



## Tribological behavior of low-alloyed steel after nitriding

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### Abstract

The tribological properties of the nitride layer applied to the low-alloyed steel were investigated in this research. Experimental work included determination of the chemical composition, wear resistance, Rockwell, Vickers and nano-indentation tests, both of the substrate material – the low-alloyed steel and the deposited nitride layer. From the results obtained in those experiments authors concluded that applying the nitride layer does not significantly improve the tribological properties of the tested low-alloyed steel samples, thus this process is not recommended for achieving that purpose.

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## 1. Introduction

The low-alloyed, high-graded steels are the most applied steels in transportation industry. They must fulfill requirements for a minimum failure rate, stability at high-temperatures and in aggressive environments, as well as for high mechanical properties. The high strength and, at the same time, high hardness of steel ensures the higher wear resistance of the contact surfaces. An increase in wear resistance can also be caused by the frictional properties of the surface, i.e. the surface layer. Therefore, various surface treatments are being applied to steels. One of the possibilities for the surface treatment, which is actually the most used method, is application of the friction Diamond Like Carbon (DLC) coatings. Those coatings are mostly formed by Physical Vapor Deposition (PVD) technologies. They are characterized by the high wear resistance, high hardness, excellent tribological properties and high corrosion resistance. A disadvantage of these coatings is coating of the complex shaped components, while dimensions of the coated components are often limited, as well (Hazlinger and Moravčík, 2013; Bronček et al., 2020; Drábik et al., 2018).

Another possibility of treating the surface to reduce friction is to create a nitride layer. Like the DLC coatings, the nitride layer is characterized by high hardness, good corrosion resistance and good tribological properties (Hazlinger and Moravčík, 2013; Drábik et al., 2016). The nitriding process is executed in a gaseous medium in which the working gas is also

present. That is why it is possible to nitride the complex parts, as well as internal diameters, cavities and holes (Bronček et al., 2020; Drábik et al., 2018).

In the nitriding process, an interface between the layer and the substrate is not formed, since this process is strictly diffusional. For this reason, the layer adhesion is not measured as in coatings. For a coating, adhesion is one of the most important requirements, which provides for its functionality in industrial applications. In nitriding, this requirement is excluded (Hazlinger and Moravčík, 2013; Binder et al., 2015).

Here is presented a short review of the most relevant literature sources related to the subject of this work.

Li et al., 2000, were performing the friction tests of inorganic bonded composite solid lubricant films (WS<sub>2</sub>, graphite, BN) in laboratory air and in 10<sup>-4</sup> Pa vacuum. The wear traces and transfer films were characterized by the scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). Experimental results suggest that when the friction tests were conducted in air, graphite plays a governing role, while in vacuum WS<sub>2</sub> plays a governing role. In case of changing atmosphere from air to vacuum or from vacuum to air, the composite film showed better friction behaviors in vacuum than in air. Takeichi et al., 2010, were examining effect of molybdenum trioxide MoO<sub>3</sub> powder on the tribological properties of sliding pair exposed to the temperature up to 700 °C. The experiment showed that MoO<sub>3</sub> powder, placed directly on the sliding surface of main tribological body, reduces friction values of

tested materials. A clear minimum of the friction coefficient was observed around 600 °C. The X-ray diffraction analysis of friction and wear traces showed mixture of different elements, which are the product generated during the tribological processes at high temperature.

Work of Ulewicz et al., 2014, presents a study of the fatigue properties of the Hardox 400 steel. The fatigue tests were carried out in the high and ultra-high cycle regions. Some components in the automotive industry and similar technical applications such as special semitrailers are exposed to cycle range between  $10^8$  and  $10^{10}$  cycles. However, only a few experimental results beyond  $10^7$  cycles were available. Thus, the main objective was to provide results on selected mechanical properties in these regimes. The stress amplitude decreases with an increase in cycles number beyond the conventional fatigue limit of  $10^7$  cycles. Based on obtained results the fatigue limits for Hardox 400 reached the level 490 MPa, while the stress amplitude decreased for about 233 MPa. The fatigue properties of Hardox strongly depend on the martensitic transformation conditions. The increase of the tensile strength is not accompanied by a corresponding increase of fatigue properties.

Kuffova and Celko, 2015, focused their research on studying the fatigue endurance improvement by using the plasma nitriding. They evaluated the microstructure and fatigue properties of low-alloyed steel 50CrV4+QT, used for highly loaded machines and parts of road vehicles were evaluated. The fatigue limit improvement at  $1 \times 10^7$  cycles was 44 %, which is explained by stabilized gradient of properties in treated layer.

Binder et al 2015 were investigating effect of the nature of the iron nitrides ( $\gamma'$ -Fe<sub>4</sub>N or  $\epsilon$ -Fe<sub>2</sub>-3N) on the sliding wear of plasma nitrided unalloyed sintered iron. The wear loss and wear rate were evaluated and the wear mechanisms were characterized. Analysis of the worn surfaces showed that several wear mechanisms operate simultaneously during the wear process, with the most significant mechanisms being oxidative and abrasive wears.

Drabik et al., 2016, were considering different surface pretreatment procedures of the 100Cr6 bearing steel substrates using the DC magnetron sputtering and high-power impulse magnetron sputtering. It is shown that the pretreatment method does not influence the structure and composition of the coatings; however, it strongly affects the surface structure and more importantly adhesion and the tribological properties of the coatings.

Terres et al., 2017, studied influence of the gas nitriding time (12, 24, 36 and 48 h) on the wear behavior of 42CrMo4 steel. It was assessed by micro hardness, pin-on-disc tribosystem and SEM through the nitrided layer for each nitriding time. They observed that wear rate varies as a function of the tests conditions due to the presence of different wear mechanisms. For short tests conditions wear rate depends on two mechanisms: plastic deformation and adhesive wear, whereas for large tests conditions the mechanisms controlling wear rate are abrasive and oxidative wear. The SEM examination of worn surfaces revealed signatures for the adhesion, abrasion, delamination and tribochemical (oxidative) modes of wear.

Landova and Brezinova, 2017, dealt with influence of tribological conditions on coating quality. They analyzed the two types of coatings WC-WB-CO and WC-FeCrAl, which were applied to the base material AISI 316L by the High velocity oxygen fuel (HVOF) technology. The aim of the experimental study was to determine the quality of coatings and their resistance to abrasive wear, depending on the number of thermal cycles. Results of experiments showed that the WC-Co-WB coating exhibited higher wear resistance.

Drabik et al., 2018, were depositing the WC/a-C:H coating (that consists of nanometer-sized  $\beta$ -W<sub>2</sub>C precipitates in an amorphous hydro-carbon matrix) on substrates of various materials by various magnetron plasma-based techniques in order to evaluate their efficiency in promotion of coating adhesion. They concluded that magnetron plasma-based pretreatment and deposition processes might involve potential practical problems in industrial coating of various objects in the same process batch.

Atapour and Ashrafizadef, 2018, have studied the tribology and cyclic oxidation behavior of plasma nitrided DIN 1.4871 austenitic valve steel were investigated. The nitriding cycles of 400,450, 500 and 550 °C for 7 h were selected and the pin-on-disc sliding wear experiments were performed at a load of 6 N and sliding velocity of 0.1 m/s in normal atmosphere under dry condition. The results indicated plasma nitriding at all temperatures increased the wear resistance of valve steel when sliding against bearing steel.

Zhou et al., 2018, proposed a new approach to quick preparation of a nitrided case for low-carbon low-alloy steels, based on cold hardening and pressurized gas nitriding. They investigated microstructure, surface hardness, thickness, and corrosion resistance of the nitrided layer on low-carbon low-alloy steel (20CrMnTi) after the nitriding at 510°C for 5 h under different cold rolling reduction (0–60% CR) and nitriding pressure (1–5 atm). Their results show that this technique can significantly improve the nitriding steel efficiency with the nitrided layer mainly composed of Fe<sub>2</sub>-3N and Fe<sub>4</sub>N nitrides.

Broncek et al., 2020, studied the tribological properties of the nitride layer deposited on the heat-treated bearing steel 100Cr6. Reason for formation of the nitride layer on this steel was decrease of the friction coefficient and simultaneous increase of the lifetime of the rings and elements of roller bearings.

The objective of this study was to verify experimentally the tribological and mechanical properties of the nitride layer applied to the low-alloyed steel.

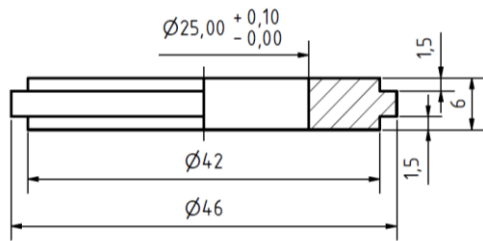
## 2. Experimental procedure

The low-alloyed steel was used as experimental material, the chemical composition of which is given in Tab. 1. Verification of the chemical composition was done on the SPEKTROMAXX device. The test specimens were then produced from the supplied rod of a  $\varnothing$  60 mm diameter and length of 500 mm. Appearance and geometry of samples are presented in Fig. 1. The low-alloyed steel was used as a substrate material for creating the nitride layer at its surface. The wear resistance is caused by the heat treatment of the low-alloyed

steel. It was executed according to the procedure recommended for this particular steel. Hardness of samples was measured after the heat treatment on a Rockwell RR-1D/AQ device.

**Table 1.** Chemical composition of low-alloyed steel [in wt. %]

Elements	C	Mn	Si	Cr
[wt. %]	1.2	0.52	0.36	1.38
Elements	P	S	Ni	Fe
[wt. %]	0.027	0.03	0.19	95.94



a) dimensions

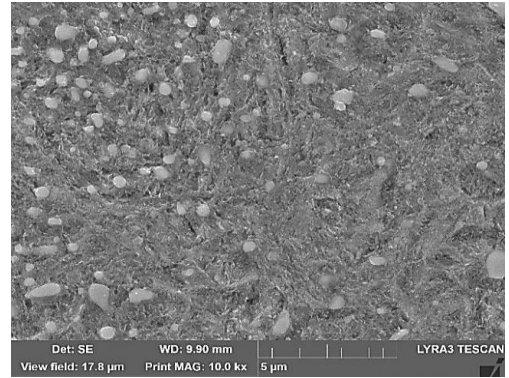


b) real tribology pair

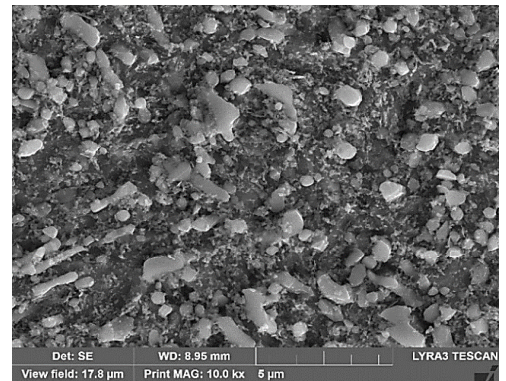
**Fig. 1.** Experimental sample

The nitriding of samples was performed after the heat treatment (quenching and low-tempering). The gas nitriding of the quenched samples was executed in the hermetically closed working chamber, for which the heating, control and regulation of heat, pressure and ammonia dissociation degree, were provided. The nitriding time was 10 hours during which a nitride layer of approximately 0.3 mm thickness was formed.

The microstructure of the samples and the nitride layer were evaluated after the heat treatment and are presented in Figs. 2 and 3, respectively. Evaluation was performed by electron microscopy on a Tescan LYRA 3 device. The low-alloyed steel microstructure consists of low-tempered martensite, complex carbides and residual austenite. Fig. 3b shows in detail a thin, continuous  $\epsilon$ -phase of a nitride layer of a thickness of approximately 10  $\mu\text{m}$ . Below this continuous layer, in the direction towards the base metal, there is a diffusion zone, which is formed of nitrides of the  $\gamma$  and  $\alpha$  - phases.

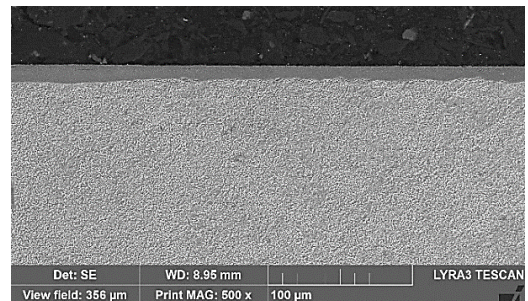


a) low-alloyed steel after heat treatment

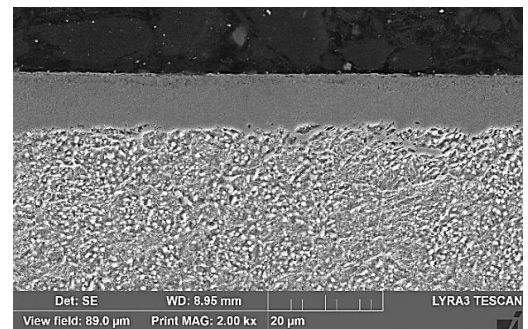


b) low-alloyed steel after nitriding

**Fig. 2.** Microstructure of samples, etch. 2 % Nital, SEM



a) actual appearance



b) detail

**Fig. 3.** Microstructure of nitride layer, etch. 2 % Nital, SEM

The chemical composition of the  $\epsilon$ -phase (hexagonal nitride) at the eutectoid temperature is  $\text{Fe}_{2-3}(\text{N})$ , which represents 7.1 to 11 wt. % of nitrogen. This layer is rich in iron



nitrides, which are characterized by high hardness (Hazlinger and Moravčík, 2013, Atapour and Ashrafizadef, 2008).

The friction coefficient of the nitride layer and the low-alloyed steel was obtained on the tribological device T-01M. The tribological system in experiments consisted of a stationary ball and a rotating disc, the Ball-on-Disc method was applied. Normal loading was realized by a set of weights of 5 N, 10 N and 15 N. The samples were rotating at  $n = 0.8$  m/s speed, while the experiment's duration was 5400 s. The counterpart was a hardened steel ball made of the 100Cr6 steel of 64 HRC hardness.

After the tribological tests, evaluation of wear of the nitride layer and the low-alloyed steel was performed. The primary profile of samples was evaluated, based on which one determines the depth of the tribological trace. The wear was rated on the Infinite Focus G5 device, produced by Alicona. The principle of measurement is shown in Fig. 4.

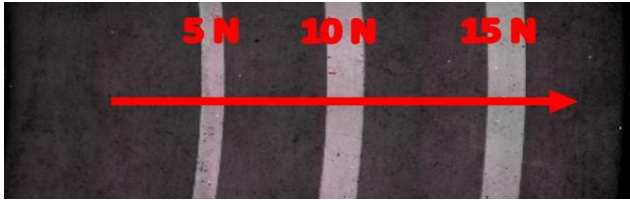


Fig. 4. The principle of wear measurement

At the end, the hardness HIT of the nitride layer and the low-alloyed steel was measured. Hardness was measured on the samples' surfaces on the Anton Paar NHT device. The applied force for hardness measurement of the nitride layer was 5 mN, while for the low-alloyed steel the force was 4 mN, acting for 5 s.

### 3. Results and discussion

Results of the dry friction of the nitride layer and the low-alloyed steel are presented in Fig. 5 and summarized in Tab. 2.

If the results were compared, one can see that the friction coefficient is smaller in the nitride layer. For the test with applied force of 5 N, the friction coefficient of the nitride layer was lower than that of the low-alloyed steel during the whole tribological test (Fig. 5b). At loads of  $F_N = 10$  N and 15 N, an increase of the contact pressure occurred, what caused the change in the friction conditions. Approximately at the half of the test time period a significant increase of the friction coefficient occurred (Figs. 5c, d). The measured friction coefficient of the nitride layer, at normal load of 5N, was  $\mu = 0.65$ ; at 10 N was  $\mu = 0.79$  and at 15 N was  $\mu = 0.71$ . Under the same nitriding conditions, the same values of the friction coefficient were measured by the authors in the work (Atapour and Ashrafizadef, 2008). That increase was probably caused by the  $\epsilon$ -phase wear, (Binder et al., 2015).

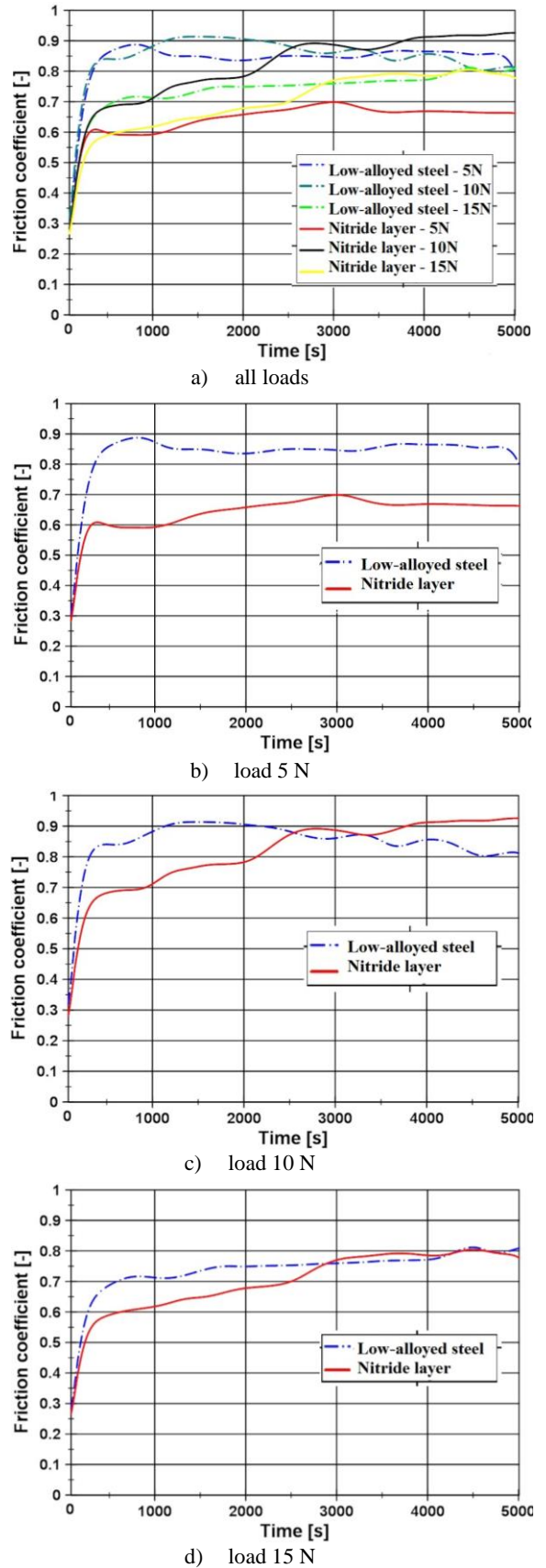
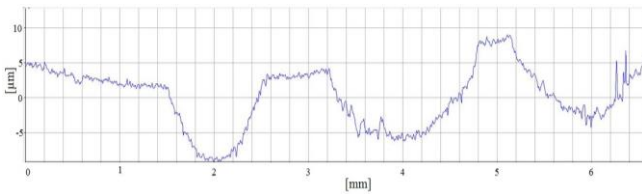


Fig. 5. Comparison of the friction coefficients of the nitride layer and low-alloyed steel

**Table 2.** Measured values of the friction coefficients of the nitride layer and low-alloyed steel

Load [N]	Average friction coefficient [-]	
	nitride layer	low-alloyed steel
5	0.65	0.86
10	0.79	0.80
15	0.71	0.74
Total friction coefficient	0.72	0.80

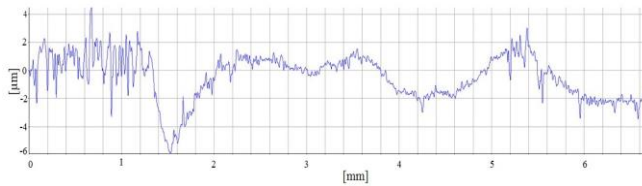


a) wear profile



b) actual appearance

**Fig. 6.** Wear of the nitride layer



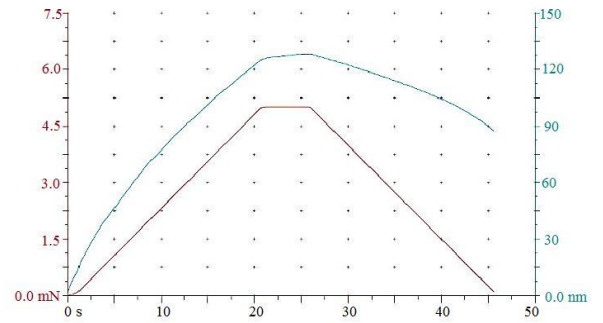
a) wear profile



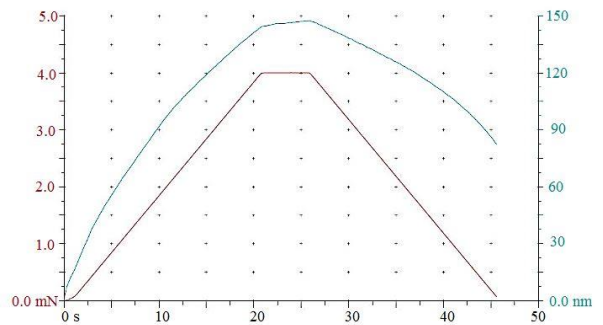
b) actual appearance

**Fig. 7.** Wear of the low-alloyed steel

The depth of the tribological traces of the nitride layer and low-alloyed steel was significant at all the three loads. From Fig. 6 and Fig. 7 is obvious that the maximal wear depth for samples with the nitride layer was 15  $\mu\text{m}$  and in low-alloyed steel 6  $\mu\text{m}$  and it was reached at maximal applied load.



a) nitride layer



b) low-alloyed steel

**Fig. 8.** Hardness measurements process, the nano-indentation method

Significant wear of samples with nitride layer is also caused by the hardness decrease of the substrate material. The decrease in Rockwell hardness HRC of samples after nitriding (influence of temperature  $T = 530\text{ }^\circ\text{C}$ ) was 45 HRC. Before nitriding the hardness HRC of samples after the heat treatment (quenching and low-tempering) was 63 HRC. Results of the hardness measurements by the nano-indentation method of the nitride layer and the low-alloyed steel are given also in Tab. 3. The nitride layer is harder at the surface than the low-alloyed steel. The measurement process is shown in Fig. 8.

**Table 3.** Hardness  $H_{IT}$  measurements results, the nano-indentation method

Sample	Hardness $H_{IT}$ [GPa]						Average value [GPa]
	9.8	9.7	10	10.3	10.2	9.9	
Nitride layer	8	7	10	10.3	10.2	9.9	10
Low-alloyed steel	8.1	7.9	7.9	8.2	8.1	8	8

When the hardness was measured in the cross-section, it reached the value of 970 HV0.025 in the nitrided samples just below the surface. Atapour and Ashrafizadef, 2008, reported the measured hardness in samples just below the surface of 1200 HV0.025 to 1350 HV0.025. Towards the core of the samples, the hardness gradually decreased to 415 HV0.025.

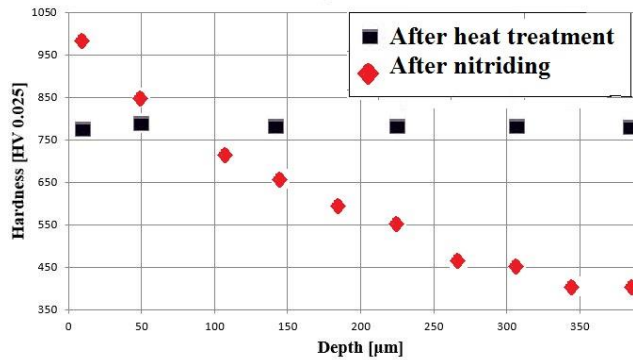


Fig. 9. Hardness HV0.025 in the samples cross-section

The decreasing course in hardness values is caused by the structural changes. The hardness values of the low-alloyed steel did not change in the cross section.

#### 4. Conclusions

Results show that the nitride layer obtains better friction properties than the low-alloyed steel. The measured friction values of the nitride layer exhibit a 10% reduction with respect to the low-alloyed steel. This decrease in friction is due to a hard layer of the  $\epsilon$ -phase (with hardness  $H_{IT} = 10$  GPa), located on the surface of the sample. After the nitriding of samples, an unfavorable decrease in substrate hardness from 63 HRC to 45 HRC, was recorded. This decrease in the samples' hardness was caused by the nitriding temperature of 530 °C, which was reflected in their higher wear rate. The nitride layer applied to low-alloyed steel does not significantly improve its tribological properties. On the contrary, it significantly deteriorates the quality of the substrate material by decreasing its hardness. From the obtained results it can be stated that it is not appropriate to recommend nitriding of the low-alloyed steel for the purpose of improving its friction properties.

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### 低合金钢渗氮后的摩擦学行为

#### 關鍵詞

低合金钢  
氮化  
摩擦学  
行为

#### 摘要

本研究研究了应用于低合金钢的氮化层的摩擦学性能。实验工作包括确定基材材料（低合金钢和沉积的氮化物层）的化学成分，耐磨性，洛氏硬度，维氏硬度和纳米压痕测试。从这些实验中获得的结果，作者得出结论，施加氮化物层不会显著改善所测试的低合金钢样品的摩擦学性能，因此不建议将此方法用于实现该目的。