

## PITTING CORROSION OF AISI 316Ti STAINLESS STEEL WITH POLISHED SURFACE

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### Abstract

AISI 316Ti is Cr–Ni–Mo austenitic stainless steel with the high Pitting Resistance Equivalent Number (PREN). The effect of the surface finishing by polishing on the pitting corrosion resistance was tested in aggressive 5% FeCl<sub>3</sub> solution. The immersion tests were carried out at the temperature 30, 50, 80 °C. The electrochemical cyclic potentiodynamic tests were carried out in the same solution at temperature 30 and 50 °C. The evaluation of the corrosion resistance arose from the comparison of the results of the immersion and the cyclic potentiodynamic tests.

**Key words:** Pitting corrosion, polished surface, AISI 316Ti stainless steel, immersion test, cyclic potentiodynamic test.

### 1. Introduction

AISI 316Ti is Cr–Ni–Mo stainless austenitic steel stabilized by Ti. It is held to be the steel with the strong pitting corrosion resistance [1] because of its high Pitting Resistance Equivalent Number (PREN = 23.688, calculated from the equation  $PREN = \%Cr + 3.3 \times \%Mo + 16 \times \%N$ ) [2]. Therefore this type of steel is generally used in aggressive environment (transportation tanks, equipment for chemical and petrochemical industry). Despite of high PREN, AISI 316Ti often underlies local corrosion in the strong operating conditions (chemical composition - namely Cl<sup>-</sup>, Br<sup>-</sup>, ClO<sup>-</sup>, temperature, mechanical loading) [3, 4, 5].

This paper concentrates on the effect of the surface finishing by polishing on the corrosion resistance of AISI 316Ti at various temperatures (30, 50, 80 °C) in aggressive 5 % FeCl<sub>3</sub> solution.

Evaluation of the corrosion resistance is based on the results of exposition immersion tests (visual and microscopic observation of failed surfaces, mass losses of specimens) and on the results of the cyclic potentiodynamic tests.

### 2. Experimental material

As experimental material was used AISI 316Ti steel with the chemical composition in Tab.1.

Microstructure of the original material was observed on the optical metallographic microscope Neophot 32 in transversal and longitudinal cut (Figs. 1, 2).

Microstructure is created by polyedric austenitic grains with observable twins, which could be created by annealing or by rolling. Strong lines visible in longitudinal cut arose by the rolling during the technologic process.

### 3. Course of the experiments

#### Immersion tests (ASTM G 48, [2]):

The specimen's shape was rectangular with dimensions 30 mm x 80 mm x 1.5 mm. The surface was treated by electrolytic polishing (70 °C, 9A, 1.5 minutes, electrolyte composed of glycerine, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>O). A half of specimens were consequently passivated in 20 % HNO<sub>3</sub> (30 minutes, 50 °C) [6, 7, 8].

Tab. 1

Chemical composition of the AISI 316Ti steel

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

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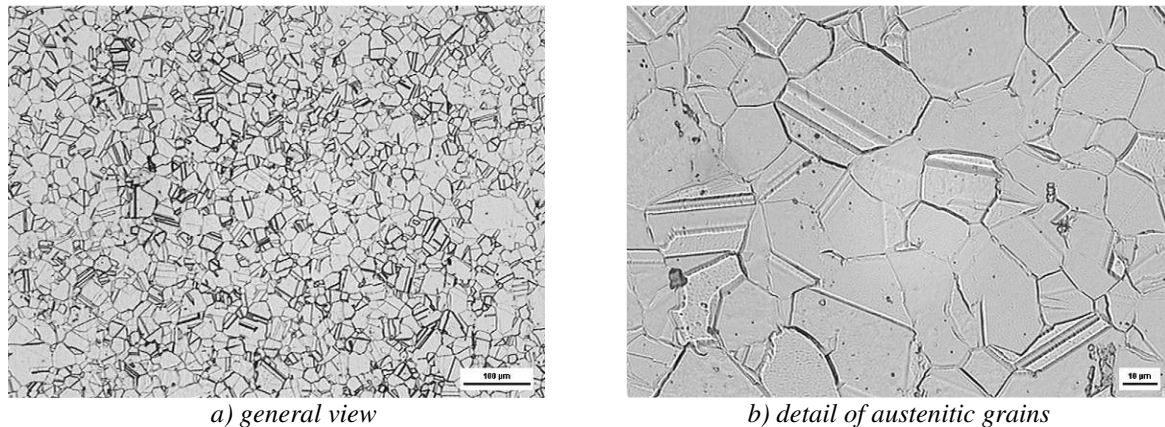


Fig. 1. Microstructure of the steel AISI 316Ti, transversal cut, etch. 10ml HNO<sub>3</sub>, 30ml HCl, 30ml glycerine

Immersion tests were carried out in 5% FeCl<sub>3</sub> solution (0.9624 mol.dm<sup>-3</sup> of Cl<sup>-</sup> concentration) at the temperature 30, 50 and 80°C. The duration of the tests was 24 hours. The group of three parallel specimens was observed for each combination of conditions (temperature, HNO<sub>3</sub> passivation). The tests were accomplished globally for 18 specimens. The tested specimens were ungreased by diethyl ether. Then they were weighted out (analytical balance Mettler Toledo XS 205, with accuracy of ± 10<sup>-5</sup>g). After 24 hours of exposure, the specimens were carefully brushed, washed by de-mineralized water, dried up and weighted up again.

#### Electrochemical tests (ASTM G 61, [2]):

The surface treatment of used specimens (10mm x 10mm x 1.5mm) was the same as mentioned by immersion tests (electrolytic polishing, passivation in 20 % HNO<sub>3</sub> solution).

The electrochemical cyclic potentiodynamic

tests were carried out in the same solution at the temperature 30 and 50°C.

Duration of the open circuit potential was 10 minutes, rotation of the sample was 1000 rpm, start potential was -200 mV, reverse potential was +900 mV, finish potential was -200 mV and scan rate of the potential was 10 mV. s<sup>-1</sup>.

#### 4. Results and discussion of the experiments

The specimens were locally attacked by pitting corrosion during the immersion tests. The density of pitting rose with the temperature (Fig. 3). Very remarkable change in appearance of pitted surfaces was observed between temperature 30 and 50°C. At 30°C, the pits were strongly bigger than at 50°C (Figs. 3, 4, 5). Combination of the low density and the “big” pits (30°C) can be probably related to the sporadic penetration of Cl<sup>-</sup> anions through the passive film and to the follow intensive corrosion by the “small” area of anode and the “big” area of cathode [9].

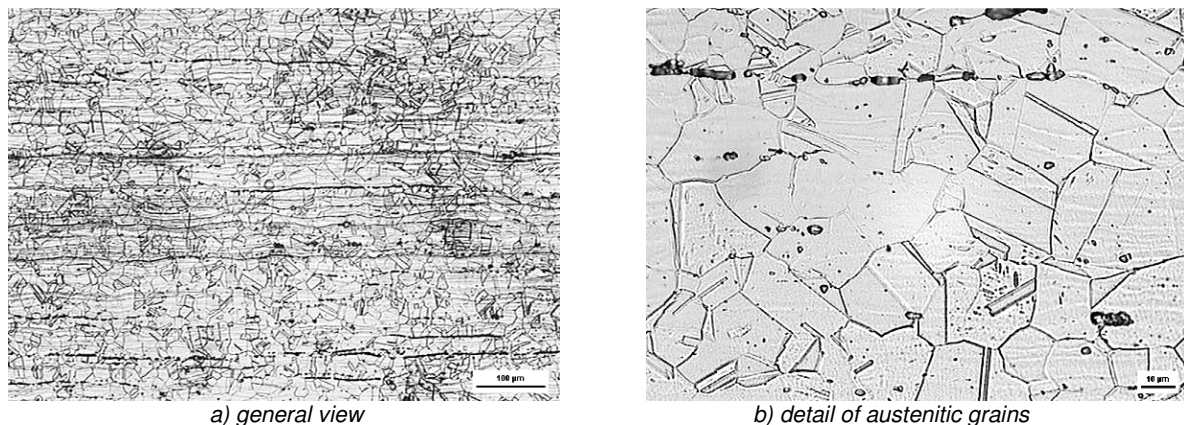


Fig. 2. Microstructure of the steel AISI 316Ti, longitudinal cut, etch.10ml HNO<sub>3</sub>, 30ml HCl, 30ml glycerine

Average corrosion rates ( $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , calculated from mass losses during the immersion tests) in dependence of the temperature are shown in Fig. 6. The behaviour of corrosion rates as a function of temperature can not be generally considered to be the essential factor for evaluation of pitting corrosion.

However, it helps to make conception about probable changes in controlling processes of the pitting corrosion kinetics [9]. The lowest values of average corrosion rates are observed at 30°C.

Specimens passivated in  $\text{HNO}_3$  have higher corrosion rates than equivalent specimens without passivation at this temperature. So the  $\text{HNO}_3$  passivation does not have positive influence on the pitting corrosion resistance in very aggressive solution (5 %  $\text{FeCl}_3$ ). The increase of corrosion rates between 30 and 50 °C (Fig. 6) clearly correlates with the change in appearance of pitted surfaces in the same range of temperature (Fig. 3).

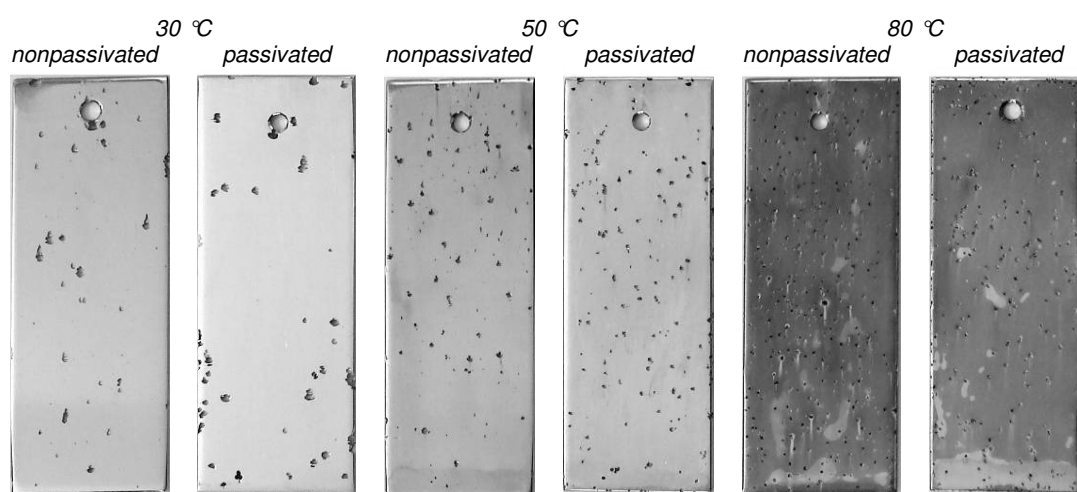


Fig. 3. The pitted surfaces after 24-hours immersion test in 5 %  $\text{FeCl}_3$  solution

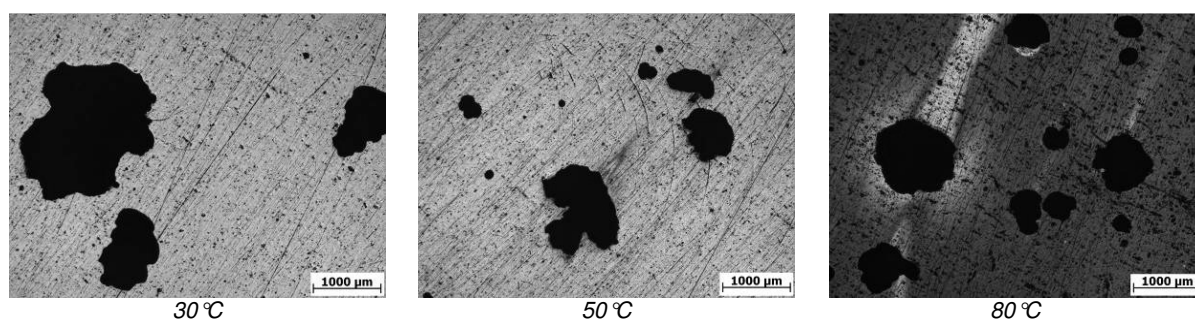


Fig. 4. Size and shape of pits observed microscopically (microscope Zeiss Axio Imager A1m, foto AxioCam MR5)

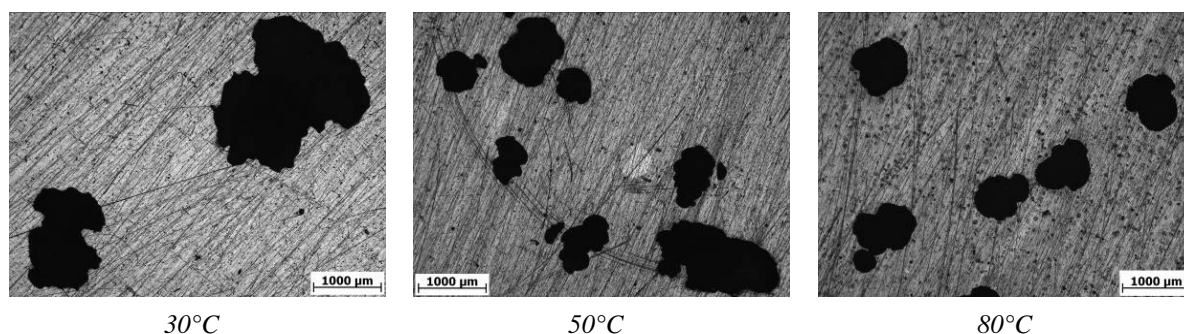


Fig. 5 Size and shape of pits on surfaces passivated in  $\text{HNO}_3$ , observed microscopically (microscope Zeiss Axio Imager A1m, foto AxioCam MR5 )

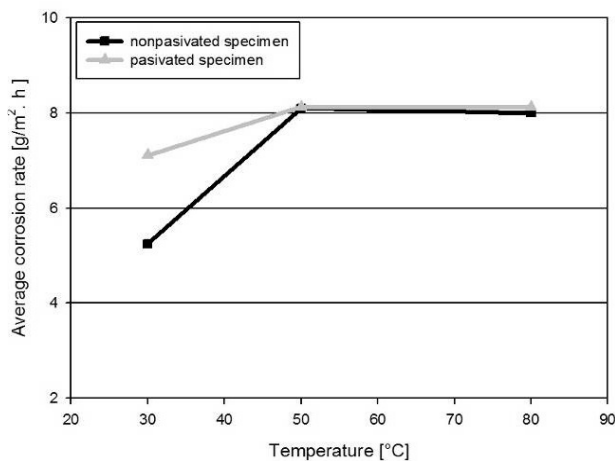


Fig. 6. Average corrosion rates in dependence on the temperature

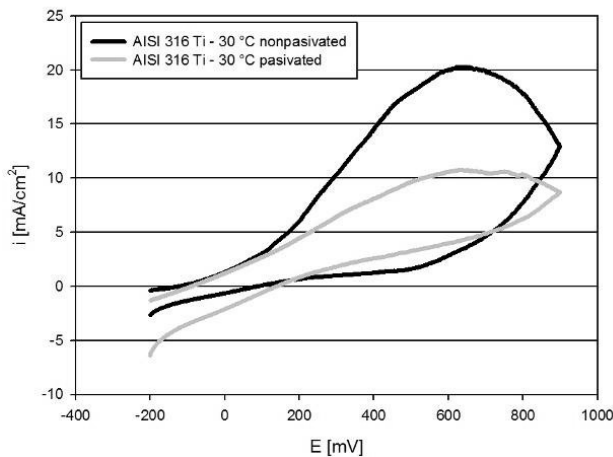


Fig. 7. Cyclic potentiodynamic curves, 5 %  $FeCl_3$ , 30 °C

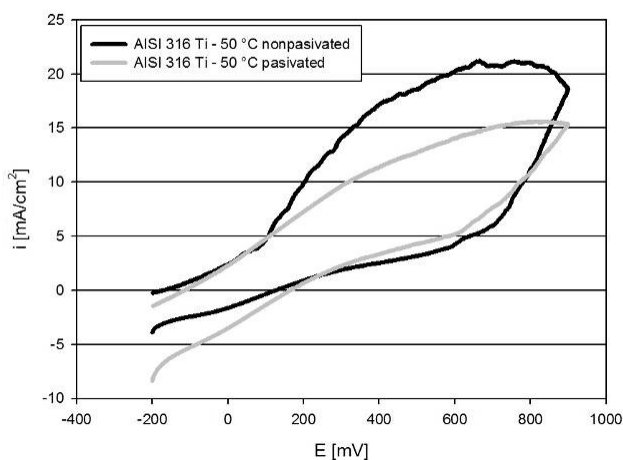


Fig. 8. Cyclic potentiodynamic curves, 5 %  $FeCl_3$ , 50 °C

The pitting potential  $E_p$  is considered to be the main electrochemical characteristic of the pitting corrosion resistance. It can be located as the potential of the strong rising of current density on the polarisation curve of direct measurement [2, 8]. This potential is not equilibrium but rather it describes the state of the pitting corrosion. The move of  $E_p$  to more positive values on the polarization curve means the rise of pitting stability [3, 4, 5].

According to cyclic polarisation curves (Figs. 7, 8), the surface passive film was probably broken at the start potential -200 mV. There is evident increase of current density immediately after overreaching of its zero value. Therefore it was not possible to determine the pitting potential  $E_p$  and the pitting corrosion resistance was considered from the shape of cyclic polarisation curves (Figs. 7, 8). Changes in corrosion kinetics were estimated according to the values of current density reached at the potential of reverse (+900 mV) [9]. The passivation in  $HNO_3$  at both temperatures reduced the current density reached at the potential of reverse. It could point to a fall of the pitting corrosion rate (however it is in variance with results of immersion tests, Fig. 6).

## 5. Conclusions

- The electrolytic polishing of surface does not effect positively on the pitting corrosion resistance of AISI 316 Ti stainless steel in aggressive 5 %  $FeCl_3$  solution at the temperature range 30 - 80°C.
- The appearance of pitted surfaces changes with the rise of the temperature (a density of pitting increases, a size of pits decreases). The strongest change in appearance is observed between 30 and 50°C (Fig. 3)
- Behaviour of the average corrosion rates (as a function of temperature) points to the sharp changes in kinetics of pitting corrosion process in range 30 - 50°C (Fig. 6).
- The shape of cyclic potentiodynamic curves is not typical, it differs from the shape of curves for passive metals (Figs. 7, 8). A current density increases immediately after overreaching of its zero value. It shows evidence of the breaking of passive film and of active local dissolving of metal at the beginning of the experiment at the start potential of -200 mV (it is not possible to locate  $E_p$ ).

- The shape of cyclic potentiodynamic curves (Figs. 7, 8) does not indicate a positive effect of HNO<sub>3</sub> passivation on the thermodynamic stability of polished surface of AISI 316Ti stainless steel in aggressive 5 % FeCl<sub>3</sub> solution at the temperature 30 - 80°C.
- The rise of current density at the potential of reverse (+900 mV) in dependence of temperature (30 - 50°C, Figs. 7, 8) points to changes in kinetics of corrosion and correlates with the rise of corrosion rates calculated by mass losses (Fig. 6).

#### Acknowledgements

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