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ANTI-WEAR PROPERTIES OF MEDIUM CARBON STEEL AFTER CARBURIZING WITH SUBSEQUENT DIFFUSION CHROMIZING AND PVD TREATMENT

PRZECIWZUŻYCIOWE WŁAŚCIWOŚCI STALI ŚREDNIOWĘGLOWEJ PO NAWĘGLANIU Z NASTĘPNYM DYFUZYJNYM CHROMOWANIEM I OBRÓBKĄ PVD

Key words: diffusion chromizing, gas carburizing, PVD treatment, layer, wear.

Abstract The paper discusses the results of research on the structure and tribological properties of hybrid layers produced on the surface of medium-carbon steel in hybrid treatment, combining gas carburizing process with the next treatment, i.e. diffusion chromizing and PVD treatment. A comparison was made of the structure and tribological properties of the layers obtained as a result of hybrid treatment with the layers produced in a single diffusion chromizing process. The studies of the layers concerned their structure, chemical composition, thickness, and hardness. Linear wear of the layers were performed by means of three-cylinder-cone method. It has been shown that the linear wear of samples with hybrid layers, produced on medium carbon steel, is less than 50% of samples with single carbide layers. This indicates very good anti-wear properties of hybrid layers.

Słowa kluczowe: chromowanie dyfuzyjne, nawęglanie gazowe, obróbka PVD, warstwa, zużycie.

Streszczenie W pracy omówiono wyniki badań dotyczących budowy oraz właściwości tribologicznych warstw hybrydowych, wytwarzanych na powierzchni stali średniowęglowej, w obróbce hybrydowej łączącej nawęglanie gazowe z następną obróbką – chromowaniem dyfuzyjnym oraz obróbką PVD. Przeprowadzono porównanie budowy i właściwości tribologicznych warstw otrzymanych w wyniku obróbki hybrydowej z warstwami, wytworzonymi w pojedynczym procesie chromowania dyfuzyjnego. Badania warstw dotyczyły ich budowy, składu chemicznego, grubości i twardości. Zużycie liniowe warstw oceniano metodą trzy wałeczki-stożek. Wykazano, że zużycie liniowe próbek z warstwami hybrydowymi, wytworzonymi na stali średniowęglowej, jest ponad dwukrotnie mniejsze niż próbek z pojedynczymi warstwami węglikowymi. To świadczy o bardzo dobrych właściwościach przeciwzużyciowych warstw hybrydowych.

INTRODUCTION

The object of investigation in this work was the modification of microstructure of chromized carbide layers, generated on medium carbon steel by means of application of hybrid treatment, consisting of combining gaseous carburization with subsequent diffusion chromizing and a final PVD (Physical Vapour Deposition) treatment.

Hybrid technologies, consisting of a combination of several different treatments, e.g., thermochemical treatment with PVD or electrochemical processes, enable the formation of hybrid layers whose excellent service properties, obtained thanks to the synergy effect, are impossible to achieve with the application of single processes **[L. 1–6]**.

Problems related to the formation of diffusion chromized layers by means of different methods (pack, gas or vacuum, etc.) as well as with the service properties of obtained layers constitute the subject of several projects **[L. 7–11]**. The microstructure of diffusion chromized layers formed on the surface of steel depends

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significantly on the carbon content of the given steel grade. Diffusion chromizing of steel with a high carbon content results in obtaining of carbide-type layers with high hardness (1600–2000 HV) and wear resistance **[L. 12, 13]**.

In diffusion chromizing processes, chromium is delivered to the steel surface from the chromizing source, as the result of chemical reactions of exchange, reduction or dissociation, while the carbon, which is essential to the formation of chromium carbide, migrates from the steel substrate **[L. 7, 14, 15]**. Because of migration of carbon in the direction of the carbide layer being formed, known as „up-hill diffusion", the steel substrate is depleted of carbon, which adversely affects its mechanical properties.

Medium carbon steels are often used in the industry for components designated for medium loading and resistance to wear by friction, e.g., shafts or pump rotors. In the process of diffusion chromizing, the deficiency of carbon in the steel substrate causes deep decarburization and adversely affects the kinetics of growth of carbide-type diffusion chromized layers **[L. 7]**. The assurance of retaining of the appropriate level of carbon in medium carbon steel by the application of initial carburization prior to diffusion chromizing may positively affect growth kinetics of the carbide layer, as well as prevent excessive decarburization of the substrate. Investigations by the authors have shown that very good tribological properties may be achieved by the combination of the diffusion chromizing process with a subsequent treatment in the form of deposition of CrN chromium nitride by the electric arc vaporization method, known as Arc-PVD (Arc Physical Vapour Deposition), **[L. 16–18]**.

The object of investigations of the current work was the modification of the microstructure of diffusion chromized carbide layers formed on medium carbon steel by combining the process of gaseous carburizing with subsequent process of diffusion chromizing, followed by Arc-PVD treatment, aiming at the formation of hybrid layers of the CrC+CrN type, characterized by excellent anti-wear properties. Investigations were conducted of microstructure and wear resistance of hybrid CrC+CrN layers obtained in subsequent processes of gaseous carburizing, diffusion chromizing by the powder pack method, combined with the next treatment, which was the deposition of CrN chromium nitride by the Arc-PVD method.

EXPERIMENTAL PROCEDURE

Diffusion chromized carbide layers were formed on 1045 grade medium carbon non-alloyed steel containing 0.45% C. Diffusion chromizing processes were carried out by the traditional powder pack method, described in detail in reports **[L. 7, 13–17]**. Hybrid treatment of medium carbon steel was achieved in three stages that are essential to the carrying out of three consecutive processes of gaseous carburizing, diffusion chromizing, and Arc-PVD treatment.

In the first stage, gaseous carburizing processes were carried out. Carburizing of medium carbon steel samples designated for diffusion chromizing was accomplished in a shaker hearth continuous furnace. The carburizing processes were carried out in an endothermic atmosphere enriched by methane at a temperature of 900°C, in a time of 6 h, maintaining a carbon potential of 1% C.

In the second stage, diffusion chromizing processes were carried out on previously carburized steel samples. Samples designated for diffusion chromizing were placed in a prior prepared powder mixture pack containing 60% chromium powder of 0.063 mm grain size, 39% kaolin, and 1% ammonium chloride – NH_4Cl, situated in boxes of special design and subsequently heated in an electric furnace at a temperature of 900°C for a time of 10 h. The design of the boxes allowed for a hermetic seal during processing by utilizing enamel which melts above 600°C. Following the chromizing process, if needed, heat treatment was carried out consisting of quenching from 860°C after soaking for 0.5 h and tempering at 580°C for 2 h.

During the third stage, in order to form hybrid layers of the CrC+CrN type, deposition of CrN chromium nitride was carried out on the surface of the chromized steel. Coatings of chromium nitride were deposited by the Arc-PVD method. Processing parameters of the Arc--PVD deposition of chromium nitride coatings are given in **Table 1.**

Table 1. Parameters of the chromium nitride deposition processes by Arc-PVD method

Tabela 1. Parametry procesów osadzania azotku chromu metodą Arc-PVD

Type of process	Substrate temperature T [°C]	Substrate polarization voltage U_{BIAS} [V]	Pressure p [Pa]	Time of deposition [min]	Atmosphere
Heating	300	–	$<1 \times 10^{-3}$	30	–
Etching by Ar ions	300	–300	$5.0 \cdot 10^{-1}$	25	Ar
Etching by Cr ions	400	–300	$5.0 \cdot 10^{-1}$	15	Ar
Deposition of CrN	380	–150	3.5	120	N_2

METHODS OF INVESTIGATION

Investigations of layer properties encompassed the following: determination of their microstructure and chemical composition as well as measurements of layer thickness and hardness. Microstructure was studied on polished and Nital etched cross sections of samples, with the aid of an optical microscope manufactured by Nikon, model LV150. Scanning electron microscope images, coupled with analysis of their chemical composition in selected micro-regions, were obtained with the help of an SEM manufactured by Hitachi, with a resolution of 3 nm, equipped with an X-ray spectrometer with EDS dispersion energy as well as a BSE detector of backscattered electrons.

Hardness measurements were carried out by the Vickers method using the HV 0.02 scale on cross sections perpendicular to sample surfaces with the help of a Zwick microhardness tester.

Tribological properties (linear wear) of layers were determined by means of sliding wear tests with a concentrated contact point **[L. 19]**. Frictional wear tests were carried out by means of the thee cylinder-cone method, employing a K-54 machine, in accordance with the PN-83/H-04302 Polish Standard **[L. 20]**. Measurements were taken with cone rotational speed of 576 r.p.m. with unit loading of 50, 100, and 300 MPa, over a time of 100 min, with lubrication by Lux 10 oil.

RESULTS AND DISCUSSION

Layer microstructure

Figure 1 shows the microscopic image of 1045 grade medium carbon steel with a hybrid layer of the CrC+CrN type, formed by the process of diffusion chromizing of an initially carburized steel sample, subjected subsequently to Arc-PVD treatment to deposit CrN chromium nitride on the surface of the carbide-type chromized layer. Etching by Nital of metallographic sections of samples revealed the presence of a hybrid layer with a two-zone microstructure, separated by a distinct boundary from the pearlitic substrate of the steel. The external zone of the hybrid layer with a thickness of approx. 5 μm corresponds to chromium nitride. The internal zone of the layer in the region between the chromium nitride and the steel substrate with a thickness of approx. 19 μm corresponds to chromium carbide.

The total thickness of the CrC+CrN-type hybrid layer was approx. 24 μm, while its hardness in the immediate subsurface zone reached ca. 2040 HV0.02. Similar microstructures and hardnesses of hybrid layers formed in processes combining diffusion chromizing with subsequent deposition of chromium nitride were also obtained by the authors in projects carried out on other grades of steel **[L. 16, 17]**.

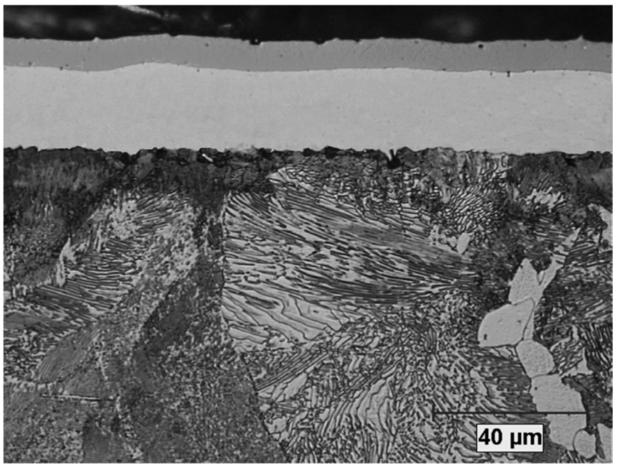

Fig. 1. Microscopic image of the Cr+CrN type hybrid layer formed on medium carbon steel in subsequent processes: carburizing with next diffusion chromizing and Arc-PVD treatment. Etched with 2%HNO_3

Rys. 1. Obraz mikroskopowy warstwy hybrydowej typu Cr+CrN, wytworzonej na stali średniowęglowej w kolejnych procesach: nawęglania z następnym chromowaniem dyfuzyjnym i obróbką Arc-PVD. Traw. 2%HNO_3

The scanning electron image obtained by the BSE+EDS mode of the CrC+CrN – type hybrid layer formed on medium carbon steel, obtained on a metallographic cross-section, perpendicular to the sample surface (a) as well as results of chemical analysis to determine the content of chromium, iron, carbon, and nitrogen in selected zones of the layer and substrate (b), marked by points 1 through 21, are shown in **Fig. 2**.

The analysis of chemical composition carried out confirmed the presence of CrN chromium nitrided in the external zone of the hybrid layer, since its main constituents are nitrogen and chromium (see Points 1–4 in **Figs. 2a and b)**. In the region between the chromium nitride and the steel substrate, the presence of chromium, iron, and carbon was determined. The maximum concentration of chromium in the region between the CrN coating and the steel substrate, corresponding to the CrC-type chromium carbide, was approx. 63 wt.% Cr and diminished to approx. 49 wt.% Cr with distance from the surface (see Points 5–16 in **Figs. 2 a and b**). At the same time, the content of iron increased. The content of carbon remained at a stable level of approx. 8 wt.% **[L. 7]**. It should be emphasized that the result of chemical analysis by the EDS method is averaged over the area affected by the electron beam of the scanning electron microscope, and this affects the error in determination of element concentration, especially of light elements, such as C or N.

a)

b)

Chemical composition [weight %]				
Number of the point	C	N	Cr	Fe
1	0.30	5.86	93.79	0.05
2	0.15	9.52	90.29	0.04
3	0.08	9.45	90.40	0.07
4	0.04	8.89	89.27	1.80
5	6.58	0.86	63.09	29.47
6	8.90	0.73	63.21	27.16
7	8.16	0.42	62.74	28.68
8	7.89	0.00	61.55	30.56
9	8.26	0.00	60.67	31.07
10	7.35	0.00	59.45	33.20
11	8.52	0.31	58.23	32.94
12	8.76	0.18	56.27	34.79
13	8.34	0.54	54.11	37.01
14	7.82	0.43	53.69	38.06
15	6.93	0.33	51.72	41.02
16	5.47	0.12	49.30	45.11
17	2.41	0.00	25.17	72.42
18	1.96	0.21	4.67	93.16
19	1.68	0.00	2.69	95.63
20	1.55	0.00	1.77	96.68
21	0.98	0.00	0.72	98.30

Fig. 2. Scanning image (SEM+BSE+EDS) of the CrC+CrN hybrid layer (a) and concentration of elements in the micro-areas of the layer and its substrate (b), marked with points 1–21 on the scanning image

Rys. 2. Obraz skaningowy (SEM+BSE+EDS) warstwy hybrydowej typu CrC+CrN (a) oraz stężenie pierwiastków w mikroobszarach warstwy i jej podłoża (b), zaznaczonych punktami 1–21 na obrazie skaningowym

Similar results of analysis of chemical composition of hybrid layers formed in combined processes of diffusion chromizing and subsequent deposition of chromium nitride were also obtained in investigations carried out on other steel grades **[L. 16, 17]**.

Figures 3 and 4 show microscopic images of layers formed on the surface of 1045 grade medium carbon steel in a process of diffusion chromizing, as revealed by Nital etching of metallographic sections cut perpendicularly to the sample surface. In both images, one can see the white, non-etching carbide-type chromized layers, separated from the steel substrate by a distinct boundary. As can be seen in **Fig. 3**, the substrate of diffusion chromized medium carbon steel, without prior carburization, has a ferritic-pearlitic microstructure, typical of unalloyed steel with medium carbon content **[L. 7, 10]**. On the other hand, the substrate of the 1045 steel subjected to carburization prior to the diffusion chromizing process has a totally pearlitic microstructure **(Fig. 4)**, characteristic of unalloyed steel with a high carbon content **[L. 7, 11]**.

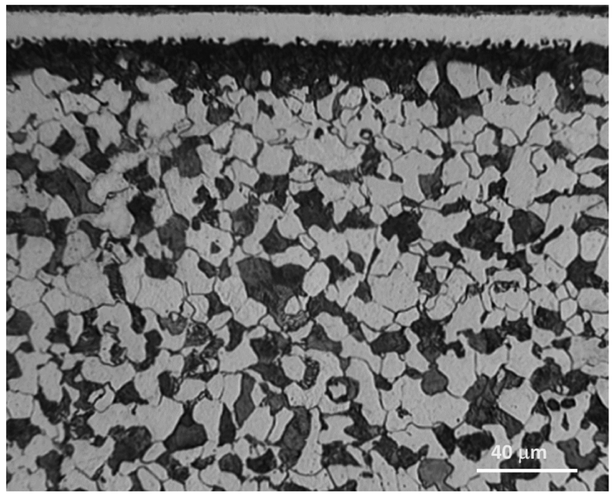

Fig. 3. Microscopic image of the carbide layer produced in diffusion chromizing process on medium carbon steel. Etched with 2%HNO_3

Rys. 3. Obraz mikroskopowy warstwy węglikowej wytworzonej w procesie chromowania dyfuzyjnego na stali średniowęglowej. Traw. 2%HNO_3

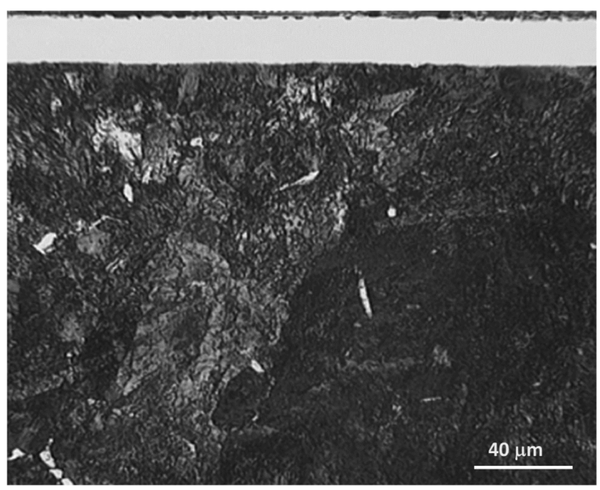

Fig. 4. Microscopic image of the carbide layer produced in diffusion chromizing process on carburized medium carbon steel. Etched with 2%HNO_3

Rys. 4. Obraz mikroskopowy warstwy węglikowej wytworzonej w procesie chromowania dyfuzyjnego na wstępnie nawęglonej stali średniowęglowej. Traw. 2%HNO_3

The thickness of carbide-type layers on initially carburized medium carbon steel was approx. 19 µm and was thus ca. 60% greater than that of layers obtained by the same diffusion chromizing process (900°C/10h), but without prior carburization of steel, which amounted to barely 8 µm. The hardness of carbide-type layers formed on 1045 grade steel subjected to prior carburization was approx. 1780 HV 0.02; thus, it was significantly higher than that of layers obtained without prior carburization which amounted to 1690 HV0.02. Carburizing of medium carbon 1045 steel prior to diffusion chromizing caused a modification of the substrate microstructure from ferritic-pearlitic to totally pearlitic which, as is known, is beneficial from the point of view of mechanical properties of the steel **[L. 7, 13–15]**. Moreover, it allowed the obtaining of carbide-type chromized layers with greater thickness and higher hardness than on that same grade of steel without carburization.

Tribological properties

Investigation of resistance to frictional wear by the three cylinder-cone method was carried out on samples of medium carbon steel with the following versions of layers:

- CrC-type carbide, formed on steel surface in a process of diffusion chromizing; and,
- CrC+CrN-type hybrid, formed in three consecutive processes, i.e. carburizing + diffusion chromizing + deposition of a CrN coating by the Arc-PVD method.

The dependence of linear wear of samples with CrC+CrN hybrid layers on the duration of the application of friction for different levels of unit loading is shown in **Fig. 5**.

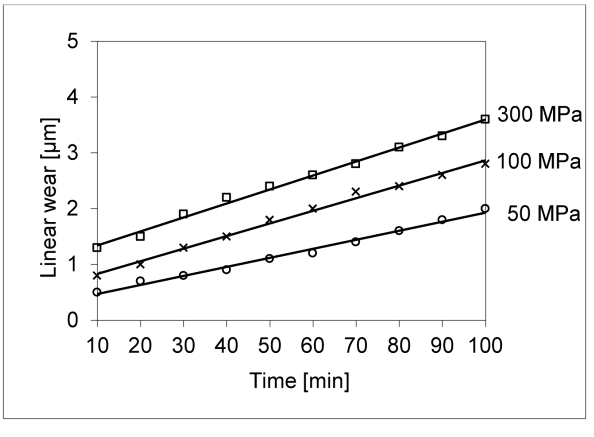

Fig. 5. Linear wear of the medium carbon steel samples with the CrC+CrN type hybrid layers vs. friction time and units pressure

Rys. 5. Zużycie liniowe próbek ze stali średniowęglowej z warstwami hybrydowymi typu CrC+CrN w zależności od czasu tarcia dla różnych nacisków jednostkowych

A comparison of linear wear of tested steel samples under different levels of unit loading for 100 min time of application of friction is shown in **Fig. 6**.

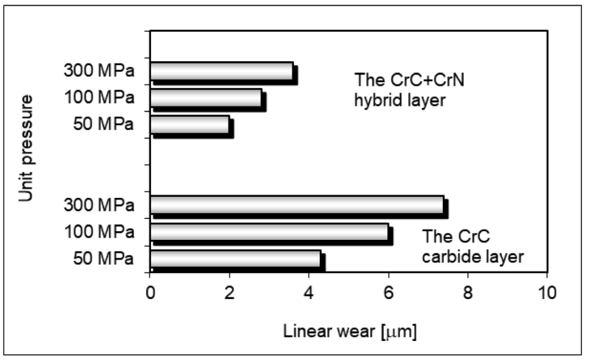

Fig. 6. Linear wear of the medium carbon steel samples with the CrC+CrN type hybrid layers and the CrC type carbide layers, vs. units pressure

Rys. 6. Zużycie liniowe próbek ze stali średniowęglowej z warstwami hybrydowymi typu CrC+CrN oraz warstwami węglikowymi typu CrC, dla różnych nacisków jednostkowych

This comparison showed that the linear wear of samples of 1045 grade steel with CrC+CrN hybrid layers is less than 50% of that of the same steel with chromized CrC-type carbide layers, e.g., linear wear of samples with a CrC-type carbide layer, under unit loading of 300 MPa after 100 min is 7.4 µm, while that of samples with hybrid layers of the CrC+CrN type is only 3.6 µm. This speaks of very good anti-wear properties of hybrid layers.

CONCLUSIONS

In the investigations carried out, the focus was on the modification of microstructure of chromized layers of the CrC carbide type on medium carbon 1045 grade steel, accomplished by the combination of three successive processes, i.e. gaseous carburizing, diffusion chromizing, and Arc-PVD treatment, with an aim at enhancement of that steel's wear resistance.

Diffusion chromizing processes were carried out by means of a technologically easy and inexpensive powder pack method. A simple and inexpensive method was also employed in the case of gaseous carburizing.

Gaseous carburizing of medium carbon steel prior to diffusion chromizing caused a modification of substrate microstructure of that steel from ferritic--pearlitic to only pearlitic, which is beneficial from the point of view of mechanical properties. Moreover, owing to the assurance of a high carbon content in the steel's substrate, essential to the formation of chromium carbide in the process of diffusion chromizing, carbide layers were obtained which featured greater thickness, approx. 19 µm, and higher hardness, approx. 1780 HV

0.02, than those obtained on the same grade of steel without prior carburizing which featured a thickness of only 8 µm and a hardness of 1690 HV 0.02.

Hybrid layers of the CrC+CrN type formed by means of deposition of chromium nitride by the Arc-PVD method on the surface of chromium carbide were composed of two zones, i.e the first – external, subsurface zone containing the CrN chromium nitride, and a second zone – internal, situated in the region between the CrN coating and the steel substrate, containing mainly chromium carbide. The thickness of hybrid layers was approx. 24 µm, while hardness taken in the zone immediately below the surface was approx. 2040 HV 0.02. Linear wear tests carried out by the three cone-cylinder method with a point contact showed that wear resistance of hybrid layers of the CrC+CrN type is more than twice as high as that of single carbide layers which speaks of their very good anti-wear properties.

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