NANOINDENTATION TEST FOR DLC COATING ANALYSIS

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Resume
In this report the effects of the substrate on the microhardness of Diamond like carbon (DLC) thin films were investigated. The DLC coatings were deposited by Radio Frequency Plasma Actived Chemical Vapor Deposition (RF PACVD; 13,56 MHz) process on three mechanically polished substrates, which were chosen for comparison; hardened molybdenum high speed steel AISI M2, unhardened tool steel AISI L2 and titanium alloy TiAl6V4. The aim of the present investigation was to determine the influence of substrates on microhardness and other mechanical properties of DLC layer. These properties especially microhardness were studied and compared from nanoindentation load – displacement curves. Results show that the hardness of the substrate is the crucial value for the hardness of the DLC films.

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1. Introduction

Diamonds like carbon (DLC) films have received considerable interest for more than a decade because of their excellent tribological properties such as low-friction coefficient, high wear resistance and high hardness [1]. Applications were reported for numerous high precision components and tools. One problem is their poor adhesion on steel substrates without intermediate layers. The mechanical and tribological properties of pure DLC films like hardness and wear resistance are superior to those of metal-containing carbon hydrogenated films (Me-C:H). However, the productivity of the deposition process is not as good because Me-C:H can be deposited by well known Physical Vapor Deposition (PVD) methods like magnetron sputtering. The most common method for depositing pure DLC films is Radio Frequency Plasma Actived Chemical Vapor Deposition (RF PACVD; 13,56 MHz) which is known to be technically difficult and expensive to scale up to industrial dimensions [2].

The classical microhardness is determined by the resistance to local deformation by a hard diamond indenter, pressed into the material. A fast development in the analysis methods is appearing at this time. Improved methods could help solving many technical problems. Whereas indentation methods are used for evaluating some mechanical properties, such as nanohardness, adhesive and cohesive behavior, wear resistance and fracture. Their big advantage is that they can be used for analyzing surfaces of real components or tools, which then do not have to be cut. However, knowledge of the true

hardness of the thin film with a thickness of 1 μm or less continues to be a quite a challenge. The nanoindentation offers a solution for this problem.

The nanohardness can be measured directly on the tool surface without breaking the surface, because the indentation is too small to cause any damage. The indentation microhardness measurement is a simple, reproducible, and cheap method, which is often used for the characterization of surface for mechanical applications. Measuring the elastic and plastic properties of thin films is always the first critical step to analyze their mechanical integrity and among alternative techniques, nanoindentation is arguably the simplest approach for measuring the mechanical properties of small material structures including thin films [3,4]. For indentation loading of a typical elastic and hard thin film on a ductile substrate, the mode of deformation of the film is assumed to be controlled by the plastic deformation of the underlying substrate [5-8]. Bending and stretching of the film due to yielding of the substrate induce stresses that lead to fracture in the brittle film [1]. Analysis DLC coating from nanoindentation load – displacement curve has not been yet described in details. As well it is very important to know behavior of substrates of thin films. The general aim of the present investigation was to determine the influence of substrates on microhardness and other mechanical properties of layers. That aim was achieved by help of nanoindentation tests.

2. Experimental

2.1 Choice of materials

There were three materials (substrates) chosen for experiment. First material was high molybdenum speed steel for cold work applications AISI M2 which is useful for example for tools, punching, forming and pressing, etc.

Table 1

Average concentration of materials

	AISI M2	**AISI L2**	**TiAl6V4**
Al	-	-	6
C	0,8-1	0,4 -1	
Mn	0,2-0,4	0,1-0,9	
Si	0,35	0,5	
P	0,03	0,03	
S	0,03	0,03	
Cr	3,8-4,5	0,7-1,2	
Mo	5	0,25	
W	6	-	
V	1,8-2,2	0,1-0,3	4
Ti	-	-	rest

Unhardened low-alloy special-purpose tool steel AISI L2 was chosen as second material. Materials AISI M2 and AISI L2 have a suitable combination of wear resistance, toughness and compressive strength. Titanium alloy TiAl6V4, which is very unique material for biomedical applications, was chosen as third substrate. Table 1 shows the average concentration of above mentioned materials. The substrates with size 20 mm in diameter × 5 mm in thickness were polished prior to deposition to a surface roughness in the range of R_a = (0,02 – 0,03) μm.

2.2 Deposition process

Amorphous carbon films were deposited in a PACVD apparatus, which is shown in Fig.1. The chamber was 110 mm in diameter and 970 mm in long. Before loading in the chamber the polished substrates were chemically cleaned with acetone and isopropyl alcohol respectively in ultrasonic bath for 15 min. Then the samples were dewatered very carefully and they were loaded into the reaction chamber and mounted on working electrode.

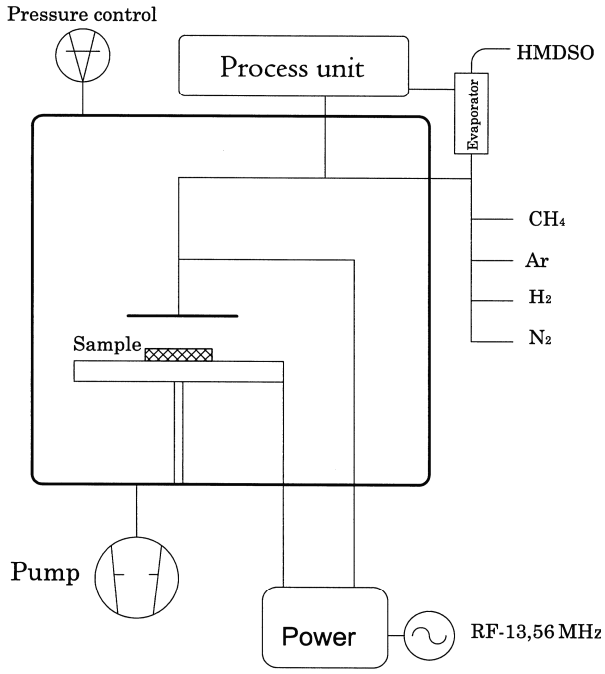

Fig. 1. A Schema of RF PACVD (13,56 MHz) equipment

The substrates were additionally cleaned in argon and then in nitrogen discharge at 0.16 Torr and 0.20 Torr respectively by Direct Current Plasma Actived Chemical Vapor Deposition (DC PACVD) plasma in order to remove impurities. For improvement of adhesion we decided to dope to introduce both silicon and nitrogen into carbon layers. Silicon was introduced from Hexamethyldisiloxane (HMDSO) - 98 % purity.

Methane was chosen as precursor for carbon deposition. So, the gas mixture of CH_4 (30 sccm), HMDSO (0.5 g/h) and N_2 (15 sccm) was introduced into RF PACVD reactor. The total work gas pressure was 1 Pa and during the deposition processes the total pressure was held constant. The applied RF 13,56 MHz power input was kept at 200 W. The process parameters such as pressure and gas flows were controlled by mass flow controllers and the pressure was controlled by a butterfly valve independently of the total gas flow.

A DLC films thickness of 1,3 μm was achieved after 35 minutes of RF PACVD deposition.

2.3 Nanoindentation

Determination of micro-hardness of the coatings has been carried out by nanoindentation. In this study, Vickers nanoindentation tests using the nanoindenter Shimadzu DUH 202 (mode 2) equipment were performed. This equipment had a Vickers shaped diamond tip with load resolution of 0.1 mN. Distinguishing resolution is 0.2 nm. Microhardness was calculated from the load-displacement curves using an analysis program. The specimen was put on the horizontal holder with a microscope directly located above the selected area. The conditions of the measurement are following: at a room temperature (25°C) and at a relative humidity around 55 %. The displacement during loading gives the so-called dynamic hardness H_D, which is expressed by the following equation:

$$H_D = \frac{F_{\max}}{26{,}43.h^2}\ , \qquad (1)$$

where $F_{\max}$ is the peak indentation load and h is the indenter penetration depth at $F_{\max}$. The load – displacement experiments were repeated on 2 independent locations of the surface of each specimen.

3. Results

In Vickers nanoindentation test, the following three samples were used. Measurements were performed gradually under the maximum load of 200g to obtain the microhardness values occurring on the top of the surface of the substrate under the thin film, and under 25g load to obtain the microhardness values occurring near the borderline of the thin film and the substrate as well as under the load of 5g and 2g to obtain the microhardness values particularly on the surface. Microhardness was calculated along formula (1).

The load/unload displacement curves for three different samples are shown in Fig. 2. This figure shows record of dependence of depth of

indent on the load during nanoindentation investigation of coating hardness. In this case the maximal loading 200 g was used. The microhardness was highest at speed steel AISI M2. Microhardness of system substrate-coating for AISI M2 is approximately 900 DHV, for AISI L2 is approximately 370 DHV and for TiAl6V4 is approximately 300 DHV.

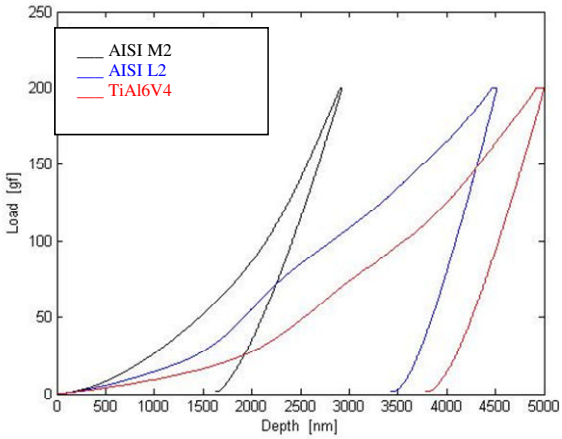

Fig. 2. Nanoindentation load-displacement curves of DLC films. Max. load 200 g was used
(full colour version available online)

The nanoindentation of curve with a maximal load 25 g (Fig.3) has a typical behavior during the nanoindentation test. Curves demonstrate higher microhardness than at 200 g load/unload. The microhardness was again highest at speed steel AISI M2. Microhardness of system substrate-coating for AISI M2 is approximately 1170 DHV, for AISI L2 is approximately 480 DHV and for TiAl6V4 is approximately 300 DHV.

In Fig. 4 is shown at further load reduction by a maximum of 5 g a share of substrate goes down, although it is marked. The highest hardness and further rising elastic deformation is shown in the first specimen (AISI M2) though it is smaller difference between steel AISI M2 and steel AISI L2.

In the other two specimens there is still a strong plastic deformation. A higher hardness is in the second specimen but a stronger elastic deformation is in the third specimen. Microhardness of system substrate-coating for AISI M2 is approximately 1180 DHV, for AISI L2 is approximately 750 DHV and for TiAl6V4 is approximately 480 DHV.

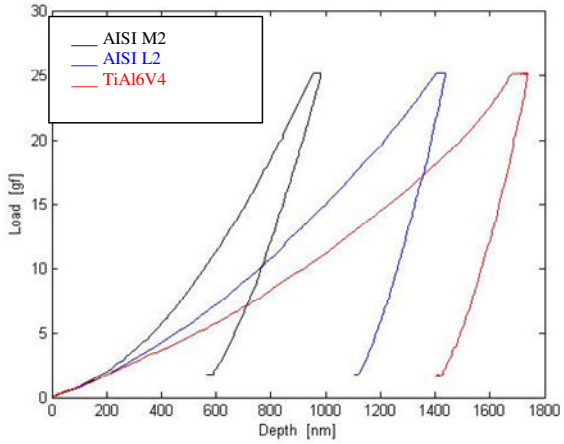

Fig. 3. Nanoindentation load-displacement curves of DLC films In this case the maximal loading 25 g was used
(full colour version available online)

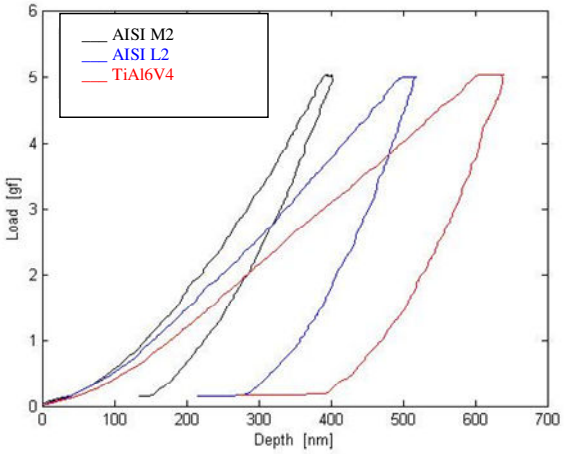

Fig. 4. Nanoindentation load-displacement curves of DLC films. In this case the maximal loading 5 g was used
(full colour version available online)

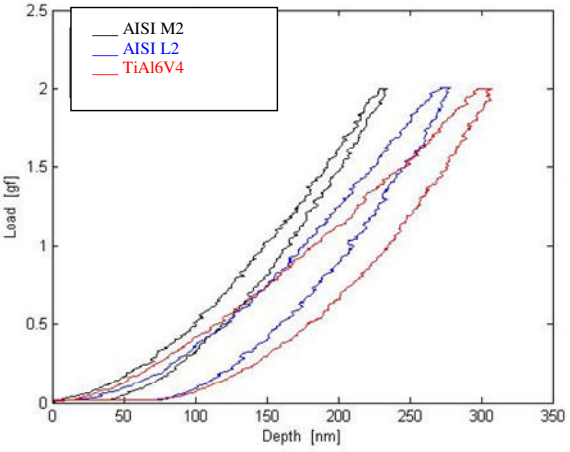

Fig. 5. Nanoindentation load-displacement curves of DLC films. In this case the maximal loading 2 g was used
(full colour version available online)

In Fig. 5 is shown registration of dependence of depth of indent on the load/unload during nanoindentation investigation of coating hardness at the maximal loading 2 g. A growth of elastic deformation of surface layers is still manifested with next decline of a standard load to 2 g. It was seen that all the data points are almost identical. The 2g load ensures that the substrate has minimal influence on the microhardness of the system substrate-film. All specimens, strictly speaking all films show evident elastic deformation. Although the influence of substrate is reducing, is still evident influence of substrate.

Microhardness of system substrate - coating for the specimen AISI M2 is 1460 DHV, for AISI L2 is 1000 DHV and for TiAl6V4 is 850 DHV.

4. Conclusions

We achieved DLC solid lubricant coatings by RF PACVD technology on three various substrates. The roughness of the coatings in the range R_a = (0,02 -0,03) μm, was approximately the same as the roughness of the substrate. The thickness of coatings was 1300 nm. The nanoindentation load-displacement curves of thin DLC films were determined using nanoindentation with Vickers diamond indenter, specifically by equipment nanoindentor Shimadzu DUH 202. The coatings DLC were adherent, hard and wear resistant.

- The loading part of the curve is a combination of elastic and plastic deformation, while the unloading curve is mainly dominated by the elastic deformation. Analyses of the loading curves are demonstrated by the significant dependence on the hardness of the substrate.
- The microhardness of all coatings increased with decreasing penetration load. In order words, influence of the substrate descends with the decline of the load, especially in the case, when the load/unload is extremely small, 5 g or 2 g. This verification is evident from records. It is obvious that the distance of single maximum decreases with decreasing load/unload.
- The hardened high speed steel AISI M2 shows more elastic deformation than the other materials. A significant plastic deformation is shown in the second specimen (unhardened tool steel AISI L2) and third titanium alloy specimen TiAl6V4**.**
- Finally, the microhardness values and elastic-plastic behavior of DLC system are significantly influenced by hardness of the substrates.

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