Effect Of SiC Ceramic Nanoparticles on Mechanical Properties of Nanocomposite SiC/a-C:H Coatings

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Abstract
The paper presents the results of the mechanical and tribological properties of hydrogenated amorphous carbon coating a-C:H and coatings, where SiC ceramic nanoparticles were introduced into a-C:H matrix. Coatings were deposited by magnetron sputtering and the ratio of nanoparticles in the matrix was varied by changing the acetylene flow in the vacuum chamber within the 5-20 sccm range. Results of indentation tests, scratches and wear tests of tested systems allowed to optimize the deposition process.

Keywords: scratch test, coating, friction, wear, cracking.

1 Introduction
The rapid development of PVD and CVD vacuum methods of coatings deposition has enabled their applications in almost all branches of industry. One of the most commonly used coatings are coatings called diamond-like carbon (DLC). They are used on surfaces of cutting tools, moving machine parts, components, artificial joint prostheses and as anti-reflective layers in optics and photovoltaic cells. DLC coatings contain a mixture of carbon atoms of different bonds hybridization sp³, sp² and sp¹ (Voevodin A.A., Zabinski J.S., 2005; Dobrzański L.A., Dobrzańska-Dnikiewicz A.D, 2011; Gilewocz A., Warcholiński B., 2010). The mechanical properties of carbon coatings are depend mainly on the ratio of sp³ to sp² bonds, characteristic for diamond and graphite respectively. Coatings with dominating sp³ bonds have a high hardness 40-100 GPa, but they are prone to brittle fracture and have a poor adhesion to metal substrates as a result of high residual stress, up to several GPa (Roberson J., 2002; Escudeiro A., Polcar T., Cavaleiro A., 2013). Whereas, the increasing amount of sp² bonds cause its softening, but the graphite on the surface can significantly reduce friction coefficient. If during carbon
coatings deposition hydrogen is introduced, the coatings becomes less brittle. Further improvement of fracture toughness and adhesion of coatings could be obtained by introduction of hard ceramic particles like metal e.g. Ti, Si, N, W carbides or nitrides. Suitable coatings composition and nanoparticles amount can significantly modify the properties of coatings (Escudeiro A., Polcar T., Cavaleiro A., 2013; Martinez-Martinez Z., et al., 2008; Bharathy P., Vijai, et al., 2010; Dąbrowski, M., et al., 2009). The hardness of such nanocomposite coatings may reach a value of 50 GPa (Voevodin A.A., Zabinski J.S., 2005), while for a-C:H hydrogenated carbon matrix coating this parameter is typically in the range of 10-30 GPa (Dobrzanowski L.A., Dobrzanska- Danikiewicz A.D, 2011; Gilewocz A., Warcholinski B., 2010). The enhancement of mechanical properties of nanocomposite coatings are observed only for optimum amount of nanoparticles in the microstructure. The size of nanoparticles should be 3 to 10 nm and the distance between them should not be longer than 1-3 nm (Voevodin A.A., J.S. Zabinski, 2000; Lukaszkowicz K., 2012) (Fig. 1). If the amount of nanoparticle is too large they can form aggregates prone to fracture and spallation. On the other side little share of hard particles will not improve wear resistance of coatings. This crucial amount of particles in the carbon matrix is usually controlled by controlling the hydrocarbon gas flow being the source of carbon and hydrogen atoms (e.g., C₂H₂) in a chamber. However, due to the complexity of coating deposition process it is difficult to quantitatively predict their microstructure, thus coating optimization is carried out based on the results of appropriate tests.

Within this work the mechanical and tribological properties of SiC/a-C:H coatings were analysed in order of find the optimal parameters of the deposition process.
2 Experimental part

Tests were performed on single a-C:H coatings and SiC/a-C:H nanocomposite coatings, all 1μm thick. Coatings were deposited by magnetron sputtering with an additional pulsed laser at 5, 10, 15 and 20 sccm (standard cubic centimetre) reactive gas flow - acetylene C₂H₂ in a vacuum chamber. Coatings were deposited on austenitic stainless steel AISI 304 substrate. For all tested coating-substrate systems hardness and elasticity modulus was determined by nanoindentation experiments using CSM Instrument equipment. The Berkovich geometry diamond indenter (Kot M., Lacki P., 2012; Chronowska-Przywara K., Kot M., Zimowski S., 2014) and two 2 and 5 mN maximum loads were applied. Indentation curves were analyzed according the ISO standard (ISO 14577-1; Chronowska-Przywara K., Kot M., Zimowski S., 2014) and Oliver-Pharr method. Scratch testing allow to determine the deformation and fracture resistance of coated surfaces (EN 1071-3; Chronowska-Przywara K., Kot M., Zimowski S., 2014). Rockwell C indenter with 0.2 mm tip radius was pressed into the surface under linearly increasing load from 0.01 to 30 N. Microscopic analysis of scratch tracks and acoustic emission signal allow to find the characteristic forms of failure. Hereby, critical loads L<sub>C1</sub> and L<sub>C2</sub> corresponding to the first cohesion and adhesion cracks of the coating (Bull S.J., Beresetegui E.G., 2006) were designated. Studies of tribological properties were carried out based on ball-on-disc test results (ISO 20808:2004; Kot M., et. al., 2014; Chronowska-Przywara K. et. al., 2014; Holmberg K., Matthews A., 2009) using 6 mm diameter Al₂O₃ ball at 1N normal load, 0.03 m/s linear speed and 20000 cycles that gives 750 m wear track length. The wear track profiles were measured with a contact profilometer at 4 points at 90° on the circumference of the ring (Fig. 2).

The profiles allow to calculate the volume of removed material V, and further a wear index Wᵥ according to equation (1):

\[
Wᵥ = \frac{V}{Fᵥ \cdot s} \left[ \frac{mm^3}{N \cdot m} \right]
\]

(1)

![Fig. 2. Scheme of the measurement of wear track profiles](image-url)
3 Test results

Fig. 3 shows the results of indentation tests, where higher hardness of nanocomposite SiC/a-C:H coatings than hydrogenated carbon a-C:H coating is clearly seen. Coatings deposited at 15 and 20 sccm acetylene gas flow exhibit the highest hardness 16-19 GPa, compared to 7 GPa for a-C:H. Rise of C_2H_2 gas flow leads to a significant hardness rise of nanocomposite coatings. This is due to the increasing amount of SiC hard carbide particles. The increase in hardness is accompanied by a relatively low rise of elasticity modulus from 150 to 175 GPa. The unreinforced a-C:H coating has this parameter almost two times lower 95 GPa (Fig. 3b).

![Fig. 3. Results of indentation tests: a) hardness, b) elasticity modulus](image)

The results of scratch tests enable to compare the load values leading to coating fracture and to evaluate the strength of coating-substrate interface and the summary of results are given in Fig. 4a and 4b. The first cohesive crack in a case of coating deposited at 5sccm gas flow was observed under 0.3 N load. For other coatings LC1 parameter was in a range of 0.6-0.7 N. This is likely the result of high amount of ceramic nanoparticles in 5sccm coating, which are not separated by carbon matrix what facilitates crack formation and propagation. The adhesive failure (LC2 load) appeared as a shell shape cracks when load reached 2.5-5.5 N (Fig. 5a, c, d). Contrary to other coating the best adhesion to the substrate indicates coating produced at 10 sccm gas flow (Fig. 5b) for which no adhesive cracks and coating removal were observed even at maximum applied load 30N. Further increase of gas flow to 15 i 20 sccm leads to significant deterioration of coatings adhesion. So what could be the reason of better adhesion coating deposited at 10 sccm gas flow? Authors explain it by higher stiffness and hardness and hence lower fracture resistance 15 and 20 sccm coatings. The cause may also lie in probably smaller residual stresses, which add to the contact stress derive from
external loading by indenter leads to exceeding the strength of coating-substrate interface. However this hypothesis requires additional testing to confirm it.

Fig. 4. Critical loads: a) cohesive cracks $L_{C1}$, b) adhesive cracks $L_{C2}$.

Fig. 5. Images of a scratch cracks at $L_{C2}$ critical load: a) 2.5N - 5sccm coating, b) 30 N - 10sccm coating, c) 5 N - 15sccm coating, d) 4 N - 20sccm coating

Tribological test results as wear index (equation 1) for nanocomposite coatings are shown in Fig. 6. Among the tested coatings the worst was a coating with the smallest amount of carbon phase deposited at 5sccm gas flow. It has been completely removed after 12,000 cycles (Fig. 7a). Wear index of the rest coatings produced at a higher 10-20 sccm acetylene flow was at the range 11÷17•10$^6$
[mm$^3$/Nm] similar to a value corresponding to carbon coating. For all nanocomposite coating the abrasive wear mechanism was dominating (Fig. 7a-d), what was confirmed by the regular profiles of wear tracks. However, in the case of a-C:H carbon coating the network of small cracks and small area spallations on the surface were visible (Fig. 7e). Despite the similar wear resistance to a-C:H coating, the nanocomposite ones are characterized by higher values of friction coefficient 0,6-0,9 while for a-C:H $\mu = 0.15$.

Fig. 6. Wear index of tested coating-substrate systems

Additionally the characteristic decrease of friction coefficient with increasing fraction of carbon phase was found, thus with the increase of the reactive gas flow. The results may indicate that highly expected graphitization phenomenon
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(Holmberg K., Matthews A., 2009; Liu Y., Erdemir A., Meletis E.I., 1996) observed for carbon coatings did not appear on the surface of carbon based nanocomposite coatings. This may be due to the presence of hard ceramic particles on the surface which remains in the friction zone and removes thin graphite layer.

4 Summary

Carbon based nanocomposite coatings with SiC nanoparticles strongly change their mechanical and tribological properties with the change of carbon and ceramic nanograins share. This composition varied and can be controlled by changing the amount of \( \text{C}_2\text{H}_2 \) (or other hydrocarbon) gas flow through the vacuum chamber during the deposition. The performed tests have shown that optimum properties exhibited coating deposited at 10 sccm gas flow. Despite the intermediate hardness \( H = 13 \text{ GPa} \), it has a comparable to harder coatings produced at 15 and 20 sccm gas flow rate, wear resistance. Whereas its the greatest advantage is significantly better fracture resistance and adhesion to steel substrate. However, still the higher friction of nanocomposite coatings remains a problem to solve. Further planned studies will be conduct to reduce the friction coefficient of SiC/a-C:H coatings with maintaining or further reduced wear rate. Authors expected that deposition of outermost thin a:C:H carbon layer on the surface of SiC/a-C:H will improve the tribological properties and underneath nanocomposite coating will provide a sufficient load bearing capacity and high wear resistance.

Acknowledgements

The authors would like to thanks Dr. habil. Jurgen Lackner from Joanneum Research Forschungsge. mbH, Institute for Surface Technologies and Photonics, Functional Surfaces, Niklasdorf, Austria for coatings deposition

References


Dąbrowski, M., et al., 2009, Powłoki (Cr, Si) N/Tin na płytach z węglików spiekanych. Elektronika: konstrukcje, technologie, zastosowania, 50.1 pp. 66-68.

EN 1071-3: Advanced technical ceramics – Methods of test for ceramic coatings – Part 3: Determination of adhesion and other mechanical failure modes by a scratch test.


ISO 20808:2004. Fine ceramics (advanced ceramics, advanced technical ceramics) - Determination of friction and wear characteristics of monolithic ceramics by ball-on-disc method.


Martinez-Martinez Z., wt.al., 2008, Comparative performance of nanocomposite coating of TiC or TiN dispersed in aC matrixes, Surface and Coatings Technology, 203.5 pp. 756-760.


