Antifriction coatings based on a-C for biomedicine applications

Y N Yurjev[1], D V Kiseleva[1], D A Zaitcev[1], D V Sidelev[1] and O S Korneva[2]

[1] Department of Experimental Physics, National Research Tomsk Polytechnic University, Tomsk, 634050, Russian Federation

[2] Materials Properties Measurement Centre, National Research Tomsk Polytechnic University, Tomsk, 634050, Russian Federation

E-mail: sidelevdv@tpu.ru

Abstract. This article reports on the investigation of mechanical properties of carbon films deposited by dual magnetron sputtering system with closed and mirror magnetic field. There is shown that a-C films with predominantly sp^2-phase have relatively high hardness (up to 20 GPa) and low friction index (~0.01). The influence of magnetic field on friction index is determined. The analysis of experimental data shows the obtained a-C samples can be used for biomedicine applications.

1. Introduction

Interest in increase of life-time of medical implants by improving wear resistance has been enhanced. The promising approach in this way is surface modification by deposition thin films. The most medical applications require good adhesion and reduction of friction index of operation surface to 0.1 and lower.

Coatings based on a-C films have high mechanical and tribological properties, high wear resistance, biocompatibility and chemical inactivity. Such films can be used in biomedicine in case of modification surface of medical implant or prostheses [1-3]. Moreover, carbon films have properties of ideal lubricant and prevent the formation of wear products by friction. There are many ways to deposit such coatings with required mechanical properties: plasma assisted chemical vapor deposition [4], cathode vacuum arc deposition [2], magnetron sputtering [5] and etc.

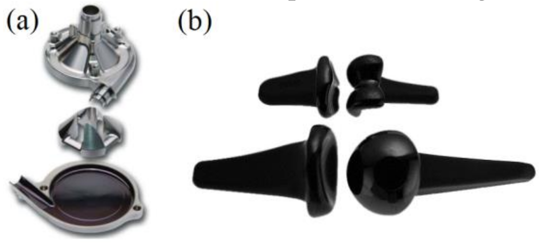

Figure 1. Carbon-coated products: (a) ventricular assist device heart pump, (b) artificial and hip joints.

High-quality antifriction coatings usually deposit by means of magnetron sputtering systems with advanced plasma density (10^{11}-10^{13} cm^3) [5]. For this purpose, magnetron systems with unbalanced magnetic field are often used. Such diode systems have relatively high density of ion current on substrate (more 5 mA/cm^2).

The dual magnetron sputtering system is an especial deposition tool. It is consisted of two planar magnetron systems operating in antiphase with bipolar mid-frequency power supply (~20-80 kHz). Dual magnetron sputtering systems have higher operation stability, provide increased energy of sputtering atoms (~10-50 eV) and improved adhesion of coatings to substrate. These aspects are important to biomedicine applications.

This article is devoted to investigation of mechanical properties of carbon films deposited by dual magnetron sputtering system in Ar atmosphere.

2. Experimental

2.1. Magnetron sputtering

The carbon films were deposited on steel substrate AISI 321(30x30x1 mm^3) by an ion-plasma installation «Yashma-5». The base pressure was 10^{-3} Pa. Steel substrates were treated in plasma of ion source with closed electron drift prior to deposition. The operation parameters of ion source were: voltage ~ 2.5 kV and current ~ 250 mA. For increase adhesion, sublayer Ti (100 nm) was deposited by planar magnetron sputtering system.

The deposition of a-C films (1 μm) were by sputtering carbon targets (MPG-6) in Ar atmosphere (99.95%) by dual magnetron sputtering system (Fig. 2). The distance between target and substrate was 100 mm. The a-C films were deposited at different values of pressure: from 0.1 to 1.6 Pa.

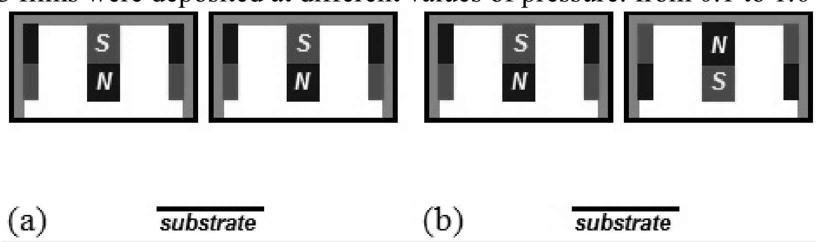

Figure 2. Dual magnetron sputtering systems with mirror (a) and closed (b) magnetic fields.

The dual magnetron sputtering system with mirror magnetic field has equivalent polarity of magnetic system [6]. For this reason, plasma flows bounce off relatively central axis. Conversely, the closed magnetic field dual magnetron has opposite polarity of magnetic system. Plasma flows in such case combine and create an additional magnetic trap for electrons. The change of magnetic system is resulted in variation of ion current density on substrate and impact of the growing film.

2.2. Films characterization

The coating thickness was controlled by quartz gauge «Micron-5». The microstructure of carbon samples was characterized by Raman spectroscopy (Centaur U-HR) in spectral range 100…2000 cm^{-1}. For resonance excitation, laser radiation (532 nm) was used. The film hardness was measured by Vickers method on Nano Hardness Tester (maximum load was 10 mN). The adhesion of coatings to substrate was characterized by scratching the surface by diamond indenter (Micro-Scratch Tester, CSEM). The friction index was tested by PC-Operated High Temperature Tribometer (CSEM) with friction pair ball-disk at atmospheric pressure.

3. Results and discussion

For microstructure identification, Raman spectra expand on two Gaussian components. The high intensities of D- (1310-1420 cm^{-1}) and G-lines (1500-1580 cm^{-1}) show content of graphite bonds (carbon in sp^2-hybridization). The data of samples structure is shown in Table 1.

According to research in the article of Chu P. K., Li L. [7]:

- cathode material is a commercial graphite (equivalent of MPG-6);
- experimental samples are a-C coatings.

Table 1. Structure characterization of carbon films.

magnetic field	P, Pa	G-line		D-line		I_D[c]/I_G[d]
		ν[a], cm^{-1}	$\Delta\nu_{1/2}$[b], cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	
closed	0.1	1535	176	1347	390	0.88
	0.13	1551	232	1379	350	0.89
	0.18	1569	140	1372	369	0.87
	1.1	1578	101	1356	250	0.86
mirror	0.1	1511	179	1357	365	0.9
	0.13	1501	206	1328	418	0.89
	0.18	1506	194	1324	431	0.88
	1.1	1517	183	1338	405	0.88
cathode	-	1544	29	1315	47	0.85

[a] ν – frequency of Raman spectrum line
[b] $\Delta\nu_{1/2}$ – half-width of line
[c] I_D –intensity of D-line
[d] I_G – intensity of G-line

The shift of G-line maximum in 1581 cm^{-1} and higher shows disintegration of crystal grain (up to 2.5 nm). In contrast, the change of D-line maximum in lower frequency indicates growing size of graphite clusters [8]. According to experimental data, samples deposited by mirror magnetic field dual magnetron have higher crystal grain size. This effect is related to imbalance of the magnetic field of the dual magnetron.

Carbon films deposited by magnetron sputtering systems can have properties of hard or mild materials. It depends on operation pressure in vacuum chamber during deposition process. Results of hardness measurements are presented in Fig. 3. The indenter penetration distance in carbon films is about 180 nm. The hardness of experimental samples is higher at lower operation pressures. This dependence is a nonlinear for both configurations of magnetic field of magnetron systems. The hardest coatings (up to 20 GPa) are deposited at 0.1-0.13 Pa. The cause of coatings hardness drop at higher pressure is Ar atoms building in coatings structure. It leads to formation of loose and more porous structure.

Results of friction index measurements are presented in Fig. 4. The operation load of Tribometer was 5 N. The friction index of original steel substrates was 0.55.

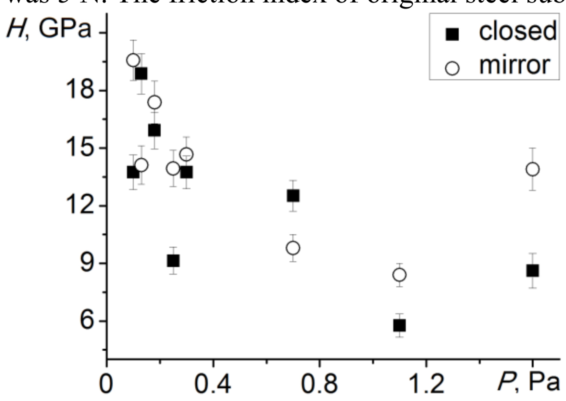

Figure 3. Hardness measurements of a-C films deposited by closed and mirror magnetic field magnetron.

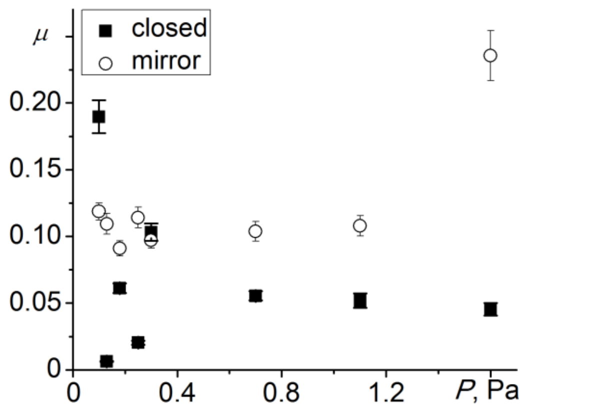

Figure 4. The friction index of experimental samples.

In accordance with Fig. 4, the friction index of a-C films doesn't change in the case of deposition by mirror magnetic field magnetron (0.08-0.12). For the second case, friction properties get worse at increase operation pressure. The average friction index for experimental samples is about 0.1.

Adhesion measurements demonstrate high results. The a-C coatings are stable at load 10 N. It explained by predominantly content of sp^2-phase in experimental samples. Otherwise, carbon films have high internal stress and it leads to decrease coatings stability.

According to results in [9,10], the friction index and hardness of human bone are 0.05 and 15-18 GPa, respectively. In this way, deposited a-C films satisfy requirements of the artificial impants.

4. Conclusions

Main results of our investigation can be summarized as follows:

- experimental samples have predominantly sp^2-phase and good adhesion properties;
- the hardness of a-C films is varied in 5…20 GPa and depends on operation pressure;
- the friction index of a-C films is lower for closed magnetic field magnetron sputtering system and the average friction index is about 0.1.

The deposited a-C films can be used to biomedicine applications.

References

[1] Thomson L A, Law F C, Rushton N and Franks J 1991 *Biomaterials* **12** 37
[2] Ren Y, Erdmann I, Khlopyanova V, Deuerler F and Buck V 2014 *Diamond and Related Materials* **44** 38
[3] Jones M I, McColl R, Grant D, Parker K G and Parker T L 1999 *Diamond and Related Materials* **8** 457
[4] Salvadori M C, Martins D R and Cattani M 2006 *Surface & Coatings Technology* **200** 5119
[5] Oskomov K V, Solov'ev A A and Rabotkin S V 2014 *Technical Physics* **59** 1811
[6] Musil J and Baroch P 2005 *IEEE Transactions on Plasma Science* **33** 338
[7] Chu P K and Li L 2006 *Materials Chemistry and Physics* **96** 253
[8] Ferrari A C, Meyer J C,Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S and Geim A K 2006 *Physical Review Letters* **97** 187401
[9] Merkher Y, Sivan S, Etsion I, Maroudas A, Halperin G and Yosef A 2006 *Tribology Letters* **22** 29
[10] Pal S 2014 *Mechanical Properties of Biological Materials* **2** 23