

CORROSION, FRICTION AND WEAR PERFORMANCE OF DIAMOND – LIKE CARBON (DLC) COATINGS

Received – Prispjelo: 2016-02-03

Accepted – Prihvaćeno: 2016-05-20

Original Scientific Paper – Izvorni znanstveni rad

The a - C:H:W, TiN/a - C:H:W and the CrN/a - C:H:W coatings were deposited on steel surface by physical vapour deposition methods and studied for corrosion and tribological properties, after elemental and structural analysis. In friction pairs the elements coated with diamond-like carbon showed better tribological properties than the elements without coatings. The presence of interlayers in coatings contributed to an improvement in the tribological properties but decreased corrosion resistance.

Keywords: diamond-like carbon coatings, corrosion, microstructure, friction, wear.

INTRODUCTION

One way to increase the stability and operational reliability of machine parts and equipment is improving the tribological properties and corrosion cooperating elements [1,2]. Some properties are desirable only on the surface of the material obtained by applying the surface layers [1, 3, 4]. Currently there is high interest in thin coatings obtained by methods of chemical deposition (CVD) and physical vapor deposition (PVD), which improves the utility because the coated part does not increase its volume, and at the same time not affect the structural substrate [1, 3].

The tribological systems improve the performance characteristics can be achieved by the use of properly selected diamond coatings and lubricants [3,5]. DLC coatings are widely used in various industries: medical electronics, automotive, utility [3- 6]. Remarkable mechanical properties, high surface smoothness and chemical inertness of the DLC coatings, enable excellent performance of tribological systems in special environments. Their engineering applications are becoming more and more popular due to the excellent tribological properties: low-friction and anti-wear, stability and corrosion resistance, high hardness, thermal stability and biocompatibility [3-5]. The aim of the study was to conduct a comparative analysis of the impact of the type of coating on tribological and corrosive properties.

MATERIALS AND METHODS

The coatings have been deposited on HS6-5-2 steel characterized by a very good ductility, toughness, and

abrasion resistance. Its hardness after improving heat at temperatures 500 - 550 ° C is 65 HRC. The coatings have been obtained in the following processes of physical vapor deposition PVD:

- TiN by arc evaporation - Arc Evaporation at a temperature of 500 ° C,
- CrN temperature by sputtering at a temperature of < 270 ° C,
- a - C: H: W at a temperature of < 250 ° C by sputtering.

In the study of the structure a scanning electron microscope (SEM) FEI XL30 SEM equipped with of energy dispersive spectrometer (EDS) EDAX GEMINI 4000, with the possibility of testing in low vacuum has been used. The research included observations of surface topography, and the point microanalysis allowed to investigate the elemental composition.

The most popular device for evaluation of tribological properties of material combinations in concentrated point contact is a Test ball-on-disc machine.

The tested combination consists of a stationery ball compressed with a force P to the rotating one with the defined speed n of the disc. The study has taken into account the effect of lubricants on the tribological properties of the analyzed systems with diamond-like coatings. Tribological tests using T-01M, have been conducted with the following parameters:

- the combination of friction: steel ball 100Cr6 – steel disc made of SW7M or SW7M covered with DLC coating,
- load P = 10 N,
- slip velocity v = 0,1 m/s,
- friction track s = 1 000 m,
- lubrication: no oil or polyalphaolefin PAO - 6,
- relative humidity conditions 55 ± 5 %,
- ambient temperature T₀ = 22 ± 1 ° C.

M. Madej, D. Ozimina, Kielce University of Technology, Poland
R. Gałuszka, The Jan Kochanowski University in Kielce, Poland
G. Gałuszka - School of Economics, Law and Medical Sciences in Kielce, Poland

Electrochemical corrosion tests have been carried out at 20 °C in a 3% aqueous solution of NaCl. It was used during measurements a three-electrode system has been used. Working electrodes on the surface of $s = 0,390 \text{ cm}^2$ were tested diamond-like coatings. The counter electrode of $s = 1,5 \text{ cm}^2$ and the saturated calomel reference electrode (SCE) were used. Polarization measurements of tested electrodes have been made using the electrochemical test kit ATLAS 0531. The stationary potential E_{cor} has been measured after 60 minutes, it has been applied rate of change of the potential of $10 \text{ mV} / \text{min.}$ and a sampling frequency of 1 mV.

DC Electrochemical tests included polarized testing involving the determination of the current corrosion density and registering the voltammetric characteristics of the corroding steel electrode of $0,390 \text{ cm}^2$ and electrode with coatings. If the cathodic and anodic corrosive reactions occur with activation overpotential, the dependence of the current density on the electrode potential describes the Butler-Volmer equation:

$$j = j_{cor} \left\{ \exp \left[\frac{2,303(E - E_{cor})}{b_a} \right] - \exp \left[\frac{2,303(E - E_{cor})}{b_c} \right] \right\} \quad (1)$$

where: E - electrode potential, E_{cor} - corrosion potential, b_a , b_c - Tafel coefficients for anodic and cathodic reactions, j_{cor} - corrosion current density [3, 7].

The values of j_{cor} and b_a , b_c have been determined using an iterative method by adjusting the parameters of the equation (1) to the registered ones in the so-called Non - Tafel area of current-voltage data [3, 7]. The values of polarization resistance R_p was calculated using Stern-Geary equation:

$$j_{cor} = \frac{b_a b_c}{2,303(b_a + b_c) R_p} \quad (2)$$

The voltammetric characteristics have been prepared in the range of -800 mV to 1600 mV at a sample rate of 1 mV and a rate of change of potential of $100 \text{ mV} / \text{min.}$ The stationary potential E_{cor} has been measured after 20 minutes of immersion of the sample in a 3% NaCl solution, registration of impedance data has been started after 20 minutes after immersion of the tested electrode in the solution. The evaluation of the corrosive properties of the samples is based on the juxtaposition of the corrosion current density, corrosion potential and polarization resistance.

RESULT AND DISSUSSION

Figure 1 summarizes the images of the surface topography of coatings of diamond, Figure 2 shows an illustrative X-ray of a-C:H:W coating, since for two-layer coatings they were very similar. In Figure 3 was presented cross-section with the measurement of their thickness.

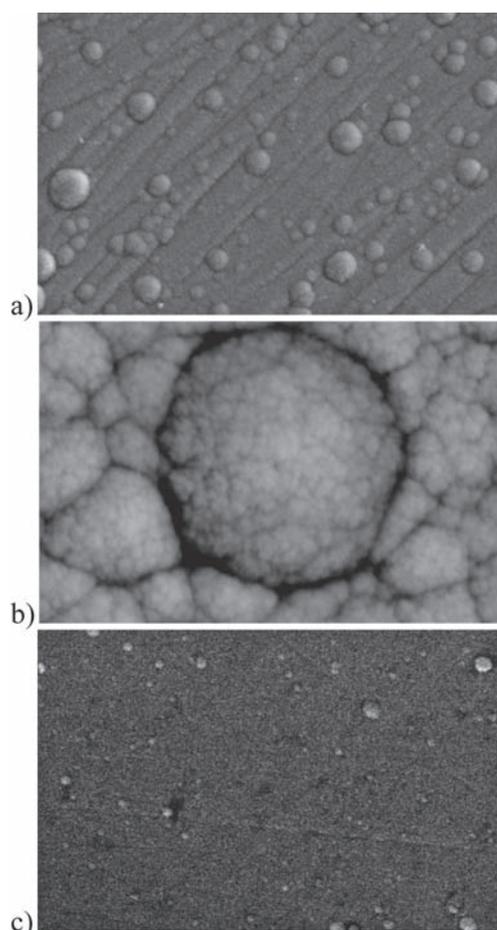


Figure 1 SEM - images of the surface of diamond - like coatings: a) a - C:H:W, b) CrN/a - C:H:W, c) TiN/a - C:H:W

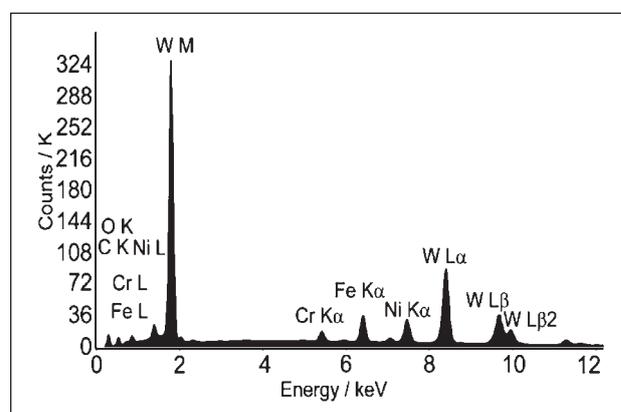


Figure 2 The EDS point analysis of elemental composition of a - C:H:W coating

SEM photographs of the surface of diamond - like coatings presented in Figure 1 show that the tested coatings have different microstructures. The coatings have distinct inclusions probably tungsten carbide. The use of TiN or CrN interlayer didn't improve the roughness of coatings.

EDS spectrum of a - C:H:W coating shown in figure 2 confirmed the composition with the one assumed the during the manufacturing process.

Thickness measurements show that depending on the type of the coating they differ from one another and take the following values:

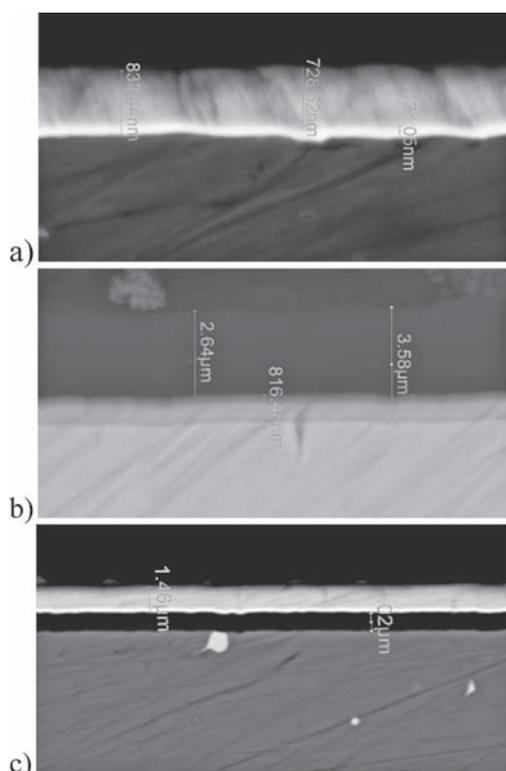


Figure 3 SEM microstructure of the cross-sectional measurement of the coating thickness: a) a - C:H:W, b) CrN/a - C:H:W, c) TiN/a - C:H:W

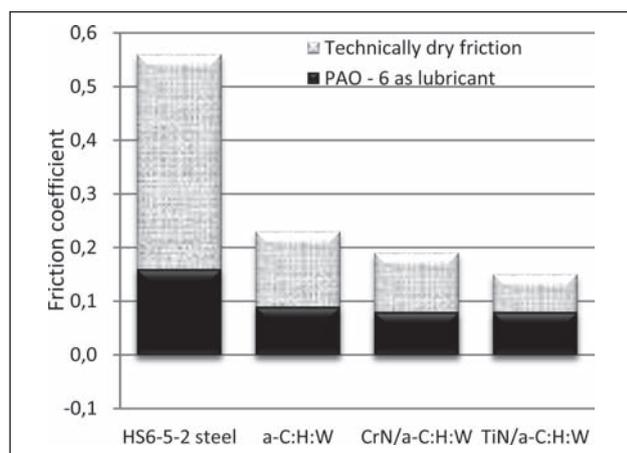


Figure 4 The friction coefficients obtained for the tested materials.

- a - C:H:W coating about 0,8 μm,
- CrN/a - C:H:W coating 0,8 + 2,6 = 3,4 μm,
- TiN/a - C:H:W coating 1,1 + 1,4 = 2,5 μm.

The evaluation of tribological properties of the research carried out on the device ball-on-disk - camera

T-01M in sliding motion. The results of the study are presented in the form of summaries of collective coefficient of friction (Figure 4), while maintaining constant parameters of environment microclimate. They are very important during conducting of tests and determining the tribological characteristics, especially in conditions of dry friction. This is due to the fact that the exposed, without passive layers, the surface of friction couples elements demonstrates big adsorptive-reaction activity with the components of the environment.

Diagrams shown in Figure 4, obtained under the conditions of dry friction a frame of reference for the study of eligible lubricants. It was found that for all tested coatings the friction coefficients are smaller than for steel. Similarly, using a synthetic polyalphaolefin PAO - 6 oil. For DLC coatings modified with tungsten, as a result of using the interlayer CrN and TiN, the frictional resistance is less than a monolayer of the coating.

In the last step electrochemical corrosion tests have been performed. Voltammetric characteristics obtained in 3 % NaCl solution at 20 ° C for the substrate and the coating are shown in Figure 5. Current-voltage characteristics of the steel electrode and diamond – like coatings indicate the active-passive behavior of coatings.

Corrosion resistance of the tested surfaces of elements diamond – like coatings and elements without coverage varies depending on the type of coating. The results summarized in Table 1 show that the corrosion current density of steel is more than five times higher than for a - C:H:W coating.

The values of Tafel coefficients b_a and b_c denote the anodic or cathodic control of corrosion process. The use of TiN and CaN interlayers had a negative impact on the corrosion current density, corrosion potential and polarization resistance. All polarizing tested diamond-like DLC coatings have better parameters of corrosion resistance with reference to the steel HS6-5-2.

CONCLUSIONS

The observations of the structure have shown the compliance of the construction of the structure of the coatings with the one that was assumed during the processes of their preparation, and EDS analysis gave information about the chemical elemental composition of the coatings. Their thickness measured during testing on the SEM microscope has also been verified.

Table 1 Results of the analysis of polarization

Material / parameter	HS6-5-2 Steel	a - C:H:W	CrN/ a - C:H:W	TiN/ a - C:H:W
Corrosion current density j_{cor} / A/cm ²	58,6·10 ⁻⁶	10,6·10 ⁻⁶	14,9·10 ⁻⁶	13,2·10 ⁻⁶
Tafel coefficient for the anode reaction b_a / mV	106	151	158	194
Tafel coefficient for the cathode reaction b_c / mV	147	280	240	486
Corrosion potential E_{cor} / mV	-591	-506	-484	-509
Polarization resistance R_p / Ω·cm ²	459	4082	2748	4607

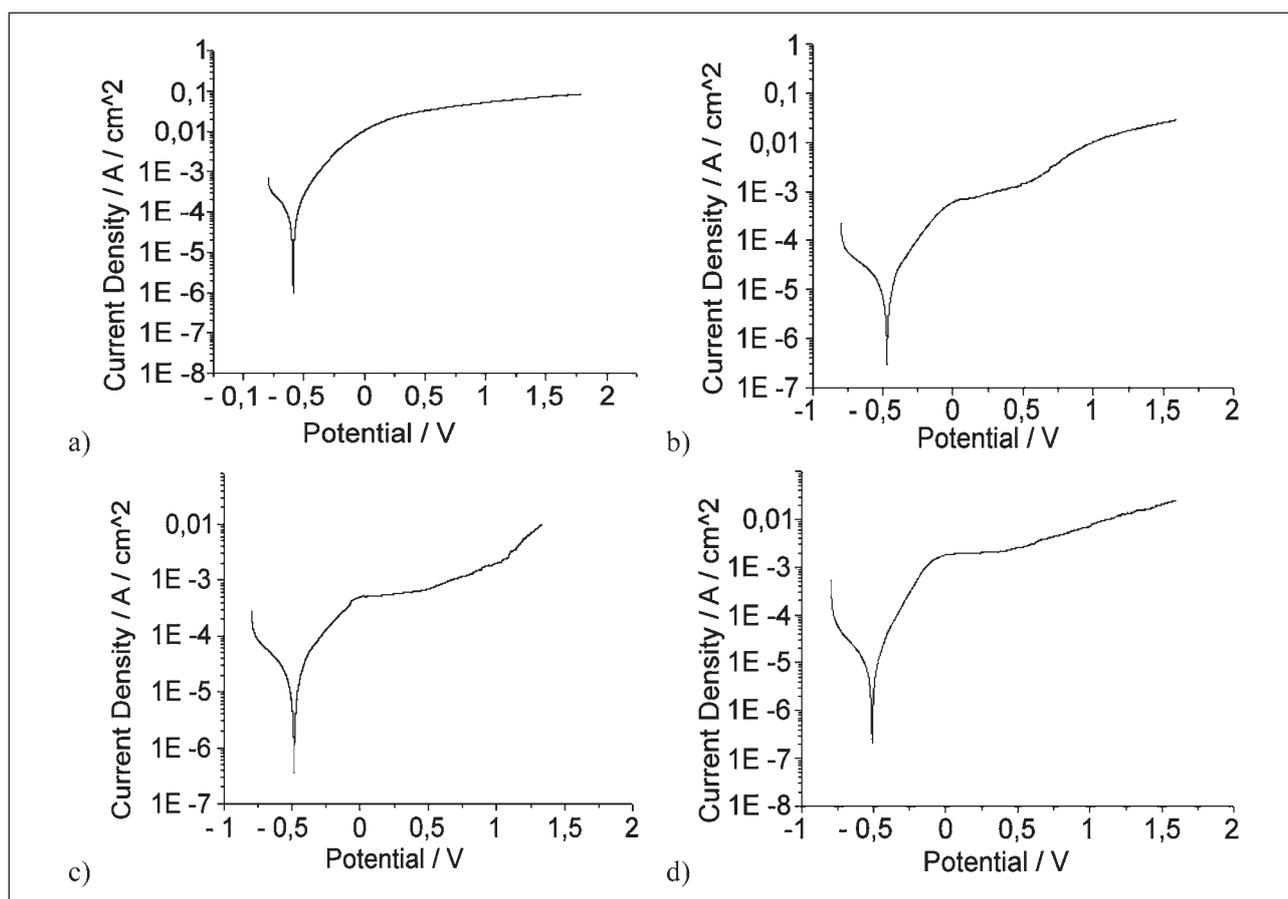


Figure 5 Voltammetric characteristics for: a) - HS6-5-2 steel and b) a - C:H:W; c) CrN/a - C: H: W; d) TiN/a - C:H:W coatings

Electrochemical corrosion tests, expressed through voltammetric characteristics showed that the tested diamond-like coatings have significantly better parameters of corrosion resistance than steel, with the highest corrosion resistance characterized by coating a - C:H:W.

Friction couples of elements coated with DLC coatings have better tribological properties in comparison to the tribological properties in comparison to the uncoated nodes under dry friction conditions and lubricating polyalphaolefins PAO - 6. In addition, PAO - 6 oil has contributed to the improvement of tribological properties of all tested systems.

The study showed that thin diamond-like coatings embed on the elements exposed to tribological and corrosive wear perfectly meet the protective functions.

REFERENCES

- [1] T. Burakowski, T. Wierzchoń: Surface engineering of metals: principle, equipment, technology. CRS Press, Boca Raton, New York, London. 1999.
- [2] D. Golubović, P. Kovač, D. Ješić, M. Gostimirović, V. Pucovsky, Wear intensity of diferent heat treated nodular cast irons, Metalurgija 51 (2012) 4, 518-520.
- [3] K. Bobzin, N. Bagecivan, S. Theiß, R. Weiß, U. Depner, T. Troßmann, J. Ellermeier, M. Oechsner, Influence of the layer architecture of DLC coatings on their wear and corrosion resistance, International Journal of Materials Research 103 (2012) 6, 774-782.
- [4] M. Madej, The effect of TiN and CrN interlayers on the tribological behavior of DLC coatings, Wear 317 (2014) 1-2, 179-187.
- [5] M. Kalin, E. Roman, L. Ožbolt, J. Vižintin, Metal-doped (Ti, WC) diamond-like-carbon coatings: Reactions with extreme-pressure oil additives under tribological and static conditions, Thin Solid Films 518 (2010) 15, 4336-4344.
- [6] A. Bąkowski, L. Radziszewski, Determining selected diesel engine combustion descriptors based on the analysis of the coefficient of variation of in-chamber pressure, Bulletin Of The Polish Academy Of Sciences Technical Sciences 63 (2015) 2, 457-464.
- [7] ISO 8044:2015 Corrosion of metals and alloys. Basic terms and definitions.

Note: The responsible translator for English language is Przemysław Szczepańczyk, Kielce, Poland