PITTING CORROSION OF STAINLESS STEEL AT THE VARIOUS SURFACE TREATMENT

Viera Zatkalíková[1,*], Tatiana Liptáková[1]

[1]Department of Materials Engineering, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 1, 010 16 Žilina, Slovak Republic
[*]corresponding author: Tel.: +421 41 513 2610, e-mail: viera.zatkalikova@fstroj.uniza.sk

Resume

The stainless steel surface treatment is very important with regard to its pitting corrosion susceptibility. An effect of various types surfacing on pitting corrosion resistance of AISI 304stainless steel is investigated in this work. The samples of the tested material are turned, blasted, peened, grinded and a half of them are pickled to achieve higher purity of surfaces and better quality of passive film. Eight types of different finished surfaces are tested by electrochemical and immersion tests to determine corrosion behaviour in conditions where pitting is evoked by controlled potential and second by solution with high redox potential. By this way the effect of mechanical and chemical surface treatment on the resistance to pitting corrosion, character, size and shape of pits are compared in the conditions of different mechanisms of corrosion process.

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1. Introduction

In spite of the fact the pitting corrosion has been investigated for many years there is no generally established definition of its mechanism and effect of various factors (temperature, concentration of aggressive components, surface finishing etc.). Many authors have obtained precious and generalized results by experimental works, but even through behavior of stainless steels in working conditions, they were very surprising.

The reason is that not all the factors variable in practice and evoking pitting can be involved in experiments. The resistance of stainless steel is generally determined by PREN (Pitting Resistance Equivalent Number), but it does not seem to be sufficient. Similar conditions in practice can evoke different development of local corrosion failure of the same stainless steel with different surface treatment. The metal surface quality is an important parameter affecting the nucleation of metastable and stable pits [1, 2, 3, 4]. More homogeneous the surface is, both chemically and physically, the higher is the pitting potential, the lower is the pit number and the better the metal resistance is to pitting [1]. Pistorius and Burstain [5] indicated by the investigation of the effect of surface roughness on metastable pitting of stainless steel, that the number of metastable pits decreases with an increasing grit number of silicon carbide paper at a given potential. Similar results were obtained by Zuo et al [6]. Coates [7] concluded that a mechanical treatment decreases the surface roughness and therefore improves the pitting resistance however the chemical passivation (pickling treatment) causes greater improvements.

Sasaki and Burstein [8] reported that the pitting potential is lower for rougher surfaces than for smoother ones. By Asami and Hashimoto [9], the chemical surface treatment (pickling, passivation) appears to affect the chromium content in the passive film. According to Sydberger [10] the beneficial effect of chemical surface treatment consists in the removal of sulfide inclusions.

In our work the resistance to pitting is searched by two methods with different mechanisms (potentiodynamic and immersion test). The probability of pitting creation can be expressed by electrochemical characteristic (E_p – pitting potential, E_{corr} – corrosion potential) in the terms 1 [11]:

$$\Delta E_p = E_p - E_{corr} \tag{1}$$

The positive value of ΔE_p suits to pitting resistance.

In the case that pitting is evoked by solution with high redox potential E_{redox}, probability of pitting creation is given by terms (2) [11]. More positive value characterizes the higher pitting resistance.

$$\Delta E_p = E_p - E_{redox} \tag{2}$$

The solution $FeCl_3$ is used in our experiments as the one with high positive redox potential coursed by Fe^{3+} content.

2. Experiments and results

The chemical composition of tested steel is in Table 1. By metalographical method the polyedric austenitic grains with visible twins were identified. In structure the cubic carbides (Ti,Mo)C and $(Cr,Mo)_{23}C_6$ carbides were observed too.

The tested samples were made of the AISI 304 rolled sheets.

2.1. Surface treatment of the tested samples

The surfaces of the AISI 304 samples were worked by various ways [12]:

- Turning at operating speed 300 min^{-1}, advance of tool 0.117 $mm\cdot min^{-1}$, cutting depth 0.3 mm (A).
- Peening by stainless steel balls (AISI 304) of diameter 0.6 mm, peening angle 90° in the distance 80 mm in blast machine with power 45 g of $balls\cdot s^{-1}$, diameter of air jet 6 mm and work jet 13 mm (B).
- Blasting by white corundum with the grain size 0.25 mm, blasting angle 45° (C) and 90° (D) in the distance 100 mm, working pressure 0.4 MPa, diameter of air jet 8 mm and work jet 13 mm.

A half of these samples were chemically treated by pickling so there were prepared 8 types of different surfaces. Pickling is used to achieve higher surface purity and higher quality of passive layer. The pickled samples were exposed to the 20 % solution of HNO_3 + 1 % HF at the temperature 23 ± 2° C for 30 minutes [12]. After pickling the samples were thoroughly washed by distilled water and dried on the free air at laboratory temperature. The roughness was measured by surface measurement device Hommel Tester T10, absolute scanner TKL 300 on the all tested surfaces. Selected roughness characteristic *Ra* (arithmetical mean deviation of the assessed profile) is presented in Table 2. The magnitude of the *Ra* is not changed by pickling very much but topography of all surfaces is more rugged. The surface geometry significantly influences corrosion behaviour because it changes mainly its magnitude of real area. The change of the surface mould after pickling is clear from the figures 1 - 4. The measurements were made by the laser three-dimensional surface measurement device RODENSTOCK LASER SYSTEM type RM 600.

Table 1

Chemical composition of tested steel (in wt. %) and PREN

Cr	Ni	Mo	Mn	N	Ti	C	Si	P	S	Fe	PREN
16.87	9.9	0.16	1.49	0.011	0.49	0.08	0.52	0.027	0.019	balance	17.046

Table 2

Ra (μm) *roughness characteristic of the tested surfaces*

A	A + pickling	B	B + pickling
3.0	2.44	3.24	3.48
C	C + pickling	D	D + pickling
2.64	2.24	4.32	2.3

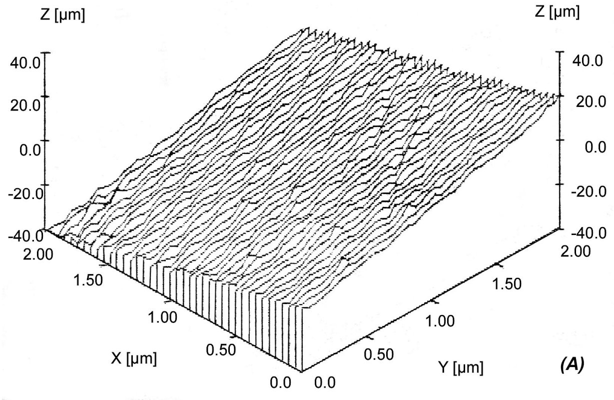


Fig. 1. Topography of the AISI 304 surface after turning (A)

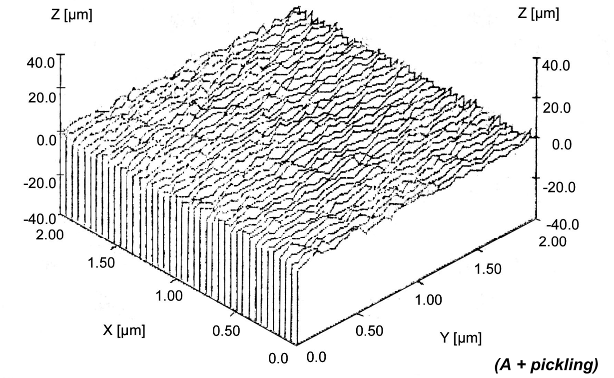


Fig. 2. Topography of the AISI 304 surface after turning and pickling (A + pickling))

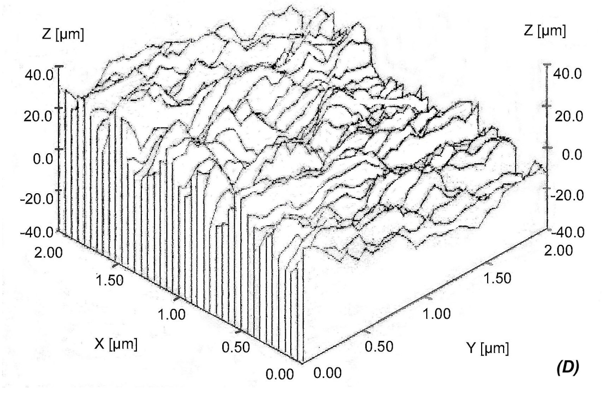


Fig. 3. Topography of the AISI 304 surface after blasting by white corundum, blasting angle 90º (D)

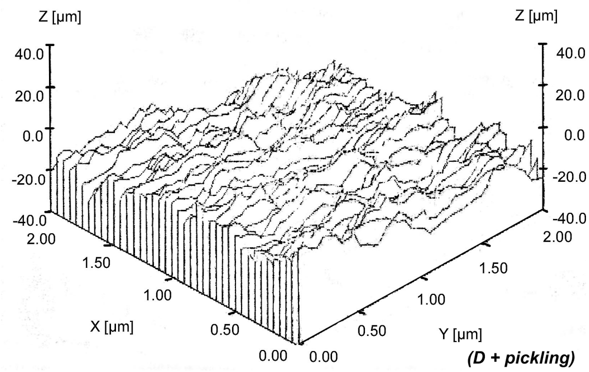


Fig. 4. Topography of the AISI 304 surface after blasting by white corundum, blasting angle 90º and pickling (D + pickling))

2.2 Corrosion tests

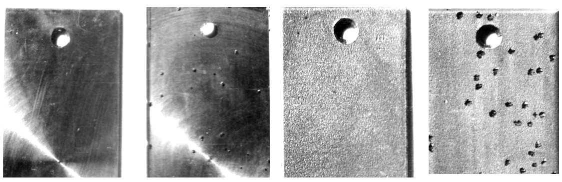
The samples with different surface finishing were investigated by electrochemical and immersion tests used for evaluation of pitting corrosion resistance. The potentiodynamic cyclic tests were performed on the laboratory apparatus VoltaLab 10, curves and results were recorded in the programme Voltamaster 4. The main unit PGZ 100 is the fundamental of the equipment. The measurements were completed on the area 1 cm^2 to the saturated calomel electrode SCE in the 0,5 M solution of NaCl at the temperature 23 ± 2° C with the shift rate of potential 5 $mV \cdot s^{-1}$. Comparison of pitting corrosion resistance by values of pitting potential E_p and repassivation potential E_{rp} is in the Table 3. The standard exposition 5 hour lasted test in the 6 % $FeCl_3$ solution (ρ = 1.49 $g \cdot cm^{-3}$) was carried out too (size of samples is 80 x 30 mm) to appreciate objectively the pitting resistance of the steel with various surface finishing. The reason is a different mechanism of corrosion in both tests. After immersion tests the corrosion rates v_{corr} were calculated (table 3) and the pits densities were established on the surface areas. The shape and arrangement of the ones was documented in Fig. 5.

According to the obtained results it is obvious that the electrochemical tests give sufficient information on thermodynamic stability. By comparison of the electrochemical test results it can be said that pickling improves quality of passive layers of the all various mechanically finished surfaces. It can be seen on the values of the pitting potential E_p and repassivation potential E_{rp}. They are more positive on samples with chemical treatment. These results correlate with other ones published in this research area [5, 6, 13, 14]. In the condition of immersion tests with a different corrosion mechanism the corrosion rate and density of pits are higher on the pickled surfaces (Fig. 5).

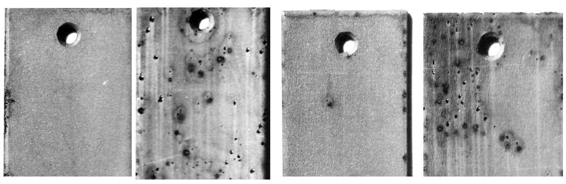
Table 3

Parameters for evaluation of resistance to pitting corrosion

Surface treatment	E_p (mV)	E_{rp} (mV)	v_{corr} ($g.m^{-2}.h^{-1}$)	Pit density on the area of sample ($10^4 \cdot m^{-2}$)
A	+ 423	-123	5.37	0
A + pickling	+ 513	-82	11.4	1.3
B	+ 210	-150	16.22	0
B + pickling	+ 490	-72	29.84	3
C	+ 140	-180	15.6	0
C + pickling	+ 600	-3	30.14	6.3
D	+ 120	-185	17.69	0
D+ pickling	+ 473	-13	29.65	5.7



A A+ pic. B B+ pic.



C C+ pic. D D+ pic.

Fig. 5. The documentary photos of the pitting corrosion attack of the AISI 304 with various surface treatment after immersion test (2/3 of real size)

Corrosion pits are situated mostly on edges of samples on the only mechanically finished surfaces but whole surface is attacked on chemically treated samples. By comparison of the surface roughness parameters after mechanical and chemical working it can be said they are not very different in contrast to their topography. It changes the real magnitude of surface what is an important factor of pitting in the immersion test. This way the concentration of reactants grows and the number of pit nucleation places, too. The higher surface segmentation after pickling can affect transport phenomena during initiation and propagation of pits (capillaries, narrow crevices). The smallest effect of pickling on the surface segmentation was proved on the peened surface.

It was necessary to compare the surface size of tested samples in order to confirm the effect of surface real size on process of pitting corrosion. The size of surface area is measured on the variously mechanically finished surfaces by the relative method of polarization resistance measurement. According to this method a polarization resistance of a metal surface is compared with standard (surface of the same steel grinded with abrasive paper 400). Its polarization resistance is considered to be unit. The measurement was carried out in the 3 $mol \cdot dm^{-3}$ solution of NH_4Cl + $K_4[Fe(CN)_6]$ 0,01 $mol \cdot dm^{-3}$ + $K_3[Fe(CN)_6]$ 0,01 $mol \cdot dm^{-3}$ [11, 12]. The values of the determined polarization resistances are in the Table 4. The relative surface areas (*SRF*) are calculated after the equation (3):

$$SRF = \frac{R_s}{R_m} \tag{3}$$

R_s - polarization resistance of the standard, R_m - polarization resistance of the tested sample.

Graphically expressed dependences of corrosion rates on the area size are in figure 6. Corrosion rates are calculated from the weight losses after immersion test. From our results the relation between area size and corrosion rate can be seen. Comparing the samples B, C, D, the differences of corrosion rate and size area are not great, but the sample A is expressively different. The pickled surface areas could not be measured by the method of polarization resistance. But according to the determined corrosion rates and evaluation of corrosion attack intensity it can be stated that pickling expands real areas of the all differently mechanically treated samples and so increases corrosion rate and number of pits too. On the other hand pickling makes the passive layer more qualitative but it is not the guaranty of higher resistance to pitting corrosion in all conditions.

Table 4

Surface area measurement of different treated samples of the AISI 304

Surface treatment	Polarization resistance R_m [Ω. cm^2]	*SRF*
A ■	2650	1.06
B ♦	147	19.1
C ▲	130	21.6
D ●	120	23.4

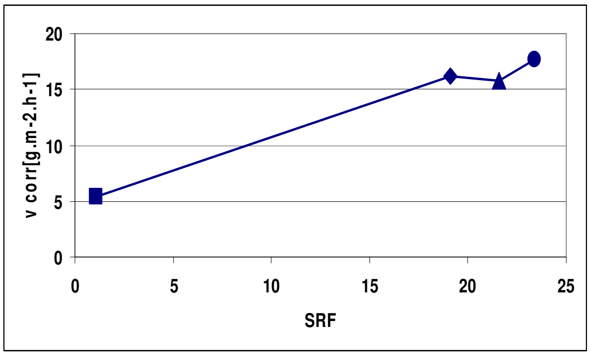


Fig. 6. Dependence of corrosion rate on size of surface

The same tests were made on the AISI 316 Ti steel to find if the chemical treatment (passivation) had a similar effect on corrosion behaviour of different stainless steel. The obtained results were similar [15, 16].

3. Conclusions

1. The chemical surface treatment (pickling and passivation) improves the protective passive film of stainless steels. It was clearly seen on the values of electrochemical characteristics of pitting corrosion (the corrosion reaction was controlled by anodic oxidation).
2. The different results of electrochemical and exposition tests carried out at normal working temperatures are connected with the conversion of mechanism of the pitting corrosion process (different control step in corrosion process). In spite of the fact that chemical treatment improves passive layer, its effect on susceptibility of stainless steels to pitting corrosion in various conditions is different.
3. The mentioned chemical treatment (pickling and passivation) of variously mechanically treated surfaces transforms their roughness and segmentation. It creates the capillary effect in close crevices and this fact changes kinetics of the pitting corrosion. According to results of immersion tests the main reason of pitting corrosion rate increasing is extension of real surface size.
4. The size and the shape of pits are evidently related to the form of mechanical finishing (blasting, turning).

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References

[1] Z. Szklarska – Smialowska: Pitting and crevice corrosion. NACE International, Houston, Texas, 2005.

[2] T. Liptáková: Základy korózie a ochrany kovov v plynárenstve. *(Fundamentals of corrosion and metals protection in gas industry)* EDIS - Žilinská univerzita, Žilina 1997. *(in Slovak)*

[3] T. Liptáková: Mater. Eng. / Mater. Inž. 7(3) (2000) 31-37.

[4] B. Hadzima, T. Liptáková: Základy elektrochemickej korózie kovov *(Fundametals of electrochemical corrosion of metals)*, EDIS - Žilinská univerzita, Žilina 2008 *(in Slovak)*

[5] G. T. Burstein, P. C. Pistorius: Corrosion 51 (1995) 380-385.

[6] Y. Zuo, H. T. Wang, J. M. Zhao: Corr. Sci. 44 (2002) 13-24.

[7] G. E. Coates: Mater. Perform. 29 (1990) 61-65.

[8] K. Sasaki, G. T. Burstein: Corr. Sci. 38 (1996) 2111-2120.

[9] K. Asami, K. Hashimoto: Corr. Sci. 19 (1979) 1007-1017.

[10] T. Sydberger: Werks. Korr. 32 (1981) 119-128.

[11] M. Pražák: Research work 57/89, SVÚOM Praha, Praha 1989.

[12] T. Liptáková: Vplyv opracovania a pracovných podmienok na odolnosť nehrdzavejúcich ocelí proti bodovej korózii. *(Influence of treatment and working conditions on pitting corrosion resistance of stainless steels),* PhD thesis, VŠDS Žilina, Žilina 1990 (in Slovak)

[13] N. B. Salah-Rousset, M.A. Chaouachi:. Mater. Eng. Perform. 5(2) (1996) 225-231.

[14] L. Škublová, B. Hadzima, L. Borbás, M. Vitosová: Mater. Eng. / Mater. Inž. 15(4) (2008) 18-22

[15] V. Zatkalíková: Bodová korózia ocele AISI 316Ti pri rôznych prevádzkových podmienkach *(Pitting corrosion of AISI 316Ti steel at various operating conditions)*. PhD Thesis, ŽU v Žiline, Žilina 2008 *(in Slovak)*

[16] B. Hadzima, V. Škorík, L. Borbás, L. Oláh: Mater. Eng. / Mater. Inž. 15(3) (2008) 27-30.