INFLUENCE OF AISI 316Ti STAINLESS STEEL SURFACE TREATMENT ON PITTING CORROSION IN VARIOUS SOLUTIONS

Pavol Fajnor¹, Tatiana Liptáková¹, Viera Konstantová²

Received 25th October 2010; accepted in revised form 5th December 2010

Abstract

Investigation of the surface treatment effect on the resistance of AISI 316Ti stainless steel to pitting corrosion is presented in this paper. The grinded surfaces without additional chemical treatment, grinded and pickled, grinded, pickled and passivated surfaces are tested. The corrosion tests are carried out by exposition in solution which evoke pitting and by electrochemical cyclic potential - sweep method. According to the results the surface treatment has a great influence on the resistance of the tested material to pitting. It is not possible to estimate the best surface treatment because behavior of AISI 316Ti stainless steel with different surface state depends on the mechanism of corrosion processes which vary in the used experimental methods.

Keywords: stainless steel, pitting corrosion, surface treatment, passivation, pickling, depassivation potential, repassivation potential.

1. Introduction

The quality of passive layers, formed by the reaction of stainless steel with oxygen, determines their corrosion resistance. A passive layer is stable, thin, nonporous, adhering well to the metal and protects the metal in usual environments (atmosphere, water, soil) against corrosion. Protective efficiency of passive layers depends on many factors, which significantly modify the surface, because they affect:
- The real size of the surface that determines the concentration of reacting metal,
- The surface morphology, which creates localities with different corrosive characteristics [1].

Many previous investigations [2, 3] have reported that the corrosion resistance of stainless steels depends on the composition, structure and thickness of the passive film. Unfortunately, few reports could establish a kind of direct correlation between the protective quality of films and a well-defined composition or structure factor. The composition and structure of the passive film formed on a stainless steel in methanol solution with chloride ions under high temperature and high pressure indicating that the film was a double-layer structure consisting of a Fe oxide-rich outer layer and a Cr oxide-rich inner layer [4].

The aim of this work is to study the effect of surface treatment of AISI 316Ti stainless steel on pitting corrosion resistance. Statistical data classify pitting corrosion in terms of frequency caused emergencies in different industries to the third place in the overall corrosion and corrosion cracking. The attack of pitting corrosion affects only a small fraction of the surface but it penetrates into the depth of the material and significantly reduces the effective cross-section components or changes properties of equipment.

¹P. Fajnor, Ing., T. Liptáková, assoc.prof. RNDr, PhD. – Department of Materials Engineering, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 1, 010 26 Žilina, Slovak Republic.
²V. Konstantová, Ing. PhD. – Department of Design and Mechanical Elements, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 1, 010 26 Žilina, Slovak Republic.
*Corresponding author, e-mail address: pavol.fajnor@fstroj.uniza.sk
In practice this kind of corrosion often causes collapses and large economic and environmental damages [1]. In practice, shot-peening by metallic and non-metallic particles, grinding or cutting operations are used for surface treatment of stainless steel. It is necessary to realize all mechanical treatments to avoid unacceptable oxidation, excessive roughness of surface, contamination, especially by metallic materials with different potential. In many cases, it is acceptable to combine mechanical treatment with chemical treatment (pickling, passivation) [5].

Chemical treatment is used for the elimination of mechanical and chemical impurities from the surface and for decreasing roughness of the surface. This creates better conditions for the passive layer formation. According to many scientists following surface treatment influence on pitting resistance of stainless steels, one can agree that it could have an important effect on individual stages of pitting (e.g., nucleation, metastable and stable growth of corrosion pits, repassivation) [6].

2. Experimental material

The AISI 316Ti austenitic Cr-Ni-Mo stainless steel stabilized by Ti was used as an experimental material (STN 41 7348). The chemical composition is shown in Table 1.

<table>
<thead>
<tr>
<th>Content element [wt %]</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>16.5</td>
<td>10.6</td>
<td>2.12</td>
<td>1.69</td>
<td>0.012</td>
<td>R</td>
</tr>
<tr>
<td>C</td>
<td>0.41</td>
<td>0.04</td>
<td>0.43</td>
<td>0.026</td>
<td>0.002</td>
<td>E</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Due to molybdenum additives, AISI 316Ti stainless steel has good plasticity and high resistance against acids and deep local corrosion. It is a non-ferromagnetic steel, with higher yield stress and strength. After welding of thin plate heat treatment is not necessary, because the steel is stabilized by Ti. All methods of arc-welding are possible to be used for this steel except gas-welding. Mechanical properties are shown in Table 2.

<table>
<thead>
<tr>
<th>Mechanical properties of AISI 316Ti stainless steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rp0.2 [MPa]</td>
</tr>
<tr>
<td>282</td>
</tr>
</tbody>
</table>

AISI 316Ti stainless steel is commonly used for the production of construction parts and machines, especially in chemical, petrochemical and pharmaceutics industry, and also for the production of tanks for the transport of aggressive substances. The higher yield strength in tension is advantageous in mechanical stressed constructions (for example in building industry). The experimental material was annealed and pickled after rolling. Dimensions of plates were 1500 x 1000 mm with thickness of 1.5 mm.

2.1 Metallography of experimental material

The specimens obtained from the middle of the plate (transverse and longitudinal section) are used for microstructural analysis of the experimental material (Fig. 1). Preparation of metallographic specimens includes sample preparation, grinding, polishing and etching [7].

![Fig. 1 AISI 316Ti stainless steel microstructure, etch. 10 ml HNO₃ + 30 ml HCl + 30 ml glycerine](image)

The microstructure of the steel is created by polyedric grains of austenite with deformation
and annealing twins formed during rolling and annealing. The significant lining is caused by rolling. Sharp coarse particles of a cuboid shape can be observed in the microstructure too. AISI 316Ti stainless steel is stabilized by Ti (0.41 %) and also some content of Mo (2.12 %) tends to enter into carbides of Ti. There are the carbides of the type (Ti, Mo)C [8].

2.2 Surface treatment of AISI 316Ti

The experimentally tested surfaces were mechanically and chemically modified. The mechanical treatment consisted of grinding by SiC paper with granularity of 320 in transverse section and by SiC paper with granularity of 500 in longitudinal section (Fig. 2). The chemical treatment consisted of pickling and passivation.

Pickling parameters: solution of composition - 144 ml of 65% HNO₃ + 8.9 ml of 40% HF + 790 ml of H₂O, time of 30 min, temperature of 21 ± 1 °C.

Passivation parameters: solution of composition - 247 ml of 65% of HNO₃ + 753 ml H₂O, time of 120 min, temperature 21 ± 1 °C.

According to the surface treatment the specimens are divided into three groups:

- grinding (mechanical treatment) – B specimen
- grinding + pickling (mechanical + chemical treatment) – BM specimen
- grinding + pickling + passivation (mechanical + chemical treatment) – BMP specimen

2.3 The topography of surface

The topography of treated surface was measured by University of Žilina, in department design and mechanical elements. Photo documentation was made on atomic force microscope Cantilever NG10 in semicontact mode. The Atomic Force Microscopy used three scanning techniques: contact, semicontact and non-contact mode. In this study the semicontact mode was used for analysis of sample topography (Fig. 3). Conditions of scanning: Cantilever NG 10, Resonance - Mag 9.67 nA, Frequency - 246.68 kHz, scan area - 50x50 µm.

---

a) topography of surface – B specimen

b) topography of surface – BM specimen
c) topography of surface – BMP specimen

Fig. 2 Specimen shape for experiment
Observation of surface morphology and comparison of real surface area was evaluated by the topography. Fig. 3 shows waviness of tested materials after mechanical and mechanical-chemical treatments. B specimen (mechanical treatment) has highest waviness of surface and also the largest real surface area for contact with experimental solution. The waviness of surface on BM and BMP specimens is less than surface waviness of B specimen.

3. Electrochemical characteristics of the tested surfaces

The electrochemical tests are performed by using the electrochemical impedance spectroscopy (EIS) in solutions of 0.9% NaCl and 1.0% FeCl$_3$ at laboratory temperatures (21 ± 1 °C). This method allows establishing the value of polarization resistance of less conductive corrosion systems, for example when a passive layer with good adhesion is created on the metal surface. The polarization resistance ($R_p$) is an electrochemical property characterizing the material resistance to polarization in the experimental environment. The higher value of $R_p$ represents better corrosion resistance of the material in corrosion environment. The electrochemical experiments were 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 with PGZ 100 measuring unit. The scheme of circuit connection and measuring principle are described in detail in [10].

The time for potential stabilization between the specimen and electrolyte is set to 10 minutes. The measurement frequency ran in a range from 100 kHz to 1 mHz with 10-times frequency change per decade. The amplitude of AC voltage was 20 mV for specimen. DC voltage which polarizes the specimen during the test, is set to the measured value of free potential after 10 minutes of stabilization [11, 12].

Nyquist diagrams resulting from the electrochemical impedance spectroscopy measurements are in the coordinates of the imaginary and real components of impedance (Figs. 4, 5). Impedance is the resistance of electrical components and phase shift versus voltage current passing alternating electric current of the frequency. Nyquist diagrams
analysis characterizes the material resistance to influence of surrounding environment. Diameter of determined semicircle represents the value of material resistance.

According to the results in Figs 6 and 7 it can be seen that the redox potential of experimental solution significantly influences the resistance of metal to polarization. In the solution of the ferric chloride the grinded surface is the most stable. In the natrium chloride solution the values of $R_P$ of the tested surfaces are evidently higher but the differences among the surfaces are not so essential. The ferric chloride solution with higher redox potential than the NaCl initiates the creation of pit much more intensively on the chemically treated surfaces.

![Fig. 6 Values of polarization resistances of AISI316Ti in 1% FeCl₃](image)

**Fig. 6 Values of polarization resistances of AISI316Ti in 1% FeCl₃**

![Fig. 7 Values of polarization resistances of AISI316Ti in 0.9% NaCl](image)

**Fig. 7 Values of polarization resistances of AISI316Ti in 0.9% NaCl**

4. Chemical and electrochemical test of pitting resistance

The immersion test is carried out in the solution of 1% FeCl₃ and 0.9% NaCl according to the standard ASTM G 48 and ASTM G 46. In general, pitting corrosion is evoked by high value of the experimental solution redox potential. The environment temperature during the test is 21 ± 1 °C in solution of 1% FeCl₃ and 37 ± 2 °C in solution of 0.9% NaCl. After exposition in the test solution the samples are cleaned in distilled water and dried. The weight losses are determined with the accuracy of $10^{-5}$ g. The calculated corrosion rates and densities and size of pits (ČSN ISO 11463) are in Table 3. It can be seen that the resistance to pitting is the best for the grinded sample. According to the results the main difference is the size of pits meaning that the surface properties affect the stage of pit growing (Fig. 8).

### Table 3

<table>
<thead>
<tr>
<th>Specimen with different surface treatment</th>
<th>Corrosion rate [g.m^{-2}.h^{-1}]</th>
<th>density (A) and size (B) of pits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solution of 1% FeCl₃</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.142</td>
<td>1A1B</td>
</tr>
<tr>
<td>BM</td>
<td>0.757</td>
<td>1A2B</td>
</tr>
<tr>
<td>BMP</td>
<td>0.494</td>
<td>1A2B</td>
</tr>
<tr>
<td><strong>solution of 0.9% NaCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.0033</td>
<td>-</td>
</tr>
<tr>
<td>BM</td>
<td>0.0037</td>
<td>-</td>
</tr>
<tr>
<td>BMP</td>
<td>0.0031</td>
<td>-</td>
</tr>
</tbody>
</table>

Corrosive attack on surface and edges of the specimens in solution of 0.9 % NaCl is not visible.

![Fig. 8 Character and intensity of corrosion attack in different treated samples of AISI 316Ti stainless steel](image)
By the cyclic potential - sweep method (cyclic polarization of specimen) the characteristics of metal pitting resistance ($E_p$ – potential of breakdown of passive layer and creation of corrosion pit and $E_r$ – potential of corrosion pits repassivation) are measured [13].

The electrochemical tests of AISI 316Ti stainless steel are performed in 1% FeCl$_3$ and 0.9% NaCl solutions at laboratory temperatures ($21 \pm 1 ^\circ C$). The cyclic potential - sweep characteristics were 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 with PGZ 100 measuring unit.

The time for potential stabilization between the specimen and electrolyte is set to 10 minutes. Cyclic potential - sweep parameters: starting potential -200 mV vs. free, potential turnover +900 mV vs. free, finish potential -200 mV vs. free, scan rate used 1 mV/s, specimen area 1 cm$^2$. The electrochemical characteristics of AISI 316Ti stainless steel with different surface treatment are in Table 4 and in figs. 9 and 10 the course of behavior of tested sample during cyclic potential - sweep test is shown.

The surface treatments significantly affect the resistance of AISI 316Ti stainless steel to pitting corrosion.

Mechanical and chemical treatments of AISI 316Ti stainless steel differently affect pitting corrosion resistance depending on corrosion mechanism. It is evident from the obtained immersion test results, that pitting corrosion, which is evoked by the solution with high redox potential of (the process is controlled by cathodic reaction) and the results of electrochemical tests (the process is controlled by anodic reaction).

In the solution of FeCl$_3$ (0.019 mol.dm$^{-3}$ of Cl$^-$) the polarization resistances of the samples with various surface treatment are about two orders of magnitude lower than in the NaCl solution (0.015 mol.dm$^{-3}$ of Cl$^-$), however concentrations of chlorides are similar.

### Table 4

| Electrochemical characteristic of AISI 316Ti |
|------------------|-------|-------|
| specimen         | $E_p$ [mV] | $E_r$ [mV] | $E_{db}$ [mV] | $E_{re}$ [mV] |
| B                | 438   | -150.8 | 282.5         | -47.42        |
| BM               | 562.8 | 50.61  | 308.6         | -64.9         |
| BMP              | 456.7 | -84.21 | 260.2         | -0.5          |

### 5. Conclusion

- The surface treatments significantly affect the resistance of AISI 316Ti stainless steel to pitting corrosion.
- Mechanical and chemical treatments of AISI 316Ti stainless steel differently affect pitting corrosion resistance depending on corrosion mechanism. It is evident from the obtained immersion test results, that pitting corrosion, which is evoked by the solution with high redox potential of (the process is controlled by cathodic reaction) and the results of electrochemical tests (the process is controlled by anodic reaction).
- In the solution of FeCl$_3$ (0.019 mol.dm$^{-3}$ of Cl$^-$) the polarization resistances of the samples with various surface treatment are about two orders of magnitude lower than in the NaCl solution (0.015 mol.dm$^{-3}$ of Cl$^-$), however concentrations of chlorides are similar.
According to the pit density and size of the pits determined after the immersion tests it can be said that the surface treatment influences mainly the stage of pit growth. From the results of the cyclic potential-sweep test it is evident that the specimens of AISI 316Ti stainless steel with treated surface by pickling and passivating have better corrosion resistance in both experimental solutions than only grinded specimens.

Acknowledgement

This research was supported partially by the grant VEGA grant No. 1/0603/08 and RAILLBCCOT, ITMS Code 26220220011 V. Authors gratefully acknowledge this support.

References