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IMPROVEMENT OF PROPERTIES OF STEELS APPLYING SALT BATH NITROCARBURIZING WITH POST-OXIDATION

IZBOLJŠANJE LASTNOSTI JEKEL PO NITROCEMENTIRANJU S POST-OKSIDACIJO

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The comparative testing of properties for the steel grade Ck45 (AISI-1045) after salt bath nitrocarburizing (TENIFER process) without and with post-oxydation (TENIFER QPQ process) was performed. To evaluate the effects of post-oxidation on differently nitrocarburized specimens metallographic testing, chemical analysis through the sample cross-section, hardness, roughness, corrosion and tribological properties were determined. The results indicate that post-oxidation has no significant effect on the hardness decrease, it lowers the friction coefficient and improves the corrosion resistance in comparison to the non-oxidized steel. That change of properties is due to the formation of iron oxide layer on the compound zone during the cooling after nitrocarburizing and especially during the subsequent treatment in the oxidizing bath.

Key words: steel properties, nitrocarburizing, nitrocarburizing, post-oxidation

Izvršena je bila primerjava lastnosti jekla Ck 45 (AISI-1045) po nitrocementiranju (postopek TENIFER) s post-oksidacijo (TENIFER QPQ-postopek) in brez nje. Za oceno vpliva post-oksidacije so bile izvršene metalografske in kemijske preiskave na prerezu preizkušanca, izmerjene so bile trdota in hrapavost ter določene korozijske in tribološke lastnosti. Rezultati kažejo, da post-oksidacija ne vpliva na trdoto, zmanjša pa koeficient trenja in poveča korozijsko odpornost v primerjavi z neoksidiranim jeklom. To izboljšanje lastnosti so posledica nastanka sloja železovega oksida med hlajenjem po nitrocementiranju in posebno med dodatno obdelavo v oksidacijski kopeli.

Ključne besede: lastnosti jekla, nitrocementiranje, post-oksidacija

1 INTRODUCTION

Nitrocarburizing is widely applied in manufacturing of machine components and tools, since improved surface hardness, fatique strength and corrosion resistance at elevated temperatures are achieved at minimal distortion. Thus, the service life of a part is significantly extended. Moreover, corrosion non-resistant steel grades attain a rather fair corrosion resistance due to compound zone [1-3]. However, additional processes of oxidizing of nitrocarburized component are also applied [1-5]. During the post-oxidation, pores in the compound zone are filled in with iron oxide, but also a thin film of oxides is formed and the corrosion resistance is improved [4,6,7,8]. This improvement indicates to a possible extended application of the process for different machine components subjected to wear and corrosion in service. One of the most popular processes of nitrocarburizing in the salt bath with post-oxidation is the TENIFER QPQ process [5,8,9,10]. The implementation of the nitrocarburizing process with post-oxidizing in the salt bath is simple, cost effective and appropriate for components made of case hardening steels, tool steels for hot work and high speed steels (piston rods of gas shock absorbers, crankshafts, valves, drive shafts of windshield wipers, etc.) [8,9].

The TENIFER QPQ process was developed as further enhancement of the TENIFER salt bath nitrocarburizing process. Within the enhanced process, after nitrocarburizing at 580 °C, treated parts are cooled down to the temperature of 350 °C to 400 °C in AB1 hydroxide bath. The following cooling to room temperature occurs in air or in water. The reduced cooling rate has a favorable effect upon the level of residual stresses and distortion. Since oxidation of cyanides and their removal from the workpiece is achived in the AB1 bath, wastewater required for cooling and rinsing need not be neutralized prior to discharging into the drain duct. Thus, the harmful effect upon the environment is reduced if compared with the common TENIFER nitrocarburizing process for which neutralization of wastewater is mandatory. Further enhancement of the nitrocarburizing process, after cooling in the AB1 bath and air or water, include the polishing of components and repeated oxidizing in the same bath. This process was named the TENIFER QPQ process. According references [2,5,7,8,10] it significantly improves the corrosion resistance, while the wear resistance and dimension tolerances are maintained. To evaluate the effects of post-oxidation upon the properties of nitrocarburized steel, an extensive research has been carried out on nitrocarburized samples with and without subsequent oxidation, i. e. applying TENIFER and TENIFER QPQ processes.

2 DESCRIPTION OF THE TESTINGS

The testings were carried on samples of steel grade Ck45, applying the test plan given in table I. Prior to nitrocarburizing, all test samples were ground to N5 roughness level and chemically degreased to provide an uniform surface roughness and cleanless. Then, the samples were preheated to 350 °C for 30 min in air. The next step was nitrocarburizing in the TENIFER salt bath at 580 °C for 2 hours. With further processing (cooling down at different modes, polishing, subsequent oxidation applied or omitted) four different conditions of treated steel samples were obtained (**Figure 1, Table 1**). The polishing was performed using emery paper of 500 and 800 grit size. To compare the properties, testing of samples in "as delivered condition" (without heat treatment) was also performed. Samples treated as specified have been subjected to the following testings:

The surface roughness was measured 12 times over the length of 4,8 mm for each sample. The measuring instrument was the "Perthometer C5D" electromecha-

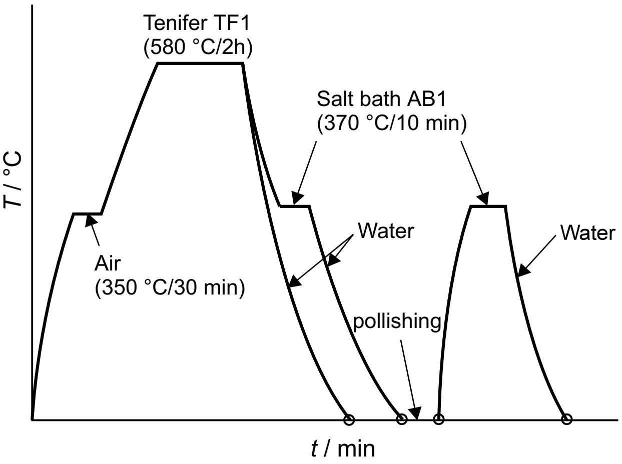

Figure 1: Heat treatment of test samples
Slika 1: Toplotna obdelava preizkušancev

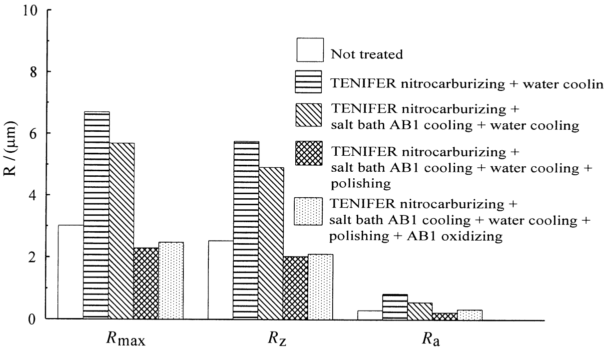

Figure 2: Surface roughness (R_{max}, R_z, R_a) for tested samples of Ck45 steel grade after TENIFER nitrocarburizing (at 580 °C for 2 h) and a different additional processing
Slika 2: Hrapavost površine za (R_{max}, R_z, R_a) za preizkušance iz jekla Ck 45 po nitrocementiranju TENIFER (580 °C, 2 h) in po dodatni obdelavi

Table I: Plan of the comparative testings for the Ck 45 steel
Tabela I: Načrt primerjalnih preizkusov jekla Ck 45

SPECIMEN DIMENSIONS Φ / mm	**PERFORMED INVESTIGATION**	SPECIMENS HEAT TREATMENT (*)				
			Nitrocarburizing (TENIFER TF1) 580 °C/2 h and			
		Non heat treated	cooling in water	cooling in salt bath AB1 + cooling in water	cooling in salt bath AB1 + cooling in water + polishing	cooling in salt bath AB1 + cooling in water + polishing + post-oxidized in salt bath AB1 + cooling in water (QPQ)
Φ (8×8×30) mm	Surface roughness tests	x	x	x	x	x
	Hardness and microstructural tests		x			x
	Analysis of constituents of the surface layer with the x-ray microanalyzer		x			x
	Solid friction tests		x			x
	Corrosion tests applaying electrochemical method	x	x			x
Φ (10×60) mm	Corrosion tests applaying gravimetric method	x	x			x

(*) All test samples were nitrocarburized (with and without post-oxidizing) in the Laboratory for Heat Treatment of the Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb.

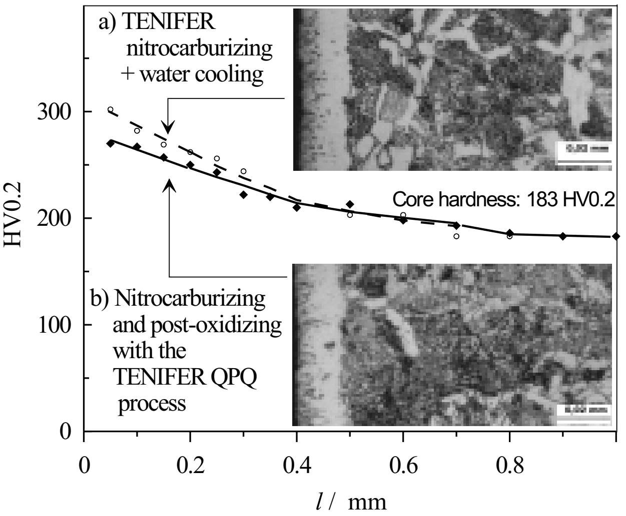

Figure 3: Microstructure and hardness distribution at the surface layer of tested samples of the Ck45 steel, nitrocarburized in the TENIFER salt bath at 580 °C for 2 h and submitted to the additional treatment: **a)** cooling in water, **b)** cooling in AB1 salt bath at 370 °C for 10 min and further cooling in water, polishing and oxidizing in AB1 bath at 370 °C for 10 min and finally cooling in water (TENIFER QPQ process).

Slika 3: Mikrostruktura in porazdelitev trdote od površine preizkušancev iz jekla Ck 45, nitrocementiranih v TENIFER-kopeli 2 h pri 580 °C in po dodatni obdelavi: **a)** ohlajeni v vodi, **b)** ohlajeni v solni kopeli AB1 pri 370 °C 10 min in ohlajeni v vodi, polirani in oksidirani v kopeli AB1 10 min pri 370 °C in končno ohlajeni v vodi (TENIFER QPQ-postopek)

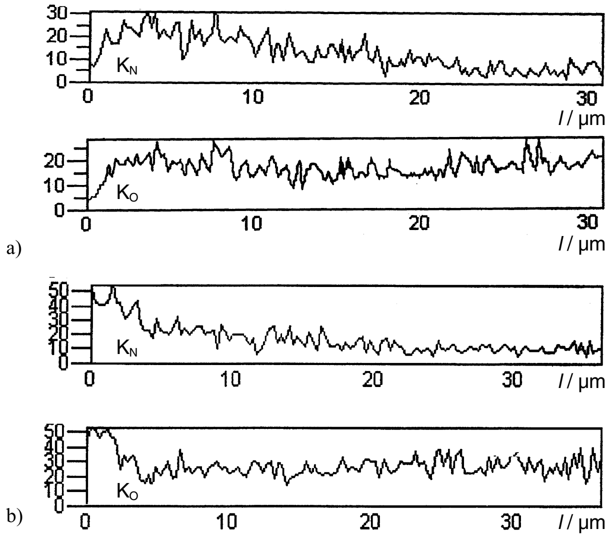

Figure 4: Distribution of nitrogen and oxygen from the surface to the inside of samples nitrocarburized in the TENIFER salt bath at 580 °C for 2 h and additionally submitted to: **a)** cooling in water, **b)** cooling in AB1 salt bath at 370 °C for 10 min and further cooling in water, polishing and oxidizing in AB1 bath at 370 °C for 10 min and finally cooling in water (TENIFER QPQ process)

Slika 4: Porazdelitev dušika in kisika od površine proti notranjosti preizkušancev, ki so bili nitrocementirani 2 h pri 580 °C v solni kopeli TENIFER in ohlajeni na enem od naslednjih načinov: **a)** ohladitev v vodi, **b)** ohladitev v solni kopeli AB1 10 min pri 370 °C, ohlajeni v vodi, polirani in oksidirani v kopeli AB1 10 min pri 370 °C in končno ohlajeni v vodi (TENIFER QPQ-postopek)

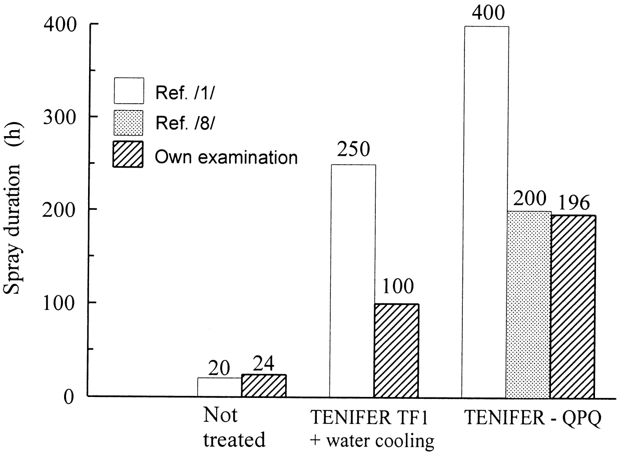

Figure 5: Time to start of the corrosion attack for samples of steel grade Ck45 after the TENIFER or the TENIFER QPQ treatment according to reference data and authors' investigations

Slika 5: Čas do začetka korozije za preizkušance iz jekla Ck 45 obdelanih po postopku TENIFER ali TENIFER QPQ po podatkih iz literature in po rezultatih v tem delu

nical device. The standard probe and RC filter for 0,80 nm wavelengths have been used. The mean depth of roughness R_z (µm), maximum roughness depth R_{max} (µm) and mean value of roughness R_a (µm) were calculated from the measured values (**Figure 2**).

The microstructure on the cross-section of the samples treated with both processes (TENIFER nitrocarburizing process and nitrocarburizing with post-oxidation applying TENIFER QPQ process) was assessed in optical microscope and the Vickers (HV0.2) hardness distribution across the samples was measured, (**Figure 3**). The distribution of nitrogen and oxygen in the edge area of the same samples was determined with electron probe microanalysis, (**Figure 4**).

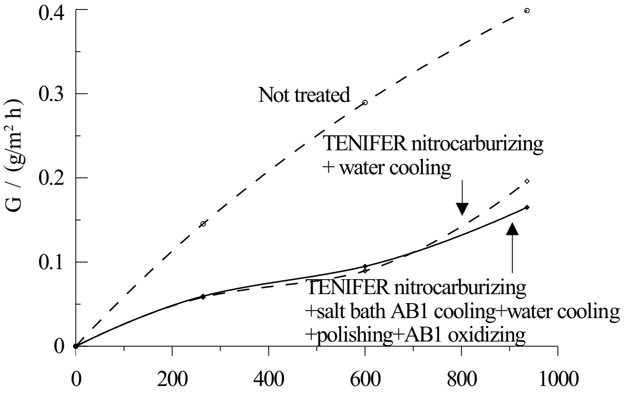

Figure 6: Corrosion rate *G* for samples of steel grade Ck45 in salt atmosphere in test chamber determined with the gravimetric method. The surface of tested sample was of 2042 mm^2

Slika 6: Hitrost korozije *G* za preizkušance iz jekla Ck 45 v slani atmosferi v korozijski komori, določena z gravimetrično metodo. Ploščina preizkušancev je bila 2042 mm^2

Table II: Corrosion resistance for differently treated samples of steel grade Ck45
Tabela II: Korozijska odpornost različno obdelanih preizkušancev iz jekla Ck 45

Heat treatment	Gravimetic testing		Electrochemical testing	
	Corrosion rate G / (g/m^2 h)	Protection level %	Corrosion current density μA/cm^2	Protection level %
Non-treated condition	0,399	0	10,8000	0
Nitrocarburizing with the TENIFER process	0,196	51	0,5445	95
Nitrocarburizing and post-oxidizing with the TENIFER QPQ process	0,165	59	0,2896	97

The corrosion velocity was determined using two methods: in the corrosion chamber and applying an electrochemical method.

– The corrosion velocity in the corrosion chamber was determined using for mass loss method (SS test according the DIN 50021 standard). The chamber atmosphere was saturated with droplets of electrolyte (5% water solution of NaCl with additions of $CuCl_2$). The acidity of the solution was of pH = 3.01, the spraying pressure was of 30 N/mm^2 and the testing temperature of 25 °C. The corrosion rate was determined with weighing of samples prior and after the exposure to the corrosive environment. The solid corrosion products were removed applying water jet prior to mass measurement. The results these testings are presented in **Figures 5** and **6** and in **Table II**.

– The determination of corrosion rate applying electrochemical method is based on the recording of changes in the electric potential between the tested sample and the reference electrode. The density of corrosion current is than calculated using Tafel's extrapolation. The saturated calomel electrode was used as the reference electrode, while the second electrode was of platinum. The working electrode (tested sample) was insulated with a teflon strip, except for the active surface, that was cleaned with ethanol prior each measurement. The potential-dynamic curves (current vs. tension) were recorded with an EG&G PARC Potentiostat/Galvanostat Model 263. A device and the Model 352/252 SoftCorr®II software was used to measure and

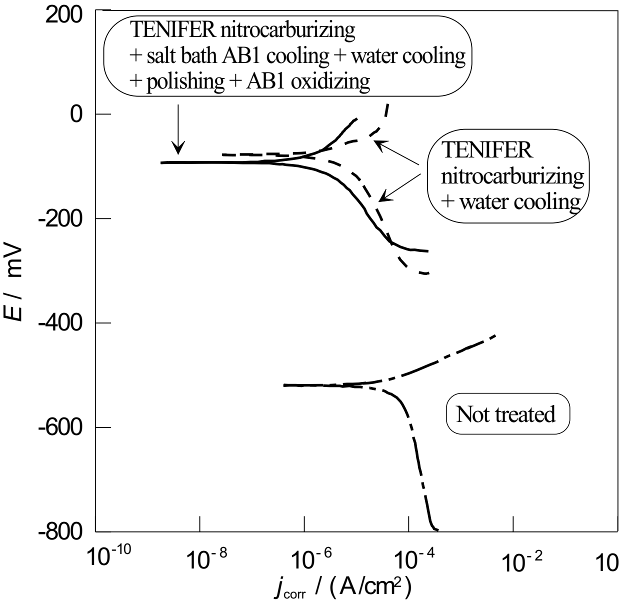

Figure 7: The potentio-dynamic curves of the electrochemical corrosion of steel Ck45 in 5% NaCl solution at 25 °C

Slika 7: Potenciodinamične krivulje elektrokorozije jekla Ck 45 v 5-odstotni raztopini NaCl pri 25 °C

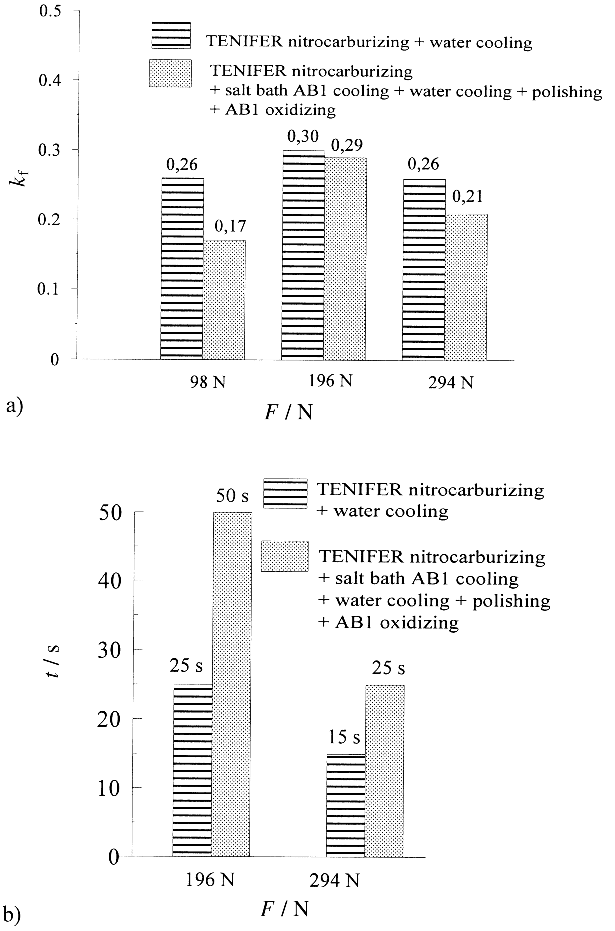

Figure 8: a) Mean value of friction coefficient; b) Start of galling in mating contact "test sample-friction wheel" – for different test conditions

Slika 8: a) Povprečne velikosti koeficientov trenja; b) Začetek trošenja pri kontaktu preizkušanec – torni prstan za različne pogoje preizkušanja process the collected data. The stationary electrochemical potential was established within 3000 s period. The results are presented in **Figure 7** and **Table II**.

– The resistance to adhesive wear and the friction coefficient were determined using the "block on ring test apparatus" with the sliding contact lasting for 1 minute, (about approximately 30 revolutions of the friction wheel). Before the start of the testing, the leverage was calibrated, i.e. the relationship between displacement of elastic spring and friction force was determined. A new friction wheel made of hardened bearing steel was used for each test. The displacement of the elastic spring was recorded during the test, and the friction force was calculated applying a calibration curve. The normal force in the sliding pair was achieved with a load hanging on an elastic spring. The mass of the sample was measured before and after testing and the wear loss determined. The results of testing are presented in **Figure 8**.

3 RESULTS AND DISCUSSION

3.1 Surface roughness

From the roughness parameters determined for the nitrocarburizing with and without post-oxidation of the surface (**Figure 2**) the following conclusions may be drawn:

- The surface roughness (all parameters) is increased when compared with the "as delivered non nitrided" condition after the TENIFER processing, no matter whether the cooling was performed in water or in AB1 salt bath. This fact can be attributed to the formation of the compound layer.
- The intermediate polishing significantly reduced the roughness, and for the applied polishing parameters, roughness equals to the original condition.
- The values of roughness parameters remain at the same level after subsequent oxidation in AB1 bath when compared to the preceding polished condition. This indicates that additional polishing after the post-oxidation in AB1 bath is not required.

After TENIFER nitrocarburizing of a component, the surface roughness is increased, and for example, dies for plastic processing must be polished after the treatment.

3.2 Hardness, microstructure and nitrogen and oxygen distribution in the surface layer

From the distribution of hardness on the transversal cross-section of the nitrocarburized sample and nitrocarburized sample with post-oxidizing (**Figure 3**) the following conclusions may be drawn:

- Approximately the same layer depth has been achieved in both samples, i.e. total depth of both layers was approximately 0,8 mm.
- There are differences in hardness closely to the sample surfaces. Merely nitrocaburized steel sample has attained a hardness for 40 HV0.2 higher than that of the sample submitted to nitrocarburizing and post-oxidizing. This can be attributed to different cooling rates from the nitrocarburizing temperature. Merely nitrocarburized sample was cooled down quickly in water, while the nitrocarburized and post-oxidized sample was cooled slowly in the salt bath. Low cooling rate achieved in AB1 bath induced the precipitation of nitrides in the diffusion zone, and subsequent heating in the AB1 bath to 370 °C for 10 min boosted the mentioned process and decreased slighty the hardness.

With metallographic analysis over the edge area of nitrocarburized samples (**Figure 3**) the following was observed:

- The compound layer is slightly deeper for samples submitted to plain nitrocarburizing (17 μm) if compared to that in the sample post-oxidized after nitrocarburizing (14 μm) due to the partial layer removal at intermediate polishing.
- The compound layer in the nitrocarburized and post-oxidized sample exhibits lesser porosity level than that in the sample merely nitrocarburized. This can be attributed to the filling of pores with oxides. This is confirmed by the results of chemical analysis of the samples (**Figure 4**).
- Differences are also spotted in the diffusion layer. If oxidizing after nitrocarburizing is applied, needle like nitrides are precipitated in this layer. Such precipitates were not found if only nitrocarburizing was performed. The slower cooling from the nitrocarburizing temperature and the following heating in the oxidizing AB1 bath promote the precipitation of nitrides. Precipitated nitrides cause a somewhat reduced hardness of the diffusion layer (**Figure 3**) and decrease the fatigue strength if compared to the merely nitrocarburized steel. However, this strength is still for approximately 100 N/mm^2 higher than that of non-treated steel samples [1,9].

The distribution of nitrogen and oxygen measured from the nitrocarburized surface to the sample core indicates that:

- The content of nitrogen in both tested samples decreases continuously from the edge towards the core indicating the diffusion of nitrogen into the steel;
- The radiation emission curves (corresponding to the oxygen content) (**Figure 4**) exhibit no changes for greater depths but they do it near the surface of the samples. For the sample treated according to the TENIFER QPQ process an increased content of oxygen is recorded in the surface layer down to the depth of approximately 5 μm, if compared with values for the greater depths. According references [2,4], finely dispersed particles of iron oxides FeO and FeO_2, and particularly Fe_3O_4 provide for the filling of pores in the ε-carbonitride layer ($Fe_2(CN)$) in the

depth range up to (5…10) µm. In the same time a compact oxide layer is produced on the very surface.

3.3 Corrosion resistance and corrosion velocity

The first traces of corrosion tests in the salt chamber were noticed with visual inspection on the edges of samples (Figure 5). Due to the subjective evaluation for the used visual method the times for the start of corrosion process was somewhat different from those reported in references [1,2,5]. Test samples treated according to TENIFER QPQ process resisted to the corrosion attack twice as long as those samples treated applying the merely nitriding process (TENIFER) as found also in references [1,2,6].

The corrosion rate after exposure of 264, 600 and 936 hours to the corrosion atmosphere was determined applying the gravimetric method (**Figure 6**). After 936 hours exposure samples treated according to TENFER QPQ exhibited lower corrosion rate (0,165 g/m^2 h) than those treated with the classic TENIFER process (0,196 g/m^2 h) and a significantly lower corrosion rate than non-treated steel samples (0,399 g/m^2 h), Table II. The level of corrosion protection (z) achieved through heat treatment of tested samples can be calculated by expression:

$$z = \frac{v_{\mathrm{corr0}} - v_{\mathrm{corrTF}}}{v_{\mathrm{corr0}}} \cdot 100\ \%$$

where v_{corrO} is the corrosion rate for non-treated sample, v_{corrTF} is the corrosion rate for nitrocarburizing applying TENIFER or TENIFER QPQ processes. The nitrocarburizing applying TENIFER process provides for a sample surface protection of the level of 51 %, while nitrocarburizing with post-oxidation (TENIFER QPQ process) provides for 59 % protection if compared to non-treated condition.

These results should be considered with caution because the removal of corrosion products from the sample surface was incomplete. Therefore the more reliable and accurate electrochemical method for determination of corrosion rate was applied and the corrosion rate was expressed as current density in the tested sample determined applying the Tafel extrapolation.

This extrapolation is performed with the recording of potentio-dynamic current-voltage curves applying a polarization (first cathodic and then anodic). The results of measurements are plotted in the semi-logarithmic scale. The density of corrosion current ($j_{\mathrm{corr}}/(\mathrm{A/cm^2})$) is determined at the intersection of the Tafel extrapolation lines.

The potentio-dynamic curves (**Figure7, Table II**) indicate significant difference in corrosion resistance. The resistance of nitrocarburized and post-oxidized sample (TENIFER QPQ process) is considerably improved when compared to the merely nitrocarburized sample. The calculation of the protection level (z) indicates that the nitrocarburizing process TENIFER provides a 95 % protection against corrosion, while the application of TENIFER QPQ process provides a 97 % protection when compared to the non-treated condition.

3.4 Coefficient of sliding friction and resistance to adhesive wear

The coefficient of sliding friction was determined for nitrocarburized samples with or without subsequent oxidation applying several different loads on the material couples test sample –friction wheel (without lubrication) using a block-on-ring test apparatus. The results are shown in **Figure 8**.

The nitrocarburized samples submitted to oxidation had a lower coefficient of friction for both lower and higher loads than samples submitted to nitrocarburizing only. This finding doesn't agree with results reported in [1]. This inconsistency may be attributed to different method of testing. The measuremet of the time to start of galling at two normal loads (196 N and 294 N) indicate that nitrocarburized and post-oxidized samples exhibit significantly longer time to start of adhesive wear than the merely nitrocarburized samples at both loads. The load of 296 N cause immediate galling of both types of samples at the very start of the test and that limits the testing load. The lower coefficient of friction and better resistance to galling for nitrocarburized and post-oxidized samples is attributed to the formation of the oxide layer at the surface of the compound zone, and lower roughness if compared to the merely nitrocarburized steel.

4 CONCLUSIONS

The comparison of the standard salt-bath nitrocarburizing and the process including the additional treatment of nitrocarburized steel parts in an oxidizing salt bath (TENIFER QPQ process), can shows that:

- The hardness in the diffusion zone were not significantly reduced.
- The smaller cooling rate in the oxidizing bath decreases the level of residual stresses and distortion. However, due to precipitated nitrides in the diffusion zone, lower fatigue strength may be expected for carbon steels.
- The surface roughness is not changed during the following oxidation. Thus, for example in manufacturing of a die, the working surfaces should be polished after nitrocarburizing and prior to the following oxidation.

During the treatment in the AB1 salt bath, iron oxide is formed in the compound zone and this additionally improves the properties:

- The coefficient of friction is reduced and resistance to adhesive wear is improved.

- The resistance to corrosion is significantly improved, indicating to a possible wider application of this process for engineering components and tools subjected both to wear and substantial corrosion attack. As an example, in the manufacturing of dies for processing of polymers, it could be possible to replace expensive stainless tool steel with less expensive steel grades (unalloyed or low-alloyed) provided that the TENIFER QPQ process is used.

Also, significantly improved corrosion resistance and resistance to adhesion wear, dimensional stability and smaller surface roughness as well as the appearance of the surface indicate that this process may replace some other surface treatment processes, such as chromizing and nickelizing.

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