

# MODIFICATION OF CARBON STEEL SURFACE BY THE TENIFER®\* PROCESS OF NITROCARBURIZING AND POST-OXIDATION

K. Marušić<sup>a</sup>, H. Otmačić<sup>a</sup>, D. Landek<sup>b</sup>, F. Cajner<sup>b</sup> and E. Stupnišek – Lisac<sup>a</sup>

<sup>a</sup> Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

<sup>b</sup> Faculty of Mechanical Engineering and Naval Architecture, Ivana Lučića 1, 10000 Zagreb, Croatia

## ABSTRACT

The surface of the non-alloyed carbon steel was subjected to thermo chemical modification by salt bath nitrocarburizing with or without post-oxidation based on the Tenifer procedure in order to improve mechanical properties, corrosion and wear resistance. Nitrocarburized layers were characterized by testing their basic properties (compound layer thickness, nitrocarburizing depth, surface hardness) according to current standards. Detailed estimation of the quality of the modified metal surface was performed by additional testing of chemical compositions by EDX and X-ray diffraction, microstructure, surface roughness and topography, and corrosion resistance. The corrosion resistance was investigated in a water solution of 5% NaCl using electrochemical polarization methods and electrochemical impedance spectroscopy. The corrosion properties of the treated and non treated samples are compared among themselves and with the properties of austenitic steel.

The surface layer obtained after nitrocarburization treatment consists mainly of  $\epsilon$ -Fe<sub>2-3</sub>N and  $\gamma'$ -Fe<sub>4</sub>N. The surface layer of the samples after post-oxidation consists also of  $\epsilon$ -Fe<sub>2-3</sub>N and  $\gamma'$ -Fe<sub>4</sub>N, but contains additionally Fe<sub>3</sub>O<sub>4</sub>.

The results obtained show that nitrocarburizing and post-oxidation treatments, based on the Tenifer procedure, result in better mechanical and corrosion properties of non-alloyed carbon steel. The corrosion properties of the thermo chemically modified non-alloyed carbon steel were improved and approach the corrosion properties of austenitic steel, known for its very good corrosion resistance.

Key words: nitrocarburizing, post-oxidation, carbon steel, corrosion resistance

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## 1. INTRODUCTION

Electrochemical and mechanical properties of a metal surface are largely responsible for the way metals can be used in a particular area. To improve corrosion properties of steel, the material is alloyed with various elements, such as chrome and nickel [1], although they are getting more and more expensive and their availability may become a problem in a foreseeable future. This is why saving energy and materials has become an issue of high concern [2]. The steel surface is modified by various heat treatments [3 – 6] in order to improve mechanical, tribological and corrosion properties of inexpensive non-alloyed steels, characterized by low resistance to corrosion in a number of media [1, 7, 8]. After appropriate surface modifications, such low-cost steels may even be considered as replacement for expensive alloyed steel materials. The purpose of surface modification treatments is to change the metal structure in a relatively thin surface layer, i. e. by diffusion of an appropriate element. The following properties of the metal can thus be improved: resistance to wear, chemical resistance, mechanical resistance and fire resistance [2].

Modification of steel surface by salt bath or gaseous nitrocarburizing is a process that is widely used in manufacturing of machine components and tools, since an improved surface hardness, fatigue strength and corrosion resistance at elevated temperatures, can thus be achieved at minimum distortion. Thus, the service life of machine components is significantly extended [9, 10 - 12]. Moreover, steel grades, that are not resistant to corrosion, attain a relatively good corrosion resistance due to the formation of a compound zone [2, 13, 14]. It should be noted that additional processes of post-oxidation after nitrocarburizing have also been applied to further improve properties of steel components and tools [2, 11 – 18].

One of the most popular processes of nitrocarburizing in a cyanide-cyanate salt bath is TENIFER TF1\* with or without post-oxidation in a nitrate-nitrite salt bath AB1\* [2, 10, 14, 17 -19]. These processes are simple, cost effective, appropriate for parts made of case hardening steels, tool steels for hot work and high speed steels, while also being environment friendly [18].

In this work, the surface of carbon steel samples is modified using nitrocarburizing in a salt bath, with or without post-oxidation. Previous investigations [9, 18, 19] have shown that a compound layer, ranging from 15 to 20  $\mu\text{m}$  in thickness, is formed during the nitrocarburizing process. This layer consists of iron nitrides. Post-oxidized samples contain iron oxide which fills the pores in about the first 5  $\mu\text{m}$ .

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Preparation of samples

The non-alloyed carbon steel samples grade C45 (non treated samples) and austenitic stainless steel grade X5 CrNi18-10 have been ground up to N5 roughness level and chemically degreased to provide uniform surface roughness and cleanness.

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The samples of C45 steel grade “1” were preheated to 350 °C for 30 min in air and then nitrocarburized in the Tenifer TF1 salt bath at 580 °C for 2 hours (Figure 1). After that a group of nitrocarburized samples marked as “2” was cooled in water (classical salt bath nitrocarburizing process) and the other group of nitrocarburized C45 samples “3” was exposed to further post-oxidation in AB1 salt bath at 350 °C for 10 min and then cooled in water to room temperature. Detailed description of the Tenifer process can be found in literature [17].

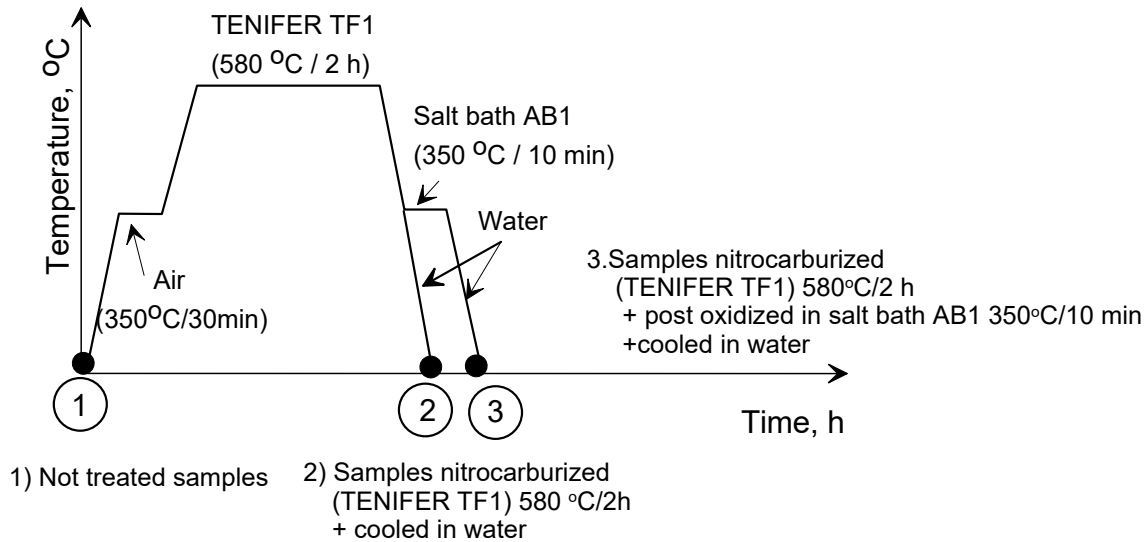


Fig. 1: Thermo chemical treatments of the test samples made of carbon steel grade C45.

## 2.2. Measurements and testing procedures

The content of nitrogen, carbon and oxygen in the studied samples was determined by EDX (Princeton Gama-Tech, model Spirit). The composition of the compound layer was analysed on Phillips X-ray Diffractometer Type PW1710.

The microstructure on the cross-section of nitrocarburized and post-oxidized samples was analyzed after metallographic preparation and etching with 3 % NITAL (3 % HNO<sub>3</sub> in ethanol). The microstructure analysis was performed by optical microscopy. Hardness distribution across the edge layer of the samples was measured by the Vickers method (HV 0.2). All hardness measurements were performed according to the standards DIN 6773:2001 and DIN 50190:1979.

Surface roughness has been measured 3 times at the length of 4.8 mm for each sample. Measuring equipment was the “Perthometer C5D” electromechanical device. Standard probe and RC filter for 0.80 nm wavelengths have been used. Maximum roughness depth  $R_{max}$  (μm) and mean value of roughness  $R_a$  (μm) have been calculated from the measured values.

Corrosion resistance of the samples was studied in 5% sodium chloride solution at 25°C. Prior to each measurement, samples were degreased in ethanol and rinsed with distilled water. The samples were insulated with Teflon tape, such that the non-insulated surface of the sample had an area of 1.76 cm<sup>2</sup>. Measurements were performed in a three electrode cell: a saturated calomel electrode was used as the reference electrode, while the counter electrode was a Pt plate. Potentiodynamic curves in the narrow (± 20 mV vs. oc.) and wide (± 150 mV vs. oc.) potential range were recorded with PAR 263A

potentiostat / galvanostat at a sweep rate  $0.166 \text{ mVs}^{-1}$ . Potential scan was performed from the most negative potentials up to the most positive potentials. The anodic polarization method was performed from open circuit potential to 1 V at a sweep rate  $0.5 \text{ mVs}^{-1}$ . Electrochemical impedance measurements were carried out in a frequency range between 10 mHz and 100 kHz, with a 10 mV amplitude, using PAR 1025 frequency response detector. After keeping the electrode at open circuit potential for one hour the measurements were performed as follows: electrochemical impedance spectroscopy and polarization in narrow and wide potential range.

### 3. RESULTS AND DISCUSSION

#### 3.1. EDX, X-ray diffraction, hardness testing and microstructure analysis

The distribution of nitrogen, carbon and oxygen measured by EDX from the thermochemically modified surface to the sample core (Figure 2) indicate that the content of nitrogen and carbon in the nitrocarburized sample decreases continuously from the edge towards the core. This is a consequence of nitrogen diffusion into the steel. It is also obvious that the radiation emission curves corresponding to the oxygen content exhibit a small increase only near the surface of the samples. For the post-oxidized sample an increased content of oxygen is recorded in the surface layer down to the depth of approximately  $6 \mu\text{m}$ , if compared with values for the greater depths. According to reference [2], finely dispersed particles of iron oxide fill the pores of the carbonitride layer in the depth range up to 5 - 10  $\mu\text{m}$ . In the same time a compact oxide layer is produced on the very surface.

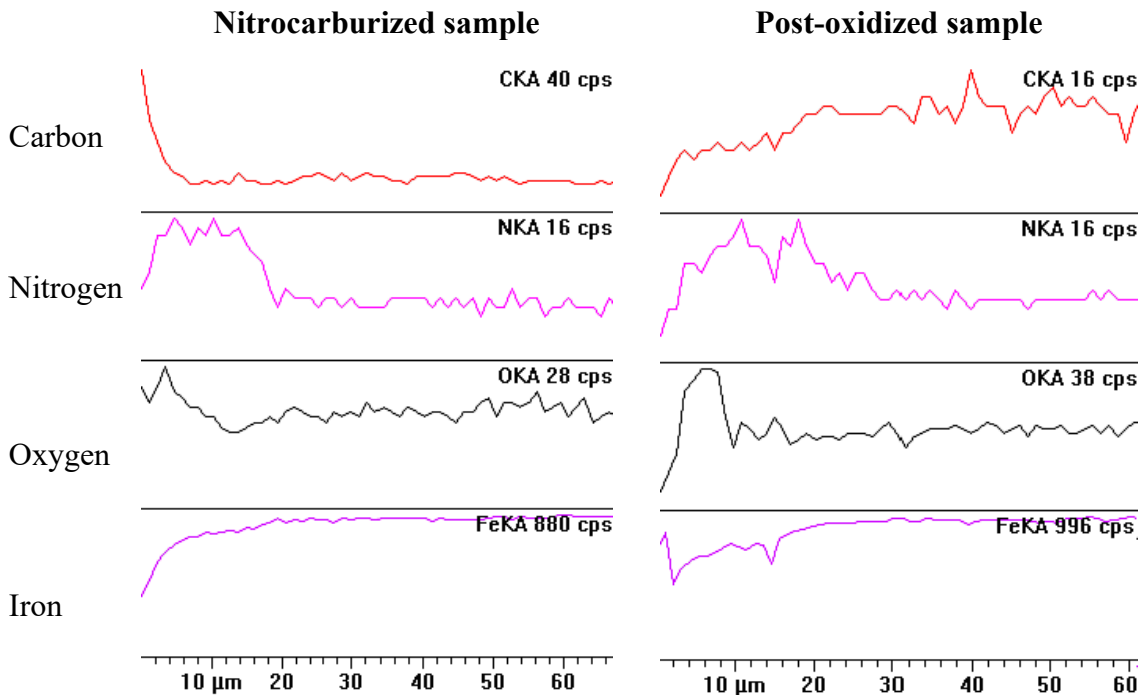


Fig. 2: EDX analysis of elemental distribution from the surface to the core of the nitrocarburized and post-oxidized samples.

The results of the X-ray diffraction analysis (Fig. 3) on the nitrocarburized sample have shown that the compound layer consists mainly of  $\epsilon$ -Fe<sub>2-3</sub>N and  $\gamma'$ -Fe<sub>4</sub>N. However, the analyses of the post-oxidized sample show the presence of iron oxide Fe<sub>3</sub>O<sub>4</sub> beside the mentioned nitrides.

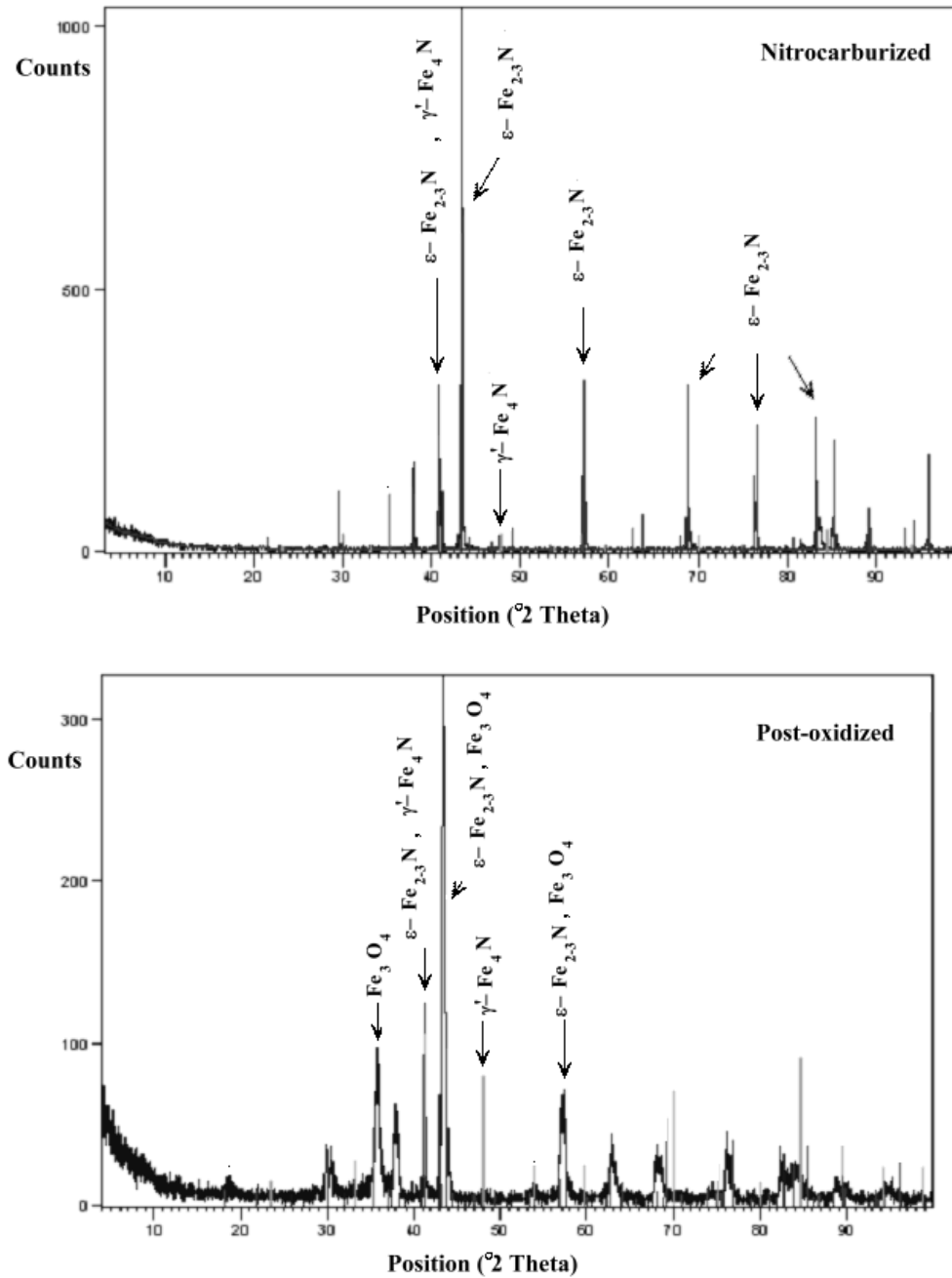


Fig. 3: Results of the X-ray diffraction analysis of the nitrocarburized and post-oxidized samples surfaces.

The distribution of hardness in the transversal cross-section of the nitrocarburized sample and post-oxidized sample (Figure 4) shows the effective depth of nitriding of about 0.45 mm. The total depth of nitriding on both samples was about 0.60 mm. There are differences in hardness in locations close to sample surfaces. The nitrocarburized sample has attained hardness that is for 40 HV0.2 higher than in the sample exposed to post-oxidation. This can be attributed to different cooling rates from the nitrocarburizing temperature. The nitrocarburized samples were cooled down quickly in water, while the post-oxidized samples were cooled slowly in the AB1 salt bath. Low cooling rate achieved in the salt bath with holding at 350 °C for 10 minutes resulted with precipitation of nitrides in the diffusion zone. By holding the nitrocarburized steel at the temperature of oxidizing bath at 350 °C, the part of interstitially dissolved nitrogen has been extracted from the iron structure at the diffusion zone and it participates at the iron nitrides formation [19]. Hardness of the diffusion zone of non-alloyed steels, as the investigated steel grade C45, is mostly determined by solubility of nitrogen in the iron structure. Post-oxidizing at 350 °C carries on to reduction of the internal stresses and diffusion of compulsory retained nitrogen atoms to more suitable energy sites at the iron body-centered cubic structure. These processes carry on to the measurable reduction in hardness which was established by conducted hardness testing.

Thermo chemical modification processes increase the hardness of the non-alloyed steel samples, so that the hardness of the treated samples is considerably higher (410 HV 0.2) than that of non treated steel samples (255 HV 0.2).

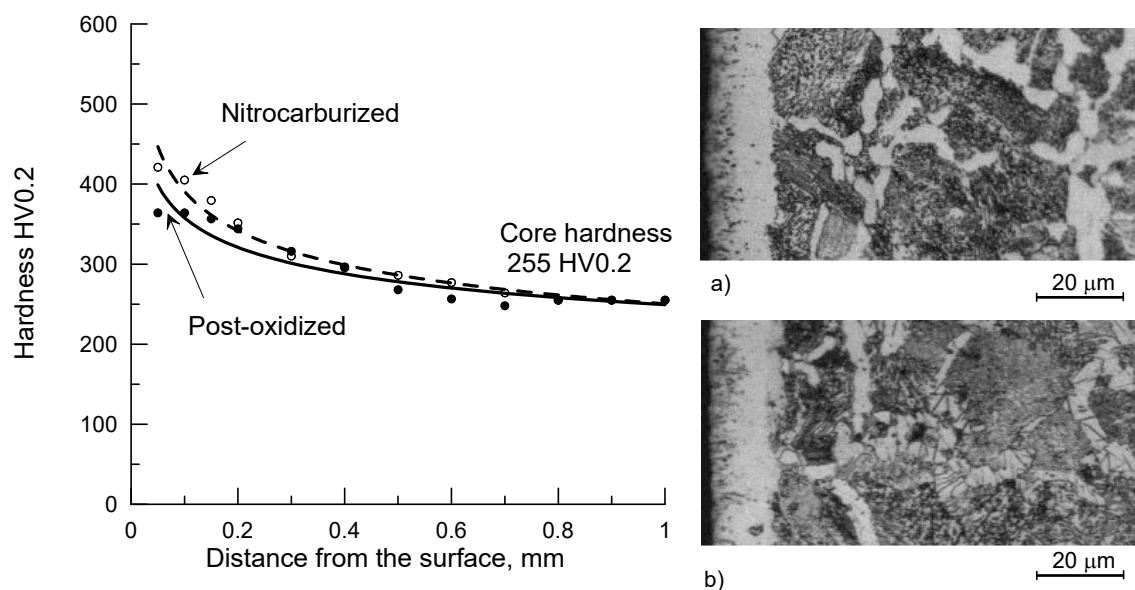


Fig. 4: Hardness distribution and microstructure in the edge area of the tested samples made of steel grade C45 after nitrocarburization (a) and post-oxidation (b).

From the optical microscopy of the microstructure at locations in the edge area of the tested samples (Figure 4) it is evident that the edge layer consists of a compound zone of about 15  $\mu\text{m}$  depth composed of  $\epsilon\text{-Fe}_{2-3}\text{N}$  and  $\gamma'\text{-Fe}_4\text{N}$  and a diffusion zone of about 0.6 mm depth with pearlite and ferrite matrices. If post-oxidation is applied after nitrocarburizing needle like nitrides are precipitated in the diffusion zone.

### 3.2. Surface roughness

Figure 5 presents the average surface roughness ( $R_a$ ,  $\mu\text{m}$ ) and the maximum height of the roughness ( $R_{\text{max}}$ ,  $\mu\text{m}$ ) on the non treated, nitrocarburized and post-oxidized samples of C 45 carbon steel.

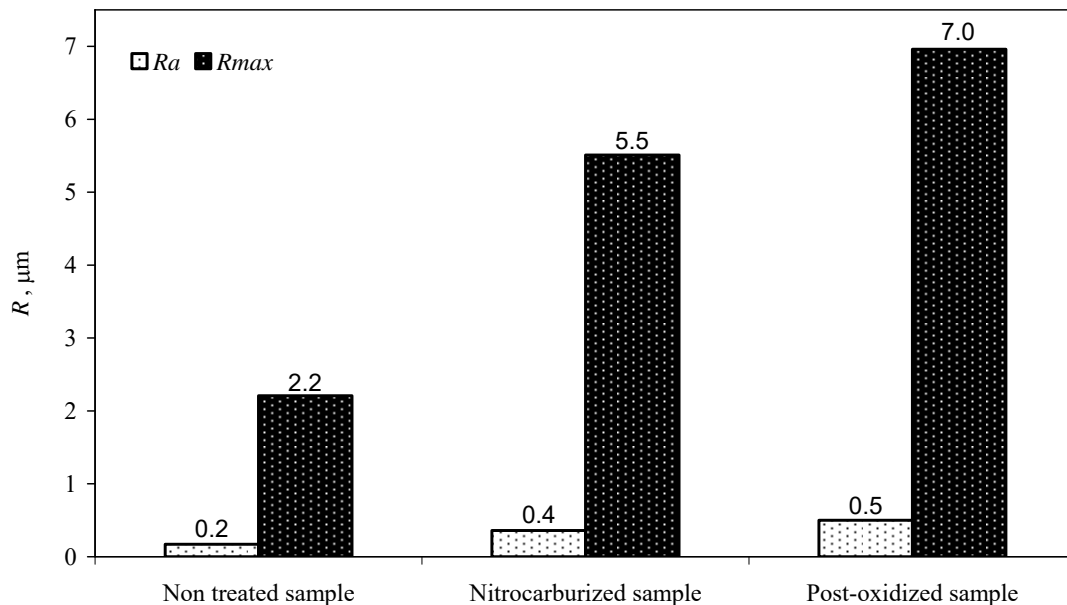


Fig. 5. Average surface roughness ( $R_a$ ) and the maximum height of roughness ( $R_{\text{max}}$ ) on the investigated samples.

The surface roughness of post-oxidized samples is greater than the roughness of nitrocarburized samples. A loose layer grows with post-oxidization and makes the reaction surface of post-oxidized samples bigger than the one of the nitrocarburized samples.

### 3.3. Electrochemical investigations of corrosion resistance

Results of the polarization measurements performed in a potential range of  $\pm 150$  mV vs. oc. are presented on Figure 6. It can be seen that the polarization curves of nitrocarburized and post-oxidized samples are shifted towards the more positive direction and towards the lower current densities when compared to the polarization curves of non treated samples. These results demonstrate that nitrocarburization and oxidation treatments have improved the corrosion resistance of carbon steel.

Polarization curve of the austenitic stainless steel sample can be observed at very low current densities, significantly lower than that of the other investigated samples.

Corrosion current densities of the tested samples were determined from the polarization curves by graphical determination of anodic and cathodic Tafel lines (Table 1). The calculated corrosion rate values of nitrocarburized and post-oxidized steel samples are about ten times lower than the corrosion rate of the non treated steel sample. In the case of the nitrocarburized samples lower corrosion current densities are obtained than for the post-oxidized samples. According to literature [2, 9, 14, 15] post-oxidized samples have better corrosion properties than only nitrocarburized samples. In our case the real surface area of the post-oxidized sample is greater than that of the only nitrocarburized sample, due to the bigger surface roughness (see Figure 5.), and which results in higher corrosion current densities. The austenitic stainless steel samples have shown the highest corrosion resistance among the tested samples.

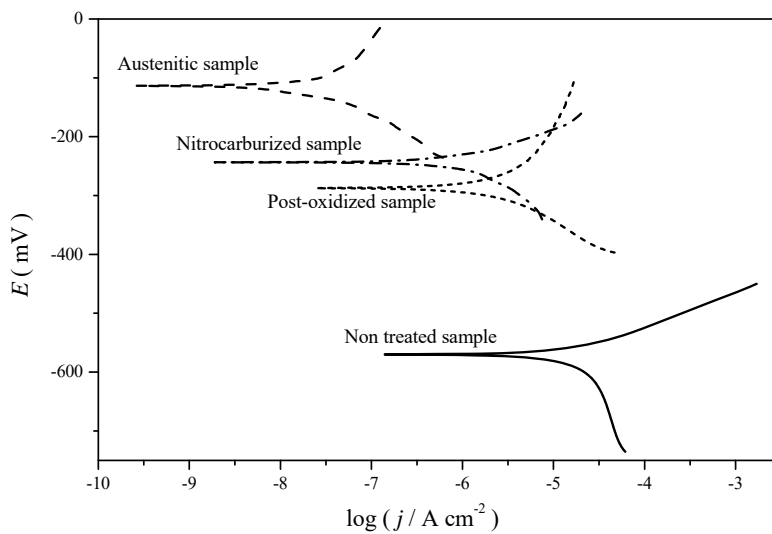


Fig. 6: Anodic and cathodic polarization curves of the investigated samples

Table 1. Corrosion parameters for the investigated samples obtained by Tafel extrapolation method.

SAMPLE	$E_{corr}$ , mV	$-b_c$ , mV dec <sup>-1</sup>	$b_a$ , mV dec <sup>-1</sup>	$j_{corr}$ , $\mu\text{A cm}^{-2}$
<b>Non treated sample</b>	-570	440	62	13.25
<b>Nitrocarburized sample</b>	-243	133	72	0.98
<b>Post-oxidized sample</b>	-287	98	162	1.86
<b>Austenitic sample</b>	-116	109	202	0.03

Linear polarization measurements were conducted over a potential region  $E_{corr} \pm 20$  mV. Polarization resistance ( $R_p$ ) was obtained from the slopes of the polarization curves, while the corrosion current densities were calculated according to the well known Stern-Geary equation [20]:

$$j_{corr} = \frac{b_a \cdot b_c}{2.3(b_a + b_c) \cdot R_p} = \frac{B}{R_p} \quad (1)$$



Values of the polarization resistance and the corrosion current densities for each sample are given in Table 2. Like the results obtained by Tafel extrapolation method, these results also show that the surface layers of nitrocarburized and oxidized samples, which have been formed during the thermo chemical modification processes, increase the corrosion resistance of the steel. The nitrocarburized sample has shown higher corrosion resistance than the post-oxidized sample. Polarization resistance of the austenitic sample is very high what confirms its excellent corrosion resistance. Although the corrosion resistance of carbon steel has been significantly improved by nitrocarburization and oxidation treatments, the extremely high corrosion resistance of austenitic stainless steel has not been reached.

Table 2. Corrosion parameters for the investigated samples obtained by polarization resistance measurements.

SAMPLE	$B$ , mV	$R_p$ , k $\Omega$ cm <sup>2</sup>	$j_{corr}$ , $\mu$ A cm <sup>-2</sup>
<b>Non treated sample</b>	24	1.35	17.47
<b>Nitrocarburized sample</b>	20	8.57	2.37
<b>Post-oxidized sample</b>	27	4.37	6.08
<b>Austenitic sample</b>	31	758	0.04

Figure 7 shows anodic polarization curves of the investigated samples in sodium chloride solution, in large potential range. It can be seen that the non treated sample corrodes very fast even at low potentials, unlike the nitrocarburized and post-oxidized sample which are very resistant, even at high potentials. The non treated sample does not show any passivation, while the nitrocarburized sample is passive up to about 0.5 V and the post-oxidized sample up to about 0.7 V. The value of the current in the passive region is about 0.13  $\mu$ A for both thermo chemically modified samples.

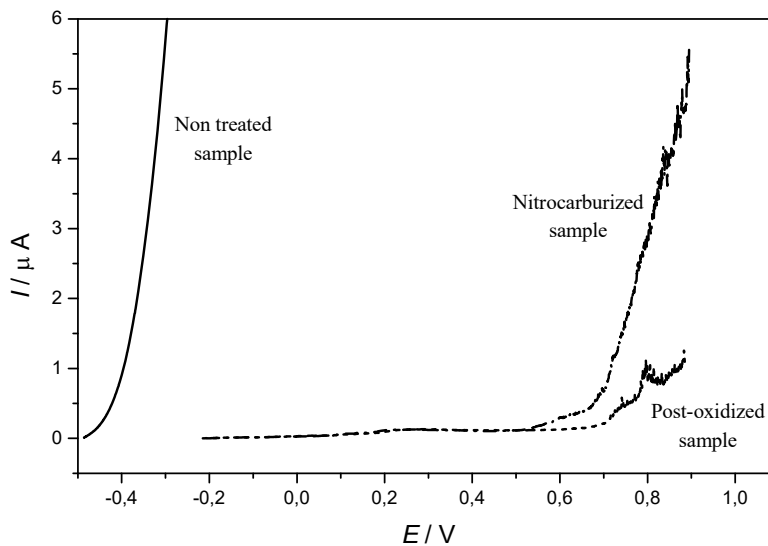


Fig. 7: Anodic polarization curves for the investigated samples.

Figure 8 presents Nyquist diagrams for the non treated sample, nitrocarburized, post-oxidized and austenitic sample. The results obtained by electrochemical impedance

spectroscopy are in accordance with previous electrochemical measurements. It is evident that the impedance loop of the post-oxidized sample shows a bigger diameter, which means a higher corrosion resistance.

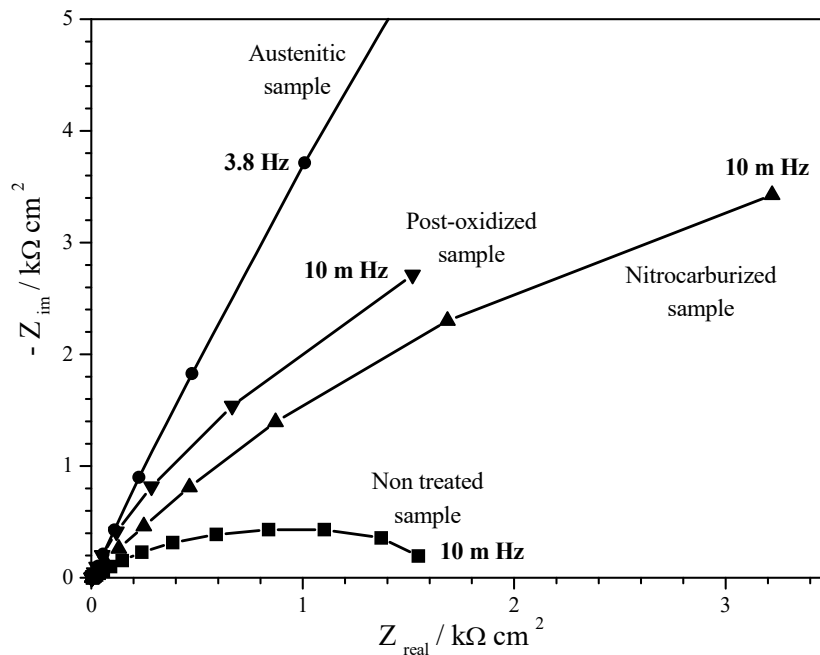


Fig. 8. Nyquist diagrams for the investigated samples.

#### 4. CONCLUSIONS

The influence of thermo chemical modification, based on the Tenifer procedure, on the mechanical and corrosion properties of non-alloyed carbon steel was investigated. Non treated sample, nitrocarburized and post-oxidized samples, and austenitic samples were tested.

The composition and properties of the surface obtained after heat treatments were estimated by EDX, X-ray diffraction analysis, hardness and microstructure analysis, roughness and corrosion resistance measurements.

The results of optical microscopy and X-ray diffraction analysis of the microstructure at locations in the edge area of the tested samples have shown that the edge layer consists of a compound zone of about 15 μm depth composed of ε-Fe<sub>2-3</sub>N and γ'-Fe<sub>4</sub>N and a diffusion zone of about 0.6 mm depth with pearlite and ferrite matrices. The surface layer of the samples after post-oxidation consists also of ε-Fe<sub>2-3</sub>N and γ'-Fe<sub>4</sub>N, but contains additionally Fe<sub>3</sub>O<sub>4</sub>. If post-oxidation is applied after nitrocarburizing needle like nitrides are precipitated in the diffusion zone.

Heat treatments applied in this testing also increase the hardness at the surface layer of the non-alloyed steel samples at the effective nitriding depth of 0.45 mm.

The electrochemical measurements have shown that the thermo chemical modification (nitrocarburization and post-oxidation) improved the corrosion properties of the non-alloyed carbon steel and approach the value of the austenitic steel. The anodic polarization of the investigated samples has shown that the non treated sample dissolves very fast and does not passivate, while the nitrocarburized sample is passive up to about 0.5 V and the post-oxidized sample up to about 0.7 V. The value of the

current in the passive region is about 0.13  $\mu\text{A}$  for both thermo chemically modified samples.

Results of these investigations confirm that the thermo chemical modification, according to the Tenifer procedure, result in better mechanical and corrosion properties of non-alloyed carbon steel.

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