Mechanical and tribological characteristics of a-C:H:SiOₓ films formed by PACVD on titanium alloy VT1-0

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Abstract. This paper is devoted to the study of the mechanical and tribological properties of a-C:H:SiOₓ films deposited on a titanium alloy VT1-0 by a plasma chemical deposition method using pulsed bipolar bias voltage. It was shown that after deposition of 2 µm-thick a-C:H:SiOₓ film on a titanium alloy VT1-0 sample, the root-mean-square surface roughness Rₐ measured using atomic force microscopy decreased from 74 to 50 nm compared to the original substrate. The surface hardness H measured using nanoindentation increased from 3.3 to 12.4 GPa with an almost unchanged elasticity modulus E. As a result, the plasticity index (H/E) of titanium samples increased from 0.03 to 0.11, and the plastic deformation resistance (H²/E) increased from 3 to 156 MPa. Deposition of a-C:H:SiOₓ film on the titanium alloy VT1-0 surface makes possible to reduce the friction coefficient from 0.3-0.6 to 0.1 and the wear rate from 6·10⁻⁸ to 7·10⁻⁶ mm³/Nm.

1. Introduction

Presently, a lot of attention is given to ensuring the durability of metal parts of machines and mechanisms by creating thin-film coatings on their surfaces. The most common coatings are nitride (TiAlN, TiAlCrYN, TiCN, TiN) and carbon-based coatings (DLC) that can reduce friction and wear rates. The addition of SiOₓ to DLC allow to reduce internal stresses in DLC films that provides excellent adhesion to many types of substrates and makes it possible to form tens of micrometers thick films [1,2]. On top of that, SiOₓ containing DLC (a-C:H:SiOₓ) films are characterized by high hardness (10-20 GPa) and elasticity modulus (30-150 GPa) [2-4], low friction coefficient of about 0.02-0.2 [1,5] and wear rate 10⁻⁵-10⁻⁸ mm³N⁻¹m⁻¹ [5,6], high transparency in the visible and near IR wavelength region (~80-85%) [7,8], excellent biocompatibility with human body [1]. Due to the unique properties of a-C:H:SiOₓ films, they can be used as wear-resistant anti-friction coatings on parts of internal combustion engines, in MEMS technologies, medicine, industry, lithography [9] and other fields.

The most common method for such films forming is the radio-frequency plasma-assisted chemical vapor deposition (RF PACVD) [5,10,11]. Koshigan et al. [1] studied influence of hydrogen and oxygen pressure on tribological characteristics of a-C:H:SiOₓ films deposited on silicon wafers. Friction experiments were performed with a linear reciprocating pin-on-flat tribometer, using 52100 steel pins. The authors showed that there are optimal values of gas pressure (H₂ and O₂) in the process of testing at which minimum values of the friction coefficient (0.02±0.01) are observed. Neerinck et
al. [12] studied tribological properties of a-C:H:SiO$_x$ films also deposited on silicon substrates. Unlubricated sliding ball-on-disk experiments were performed at room temperature using AISI L3 steel bearing ball. It was shown that in air at a relative humidity (RH) 50% the friction coefficient was 0.04–0.08, while at a relative humidity of 90% and under water, it was lower than 0.15. The wear rate calculated from the profilometry measurement of the wear track area was $2 \times 10^{-7}$ mm$^3$N$^{-1}$m$^{-1}$ in air of 50% RH and only $3.5 \times 10^{-8}$ mm$^3$N$^{-1}$m$^{-1}$ under water. Venkatraman et al. [13] studied effect of temperature annealing on the tribological properties of a-C:H:SiO$_x$ films deposited on silicon. The wear rate of the annealed films was measured in air at room temperature with a relative humidity of ~35% using a ball-on-disk tribotester with WC ball. The authors showed that with an increase in the annealing temperature in air, graphitization of a-C:H:SiO$_x$ films occurs, as a result of which mechanical and tribological properties deteriorate, in particular, an increase in wear rate from $(1 \div 10) \times 10^{-8}$ to $(8 \div 50) \times 10^{-7}$ mm$^3$N$^{-1}$m$^{-1}$ is observed. Jana et al. [14] studied tribological properties of a-C:H:SiO$_x$ films deposited on glass substrates at different relative humidity of the environment. The wear and friction characterization was performed using ball-on-disc tribotester with WC ball. In this paper the authors showed that an increase in relative humidity from 35 to 80% leads to an increase in the friction coefficient from 0.005 to 0.074, while the wear rate is reduced from $9.8 \times 10^{-8}$ to $2.7 \times 10^{-9}$ mm$^3$N$^{-1}$m$^{-1}$ with increasing relative humidity from 35 to 50%. A further increase in relative humidity up to 80% leads to an increase in the wear rate. Bhowmick et al. [6] have studied tribological characteristics of a-C:H:SiO$_x$ films deposited on M2 grade tool steel coupons. Pin-on-disc type sliding tests were performed with 319 Al alloy pins. At a room temperature, a-C:H:SiO$_x$ films had friction coefficient of 0.17 and wear rate of $2.86 \times 10^{-5}$ mm$^3$N$^{-1}$m$^{-1}$. At temperature of 400$^\circ$C, the friction coefficient was 0.11, and wear rate was $16.23 \times 10^{-5}$ mm$^3$N$^{-1}$m$^{-1}$. Jedrzejczak et al. [5] have studied tribological characteristics of a-C:H:SiO$_x$ films deposited on cylindrical samples of Ti6Al7Nb alloy in combination with different counterbodies. A ball-on-disc tribotester with AISI 316L and ZrO$_2$ balls was used. The relative humidity was 30%. In this paper, the authors have shown that a-C:H:SiO$_x$ films have a minimal friction coefficient of 0.04–0.07 at using of both balls. In this case, the wear rate for a-C:H:SiO$_x$ films was from $1.43 \times 10^{-7}$ to $3.97 \times 10^{-7}$ mm$^3$N$^{-1}$m$^{-1}$.

This paper is devoted to the study of the mechanical and tribological properties of a-C:H:SiO$_x$ films deposited on a titanium alloy VT1-0 by plasma chemical deposition method using pulsed bipolar bias voltage applied to substrate. The titanium alloy VT1-0 (Ti content is ~99.24-99.7%) is widely used in aircraft and rocket production, medicine and other areas. However, it is known that titanium alloys have the high surface reactivity, low work hardening coefficient, low shear strength, high value of a friction coefficient and a wear rate [15].

2. Materials and Methods
Deposition of a-C:H:SiO$_x$ films was realized on vacuum installation equipped with plasma generator with heated cathode working in mixture of argon and polyphenyl-methylsioxane (PPMS) vapor. PACVD deposition system has been described in detail in [16]. Vacuum in the chamber to a pressure of $10^{-2}$ Pa was realized by turbomolecular pump.

Made from titanium alloy VT1-0 samples (size 2\times2 cm$^2$ and thickness 0.4 cm) were used as the substrates. The distance between the plasma generator and the substrate was 100 mm. Before a-C:H:SiO$_x$ films deposition, the substrates were pre-cleaned in argon plasma for 6 minutes. In this case argon pressure in chamber was 0.3 Pa, discharge voltage - 100 V, discharge current - 11 A, magnetic induction in the substrate area - 3 Gs. Bipolar bias voltage with negative pulse amplitude of 1000 V, with frequency of 100 kHz and the positive impulse duration of 4 \mu s was applied to the substrate during plasma cleaning. After that, a-C:H:SiO$_x$ film was deposited at argon pressure of 0.1 Pa, PPMS flow rate of 95 \mu l/min, discharge voltage of 140 V, discharge current of 6 A and magnetic induction of 3 Gs. During the film deposition, the negative pulse amplitude of the bipolar bias voltage was reduced to 500 V. Film deposition rate was $3 \pm 0.3 \mu$m/h. In [16], we showed that in this deposition regime, the hardest films with the highest sp$^3$-bonded carbon content are formed on Si substrates.
The deposited a-C:H:SiO$_x$ films were investigated by different characterization techniques. Raman spectroscopy (Centaur U HR complex) with 532 nm Ar laser (beam cross-section of 50 μm) was used for recording of spectra. These spectra were obtained in a spectral range of 800–1800 cm$^{-1}$ with a resolution better than 1.5 cm$^{-1}$. From the Raman spectra it is possible to obtain information about the carbon bonds in the film. For this, the spectra were divided into Gaussians and the position, width, and intensity of the $D$ and $G$ Raman peaks were determined. Hardness ($H$) and coefficient of elasticity ($E$) of the a-C:H:SiO$_x$ films were determined by NanoTest 600 device (MicroMaterials, Great Britain) at 2 mN load by Oliver–Pharr method [17]. The surface morphology of the samples was studied by atomic force microscopy using AFM Solver P47 (NT-MDT, Russia) microscope. The friction coefficient was determined using the THT-S-AX0000 (CSM Instruments, Switzerland) tribometer in the "ball on disk" geometry. A ball with a radius of 3 mm made of VK-6 alloy was used as counterbody. The rotation speed of the disk was 5 cm/s, and rotation frequency was 2 Hz at normal load 5 N. Air temperature was 25 °C during the test, and the relative humidity was 50%. Wear rate was estimated by method described in [18]. The film thickness was measured by a Linnik microinterferometer MII 4 (LOMO, Russia).

3. Results

3.1. Atomic force microscopy results

The surface morphology of the samples was studied on initial substrate made from titanium alloy VT1-0, polished by an abrasive paper, and the same substrate coated by a-C:H:SiO$_x$ film. The surface of initial sample had a granular structure with grains of approximately 100 nm in width and 50–100 nm in height (figure 1.a). After deposition of a-C:H:SiO$_x$ film with the thickness of 2±0.2 μm, the substrate surface became smoother. Root-mean-square surface roughness $R_q$ decreased from 74 to 50 nm. Table 1 presents samples surface roughness values before and after film deposition. In [19] it was shown that the wear rate of DLC films depends on the substrate surface roughness, and latter is the decisive parameter for the wear resistance of the DLC to external loads.

| Sample               | $R_{mean}$ (nm) | $R_{max}$ (nm) | $R_q$ (nm) | $R_a$ (nm) |
|----------------------|-----------------|----------------|------------|------------|
| Initial substrate    | 258             | 461            | 72         | 57         |
| Coated substrate     | 134             | 412            | 54         | 43         |

$R_{mean}$ – mean peaks height, $R_{max}$ – maximum peaks height, $R_q$ – root-mean-square surface roughness, $R_a$ – arithmetic-mean surface roughness.

![AFM images of initial VT1-0 sample (a) and coated with a-C:H:SiO$_x$ film (b)](image_url)
3.2. Mechanical characteristics research

The comparison was made between the hardness and the elastic modulus of the initial VT1-0 sample and a sample with a-C:H:SiO\textsubscript{x} film (figure 2). It is noticeable that after deposition of a-C:H:SiO\textsubscript{x} film, the surface hardness increased from 3.3 to 12.4 GPa. Herewith the elastic modulus of both samples remains almost unchanged – 112.9 and 110.5 GPa. Although hardness is important material property which defines wear resistance, it is considered that the elastic modulus also has an important influence on wear behavior. In particular, the elastic strain to failure, which is related to the ratio of hardness and elastic modulus, is a more suitable parameter for predicting wear resistance [20].

![Figure 2. Mechanical characteristics of initial VT1-0 sample and coated with a-C:H:SiO\textsubscript{x} film](image)

Since the hardness grew almost 4 times with a practically unchanged elasticity modulus on the sample with a-C:H:SiO\textsubscript{x} film, then the elastic-plastic characteristics of the surface (elastic index H/E and plastic resistance H\textsuperscript{3}/E\textsuperscript{2}) changed significantly. In particular, elastic index increased from 0.03 to 0.11 and plastic resistance increased from 3 to 156 MPa. The increase in these characteristics indicated an improvement in the wear resistance of the sample surface. Table 2 gives mechanical and elastic-plastic characteristics of the samples surface.

| Sample           | H (GPa) | E (GPa) | H/E  | H\textsuperscript{3}/E\textsuperscript{2} (MPa) |
|------------------|---------|---------|------|----------------------------------|
| Initial substrate| 3.3     | 112.9   | 0.03 | 3                                |
| Coated substrate | 12.4    | 110.5   | 0.11 | 156                              |

3.3. Tribological properties research

After deposition a-C:H:SiO\textsubscript{x} film, the friction coefficient of the sample surface decreased from 0.3-0.6 to 0.1 (figure 3). The initial sample had a friction coefficient that varied in the range from 0.3 to 0.6 and was not stable with time. The reason of the friction scattering was not clear. After film deposition, the friction coefficient not only decreases, but also its oscillations become less pronounced. Except for a short running-in period at the beginning, the sliding on the films soon turns to a stable friction.
Figure 3. Friction behaviours of initial VT1-0 sample (a) and coated with a-C:H:SiO$_x$ film (b)

Figure 4 show the optical images of wear track of both samples. Wear rate of the sample with a-C:H:SiO$_x$ film, calculated from profile of wear track, decreased from $6 \cdot 10^{-4}$ to $7 \cdot 10^{-6}$ mm$^3$/N·m in comparison with initial sample. It is clearly seen that the wear track on the VT1-0 sample (figure 4-a) is wider and deeper, while on the sample with the film it is narrower and less deep.

We have previously shown that a-C:H:SiO$_x$ film deposited on the GaAs substrate has higher friction coefficient (0.16) and greater wear rate ($1.3 \cdot 10^{-5}$ mm$^3$/N·m) [21]. Such a difference in film characteristics may be caused by a difference in film deposition conditions, namely another negative pulse amplitude of the substrate bias voltage and Ar pressure during deposition.

3.4. Raman spectroscopy
Raman spectroscopy is one of the simplest methods for determining the structure of carbon-based thin films and gives information about the content of sp$^3$- and sp$^2$-hybridized carbon atoms in film. Properties of the deposited films depend on the prevalence of one or another hybridization type. Raman spectrum of a-C:H:SiO$_x$ film has wide peak in wavenumber range 1000-1700 cm$^{-1}$ typical for
DLC films (figure 5). This peak was decomposed on two Gaussians, corresponded to D (disordered) and G (graphite) peaks and their position, full width at half-maximum (FWHM), peak intensity ratio $I_D/I_G$ were determined (table 3).

![Figure 5. Raman spectrum of a-C:H:SiO$_x$ film deposited on VT1-0 sample](image)

**Table 3.** Results of analysis of Raman spectrum of a-C:H:SiO$_x$ film.

| $\omega_D$ (cm$^{-1}$) | $\Gamma_D$ (cm$^{-1}$) | $\omega_G$ (cm$^{-1}$) | $\Gamma_G$ (cm$^{-1}$) | $I_D/I_G$ |
|-----------------------|-----------------------|-----------------------|-----------------------|------------|
| 1330                  | 334                   | 1494                  | 189                   | 0.83       |

$\omega$ – peaks position, $\Gamma$ – full width at half maximum (FWHM), $I_D/I_G$ – intensity ratio.

**Conclusions**

The results of this study showed that the deposition a-C:H:SiO$_x$ films on the VT1-0 samples allows:

- to increase the surface hardness from 3.3 to 12.4 GPa with a practically unchanged elasticity modulus (110-113 GPa) and, consequently, to increase plasticity index $H/E$ from 0.03 to 0.11 and plastic resistance $H^2/E^2$ from 3 to 156 MPa;
- to reduce friction coefficient and wear rate by 3.7 times and 85 times, respectively.

Consequently, obtained a-C:H:SiO$_x$ films can be used to increase the durability of products made from titanium alloy VT1-0 in aircraft manufacturing, medicine and other industries.

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