THE INFLUENCE OF N2 AND Si ON PROPERTIES OF WC/C COATINGS DEPOSITED BY DC MAGNETRON SPUTERING TECHNIQUE

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Summary. In this article, various coating properties (thickness, COF, hardness) of WC/C layer deposited on steel and Si based substrate material by process of direct current magnetron sputtering (DC MS) without reactive gas as well as with employed reactive gases (N_2 and SiH_4+N_2) were investigated.

Keywords: WC/C coating; DC magnetron sputtering; properties; COF

1. INTRODUCTION

WC/C is a attractive material for industrial applications of thin hard layers because it has excellent properties, such as high hardness, Young´s modulus, corrosion resistance, and low coefficient of friction (COF). WC/C films are deposited using chemical vapor deposition (CVD) [1–7] and physical vapor deposition (PVD) techniques [8–14]. Plasma enhanced CVD of tungsten hexacarbonyl has been used for deposition of WC-C layers at lower deposition temperatures than those used in CVD techniques [2-7].)

Abad et al [8] obtained in WC/a-C coating, a maximum hardness, thickness and COF of 40 GPa, 2 μm and 0.8, respectively. Mrabet et al [9] obtained in WC/C coating a maximum hardness and COF of 35 GPa and 0.83, respectively. Shengguo Zhou et al. [10] evaluated nc-WC coating with C=75% and employed technical parameters within experimental process are listed in Tab. 1. Used temperature of deposition was not mentioned in their paper. Following properties of investigation were considered: coating thickness, hardness and COF, see Tab. 1. Kosinskiy et al. [11] investigated WC/C coating and the measured values were H=6.9GPa and E=212GPa. Novák et al. [12] studied nanohardness of DC magnetron sputtered W–C layers as a function of composition and residual stresses. Maximum measured values were as follows: H=19.5GPa and E=192GPa. Agudelo-Morimitsu et al. [13,14] evaluated WC/C coatings deposited at temperatures from room temperature (RT) to 300°C. Following values were obtained, for the parameters of interest: COF=0.35-0.75, H=16-29GPa, E=256-448Gpa.

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The aim of this work is to study of the influence of N_2 and N_2+SiH_4 on thickness as well as selected properties (indentation hardness and COF) of WC/C coatings deposited by DC magnetron sputtering technique. Obtained results were compared with the values reported by the above mentioned authors.

Table 1 Selected technological parameters of WC/C coatings and their measured values, based on literature survey.

Ref.	Pressure [Pa]	Bias [-V]	Temperature [°C]	Substrate material	Thickness [μm]	Hardness [GPa]	COF
[10]	10^{-3}	300	-	stainless steel	2.1	24	0.12
[11]	0.85	0	298K	90MnCrV8 steel	0.4	6.9	0.2-0.3
[12]	0.25	-	-	-	0.6	16-19.5	-
[13]	-	-	RT, 100, 200, 300	AISI 316	up to 0.9	-	-
[14]	-	-			up to 0.9	16-29	0.35-0.75

2. EXPERIMENTAL SETUP

Medium carbon steel C45 (chemical composition: C=0.42-0.50%, Si max.0.40%, Mn=0.50-0.80%, Cr max. 0.40%, Mo max. 0.10%, Ni max. 0.40%, P max. 0.035%, S max. 0.35%) was used as a substrate material for coating deposition. Experimental samples were cut from workpiece material (bar with diameter of 25 mm) using wire electro discharge machining (WEDM) technology. Functional surfaces were mechanically grinded to thickness of 3 mm. After that the substrates were hardened (in oil) at temperature of 890°C and then annealed (200°C). Substrates were polished with diamond paste to roughness $R_a \approx 12$ nm. Prior to deposition, the substrates were electrosonically cleaned in acetone for 10 minutes and then dried with an electric hair dryer for 5 minutes. An argon ion discahrge is used to sputter clean the substrate surface (for the duration of 10 minutes). Coatings were deposited on Si substrate to evaluate and measure their thickness.

DC magnetron sputtering (MS) technique was applied for coatings deposition. One set of the test samples was deposited without reactive gas (only sputtering gas Ar was employed). Second batch of the samples was deposited using reactive gas N_2, third one with the mixture of gases N_2+SiH_4. The amount of silane contained in the reactive gas represetns value of 1.5 %. The ratio between a sputtering gas (Ar) and reactive gas (N_2 and N_2+SiH_4, respectively) is 1:1, while keeping the pressure inside vacuum chamber constant during the process of deposition. Stoichiometric WC target (97 %, 90 mm in diameter) was used for the deposition process. Target-to-substrate distance was kept constant on value of 100 mm. The molecules from the target were ionized in Ar (99.999% purity) glow discharge and accelerated toward the substrate with the negative substrate bias voltage 300 V. Other parameters of deposition were as follows: power on target 175 W (350 V, 0.5 A), current density 2.75 W/cm^2, chemical composition of target – WC, current on the target coil 1.5 A, pressure inside vacuum chamber was 0.2 Pa; DC current was about 0.03 A and deposition time was 90 min. The temperature was varied between 400 and 500°C.

Thickness and microstructure of deposited coatings under consideration was investigated by SEM microscope JOEL 7000F with the EDX analyser unit.

Hardness measurements of PVD coated layers was perfomed with nanoindentation device NHT with Berkovich tip (CMT Instruments, Switzerland). Sinus testing mode (15 Hz) with aplitude of 1 mN and load ranging from 20 to 60 mN, depending on the coating thinkness was applied in the process of nanoindentation.

The coefficient of friction (COF) was obtained in ball-on-disc testing using HTT tribometer (CSM Instruments, Switzerland). Following experimental process conditions were applied: normal load 0.5 N, air temperature 23 °C, sliding speed of 10 cm/s, the radius of the wear tracks on the discs (5 mm) and the sliding distance (50 m) were kept constant during all ball – on – disc experiments,. Deposited substrates under research consideration were worn against bearing steel ball (100Cr6) with diameter of 6 mm. The evaluation of the ball wear is not the focus of this article´s research.

3. RESULTS AND DISCUSSION

Influence of various reactive gases on mechanical and tribological properties of WC/C deposited layers was examined and the results outlined are presented in the text below. All the technological conditions during deposition of WC/C coatings by employing various mixture of gases (no reactive gas, N_2 and N_2+SiH_4) were kept as a constant. During the experiments, Ar was used as a sputtering gas.

3.1. Evaluation of the coating properties deposited without using reactive gas

Obtained coating thickness was 1.5 μm (Fig. 1), which is significantly less than in literature [8,10], but 3 to 4 times higher than in literature [11,12] and about 60 % more in comparison with [13,14]. The coating surface layer features amorphous structure and its cross-section view indicates columnar structure. The differences between the measured coating thickness and the above mentioned values are mainly due to the pressure and temperature in the vacuum chamber during the process of deposition as shown in Table 1. Another influencing parameter may be the distance between substrate surface and target surface in the magnetron as well as deposition temperature, which was about 100 °C higher than ones employed in the above mentioned literature sources.

Measured hardness values were found to be in the range from 30.1 GPa to 32.0 GPa. These values are in accordance with results published in literature [14], where max. hardness was 29 GPa. On the other hand, this value is about 50 and 30 % higher when comparing to literature [10] and [12], respectively. The coefficient of friction was equal to 0.63±0.1, which is 20 % less in comparison to [8, 9], but about 50 % more than in literature [11]. It can be also concluded, that variances between measured values of the hardness and COF in comparison to those presented in the above mentioned literature sources is due to the divergences of the technological parameters employed in the process of WC/C deposition.

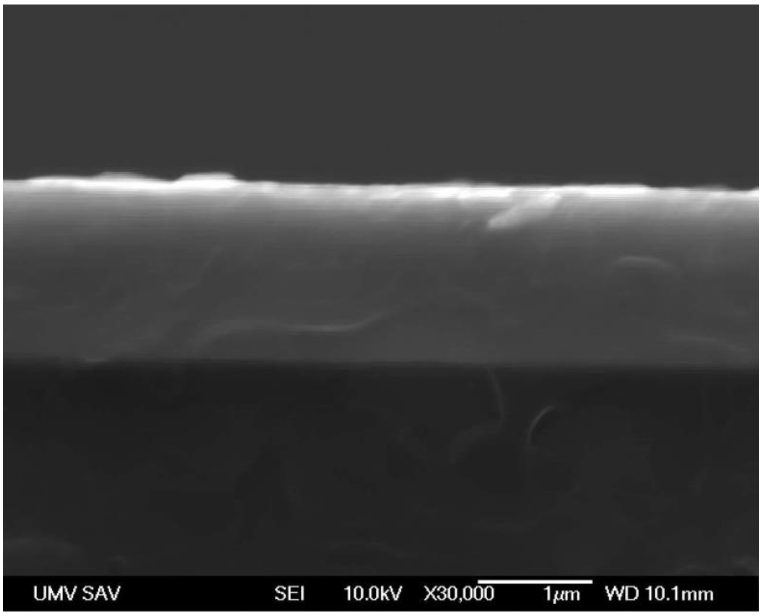

Figure 1 Cross-section view of WC/C coating deposited without reactive gas, measured thickness 1.5 μm

3.2. Influence of the reactive gas on mechanical and tribological properties of the WC/C deposited layers

In the experiment, as first, the effect of reactive gas N_2 was investigated. Deposited layer thickness was significantly reduced to the value of 1.0 μm (Fig. 2). Measured value of the coating hardness in a case of N_2 reactive gas was equal to 16.0±1.2 GPa. The COF parameter was measured after the total sliding distance in accordance with experimental setup (50 m). Obtained value of the COF was 0.26. Compared to deposition without reactive gas, reduction of friction coefficient by over more than 60% was observed using nitrogen reactive gas.

After deposition of WC/C layer with a use of the reactive gas mixture N_2+SiH_4 the measured coating thickness was equal to 0.9 μm (Fig. 3), so it was approximately the same as coating thickness deposited without the use of Si. On the other hand, obtained coating hardness was significantly higher and measured value was equal to 26 ± 1.0 GPa. There is no significant difference in a case of COF**,** where the measured value was equal to 0.26. Moreover, it can be concluded, that nitrogen N_2 (alone as well as with Si) dramatically reduce the value of the COF. However, gas mixture SiH_4 reduces coating hardness. It should be emphasized, that the gas mixture contains only 1.5% SiH4 (silane), because the silane itself is explosive. Therefore, in the process of WC/C coating deposition a mixture of nitrogen containing about 1.5 % of silane is used.

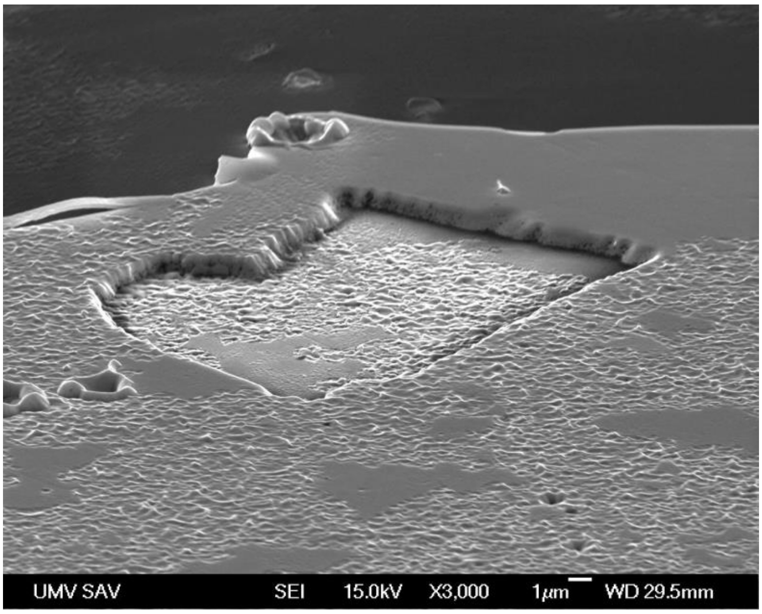

Figure 2 Cross-section view of WC/C coating deposited with N_2, thickness 1.0 μm

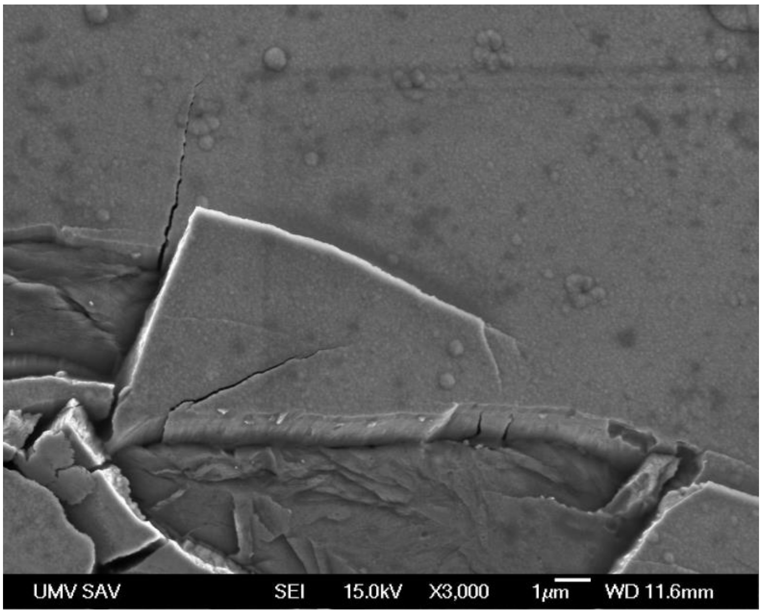

Figure 3 Cross-section view of WC/C coating deposited with N_2+SiH_4, thickness 0.9 μm

4. CONCLUSIONS

Using predetermined technological parameters, WC/C layer, deposited by DC magnetron sputtering was investigated. Properties such as deposited layer thickness, hardness and COF were evaluated. The effect of reactive gases in the process of deposition on the mechanical, tribological properties of the coatings was investigated within the proposed research. Based on experimental research, following conclusions can be drawn:

- coating parameters such as thickness of 1.5 μm, hardness of 31.6±0.5 GPa and COF of 0.63±0.1were obtained during the evaluation of WC/C layer deposited without using reactive gas
- reactive gases like N_2 and N_2+SiH_4 significantly decrease coating hardness, its thickness and COF in comparison to WC/C coating deposited without reactive gases,
- the nanoindentation test results show that N_2 decreases the value of coating hardness to 16.0±1.2 GPa and gas mixture N_2+SiH_4 to value of 26±1.0 GPa.
- it was also found that reactive gases decrease layer thickness, N_2 decreases coating thickness to value of 1.0 μm and N_2+SiH_4 to 0.9 μm.
- moreover, the COF was found to be lower when using reactive gases N_2 and N_2+SiH_4 (measured values 0.26 and 0.27, respectively) compared with COF of the deposited layer without using reactive gas (measured value 0.63)

Acknowledgement

The work presented in this paper was financially supported by the Slovak Grant Agency under the grant VEGA No 1/0432/17: The research of nanocomposite hard coatings to improve the functional properties of engineering parts and APVV-16-0359: The utilization of innovative technology for repair functional surfaces of mold casting dies for castings in automotive industry. Moreover, authors wish to thank Faculty of Mechanical Engineering of TU in Kosice for the material and financial support within the project "Development of the intelligent monitoring system for zero defect production"

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