Influence of chemical removal of oxide films, formed by exposure of high-alloy steel to air at high temperatures, on their pitting liability

Ivan Budić[1], *Vesna Alar*[2] *and* ***Ivan Esih***[3]

1. *University of Osijek, Faculty of Mechanical Engineering, Trg Ivane Brlić Mažuranić 2, 35000 Slavonski Brod, Croatia, ivan.budic@sfsb.hr*
2. *University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, I.Lučića 1, 10000 Zagreb, Croatia, vesna.alar@fsb.hr, corresponding author*
3. *Croatian Society for Materials Protection, I.Lučića 1, 10000 Zagreb, Croatia, hdzama@fsb.hr*

Summary

Oxide film or scale, formed on stainless steels in hot air during manufacture or in exploitation, affect their corrosion resistance harmfully. This effect has been studied by testing the liability of stainless steels with thermal oxides to pitting in $FeCl_3$-solution according to ASTM G48-99a. For evaluation of results eight pitting criteria, based on determination of pits number, their depths and mouths areas, have been used. Stainless steel specimens were exposed to testing solution

- in the initial state (ie. without thermal oxides),
- after heating in air (ie. with thermal oxides), and
- after heating in air and subsequent pickling in agents containing HNO_3 and HF.

Beside sheet specimens, welded pipe specimens have been tested, too. Thereby it was established that pitting criteria vary considerably on the weld itself, on heat tints zones and on base metal. The discussion of results shows that the removal of thermal oxides by pickling decreases general pitting tendency but it is impossible to achieve initial localised corrosion resistance therewith. After all, it may be concluded that the investigation confirms modern concepts about nucleation and growth of pits on stainless steels, elaborated by G.T.Burstein and collaborators.

1 Introduction

Exposure of stainless steels (SS) in exploitation or during manufacturing procedures (like casting, welding, rolling, drawing, forging, grinding, heat treatment etc.) to hot air or gaseous mixtures containing O_2, CO_2 and /or water vapour results in formation of oxide films or scales on SS surfaces that affects their corrosion behaviour in water solutions [1]. The existence of the mentioned oxide layers on SS substrates is usually technically or commercially unacceptable. Frequently it increases the propensity to localised corrosion, too [2]. It is possible to remove oxide layers by several chemical or mechanical techniques but their usefulness is often questionable, especially regarding the liability of SS to pitting in chlorides containing solutions [3].

This paper reports about a study of effects of thermal oxide layers and their chemical removal from austenitic CrNi- and CrNiMo-SS surfaces on susceptibility to pitting corrosion in $FeCl_3$-solution. After exposure to the solution characteristic criteria of pitting progress on specimens have been determined.

2 Experimental and results

Pitting corrosion liability of austenitic SS has been investigated by exposure to $FeCl_3$-solution at room temperature according to ASTM G 48-99a, and that in the form of

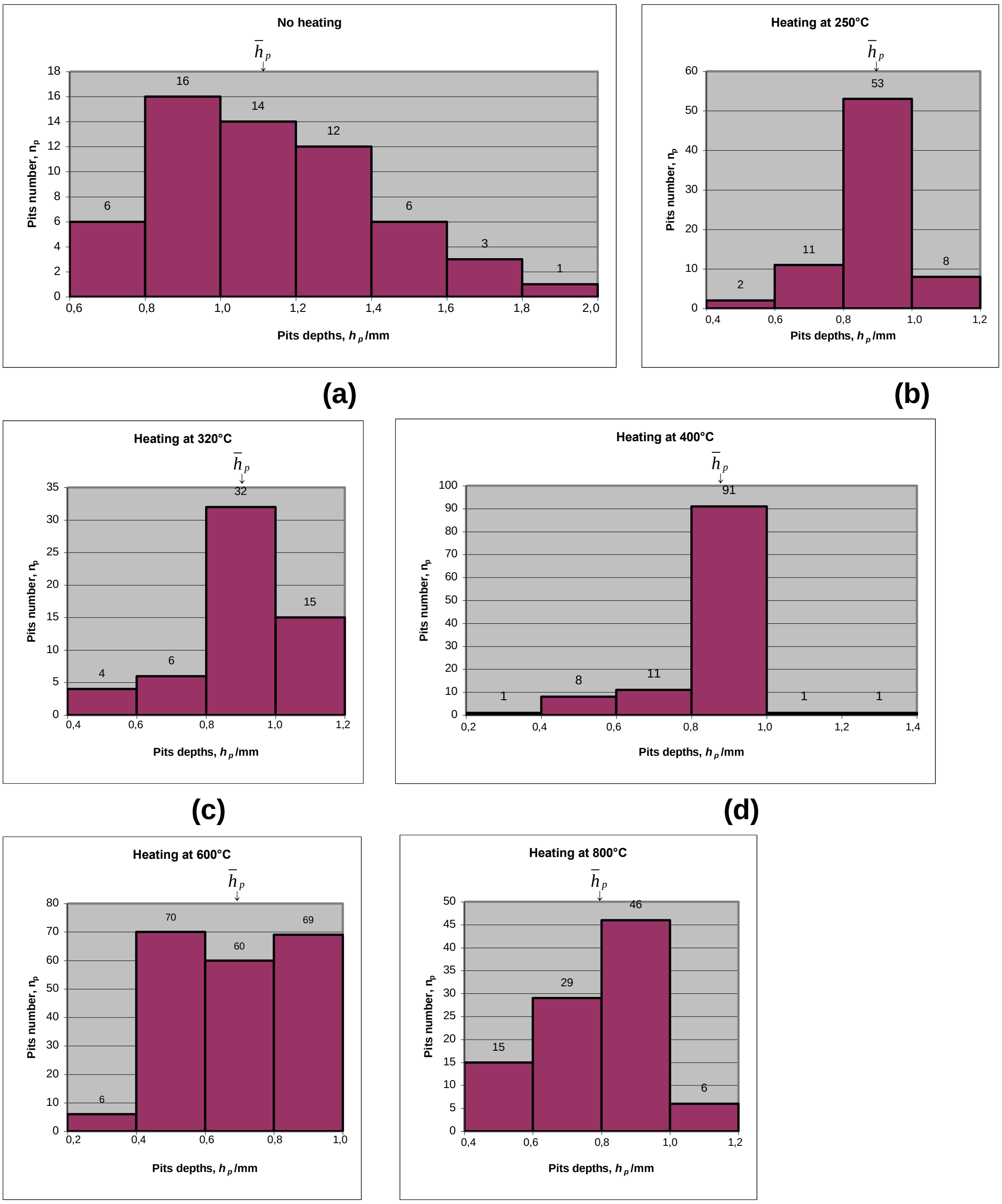
- **a)** sheet specimens of AISI 304 SS oxidised by heating in air for 20 min at 250, 320, 400, 600 and 800˚ C
- **b)** sheet specimens of AISI 316L SS oxidised by heating in air for 20 min at 200, 400, 600, 800 and 1000˚C without further treatment or after removal of oxide layers by pickling with a paste containing HNO_3 and HF, as well as
- **c)** pipe specimens of AISI 316L SS prepared by circumferential TIG-welding from two pieces of pipe without further treatment or after removal of oxide layers by rinsing/pickling with a solution containing HNO_3 and HF at room temperature.

For comparison, identical specimens in the initial state, ie. without heating and pickling, have been tested, too. After pull-out of specimens from the $FeCl_3$-solution necessary measurements for the evaluation of pitting tendency have been accomplished. The results of measurements on specimens mentioned under **a)** are summarised as pitting criteria in **Table 1**. The distribution of pits depths for such specimens is presented in **Figure 1** and appearance of specimens tested in the initial state and after heating at 600˚ C is shown in **Figure 2**.

Table 1: Geometry of pitting on specimens under **a)** after 24 h of exposure to $FeCl_3$-solution; observed surface area S=283.5 cm^2

Heating (˚C)	Pits number n_p	Pits depths (mm) average $\bar{h}_p$	Pits depths (mm) maximum $h_{p\,max}$	Average pit mouth area $\bar{S}_p$ mm^2
no	58	1.12	1.85	3.01
250	74	0.91	1.11	3.32
320	57	0.92	1.07	3.53
400	113	0.87	1.30	2.76
600	205	0.67	1.00	2.65
800	96	0.80	1.04	2.26

Heating (˚C)	Pitting area fraction (%) $n_p \bar{S}_p / S$	Pitting penetration density $n_p \bar{h}_p / S$ (mm/cm^2)	Average pit severity $\bar{h}_p / \bar{S}_p$ (mm^{-1})	Apparent pits volume(mm^3) $n_p \bar{h}_p \bar{S}_p$
no	0.62	0.229	0.372	196
250	0.87	0.238	0.274	224
320	0.71	0.185	0.261	185
400	1.10	0.347	0.315	271
600	1.92	0.484	0.253	364
800	0.77	0.271	0.354	174

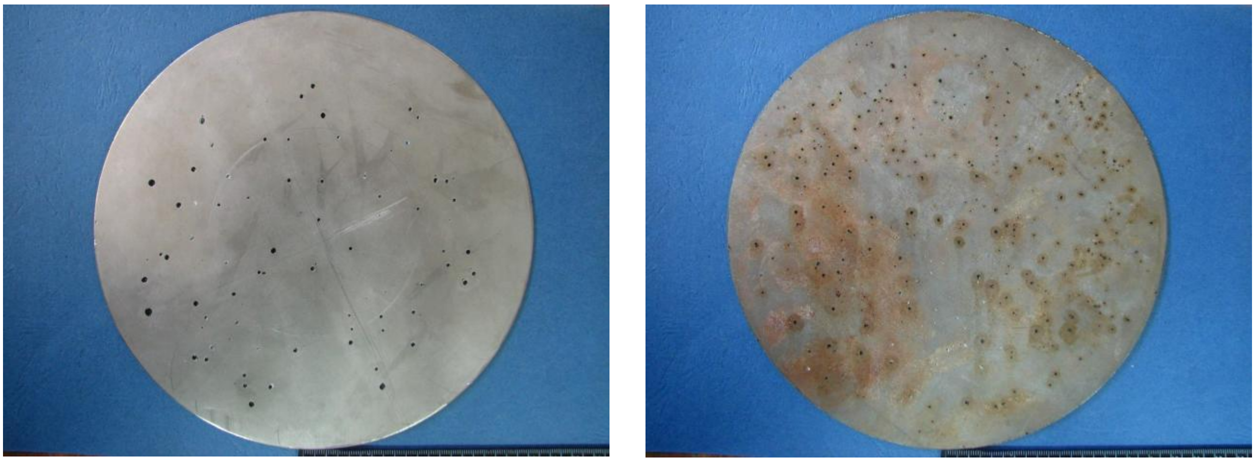


(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 1: Distribution of pits depths for specimens from **Table 1**



a **b**

Figure 2: Appearance of specimens from **Table 1** tested without heating (a) and after heating at 600˚ C (b)

The results of pitting testing on specimens under **b)** are displayed in **Table 2**. Appearance of specimens from this **Table** after heating and after heating, pickling and pitting testing is shown in **Figure 3.**

Table 2: Geometry of pitting on specimens under **b)** after 72 h of exposure to $FeCl_3$-solution; observed surface area S = 90 cm^2

Specimens Heating (˚C)	Pickling	Pits number n_p	Pits depths (mm) average $\bar{h}_p$	Pits depths (mm) maximum $h_{p\ max}$	Average pit mouth area $\bar{S}_p$ mm^2
400	no yes	50 4	0.96 0.98	2.03 1.56	2.14 1.40
600	no yes	121 3	0.93 1.49	1.83 2.26	1.70 1.17
800	no yes	80 5	1.00 1.28	1.74 1.41	1.72 2.44
1000	no yes	25 62	1.43 0.95	2.28 1.80	1.77 0.75

Specimens Heating (˚C)	Pickling	Pitting area fraction (%) $n_p \bar{S}_p / S$	Pitting penetration density $n_p \bar{h}_p / S$ (mm/cm^2)	Average pit severity $\bar{h}_p / \bar{S}_p$ (mm^{-1})	Apparent pits volume(mm^3) $n_p \bar{h}_p \bar{S}_p$
400	no yes	1.19 0.062	0.533 0.044	0.449 0.700	102.7 5.49
600	no yes	2.29 0.039	1.25 0.050	0.547 1.27	191.3 5.23
800	no yes	1.53 0.136	0.889 0.071	0.581 0.525	137.6 15.6
1000	no yes	0.492 0.079	0.397 0.654	0.808 1.27	63.3 44.2

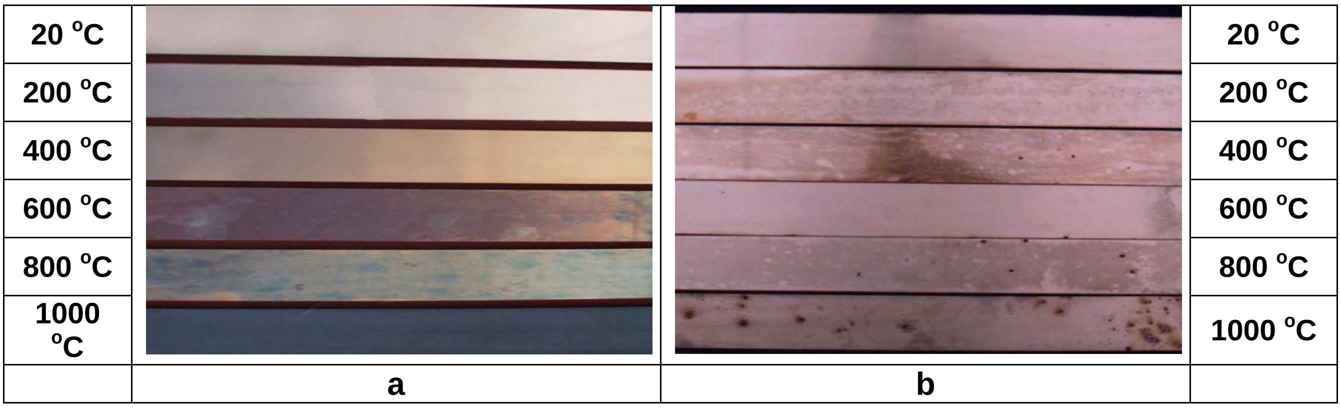


Figure 3: Appearance of specimens from **Table 2** after heating (a) and after heating, pickling and pitting testing (b)

Pitting testing of welded pipe specimens, referred to under **c)**, has been carried out

- without any rinsing/pickling (variant A),
- after rinsing/pickling with solution containing 15% HNO_3 and 1.5 % HF during one or two hours (variants B-1 and B-2), or
- after rinsing/pickling with solution containing 20% HNO_3 and 3% HF during one or two hours (variants C-1 and C-2).

The rinsing has been applied at 22° C and flow velocity 0.18 m/s. Pitting liability of welded pipe specimens has been evaluated separately for

(1) weld seam zone (**W**) with opaque dark grey oxide scale covering about 11% of the observed surface area,

(2) heat tints zone (**HT**) surrounding both sides of the weld seam with different interference colours covering about 14% of the observed surface area (interference is caused by semitransparent oxide films), and

(3) base metal zone (**BM**) with unchanged SS, ie. the rest of the observed surface area (about 75%).

Testing results for pits depths and densities are presented in **Figure 4**. The appearance of weld seam and its surroundings before and after pitting testing is visible in **Figure 5**.

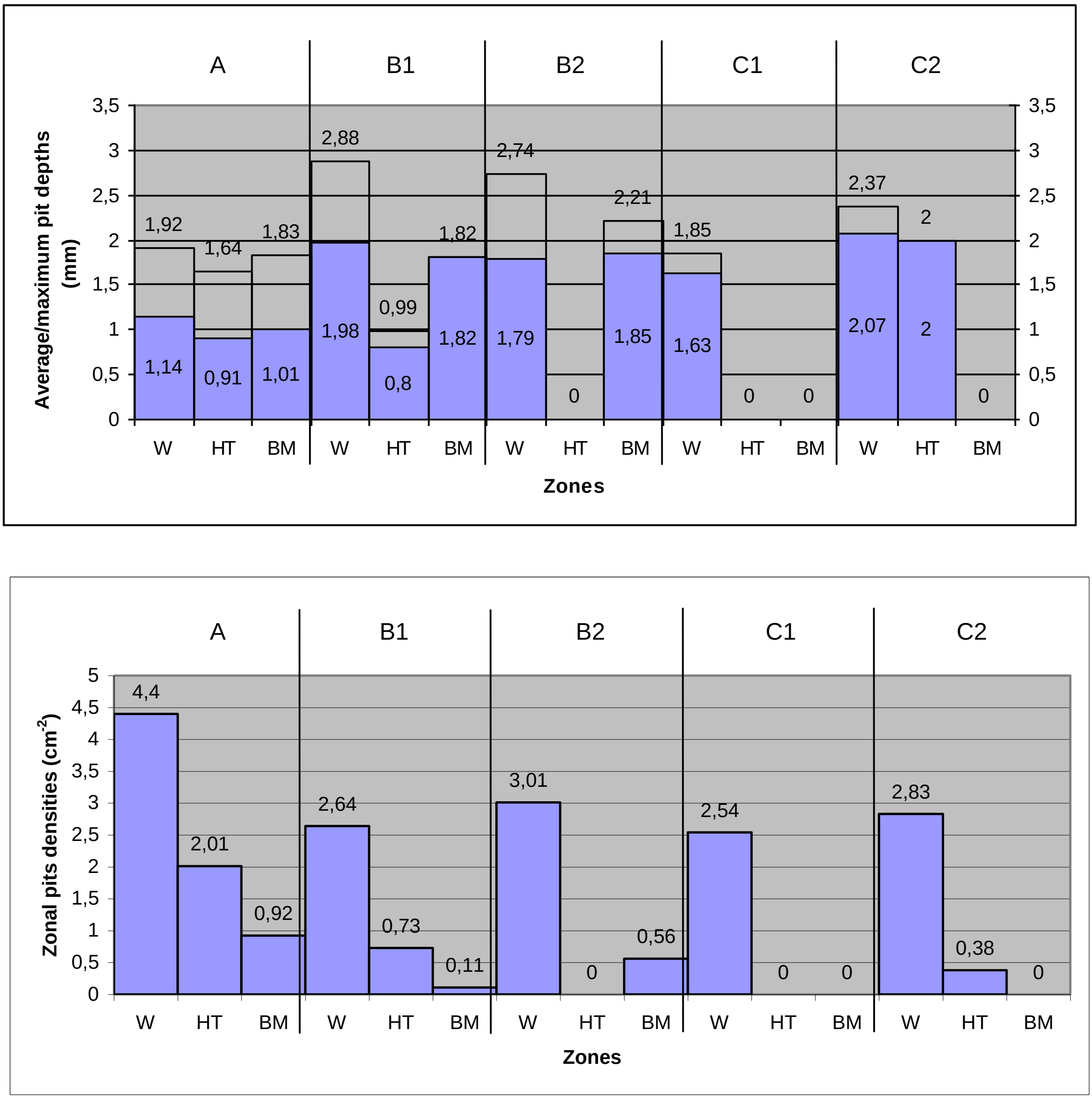
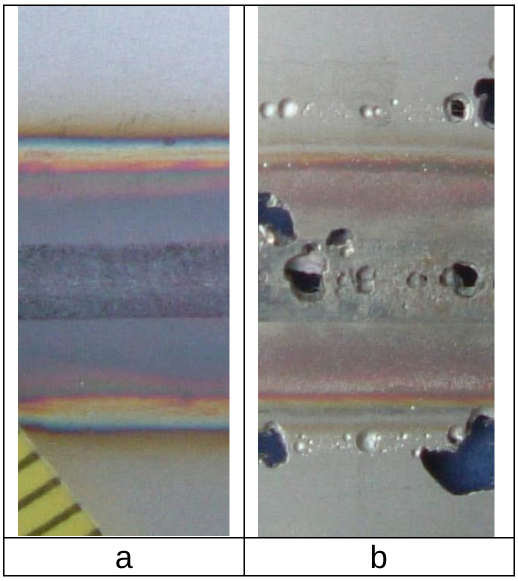


Figure 4: Average and maximum pits depths and densities on welded pipe specimens after 96 hours of exposure to $FeCl_3$-solution



a b

Figure 5: Appearance of seam welded specimens before (a) and after (b) pitting testing.

The pits obviously accumulate on weld and heat tints zones that justifies separate consideration of pitting criteria for W-, HT- and BM-zones.

3 Discussion

As follows from **Table 1** as well as from **Figures 1** and **2** thermal oxides formed by heating of AISI 304 SS at 400, 600 or 800° C significantly increase pits number, n_p, after testing of a specimen in $FeCl_3$-solution contributing considerably to external (superficial) and internal (penetrating) damage of the metal (especially after heating at 600° C). External damage impairs surface quality of SS provoking numerous technical problems particularly if perfectly clean and smooth metal surfaces are indispensable (like in potable water systems, in the production of foodstuffs, medicines, fine chemicals etc.). Internal damage results in deformations, cracking and fracture of mechanically loaded structures or in perforations of thin-wall constructions (as tubes, containers etc.) causing leakage of valuable and/or dangerous (eg. poisonous or inflammable) fluids provoking enormous economic losses or even catastrophic disasters (like 1984 in Bhopal, India, and many others). Detrimental influence of thermal oxides is revealed also by increasing values of pitting area fraction and of penetration density, $n_p\bar{S}_p/S$ and $n_p\bar{h}_p/S$. Therefrom it may be concluded that the formation of thermal oxides on SS at sufficiently high temperatures (probably over 350° C) produces many inhomogeneities on metal surface beneath oxide film or scale growing thereupon [4].

After removal of thermal oxides (eg. by pickling or by dissolution during pitting testing) mentioned inhomogeneities can act as pits nuclei. It is therefore necessary that the pickling removes not only thermal oxides but metal inhomogeneities underneath, too. On the other hand, the effect of thermal oxides on some pitting criteria is ambiguous or negligible (eg. on pit mouth area and apparent pits volume) and sometimes even slightly favourable (eg. regarding pits depths and their severity).
According to **Table 2** and **Figure 3** the presence of thermal oxides on AISI 316L SS and their removal by acid pickling have a strong influence on pitting liability in $FeCl_3$-solution. However, this type of SS is more resistant to localised corrosion than AISI 304. So, in the initial state or after heating at 200° C no pitting is provoked on AISI 316L SS in spite of the prolongation of exposure to $FeCl_3$-solution from 24 up to 72 hours.

The pickling of specimens heated at 400, 600, 800 and 1000˚ C decreases remarkably following pitting criteria: pitting area fraction $n_p\bar{S}_p/\bar{S}$ and apparent pits volume $n_p\bar{h}_p\bar{S}_p$ that is a roughly approximated measure of the electrochemical activity of pits on the specimen. It is interesting that the maximum value of $n_p\bar{h}_p\bar{S}_p$ for an unpickled specimen appears after heating at 600˚ C. Heating at the same temperature gives maximum value for $n_p\bar{h}_p\bar{S}_p$ on AISI 304 SS, too (as visible in **Table 1**). The pickling after heating of AISI 316L SS at 400, 600 or 800˚ C diminishes enormously pits number n_p on a specimen and corresponding pitting penetration density $n_p\bar{h}_p/S$ (**Table 2**). On the contrary, the pickling after heating at 1000˚ C causes the increase of pits number and their penetration density. It could be explained by an enormous increase of inhomogeneity of metal surface under oxide scale arising by heating of AISI 316L SS at 1000˚ C resulting in tensile stresses in the metal caused by the growth of voluminous oxide layer which is later crumbled by compressive stress (as presented in **Figure 6)** or dissolved by pickling acid and the $FeCl_3$-solution. Such an explanation is in accordance with results and conceptions of G.T. Burstein and collaborators [5, 6 etc .] about pits nucleation and propagation.

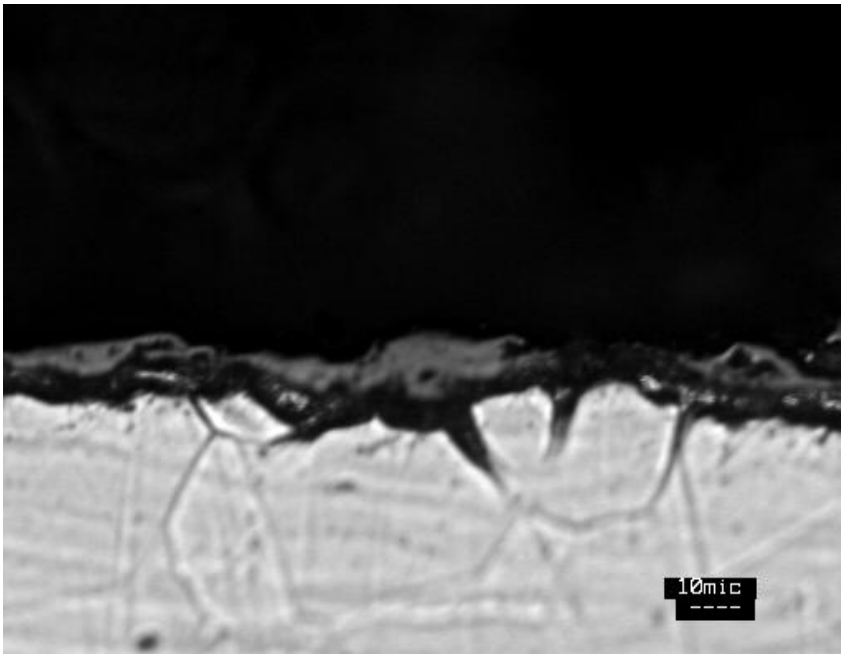


Figure 6. Crumbled oxide layer after heating of AISI 316L SS at 1000 ^{o}C

Additional pitting testing of welded pipe specimens was carried out because similar elements are very often used in technical practice and distinguish themselves by peculiar corrosion behaviour as presented in **Figures 4** and **5** and in the reference [7] as well. Besides, during manufacture or in exploitation many SS objects are subjected to powerful temperature gradients similar to those appearing in weld and heat tints zones in the course of pipe specimens preparation. In such cases it is often recommendable to perform only local pickling in certain zones, using pastes and gels, optimising thereby agent´s composition and treatment time.

The highest values of maximum pits depths and densities on welded specimens are always observed in W-zones as visible in **Figure 4** that points out at significantly increased electrochemical inhomogeneity of SS after casting and welding contributing essentially to pitting susceptibility by increased number of potential nucleation sites. That is in conformity with technical practice. Therefore it is recommendable to perform pickling of weldments and periodic passivation of welded SS constructions.

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