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TRIBOLOGICAL PROPERTIES OF MEDIUM-CARBON STEEL AFTER NITRIDING COMBINED WITH SUBSEQUENT OXIDATION AND IMPREGNATION

WŁAŚCIWOŚCI TRIBOLOGICZNE ŚREDNIOWĘGLOWEJ STALI PO AZOTOWANIU POŁĄCZONYM Z NASTĘPNYM UTLENIANIEM I IMPREGNACJĄ

Key-words: nitriding, oxidation, nitriding layer, wear, corrosion.

Abstract The paper presents the results of examinations of tribological and corrosion properties of the layers produced on a C45 medium-carbon steel surface in the gas nitriding process combined with subsequent treatment – oxidation and impregnation of corrosion inhibitor. Investigations of the microstructure of these layers and their phase composition were carried out. Hardness of the layers was measured by Vickers method. Tribological properties (linear wear) of the layers were performed by means of the three-cylinder-cone method. Resistance to corrosion was determined by electrochemical methods. The investigations showed that the linear wear of the C45 steel samples with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation was smaller than that of steel samples without layers. Moreover, the corrosion resistance of these layers in aggressive solutions containing chloride ions was very good.

Słowa kluczowe: azotowanie, utlenianie, warstwa azotowana, zużycie, korozja.

Streszczenie W pracy omówiono wyniki badań właściwości tribologicznych i korozyjnych warstw wytwarzanych na powierzchni stali średniowęglowej C45 w procesie azotowania gazowego połączonym z następną obróbką – utlenianiem i impregnacją inhibitorem korozji. Przeprowadzono badania mikrostruktury tych warstw, jak również ich składu fazowego. Twardość warstw była mierzona metodą Vickersa. Właściwości tribologiczne (zużycie liniowe) warstw oceniano metodą trzy wałeczki–stożek. Badania odporności na korozję przeprowadzono metodami elektrochemicznymi. Badania wykazały, że zużycie liniowe próbek ze stali C45 z warstwami wytworzonymi w połączonych procesach azotowania z następnym utlenianiem i impregnacją, było mniejsze niż próbek ze stali bez warstw. Ponadto odporność korozyjna tych warstw w agresywnych roztworach zawierających jony chlorkowe była bardzo dobra.

INTRODUCTION

Gas nitriding of steel, based on the diffusion of nitrogen on the steel surface, serves to improve fatigue life and resistance to wear by friction tools and machine parts **[L. 1–6]**.

The nitriding process represents a low-temperature thermo-chemical treatment (500–650°C) that is widely applied in industry to various products, mainly made of steel, both to single units and to mass or serial production **[L. 7–9]**. It is a cost-effective alternative to widespread high temperature technologies (800–950°C) and thermo-chemical treatment methods, such as carburizing or carbonitriding.

The nitriding processes are most often carried out in a gas atmosphere produced from partially dissociated ammonia [**L. 10–12**]. As the result of nitriding, a diffusion layer is formed, the microstructure and phase composition of which depend on temperature and process time, the chemical composition of steel on which

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the layer is generated, and on atmosphere composition [**L. 13, 14**].

Steels for nitriding should be in the quenched and tempered condition, because nitriding takes place at a lower temperature than that of the last tempering. Lower temperatures of nitriding enable the following: significant reduction of deformations and dimensional changes of treated components, the reduction of finishing costs, and the reduction of costs connected with the wear of equipment used for heat treatment at high temperatures [**L. 15**, **16**]. The mentioned advantages cause the range of applications of traditional and modern nitriding techniques in industry worldwide to expand systematically.

A significant interest was lately focused on developing nitride layers enhancing corrosion resistance. It is well known that nitrided layers have relatively good corrosion resistance in atmospheric conditions, but it is not sufficient when exposed on severe corrosive media, e.g., containing chloride ions [**L. 17–19**].

There are two reasons causing weak corrosion resistance of steels with thin and porous nitrided layers on it. The first reason is porosity in the case of carbon and low-alloyed steels, and the second reason is the damage of alloyed structure by the high temperature nitriding process in the case of corrosion resistant stainless and highly alloyed steels **[L. 20]**.

As is known, very good corrosion resistance in aggressive environments containing chloride ions are shown in the combined processes of gas nitriding with subsequent treatment – oxidation and impregnation of corrosion inhibitors **[L. 21–26]**. The surface zone of the nitrided layers is characterized by a particular porosity; therefore, to ensure better corrosion resistance, these layers are impregnated with corrosion inhibitors. In the oxidation process performed on the surface of the nitrided layer, thin protective oxide coatings are formed, which ensure the tightness of the porous nitrided layer.

Iron forms three oxides with oxygen: Fe_2O_3 (hematite), Fe_3O_4 (magnetite), and FeO (wustite) [**L. 23**]. The highest corrosion resistance is demonstrated by oxide coatings produced at temperatures above 500°C, containing a large amount of iron oxides Fe_3O_4 [**L. 22**].

The article discusses the results of examinations of tribological properties and corrosion resistance of the layers produced on the steel surface in gas nitriding process with subsequent treatment – oxidation and then impregnation of corrosion inhibitor. The investigations were carried out for medium-carbon steel of the C45 grade, which is often used for machine parts exposed to severe conditions due to wear by friction and corrosion damages.

EXPERIMENTAL

Nitrided layers were developed on samples made of the structural grade C45 steel (non-alloyed steel containing 0.45% C). To improve the properties of the parent steel, the samples were subjected to the processes of thermal treatment, namely quenching at 860ºC (0.5 h) and tempering at 480ºC for 2 hours. The controlled gas nitriding processes were carried out at the temperature of 570ºC for 5 hours in the atmosphere of 100% dissociated ammonia. After nitriding, the samples were oxidized at 550ºC in steam and then impregnated with an oil corrosion inhibitor.

The microstructure of these layers was examined by means of an optical microscope on mounted and polished metallographic cross-sections. Phase composition of the layers was determined by X-ray phase analysis. Hardness of the layers was measured by Vickers method.

Tribological properties of the samples and their wear resistance were evaluated by the three-cylinder-cone method, employing an I-47-K-54 apparatus, in accordance with the PN-83/H-04302 standard **[L. 26–29].**

Measurements were taken with a rotating speed of the cone at 576 r.p.m. and unit loading pressures of 50, 100, and 300 MPa during a time of 100 min, applying lubrication by Lux 10 oil, metered at 30 drops per minute. Three samples were used for each variant.

Electrochemical corrosion measurements of the samples were performed in 0.5 M NaCl solution at a temperature of 24ºC during 26 h. The solution was exposed to air. The exposed area of the sample was 1 cm^2. Potentiometric testing was employed to determine the time dependencies of the open circuit potential of the samples in the corrosive solution. Measurements were performed in a three-electrode cell with a saturated calomel electrode as the reference and Pt wire netting as the counter electrode. All potential values are expressed in relation to the saturated calomel electrode. Three samples were used for each variant.

RESULTS AND DISCUSSION

Layer microstructure

An X-ray phase analysis of the surface of nitrided and then oxidized samples made of C45 steel showed the presence of Fe_2O_3 and Fe_3O_4 iron oxides and Fe_2N type iron nitride, indicating the presence of a nitrided layer, **Fig. 1**. Similar results of X-ray phase analysis were obtained in other publications regarding this type of layers [**L. 1–3, 8, 11**].

A microscopic image of the layer, produced on nitrided and then oxidized steel, revealed by Nital etching of metallographic cross-section, is shown in **Fig. 2**.

Investigations of microstructure of this layer revealed the presence of two zones: the first zone, (outer zone) of the layer, counting from the surface of the sample, is an oxide layer containing iron oxides, while the second zone (inner zone) is a nitrided layer, located in the area between the oxide layer and the C45 steel substrate (**Fig. 2**). Similar microscopic images of such layers were also observed in other investigations [**L. 18–22**].

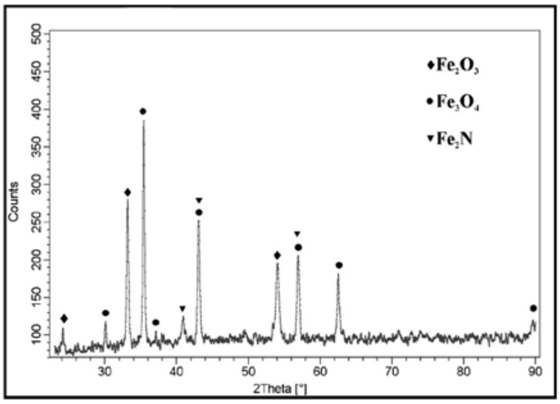

Fig. 1. **X-ray diffraction pattern (CuKα) of the nitrided and then oxidized C45 steel sample**

Rys. 1. Dyfraktogram (CuKα) z powierzchni próbki ze stali C45 azotowanej a następnie utlenianej

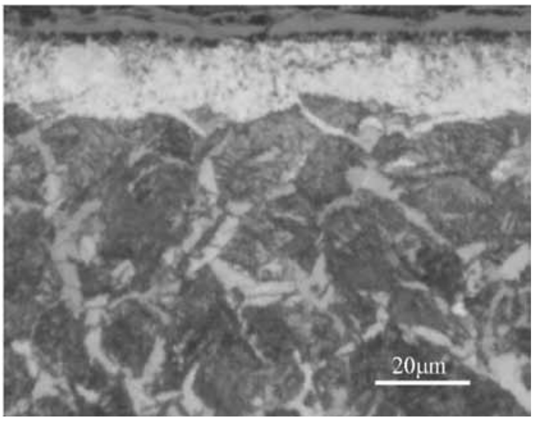

Fig. 2. **Microstructure of the C45 steel after nitriding with subsequent oxidation. Etched with 2% HNO_3**

Rys. 2. Mikrostruktura stali C45 po azotowaniu i następnym utlenianiu. Traw. 2% HNO_3

The thickness of the oxide layer (outer zone) was about 5 µm. The thickness of nitrided layer (inner zone) was about 18 µm, and its hardness was approx. 820 HV. The total thickness of the layer produced by nitriding and subsequent oxidation was about 23 µm.

Tribological properties

Tribological properties (linear wear) of samples were evaluated on the basis of sliding wear tests with concentrated contact [**L. 26–28**].

Wear resistance testing by the three cylinder-cone method was carried out on samples of the C45 steel with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation. For comparison, the wear resistance of the C45 steel samples without layers was also measured.

Figure 3 presents the linear wear of the C45 steel samples, with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation vs. friction time and units pressure. The linear wear of the tested samples at unit pressures of 50 and 100 MPa is small and amounts to 5.3 and 6.0 µm, respectively, for a friction time of 100 min, in contrast to the linear wear of samples at 300 MPa, which is more than twice as thick – 12.8 µm. At low unit pressures (50 and 100 MPa), the hard nitrided layer provides good wear resistance; however, it is destroyed due to friction at high unit pressure (300 MPa). Similar results were reported in other publications [**L. 8, 9, 17–20**].

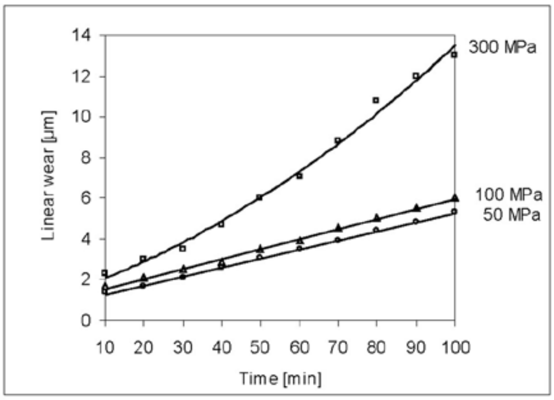

Fig. 3. **Linear wear of the C45 steel samples with the layers, produced in the combined processes of nitriding with subsequent oxidation and impregnation, vs. friction time and units pressure**

Rys. 3. Zużycie liniowe próbek ze stali C45 z warstwami wytworzonymi w połączonych procesach azotowania z następnym utlenianiem i impregnacją, w zależności od czasu tarcia i nacisków jednostkowych

A comparison of the linear wear of the C45 steel samples with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation, with that of the steel samples without layers, for various values of unit loadings of 50, 100, and 300 MPa and a wear time of 100 min, is shown in **Fig. 4.**

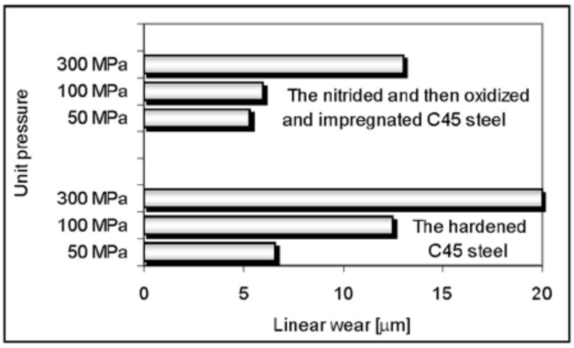

Fig. 4. **A comparison the linear wear of steel samples with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation with that of the steel samples without layers, for various values of unit pressure and 100 min friction time**

Rys. 4. Porównanie zużycia liniowego próbek ze stali z warstwami wytworzonymi w połączonych procesach azotowania z następnym utlenianiem i impregnacją oraz próbek ze stali bez warstw dla różnych nacisków jednostkowych i czasu tarcia 100 min

The investigations showed that the linear wear of the C45 steel samples with the tested layers was smaller than that of the steel samples without layers, **Fig. 4**. For example, the linear wear of the C45 steel samples with the layers was 6.0 µm under 100 MPa unit pressure for a friction time of 100 min, while that of the steel samples without layers under the same conditions was twice as thick – 12.5 µm.

CORROSION RESISTANCE

Corrosion tests were performed for the following samples:

- Bare C45 steel without a layer, and
- Nitrided and subsequently oxidized C45 steel after impregnation with a corrosion inhibitor.

Anodic polarization curves were taken after the stabilisation of the open circuit (26 h exposure). **Fig. 5** shows representative anodic curves for the samples under tests. For the bare steel, a fast increase in anodic current was observed, which is indicative of an intense active dissolution.

All nitrided and subsequently oxidized C45 steel samples after impregnation exhibited a suppression of anodic dissolution, which is typical for a spontaneous passivity. These samples remained passive in wide ranges of potentials.

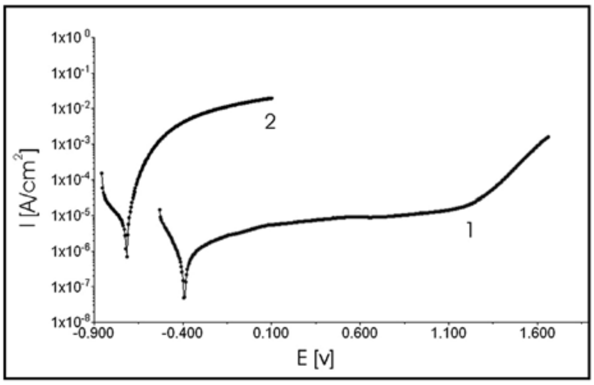

Fig. 5. Anodic polarisation curves of steel samples with the nitrided and subsequently oxidized and impregnated layers (Curve 1), and samples of bare steel without layers (Curve 2)

Rys. 5. Przebieg krzywych polaryzacji anodowej próbek stalowych z warstwami azotowanymi, następnie utlenianymi i impregnowanymi (krzywa 1) oraz próbek ze stali bez warstw (krzywa 2)

Some parameters extracted from polarization data and remarks about the appearance of the sample surface after the test are given in **Table 1**. The very high value of the anodic current density of the bare steel reflects the intense and active dissolution of this material. The steel samples with tested layers show much lower anodic currents, which is typical for passive dissolution.

Table 1. Results of analysis of anodic polarisation curves

Tablica 1. Wyniki analizy krzywych polaryzacji anodowej

Sample	E_{corr}	I_{corr}	Surface appearance
	[mV]	[µA/cm^2]	
The C45 steel without layer	- 715	12	Grey-rusty
The nitrided and then oxidized and impregnated C45 steel	- 375	0,71	No changes

This intense dissolution (lack of passivation) resulted in the roughening and grey-rusty coloration of the sample surface after the tests. In contrast, the surface of the nitrided and subsequently oxidized C45 steel samples after impregnation remained almost unchanged after the tests (**Table 1**).

A very good corrosion resistance of the C45 steel samples with nitrided and subsequently oxidized and impregnated layers according literature data [**L. 22, 23**] is ensured by the presence of a large amount of Fe_3O_4 oxides in the oxide coating, which was confirmed by X-ray results (**Fig. 1**).

CONCLUSIONS

The subjects of the study were the tribological and corrosion properties of the C45 medium-carbon steel after gas nitriding with subsequent oxidation and inhibitor impregnation. An X-ray phase analysis of the surface of nitrided and then oxidized samples made of C45 steel showed the presence of Fe_2O_3 and Fe_3O_4 iron oxides and Fe_2N type iron nitride, indicating the presence of a nitrided layer.

The layer produced on the C45 steel in the controlled gas nitriding process with subsequent oxidation consisted of two zones: the first zone, (outer zone) of the layer, counting from the surface of the sample, was an oxide layer, while the second zone (inner zone) was a nitrided layer, located in the area between the oxide layer and the steel substrate. The thickness of the oxide layer was about 5 µm. The thickness of nitrided layer was about 18 µm, and its hardness was approx. 820 HV. The total thickness of the layer, produced by nitriding and subsequent oxidation was about 23 µm.

The investigations of tribological properties (linear wear), using the three cylinder-cone method, showed that the linear wear of the C45 steel samples with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation was smaller than that of steel samples without layers.

The linear wear of these samples at unit pressures of 50 and 100 MPa for a friction time of 100 min was more than two times smaller than that of the samples tested at 300 MPa.

Electrochemical corrosion tests revealed that the C45 medium-carbon steel with the layers produced in the combined processes of nitriding with subsequent oxidation and impregnation could offer an effective protection against corrosion in a 0.5 M NaCl solution. The C45 steel samples with layers exhibited spontaneous passivation and remained passive in a wide range of potentials, whereas the bare steel without layers corroded actively.

The surface of the nitrided and subsequently oxidized C45 steel samples after impregnation remained almost unchanged after the corrosion tests. In contrast, the surface of bare steel samples without layers, due to intense dissolution (lack of passivation), became rough and grey-rusty after tests. A very good corrosion resistance of the C45 steel samples with nitrided and then oxidized and impregnated layers is assured, among others, by the presence of Fe_3O_4 oxides in the oxide coating, which was confirmed by X-ray results.

Therefore, economical C45 medium-carbon steel after nitriding with subsequent oxidation and impregnation can be used in the industry instead of expansive alloy steels for machine parts exposed to severe conditions due to corrosion damages in aggressive environments containing chlorine ions and wear by friction, but they cannot be used at very high unit pressures, e.g., 300 MPa.

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