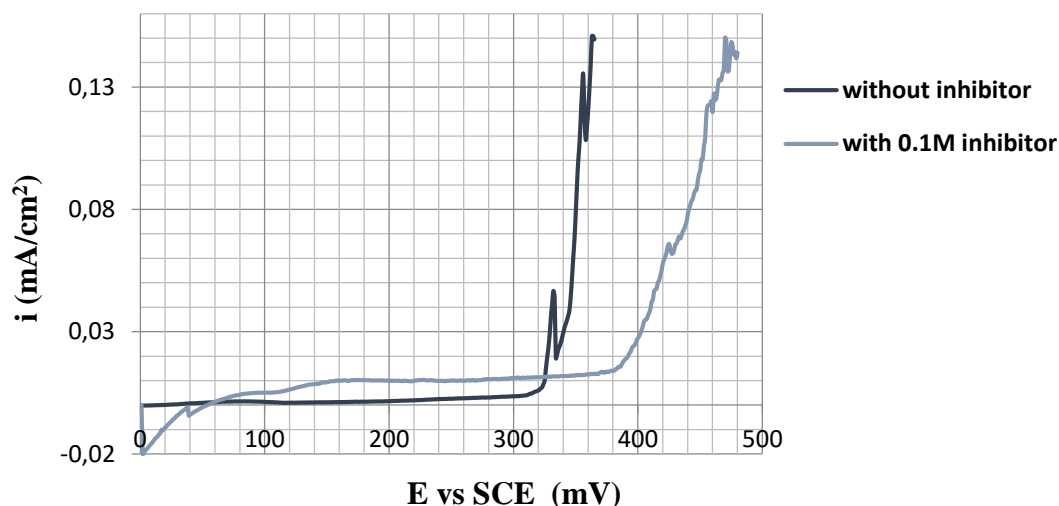
Fig. 4 Potentiodynamic polarization curves

Table 3
Values of the pitting potentials

Presence/absence of molybdate inhibitor	Pitting potential E_p (mV vs SCE)
Without inhibitor	310
With 0.1M inhibitor	380

4. CONCLUSION

Based on the performed experiments can be concluded:

- Addition of 0.1M molybdate inhibitor in 1 M chloride solution (represented by 5 % $FeCl_3$ solution) did not prevent a local surface failure by the pitting corrosion during 24-hours immersion test. However, the inhibitor positively affected the size and shape of pits (rounder and better bounded pits) and also caused the significant decrease of the average corrosion rate.
- According to the potentiodynamic polarization a marked shift of the pitting potential to higher positive values in the case of inhibitor addition was recorded which reflects the higher resistance to pitting. Taking to the account that the aggressiveness of 1M chloride solution for potentiodynamic polarization was lower than for exposure test (explained in Chapt. 2), a use of the molybdate inhibitor for improving of the pitting corrosion resistance seems to be more reliable in less aggressive chloride solutions.

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