ELECTROCHEMICAL CHARACTERIZATION OF AISI 304 STAINLESS STEEL SURFACE DURING INDUSTRIAL PICKLING PROCESS

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Abstract

The present work deals with the possibility of the evaluation of the descaling rate of the AISI 304 stainless steel. The samples were pre-treated in the reduction melt containing NaOH, Na_2O and NaH and the final pickling took place in the mixtures of acids. The cross - sections of the scales formed on the steel as received and those remained after reduction bath treatment and acid pickling were examined by using a scanning electron microscope. The surface analysis was performed by the Raman microspectroscopy and the presence of magnetite was proved for all the samples. The occurrence of this electroactive substance enabled using of the electrochemical methods (cyclic voltammetry, electrochemical impedance spectroscopy and chronocoulometry) for monitoring of the redox reactions taking place on the working electrode formed by the steel sample in 1 M NaOH solution. The application of whichever method provides a quick estimation of the pickled surface state.

Keywords: Stainless steel pickling, Raman spectroscopy, voltammetry, **c**hronocoulometry, electrochemical impedance spectroscopy

1.   INTRODUCTION

Austenitic stainless steel is often used for its excellent mechanical properties and its high corrosion resistance. This type of steel is usually continually casted with following re-heating, rolling and annealing [1]. During this process the oxide layer is being formed at the surface. The chromium-depleted layer is coming into being between this oxidic layer and the base metal. Both layers are undesirable and have to be removed.The pickling process consists of several parts -a mechanical pickling, preliminary and final pickling and surface passivation if need be. The processes of the preliminary pickling, resulting in the higher solubility of the particular components of the oxide layer in the subsequently applied solutions, are either electrochemical or chemical. The chemical pickling can be performed in a reducing or oxidising molten bath. The advantages of the technology of the hydride pickling of high-alloy steels and alloys were described in [2]. The reduction melt consisting of NaOH-Na_2O-NaH at 400 °C was electrochemically characterised in [3]. Descaling of stainless steels in an oxidising salt bath was described in [4].The procedure of the final pickling consists in the removal of silicon cumulated in the in the interphase between the oxide layer and chromium-depleted layer. The mixture of the acids and oxidizing agent (e.g. HF + HNO_3) is usually applied. Subsequently the chromium-depleted layer is being dissolved in this mixture. The oxide film can be studied by means of the electrochemical and spectroscopic methods [1, 5]. Nowadays the methods capable to distinguish the oxidised and blank surface on the basis of the electrochemical measurenent in the neutral and acid electrolytes are being developed. The electrochemical measurements comparing the behaviour of the oxidised and blank surface of the AISI 304 stainless steel have not been sufficiently studied yet.In practice, the descaling rate can be evaluated by the observation of the metallographic scratch pattern. This multi-step technique is very time-consuming with a very long feedback. Hence the simpler and faster electrochemical method was searched.

2. EXPERIMENTAL

2.1. Materials

The stainless steel bar (ϕ 9 mm) under investigation was of AISI 304 type produced by BGH Edelstahl Lugau Gmbh. The way of treatment is summarized in **Table 1**. The steel bars were treated in the reduction bath containing NaOH, Na_2O and NaH at 400 °C (step A) and consequently rinsed with the solutions of 15 % HCl at 50 °C (step B) and the mixture of 15 % HNO_3 and 3 % HF (wt. %) at 21 °C (step C).

Table 1 Time of pickling of samples No. 1-5 (min) for follow-up steps A-C

Sample	A	B	C
1	-	-	-
2	15	-	-
3	15	5	-
4	15	5	1
5	15	5	3

2.2. Surface analysis

The cross - sections of the scales formed on the steel as received and those remained after reduction bath treatment and acid pickled samples were examined by using a scanning electron microscope (SEM) JEOL JSM-6490LV (Japan) in the reflected electrones. The presence of Fe_2O_3 and Fe_3O_4 on the surface of the samples 1 - 5 was detected by Raman microspectroscopy. The method was performed using Raman microscope XploRA™ (HORIBA Jobin Yvon, France) equipped with 532 nm excitation laser source, with 1200 gr./mm grating and 100x objective. Intensity of the laser beam was set at 1%.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using the potentiostat-galvanostat Voltalab VM 40 Radiometer-Analytical (France). The experiments took place in the 1 M NaOH solution in a glass beaker at ambient temperature (20 °C). The auxiliary electrode was a nickel wire the reference electrode was a Hg / HgO (1M NaOH). The working electrodes were prepared from the 304 stainless steel bars, the area was 0.85 cm^2. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronocoulometry (CC) were applied to verify the possibility of evaluation of the pickling process efficiency.

3. RESULTS AND DISCUSSION

3.1. Microscopic observations and Raman spectroscopy

The surface was analysed using SEM. **Figures 1, 2** demonstrate the composition of the corrosion layers of the appropriate samples. The presence of iron and chromium oxides can be seen on the surface of the untreated sample 1 (**Figure 1**). The point oxides can be seen in the interface between the oxide layer and metallic matrix. Only imperceptible traces of nickel were found. After the treatment in the reduction melt at 400 °C the layer becomes thinner. The coherent iron-chromium oxide layer was removed and incoherent layers of pure metal with the high iron content appeared. The alternating iron, chromium and nickel oxide sub-layers remained and their morphology changed into the porous one. The oxides were still present after the pickling in the hydrochloric acid solution. The oxide layer and the metal originated by reduction partly decreased. Only small residues of the oxide layer remained after the mixed acid pickling after three minutes, the oxide layer was completely removed (**Figure 2**). The surface was etched sporadically and the intergranular corrosion along the austenitic grains occurred.

Point / Element	O	Cr	Fe	Ni	Point / Element	O	Cr	Fe	Ni
1	64.0	17.6	16.6	0.3	1	-	19.9	68.7	8.1
2	44.5	13.5	34.5	5.6	2	50.1	24.2	19.6	1.2
3	62.3	18.0	15.7	1.2	3	42.9	13.7	35.4	6.4
4	63.0	21.6	13.6	0.2	4	61.0	21.7	14.0	0.8
5	-	20.1	68.8	8.1	5	-	18.6	70.4	8.2
6	-	19.9	68.9	8.0	6	-	19.8	68.8	8.1
7	-	19.9	68.7	8.0	7	-	20.0	68.6	8.0
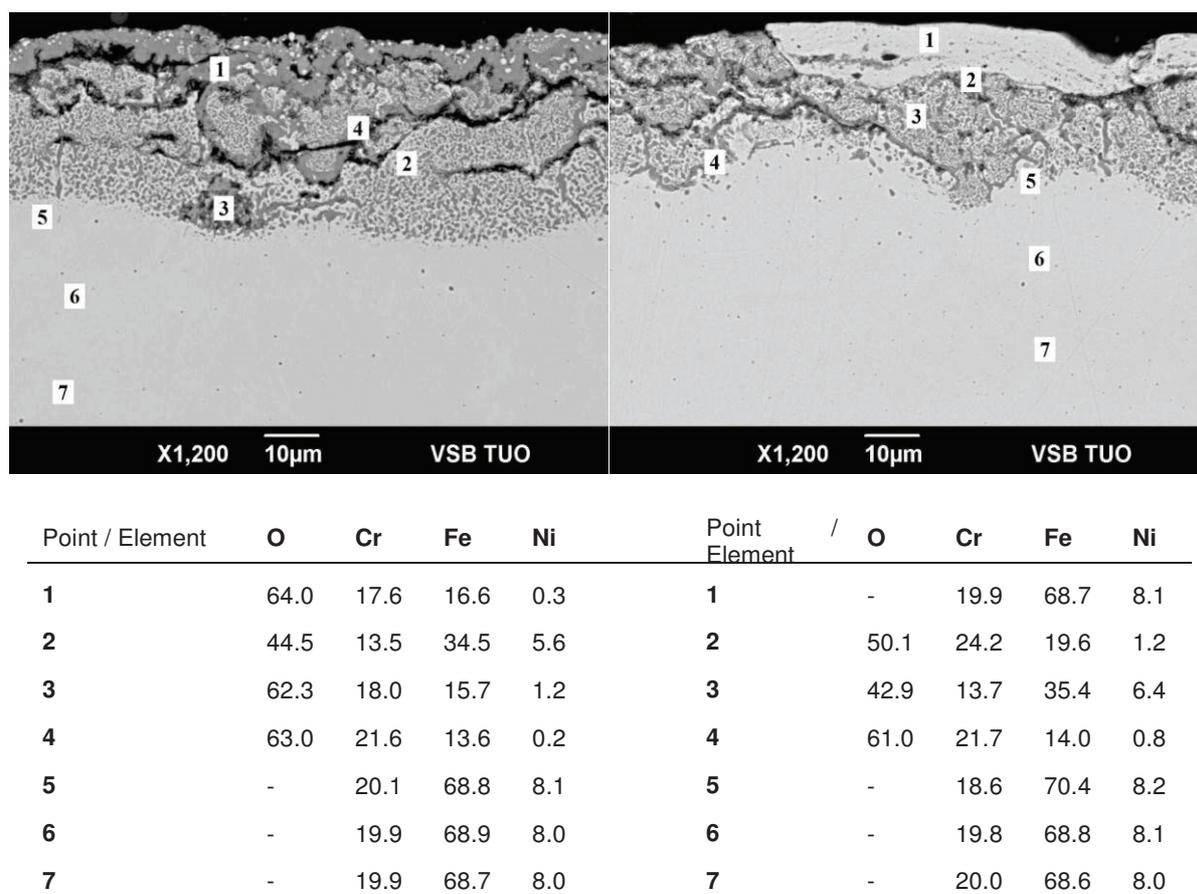
Figure 1 SEM and EDS analysis of the cross section of the oxide scale of the original corroded material (sample 1) and the sample 2 (after hydride pickling step A from **Table 1**)
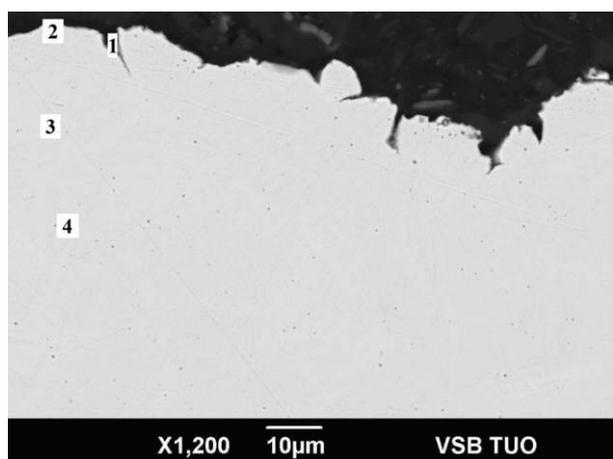
Point / Element	O	Cr	Fe	Ni
1	54.1	19.4	21.9	1.0
2		18.7	70.0	8.3
3		19.9	68.8	8.1
4		20.0	68.6	8.0

Figure 2a SEM and EDS analysis of the cross section of the oxide scale of the sample 5 (after steps A+B+C from **Table 1**)

The results of the Raman spectroscopy can be seen in **Figure 3**. The presence of Fe_2O_3 and Fe_3O_4 on the surface of the samples was detected. Fe_3O_4 is a poor Raman scatterer, therefore only one very intensive band at 670 cm^{-1} was observed in all measured samples. Other characteristic band of Fe_3O_4 was observed at 531cm^{-1}, but it was less intensive. In the case of the sample 1, Fe_2O_3 was detected in some measured point (sample 1a). Only the most intensive bands at 217 and 276 cm^{-1} corresponded to the hematite. A surface hematite layer in the samples 2 - 5 was probably reduced during the reduction descaling bath treatment. Two more bands in the samples 304-3 and 304-5 (1337 and 1590 cm^{-1}) correspond to the amorphous carbon. The surface was depleted by chromite due to the dissolution in the melt.

3.2. Electrochemical measurements

At first the cyclic voltammetry was applied. **Figure 4** shows the polarization curve at the polarization scan rate of 200 mV / s in 1M NaOH solution at 20 °C for the samples 1 and 2. A cathodic reduction of Fe_3O_4 in the alkaline solutions is explored thoroughly because it can be used for the direct iron production in the so called green metallurgy [6]. The first cathodic peak can be related to the reaction (1) [6].

$$Fe_3O_4 + 2e^- + 4H_2O + OH^- = 3Fe(OH)_3^- \qquad (1)$$

Because the presence of $Fe(OH)_3^-$ ions has not been proved yet, the reaction can be also described by the equation (2) according to [7, 8].

$$Fe_3O_4 + 2e^- + 4H_2O = 3Fe(OH)_2 + 2OH^- \qquad (2)$$

Than the subsequent cathodic reaction of the iron formation can be described by the equation (3).

$$Fe(OH)_3^- + 2e^- = Fe + 3OH^- \qquad (3)$$

Two anodic peaks can be found for the synthetically formed Fe_3O_4. The first anodic peak can be probably attributed to the reverse reaction (3) and the second one, which is much more remarkable, to the reaction 4.

$$Fe_3O_4 + 4H_2O + 4OH^- = 3Fe(OH)_4^- + e^- \qquad (4)$$
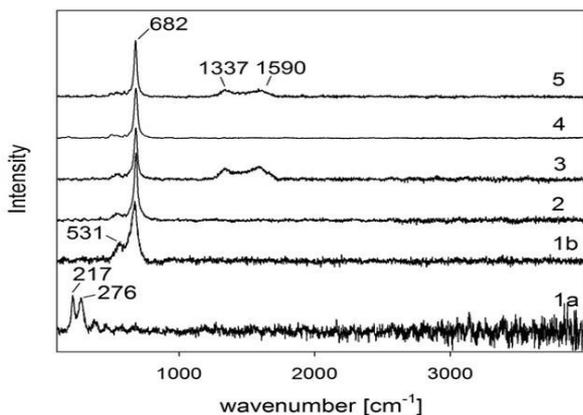
Figure 3 Raman microspectroscopy of the samples 1- 5
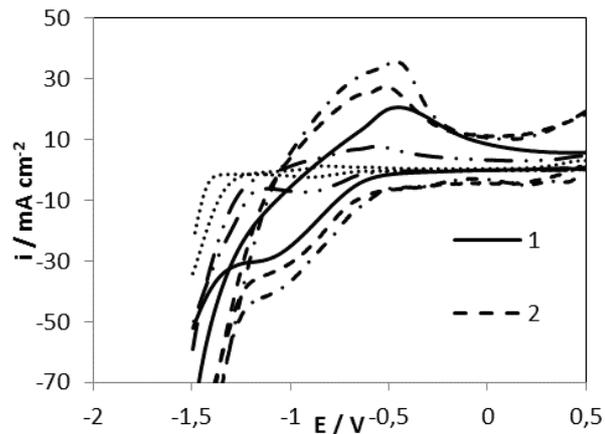
Figure 4 Voltammetric curves of the samples1 - 5 in the 1M NaOH solution, scan rate 200 mV/s

These peaks can be hardly distinguished at real samples. **Figure 4** demonstrates the voltammetric curves for the real samples 1-5. The total thickness of the oxide layer decreased. The anodic maximum height and the corresponding cathodic minimum height are related to the surface amount of magnetite, which increased after the reduction of hematite by sodium hydride. The hydrochloric acid caused the formation of micro-channels and the oxide layer became less compact. The electrode-electrolyte interface increased and the peak heights increased. In HF-HNO$_3$ bath, various ionic or molecular species can occur [1]. Sample 4 is partly free from oxide layer, which corresponds with the decreasing peak heights. Sample 5 is almost clear and the intergranular corrosion is more pronounced with increasing pickling time in HF-HNO$_3$ mixture. Also the slopes of the curves 3 - 5 at the corrosion potential (zero current density) decreased with the proceeding pickling process which means that the corrosion rate in 1M NaOH at 20 °C decreased. Of course, the corrosion rate must be measured at the low scan rate but the current density was very low under these conditions. Also the anodic current density in the passive state progressed analogously. These results show that the cyclic voltammetry enables to estimate the surface state, mainly during the final acid pickling.
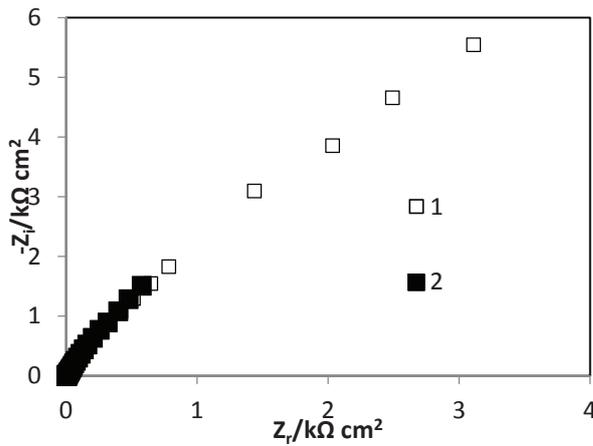
Figure 5 Nyquist plots of the samples 1 - 2 at 0.0 V
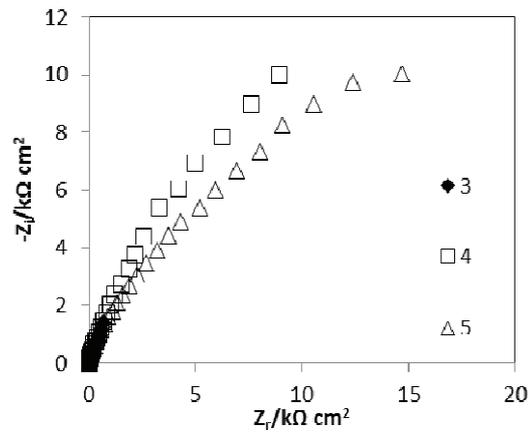
Figure 6 Nyguist plots of the sample 3 - 5 at 0.0 V

On the basis of the previous results, the conditions for the next electrochemical methods (EIS and CC) were chosen. The impedance values were measured at the potential 0.0 V which corresponds to the passive region. From Nyquist plots- **Figure 5**, it can be seen that the process is controlled by diffusion through the oxide layer for the sample 1 and 2 - the dependence of the imaginary part of the impedance on the real one is almost linear. The sample 3 (**Figure 6**) still contains a compact oxide layer (from 10 to 25 μm) and the Nyquist plot is almost linear, too. For the samples 4 and 5, where the diffusion layer is not compact, the dependence approaches the circular shape and the process is controlled mainly by the kinetics of the charge transfer.
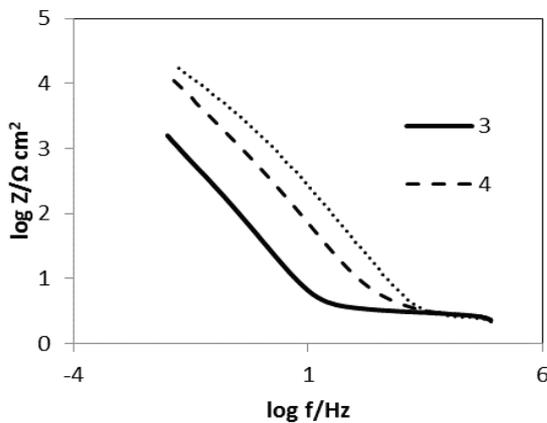
Figure 7 Bode plots of the samples 3 - 5 at 0.0 V
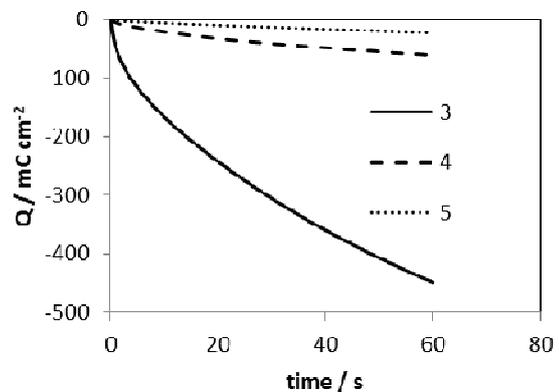
Figure 8 Chronocoulometric curves at -1.140 V - samples 3 - 5

The highest values of impedance were found for the sample 5 (**Figure 7** - Bode plots) which can be explained by the decrease of the amount of the charge carriers and the best passive behaviour. The amount of the charge passed at the cathodic reduction for the samples 3-5 can be seen in **Figure 8**. The smallest value was measured for the sample 5 with a minimal non compact layer of Fe_3O_4. The curve of the sample 3 with an eroded scale layer and large amount of Fe_3O_4 on the surface available for the reduction exhibited the highest amount of the consumed charge. The layer is not homogenous and the reduction takes place only at the surface, hence the layer thickness cannot be determined exactly. Nevertheless, the chronocoulometric method can be used for the estimation of the descaling rate.

4. CONCLUSIONS

The cyclic voltammetry, electrochemical impedance and chronocoulometry proved to be suitable for the evaluation of the descaling process. The results of the Raman spectroscopy and scanning electron microscopy

showed the presence of Fe_3O_4 which is electrochemically active. Magnetite can be subjected to the anodic oxidation and cathodic reduction. The electrochemical responses obtained by CV (the anodic peak height, the current density in the passive state, the slope of the linear part of the voltammetric curve at the corrosion potential), EIS and CC have the same sequence and correspond to the way of sample treatment and time of pickling in the acids. The precise determination of the layer thickness is not possible because the layer is not homogenous and the reduction takes place only at the surface. Nevertheless, the applied electrochemical methods can be used for the estimation of the descaling rate.

ACKNOWLEDGEMENTS

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