EFFECT OF SUBSTRATE BIAS VOLTAGE PARAMETERS ON SURFACE PROPERTIES OF ta-C COATINGS

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The study presents the technology of the formation of amorphous ta-C films, deposited by pulsed vacuum-arc method with the use of a water-cooled electromagnetic Venetian blind plasma filter. The effect of the substrate bias voltage, in the range of -25 to -200 V, on the structural and surface properties of ta-C coatings was analyzed. The strong correlation between surface properties of amorphous ta-C films depending on substrate bias voltage variations and characteristic changes in the content of the diamond-like sp^3 fraction was observed.

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INTRODUCTION

The surface of material plays a basic role in determining various processes such as dyeing penetration, chemical absorption, biocompatibility and others. Properties of material surface - composition, roughness, topography, wettability can influence phenomena at material interface and are very important for various advanced applications. Modern techniques are widely used for surface parameters modification. Filtered vacuum-arc evaporation is one of the most widespread industrial methods of hydrogen-free ta-C thin film deposition [1, 2]. Thin films of tetrahedral carbon (ta-C), with high content of sp^3 bonds, are very attractive materials due to advanced characteristics such as high hardness, high resistivity, chemical inertness and low friction coefficient [3]. Results on the formation of amorphous ta-C films with a minimum amount of defects, deposited by pulsed vacuum-arc method with the use of a water-cooled electromagnetic Venetian blind plasma filter were presented in the previous study. The subject of the research was the influence of the substrate bias voltage, in the range of -25 to -200 V, on the mechanical properties of ta-C coatings, such as adhesion, hardness and Young's modulus. As it is known, the basic physico-mechanical properties of ta-C thin films are directly connected to the content of carbon atoms in sp^3 hybridization [4]. The highest content of sp^3 bonds was obtained at the substrate bias potential of -100 V, which also showed the maximum hardness and Young's modulus. Furthermore, the ta-C coating synthesized at this bias potential had excellent adhesion up to 41 N. The aim of the present study was the comparative analysis of the surface properties of ta-C coatings depending on the substrate bias voltage, in the range of -25 to -200 V.

1. MATERIALS AND METHODS

Experiments were performed on a modernized industrial vacuum arc device C55CT. Two graphite cathodes, with a DC-arc current of 50 A, high-current arc pulses of 1400 A, were used for carbon (ta-C) deposition.

Samples of high-speed steel (HSS), with the dimensions of 30 mm in diameter and 3 mm in thickness, polished to a roughness of Ra = 0.02 μm were used as substrates. The vacuum chamber was pumped out to a pressure of 1×10^{-3} Pa. The main process parameters were previously presented [5, 6]. At such parameters the thickness of ta-C film was about 0.8 μm.

The surface topography and structure of the ta-C coatings were evaluated by scanning electron microscopy (QUANTA 600 FEG) (SEM) method at different magnifications.

The main surface parameters such as surface roughness, wettability, surface free energy were investigated. The surface roughness was measured by means of profilometer Talysurf CCI (according to ISO 3287). The contact angles were measured by means of tensiometric method in Kruss K12 Tensiometer at temperature 20 °C. Prior to contact angle measurements, samples were ultrasonically cleaned in acetone and deionised water and dried. The standard liquids with well-known values of surface tension, component of dispersion and polar interaction such as water, formamide, diiodo methane, ethylene glycol, α-bromo naphthalene and glycerol were used. Also the surface free energy (SFE) and its polar and dispersion components were determined by means of Owens-Wendt-Rabel-Kaeble', Van Oss and Fowkes methods [7-9]. Raman spectra were measured by using the Raman scattering spectrometer Renishaw in Via, with the wave lengths of 514 and 785 nm in the geometry of the reverse scattering.

2. RESULTS AND DISCUSSION

The studies of surface morphology showed that the coatings deposited with the use of the plasma filter on the water-cooled substrates demonstrate different roughness parameters depending on the potential in the range from -25 to -200 V (Fig. 1).

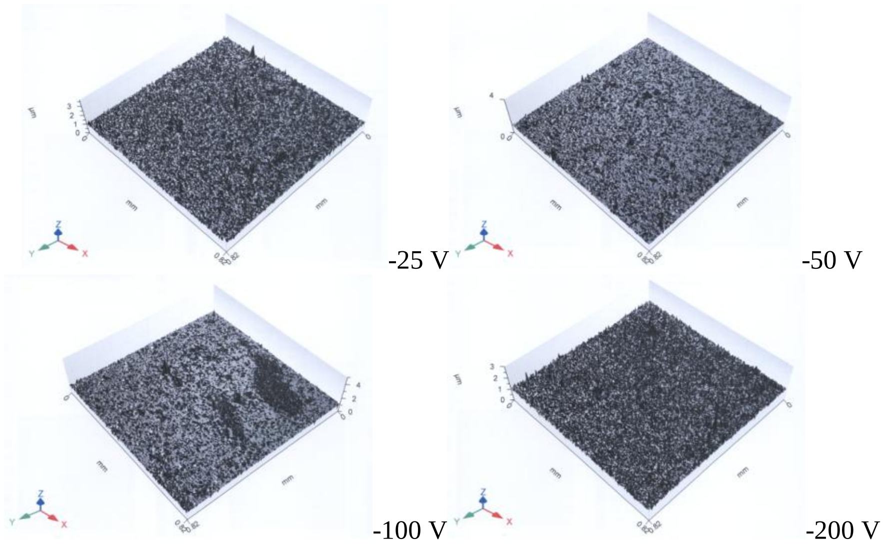

Fig. 1. Surface morphology of ta-C films depending on the potential in the range from -25 to -200 V

The values of surface roughness Ra decreased from 0.055 μm (-25 V) to 0.047 μm (-50 V) and 0.036 μm (-100 V) and then increased to 0.066 μm (-200 V). Some explanation of this phenomenon was presented in previous study [9, 10]. At the bias potential of -25 V the energy of the incident ions is insufficient to penetrate the subsurface layer of the coating, and during film growth a large proportion of the carbon atoms is retained on the surface, where surface diffusion processes contribute to the formation of a thin film with a low density and a greater proportion of sp^2 bonds, what leads to increased roughness. Under the conditions when the bias potential increased up to -100 V, the surface diffusion is not essential, and the energy of the ions is usually dissipated in the film. Such conditions result in the formation of a dense structure with diamond-like sp^3 bonds of carbon atoms. Further increase of the bias potential up to -200 V leads to reduction of sp^3 bond content and increased roughness.

The difference of surface parameters of ta-C coatings depending on the substrate bias voltage, in the range of -25 to -200 V was analyzed by SEM method (Fig. 2) in a good agreement with results of profilometer Talysurf CCI measurements.

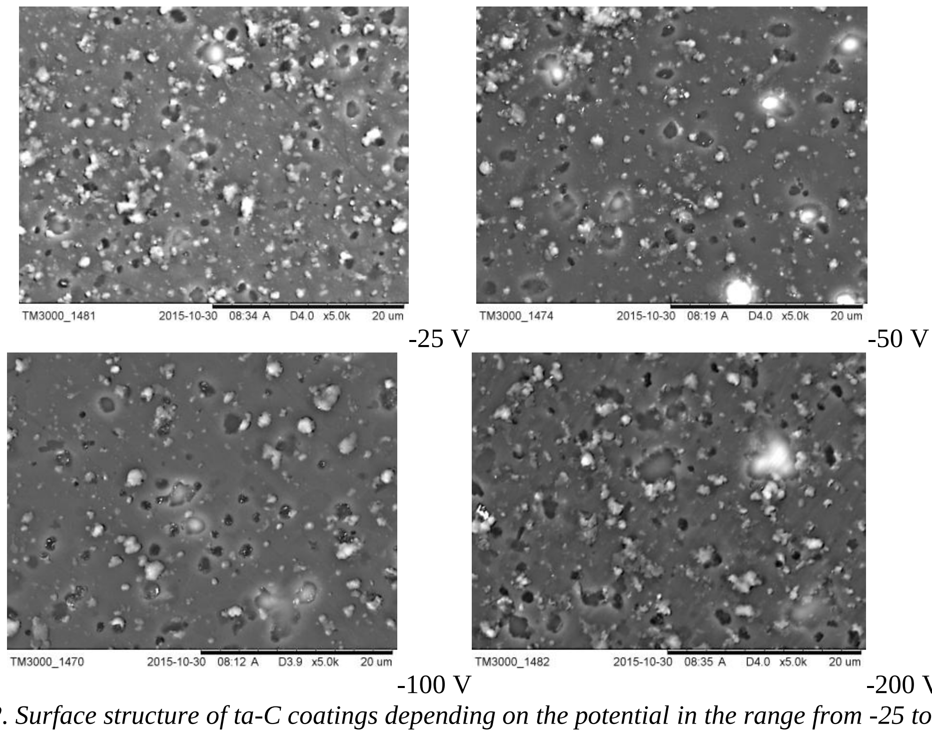

Fig. 2. Surface structure of ta-C coatings depending on the potential in the range from -25 to -200 V

Advancing contact angles were measured by Wilhelm's method (Kruss K12) at temperature 20 °C. The surface free energy SFE (γ) and its polar (γ^p) and dispersion (γ^d) parts estimations were made by Owens-Wendt-Rabel-Kaeble', Van Oss and Fowkes methods (Fig. 3).

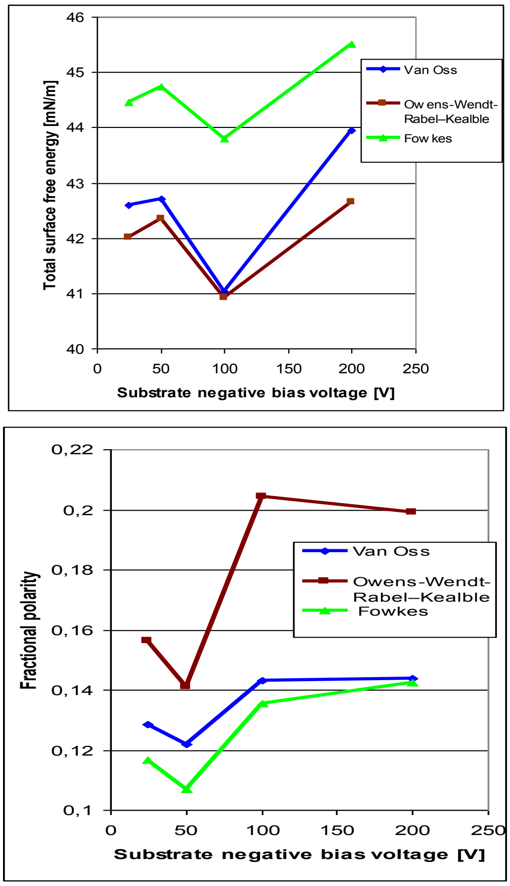

Fig. 3. Total surface free energy estimated by Owens-Wendt-Rabel-Kaeble' (a); Van Oss and Fowkes methods fractional polarity $\gamma^p / (\gamma^d + \gamma^p)$ estimated by Owens- Wendt-Rabel-Kaeble', Van Oss and Fowkes methods depending on substrate negative bias voltage (b)

The contact angles are generally large for the low-energy hydrophobic than for the higher energy, more hydrophilic materials. The SFE energy values were in the range 40…45 mN/m, polar part was grown from 4.79 mN/m to 8.49 mN/m with increasing of the bias potential.

Under the conditions when the bias potential increased up to −100 V, the surface energy decreased according to the structural changes and formation of a dense film with diamond-like sp^3 bonds of carbon atoms. Subsequent increase of the bias potential up to −200 V leads to surface energy increasing due to further structural changes and reduction of sp^3 bond content. In contrast, the maximal values of polar part of SFE and fractional polarity $\gamma^p / (\gamma^d + \gamma^p)$ (Fig. 3,b) estimated by different methods were demonstrated in the case of the ta-C films deposited at substrate bias voltage -100 V. The fact that materials with higher values of fractional polarity have higher biocompatibility is important for various biomedical applications of ta-C coatings.

The phase composition of ta-C films depending on the substrate bias voltage was analyzed by Raman spectroscopy. Raman scattering spectra in the range of 800…2000 cm^{-1} for ta-C films deposited at the bias potentials from -25 to -200 V were presented (Fig. 4).

Observed increase in the peak intensity at 1360 cm^{-1} may indicate an increase in the content of sp^2 bonds in the structure of the amorphous carbon film, as well as an increase in the size of the crystallites [11, 12]. The results suggested that the coatings deposited at the bias potential -100 V have a higher ratio of sp^3/sp^2 bonds compared to the coatings obtained at other values of the bias voltage.

The effect of the substrate bias voltage during the synthesis on the content of sp^3 bonds in the deposited ta-C films was analyzed.

The changing of structural parameters results in changes of surface characteristics and functional properties of deposited ta-C coatings.

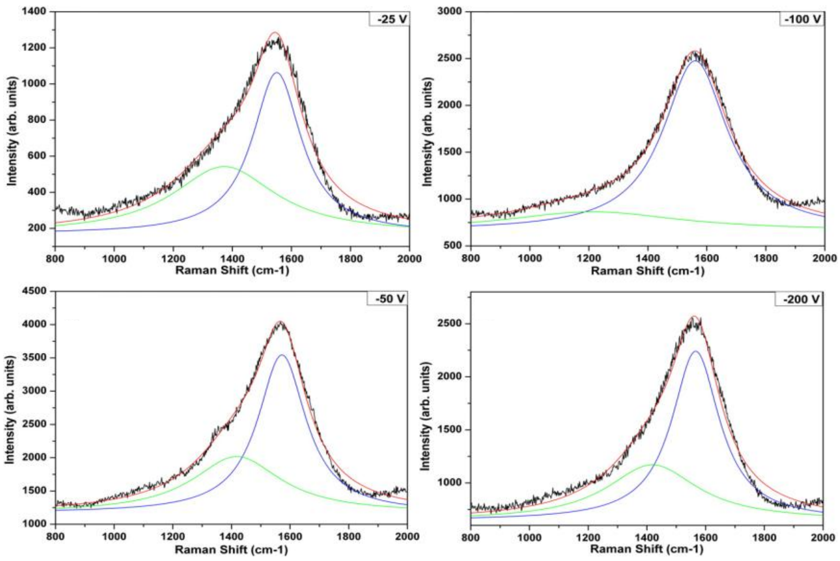

Fig. 4. Raman spectra of ta-C films prepared at different substrate bias voltages

CONCLUSIONS

The results demonstrate the possibility to modify surface parameters of ta-C coatings by changing technological parameters and the substrate bias voltage adjustment. The substrate bias potential in the synthesis process has a strong influence on the structure and surface properties of amorphous carbon coatings. The difference of surface parameters of ta-C coatings depending on the substrate bias voltage, in the range of -25 to -200 V was analyzed by SEM method in a good agreement with results of profilometer Talysurf CCI measurements.

The SFE energy values were in the range 40…45 mN/m, polar part was grown from 4.79 to 8.49 mN/m with increasing of the bias potential. The maximal values of polar part of SFE and fractional polarity estimated by different methods have been demonstrated in the case of the ta-C films deposited at substrate bias voltage of -100 V. The fact that materials with higher values of fractional polarity have higher biocompatibility is important for perspective biomedical approbations of ta-C coatings. The modification of surface properties such as roughness, surface free energy and fractional polarity is very challenging for various industrial applications of amorphous carbon coatings.

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ЭФФЕКТ ПАРАМЕТРОВ СМЕЩЕНИЯ ПОТЕНЦИАЛА ПОДЛОЖКИ НА ПОВЕРХНОСТНЫЕ СВОЙСТВА ПОКРЫТИЙ ta-C

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Представлена технология формирования аморфных покрытий ta-C, нанесенных импульсным вакуумно-дуговым методом с использованием охлаждаемого электромагнитного фильтра плазмы. Проанализирован эффект изменения смещения потенциала подложки в диапазоне значений от -25 до -200 В и его влияние на структурные и поверхностные свойства покрытий ta-C. Обнаружена корреляция между поверхностными свойствами аморфных покрытий ta-C и изменениями в содержании sp^3-фазы в зависимости от изменения потенциала подложки.

ЕФЕКТ ПАРАМЕТРІВ ПОТЕНЦІАЛУ ЗМІЩЕННЯ ПІДКЛАДКИ НА ПОВЕРХНЕВІ ВЛАСТИВОСТІ ПОКРИТТІВ ta-C

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Наведена технологія формування аморфних покриттів ta-C, нанесених імпульсним вакуум-дуговим методом з використанням охлаждаемого електромагнітного фільтра плазми. В роботі був проаналізований ефект зміни зміщення потенціалу підкладки в діапазоні значень від -25 до -200 В і його вплив на структурні і поверхневі властивості покриттів of ta-C. Була виявлена кореляція між поверхневими властивостями аморфних покриттів ta-C і змінами в змісті sp^3 фази в залежності від зміни потенціалу підкладки.