

EWA KASPRZYCKA^{*}, BOGDAN BOGDAŃSKI^{}**

PROPERTIES OF DUPLEX LAYERS PRODUCED IN A VACUUM CHROMIZING PROCESS ON STEEL COVERED WITH COBALT ALLOY

WŁAŚCIWOŚCI WARSTW DUPLEX WYTWARZANYCH W PROCESIE CHROMOWANIA PRÓŻNIOWEGO NA STALI POKRYTEJ STOPEM KOBALTU

Key words:

vacuum chromizing, duplex layers, tribological properties, corrosion

Słowa kluczowe:

chromowanie próżniowe, warstwy duplex, właściwości tribologiczne, korozja

Abstract

The paper presents the results of examinations of the structure and properties of duplex layers of the CrC+(Co-W) type, produced in a vacuum chromizing process on a tool steel surface covered with Co-W electrolytic alloy. A comparison of the CrC+(Co-W) type duplex layers with the CrC type single carbide layers, produced in vacuum chromizing process, were performed. Studies of layers thickness, their hardness, structure, and concentration depth profiles of elements in the diffusion zone of these layers were carried out.

^{*} Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry, ul. Łukasiewicza 17, 09-400 Płock, Poland.

^{**} Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warszawa, Poland.

Tribological properties of the layers and corrosion resistance were determined. It has been proven that the wear resistance by friction of the CrC+(Co-W) type duplex layers, produced by means vacuum chromizing of tool steel covered with Co-W alloy electrolytic coating, is as good as single carbide layers of the CrC type, but their corrosion resistance is higher.

INTRODUCTION

This work pertains to diffusion layers with a carbide microstructure, formed during the vacuum chromizing process, combined with an initial galvanic treatment. Owing to the synergy effect, the combination of thermo-chemical treatments with other technologies, e.g., electrolytic, enables the obtaining of duplex-type layers with significantly enhanced service properties in comparison with those in the case of single processes [L. 1–6]. Vacuum chromizing, as opposed to other methods of diffusion chromizing, e.g., powder pack, gas or salt bath, is an energy and material efficient technology, which does not cause any contamination of the natural environment [L. 7, 8]. Carbide layers formed on steels in vacuum chromizing processes are characterized by very high wear resistance, but their corrosion resistance in aggressive environments, containing, among other, chloride ions, is insufficient [L. 8–10]. Investigations have demonstrated that electrolytic deposition of nickel alloys, containing carbide forming elements on the surface of steel prior to the vacuum chromizing process enables the formation of duplex layers featuring high corrosion resistance, as well as good tribological properties [L. 11]. Very good anti-corrosion and anti-wear properties are exhibited by coatings composed of cobalt alloys, which contain carbide-forming elements, e.g., Co-W type electrolytic coatings, which contain tungsten [L. 12, 13]. Cobalt-chromium alloys (Vitalium), thanks to their resistance to biological corrosion and good mechanical properties, have found application in medicine [L. 14].

The aim of investigations conducted in this project was the assessment of wear resistance and corrosion resistance of CrC+(Co-W) – type duplex layers formed in a joint galvanic and diffusion treatment, combining two processes, i.e. electrolytic deposition of the Co-W alloy on the steel surface and a subsequent diffusion chromizing process.

EXPERIMENTAL PROCEDURE

Chromized carbide layers (CrC type layers) were formed in vacuum chromizing processes on samples made from alloy tool steel – grade X210Cr12. The chromizing processes were carried out in a vacuum furnace at temperatures within the range of 1100–1150°C, at a pressure lowered to 10–10⁻² Pa. The method of vacuum chromizing, developed as the result of own investigations, is the subject of a patent [L. 15]. Following the vacuum chromizing processes, if needed, heat

treatment was carried out (austenitization at 980°C for 0.5 h, quenching and tempering at 200°C for 2 h).

Duplex layers of the CrC+(Co-W)-type were obtained by combining two processes in sequence, i.e. galvanic treatment, consisting of deposition of an electrolytic coating of a cobalt-based Co-W alloy on the surface of X210Cr12 grade steel with subsequent vacuum chromizing.

The electrolytic coating made from the cobalt-based Co-W alloy, deposited on the surface of X210Cr12 grade steel, contained 70% Co and 30%W, and its thickness was approx. 5 μm .

METHODS OF INVESTIGATION

Investigations of the layers comprised the following: their microstructure and phase composition, element concentration profiles, as well as measurements of layer thickness and hardness. The microstructure of layers was observed on mounted and polished metallographic cross-sections, etched with nital, with the aid of an optical microscope. Phase composition of chromized layers was determined by means of X-ray phase analysis with the aid of a diffractometer, employing CoK_α radiation. Linear analysis of element concentration in the layers was carried out with the aid of a Cameca X-ray microanalyzer, manufactured by the WDS Company. Hardness tests were made on polished sections perpendicular to the surface of the samples, employing a Zwick microhardness tester.

Tribological properties (linear wear) of layers were determined by means of sliding wear tests with concentrated contact [L. 16]. Wear tests were carried out by the three-cylinders-cone method, employing the I-47-K-54 equipment, in accordance with the Polish Standard PN-83/H-04302 [L. 17]. Measurements were taken with a rotating speed of the cone at $n = 576$ r.p.m. and unit loading pressures of 50, 100, 300 and 400 MPa during a time of 100 min, applying lubrication by Lux 10 oil. Corrosion resistance tests of chromized samples made from X210Cr12 grade tool steel were carried out in an aqueous solution containing 10% NaCl. The rate of the corrosion of the tested samples was determined based on loss of mass. In parallel with corrosion tests of chromized layers, tests were carried out on samples of 1H18N9T grade austenitic stainless steel. A period of half-year exposure was assumed. The corrosive medium was changed every 10 days.

RESULTS AND DISCUSSION

Layers structure

Investigations of microstructure of carbide layers of the CrC type, and of duplex CrC+(Co-W), formed on tool steel surface, and carried out on metallographic

mounted, polished and natal-etched cross-sections, revealed the presence of bright non-etching layers, separated by a clear cut border from the steel matrix (Figs. 1a and b).

X-ray phase analysis of the surface of chromized samples with CrC carbide layers obtained in a vacuum chromizing process showed the presence of mainly the $(Cr, Fe)_7C_3$ carbide. The concentration of chromium in the carbide reached approx. 75 wt.% with an iron content of approx. 25 wt.% (Fig. 2).

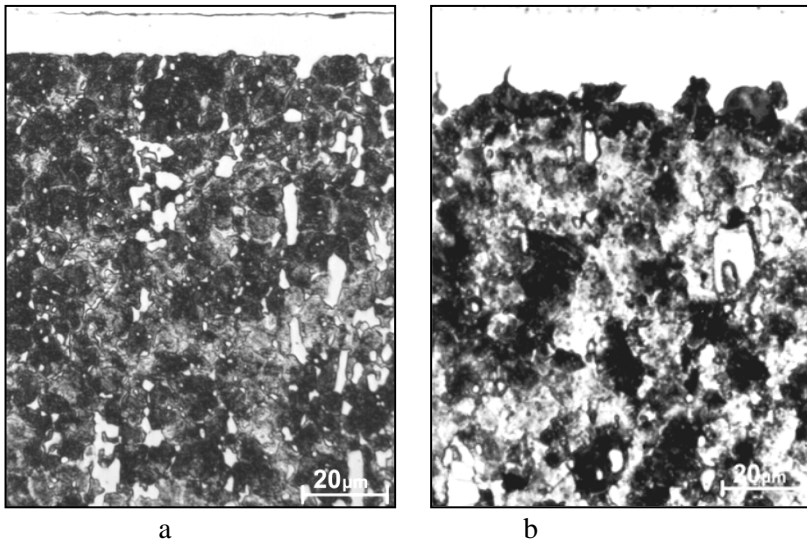


Fig. 1. Microstructure of tool steel with chromized layer: a – carbide layer of the CrC type, b - duplex layer of the CrC+(Co-W) type. Etched with 2% HNO_3

Rys. 1. Mikrostruktura stali narzędziowej z warstwą chromowaną: a – węglkową typu CrC, b – warstwą duplex typu CrC+(Co-W). Traw. 2% HNO_3

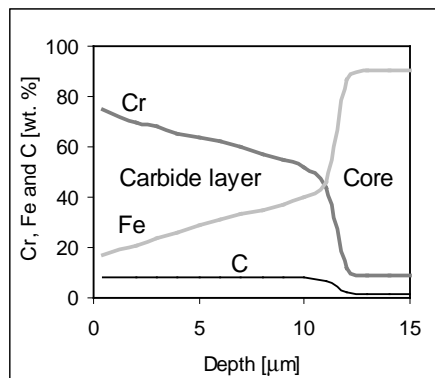


Fig. 2. Depth profiles of elements concentration of the CrC carbide layer

Rys. 2. Rozkłady stężenia składników w warstwie węglkowej typu CrC

The content of carbon in the carbide was ca. 9%, which is characteristic of the Cr_7C_3 type carbide [L. 7]. Layer thickness was 13 μm , while its hardness was 1800 HV0.02.

X-ray phase analysis of the surface of chromized samples with type $\text{CrC}+(\text{Co}-\text{W})$ duplex layers showed the presence of the $(\text{Cr}, \text{Fe})_7\text{C}_3$ chromium carbide, as well as of type $(\text{W}, \text{Me})\text{C}$ tungsten carbides.

Element concentration profiles in the $\text{CrC}+(\text{Co}-\text{W})$ duplex layer, obtained by means of an X-ray microanalyzer, indicate that it is possible to distinguish two separate zones with significantly differing microstructures (Fig. 3).

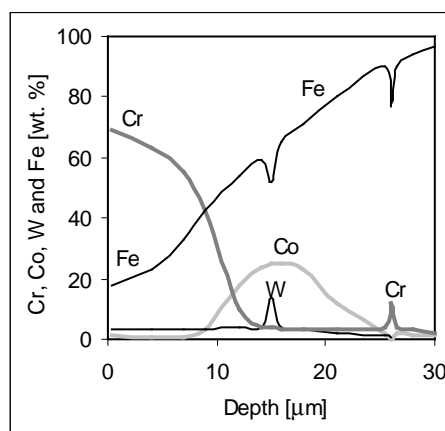


Fig. 3. Depth profiles of elements concentration of the $\text{CrC}+(\text{Co}-\text{W})$ duplex layer

Rys. 3. Rozkłady stężenia składników w warstwie duplex typu $\text{CrC}+(\text{Co}-\text{W})$

The first zone is constituted by an area adjacent to the surface of the layer, having a thickness of ca. 10 μm and containing the $(\text{Cr}, \text{Fe})_7\text{C}_3$ chromium carbide. The content of chromium in this carbide in the area adjacent to the surface is approx. 70 wt.%.

In the second zone of the duplex $\text{CrC}+(\text{Co}-\text{W})$ layer, the presence of cobalt was determined, taking up the space between the chromium carbide and the steel matrix with a thickness of ca. 20 μm . Its content attains ca. 25 wt.%. The presence of tungsten and chromium was also determined. This zone also contains tungsten and chromium carbides, revealed each time in concentration profiles in the form of a characteristic leap increment of tungsten or chromium concentration with a simultaneous drop in the concentration of iron (Fig. 3).

The border separating the $\text{CrC}+(\text{Co}-\text{W})$ type duplex layer from the steel matrix is not uniform, as opposed to the border separating the CrC -type carbide layer (Fig. 1). For this reason, an accurate measurement of the thickness of this layer is difficult. Nevertheless, it can be stated with approximation that this thickness is ca. 30 μm , because it is down to that depth that changes in

microstructure are observed under the microscope in the surface layer (**Fig. 1b**). These changes are caused by the diffusion of the electrolytic Co-W coating into the steel during the vacuum chromizing process at an elevated temperature and lowered pressure. The hardness of the duplex layer in the subsurface zone, corresponding to the $(Cr, Fe)_7C_3$ chromium carbide, was 1740 HV 0.02.

Tribological properties

Tribological characteristics, portraying linear wear of samples with CrC+(Co-W) – type duplex layers versus friction time for unit pressure loading of 50, 100, 300 and 400 MPa, are shown in **Fig. 4**. Linear wear of samples with duplex layers increases with the rise of unit loading from 3.8 μm at 50 MPa to 9.6 μm at 400 MPa during the 100 min. test. In **Fig. 5**, a comparison is given of the linear wear of CrC+(Co-W) – type duplex layers with that of carbide layers of the CrC type, as well as of samples made from X210Cr12 steel, without any layer, only after heat treatment, i.e. quenched and tempered. As can be seen, the values of linear wear obtained on samples with CrC+(Co-W) – type duplex layers are of the same order as those obtained on samples with carbide layers of the CrC type.

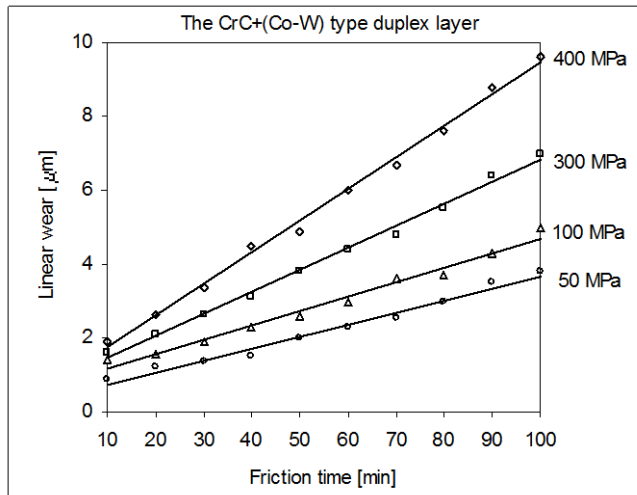


Fig. 4. Linear wear of the tool steel samples with the CrC+(Co-W), type duplex layers vs. friction time and units pressure

Rys. 4. Zużycie liniowe próbek ze stali narzędziowej z warstwami duplex typu CrC+(Co-W), w zależności od czasu tarcia dla różnych nacisków jednostkowych

In both cases, the linear wear of samples is significantly less than that of steel samples without layers, subjected only to heat treatment, i.e. quenching and tempering. The investigations of wear resistance of CrC+(Co-W) – type

duplex layers and of CrC – type carbide layers showed their good tribological properties.

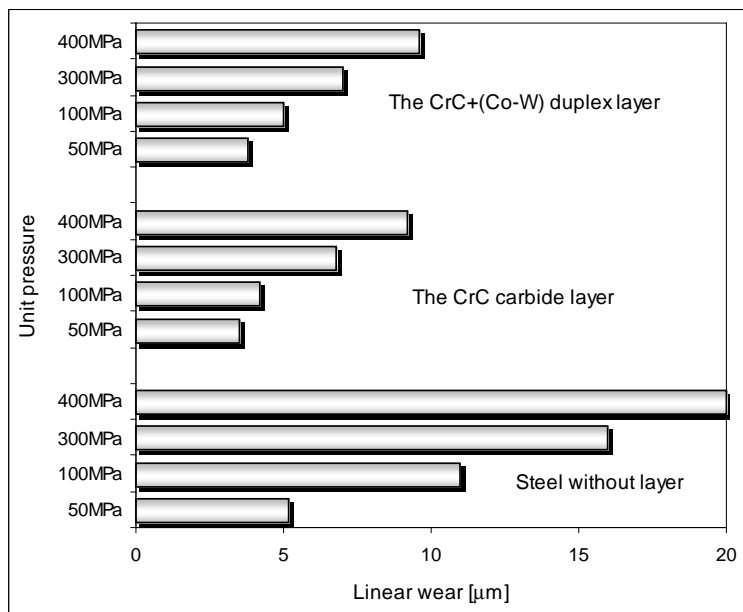


Fig. 5. Linear wear of the tool steel samples with the CrC type carbide layers, the CrC+(Co-W) duplex type layers and hardened steel samples without any layers, for different units pressure and 100 min friction time

Rys. 5. Zużycie liniowe próbek ze stali narzędziowej z warstwami węglowymi typu CrC, warstwami duplex typu CrC+(Co-W) oraz utwardzanych cieplnie próbek ze stali, bez warstwy, dla różnych nacisków jednostkowych i czasu tarcia 100 min

Corrosion resistance

Investigations of corrosion resistance in an aqueous solution containing 10% NaCl were carried out on the following types of samples:

- Samples with CrC+(Co-W) – type duplex layers, obtained in a process of vacuum chromizing on the surface of X210Cr12 steel, overlaid with a Co-W alloy;
- Samples with CrC – type carbide layers, obtained in a process of vacuum chromizing directly on the surface of X210Cr12 steel; and,
- Samples made from corrosion resistant 1H18N9T grade steel, without a diffusion layer.

For these investigations, a half-year time of exposure was assumed. The rate of corrosion of chromized samples and that of samples made from 1H18N9T grade steel is given in **Table 1** for comparison.

Changes of mass (decrements) of samples, caused by the action of the corrosive environment, indicated a uniform course of the corrosion process. The corrosion resistance of chromized samples made from X210Cr12 steel with CrC+(Co-W) – type duplex layers in an aqueous solution of 10% NaCl was significantly greater than that of samples with only CrC – type layers. As an example, the rate of corrosion of samples with CrC+(Co-W) – type layers, which amounted to 0.0035 g/m² per 24 h, was almost 4 times less than the rate of corrosion of samples with CrC – type carbide layers (0.0134 g/m² per 24 h). The rate of corrosion of samples with duplex-type layers was of the same order as that of corrosion resistant 1H18N9T grade austenitic steel.

Table 1. Corrosion rate of chromized the X210Cr12 steel samples and the 1H18N9T steel in the aqueous solution of 10% NaCl

Tabela 1. Szybkość korozji chromowanych próbek ze stali X210Cr12 i stali 1H18N9T w roztworze wodnym 10% NaCl

The exposure time: 6 months

Kind of process /steel	Kind of layer	Corrosion rate [g/m ² doba]
Electrolytic deposition of the Co-W alloy on the X210Cr12 steel surface + Vacuum chromizing	The CrC+(Co-W) type duplex layer	0.0035
Vacuum chromizing	The CrC type carbide layer	0.0134
The 1H18N9T steel	Steel without layer	0.0027

CONCLUSIONS

Duplex layers of the CrC+(Co-W) type, generated thanks to the combination of two successive processes, i.e. electrolytic treatment, consisting of deposition of a coating of Co-W cobalt-base alloy on the surface of X210Cr12 steel, with subsequent vacuum chromizing, exhibit a zone build, as shown by the investigations carried out. The first zone counting from the surface of the layer is constituted by chromium carbide of the (Cr, Fe)₇C₃ type, which is formed during the vacuum chromizing process [L. 8].

The second zone, situated between the chromium carbide and the steel matrix, is rich in cobalt, with a concentration of ca. up to 25 wt.%, as well as tungsten. This zone is formed during the process of vacuum chromizing, as the result of diffusion of constituents of the Co-W galvanic coating in the direction

of the core, thus there is a diffusion of cobalt and tungsten at an elevated temperature and low pressure [L. 8]. In this second zone, the presence is observed of tungsten carbides, originating from the electrolytic coating, as well as of chromium carbides, which constitute a structural component of the alloy steel.

Investigations of wear resistance of CrC+(Co-W) – type duplex layers have shown that their tribological properties are as good as those of CrC – type carbide layers, obtained in the vacuum chromizing process, but that their corrosion resistance in the 10% NaCl aqueous solution is almost four times higher.

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Streszczenie

W pracy omówiono wyniki badań dotyczących struktury oraz właściwości warstw duplex typu CrC+(Co-W) wytwarzanych w procesie chromowania próżniowego na powierzchni stali narzędziowej pokrytej elektrolitycznie stopem Co-W. Przeprowadzono porównanie pomiędzy warstwami duplex typu CrC+(Co-W) oraz pojedynczymi warstwami węglowymi typu CrC, wytwarzanymi w procesie chromowania próżniowego. Przeprowadzono pomiary grubości warstw, ich twardości oraz badania struktury i rozkładów stężenia pierwiastków w strefie dyfuzyjnej. Określono odporność na zużycie przez tarcie warstw oraz ich odporność korozyjną. Wykazano, że odporność na zużycie przez tarcie warstw duplex typu CrC+(Co-W), wytwarzanych w procesie chromowania próżniowego na powierzchni stali pokrytej powłoką elektrolityczną ze stopu Co-W, jest równie dobra, jak węglowych warstw chromowanych typu CrC, ale ich odporność korozyjna jest znacznie większa.