Marcin KOT[*], Łukasz MAJOR[**], Jurgen LACKNER[***], Kinga CHRONOWSKA-PRZYWARA[*]

TRIBOLOGICAL PROPERTIES OF TI/A-C:H NANOCOMPOSITE CARBON BASED COATINGS

WŁAŚCIWOŚCI TRIBOLOGICZNE NANOKOMPOZYTOWYCH POWŁOK WĘGLOWYCH TI/A-C:H

Key words:

carbon coatings, fracture resistance, friction, wear

Słowa kluczowe:

powłoki węglowe, odporność na pękanie, tarcie, zużycie

Abstract

The paper presents the results of mechanical and tribological tests of Ti/a-C:H nanocomposite carbon coatings and a-C:H hydrogenated carbon coating. All coatings were deposited by magnetron sputtering technique at various acetylene gas flows in a vacuum chamber, resulting in different coatings properties.

The conducted study determines hardness, elasticity modulus, fracture resistance, and tribological properties – wear and friction coefficient of deposited coatings. The lowest wear and coefficient of friction were exhibited

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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@imir.agh.edu.pl.

[**] Polish Academy of Sciences, Institute of Metallurgy and Materials Sciences, Reymonta 25, 30-059 Krakow, Poland.

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

coatings deposited at higher acetylene flows, 15-20 sccm. However, they are brittle and the critical load in scratch testing is several times smaller than in a case of softer coatings deposited at lower acetylene flow up to 10 sccm.

INTRODUCTION

Carbon coatings are of great interest in many branches of industry, and as tribological coatings, they have found many applications. By appropriate control of the deposition process, it is possible to obtain coatings with predetermine sp^2 (graphite) and sp^3 (diamond) bonds and suitable mechanical and tribological properties **[L. 1, 2]**. Depending on the sp^2/sp^3 bonds ratio and the presence of hydrogen (or nitrogen), carbon coatings can be divided into several groups like: a-C, ta-C or a-C:H with hardness varying within the 5 to 50GPa range **[L. 1, 3–5]**. Unfortunately, the worst disadvantage of all carbon coatings is their low fracture resistance. Hence, such coatings have to be deposited on hard surfaces that provide them adequate support and restrict the deformation of the whole coating-substrate system. Therefore, a lot of effort by research laboratories is focused on designing new types of carbon coatings that contain barriers to easy microcracks propagation but do not reduce their excellent tribological properties. One of the solutions may be a modern nc-MC/a-Mtr nanocomposite coating, where nc-MC means nanoparticles of transition metal carbides, i.e. Ti, Cr, W **[L. 4, 6]**, while a-Mtr amorphous carbon matrix a-C or a-C:H. Voevodin and others **[L. 7]** have postulated that the coatings exhibit optimal properties when the size of nanoparticles is 5-10 nm and a carbon matrix perfectly separates them. Moreover, the low thickness of carbon layers (1~2 nm) should lead to a significant improvement in the coating's fracture toughness. In such a material, the nanocracks that could appear in carbon matrix are too small to be able to propagate. Even if these nanocracks join into larger microcracks, the large amount of hard nanoparticles considerably increase the critical stress necessary for crack growth. Furthermore, the improvement of the fracture toughness of nanocomposite coatings could be obtain when the high strength of a nanoparticle-matrix interface is provided. Additionally, a large amount of nanoparticles for which the deformation cannot occur through the dislocation motion on slip planes, results in the high hardness of these coatings **[L. 8]**.

Within this study, the mechanical and tribological properties of Ti/a-C:H were analysed. The coatings' microstructures were changed by varying the reactive C_2H_2 gas flow rate through the vacuum chamber during deposition.

MATERIALS AND RESEARCH METHODOLOGY

Ti/a-C:H nanocomposite coatings and an a-C:H coating were deposited on X5CrNi18-10 austenitic stainless steel. Plates with a 1.5 mm thickness and dimensions of 20x20 mm were used as substrates. Coatings were deposited in an industrially scaled sputtering machine (Leybold, Cologne, Germany) equipped with 4 rectangular 3”x17” unbalanced magnetrons with -50V bias. Due to the low hardness of the substrate, multilayers of 4 μm thick Cr/CrN were deposited first on the steel as a coating that provides appropriate support for carbon coatings. The thicknesses of the successive layers t_{Cr}=83nm and t_{CrN}=167nm in multilayers were chosen based on previous studies of multilayer coatings with different periods and different thickness ratios of ceramic and metal layers **[L. 9]**. During the deposition of the nanocomposite coating, a mixture of C_2H_2 and Ar with pressure of $1 \cdot 10^{-3}$ mbar was used; however, the gas flow of acetylene, the source of carbon atoms, was changed within 1-20 sccm range. The titanium atoms were derived from sputtered a high purity titanium target. The thickness of all Ti/a-C:H nanocomposite coatings and a-C:H carbon coating was 1μm. Hardness and elasticity moduli of all coatings were determined by nanoindentation using a CSM Nanoindenter. A Berkovich geometry indenter at 2mN maximum load was used. Indentation curves were analysed according to the procedure given by Oliver-Pharr'a **[L. 10]**, recommended by ISO standard **[L. 11]**.

Fracture toughness studies were conducted by spherical indentation with a 20 μm indenter tip radius. The maximal load was selected to induce the crack formation in the coating, which was observed as a sudden increase of the penetration depth on indentation curves (pop-ins) **[L. 12]**. The compared parameter, as a measure of the coating’s fracture resistance, was load L_{FR} that caused the first crack event and corresponding penetration depth h_{FR}. The deformation behaviour and adhesion of carbon coatings to multilayers were determined by scratch testing **[L. 13]** with a standard Rockwell C 0.2 mm tip radius indenter. The tribological properties were analysed based on the test results carried out on ball-on-disc tribometer with Al_2O_3 6 mm diameter spheres. Test were performed within 20000 cycles with an r=5 mm track radius producing an s=630 m length wear track. Normal load F_N was 1 N, which corresponded (assuming the properties of the coating in calculations) to the initial pressure 0.3-0.4 GPa in the contact zone. The measured cross-sectional profiles of wear tracks allowed the determination of the W_V wear index, calculated from the following formula:

$$W_V = \frac{V}{F_N \cdot s} \; \left[\frac{mm^3}{N \cdot m}\right] \tag{1}$$

RESULTS OF MECHANICAL AND TRIBOLOGICAL TESTS

The hardness of nanocomposite coatings, measured by instrumented indentation, increased with the C_2H_2 gas flow from 6 GPa for Ti/a-C:H 1sccm up to 19 GPa for Ti/a-C:H 20 sccm (**Fig. 1**). However, the hardness of a-C:H

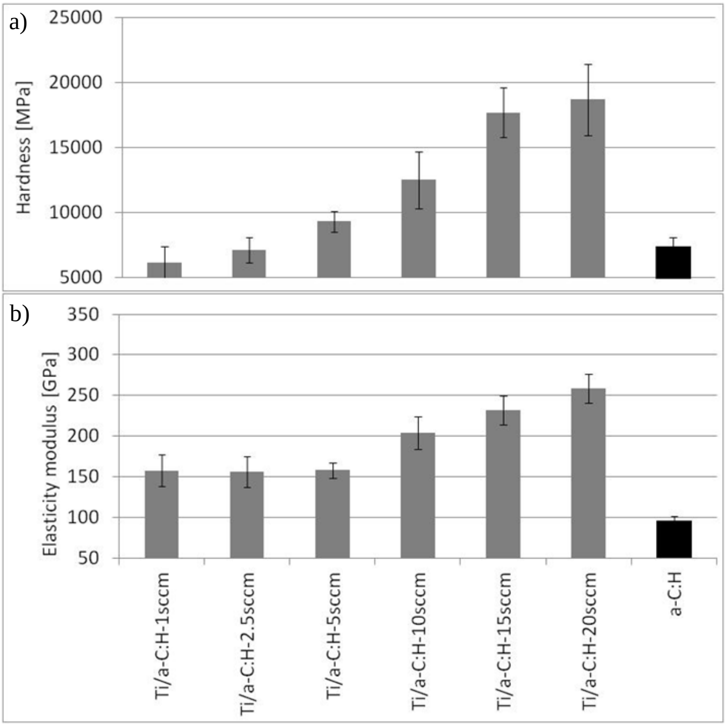

Fig. 1. Indentation test results of tested carbon coatings: a) hardness, b) elasticity modulus
Rys. 1. Wyniki testów indentacyjnych badanych powłok węglowych: a) twardość, b) moduł sprężystości

coating was 7.5 GPa. A similar correlation was found for the elasticity modulus that changed from 155 to 260 GPa. For all nanocomposite coatings, it was higher than E = 95 GPa measured for a-C:H. The spherical indentation tests showed the highest fracture resistance for the Ti/a-C:H 2.5 sccm coating for which first the crack appeared at a load of 800 mN. This value was four times greater than for the a-C:H coating (**Fig. 2**). It was found that nanocomposite coatings produced at a higher acetylene flow (10-20 sccm) did not exhibit an enhancement of fracture toughness despite their significantly different hardness and elasticity modulus than the a-C:H carbon coating. **Figure 3** shows the indent images of selected coatings after indentation with a 500 mN maximum load. The absence of cracks on the surface of Ti/a-C:H-2.5 sccm coating is clearly seen. For other coatings, this load led to a network of radial and circumferential cracks. Significant differences in failure modes of coatings deposited at low acetylene flow rates starting at 10 sccm and above this value were observed. Furthermore, coatings deposited at 1-10 sccm showed better adhesion to the substrate, which was proved by the complete absence of adhesion cracks up to 30 N maximum load used during the scratch tests

(**Fig. 4**). In contrast, large adhesive cracks were appeared at 4-5 N load for 15 and 20 sccm nanocomposite and a-C:H coatings. This may be due to their large residual stresses that results from the low adhesion of carbon coatings particularly to metallic substrates. This clear division into two groups of Ti/a-C:H coatings was also confirmed by the results of wear tests.

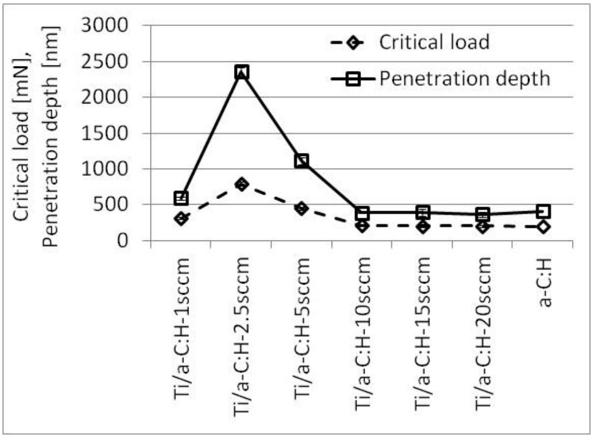

Fig. 2. Spherical indentation test results of carbon coatings
Rys. 2. Wyniki testów indentacji sferycznym wgłębnikiem badanych powłok

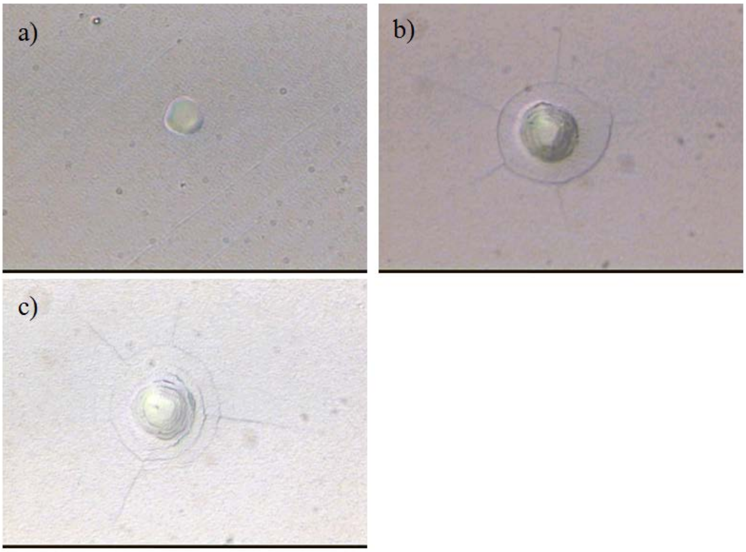

Fig. 3. Images of spherical indents performed at 500 mN on (a) Ti/a-C:H-2.5 sccm, (b) Ti/a-C:H-10 sccm, and (c) Ti/a-C:H-20 sccm coatings
Rys. 3. Obrazy odcisków po sferycznej indentacji z obciążeniem 500 mN powłoki: a) Ti/a-C:H-2,5 sccm, b) Ti/a-C:H-10 sccm, c) Ti/a-C:H-20 sccm

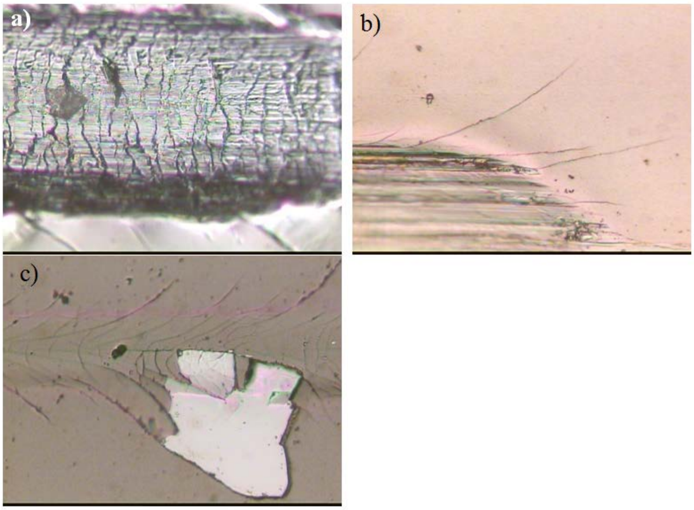

Fig. 4. Scratch track image on coatings, (a) Ti/a-C:H-1sccm-30N, (b) Ti/a-C:H-10sccm-30N, and (c) Ti/a-C:H-20sccm-5N

Rys. 4. Obrazy po teście zarysowania powłoki: a) Ti/a-C:H-1sccm-30N, b) Ti/a-C:H-10sccm-30N, c) Ti/a-C:H-20sccm-5N

Coatings deposited at 15 and 20 sccm had a wear index of $W_V=6 \cdot 10^{-6}$ mm^3/Nm, which was about 50% greater than coatings without the addition of titanium carbide nanoparticles (**Fig. 5**). Furthermore, the coefficient of friction of these nanocomposite coatings in contact with an Al_2O_3 ball was between 0.15 and 0.2 (**Fig. 6**). Whereas, for coatings deposited at low acetylene flows (1-10 sccm), wear was higher at $W_V=12\text{-}50 \cdot 10^{-6}$ mm^3/Nm and the coefficient of friction was also higher, reaching 0.8.

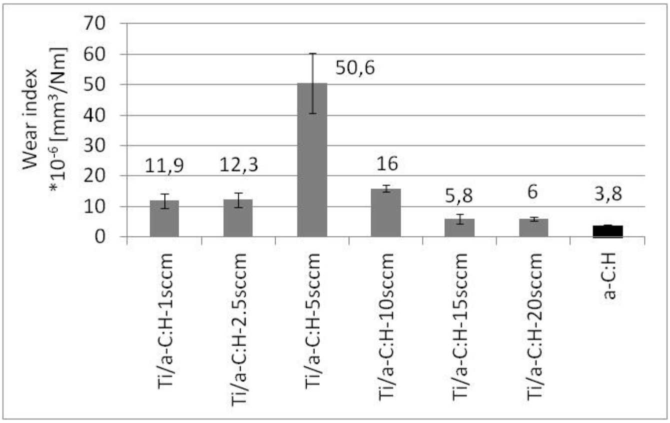

Fig. 5. Wear index of tested coatings

Rys. 5. Wskaźnik zużycia badanych powłok

ANALYSIS OF TEST RESULTS AND CONCLUSIONS

The conducted research program on Ti/a-C:H coatings and previously performed tests on Cr/a-C:H coatings presented in **[L. 6]** allowed us to describe the changes of a coating's mechanical properties as a function of the amount of the carbon atoms supplied to the vacuum chamber, and linking them with the coatings microstructure. **Figure 7** shows typical changes in hardness, wear resistance, and the friction coefficient as a function of the amount of metal in the coating's microstructure. At a low carbon content, coatings have a columnar structure similar of metallic coatings (**Fig. 7**, square (a)) – in this work Ti

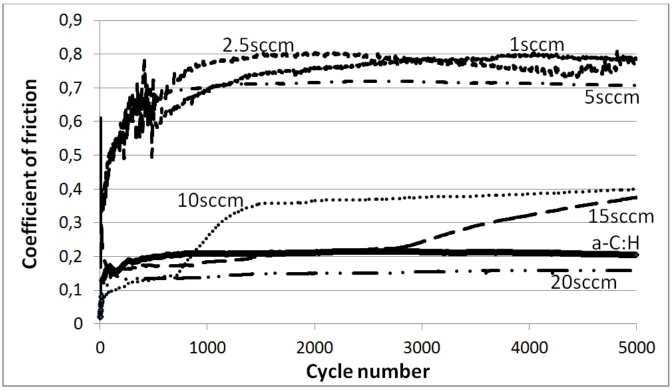

Fig. 6. Friction coefficient changes of tested carbon coatings during the tribological tests
Rys. 6. Zmiany współczynnika tarcia badanych powłok podczas testu tribologicznego

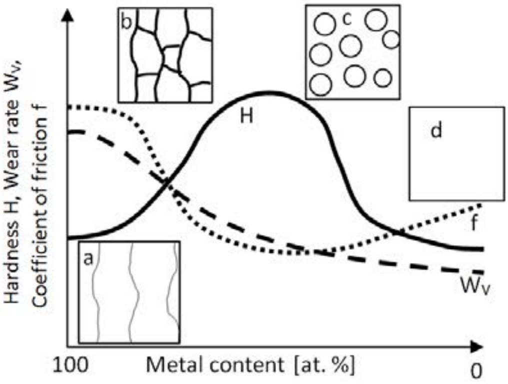

Fig. 7. Evolution of the coating's mechanical and tribological properties with changes the amount of metal in the microstructure
Rys. 7. Zmiany właściwości mechanicznych i tribologicznych powłok węglowych wraz ze zmianą udziału ilości metalu w strukturze powłoki

coatings. These coatings have a low hardness up to a few GPa, which leads to its plastic deformation at low contact stress, high wear caused by creation of adhesive joints, and a high friction coefficient. The rise in carbon content results from the formation of TiC ceramic coating with a higher hardness and wear resistance; however, it is more prone to fracture than metal layers or metal with ceramic inclusions (**Fig. 7**, square (b)).

A further increase in carbon changes the microstructure into a nanocomposite, where amorphous carbon plays a matrix role. Such coatings exhibit very low wear and a low coefficient of friction, which is a characteristic for carbon coatings (**Fig. 7**, square (c)). An even larger amount of carbon reduces the number of TiC nanoparticles in the coating, which deteriorates its fracture toughness and adhesion to metallic substrates (**Fig. 7**, square (d)). An interesting phenomenon is the significantly higher coefficient of friction of the nanocomposite coating, compared to carbon coatings. In the case of coatings with a large amount of carbon in the structure, under favourable conditions, the formation of a third body through the graphitization process occurs, as shown in the previous papers **[L. 6**, **14]**. However, the graphitization process was not observed for nanocomposite coatings with a large amount of nanoparticles. This can be explained by the presence of hard nanoparticles in the contact zone that effectively remove the thin graphite layer.

The results of the tested Ti/a-C:H nanocomposite coatings indicate a strong effect of acetylene flow on the mechanical and tribological properties of deposited coatings. It seems to be possible to deposit coatings with pre-planned properties. This allows the selection the appropriate coating, when the load character and level are known for a particular application.

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Streszczenie

W pracy przedstawiono wyniki badań mechanicznych i tribologicznych nanokompozytowych powłok węglowych Ti/a-C:H, które porównywano z właściwościami powłok węglowych a-C:H. Powłoki wytwarzano techniką magnetronowego rozpylania przy różnym przepływie acetylenu od 1 do 20 sccm przez komorę próżniową, co skutkowało różnymi właściwościami powłok. Przeprowadzone badania umożliwiły określenie twardości, modułu sprężystości, odporności na pękanie oraz właściwości tribologicznych – wskaźnika zużycia i współczynnika tarcia wytworzonych powłok. Najmniejszym zużyciem oraz najmniejszymi wartościami współczynnika tarcia charakteryzowały się powłoki wytworzone przy największych przepływach acetylenu 15–20 sccm. Natomiast są one kruche, a obciążenie krytyczne określone w teście zarysowania jest kilkukrotnie mniejsze niż dla miększych powłok osadzanych przy przepływie acetylenu do 10 sccm.