Improvement of wear resistance for C45 steel using plasma nitriding, nitrocarburizing and nitriding/manganese phosphating duplex treatment

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Abstract: This article focuses on effect of plasma nitriding, nitrocarburizing and nitriding/manganese phosphating duplex treatments to wear resistance of C45 steel substrate. The wear test "ball on disc" was conducted to evaluate the coefficient of friction and wear rate using the BRUKER UMT-3 tribometer. The analysis results indicated that nitrocarburizing obtained the best wear resistance; the worst wear resistance was plasma nitriding. Manganese phosphating coating enabled to reduce the coefficient of friction enhanced wear resistance nitrided layer. The used surface treatments also improve non-equal wear of tempered surface over the sliding track.

1 Introduction

During the relative motion, the frictional ways present between two parts and it leads to wear and damage of those parts or one of them [1]. Although wear can be reduced by lubrication, in many cases we have to figure machine working in unlubricated condition (dry friction). In the history of surface treatments, hard chrome plating, a very effective method to enhance corrosion and wear resistance has been used widely in airspace, automotive and armament industry. However, during the chrome plating procedure, the used hexavalent chrome affects seriously to the human health and ambient environment. Amount of surface treatments is suggested to replace the hard chrome plating in industry.

Nitrocarburizing and plasma nitriding are among the great ways to increase corrosion resistance, wear resistance and service life of mechanical components. Mechanical and tribological properties of nitrided parts depend on process parameters, such as treatment duration, atmosphere, temperature, pressure, etc. and the composition of particular nitride phases has a direct influence to the wear resistance [2, 3]. During plasma nitriding process, two layers with distinct properties are formed: the outer compound layer consisting of ε-Fe2,3N and γ'-Fe4N phase, and the thick inner diffusion layer. Phosphating is the most important surface treatment to improve corrosion resistance of material. In which, manganese phosphate coating exhibits high hardness, superior corrosion and wear resistance. Due to ability to absorb lubricants, manganese phosphating is mostly used for pistons and in weapon industry to ease the sliding of moving parts, which are running in lubricants by reducing the friction between metal parts.

C45 steel is a plain carbon steel for quenching and tempering, widely used in mechanical engineering and automotive components due to low cost and good combination of mechanical properties. In weapon manufacture, C45 steel is applied to product barrel of pistols or shotguns and other parts.
This article focused on investigating wear resistance of selected surface treatments for C45 steel: plasma nitriding, nitrocarburizing and duplex treatment of nitriding/manganese phosphate. The wear test “ball on disc” during unlubricated sliding was conducted to investigate the coefficient of friction and wear resistance of substrate and surface treatments. The metallographic documentation was performed by optical microscopy. The surface hardness and microhardness test were carried out to determine formation of nitride layer and coating.

2 Methods and experiments

The samples were shaped as rotary disc with diameter of 70 mm, thickness of 6.6 mm and surface roughness Ra of 0.54 µm. The samples were quenched and subsequently tempered. Prior to nitriding process, samples were plasma cleaned and activated in plasma under gas mixture of 20H₂ : 2N₂ (l/h) for 30 minutes. The plasma nitriding PN1 was treated under gas ratio of 3H₂ : 1N₂ for 15 hours, nitriding process PN2 under ratio of 1H₂ : 3N₂ (reverse ratio atmosphere) for 15 hours; the sample marked as DUPLEX1 represents duplex treatment of nitriding PN1 and manganese phosphating, likewise, sample DUPLEX2 is duplex treatment of PN2 and manganese phosphating. The nitrocarburizing Tenifer® was treated as two separate processes: nitrocarburizing in salt bath for 45 min under temperature 590 °C and followed oxidation process for 10 min at 430 °C.

The chemical composition of used steel was verified using the spectrometer LECO SA-2000 (on principle GDOES - Glow discharge optical spectroscopy). The surface hardness was measured by Vickers method with a load of 1 kg and 10 seconds dwell time. The structure observation and documentation was realized using the optical microscopy. Based on outstanding contrast between compound and diffusion layer, the thickness of compound layer could be determined. However, this method does not work in order to measure thickness of manganese phosphate coating and diffusion layer. Therefore, Vickers microhardness profile measurement was used to determine the thickness of diffusion layer with a load of 50 g and 10 seconds dwell time [4]. The thickness of manganese phosphate coating was investigated by the GDOES/QDP method (Glow discharge optical spectroscopy/ Quantitative Deep Profiling).

The wear test “ball on disc” was conducted using the tribometer BRUKER UMT-3 in accordance with ASTM G99-95a standard [5]. During the test, the normal load was kept in a value of 20 N. The used ball in diameter of 6.3 mm was made of carbide wolfram, which has the hardness value of 92 HRA. The test parameters were set as following: disc rotary velocity of 500 rpm corresponding to the circumferential velocity of 1.26 m/s, the cycle number of 13500 and humidity of 55%. The profilometer Taylor Hobson CLI 1000 with the software TALYSURF was used to evaluate depth and area of wear track profile.

The wear rate, which represents the wear resistance, is calculated according to the Archard equation [6]:

\[ K = \frac{V}{W \cdot s} \]

where:
- \( K \) is the wear rate \([\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}]\),
- \( W \) is the normal load \([\text{N}]\),
- \( s \) is the sliding distance \([\text{m}]\),
- \( V \) is the volume of removed material \([\text{mm}^3]\) calculated from profile area of wear and rotary radius.

3 Results and discussions

3.1 Chemical composition

The results measured by GDOES method are in accordance with chemical composition of CSN 41 2050 standard (see table 1).
Table 1. Chemical composition of C45 steel (in wt%).

| Element          | C%  | Mn%  | Si%  | Cr%  | Ni%  | Cu%  | P%   | S%   |
|------------------|-----|------|------|------|------|------|------|------|
| CSN 41 2050      | 0.42-0.50 | 0.17-0.50 | max. | max. | max. | max. | max. | max. |
| GDOES/BULK       | 0.45 | 0.635 | 0.233 | 0.168 | 0.22 | 0.0053 | 0.023 |      |

Parameters of GDOES/Bulk analysis: U = 800 V, I = 30 mA, p(Ar) = 314 Pa

3.2 Microstructure and microhardness of layers/coating

The etched crosswise documented by optical microscopy are shown in figure 1 and figure 2. It can be seen the sorbitical structure of tempered substrate and the layer structure of nitrided and nitrocarburized samples. The nitrided layer is consisted of a very thin white colour so-called compound layer and diffusion layer, which has darker colour than substrate (see figure 1). In case of nitrocarburizing Tenifer®, an oxide layer is formed outer of compound layer (see figure 2), while the DUPLEX1 and DUPLEX2 samples were covered by a manganese phosphating coating outer compound layer. The crystal structure of manganese phosphate coating is presented in figure 3.

![Figure 1. Microstructure of nitrided sample.](image1)

![Figure 2. Microstructure of nitrocarburized sample.](image2)
nitrided. The nitriding sample PN1 in classic nitriding atmosphere obtained thinner compound layer but greater case depth than the nitriding sample PN2 in reverse nitriding atmosphere. Moreover, in the same process parameters for the nitrided 42CrMo4 steel, nitriding PN1 also obtained greater case depth than nitriding PN2 [7].

![Image](image_url)

**Figure 3.** The structure of manganese phosphating.

The surface hardness as average value of five measurements is summarized in table 2. Both the plasma nitriding and nitrocarburizing technologies increase surface hardness of substrate, in which the hardness of nitrocarburized sample is lower than nitrided ones and manganese phosphate coating reduces surface hardness of nitrided layers. Conversely, the microhardness of nitriding PN2 obtains greater surface hardness than PN1.

| Sample            | Surface hardness [HV1] | Compound layer [µm] | Coating [µm] | Case depth [mm] |
|-------------------|------------------------|---------------------|--------------|-----------------|
| Tempered          | 303.86 ± 12.34         | -                   | -            | -               |
| Nitrocarburized   | 444.62 ± 28.99         | 14.68               | -            | 0.2562          |
| PN1               | 461.34 ± 18.28         | 4.31                | -            | 0.3938          |
| DUPLEX1           | 357.86 ± 22.22         | 4.61                | 2.0          | 0.3497          |
| PN2               | 523.06 ± 10.4          | 5.80                | -            | 0.2815          |
| DUPLEX2           | 389.92 ± 16.7          | 5.10                | 2.0          | 0.2980          |

The maximal obtained microhardness reached value of 510 HV0.05 (nitrocarburizing), the other samples have lower microhardness than 500 HV0.05, which is low for nitrided and nitrocarburized steel because C45 steel is a plain carbon steel, nitrogen just reacts with iron, not with alloying elements as alloyed steels. On the other hand, microhardness value reduces regard to the distance from surface to substrate. Substrate microhardness is in interval of 300-320 HV0.05.

### 3.3 Tribological performance

#### 3.3.1 The coefficient of friction

The coefficient of friction of steel-carbide wolfram tribological system is plotted in the Figure 4. In general, the curve of friction coefficient gains the maximal value in a very short duration, i.e. running-in period, then the curve becomes steady. By a large number of cycles, the coefficient of friction may increase or oscillate hardly cause of the degraded contact surfaces.

Nitrocarburized samples exhibited the greatest coefficient of friction. About first 6000 sliding cycles, the friction coefficient of nitrocarburizing increased continually from 0.0001 to 0.81. Then the coefficient of friction became steady, but still the highest of all samples.
For the tempered sample and other surface treatments, the difference in friction coefficient is obvious in the running-in period. The tempered sample spent longer time (about 1200 cycles) than nitrided samples (about 450 cycles) to get the maximal value of $\mu$ (0.61). The duplex treated samples have lower coefficient of friction than tempered sample all the first 3100 cycles. For the nitrided samples, about first 450 cycles of sliding, the value of $\mu$ increases quickly up to 0.6 and then quickly decreases to value 0.4. Three samples nitrocarburizing, DUPLEX1 and DUPLEX2 do not exhibit so steep progress of coefficient of friction as nitrided and tempered samples. Manganese phosphate coating ensures the nitrided surface having lower values of friction coefficient at the beginning of wear test. After running-in period, the friction coefficient of all samples (except nitrocarburized sample) was in the narrow range of 0.5-0.6. The duplex treated samples exhibited lightly higher value of friction coefficient than nitrided samples.

![Figure 4. Progress of friction coefficient.](image)

3.3.2 Wear
Wear resistance of the samples was evaluated by the shape and size of wear track. The wear track of tempered sample was significant and its width was changed along the track (see Figure 5) with uncertain period. Because during sliding, the particles were continually removed from material and transferred to other positions on over the trail of ball. By a number of cycles, the material particles were accumulated, the width of wear track increased. Parallel process with formation of particles was interactions between removed particles, ball and disc surfaces, e.g. plastic deformation and surface hardening. When the material particles were accumulated to a critical level, the ball could not transfer the particles forward, it overran the accumulated material. As consequence, the particles were detained and pressed down. Therefore, a wear track with non-uniform width was formed. In advanced, on surface of nitrided, nitrocarburized and duplex treated samples, more uniform wear track than tempered sample was created. The width of wear track measured by microscopy, the wear depth and wear profile area measured by profilometer are given in table 3. The value of wear depth and wear profile area is sorted ascending.
Table 3. The width and profile area of wear track

| Sample        | Width (µm) | Wear depth (µm) | Profile area (µm²) |
|---------------|------------|-----------------|--------------------|
| Nitrocarburized | 888 ± 26   | 3.25            | 1158.20            |
| DUPLEX2       | 517 ± 14   | 4.04            | 1665.25            |
| DUPLEX1       | 582 ± 43   | 4.68            | 1944.50            |
| PN2           | 794 ± 35   | 5.21            | 2523.80            |
| PN1           | 655 ± 16   | 6.45            | 3008.50            |
| Tempered      | 814 ± 58   | 24.78           | 14188.50           |

The wear rate calculated according to equation (2) and the coefficient of friction (considered as an average value of stable section in the figure 4) is showed in figure 6. The sample is sorted by smaller to greater value of wear as following sequence: Nitrocarburizing, DUPLEX2, DUPLEX1, PN2, PN1 and tempered. Nitrocarburizing technology was the best treatment to enhance wear resistance of material (the wear rate value smaller than 12-times). Thanks to 2 µm thickness of manganese phosphate coating, duplex treatment reduce markedly coefficient of friction and wear rate (8-times). Plasma nitriding was the worst among used surface treatment but its wear rate was 5-times less than tempered sample.

Figure 5. The wear track of tempered sample.

Figure 6. The coefficient of friction and wear rate.
Holemar et al. [9] pointed that, the ε-phase improves better friction properties than γ' phase, and nitriding in enriched nitrogen atmosphere formed compound layer consisted of ε-phase. Presented results also confirmed that nitriding PN2 treated in reverse atmosphere 1H$_2$: 3N$_2$ (enriched nitrogen atmosphere) provides better wear resistance than plasma nitriding PN1 treated in classic atmosphere 3H$_2$: 1N$_2$. Therefore, the composition of nitriding atmosphere has an influence to coefficient of friction and wear resistance.

The coefficient of friction is considered very meaningful characteristics of tribological system. Generally, it is believed that the lower coefficient of friction leads to reduce of material degradation during sliding. However, in this article, the obtained results showed that, the wear rate (resistance) was not proportional to coefficient of friction: the tempered sample exhibited a relatively low friction but very extensive wear rate, in adverse, nitrocarburized sample reached the greatest coefficient of friction but the lowest wear rate (see figure 6), resp. the best wear resistance.

Figure 7 shows correlation of the wear rate to thickness and microhardness of compound layer. It is easy to determine that, the biggest bubble - the highest value of wear rate is tempered sample, on which is not formed any layer or coating, and its hardness is the least of all. In adverse, the smallest bubble – nitrocarburizing having the least wear rate is on the right top of graph (the greatest hardness and compound layer). The nitrided samples PN1 and PN2 have lightly greater wear rate than the duplex treated samples. In terms of experiment, the used load was relatively small (20N), the main mechanism was mild wear. It can be stated that, the thicker and harder is the layer, the better wear resistance of surface is reached. However, if the used load will higher, the main wear may change to severe mechanism, the hard and brittle layers can be peeled off and play a role as abrasive agent. The wear process may be accelerated.

**Figure 7.** The wear rate in relation to microhardness and thickness of compound layer.

## 4 Conclusions

This article focused on evaluating the coefficient of friction and wear resistance of C45 steel treated by plasma nitriding under different nitriding atmospheres, nitrocarburizing (Tenifer®) and nitriding/manganese phosphating duplex treatment. Experimental results can be summarized in following conclusions:

- During sliding of tempered sample, the removed particles were transferred, accumulated, pressed down and formed non-equal wear track.
- Nitrocarburizing is the best technology in enhancing wear resistance of material (12-times better) though of high coefficient of friction. The duplex treatment nitriding/ manganese phosphating showed the best trend of friction coefficient and very high wear resistance. Plasma nitriding obtained
the worst wear resistance but still 5-times better than tempered sample. Moreover, the wear track of these treated surfaces created more uniform wear track than tempered sample, this characteristic may be useful in practice in improving vibration of machinery parts during operations.

The obtained results are an example to interpret that, the wear rate (resistance) may not be proportional to coefficient of friction: tempered sample exhibited a low friction but very high wear rate, on the contrary, nitrocarburized sample exhibited the greatest friction coefficient but the lowest wear rate.

The plasma nitriding and nitrocarburizing technologies formed on substrate nitrided layers with hardness about 100-200 HV higher than tempered surface. Two different gas atmospheres were used for plasma nitriding, in which the nitriding PN2 (1H₂ : 3N₂) obtains thicker compound layer, higher surface hardness than nitriding PN1 (3H₂ : 1N₂).

A relationship of wear rate to thickness of compound layer and microhardness is evaluated. The thicker compound layer with greater hardness could reduce the wear rate. The optimal thickness of compound layer is a subject remained for other studies.

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