

DUPLEX TREATMENT OF PLASMA NITRIDING AND MANGANESE PHOSPHATING OF 42CrMo4 STEEL FOR CORROSION RESISTANCE INCREASING

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Abstracts

Plasma nitriding is widely used as a final operation to improve wear, fatigue and corrosion resistance of industrial parts. Nevertheless, corrosion resistance can be further increased by post-oxidizing or by manganese phosphate conversion coating. This paper considers the duplex treatment of plasma nitriding and manganese phosphating of 42CrMo4 steel surface, widely used for manufacturing of breech mechanism in the armament production. Plasma nitriding was carried out at 500 °C for 15 h in different nitriding atmosphere having hydrogen and nitrogen gas flow ratio with 3 to 1 (l/h) and of 1 to 3 (l/h). Plasma nitrided steel samples were manganese phosphated (without lubrication). The treated samples were characterized using metallographic techniques, microhardness, and NSS corrosion tests. Different compound layer thickness under different nitriding gas ratio was confirmed. The X-ray diffraction analysis (XRD) confirmed different volumes of ϵ -Fe₂₋₃N, γ' -Fe₄N nitrides in the compound layers and hureaulite Mn₅ (PO₃ (OH))₂ (PO₄)₂ (H₂O)₄ in the manganese phosphate coatings. The visual and gravimetric evaluation was carried out and corrosion rates modified to weight gains were calculated for corrosion evaluation. After removing of corrosion products weight losses were measured and pitting factors were calculated. Duplex treatment (manganese phosphating after plasma nitriding) also displayed increased corrosion resistance and suppressed pitting propagation in comparison with the plasma nitrided steel samples and a potential to further increase of corrosion resistance of plasma nitrided structural steels.

Keywords: Plasma nitriding, manganese phosphate, corrosion resistance

1. INTRODUCTION

Plasma nitriding (ion nitriding) is a chemical-heat treatment process that is generally employed to increase the surface hardness, fatigue strength, corrosion resistance and to improve the tribological behavior of various steels [1, 2]. Nevertheless the notch toughness is reduced [3]. After nitriding process a surface compound layer on the surface is created, usually composed of nitride phases γ' -Me₄N and/or ϵ -Me₂₋₃N, (iron and alloying elements nitrided like Al, Cr, Mo, V) [4, 5]. The created compound layer is characterized by increased hardness and good corrosion resistance, which can be decreased by porosity. Porosity is evident with increased nitriding duration, the negative effect of porosity can be suppressed by the post-oxidation process used after the nitrocarburizing process (known as Tenifer® or Arcor®) [6]. Another type of conversion coating like phosphating can be applied for increasing the corrosion resistance of various steels, cast irons or zinc, magnesium, cadmium and often also aluminum [7]. Phosphating is usually applied for facilitating running-in of rotating machine parts, decrease drag friction and also reduce the risk of seizure of coated gear wheel as well. The most frequently used process is zinc phosphating process (coating formed mainly by hopeite Zn₃ (PO₄)₂ (H₂O)₄), mixed zinc-calcium phosphate (formed by scholzite Zn₂Ca(PO₄)₂ (H₂O)₄), so-called "three-cations" phosphating (formed by phosphophyllite) and manganese phosphating (formed usually by dense crystalline coating of hureaulite Mn₅ (PO₃ (OH))₂ (PO₄)₂ (H₂O)₄). In the temperature range of 160 °C - 400 °C the dehydration of phosphates occurs. Hureaulite (manganese phosphating) deals for the most thermal stable type of phosphating. The weight-loss of hopeite (zinc phosphate) at 400 °C reached 12 wt%, for scholzite (zinc-calcium) 14 wt%, for tri-cation phosphate 14 wt% and for hureaulite (Mnph) approximately 10 wt% [8].

This paper is focused on the comparison of corrosion resistance of tempered, plasma nitrided and duplex treated (plasma nitrided and further manganese phosphated) 42CrMo4 (AISI 4137/4140) steel. The corrosion resistance was tested using the NSS corrosion test according to ISO 9227 standard and visually and gravimetrically evaluated. After removing the corrosion products, the surface was evaluated using the laser confocal microscopy. Results of corrosion tests were further supplemented by metallographic documentation and measuring of compound layer thickness using light microscopy. Thickness and microhardness of created layers were measured by Vickers microhardness method in accordance with DIN 50190 standard.

2. EXPERIMENTAL

For the study was used the 42CrMo4 (AISI 4137/4140) steel, widely used for manufacturing of breech mechanism and gun barrels in the armament production, 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 Fe 130 and Fe 140 standards. The steel bar was cut into discs of diameter 80 mm and 4 mm thick. Steel samples were normalized at 870 °C, oil hardened at 850 °C for 20 min and air tempered at 550 °C for 40 min to achieve standard mechanical properties. All the surfaces of samples were grinded to roughness Ra = 0.4 µm and degreased in ethanol prior plasma nitriding and following duplex treatment (plasma nitriding and manganese phosphate coating).

Plasma nitriding was performed at 500 °C for 15 hours under different plasma nitriding atmosphere gas ratio in the RUBIG PN 60/60 device, marked as PN3H:1N for 24H₂:8N₂ (l/h) and PN1H:3N for 8H₂:24N₂ (l/h). Prior each plasma nitriding process were the samples plasma cleaned at 480 °C for 0.5 hour in the 20H₂:2N₂ (l/h) atmosphere.

The manganese phosphate coating was created in a standard solution containing H₃PO₄, MnO₂ and demineralised H₂O, marked as PN3H:1N + Mnph and PN1H:3N + Mnph. Plasma nitrided and duplex treated steel samples were compared to not treated samples (marked as Tempered) and to manganese phosphated one (marked as Mnph). The mean value of measured Mnph coating.

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All prepared samples were crosswise cut, with SiC paper wet grinded (with grit size from 80 to 2000), polished by diamond paste with grit of 1 µm and finally etched by 2% Nital. The cross-sectional martensitic-carbidic microstructures of prepared tempered (not-nitrided), nitrided and Mnph coated were grinded, studied by optical microscopy and the microstructures are shown in **Figure 1**.

Table 1 The nitride layer depth

Process	Layer depth (µm)	Compound layer (µm)
PN3H:1N	200	6.6±0.4
PN1H:3N	240	8.9±0.6
PN3H:1N + Mnph	180	5.1±0.4
PN1H:3N + Mnph	200	8.8±0.6

The compound nitride layer porosity is visible after 15 hours of plasma nitriding process (see the arrow in **Figures 1 a, b**). Increased porosity of compound layer has a negative influence on corrosion resistance for

predominantly ϵ -Fe₂₋₃N nitride formed compound layer. As well as the compound layer thickness increases with increasing ratio of N₂ to H₂ in nitriding atmosphere, from 6.6 μ m (PN3H:1N) to 8.9 μ m (PN1H:3N). Compound layer thickness and Mnph coating measuring were confirmed by light microscopy measurement using Olympus DSX 500 (see **Figure 1** and **Table 1**). The depth of diffusion layer was evaluated by microhardness measuring using automatic microhardness tester LECO LM 247 AT equipped with the software AMH43 in accordance with DIN 50190 standard in the direction from the surface to the core at 50 g load and 10 s dwell defined by 18 indentations (summarized in **Table 1**).

Mnph converse coating was carried out to eliminate the porosity of compound layer on plasma nitrided and tempered steel samples. After applying a coating on the samples, as shown in **Figure 2**, the phase analysis was performed. The phases were analysed by XRD Rigaku Miniflex 600 device (Rigaku D/teX Ultra 250, Cu K α radiation), using PDXL software with PDF-2 and Crystallographic Open Database for quantitative analysis. As seen in **Figure 3**, hureaulite Mn₅ (PO₃ (OH))₂ (PO₄)₂ (H₂O)₄ was created, detected between the 5° and 30° on the plasma nitrided steel surfaces.

X-ray phase analyses proved also nitrides composition of the compound layer of plasma nitrided 42CrMo4 steel, dependent on the nitriding gas ratio. It is evident, that increased ratio of N₂ to H₂ (l/h) promotes the creation of ϵ -Fe₂₋₃N nitrides.

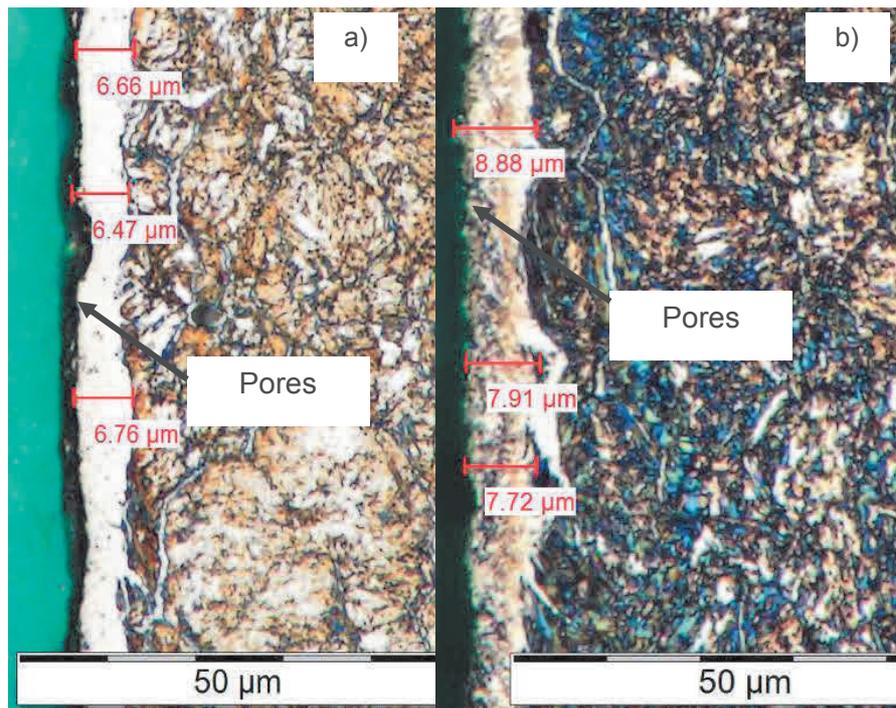


Figure 1 Cross-sectional microstructures a) PN 3H:1N, b) PN 1H:3N

The corrosion tests were performed in the 5 % neutral sodium chloride solution (NSS) in accordance with ISO 9227 standard in the VLM GmbH SAL 400-FL corrosion chamber. Corrosion test conditions: the temperature of 35 ± 2 °C, 5 % neutral sodium chloride solution, the amount of vapor condensation was set for $1 \div 2$ ml.h⁻¹ on square of 80 cm², pH 6.5 \div 7.2, the suspension angle of 20° from the vertical line, the exposition period 2, 4, 8, 24, 48, 72, 96, 144 and 196 hours. The samples were degreased by ethylalcohol before the corrosion testing.

During the corrosion tests the corrosion rate K_{corr} (mg. cm⁻².h⁻¹) was calculated, modified to weight gain measured during every testing corrosion period as the El-Sayed [9]:

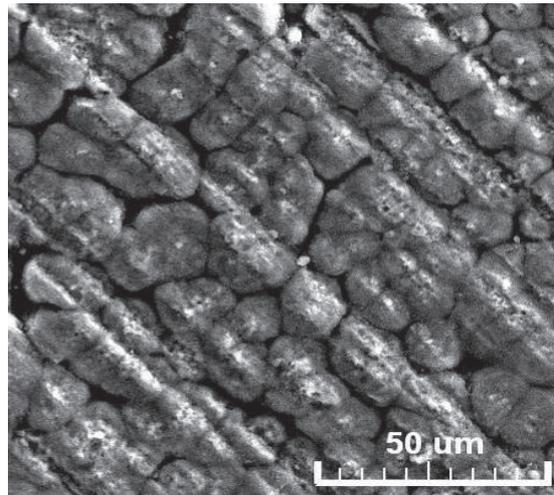


Figure 2 Mnph coating on the PN 1H:3N (SEM 1000x Tescan Vega)

$$K_{corr} = \frac{m_t}{S \cdot t} [mg \cdot cm^{-2} \cdot h^{-1}] \quad (1)$$

where the m_t (mg) is weight gain in evaluated time period defined by $m_t = m_h - m_{int}$ (mg), the m_h (mg) is the measured weight in evaluated time period and m_{int} (mg) is the initial weight before corrosion test, S (cm^2) is the total surface area and t (h) is the evaluated time period.

Weight-loss evaluation for all corroded samples was performed reaching the 196 h testing exposure after removing corrosion products (in accordance with ISO 8407 standard). Weight-loss evaluation after finish the corrosion tests was expressed by Δm_x ($mg \cdot cm^{-2}$) (2) given by ISO 9227 standard:

$$\Delta m_x = \frac{m_{int} - m_k}{S} [mg \cdot cm^{-2}] \quad (2)$$

where the m_{int} (mg) is the initial weight before corrosion test, m_k (mg) weight after removing corrosion products and S (cm^2) is the total surface area. All values of m_t , m_{int} and m_k used for K_{corr} and Δm_x calculation represents average values of five weight measurements.

Finally, the corrosion-free surfaces were additionally by the laser scanning microscope OLYMPUS OLS 3000 evaluated to study of the type of corrosion and pitting factor (PF) given by ISO 11463 standard was calculated, as a ratio of the deepest penetration to the average penetration of 10 measured penetrations.

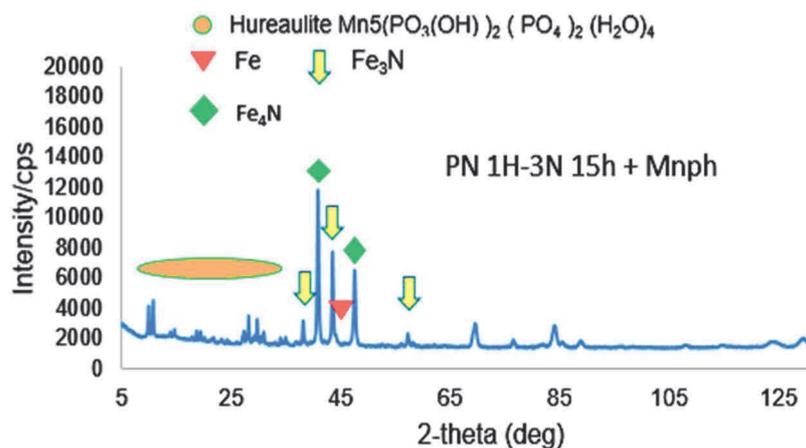


Figure 3 XRD patterns of plasma nitrided and further Mnph coated samples

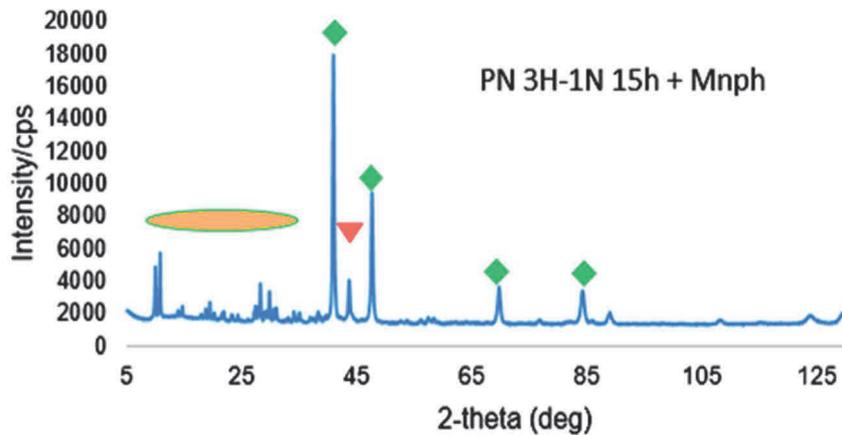


Figure 3 XRD patterns of plasma nitrided and further Mnph coated samples

3. RESULTS AND DISCUSSION

Different trends of corrosion propagation were observed during the NSS corrosion tests. The difference of corrosion resistance of plasma nitrided samples was related to plasma nitriding conditions and parameters of created nitride layers. The corrosion resistance was during the exposition periods (2, 4, 8, 24, 48, 72, 96, 144 and 196 h) after drying visually evaluated using the QuickPHOTO Industrial 2.3 software with Phase analyses application and corroded surface (in %) was calculated as seen in **Figure 4**.

The progress of surface corrosion attack (in %) during the NSS corrosion test and correlation to weight gain (in mg) is summarized in **Figure 5**. There is no correlation between the progress of corroded surface (line plotted) and the weight gain (point plotted) for plasma nitrided steel samples (PN3H:1N and PN1H:3N) as seen in **Figure 5**. Very good correlation was found for the duplex treatments, resp. for PN3H:1N + Mnph and PN1H:3N + Mnph).

The disagreement between the corroded surface (%) and weight gain (mg) is related the compound layer porosity and to the type of corrosion. After corrosion products removing can be determined the corrosion mechanism (**Figure 6**).

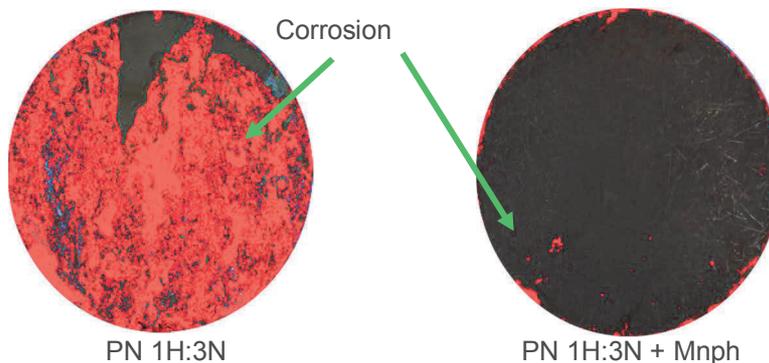


Figure 4 Visual evaluation QuickPHOTO application, after 48h in NSS

It is evident, that the mechanism of corrosion propagation was changed. For tempered samples is the typical uniform type of corrosion, in 48 h of exposure whole surface was corroded (see **Figure 5** and **Figure 6**). For plasma nitriding was the corrosion propagation changed and shifted into the localized (pitting) type of corrosion.

As seen corroded surface reached 100% in 144 h of exposure (PN3H:1N), respectively 90% in 196 h (PN1H:3N), but with highest weight gain related to deeper penetration (**Figures 5 and 6**).

The level of localized corrosion (pitting) can be expressed as so-called “Pitting factor” (PF). The value of PF = 1 represents the uniform type of corrosion and PF > 1, represents increasing of pitting. Comparing the corrosion resistance evaluation plotted in **Figure 5** and **Figure 7** can be summarized as following: untreated steel (Tempered) and Mnph coated steel showed wide uniform corrosion with PF = 1 and K_{corr} - weight gain 0.114, resp. 0.095 ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$).

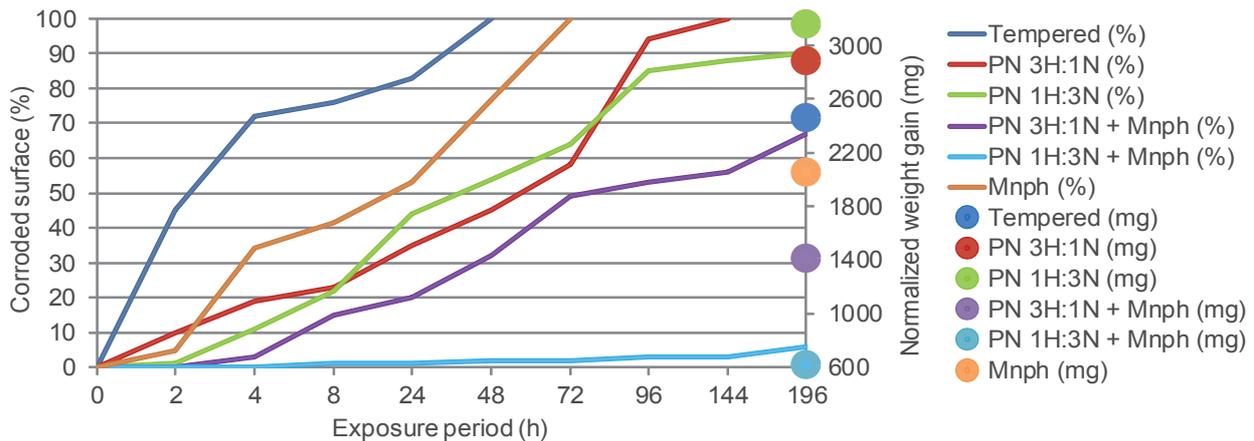


Figure 5 Corroded surface (%) and Weight gain (mg) - NSS corrosion tests

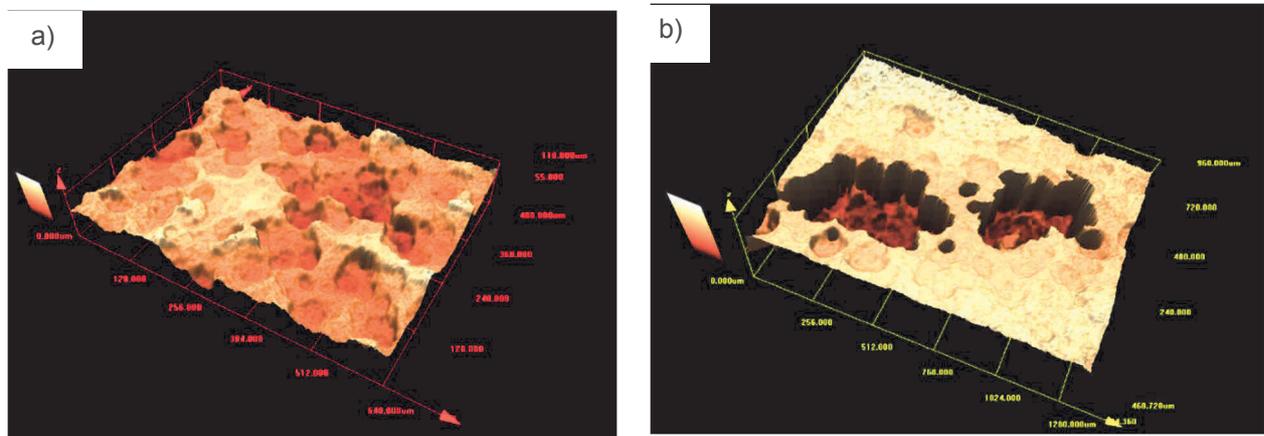


Figure 6 Laser confocal microscopy 3D surface evaluation of chemically cleaned samples
a) Tempered (uniform corrosion); b) PN1H:3N (uniform and localized corr.)

Application of plasma nitriding (PN 3H:1N and PN1H:3N) reduces the propagation of uniform type of corrosion but tends the localized one (pitting), which was characterized by increased K_{corr} - weight gain 0.133 resp. 0.146 ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) and PF = 1.34, resp. PF = 1.22. Significant reduction of uniform corrosion propagation and K_{corr} - weight gain ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) can be achieved by duplex treatment (PN + Mnph coating). K_{corr} was reduced to value 0.065, resp. 0.029 ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$), even the PF was reduced to PF = 1.2 (for PN3H:1N + Mnph) and PF = 1 (for PN1H:3N + Mnph). The lowest weight-loss $\Delta m_x = 10.5$ ($\text{mg}\cdot\text{cm}^{-2}$) was found for PN1H:3N + Mnph, followed by $\Delta m_x = 20.6$ ($\text{mg}\cdot\text{cm}^{-2}$) for PN3H:1N + Mnph, $\Delta m_x = 29.15$ ($\text{mg}\cdot\text{cm}^{-2}$) for Mnph, $\Delta m_x = 31.7$ ($\text{mg}\cdot\text{cm}^{-2}$) for Tempered, $\Delta m_x = 32.5$ ($\text{mg}\cdot\text{cm}^{-2}$) for PN3H:1N and highest $\Delta m_x = 37.9$ ($\text{mg}\cdot\text{cm}^{-2}$) for PN1H:3N.

4. CONCLUSION

The present work describes the corrosion resistance of plasma nitrided and duplex treated (plasma nitrided and Mnph coating) 42CrMo4 steel and evaluation methods of realized exposure NSS corrosion test. The most relevant conclusion is as follows:

- Corrosion resistance evaluation by surface propagation (corroded surface in %) is not relevant, it is necessary to complete the evaluation by gravimetric measurement;
- Plasma nitrided 42CrMo4 steel tends to increased K_{corr} -weight gain and localized corrosion, caused by compound layer incompactness expressed by pitting factor (see **Figure 7**);
- Manganese phosphating of plasma nitrided structural steel rapidly decreases the surface corrosion propagation, K_{corr} , weight losses and even decreases the level of pitting factor (localized corrosion).

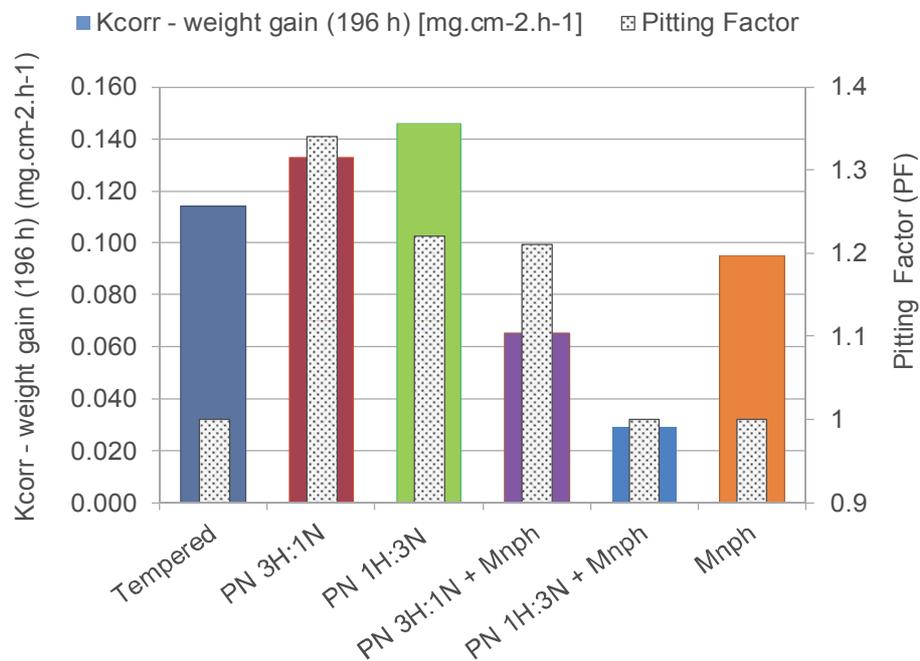


Figure 7 Pitting Factor (PF) correlation to K_{corr} ($\text{mg.cm}^{-2}.\text{h}^{-1}$)

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