Corrosion and Wear Resistance of Plasma Nitrided and Duplex Treated 42CrMo4 Steel

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Plasma nitriding is generally used as a final operation to improve wear, corrosion resistance and fatigue limit of machine parts. The corrosion and wear resistance of nitrided steels can be further increased by converse coating. This paper reports the results of corrosion and wear tests of plasma nitrided and duplex treated (plasma nitriding and manganese phosphate coating) 42CrMo4 steel. Plasma nitriding was carried out at 500 °C in different nitriding atmosphere ratio of $3H_2:1N_2$ and $1H_2:3N_2$ [l/h] for 15 hours. Plasma nitrided samples were subsequently manganese phosphated (without lubrication). The experimental samples were exposed to neutral sodium chloride solution, visually and gravimetric evaluated during exposure tests and after removing corrosion products. The wear test "ball on disc" was carried out at temperatures of 21 °C, 150 °C, and 300 °C, under a load of 20 N. The results confirmed the possibility of applying manganese phosphate coating to plasma nitrided steel to enhance its properties. X-ray diffraction phase analysis found the different volumes of ϵ -Fe₂₋₃N and γ '-Fe₄N nitrides in the compound layers and hureaulite Mn5 (PO₃ (OH))₂ (PO₄)₂ (H₂O)₄ in the manganese phosphate coatings. The results were supplemented by metallographical documentation, thickness and microhardness test.

Keywords: Plasma Nitriding, Duplex Treatment, Corrosion, Wear

1 Introduction

Plasma nitriding as a chemical heat treatment process is generally used to increase the surface hardness, fatigue strength and corrosion resistance [1, 2]. According to some authors, plasma nitriding increases the wear resistance [3], but it also reduces the notch toughness [4]. After nitriding process, a compound layer, usually composed of nitride phases γ' -Me₄N and/or ϵ -Me₂₋₃N, (supplemented by alloying elements like Al, Cr, Mo, V) [5], is created on the surface. The compound layer is characterised by increased hardness and good corrosion resistance, which can be decreased by porosity. An acceptable way to suppress these pores is the postoxidation process [6-10]. As well phosphating can be applied for increasing the corrosion resistance of steels, cast irons or zinc, magnesium, cadmium and often also aluminium [11-14]. Another purpose of phosphate converse coating is an improvement of running-in of rotating machine parts and decreasing of drag friction. The most frequently used process is zinc phosphating (coating formed mainly by hopeite Zn₃ (PO₄)₂ (H₂O)₄), zinc-calcium phosphate (formed by scholzite Zn₂Ca(PO₄)₂ (H₂O)₄, socalled "three-cations" phosphating (formed by phosphophyllite) and manganese phosphating (formed usually by dense crystalline coating of hureaulite Mn5 (PO₃ $(OH)_2 (PO_4)_2 (H_2O)_4$). At elevated temperatures (160 °C ÷ 400 °C), it is necessary to consider the dehydration process of phosphates, which can affect the quality and structure of phosphate coating. Hureaulite (manganese phosphating marked as Mnph in the text) deals for the most thermal stable type of phosphating [15]. The manganese crystalline structure can be modified to moderate the grain size of phosphate crystals and thus further to increase the corrosion resistance [16].

This paper is focused on the evaluation of corrosion and wear resistance of plasma nitrided and duplex treated (plasma nitriding and manganese phosphate converse coating) 42CrMo4 (AISI 4137/4140) steel and compared

to tempered one. The corrosion resistance was tested using the neutral sodium chloride solution corrosion test (marked as NSS in the text) according to ISO 9227 standard, visually and gravimetric evaluated. After removing the corrosion products, the surfaces were evaluated using the laser confocal microscopy. The wear test "ball on disc" was performed at a temperature of 21 °C, 150 °C, and 300 °C and a load of 20 N. The wear resistance and coefficient of friction during unlubricated sliding according to ASTM G99-95a standard was evaluated. Results of corrosion and wear tests were further supplemented by X-ray diffraction phase analysis, metallographic documentation and measuring of compound layer thickness. Thickness and microhardness of created layers were measured by Vickers microhardness method in accordance with DIN 50190 standard.

2 Experimental

For study was used the 42CrMo4 (AISI 4137/4140) steel with the following chemical composition [in wt.%]: 0.40 C, 1.08 Cr, 0.63 Mn, 0.27 Si, 0.15 Mo, 0.10 Ni, 0.0019 S, 0.0012 P. Chemical composition was verified using the Q4 Tasman device, calibrated by the Fe 130 and Fe 140 standards. Experimental samples were heated to 850 °C for 20 min, oil quenched, tempered at 550°C for 40 min to attain martensitic-carbidic structure. All the samples were ground to the roughness of Ra = 0.6 μ m and degreased in ethyl alcohol prior the plasma nitriding and following duplex treatment. Plasma nitriding process was applied under 3H₂:1N₂ [l/h] and 1H₂:3N₂ [l/h] nitriding gas ratio for 15 hours and marked as PN1 and PN2 in the text (see Tab. 1).

The duplex treatment of plasma nitriding process No 1 and No 2, and manganese phosphate coating (marked as PN1+ Mnph and PN2+Mnph) were prepared in a standard solution containing H₃PO₄, MnO₂, and demineralised water. The mean value of the measured thickness of Mnph coating was approximately 3.7±0.5 (μm) on

plasma nitrided steel samples. The phase analysis was performed by XRD Rigaku Miniflex 600 device (Rigaku D/teX Ultra 250, Cu Kα radiation), using PDXL software

with PDF-2 and Crystallographic Open Database for the quantitative analysis. As can be seen in Fig. 1, crystalline hureaulite Mn5 (PO₃ (OH))₂ (PO₄)₂ (H₂O)₄) was created.

Tab. 1 Plasma nitriding parameters (Rubig PN 60/60 device)

Process	Temperature	Duration	Pressure	Bias	Gas flow [l/h]	
	[°C]	[h]	[Pa]	[V]	H_2	N_2
Plasma cleaning	480	0.5	80	800	20	2
PN1	500	15	280	530	24	8
PN2	500	15	280	530	8	24

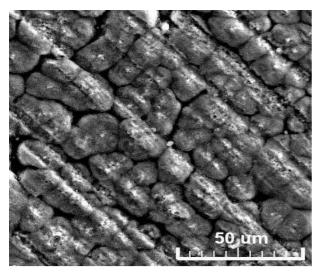


Fig. 1 Hureaulite - Manganese phosphate coating (SEM 1000x Tescan Vega)

For metallographic testing, all samples were crosswise cutted, wet ground using SiC paper with grit size from 80 to 2000, subsequently polished and finally etched by 2 % Nital,

Prior to metallographic testing, nitride layer depth was evaluated by microhardness testing in accordance with DIN 50190 standard using the automatic microhardness tester LECO LM 247 AT equipped with the AMH43 software. The microhardness depth profile was characterised by 18 indentations at a load of 0,49 N and 10 s dwell time. The nitride layer depth and the thickness of the compound layer of nitrided and duplex treated steel samples are summarised in Tab. 2.

The mircrostructure documentation and compound layer thickness measuring were realised using the optodigital microscope OLYMPUS DSX 500 (see Fig. 2 and Fig. 3). According to the X-ray phase analyses, it is evident, that increased ratio of N_2 to H_2 (l/h) in the nitriding atmosphere promotes the creation of ϵ -Fe₂₋₃N nitrides (see phase analysis in Fig. 3).

Tab. 2 Nitride layer characteristics

Process	Nitride layer depth	Compound layer (mean value)
Flocess	[µm]	[µm]
PN1	200	6.6±0.4
PN2	240	8.9 ± 0.6
PN1 + Mnph	180	4.4 ± 0.4
PN2 + Mnph	200	8.8 ± 0.6

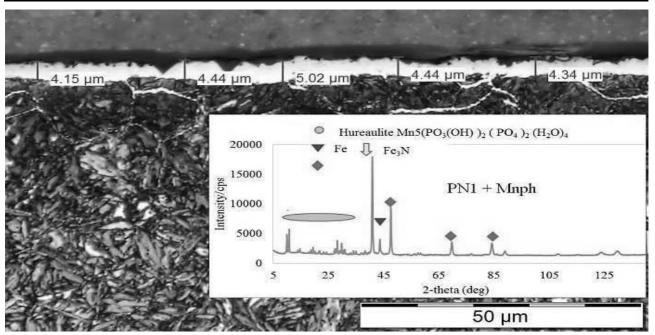


Fig. 2 Microstructure of plasma nitrided (process No 1) and manganese phosphated steel (PN 1+Mnph)

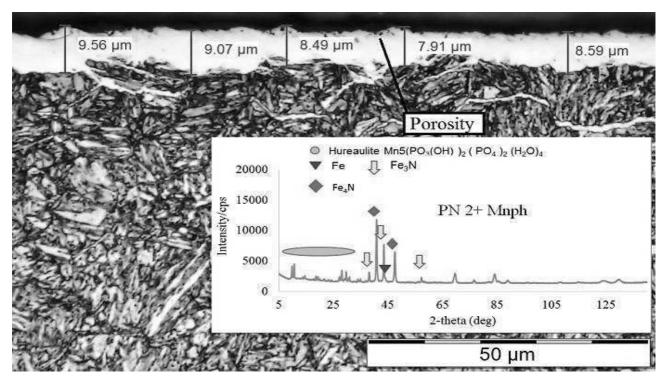


Fig. 3 Microstructure of plasma nitrided (process No 2) and manganese phosphated steel (PN 2+Mnph)

2.1 Corrosion resistance

The corrosion resistance was visually and gravimetric evaluated during 2, 4, 8, 24, 48, 72, 96, 144 and 196 hours of exposition periods. The NSS Exposure corrosion tests in the 5 % neutral sodium chloride solution were performed in accordance with ISO 9227 standard in the VLM GmbH SAL 400-FL corrosion chamber. Prior the exposure corrosion tests the samples were degreased by ethyl alcohol.

After defined exposition periods (2, 4, 8, 24, 48, 72, 96, 144 and 196 h) the exposed samples were dried and visually evaluated using the QuickPHOTO Industrial 2.3 software with phase analyses application and corroded

surface (in %) calculated. The surface corrosion propagation (full line) is summarised in Graph 1.

The corrosion resistance evaluation was supplemented by gravimetric evaluation, and the corrosion rates K_{corr} [mg.cm⁻².h⁻¹] were calculated, modified to weight gain (see dashed lines in Graph 1):

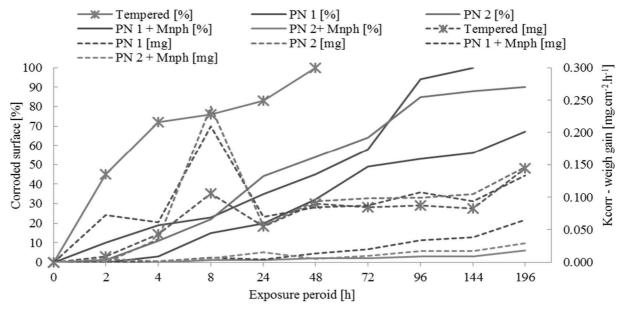
$$K_{corr} = \frac{m_t}{s \cdot t} \left[mg \cdot cm^{-2} \cdot h^{-1} \right] \tag{1}$$

Where:

m_t...Weight gain for period [mg],

S....Surface area [cm²],

t.....Evaluated period [h], (2, 4, 8, 24, 48, 72, 96, 144 and 196 hours).



Graph 1 Corrosion propagation

As seen in Graph 1 significant reduction of corrosion propagation [in % of surface] occurs after plasma nitriding process No 1 (PN1) and No 2 (PN2) compared to not nitrided steel (Tempered). This corrosion propagation was further reduced by following manganese phosphate converse coating (marked as PN1+Mnph and PN2+Mnph steel samples). After 196 h of exposures, the surface of sample PN1+Mnph was corroded of 67 % and sample PN2+Mnph of 6 %.

The visual evaluation after 196 h of exposure was compared to calculated K_{corr} [mg.cm⁻².h⁻¹] values (see Graph 1 dashed lines). As seen in Graph 1, the values of the corroded surface [in %] and values of K_{corr} – weight gain [mg.cm⁻².h⁻¹] have not the same progress as awaited. Generally, the corroded surface during the general corrosion deals with the weight gain. It means that there is another type of corrosion attack on the steel surfaces contributing to the corrosion attack, as seen peaks after 8 h of exposure. Very good correlation was found for PN1+Mnph and PN2+Mnph samples. To clarify this finding, the corrosion products were cleaned according to ISO 8407 standard from the surface. Using the laser confocal microscopy (Olympus Lext OLS 3000) the corrosion free surfaces were examined and additionally localised corrosion determined. Localised type of corrosion penetrated deeper into the surfaces especially of plasma nitrided steel (see samples PN1 and PN2), thanks to increased porosity of compound layer (see Fig. 4), and thus the values of K_{corr} – weight gain increases. This phenomenon was suppressed by Mnph converse coating (see samples PN1+Mnph and PN2+Mnph). The level of localised corrosion (pitting) can be expressed by so-called "Pitting factor" (marked as PF) given by ISO 11463 standard, as a ratio of the deepest pit depth to the average value of 10 pits depth. The value of PF = 1 represents the uniform type of corrosion and PF > 1, represents increased pitting.

After chemical cleaning, in accordance with ISO 8407 standard, the corrosion loss evaluation was expressed by Δm_x [mg.cm⁻²]:

$$\Delta m_{x} = \frac{m_{int} - m_{k}}{S} \left[mg \cdot cm^{2} \right]$$
 (2)

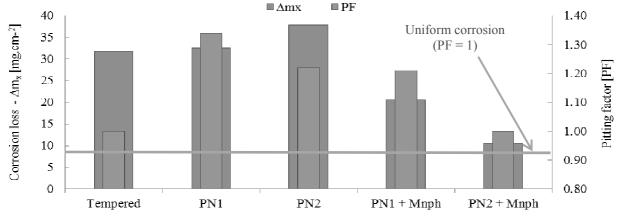
Where:

m_{int}...Initial weight [mg],

 $m_k.... Weight \ after \ removing \ corrosion \ products \ [mg],$

S.....Surface area [cm²].

The pitting factor values and total corrosion loss [mg.cm⁻²] are summarized in Graph 2. As seen after application of plasma nitriding, localised type of corrosion rises and has a significant share of corrosion loss. Application of manganese phosphate converse coating reduces this negative effect of plasma nitriding, see the reduction of corrosion loss and PF values in Graph 2 and Fig. 4.



Graph 2 Corrosion loss (\(\Delta mx \)) and pitting factor (PF) values after removing corrosion products

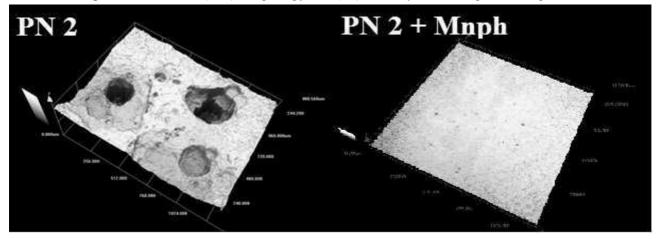


Fig. 4 3D surface evaluation of chemically cleaned samples – plasma nitriding process No 2 (PN2) deals with uniform and localised corrosion, with calculated PF = 1.21; plasma nitriding process No 2 and manganese phosphated steel (PN 2+Mnph) deals with smooth surface, with calculated PF = 1

2.2 Wear resistance

The samples for the wear test were prepared in the shape of round disk with a diameter of 70 mm and thickness of 6.6 mm. The heat treatment, plasma nitriding and following manganese phosphate converse coating were prepared in the same way as for corrosion tests.

The wear test "ball on disc", corresponded to ASTM G99-95a, was carried out on the tribometer BRUKER UMT-3. For the test was the tungsten carbide indentor used, with a diameter of 6.3 mm. Measurement parameters were set as follows: the normal load of 20 N, the rotary speed of 500 rpm, track radius of 20 mm, test duration of 27 min, 13500 cycles. In order to gain a required temperature of 21 °C, 150 °C and 300 °C, the sample (disc) and indentor were heated in the testing chamber for 25 minutes and kept at this temperature for 10 minutes to attain the same temperature as for the testing sample as well as for the indentor. After the wear test, the samples were air cooled and then cleaned in ethyl alcohol using an ultrasound cleaner for evaluation and measuring of the wear track (Fig. 5). The TALYSURF CLI 1000 profilometer was used to evaluate the wear depth and area of the wear profile (see Fig. 6).

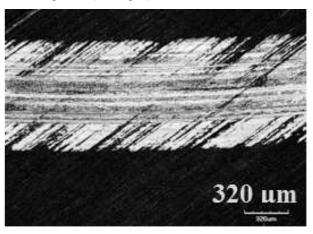


Fig. 5 The wear track, plasma nitriding process No 2 (PN2), 21 °C (measured by Olympus Lext OLS 3000)

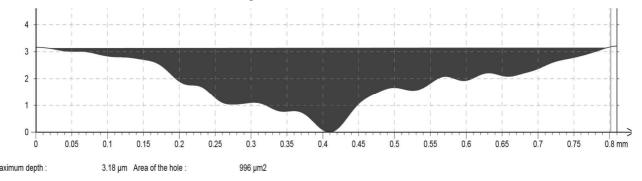


Fig. 6 Profile and area of wear profile measurement using TALYSURF CLI 1000 of (plasma nitriding process No 2, 21

Using the measured area of the wear profile the wear rates were calculated by the modified Archard' equation (summarised in Tab. 3): $w = \frac{A}{F_N \cdot \omega \cdot t} \left[mm^{-3} \cdot N^{-1} \cdot m^{-1} \right]$

$$w = \frac{A}{F_{N'}\omega \cdot t} \left[mm^{-3} \cdot N^{-1} \cdot m^{-1} \right] \tag{3}$$

w....Wear rate [mm⁻³.N⁻¹.m⁻¹],

A....Area of wear profile [mm⁻²],

 F_N ...Normal load [N],

 ΩRotary speed [rpm],

t.....Measurement time [min].

Tab. 3 Wear rate and coefficient of friction

	Wear rate [mm ⁻³ .N ⁻¹ .m ⁻¹]			Coefficient of friction [-]		
Process	21 °C	150 °C	300°C	21 °C	150 °C	300°C
Tempered	7.99 ± 0.19	2.76 ± 0.42	5.78 ± 1.49	0.92 ± 0.12	0.95 ± 0.02	0.96 ± 0.03
PN 1	3.21 ± 0.43	5.07 ± 1.25	21.53 ± 10.14	0.79 ± 0.14	0.66 ± 0.08	0.55 ± 0.06
PN 2	3.78 ± 0.76	4.94 ± 0.91	18.85 ± 5.28	0.83 ± 0.03	0.55 ± 0.03	0.55 ± 0.03
PN 1+Mnph	2.54 ± 0.36	2.94 ± 1.19	10.23 ± 5.21	0.76 ± 0.06	0.59 ± 0.04	0.61 ± 0.03
PN 2+Mnph	3.42 ± 0.72	2.43 ± 0.43	7.91 ± 1.31	0.74 ± 0.07	0.61 ± 0.05	0.62 ± 0.09

Plasma nitriding proces significantly reduces the wear rate at ambient temperature compared to the tempered steel sample as seen in Tab. 3, which can be further reduced by manganese phosphate converse coating. With increased temperature to 150 °C, the wear rates of plasma nitrided steel samples increases and duplex treated were almost unchanged, compared to decreased wear rate of tempered steel sample. At a temperature of 300 °C the wear rate of tempered steel, was slightly increased but it was lower than at ambient temperature. It is possible that

the enhanced oxidation kinetics of metallic materials during the sliding wear in elevated temperature during the sliding wear plays a role as self-lubricant, thus the wear was decreased [17, 18].

As seen in Tab. 3, the wear rate of plasma nitrided steel (process PN 1 and PN 2) at 300 °C was rapidly increased, using of manganese phosphate was the wear rate reduced to more than 50 % of plasma nitrided steel sam-

The value of friction coefficient was considered of the

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stable section of friction coefficient measurement (as plotted in Fig. 5) for testing temperatures and summarised

in Tab 3

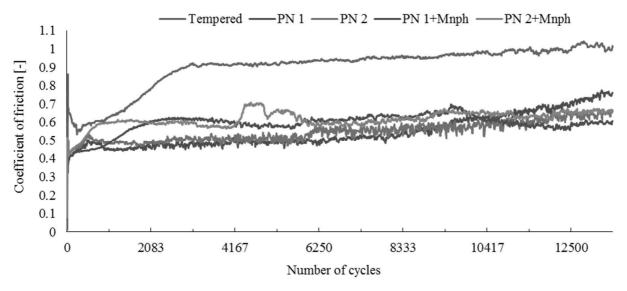


Fig. 5 Friction coefficient measurement under temperature of 300 °C

It is evident that tempered steel sample exhibits the greatest coefficient of friction, increased with temperature in the range of 21 °C \div 300 °C. Using of plasma nitriding significantly decreases the coefficient of friction for used temperature range and the lowest values were measured at 300 °C. At ambient temperature, manganese phosphate decreases the coefficient of friction of nitrided samples, however at elevated temperature duplex coating plasma nitriding + Mnph showed a higher coefficient of friction than substrate – nitrided surface (see Tab. 3). Increasing of the coefficient of friction for duplex treated steel samples can be attributed to the failure of brittle nitride compound layer and dehydration of manganese phosphate under increased temperature [15].

3 Conclusions

The tempered, plasma nitrided and duplex treated (plasma nitrided and manganese phosphated converese coating) 42CrMo4 steel samples were prepared for corrosion and wear resistance evaluation. Prepared samples were exposed to neutral sodium chloride corrosion tests up to 196 hours, continuously visually and gravimetric evaluated.

The wear tests "ball on disc", to investigate the coefficient of friction and the wear rate, were carried at temperatures of 21 °C, 150 °C, and 300 °C. For the wear test was used the tungsten carbide indentor, with a diameter of 6.3 mm. The most relevant conclusion is as follows:

- According to the visual evaluation of the corrosion propagation [in %], which was significantly reduced after application of plasma nitriding, was further reduced by following manganese phosphate converse coating;
- 2) The gravimetric evaluation proved a discrepancy with the visual evaluation thanks to the negative effect of compound layer porosity. This porosity

- caused increased ratio of localised type of corrosion, this fact was confirmed by surface evaluation after removing of corrosion products and expressed by increased "pitting factor", which was reduced by following manganese phosphate converse coating as well;
- Plasma nitriding has significantly reduced the wear rate at ambient temperature compared to tempered steel sample, which was further reduced by manganese phosphate converse coating;
- 4) The wear rate of plasma nitrided and duplex treated steel samples was increased with increased temperature but the coefficient of friction has decreased:
- 5) The wear rate of tempered steel at elevated temperatures is lower than at ambient temperature and lower than nitrided or duplex treated samples, but on the view of corrosion resistance, tempered steel cannot correspond to the requirements of the practical operation of machine parts.

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