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**PITTING CORROSION OF Cr-Ni-Mo STAINLESS STEEL IN THE
PRESENCE OF MoO_4^{2-} IONS ADDED TO AGGRESSIVE CHLORIDE
SOLUTION**

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1. Introduction

Pitting corrosion is one of most serious electrochemical corrosion phenomena. It is very common corrosion failure of stainless steels in various chloride environments. Chlorides are aggressive ions, which penetrate through weakened places of surface protective passive film and cause its local breakdown [1-3].

It has been known that some non-aggressive inorganic anions (e.g. CrO_4^{2-} , MoO_4^{2-} , PO_4^{3-} , NO_2^-) present in chloride solution play an important role in a passivation process. These anions act as anodic oxidizing inhibitors of the initial phase of pitting corrosion process by their adsorption on the metal surface [1, 4-6]. Many authors underline that a corrosion inhibitor acts effectively only above a certain concentration ratio of non-aggressive to aggressive anions. This relationship can be expressed as follows (1):

$$c_A = A + B \log c_N \quad (1)$$

where c_A is concentration of aggressive ions, c_N is concentration of inhibitive ions, A and B are constants [1, 6]. However, there are some authors, who have tested inhibitors added into solution in a very broad interval of concentration ratios, and they bring positive results about inhibitive effects as well [4, 5, 7, 8].

According to many authors, chromans are very efficient pitting corrosion inhibitors [1, 4-6], but they have an important disadvantage. These species are highly toxic and

therefore ecologically unfriendly and handling them requires very strict rules. From this point of view molybdates are much more suitable for ordinary use.

AISI 316Ti is Cr-Ni-Mo austenitic stainless steel stabilized by Ti. It is widely used in chemical, petrochemical and food industries in shipping, storage and for various biomedical applications as well [2, 3, 8, 9]. In spite of its wide use and high Pitting Resistance Equivalent Number (PREN=23.688) [10] this steel is prone to local corrosion failure in chloride solutions [2, 3, 8, 9].

This paper deals with the effect of sodium molybdate inhibitor on the resistance of AISI 316Ti steel to pitting, tested by 24-hours exposition immersion tests carried out in 5% ferric chloride solution at the temperature of 20 ± 3 °C in absence and presence of three molybdate concentrations (0.025 M, 0.05 M, 0.1 M). Resistance to pitting was evaluated on the bases of corrosion losses during immersion and by morphology of pitting (observed visually and by optical microscope).

2.Experimental material

AISI 316Ti stainless steel with the chemical composition shown in Tab. 1 was used as an experimental material. It was bought in ITALINOX company and its treatment (marked as 2B) was based on annealing and pickling after smoothing rolling [11].

Tab. 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 of experimental material observed by optical metallographic microscope Neophot 32 in longitudinal section is shown in Fig. 1. It is created by polyedric austenitic grains with observable twins (Fig. 1), which could be created by annealing or by rolling. Parallel lines arose by the rolling during the technologic process. Observed microstructure (Fig. 1,) contains numerous carbides. (Mo, Ti)C carbides are of cubic shape, (Mo, Cr)₂₃C₆ carbides are localized along the above mentioned lines [12].

3.Experimental methods

The specimen's shape for immersion tests was rectangular 30 mm x 80 mm x 1.5 mm. The specimen surface was not treated (mechanically or chemically) only the edges were grinded by abrasive paper grain 600. The grease was removed by diethyl ether. The specimens were weighted out with accuracy $\pm 0.000\ 01$ g (Mettler Toledo XS 205).

The basic solution for immersion tests was 5 % FeCl₃. It is extremely aggressive acidic solution (pH = 1.2), its specific conductivity is 58 mS.cm⁻¹, and it has high redox potential (691 mV). 5 % FeCl₃ solution was used without inhibitor and with three various sodium molybdate concentrations: 0.025 M, 0.05 M and 0.1 M. All immersion tests were

24 hours and they were carried out at the temperature $20 \pm 3 \text{ }^\circ\text{C}$ [2, 9, 10]. 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.

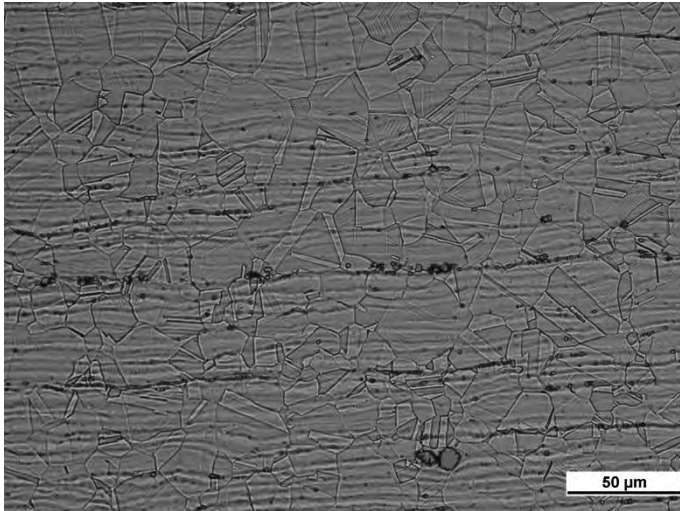


Fig. 1 Microstructure of AISI 316Ti stainless steel in longitudinal section (etch. $10 \text{ cm}^3 \text{ HNO}_3 + 20 \text{ cm}^3 \text{ H}_3\text{PO}_4 + 30 \text{ cm}^3 \text{ glycerin}$, for 5 minutes)

Pitted surfaces of specimens after immersion tests were observed by the optical microscope NIKON AZ 100.

4. Experimental results and discussion

All tested specimens were locally damaged by pitting during immersion tests (Fig. 2). The corrosion failure is localized non-uniformly. Pits seem to be situated into lines related with rolling. $(\text{Mo}, \text{Cr})_{23}\text{C}_6$ carbides occur along this lines (Fig. 1) and they may affect negatively the quality of passive film in these places. Local corrosion failure is also situated to the edges and to the holes for hanging with higher surface roughness (Fig. 2).

As we can see in Fig. 2 a), the pits on specimen immersed in 5% FeCl_3 are oblong and generally bigger than pits in Figs. 2 b), c), d). The specimens immersed in 5% FeCl_3 solution with inhibitor have similar character of pitting – the shape of pits is rounder and edges are less damaged than in case without inhibitor. The typical pit shapes are shown and can be compared in Fig. 3. This comparison confirms differences of pit shapes observed visually (Fig. 2). The adsorption of molybdate inhibitor on the steel surface probably prevented growth of pits sideways and caused better bounded rounder pits. This phenomenon can be observed on the profiles of pits presented in Fig. 4 as well. As we can see, the inhibitor limited the width of pits, but did not prevent their increase in depth.

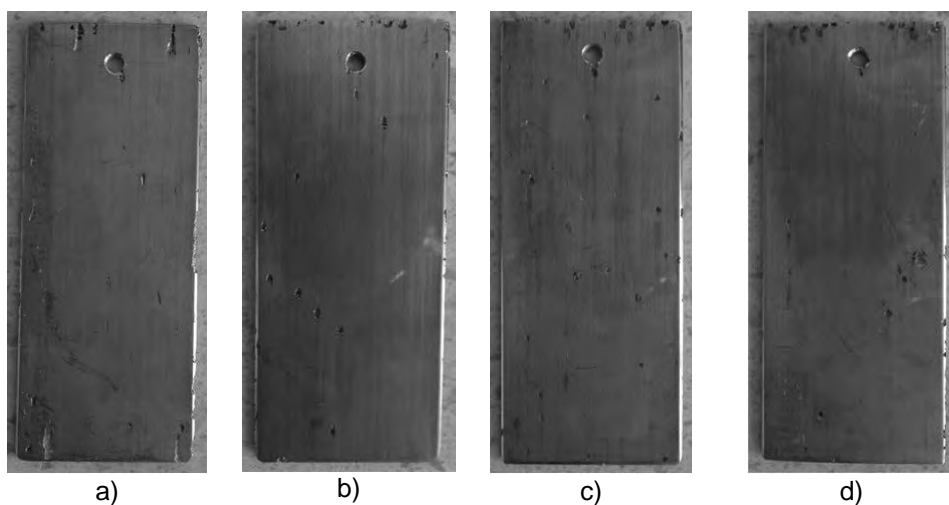


Fig. 2 Pitted surfaces of tested specimens after 24-hours immersion test in 5% FeCl_3 solution: a) without inhibitor, b) with 0.025 M molybdate, c) with 0,05 M molybdate, d) with 0,1M molybdate.

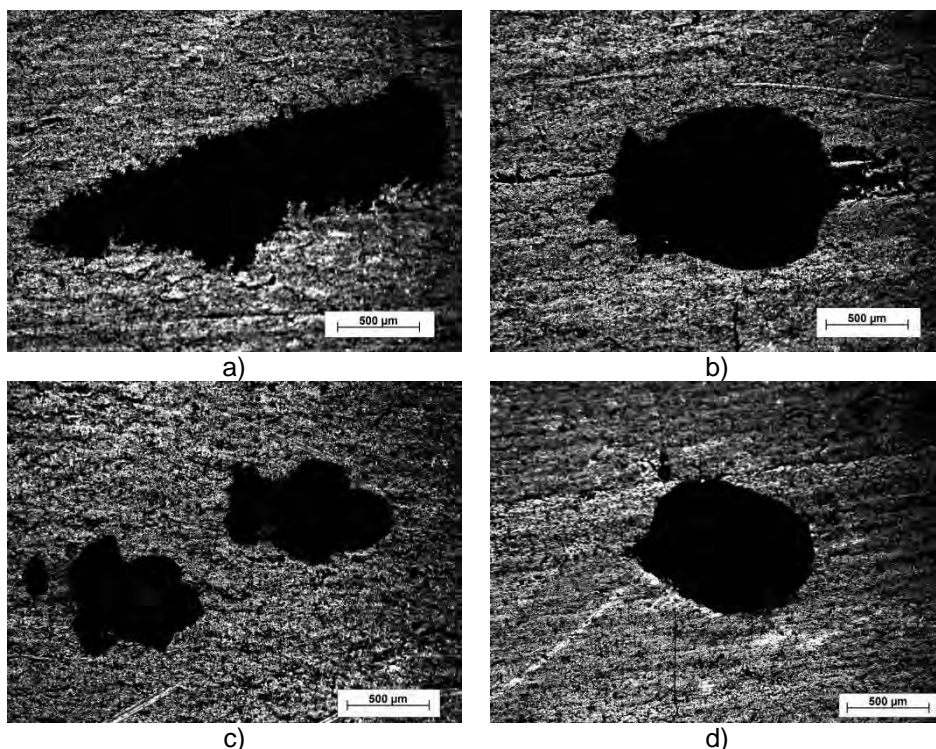


Fig. 3 Typical shapes of pits after 24-hours immersion test in 5% FeCl_3 solution: a) without inhibitor, b) with 0.025 M molybdate, c) with 0,05 M molybdate, d) with 0,1M molybdate.

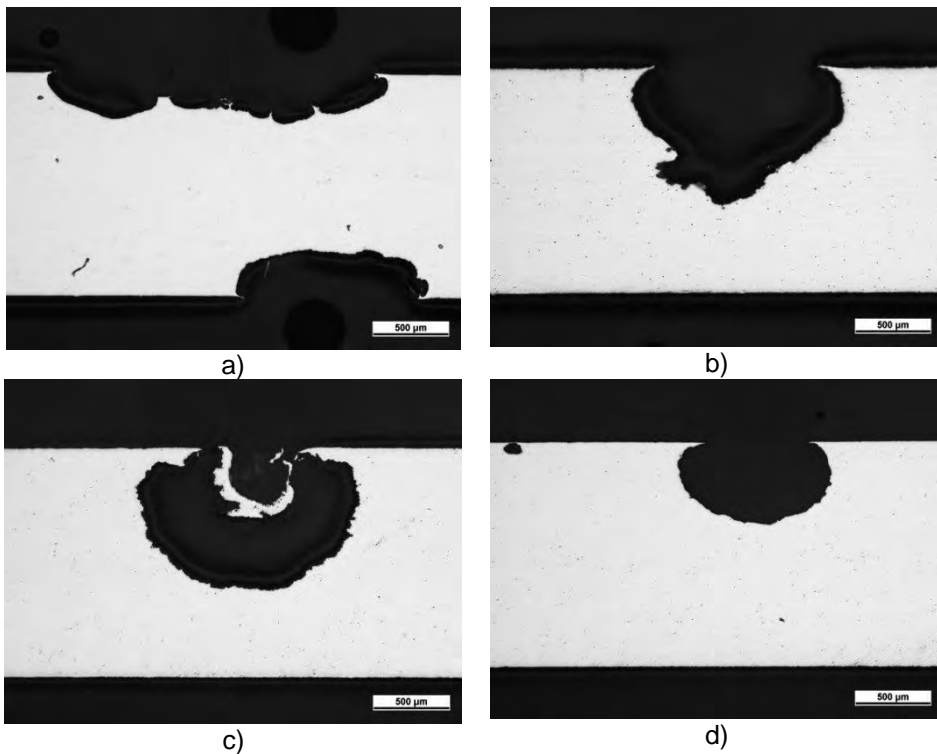


Fig. 4 Typical profiles of pits after 24-hour immersion test in 5% FeCl_3 solution: a) without inhibitor, b) with 0.025 M molybdate, c) with 0,05 M molybdate, d) with 0,1M molybdate.

Average corrosion rates ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), calculated from corrosion losses ($\text{g}\cdot\text{m}^{-2}$) during the immersion tests in dependence on the molybdate concentration are shown in Fig. 5.

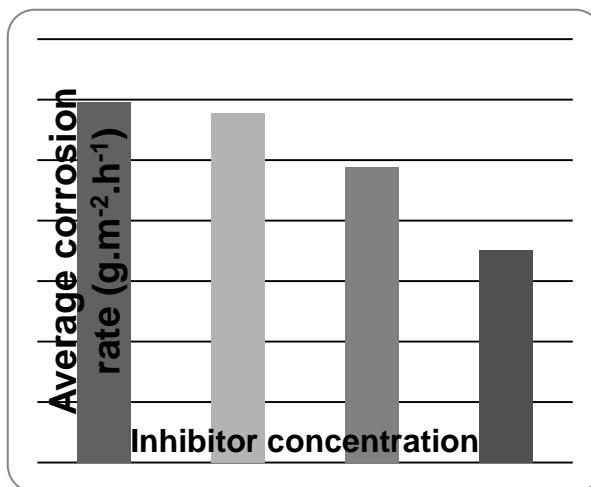


Fig. 5 Average corrosion rates in dependence on inhibitor concentration

The corrosion rate based on the corrosion loss cannot be generally considered as the essential factor of evaluation of pitting corrosion resistance because of non-uniform, local character of pitting. However, it helps make an idea about probable changes in the pitting corrosion kinetics [2, 9]. Fig. 5 shows the drop in corrosion rate in dependence on the rise of inhibitor concentration. The strongest drop is observed for the highest molybdate concentration. Lower concentrations of inhibitor probably affected the kinetics much less.

All obtained results point to very slight and not sufficient positive effect of sodium molybdate added in the above mentioned concentrations to 5% FeCl₃ solution on resistance of AISI 316Ti steel to pitting.

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Summary

Pitting corrosion OF Cr-Ni-Mo stainless steel in presence of MoO_4^{2-} ions added to aggressive chloride solution

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The submitted manuscript focuses on the pitting corrosion of AISI 316Ti steel in very aggressive chloride solution with added sodium molybdate, which is considered the effective inhibitor of the local corrosion of stainless steels. The effect of molybdate on resistance of AISI 316Ti steel to pitting was tested in 5% ferric chloride solution by 24-hour exposition immersion tests. The tests were carried out at room temperature in the absence and presence of various molybdate concentrations (0.025 M, 0.05 M, 0.1 M molybdate). Resistance to pitting was evaluated on the bases of corrosion rates calculated from corrosion losses during immersion and by morphology of pitting, which was observed visually (character of pitting, pit shapes) and by optical microscope (pit shapes and pit profiles).

