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Preparation and characterisation of a-C and a-C:H coatings deposited by pulsed magnetron sputtering

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ABSTRACT

The amorphous carbon coatings of a-C and a-C:H type were deposited by pulsed magnetron sputtering in argon and argon/acetylene atmosphere, respectively. The deposition rate, chemical composition, structure and mechanical properties of these coatings were studied as a function of acetylene flow rate. The adding of acetylene to working atmosphere caused increase of deposition rate and hydrogen content in coatings, and at the same time decrease in their hardness. The friction and wear behaviour of a-C and a-C:H coatings in ambient air are highly dependent on kind of counterparts material. The "true" friction coefficients of a-C and a-C:H coatings sliding against a-C and a-C:H coatings, respectively, are similar in values (0.06–0.08) and wear rates are similar too. Significantly higher friction coefficients (0.2–0.3) and wear rates were observed for both a-C and a-C:H coatings sliding against 100Cr6 steel. The lowest friction coefficients (0.02–0.04) and wear rates were obtained for a-C and a-C:H coatings sliding against Alumina counterpart.

1. Introduction

Carbon-based a-C and a-C:H coatings, often commonly called as DLC (Diamond-Like Carbon) coatings, due to their low friction coefficient and high wear resistance are more and more often used for tribological applications, especially under conditions of dry friction. Over recent years many investigations were focused on a friction mechanism affected by DLC coatings, hydrogenated [1–7] as well as hydrogen-free ones [3,5]. Generally, the friction mechanism of DLC coatings is conditioned by the processes of graphitization and oxidation, which resulted in forming the transfer layer and wear debris on sliding surfaces. However chemical composition of these transfer layers can be different, especially when steel counterpart is used. Some investigations show that this transfer layer is composed mainly of the graphite-like materials [1,4,6,7] but other ones, that it is composed mainly of the oxides of steel counterpart [2,3,5,7].

Magnetron sputtering is one of the most often used deposition technique of DLC coatings [8–18]. The magnetron sputtering technique, especially in pulsed mode, offers a lot of advantages (process stability, precise control) however, the deposition rate for a-C coatings using this technique is low, due to low effectiveness of graphite sputtering, which is mostly used for making the target. The deposition rate could be significantly increased by applying the carbon-carrying gas to the working atmosphere and additionally making use of the process of carbon deposition on the substrate in the form of CH radicals produced by the decomposition of this gas in magnetron discharge plasma. However, the application of such the gas simultaneously results in introducing the hydrogen into the coating, which may significantly affect its properties, especially tribological ones [19–25]. If the hydrogen concentration is high, the coefficient of dry friction at the frictional contacts with such coatings could achieve the values below 0.005 in the inert environment, e.g. nitrogen or vacuum, which was named superlow-friction [20] or superlubricity [21]. Furthermore, a phenomenon of hydrogen release leads to self-lubrication, and which results in significant reduction of friction forces [20,22]. This phenomenon, for nitrided steel subjected to hydrogenation, which led to the gasostatic micro-bearing of the roughness and in the end to the self-lubrication, was described earlier [26]. However, the occurrence of hydrogen in a zone of friction between a DLC coating and steel could have a very negative effect on the properties of such the contacts respecting the possibility of occurring a so-called hydrogen wear of steel described by several authors [27,28]. This phenomenon consists in a gradual degradation of the surface layer due to the adsorption of hydrogen on the steel surface and then its diffusion in the depths of steel. It resulted in the formation of the brittle cracks in the micro-areas of the surface layer of steel, which leads to its failure under the influence of forces generated during friction. The tribological properties of frictional contacts with DLC coatings working under the conditions of dry friction are strongly affected by the working atmosphere [29–33] and the material type of counterparts [34–36], often not allowed for in analyses. Especially for the frictional contacts of DLC coatings with steel, the possible unfavourable interaction of carbon with iron through its diffusion into the steel counterpart, like in case of diamond tools undergoing the rapid degradation during machining of the steel, should be taken into consideration.

The purpose of the present study was to investigate the effects of the acetylene added to the working atmosphere during the deposition of amorphous carbon coatings by the pulsed magnetron sputtering on their deposition rate, chemical composition, structure and mechanical

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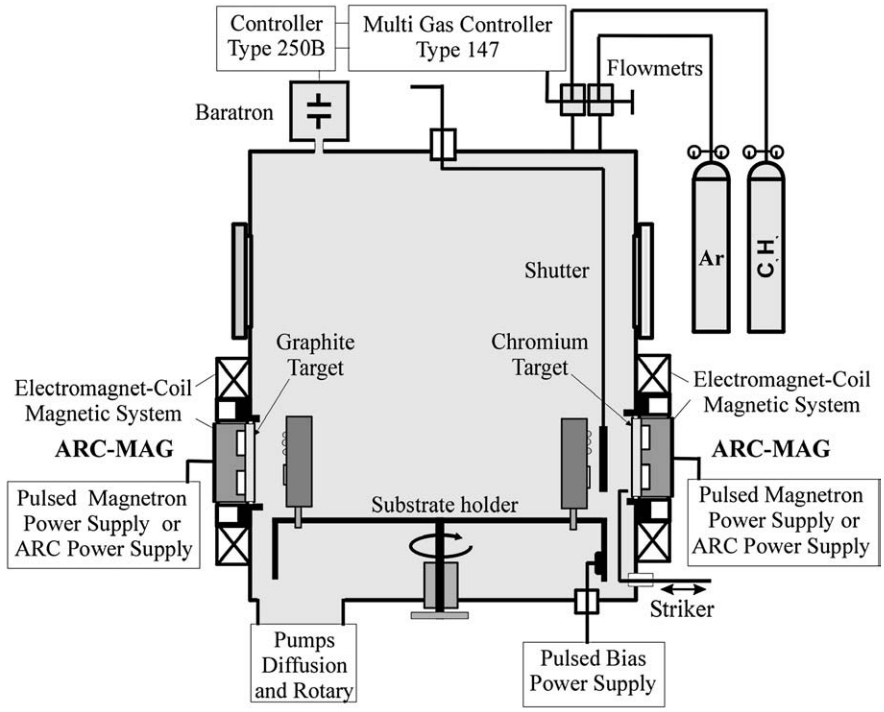

Fig. 1. Deposition system.

properties. To obtain the high adhesion of coatings, which may significantly affect the tribological properties, the adhesive gradient interlayer of a Cr/Cr–C:H type between the substrate and the coating was applied. The comparison evaluation of tribological properties of coatings at the frictional contacts with the coatings coated 100Cr6 bearing steel, uncoated 100Cr6 bearing steel and alumina in the ambient air was an important element of the investigation.

2. Experimental details

2.1. Coatings deposition

The a-C and a-C:H coatings were deposited in self-made deposition system presented on Fig. 1. The deposition chamber (700 × 700 × 600 mm) was equipped with two ARC-MAG sources with the chromium (99.8%) and graphite (99.99%) targets of 100 mm in diameter. The right ARC-MAG source with chromium target was supplied using arc power supply or pulsed magnetron power supply and left ARC-MAG source was supplied only with pulsed magnetron supply. A rotational substrate holder was also biased to a pulsed voltage. Application of pulsed power supplies with frequency of 1 kHz, modulated with medium frequency of 100 kHz, to magnetron and substrates, enables stable and arc free deposition process and limited of the over-heating of substrate as well. Gases were introduced to the deposition chamber through flowmeters controlled by a Multi Gas Controller type MGC-147 coupled with the Controller 250B-Baratron® pressure measuring system, produced by MKS Instruments. Argon of 99.995% purity and acetylene of 96.8% were used. Coatings were deposited on substrates dia. 32 × 3 mm in dimension made of 100Cr6 bearing steel subjected to the heat treatment to 8.3 GPa in hardness and then grounded and polished until the surface roughness of $R_a \leq 0.02$ μm was obtained. Bearing balls (100Cr6, 8.3 GPa, $R_a \leq 0{,}02$ μm) 10 mm in diameter were also coated. Prior to deposition the process consisted of ultrasonic-aided cleaning with organic solvents and alkaline detergents were applied to the substrates and the balls. The final operation was the cleaning with organic solvent vapours and drying with compressed nitrogen. The substrates and balls prepared according to the above procedure were placed in the deposition chamber (Fig. 1) on a rotational substrate holder. After creating a 2×10^{-3} Pa vacuum in the chamber the substrates were heated up using a radiation heater up to the temperature approx. 120 °C. In the next stage the process of ion cleaning was applied to substrates under glow discharge of argon at the pressure of 10 Pa and the bias voltage of −1000 V (pulsed D.C.) for 10 min. To improve the adhesion and crack resistance of a-C and a-C:H coatings, a transition Cr/Cr–C:H interlayer with graded hardness and Young's modulus was deposited. The deposition of this transition interlayer was done with right ARC-MAG source (Fig. 1) by a combination of vacuum arc evaporation (ARC) and pulsed reactive magnetron sputtering (MAG) techniques, in order to achieve Cr sublayer with high adhesion to metal substrate and graded intermediate Cr–C:H layer with high precision. More details of deposition procedure of Cr/Cr–C:H interlayer can be found in Ref. [36]. After deposition Cr/Cr–C:H interlayer substrates were move to left ARC-MAG source with graphite target and then a-C or a-C:H coatings were deposited by pulsed magnetron sputtering in argon or argon and acetylene atmosphere, respectively. Three kinds a-C:H coatings, named a-C:H08, a-C:H16 and a-C:H24, were deposited for 8, 16 and 24 sccm acetylene flow. Some important parameters of deposition process are presented in Table 1.

2.2. Coatings properties evaluation

The chemical compositions of coatings were determined by Elastic Recoil Deflection Analysis (ERDA). The phase composition of coatings

Table 1
Deposition parameters of a-C and a-C:H coatings

Parameters	a-C	a-C:H08	a-C:H16	a-C:H24
Residual pressure	2×10^{-3} Pa			
Working pressure	0.3 Pa	0.32 Pa	0.34 Pa	0.36 Pa
Argon flow	50 sccm			
Acetylene flow	0 sccm	8 sccm	16 sccm	24 sccm
Sputtering power	1 kW			
Bias voltage	−100 V			
Substrate temperature	<160°C			
Target-substrate distance	60 mm			