

CORROSION RESISTANCE AND TRIBOLOGICAL PROPERTIES OF PLASMA NITRIDED AND TENIFERED 42CrMo4 STEEL

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Abstract

Plasma nitriding is a great thermochemical treatment, widely used in many technical applications as a final operation to improve the mechanical, tribological and corrosion properties of steel. This article deals with wear and corrosion resistance comparison of plasma nitrided and tenifered 42CrMo4 steel, which is widely used in manufacturing of breech mechanism in the armament production. The prepared steel samples were plasma nitrided under different nitriding gas mixture at 500 °C for 10h and tenifered for 45 min at temperature 590 °C followed by oxidation process for 10 min at 430 °C. For comparing the properties of samples treated by these selected technologies, the test “ball on flat” was carried out on the tribometer device UMT-3 and the corrosion resistance evaluation was realized by the NSS corrosion tests in the condensation chamber. The results were supplemented by the GDOES concentration profiles analyses, microhardness (HV 0.05), surface hardness, and microstructure evaluation. Based on the wear and corrosion tests, it was found that above evaluated technologies are suitable for increasing of wear and corrosion resistance simultaneously, which can be useful in weapons production.

Keywords: Plasma nitriding, tenifer, wear resistance, corrosion resistance

1. INTRODUCTION

The plasma nitriding technology is based on surface saturation 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 in the past primarily to increasing of surface hardness, wear resistance and fatigue limit. So called diffusion nitride layer creation occurs inside the material as a result of the nitriding diffusion based process. So-called tie-layer (compound layer) is created on the surface of treated component, and consists of ϵ -Fe₂₋₃N and γ -Fe₄N phases. The layer is very hard (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 consist of dispersive iron nitrides and nitrides of alloying elements with high affinity to nitrogen [1, 4].

The properties and nitride layer composition are influenced mostly by the nitriding gas composition and the controllable parameters of nitriding process such as voltage, nitriding duration and the surface conditions [3, 5]. The corrosion resistance of nitrided steels depends on the phase composition and tie-layer integrity [6, 7]. A positive influence of ϵ -phase (Fe₂₋₃N) to corrosion resistance increase had been found, this increased corrosion resistance can be further increased by subsequent surface oxidation of the surface nitride layer [8-10].

This paper is focused on comparison of corrosion and wear resistance of plasma nitrided and tenifered 42CrMo4 steel (AISI 4137/4140), used in manufacturing of barrel or breech mechanism of guns. The corrosion resistance was tested by the NSS corrosion test according with ISO 9227 standard and visually evaluated using the software QuickPHOTO Industrial 2.3. After removing the corrosion products, the surface was evaluated using the laser confocal microscope Olympus LEXT OLS 3000. The “ball on flat” test, responded to ASTM G133-95 standard carried out on the tribometer CETR UMT-3, allowed to find out the adhesive wear

and friction coefficient during sliding motion [11]. The results of corrosion and wear tests were further supplemented by metallographic documentation and measuring of tie-layer thickness, which were performed using the optical microscope OLYMPUS GX 51 equipped with the 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.

2. EXPERIMENTALS

The tests were performed on experimental samples of size 50 x 50 x 5 mm. The samples were normalized (850 °C), oil quenched (850 °C) and air tempered (550 °C) to attain optimal mechanical properties. The chemical composition of mentioned steel was verified by the GDOES method using the device SA2000 LECO (see **Table 1**).

Table 1 Chemical composition of 42CrMo4 steel [in 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(Ar) = 314 Pa

Heat-treated and surface treated steel samples were numerically marked according to **Table 2**. The tenifer technology essentially is a technology including nitrocarburizing process in salt bath of SURSULF solution for 45 min under temperature 590 °C followed by oxidation process in salt bath of OXINIT solution for 10 min at 430 °C. Plasma nitriding process was carried out in two steps: The first-step, so-called plasma cleaning process, was set before each plasma nitriding process to remove the surface oxides and for surface activation, the next step was plasma nitriding process, realized under concrete nitriding conditions according to **Table 3** in the RUBIG PN 60/60 device.

Table 2 Samples marking

| Sample marking | Process (gas ratio) |
|----------------|--|
| 1 | HT |
| 2 | PN (1H ₂ :3N ₂ , 10 h) |
| 3 | PN (3H ₂ :1N ₂ , 10 h) |
| 4 | HT + Tenifer |

HT = heat treatment, PN = plasma nitriding

Table 3 Plasma nitriding process parameters

| 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 |
| Plasma nitriding PN1 | 500 | 10 | 280 | 530 | 24 | 8 |
| Plasma nitriding PN2 | 500 | 10 | 280 | 530 | 8 | 24 |

For metallographic testing, all samples were crosswise cutted, wet grinded using silicon carbide paper with grit size from 80 to 2000, subsequently polished and finally etched by Nital. The cross-structure observation and documentation was realized with magnification of 200x and 500x using the optical microscope OLYMPUS GX 51 by the software ANALYSIS. The bainitic-sorbite microstructure of heat treated sample and structure of nitrided and tenifered layers can be observed in **Figure 1**. Surface layer thickness of thin layers measuring was confirmed by concentration profile measurement, measuring was realized using the SA2000 LECO device. Thickness of diffusion layer was evaluated by microhardness testing in accordance with DIN 50190 standard. The automatic microhardness tester LECO LM 247 AT equipped with the software AMH43 allowed to investigate diffusion layer depth in direction from surface to the core at 50 g load and 10 s dwell. The final

microhardness profile and measuring of diffusion layer depth was determined by 18 indentations with variable indentation spacing. For results of microhardness depth profile measuring see **Figure 2**. The tie-layer and diffusion layer characteristics are summarized in **Table 4**.

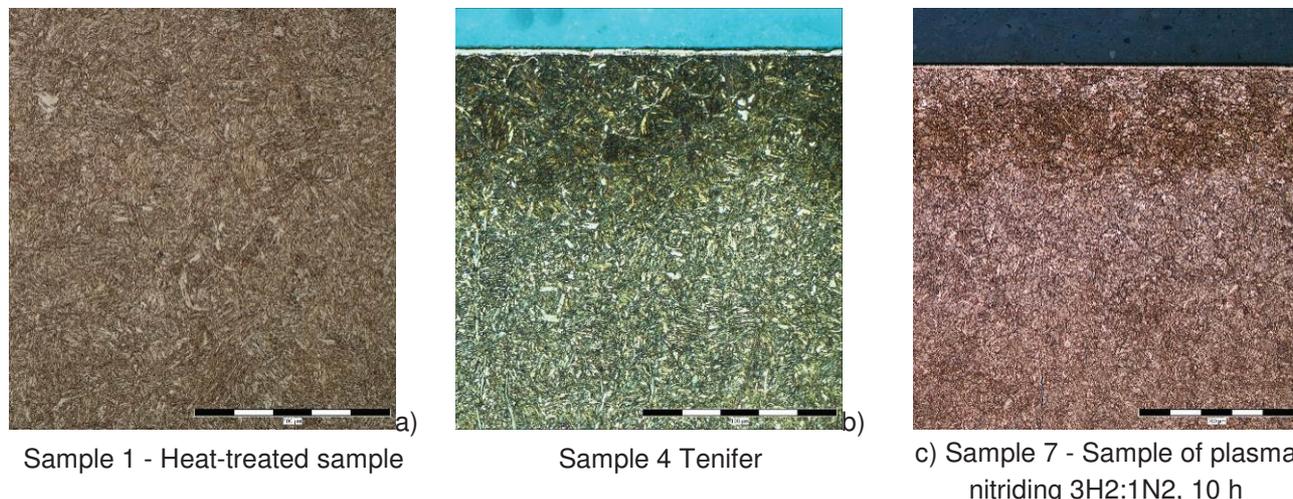


Figure 1 Cross-sectional microstructure (500x)

The corrosion resistance testing of plasma nitrided and tenifered samples was tested in the 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 °C, 5 % neutral sodium chloride dilution, the amount of vapour condensation 1-2 ml / h on square of 80 cm², 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 ethylalcohol. The edgings and the suspension apertures were conserved by FERRO COLOR U2066 resistant paint.

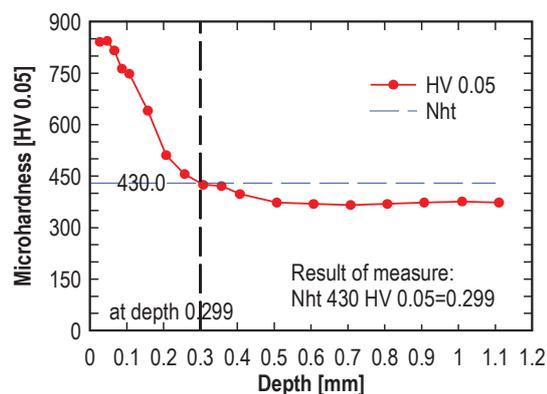


Figure 2 Microhardness depth profile - sample No. 2 (PN 1H₂:3N₂, 10h)

Table 4 Values of microhardness and layer depths

| No. | Surface hardness (HV) | Microhardness (HV0.05) | | Nht [HV0.05] | Layer depth (mm) | Tie-layer thickness (µm) |
|-----|-----------------------|------------------------|---------|--------------|------------------|-----------------------------------|
| | | Core | Surface | | | |
| 1 | 384 | - | - | - | - | - |
| 2 | 792 | 375 | 841 | 430 | 0.299 | 6.7 ^{TL} |
| 3 | 786 | 369 | 772 | 420 | 0.346 | 4.3 ^{TL} |
| 4 | 719 | 348 | 698 | 400 | 0.153 | 1 ^B +3.5 ^{TL} |

B - black oxide layer, TL - tie-layer (compound layer)

During corrosion tests, the uniform type of corrosion attack and pitting corrosion were supposed as a reason of the nitride layer incompactness. The samples were visually (photographic) evaluated, using the QuickPHOTO Industrial 2.3 software with Phase analyses application. Finally, after reaching 100% of corroded samples surface the tests were completed. Eventually, these corroded surfaces were cleaned chemically (500 ml of HCl, 3.5 ml of urotropin and 496.5 ml of H₂O solution) and mechanically (brushed) cleaned from corrosion products in accordance with ISO 8407:1991 standard. Later, corrosion products-free samples surfaces were evaluated by the laser scanning microscope OLYMPUS OLS 3000.

The wear testing based on the “ball on flat” method, responded to the ASTM G133-95 standard was carried out on the tribometer CETR UMT-3. The quenched steel ball of diameter 9.53 mm (3/8 inches) was used. Parameters of testing were set as following: applied load of 20 N, the sliding track of 20 mm, frequency of reciprocating motion 3 Hz, increasing load time of 10 seconds, loading duration of 180 seconds. This test allows to find out the adhesive wear and friction coefficient during sliding motion as a function of time.

3. RESULTS

During the NSS corrosion tests, different trends of corrosion attack were observed as corrosion resistance effect of the surface treatments. The difference of corrosion resistance of plasma nitrided samples was related to plasma nitriding conditions and parameters of created nitride layers. The progress of surface corrosion attack during the NSS corrosion tests is summarized in **Figure 3**.

The results showed that, plasma nitriding and tenifering technology significantly increased not only the surface hardness of structural steels, but also the corrosion resistance. The first signs of corrosion attack of nitrided 42CrMo4 steel samples after 2 hours of exposure were almost identical, but the corrosion attack propagation were different.

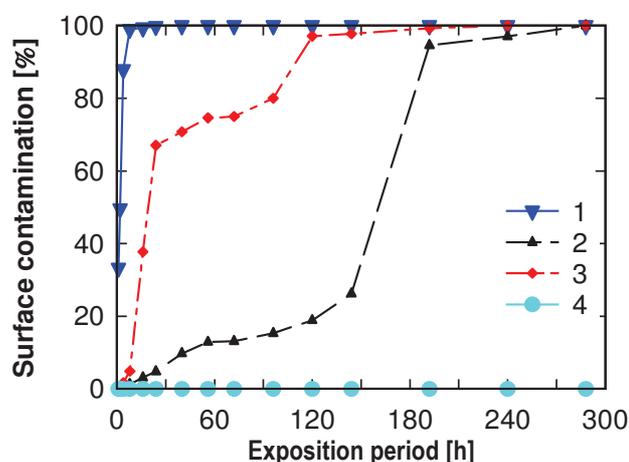


Figure 3 The progress of corrosion attack (NSS corrosion tests)



Figure 4 NSS corrosion tests after 56 h of exposure

The surface of sample No. 1 (HT - no surface treatment) was corroded from 50 % surface after 2 h of exposure while surface of sample No. 1 (HT) was fully degraded after just 24 h. The sample No. 3 plasma nitrided in standard atmosphere (PN 3H₂:1N₂) for 10 h showed after 96 h of exposure 80% of surface corrosion attack and after 240 h was fully corroded. The sample No. 2 - plasma nitrided sample in reverse nitriding atmosphere (PN 1H₂:3N₂) for 10 h reached the best results among the plasma nitrided samples. The expansion of corrosion

attack on sample No. 2 was weak in the beginning of corrosion tests, but from 144 h of exposure graduated rapidly. After 288 h of exposure in NSS this sample was fully corroded. The sample No. 4 (HT + Tenifer) reached excellent results: not even after 384 h of exposure in NSS weren't any signs of corrosion observed (see **Figure 4**). Besides, the thickness and the composition of surface layer have an obvious influence to the corrosion resistance.

The increased corrosion resistance of tenifered and plasma nitrided 42CrMo4 steel samples can be related to the surface state as well, cause of corrosion products removal. Surfaces with increased corrosion resistance tended to pitting corrosion, typical for passivable surfaces of stainless steels for example, like plasma nitrided steel samples (see **Figure 5**).

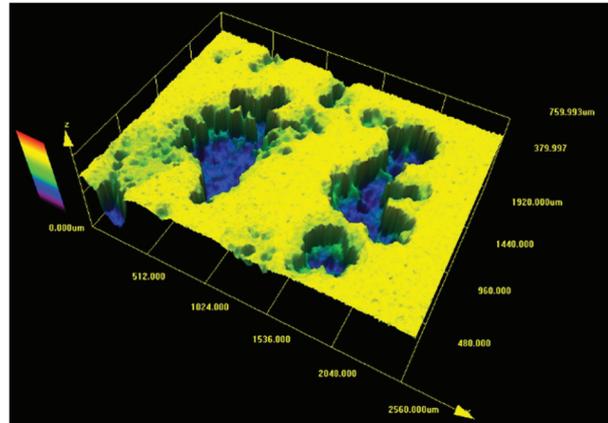


Figure 5 3D surface topography of sample No. 2

For the wear tests, when the load ball repeated again and again on the surface of samples, wear trace occurred. The tribometer device UMT-3 allowed to investigate the penetration depth reacted by the steel ball into the sample surface. It is obvious that, the shallower penetration, the better wear resistance. Degree of adhesive wear of samples are summarized in **Table 5**. The results shows that tenifered sample had lower adhesive wear level than nitrided samples, and the sample PN 1H₂:3N₂ (sample No 2) showed lower wear than the sample PN 3H₂:1N₂ (sample No 3).

Table 5 Adhesive wear

| Sample | Penetration depth (µm) | Standard deviation (µm) |
|--------|------------------------|-------------------------|
| No. 1 | - | - |
| No. 2 | 49.21 | 0.20 |
| No. 3 | 55.03 | 0.24 |
| No. 4 | 39.56 | 0.54 |

An important evaluated parameter of wear test was the friction coefficient μ . In the most machine parts, we expect the low friction coefficient during working to reduce energy waste and material degradation. Result of wear tests (see **Figure 6**) showed that, at the beginning to the time of 45 seconds, the friction coefficient of tenifered sample was lower than nitrided samples, but with increasing test duration, the value μ of this sample tended to higher value than nitrided samples. On the other hand, the sample treated by plasma nitriding 1H₂:3N₂ has lower value μ than the plasma nitriding 3H₂:1N₂ ones. The result given in **Figure 6** shows that friction coefficient of material was increased with test duration.

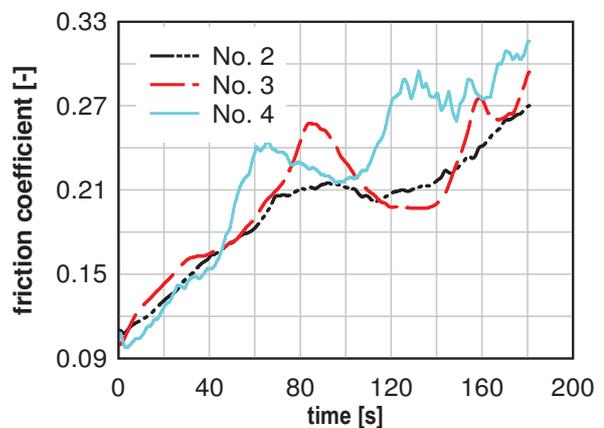


Figure 6 Friction coefficient of samples

4. CONCLUSION

The results documented that, plasma nitriding and tenifer technology significantly increases the surface hardness, corrosion and wear resistance of structural steels. Significant differences of plasma nitrided samples are derived from differences of plasma nitriding parameters (see **Table 3** and **Table 4**), which causes changes of compound layer phase composition and tie-layer thickness (see **Table 4**). Among plasma nitrided samples the sample No. 2 reached the best corrosion resistance result with compound layer thickness of 5.6 μm mainly composed of corrosion-resistant ϵ -phase (Fe_{2-3}N). But the most impressive results belong to the tenifered sample No. 4: not even after 384 h of exposure in NSS weren't any corrosion attack observed and although the friction coefficient was higher than the rest of samples, the wear level was the smallest. The tenifer tie-layer consisted of 3.5 μm thick monophasic ϵ -phase (Fe_xN) tie-layer. This increased corrosion resistance can be explained by the formation of 1 μm black oxide layer on the surface of the monophasic tie-layer. The tenifering process (nitrocarburizing process in salt bath) followed by oxidation process to form the 1 μm thin compact Fe_3O_4 oxide layer covering the surface. This surface layer is especially resistant to abrasion, corrosion and galling [12]. Additional increased corrosion resistance could be expected on plasma nitrided steel followed by oxidation process, known as PLASOX for example.

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