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Corrosion resistance of surface treated 42CrMo4 steel

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Abstract

This article deals with corrosion resistance comparison of plasma nitrided 42CrMo4 steel to another surface technologies used for breech mechanism manufacturing in the armament production. Increasing of demands on materials used for armament production and in other industrial applications leads to the innovation of technologies in the field of surface treatment, especially wear resistance, surface hardness, running-in properties and corrosion resistance, optical demands and others. For the evaluation of experimental corrosion resistance were plasma nitrided samples of 42CrMo4 steel compared with alkali blackening, manganese phosphate and Arcor® technologies. The conditions of plasma nitriding process were set to provide exactly defined nitride layers with defined parameters. In this case, the above-mentioned surface technologies were applied to individual samples of 42CrMo4 steel, which were subsequently metallographically evaluated and the hardness and microhardness were measured. The corrosion resistance comparison was realized by the NSS corrosion tests in the condensation chamber and visually evaluated. The results and comparison of corrosion resistance of plasma nitrided steel samples with above-mentioned surface treatment technologies showed significant differences in corrosion rate propagation. Thank to different plasma nitriding conditions, there are evident differences in corrosion resistance between the plasma nitrided steel samples as well. The corrosion resistance evaluation is supplemented by the surface layer characteristics.

Key words: plasma nitriding, breech mechanism, corrosion resistance

1. Introduction

The plasma nitriding technology is based on saturation of the surface of components (made of steels or cast iron) by nitrogen comprised in plasma under anomalous glow discharge conditions and deals for the most effective nitriding technology, compared to gas and liquid nitriding. The plasma nitriding technology was mostly used primarily to increasing of surface hardness, wear resistance and fatigue limit in the past. Nitrides creation occurs inside the material as a result of the nitriding process. So-called white layer (compound layer) is created on the surface of treated component and consists of ε-$Fe_{2-3}N$ and γ-Fe_4N phase. The layer is characterized by high hardness and fragility (aluminium alloyed steels reaching the surface hardness up to 1500 HV), with good wear resistance and anticorrosion properties [1–3]. Beneath the compound layer the diffusion layer is created, which consists of dispersive iron nitrides and nitrides of alloying elements with high affinity to nitrogen [4].

The properties and nitride layers composition are influenced mostly by the nitriding gas mixture composition and by the nitriding process conditions like temperature, voltage, nitriding duration and by the surface conditions [3, 5]. Monitoring of surface roughness parameters like Pa, Ra and Wa (μm) has been demonstrated an increase of these parameters after plasma nitriding process [6]. The corrosion resistance of nitrided steels depends on the phase composition and compound layer integrity [7, 8]. A positive influence of ε-phase ($Fe_{2-3}N$) to corrosion resistance increase had been found; this increased corrosion resistance can be further increased by the post-oxidizing process (surface oxidation) of the nitride layer [9–11]. Corrosion resistance of plasma nitrided 42CrMo4 steel (AISI 4137/4140), used in weapon industry for breech mechanism manufacturing, was compared with

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Table 1. Chemical composition of 42CrMo4 steel

Chemical composition (wt.%)								
Element	C	Mn	Si	Cr	Ni	Mo	P	S
DIN standard	0.38–0.45	0.50–0.80	0.17–0.37	0.90–1.20	< 0.50	0.15–0.30	< 0.035	< 0.035
GDOES/Bulk*	0.45	0.75	0.20	1.06	0.11	0.20	0.007	0.035

*Parameters of GDOES/Bulk analysis: $U = 800$ V, $I = 30$ mA, $p(\mathrm{Ar}) = 314$ Pa

Table 2. Samples marking and surface treatment

Samples marking	Process*
1	HT
2	Alkali oxidized
3	MP
4	Arcor®
5	PN ($3H_2$:$1N_2$, 5 h)
6	PN ($1H_2$:$3N_2$, 5 h)
7	PN ($3H_2$:$1N_2$, 10 h)

*Process: HT is heat treatment, MP is manganese phosphate, and PN is plasma nitriding

another surface technologies used for surface treatment of breech parts namely: alkali blackening used for optical and aesthetic reasons, manganese phosphate used for running-in improvement and nitrocarburizing (Tenifer®) for wear and corrosion resistance increasing.

The corrosion resistance was tested by the NSS corrosion test according to ISO 9227 standard and visually evaluated using the QuickPHOTO Industrial 2.3 software. After corrosion products removing was the surface by the laser confocal microscopy Olympus LEXT OLS 3000 evaluated. The results of corrosion tests and the layers properties evaluation were further supplemented: metallographic documentation and measuring of compound layers thickness were carried out using the light microscope OLYMPUS GX 51 equipped with software ANALYSIS. Thickness and microhardness of created layers were measured by Vickers microhardness method in accordance with DIN 50190 standard on automatic microhardness tester LECO LM 247 AT and later via concentration profiles measured by GDOES/Bulk method on LECO SA 2000 spectrometer were confirmed.

2. Experimental

The corrosion resistance of 42CrMo4 steel was evaluated on tempered experimental steel samples of size 50 × 50 × 5 mm^3. The chemical composition of used steel was verified by the GDOES/BULK method using the SA2000 LECO device, see Table 1.

Heat-treated and surface treated steel samples were marked according to Table 2. Some of the heat-treated steel samples were subsequently surface treated. Surface treatment of steel samples marked as 2–4 was prepared in cooperation with used treatment conditions for concrete applications.

Two-step alkali blackening process of sample No. 2 was realized by macerating in hot alkalic-oxidizing solution Brün Rekord powder at 141–143 ℃ for 10–15 s. For the creation of manganese phosphate layer of sample No. 3 was used the sodium phosphate solution of Phosphata M 111/5556 at 80–85 ℃ for 20 s. The Arcor® technology was used for the nitrocarburizing process, more accurately nitrocarburizing in a salt bath of SURSULF for 45 min under temperature 590 ℃ followed by an oxidation process in a salt bath of OXINIT for 10 min at 430 ℃ (also known as Tenifer®).

The steel samples marked as 5–7 (see Table 2) were plasma nitrided under a two-step process. The first step, so-called plasma cleaning process, was set before each plasma nitriding process to remove the surface oxides and to the surface activation. The plasma nitriding process was realized under concrete nitriding conditions according to Table 3 in the plasma nitriding RUBIG PN 60/60 device.

The corrosion resistance testing of alkali oxidized, phosphated, nitrocarburized and plasma nitrided steel samples were carried out in a fog of a 5 % neutral sodium chloride solution (NSS) in accordance with ISO 9227 standard in the VLM GmbH SAL 400-FL corrosion chamber under following conditions: the temperature of 35 ± 2 ℃, 5 % neutral sodium chloride dilution, the amount of vapour condensation 1–2 $\mathrm{ml\,h^{-1}}$ on square of 80 cm^2, pH 6.5–7.2, the suspension angle of 20° from the vertical line, the exposition period 1, 2, 4, 8, 16, 24, 40, 56, 72, 96, 120, 144, 192, 240, and 288 h. The samples were degreased before the corrosion testing by the technical benzoline and ethyl alcohol, and the edgings and suspension apertures were conserved by FERRO COLOR U2066 resistant paint. Edgings and suspension apertures conservation was proved by previous experiments [7].

During the corrosion tests, the uniform type of corrosion attack and pitting corrosion were supposed as a reason of the nitride layer incompactness. Pitting can cause fatigue of material by cracking initiation and propagation. During the evaluation periods

Table 3. Plasma nitriding process parameters

No.	Process*	Temperature (℃)	Duration (h)	Pressure (Pa)	Pulse length (μs)	Bias (V)	Gas flow H_2:N_2 ($l\,h^{-1}$)
	Plasma cleaning	480	0.5	80	100	800	20/2
5	PN	500	5	280	100	520	24/8
6	PN	500	5	280	75	520	8/24
7	PN	500	10	280	100	520	24/8

*Process: PN is plasma nitriding

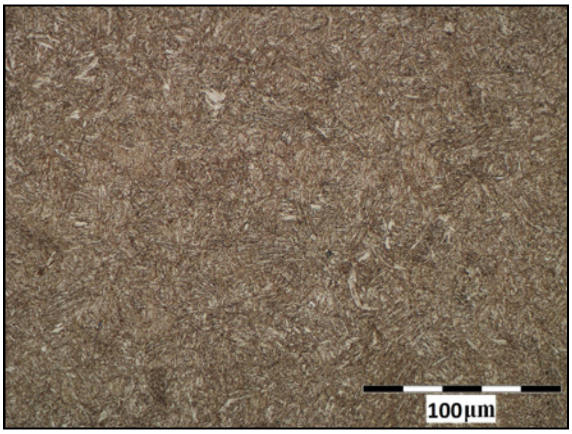

Fig. 1. The cross-sectional microstructure of heat-treated of 42CrMo4 steel (light microscope OLYMPUS GX 51).

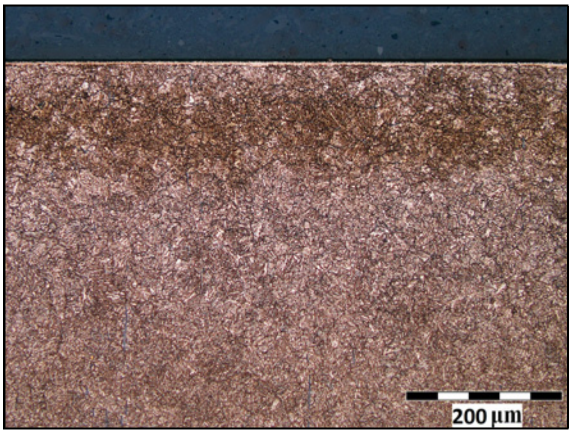

Fig. 2. The cross-sectional microstructure of 42CrMo4 steel plasma nitrided sample No. 7 – PN $3H_2$:$1N_2$ for 10 h (light microscope OLYMPUS GX 51).

were the samples visually evaluated, using the QuickPHOTO Industrial 2.3 software with Phase analysis application. Finally after reaching 100 % of corroded surface corrosion tests were completed. Finally were these corroded surfaces in accordance with ISO 8407:1991 standard chemically (500 ml of HCl, 3.5 ml of urotropine and 496.5 ml of H_2O solution) and mechanically (brushed) from corrosion products cleaned. So corrosion products-free samples surfaces were by the laser scanning microscope OLYMPUS OLS 3000 evaluated.

3. Results

Manufactured samples of 42CrMo4 steel were normalized (850 ℃), oil quenched (850 ℃) and air tempered (550 ℃) to attain optimal mechanical properties. Upper bainitic-sorbitic microstructure was confirmed using the light microscopy as can be seen in Fig. 1 on the cross-sectional chemically etched microstructure.

For metallographic testing, all samples were crosswise cut, wet ground using silicon carbide paper with grit from 80 to 2000 and subsequently polished and finally by Nital etched. The cross-structure observation and documentation were realized under magnification of 200× and 500× using the optical microscopy (as presented in Fig. 2). As well as for surface layers evaluation (samples No. 2 and 3) and measuring of compound layer thickness (samples No. 4–7) was used the optical microscope OLYMPUS GX 51 equipped with software ANALYSIS.

The surface layer thickness of thin layers was confirmed by light microscopy and by concentration profile measurement, realized using the SA2000 LECO device (GDOES/Bulk). The thickness of hard-surface layers and depth of diffusion layers were evaluated by microhardness testing using the automatic microhardness tester LECO LM 247 AT equipped with software AMH43. The microhardness testing and measuring of diffusion layers depth was carried out in the direction from the surface to the core at 50 g load and 10 s dwell time in accordance with DIN 50190 standard. The final microhardness profile and measuring of diffusion layer depth was determined by 18 indentations with variable indentation spacing, as presents Fig. 3. The surface layers and diffusion layers characteristics are summarized in Table 4.

During the NSS corrosion tests in accordance with ISO 9227 standard were different trends of corrosion attack and corrosion resistance observed, dependent on surface treatment. Different corrosion resistance of plasma nitrided steel samples is due to different

Table 4. Microhardness and layer properties

No.	Surface hardness, HV	Microhardness		Nht, HV0.05	Case depth (mm)	Surface layer thickness (μm)
		Core, HV0.05	Surface, HV0.05			
1	384	–	–	–	–	–
2	349	364	360	410	0	1.1^{B}
3	513	357	351	410	0	3.7^{MP}
4	719	347	626	400	0.132	1^{B}+ 3.5^{TL}
5	782	380	829	430	0.181	3.7^{C}
6	792	371	809	420	0.199	5.6^{C}
7	786	365	772	410	0.248	4.3^{C}

^{B} – black oxide layer, ^{MP} – manganese phosphate layer, ^{TL} – tie-layer, ^{C} – compound layer

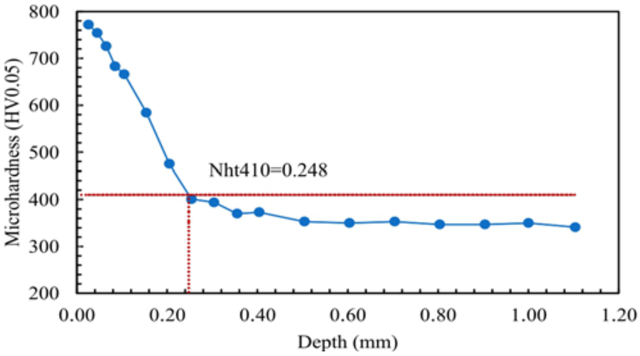

Fig. 3. Microhardness profile of 42CrMo4 steel plasma nitrided sample No. 7 – PN $3H_2:1N_2$ for 10 h.

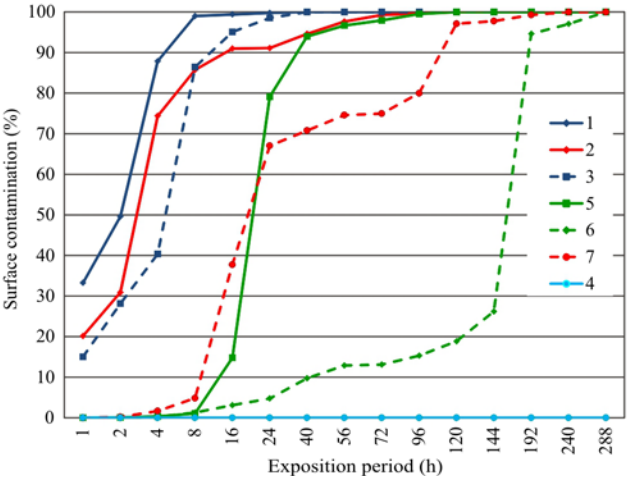

Fig. 4. The progress of corrosion propagation (NSS corrosion tests – visual evaluation).

plasma nitriding process conditions and created nitride layers parameters related. The progress of corrosion propagation during the NSS corrosion tests is summarized in Fig. 4.

The results showed that plasma nitriding and Arcor® technology significantly increase the surface hardness of structural steels, but also the corrosion resistance. The first signs of corrosion attack of nitrided 42CrMo4 steel samples at the beginning of exposure were almost identical, but the courses of corrosion attack were different.

The surface of sample No. 1 (HT – no surface treatment) was corroded from 50 % of the surface and sample No. 2 (alkali oxidized) and No. 3 (MP) about 30 % of the surface. After 40 h of exposure were exposed surfaces of samples No. 1 (HT) and No. 3 (MP) fully corroded and the sample No. 2 (alkali oxidized) after 72 h of exposure later. Sample No. 5 plasma nitrided in standard atmosphere for 5 h (PN $3H_2:1N_2$, 5 h) was fully degraded after 120 h of exposure. Sample No. 7 plasma nitrided in standard atmosphere for 10 h (PN $3H_2:1N_2$, 10 h) showed after 96 h of exposure 80 % of the corroded surface and after 240 h was fully corroded. Compared to sample No. 5 was the corrosion propagation of sample No. 7 more favourable (as shows Fig. 4). The best results among the plasma nitrided steel samples reached the No. 6 plasma nitrided steel sample in so-called reverse nitriding atmosphere for 5 h (PN $1H_2:3N_2$, 5 h). The corrosion propagation of sample No. 6 was weak at the beginning of corrosion tests, but after 192 h of exposure graduated rapidly. After 288 h of exposure in NSS was this sample fully corroded. The corrosion resistance of plasma nitrided 42CrMo4 steel can be further improved by the post-oxidizing process as well, known as Plasox®, e.g. [12–14].

Excellent results reached sample No. 4 (Arcor®) as can be seen in Fig. 5. Not even after 384 h of exposure in NSS were any signs of corrosion observed. To the corrosion resistance has a significant influence the thickness and the surface layer composition obviously. The Arcor®, a nitrocarburizing process in the salt bath, was followed by a post-oxidation process to form a thin and compact Fe_3O_4 oxide layer covering the pores in the tie-layer [15]. This surface layer is especially resistant to abrasion, corrosion and galling as well [16].

Increased corrosion resistance of nitrocarburized and further post-oxidized and plasma nitrided

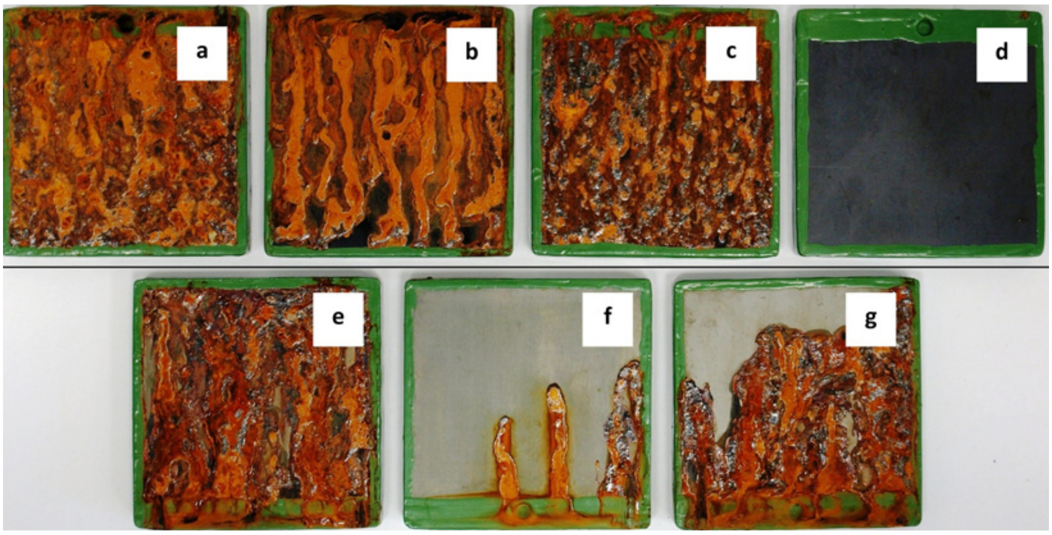

Fig. 5. NSS corrosion tests after 56 h of exposure; (a) HT, (b) alkali oxidized, (c) manganese phosphate, (d) Arcor®, (e) PN $3H_2{:}1N_2$ for 5 h, (f) PN $1H_2{:}3N_2$ for 5 h and (g) PN $3H_2{:}1N_2$ for 10 h.

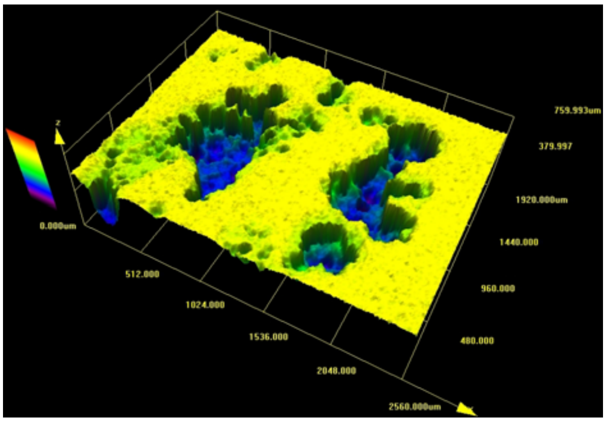

Fig. 6. 3D surface topography of 42CrMo4 steel plasma nitrided sample No. 6 (confocal laser microscopy, Olympus OLS 3000).

42CrMo4 steel can be related to the state surface after corrosion products removal as well. Surfaces with increased corrosion resistance tend to pitting corrosion, typical for passivable surfaces of stainless steels for example, like plasma nitrided steel samples as seen in Fig. 6.

The pitting is possible due to Cl^- ions, which are able to transfer through the imperfections in the thin oxide layer (cathodic surface) to the compound layer which is not micropores free. Corrosion mechanism of plasma nitrided and nitrocarburized steels is similar to nitrogen alloyed stainless steels (e.g. FeCr22Ni7Mo3N) [17].

4. Conclusions

The best corrosion resistance results of compared treatments used for 42CrMo4 steel reached the Arcor® (sample No. 4), not even after 384 h of exposure in NSS were any corrosion attacks observed. The nitrocarburized layer was composed of 3.5 μm thick monophasic ε-phase (Fe_xN) tie-layer. This increased corrosion resistance is reached thanks to 1 μm thick black oxide layer on the surface of the monophasic tie-layer and is dependent on the compactness of tie-layer as well.

The best result of plasma nitrided 42CrMo4 steel reached sample No. 6 (nitrided in so-called reverse nitriding atmosphere for 5 h) with a compound layer of 5.6 μm thick mainly composed of ε-phase ($Fe_{2-3}N$). The results showed that plasma nitriding and Arcor® technology significantly increases the surface hardness and corrosion resistance of structural steels. Significant differences of plasma nitrided steel samples thanks to different plasma nitriding parameters were found due to tie-layer phase composition and compound layer thickness.

Plasma nitrided and nitrocarburized 42CrMo4 steel tends to suppression of uniform corrosion, and local form of corrosion (pitting) contributes to the corrosion of the treated surface. The supersaturated surface layer (tie-layer) by nitrogen most likely supports the passivation mechanism. Nitrogen, in the form of negatively charged N_3^- ion, which makes possible the formation of NH_4^+ ions, slows down the initiation of uniform corrosion and growth of pits due to rise of acidity.

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References

[1] Pye, D.: Practical Nitriding and Ferritic Nitrocarburizing. Ohio, ASM International Materials 2003.

[2] Holemar, A., Hrubý, V.: Plasma Nitriding in Practice. Praha, SNTL 1989. (in Czech)

[3] Wen, D.-Ch.: Surface and Coatings Technology, *204*, 2009, p. 511. doi:10.1016/j.surfcoat.2009.08.023

[4] Nikolussi, M., Leineweber, A., Bischoff, E., Mittemeijer, E. J.: International Journal of Materials Research, *98*, 2007, p. 1086. doi:10.3139/146.101576

[5] Hirsch, T. K., Rocha, A. D. S., Ramos, F. D., Strohaecke, T. R.: Metallurgical and Materials Transactions A, *35*, 2004, p. 3523. doi:10.1007/s11661-004-0189-2

[6] Kusmic, D., Svoboda, E., Hruby, V.: In: Proceedings of Conference on Coating and Layers 2007. Trenčín, Digital Graphic 2007, p. 73. ISBN 978-80-969310-4-0

[7] Kusmic, D., Hruby, V.: Advances in Military Technology, *3*, 2008, p. 65.

[8] Pokorný, Z., Hrubý, V., Kusmič, D.: Hutnické listy, *2*, 2010, p. 46.

[9] Wen, D. C.: Applied Surface Science, *256*, 2009, p. 797. doi:10.1016/j.apsusc.2009.08.062

[10] Basu, A., Majumbar, J. D., Alphonsa, J., Mukherjee, S., Manna, I.: Materials Letters, *62*, 2008, p. 3117. doi:10.1016/j.matlet.2008.02.001

[11] Mahboubi, F., Fattah, M.: Vacuum, *79*, 2005, p. 1. doi:10.1016/j.vacuum.2005.01.002

[12] Ebrahimi, M., Heydarzadeh, S. M, Mahboudi, F.: Surface and Coatings Technology, *205*, 2010, p. S261. doi:10.1016/j.surfcoat.2010.07.115

[13] Wu, J., Ye, X., Li, H., Hu, J.: Vacuum, *111*, 2015, p. 110. doi:10.1016/j.vacuum.2014.09.021

[14] Wu, J., Liu, H., Li, J., Yang, X., Hu, J.: Journal of Alloys and Compounds, *680*, 2016, p. 642. doi:10.1016/j.jallcom.2016.04.172

[15] Marušić, K., Otmačić, H., Landek, D., Cajner, F., Stupnišek-Lisac, E.: Surface and Coatings Technology, *201*, 2006, p. 3415. doi:10.1016/j.surfcoat.2006.07.231

[16] Zábavník, V.: Chemické listy, *105*, 2011. Available at: http://chemicke-listy.cz/docs/full/2011_s4_s633-s640.pdf (accessed 3.10.2016).

[17] Rotnik, U., Doleček, V., Vehovar, L., Božič, S.: Kovove Mater., *44*, 2006, p. 89.