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## TRIBOLOGICAL PROPERTIES OF BEARING STEEL AFTER HYBRID TREATMENT, COMBINED DIFFUSION CHROMIZING WITH THE PVD METHOD

### WŁAŚCIWOŚCI TRIBOLOGICZNE STALI ŁOŻYSKOWEJ PO OBRÓBCE HYBRYDOWEJ, ŁĄCZĄCEJ DYFUZYJNE CHROMOWANIE Z METODĄ PVD

**Key words:**

diffusion chromizing, PVD treatment, hybrid layer, tribological properties.

**Abstract**

The objective of the research in this work was the modification of the structure of chromized carbide layers on a bearing steel surface by the combination of diffusion chromizing with subsequent treatment, chromium nitride deposition by the PVD method, carried out to improve their tribological properties. As a result, CrC+CrN type hybrid layers on the surface of bearing steel were obtained. For comparison, the properties of single chromized carbide layers produced on a bearing steel surface in diffusion chromizing by the pack powder method were tested. Investigations of the layers' microstructures, phase composition, depth profiles of elements in the layer diffusion zone, and hardness were carried out. Tribological properties (linear wear) of the layers were performed by means of taper-three rolls tests. It has been proved, that the resistance to abrasive wear of the CrC+CrN type hybrid layers is almost two times higher than that for single CrC carbide layers.

**Słowa kluczowe:**

dyfuzyjne chromowanie, obróbka PVD, warstwa hybrydowa, właściwości tribologiczne.

**Streszczenie**

Przedmiot badań w niniejszej pracy stanowiła modyfikacja budowy warstw chromowanych na stali łożyskowej przez połączenie chromowania dyfuzyjnego z następną obróbką, osadzaniem azotku chromu metodą PVD, przeprowadzana dla poprawy ich właściwości tribologicznych. W rezultacie otrzymano warstwy hybrydowe typu CrC+CrN. Dla porównania przeprowadzono badania pojedynczych warstw węglkowych wytwarzanych na powierzchni stali łożyskowej metodą proszkową chromowania dyfuzyjnego. Przeprowadzono badania mikrostruktury warstw, ich składu fazowego, zmian stężenia pierwiastków w strefie dyfuzyjnej warstw oraz twardości. Właściwości tribologiczne (zużycie liniowe) warstw oceniano przy wykorzystaniu metody trzy wałeczki-stożek. Wykazano, że odporność na zużycie przez tarcie stali łożyskowej z warstwami hybrydowymi typu CrC+CrN jest prawie dwa razy większa od odporności tej stali z pojedynczymi warstwami węglkowymi typu CrC.

## INTRODUCTION

The objective of the research in this work was the modification of the structure of carbide-type chromized layers on a bearing steel surface by the combination of diffusion chromizing with subsequent Arc PVD (Arc Physical Vapor Deposition) treatment, carried out to improve their tribological properties.

The 100Cr6 bearing steel is used, among others, for the manufacture of bearings, chain bolts, and

other components subject to wear during friction. The improvement of the tribological properties of this steel can be obtained by creating on its surfaces layers, such as, chromium carbide layers, produced in diffusion chromizing process characterized by high resistance to friction wear [L. 1–6].

Diffusion chromizing is applied to increase the durability of tools, which operate under wear conditions [L. 1, 7–10]. This process is conducted by different methods, i.e. powder pack, gas, vacuum, and molten salt

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baths [L. 11–17]. Industrial significance in current times has been gained by the inexpensive and technologically simple powder pack method (“pack cementation”) which consists of heating the steel in a powder mixture containing ferro-chromium, which is a source of chromium, an activator (e.g., ammonium chloride), and a ceramic filler (e.g., kaolin) preventing sintering of the powder at high temperatures [L. 1, 18–21].

In recent years, research has been undertaken to improve the properties of diffusion layers produced in thermo-chemical treatment processes, resulting from the growing requirements of the industry regarding the durability and reliability of machine parts and tools, especially those working in difficult conditions. Meeting such requirements is made possible through the modification of the layer structure by the combination of thermo-chemical treatment with PVD techniques [L. 22–25]. An example here could be hybrid layers of the type produced by nitrided layer/CrN coating with excellent useable properties, obtained in consecutive processes of gaseous nitriding, combined with a subsequent treatment, which is the deposition of chromium nitride coating by PVD method [L. 25–27]. These layers are characterized by, among others, high resistance to wear by friction, as well as high strength under heavy mechanical loading and high thermal shock resistance, have found application in the industry in the field of improving the service life of forging dies made of hot work tool steel. However, there are few publications on the subject of the possibility of combining the diffusion chromizing process with subsequent Arc-PVD treatment [L. 28, 29]. Investigations by the authors in this field have shown that, from among various coatings deposited by the Arc-PVD method, characterized by good tribological properties, e.g., TiN, CrN, Ti(C, N), (Ti, Cr)N, the best adhesion to the surface of the chromized layer was exhibited by chromium nitride CrN coatings [L. 28, 29].

The aim of the research in this work was the modification of the structure of carbide-type chromized layers on the bearing steel surface by the combination of diffusion chromizing with the next treatment, chromium nitride deposition by Arc PVD method, carried out to improve their tribological properties.

The article discusses the results of the investigations of microstructure and tribological properties of the CrC+CrN type hybrid layers, obtained as a result of this modification, as well as single chromized carbide layers.

## EXPERIMENTAL PROCEDURE

Chromized layers with a carbide microstructure (the CrC type carbide layers) were formed on samples of 100Cr6 bearing steel (containing 0.95% C and 1.45% Cr).

The traditional powder pack method of diffusion chromizing has been described previously in numerous articles on this subject [L. 1, 7, 8, 15].

The processes were carried out in an electric furnace equipped with a temperature control system. Samples for the investigation were placed in a powder mixture containing: 60% ferro-chrome powder, 39% kaolin, and 1% ammonium chloride ( $\text{NH}_4\text{Cl}$ ), inside special boxes made of heat resistant steel with lids. The application of specially designed boxes enabled achieving hermetic conditions during the process with the aid of enamel which melts at temperatures above 600°C, thus preventing oxidation of the batch. The filled boxes were placed in the furnace, heated to the temperature of the chromizing process (900°C) and soaked.

Treatment of samples made from bearing steel, indispensable for the formation of the CrC+CrN type hybrid layers, was carried out in two subsequent stages utilizing two different types of equipment.

In the first stage, diffusion chromizing was conducted on the bearing steel in order to form a CrC-type carbide chromizing layer on its surface. The diffusion chromizing processes were carried out in a GOAT-1200 electric furnace at the Institute of Precision Mechanics in Warsaw.

In the second stage, in order to form the CrC+CrN type hybrid layers, deposition was carried out of CrN chromium nitride on the surface of the chromized steel. The chromium nitride coatings were deposited by the arc-evaporation method (Arc-PVD), utilizing a Standard 1 type equipment at the Institute for Sustainable Technologies – NRI, in Radom. Process parameters of coating deposition by the Arc-PVD method are given in **Table 1**.

**Table 1. Parameters of the chromium nitride deposition process by Arc PVD method**

Tablica 1. Parametry osadzania azotku chromu metodą Arc-PVD

Type of process	Substrate temperature $T$ [°C]	Substrate polarization voltage $U_{\text{BIAS}}$ [V]	Pressure $p$ [Pa]	Atmosphere	Time of deposition [min]
Etching by Cr ions	400	–950	$5.0 \cdot 10^{-1}$	Ar	15
Deposition of CrN	380	–150	3.5	$\text{N}_2$	120

## METHODS OF INVESTIGATION

Investigations of layer microstructures were carried out on mounted and polished metallographic cross-sections.

The layers obtained were investigated by performing an X-ray phase analysis and a spectral line analysis with a microanalyser. Metallographic examinations and thickness measurements of the layers were carried out with an optical microscope. Layer microstructure was revealed by nital etching. The hardness (HV 0.02) of layers was measured by Vickers method.

Tribological properties of the samples, their wear resistance to friction, were evaluated by the three-cylinder-cone method [L. 30]. Measurements were taken with a rotating speed of the cone at  $n = 576$  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.

## RESULTS AND DISCUSSION

### Layer microstructure

The surface of samples with hybrid and chromized carbide layers was silvery and smooth. X-ray diffraction phase analysis of the surface of chromized layers made from 100Cr6 bearing steel revealed the presence of the  $\text{Cr}_{23}\text{C}_6$  type carbide, as well as traces of the  $(\text{Cr}, \text{Fe})_2\text{N}$  nitride, similarly to what has been reported in other publications [L. 1, 2, 4, 7].

Concentration depth profiles of Cr, Fe, and C in the carbide layer diffusion zone obtained by means of the X-ray microanalyses are shown in Fig. 1. The presence of iron in the chromium carbide tells us that the layer is built of the ferro-chromium  $(\text{Cr}, \text{Fe})_{23}\text{C}_6$  carbide. This is also shown by the content of carbon in the carbide (approx. 6%) which is characteristic of the  $\text{Cr}_{23}\text{C}_6$  type carbide. The thickness of the CrC type carbide layer is about 10  $\mu\text{m}$  and its hardness approx. 1800 HV.

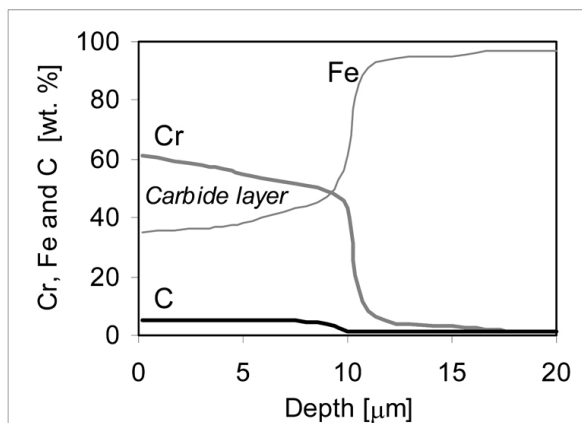


Fig. 1. Depth profiles of elements concentration in the CrC type carbide layer

Rys. 1. Zmiany stężenia pierwiastków od powierzchni w warstwie węglkowej typu CrC

X-ray diffraction phase analysis of the surface of bearing steel samples with the CrC+CrN type hybrid layers, obtained by the deposition of the CrN coatings on the CrC carbide layer, revealed the presence of both the  $(\text{Cr}, \text{Fe})_{23}\text{C}_6$  chromium carbide and of the CrN chromium nitride.

Microscopic images of the bearing steel sample with the CrC+CrN hybrid layer, revealed by nital etching of metallographic cross-sections, are shown in Fig. 2.

The microscopic image of the hybrid layer indicates its two-zone structure. The first sub-zone (outer sub-zone), counting from the surface of the sample, is the CrN chromium nitride, with a thickness of approx. 4  $\mu\text{m}$ , while the second sub-zone (inner sub-zone) is the  $(\text{Cr}, \text{Fe})_{23}\text{C}_6$  chromium carbide with a thickness of approx. 10  $\mu\text{m}$ , located in the area between the CrN and the bearing steel substrate.

Similar microscopic images of the CrC+CrN hybrid layers were also observed in other investigations [L. 15, 27, 28].

The thickness of the hybrid layer is about 14  $\mu\text{m}$  and its hardness approx. 2100 HV.

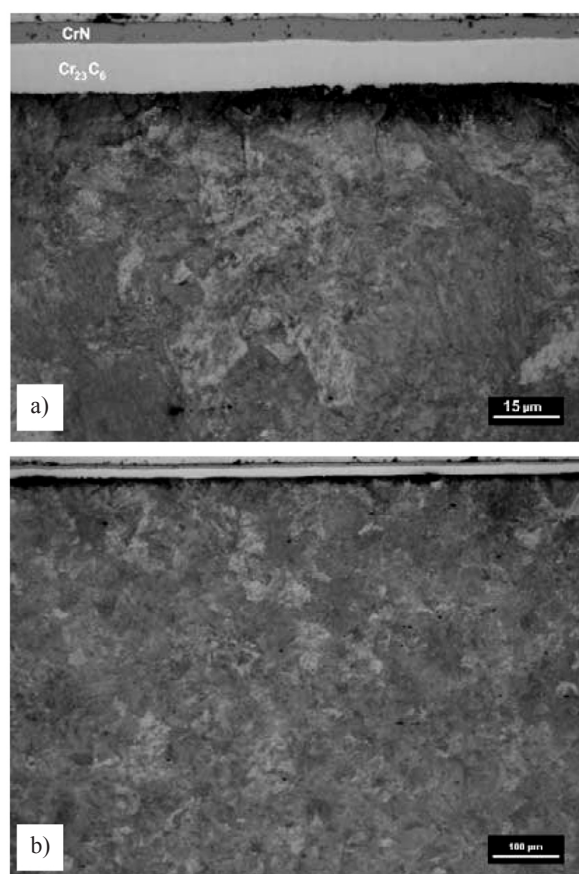
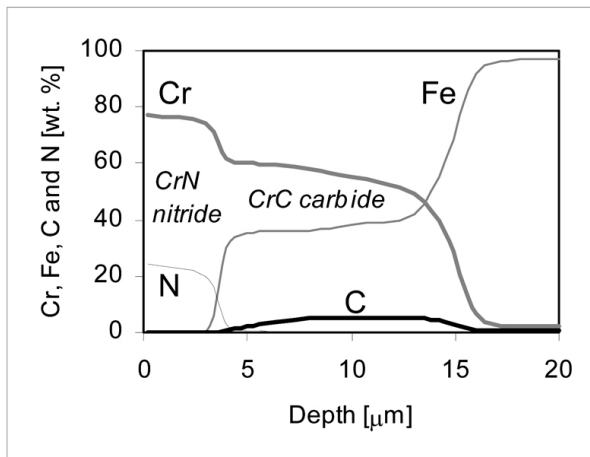


Fig. 2. Microstructure of bearing steel with CrC+CrN type hybrid layer: a – magnification: 500 $\times$ , b –magnification: 100 $\times$ . Etched with 2%  $\text{HNO}_3$

Rys. 2. Mikrostruktura stali łożyskowej z warstwą hybrydową typu CrC+CrN: a – powiększenie:  $\times 500$ , b – powiększenie:  $\times 100$ . Traw. 2%  $\text{HNO}_3$

Concentration depth profiles of Cr, Fe, N, and C in the hybrid layer diffusion zone obtained by means of the X-ray microanalyses are shown in **Fig. 3**.



**Fig. 3. Depth profiles of elements concentration in the CrC+CrN type hybrid layer**

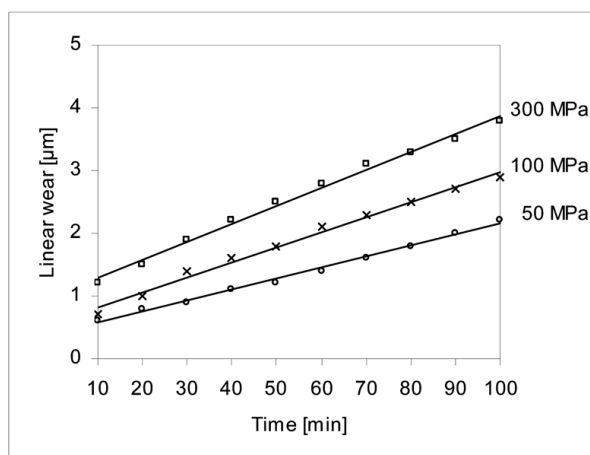
Rys. 3. Zmiany stężenia pierwiastków od powierzchni w warstwie hybrydowej typu CrC+CrN

Depth profiles of the hybrid layer indicate the presence of chromium nitride CrN directly under the surface as well as the chromium carbide in the zone between the chromium nitride and the steel substrate.

### Tribological properties

Wear testing by the three cylinder-cone method was carried out on samples of bearing steel with the CrC type carbide layers and the CrC+CrN type hybrid layers.

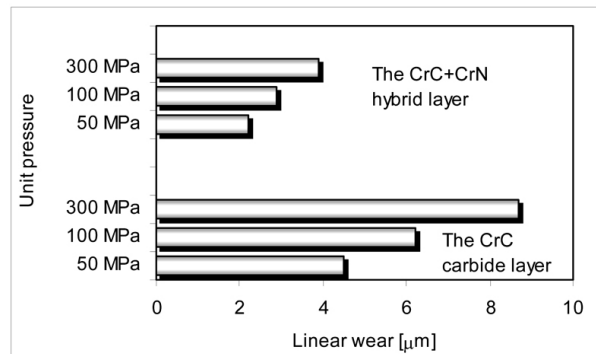
Linear wear of the 100Cr6 bearing steel samples with the CrC+CrN type hybrid layers vs. friction time and units pressure is shown in **Fig. 4**.



**Fig. 4. Linear wear of the 100Cr6 bearing steel samples with the CrC+CrN type hybrid layers vs. friction time and units pressure**

Rys. 4. Zużycie liniowe próbek ze stali łożyskowej 100Cr6 z warstwami hybrydowymi typu CrC+CrN, w zależności od czasu tarcia dla różnych nacisków jednostkowych

A comparison of the linear wear of samples made of 100Cr6 bearing steel with hybrid layers of the CrN+CrC type and the CrC type carbide layers, for different units pressure (50, 100, and 300 MPa) and 100 min friction time, is shown in **Fig. 5**.



**Fig. 5. Linear wear of the 100Cr6 steel samples with the CrC+CrN type hybrid layers and the CrC type carbide layers vs. units pressure**

Rys. 5. Zużycie liniowe próbek ze stali 100Cr6 z warstwami hybrydowymi typu CrC+CrN oraz warstwami węglowymi typu CrC dla różnych nacisków jednostkowych

The investigations showed that the linear wear of the 100Cr6 bearing steel samples with the CrC+CrN type hybrid layers was more 50% less than that of steel samples with the CrC chromized carbide layers, **Fig. 5**.

For example, linear wear of samples with the CrC+CrN hybrid layers was 3.9  $\mu\text{m}$  under 300 MPa units of pressure for a friction time of 100 min, while that of the CrC carbide layer under the same conditions was 8.7  $\mu\text{m}$ .

The linear wear of the bearing steel samples without layers was more than twice as much.

### CONCLUSIONS

In the investigations, the focus was on the modification of the microstructure of carbide layers of the CrC type, accomplished by the combination of diffusion chromizing with a subsequent treatment consisting of CrN chromium nitride deposition by the Arc PVD method in order to improve their tribological properties.

Diffusion chromizing of the 100Cr6 bearing steel by the traditional pack method enabled the formation of layers composed of the  $(\text{Cr, Fe})_{23}\text{C}_6$  chromium carbide, containing trace amounts of the  $(\text{Cr, Fe})_2\text{N}$  nitride, similarly to other known diffusion chromizing methods in which chromium halogens served as process activators [L. 1, 2, 4, 7].

The CrC+CrN hybrid layers, obtained by the deposition of a CrN coating by the Arc PVD method on the surface of the chromium carbide layer, consisted of two zones: the first (outer zone), containing the



CrN nitride, and the second (inner zone), containing  $(Cr, Fe)_{23}C_6$  carbide, located in the area between the CrN coating and the tool steel substrate (**Figs. 2 and 3**).

The thickness of the CrC+CrN hybrid layer was about 14  $\mu\text{m}$  (CrC – 10  $\mu\text{m}$ ; CrN – 4  $\mu\text{m}$ ) and its hardness approx. 2100 HV. Similar results were reported by the authors in the case of the creation of the CrC+CrN hybrid layers on the surface of tool steel [**L. 28, 29**].

The investigations showed that the linear wear of bearing steel samples with the CrC+CrN hybrid layers was two times lower than that of the CrC carbide layers, **Fig. 5**. This indicates the excellent tribological properties of the hybrid layers. Similar relationships between tribological properties of the CrC type carbide layers and the CrC+CrN type hybrid layers were reported by the authors in other publications [**L. 28, 29**].

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