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Marcin KOT[*], **Jurgen LACKNER**[**], **Łukasz MAJOR**[***], **Roman MAJOR**[***], **Konrad SKALSKI**[*], **Grzegorz WIĄZANIA**[*], **Sławomir ZIMOWSKI**[*]

ADAPTIVE COATINGS a-C/MoS$_2$

POWŁOKI ADAPTACYJNE a-C/MoS$_2$

Key words: adaptive coatings, chameleon coatings, nanohardness, friction, wear.

Abstract One of the latest ideas in surface engineering is the deposition of new kinds of coatings, called adaptive or chameleon. Based on literature review, the different mechanisms of the adaption of such coatings depend on the applied ranges of temperature and loads were compared. Moreover, the main directions of development of adaptive coatings were also presented. The paper includes results of single coatings, a-C and MoS$_2$, as well composite coatings, a-C/MoS$_2$, in which the mechanism of adaptation was expected. Indentation tests were carried out to determine nanohardness and elasticity modulus. The adhesion of coatings to steel substrates was studied by scratch testing, and tribological properties were studied using a high-temperature ball-on-disc tribometer and tests results conducted at room temperature and at elevated temperatures up to 300°C. Results showed that composite coating, a-C/MoS$_2$, can work over the entire range of temperatures with a low coefficient of friction 0.02–0.1 and wear index of $0.07–0.47 \cdot 10^{-6}$ mm^3/Nm . Whereas, a-C and MoS$_2$ coatings exhibited a low coefficient of friction and a high wear resistance at low and high temperatures, respectively.

Słowa kluczowe: powłoki adaptacyjne, powłoki kameleonowe, nanotwardość, tarcie, zużycie.

Streszczenie W pracy przedstawiono nowy kierunek w inżynierii powierzchni tworzenia powłok adaptacyjnych, zwanych także kameleonowymi. Na podstawie analizy literatury zestawiono różne mechanizmy adaptacji powłok, w zależności od zakresu stosowanych temperatur pracy i kierunki rozwoju takich powłok. Przedstawiono także wyniki badań własnych dla powłok pojedynczych a-C i MoS$_2$ i na ich tle wyniki dla powłok a-C/MoS$_2$, w których spodziewano się mechanizmu adaptacji. Przeprowadzono testy indentacyjne, z których wyznaczono ich nanotwardość i moduł sprężystości. Analizowano także adhezję powłok do podłoży stalowych przy użyciu testu zarysowania. Testy tribologiczne przeprowadzono w temperaturze pokojowej oraz w podwyższonej do 300°C. Uzyskane wyniki wykazały, że w odróżnieniu do powłok a-C i MoS$_2$ powłoki a-C/MoS$_2$ mogą pracować w całym zakresie badanych temperatur. Wskazują na to niskie wartości współczynnika tarcia 0,02–0,1 i wskaźnika zużycia $0,07–0,47 \cdot 10^{-6}$ mm^3/Nm.

INTRODUCTION

With the current, extremely rapid development of practically all industrial sectors, there is a constant need to limit friction and wear of friction pairs of machines, vehicles, and tools. This can be achieved by redesign, the use of more wear resistant materials, or better lubricants. Another solution that has been used for 50 years is surface modification by surface layers or coating deposition. Such treatments can be very effective and significantly extend the lifetime of technical facilities and increase their reliability. In many cases, friction nodes can work without lubricants or with their reduced amount and low friction force, which directly affects the energy consumption of machines or the fuel consumption of engines. First tribological coatings deposited by CVD and PVD techniques were nitrides or carbides of transition metals such as Ti and Cr, mainly used for machining tools. They are called "first generation of coatings." After that, more complex second-generation coatings appeared, such as TiCN, TiAlN and the also first carbon coatings like DLC [**L. 1, 2**]. Further development of the coatings allowed one to deposit the third generation of coatings with

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[*] AGH University of Science and Technology, Faculty of Mechanical Engineering and Robotics, Al. Mickiewicza 30, 30-059 Krakow, Poland, e-mail: kotmarc@agh.edu.pl.

[**] Joanneum Research Forschungsges.M.B.H., Institute for Surface Technologies and Photonics, Functional Surfaces, Leobner Straße 94, A-8712 Niklasdorf, Austria.

[***] Polish Academy of Sciences, Institute of Metallurgy and Materials Sciences, Reymonta 25, PL-30059 Krakow, Poland.

a complex microstructure, e.g., nanocomposite coatings CrC/a-C:H, TiC/a-C:H [**L. 3, 4**], and multilayers Ti/TiN [**L. 5**]. However, the need to exploit elements with coatings in various environmental conditions – temperature, atmosphere, and humidity, caused that a new type of coatings to be currently developing, which are called "adaptive or chameleon coatings" [**L. 6, 7**]. The latest results presented in the literature indicate that the range of operating temperatures of adaptive coatings depends mainly on the mixture of materials that create the coating and can reach even 1000°C. For the temperature range from –100°C up to 300°C, coatings based on carbon with solid lubricants and metal oxides, e.g., WC-WS2-DLC, TiCN-MoS2-Sb2O3-C, Al_2O_3-DLC-Au-MoS_2, are most often tested [**L. 8**]. The main adaptation mechanism in this temperature is the transformation of sp^3 carbon bonds into sp^2 and great tribological properties of solid lubricants MoS_2, WS_2, and oxides Sb_2O_3 and Al_2O_3. However, the high wear resistance of these coatings is mainly archived by ceramic matrices – WC, YSZ, TiCN, and Al_2O_3. If a higher service temperature is required, coatings like YSZ-Au, Mo_2N-Ag-MoS_2, CrN-Ag, and TiN-Ag [**L. 6**] with adaptation mechanism based on the diffusion of soft Ag and Au metals, the creation of metal oxides V_2O_5 and $Ag_2Mo_2O_7$ [**L. 9**] along with additional introduction of dichalkogenides could be used.

Many of tribological coatings are based on carbon materials, whose very good mechanical and tribological properties have been reported in the literature [**L. 10, 11**]. It is indicated that the low coefficient of friction and high wear resistance result from the creation of a thin layer with a graphite structure on the surface. This process of graphitization occurs as a result of the temperature increase, which depends on the coating type and starts at a temperature of 300–600°C, or due to a high pressure leading to threshold temperature in micro-regions. In the case of a-C coatings, the low friction coefficient is typical for high humidity, when the contacting surfaces are separated and there are no interactions of very strong dangling σ bonds and the creation of adhesive joints with other atoms is restricted [**L. 12**]. In a dry environment, at high temperatures, and in a vacuum, these σ bonds increase friction, and the coefficient of friction (CoF) reaches the value of 1 as well deteriorates wear resistance. Blocking the possibility of the undesirable interaction of σ bonds by hydrogen atoms is observed in the case of a-C:H hydrogenated coatings [**L. 13**]; whereas, MoS_x coatings exhibit good tribological properties at high temperatures and in a vacuum [**L. 14**]. The condition is to obtain a crystalline structure with typical planes with low shear strength between sulphur atoms. Amorphous coatings do not show low coefficients of friction with metals and ceramics, although they can locally crystallize on surfaces. An important factor for obtaining coatings with good tribological properties is the coating composition, i.e. the amount of molybdenum and sulphur atoms. The coatings with sulphur content below the stoichiometric composition are the best; therefore, the x parameter in MoS_x should be within the 1.8–2 range, while the minimum value cannot be less than 1.1. At room temperature and 40–60% humidity, the coefficient of friction of such coatings increases from 0.001–0.01, and the characteristic for a vacuum is up to 0.2. This is due to blocking the transfer of coating material to the surface of the tribological partner and the loss of friction between the S-S easy slip planes. Moreover, the low hardness and susceptibility to oxidation of MoS_x coatings results in that they are not suitable for friction nodes exploit in a humid environment at ambient temperature [**L. 15**]. The new idea is the deposition of a-C/MoS_2 nanocomposite coatings, which can exhibit good tribological properties at low and high temperatures due to the formation of graphite or MoS_2 sliding layers on the surface depending on the operating conditions of friction node.

The aim of this work is the analysis of mechanical and tribological properties of modern a-C/MoS_2 composite coatings at ambient and 300ºC temperatures and to analyse their ability to self-adaptation phenomena. The properties of such coatings were compared with a-C and MoS_2 single coatings.

MATERIALS AND RESEARCH METHODOLOGY

All tested coatings were deposited by magnetron sputtering in an industrial chamber (Leybold, Cologne, Germany) with 4 rectangular magnetrons 3"x17" and 3kW maximum power. The substrates were plates of X5CrNi18-10 austenitic stainless steel with a thickness of 0.5 mm and dimensions of 20x20 mm. The substrates prior to coating deposition were polished and ultrasonically washed in acetone and ethanol. The a-C carbon and MoS_2 molybdenum disulphide coatings were deposited in an argon atmosphere by sputtering carbon and MoS_2 targets, respectively. In a case of a-C/MoS_2 composite coating, four discs (two carbon and two MoS_2) were used simultaneously. The total coating thickness was 0.5 µm. The analysis of mechanical properties was made based on the results of nanoindentation tests, performed using a Nano-Hardness-Tester produced by CSM Instruments, Switzerland. The diamond indenter with Berkovich geometry was pressed with 2 and 5 mN maximum loads and 4 and 10 mN/min loading and unloading speeds, while the indentation curves were analysed using the Oliver-Pharr procedure [**L. 16**]. The penetration depths were up to 140 and 250 nm, so they were significantly greater than 10% of the coating thickness; hence, it should be assumed that the substrate affects the measurement results. However, the thickness of the coatings is comparable, and results can be used to compare the coatings' properties. Scratch tests on a Micro-Combi-Tester (CSM Instruments, Switzerland) were done to analyse the adhesion of coatings to steel substrates [**L. 17**]. The indenter was a Rockwell C diamond with of 200 µm tip radius, and tests were conducted with a continuously increasing normal load up to 30 N. Wear resistance at ambient and at 300°C temperatures was determined by conducting tribological tests on a high temperature tribometer T-21 (ITeE Radom). The counterbody Al_2O_3 ball with 6 mm diameter was loaded with F_N = 1 N normal force. The number of cycles, *n* = 20,000, with wear track radiusof *r* = 5 mm gave friction length *s* = 630 m. The volume of worn material, V, was determined by measuring the friction track profiles using a Profilm 3D non-contact profilometer (Filmmetrics, USA). The value of the wear index, WV, was determined from the following equation [**L. 18**]:

$$W_V = \frac{V}{F_N \cdot s} \left[\frac{\mathrm{mm}^3}{\mathrm{N \cdot m}}\right] \qquad (1)$$

For comparison with MoS_2 and a-C/MoS_2 coatings, the results for a-C coating, presented in the previous publication, were added [**L. 19**].

RESULTS OF MECHANICAL AND TRIBOLOGICAL TESTS

Analysis of a-C/MoS_2 composite coating microstructure indicated its amorphous character, which is typical for a-C carbon coatings. The presence of 6% MoS_2 in the coating was confirmed by the EDX technique (Energy Dispersive X-Ray Analysis). However, in the initial stage, coatings with MoS_2 content of up to 25% were tested, but the hardness of coatings and their wear resistance were decreasing with a rising amount of dichalcogenide. Similar phenomenon for a-C/MoS_2 coatings was presented in [**L. 20**]. That is why the properties of only one, the best nanocomposite coating, are presented. **Figure 1** shows the results of nanoindentation tests. The hardness of a-C and MoS_2 coatings is 17 and 3.5 GPa, respectively, while the composite coating with the predominant amount of carbon has a hardness of 16 GPa, and it is only slightly lower than for a-C. Assuming the rule-of-mixture, this value agrees well with the value calculated for a 6% share of the soft MoS_2 phase in the composite coating. Lower values of hardness for higher indentation loads indicates the effect of softer substrate on measured values. The hardness of substrate is 9 GPa; hence, similar values of hardness were determined at both loads for the MoS_2 coating. The values of elastic modulus are 180, 65, and 165 GPa for a-C, MoS_2, and a-C/MoS_2 coatings, respectively.

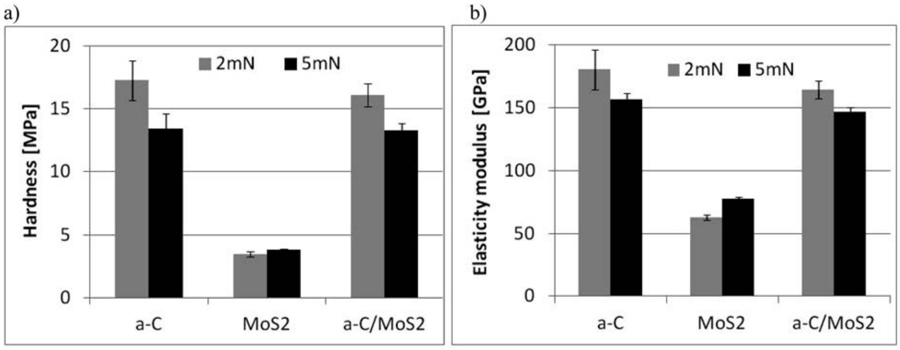

Fig. 1. Indentation test results: a) nanohardness, b) elasticity modulus

Rys 1. Wyniki testów indentacyjnych: a) nanotwardość, b) moduł sprężystości

The main application problem for carbon coatings is their poor adhesion to steel substrates, which was confirmed by scratch testing of the a-C coating. First adhesive cracks and the removal of coating fragments

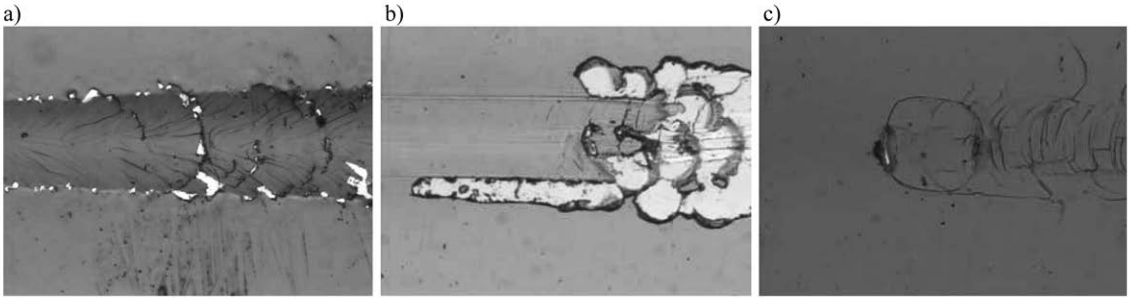

Fig. 2. Scratch track images of: a) a-C, b) MoS_2, c) a-C/MoS_2, coatings

Rys. 2. Obrazy torów zarysowania powłok: a) a-C, b) MoS_2, c) a-C/MoS_2

from the substrate were observed at 9.5 N load (**Fig. 2a**). As it was presented in many publications, the main reasons of this low adhesion are high residual stresses of carbon coatings and their low fracture toughness [**L. 21**]. The better scratch resistance with 16 N critical load (**Figure 2b**) was exhibited by the MoS_2 coating.

However, it should be emphasized that the failure character was catastrophic, because the removal of the coating was from the entire scratch width. However, for the composite coating, no adhesive cracks were created up to the maxim load of 30 N, but cohesive cracks were observed at 20 N (**Fig. 2c**).

The evolution of the friction coefficient in contact with Al_2O_3 balls for tests carried out at room temperature and 300°C is shown in **Figures 3**. At ambient temperature (**Fig. 3a**), the lowest coefficient of friction was exhibited by the a-C coating. In the initial period, up to about 7000 cycles, the coefficient of friction was 0.15 and then CoF dropped to 0.05 and remained constant until the end of the test. This is probably the result of creating a thin sliding graphite layer on the coating surface [**L. 22, 23**], known as graphitization phenomenon; whereas, for the MoS_2 coating, the coefficient of friction was the highest at 0.3–0.35. The intermediate coefficient of friction of 0.1–0.15 at ambient temperature characterized a-C/MoS_2 composite coating.

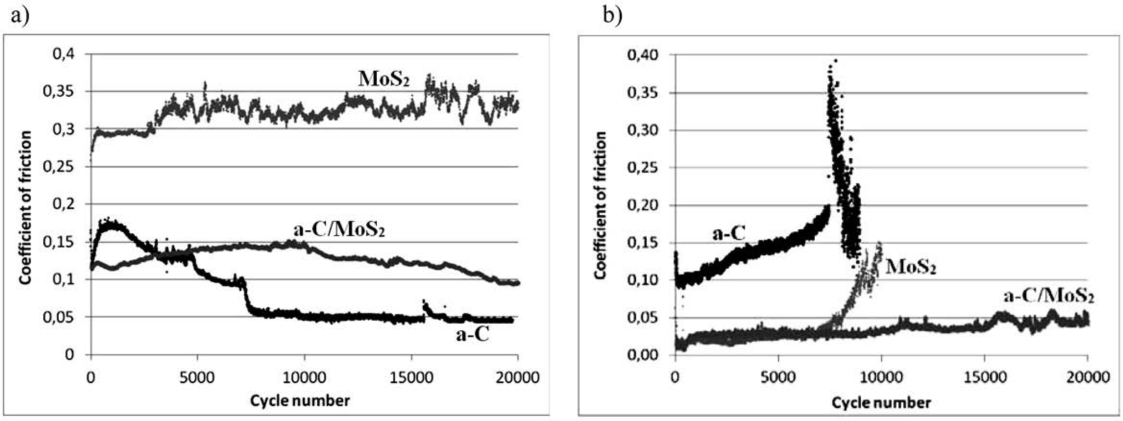

Fig. 3. Coefficient of friction evolution during tests performed at: a) 20°C, b) 300°C temperature

Rys. 3. Przebieg współczynnika tarcia badanych powłok podczas testów wykonanych w temperaturze: a) 20°C, b) 300°C

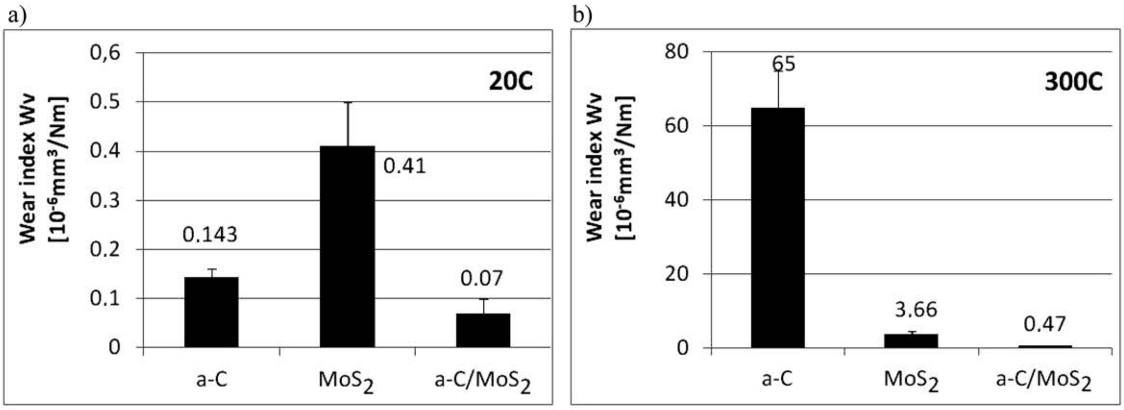

Fig. 4. Wear index of coatings at: a) 20°C, b) 300°C temperature

Rys. 4. Wartości wskaźnika zużycia objętościowego powłok przy temperaturze: a) 20°C, b) 300°C

Between tested coatings, the highest wear resistance was measured for the MoS_2 (**Fig. 4a**). However, despite the higher coefficient of friction of the composite than the carbon coating, it is characterized by the lowest wear index. Its value is $0.07 \cdot 10^{-6}$ mm^3/Nm is extremely low and indicates, similar to carbon coating, the formation of a thin sliding layer, that also confirms the decreasing coefficient of friction after 10,000 cycles of the test. Images of wear tracks showed that cracks did not occur in the coatings at room temperature and abrasive wear dominated with only fine grooves in the direction of ball motion (**Fig. 5**). For all coatings, the wear was so small that it did not led to substrate exposure, but it should be emphasized that, at room temperature and 50% humidity, the a-C and a-C/MoS_2 coatings have significantly better properties than the MoS_2 coating. An increase of temperature to 300°C led to a reverse situation and a lower coefficient of friction of 0.02–0.03 of the MoS_2 coating than a-C coating, for which CoF was growing from 0.1 to 0.2 along the test duration (**Fig. 3b**), while, both single coatings did not survive the whole number of cycles and were damaged after about 7000 cycles, which was particularly visible in wear track image of carbon coating (**Fig. 6a**). However, damage of MoS_2 coating did not cause such a drastic increase in friction, probably because of the remaining wear products in the friction zone that still protected against direct contact between the ceramic ball and substrate (**Fig. 6b**). High wear is a result of low hardness of this coating (**Fig. 1a**). However, the composite coating showed great tribological properties in these conditions. The coefficient of friction 0.02–0.05 was similar to MoS_2, but the high hardness of the composite coating derived from the dominant carbon phase significantly reduced its wear. Tribological tests were also performed at 400°C, but coatings in this condition were completely destroyed. In a view of the performed research program, the 300°C temperature seems to be a threshold because of the rapid graphitization of carbon coatings with high amount of sp^2 bonds, accompanied by a significant decrease of wear resistance.

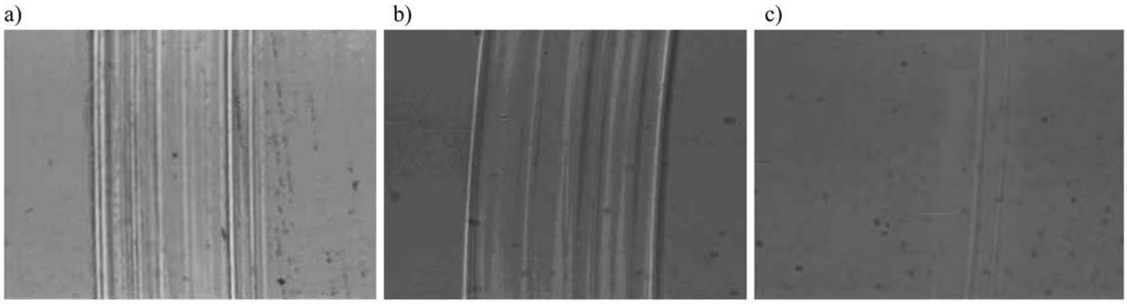

Fig. 5. Wear track images of coatings surfaces: a) a-C, b) MoS_2, c) a-C/MoS_2 after tests performed at 20°C temperature
Rys. 5. Obrazy powierzchni torów tarcia po testach tribologicznych wykonanych w temperaturze 20° powłok: a) a-C, b) MoS_2, c) a-C/MoS_2

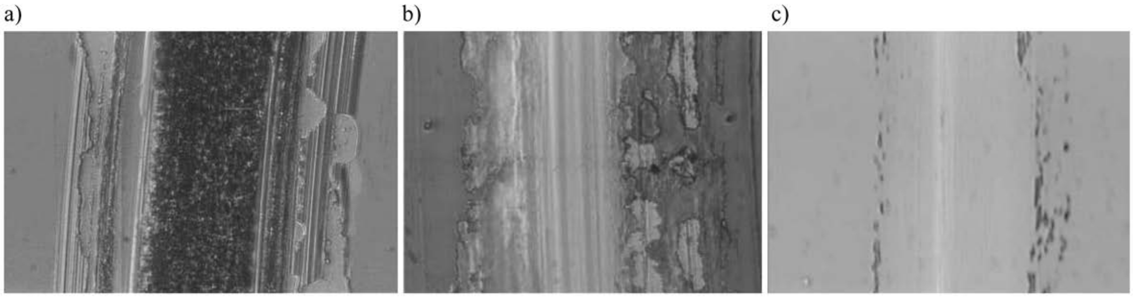

Fig. 6. Wear track images of coatings surfaces: a) a-C, b) MoS_2, c) a-C/MoS_2 after tests performed at 300°C temperature
Rys. 6. Obrazy powierzchni torów tarcia po testach tribologicznych wykonanych w temperaturze 300° powłok: a) a-C, b) MoS_2, c) a-C/MoS_2

CONCLUSIONS

Adaptive coatings, also called "chameleon coatings," are a new solution in surface engineering, which could be applied in various environmental conditions, i.e. temperature, humidity, pressure, and atmosphere. The analysis of mechanical and tribological tests presented in the paper showed that a-C/MoS_2 coatings exhibited an adaptive mechanism. They are characterized by the advantages of a-C and MoS_2 that such coatings have in suitable conditions. Hydrogen free a-C coatings have a low wear and friction coefficient at room temperature, while MoS_2 coatings have a low wear and friction coefficient at high temperatures. Carbon coatings are harder, and so they can carry higher loads, but their adhesion to steel substrates is worse. Whereas, the results of experimental tests confirmed that a-C/MoS_2 coatings are suitable for ambient and 300°C temperatures. Their hardness is similar to the a-C coating, but the adhesion to the substrate is significantly better than for both single coatings.

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