

# Microstructure and mechanical properties of hard carbon films prepared by heat treatment of a polymer on steel substrate

Xingbin Yan, Tao Xu, Xiaobo Wang, Huiwen Liu, Shengrong Yang\*

*State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*

Received 28 July 2003; accepted in revised date from 3 March 2004

Available online 14 July 2004

## Abstract

Hard carbon films were prepared on steel substrates by heat treatment of a polymer-poly(phenylcarbyne) at various temperatures in an Ar atmosphere. The influence of heat treatment temperature on the microstructure, surface roughness and mechanical properties of the resulting films was investigated by Raman spectroscopy, atomic force microscopy (AFM), nanoindenter, scratch and ball-on-disk sliding tests. The  $sp^2$  C fractions of the hard carbon films and the root mean square (RMS) roughness increased as the heat treatment temperature increased. The preparation at 800 °C gave rise to carbon films with the maximum hardness and the hardness dropped with the higher temperature due to graphitization. In addition, with increasing heat treatment temperature, critical load of the carbon films, the ability of friction reduction and wear resistance increased gradually. The influence of the heat treatment temperature on the mechanical properties of the hard carbon films is discussed in combination with the structural analysis.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Hard carbon films; Polymer precursor; Raman; Mechanical properties

## 1. Introduction

Much recent attention has been focused on diamond-like carbon (DLC) films (also known as amorphous hydrogenated carbon (a-C:H) films). Their high hardness, low friction coefficient and low wear rate make them to be attractive for tribological applications [1–6]; also their electrical and thermal properties are attractive for electronic applications [7,8]. These similarities with diamond are caused fundamentally by the fact that a greater part of DLC consists of a local  $sp^3$ -bonding configuration. DLC films can be deposited using various chemical and physical vapor deposition techniques such as filament-assisted chemical vapor deposition [9] RF-plasma-activated chemical vapour deposition [10,11], filtered cathodic vacuum arc [12], microwave plasma-assisted deposition [13], mass-selected ion beam deposition [14] and pulse laser deposition [15]. Using these methods, however, the applications of DLC films have been limited owing to the complicated equipment, rigorous condition of preparation and unsatisfactory adhesion of DLC films to metal (especially steel) substrates. Moreover, it is very difficult and costly to

deposit the DLC films on large area and complex shape substrates. A new technique for synthesizing hard carbon films on silicon and graphite substrates from a polymer precursor at low pressure was developed by Visscher et al. [16–20]. The polymer is easily soluble in many organic solvents, forming a solution that can be applied to various substrates by spinning, dipping or draining. Using this method, the polymer film can be coated on to a complex form with a large area both inside and outside, simultaneously. All previously reported results indicate that it is worthwhile continuing research on this method.

In this work, we focus on the mechanical properties of hard carbon films prepared on steel substrates by heat treatment of the polymer precursor. The influence of the heat treatment temperature on the mechanical properties of the hard carbon films was discussed in combination with the structural analysis.

## 2. Experimental

### 2.1. Preparation of hard carbon films

The poly(phenylcarbyne) polymer was inexpensively synthesized by reductive condensation of 1,1,1-trichloro-

\* Corresponding author. Tel.: +86-931-8277851.  
E-mail address: [yanxingbin@sina.com](mailto:yanxingbin@sina.com) (S. Yang).

toluene monomer with an ultrasonically generated NaK alloy emulsion in tetrahydrofuran (THF) under an inert atmosphere (argon) [14]. It is composed of randomly constructed rigid network of tetrahedral hybridized phenyl-carby units and can be converted into hard carbon films by pyrolysis. The polymer power was dissolved in THF, followed by spin coating onto the surface of polished AISI310 steel (1Cr25Ni20Si2) substrates (thickness 3.0 mm, surface roughness  $R_a < 0.2 \mu\text{m}$ ), to allow the formation of the polymer films after the removal of the THF by evaporation. Then the polymer films were inserted into a quartz tube and heated at 100 °C for a few minutes to evaporate the solvent; in the end, the target hard carbon films were obtained by sintering of the polymer films at 600–1000 °C in Ar atmosphere for 2 h and allowing to cool naturally.

## 2.2. Characterization of hard carbon films

The thickness of the polymer films after drying and after heat treatment was measured using a surface profile instrument.

Raman spectroscopic measurements were carried out to investigate the structure of the carbon films on a SPEX1403 Raman spectrometer, operating with an Ar<sup>+</sup> laser of 488 nm.

An atomic force microscope (AFM) of model SPM-9500 (Shimadzu, Kyoto, Japan) with a Si<sub>3</sub>N<sub>4</sub> probe was used to observe the morphology of the carbon films, using “constant force” mode to obtain the morphology image.

## 2.3. Mechanical properties of hard carbon films

In order to truly investigate the influence of heat treatment temperature on mechanical properties of the resulting films, we prepared the hard carbon film with the same thickness of 1000 nm. The thickness was controlled through varying the rotate speed of spin apparatus. The relative error for the thickness was not more than 5%.

The Vickers hardness of the steel substrate before and after heat treatment,  $HV_{0.05}$ , was measured on a hardness tester (MH-5-VM, China) with a load of 50g. The hardness of carbon films was determined using a Nano Indenter II indentation system (MTS Systems). Indentations were made by using a Berkovich diamond tip. The hardness ( $H$ ) was measured continuously during the indentation and the force–displacement curves were measured. In this experiment, the indenter displacement for all samples was 100 nm and average values were obtained from five indentations on the different parts of each sample in order to obtain reliable hardness values of the carbon films.

The adhesion strength was measured by the UMT-2MT tribological test system with a scratch option. The radius of a diamond indenter in the scratch test was 0.4 mm and the measurements were carried out at a table speed of 3 mm/min and a load increase rate of 170 mN/min. Film's failure is determined by an acoustic emission detector. The load at

which fracture or spalling takes place is defined as the critical load ( $L_c$ ), and has been proposed to be a parallel comparison measure for practical adhesion strength of hard carbon films prepared various heat treatment temperatures.

The friction and wear behaviors of the carbon films were evaluated on the UMT-2MT tribological test by sliding the films on steel substrate against an Al<sub>2</sub>O<sub>3</sub> ceramic ball (diameter 4 mm,  $HV$  1400 ~ 1700, RMS 5.6 nm) at a sliding frequency of 5 Hz, a sliding distance of 6 mm, and a load of 2.0 N. The friction test rig provides a reciprocoating–sliding configuration. All the tests were conducted at room temperature and a relative humidity of 40%–45%. All balls were cleaned ultrasonically by acetone prior to measurement and a new ball or a new position of the ball was used for each friction testing. The friction coefficient and sliding time were recorded automatically during the test. It was assumed that lubrication failure of the film occurred as the friction coefficient rose sharply to a higher and stable value similar to that of a cleaned bare steel substrate against the same counterpart. The sliding cycle accounted from the sliding time and sliding frequency was considered as the wear-resistance life of the film.

## 3. Results and discussion

### 3.1. Characterization of structure and morphologies of hard carbon films

Table 1 shows the thickness of the polymer films on steel substrates heat-treated with increasing temperature. We can see that the thickness of polymer film reduces obviously in the temperature range from 200 to 800 °C. It indicates that the significant weight loss of PPC occurs, which is associated with the decomposition of polymer and transformation of hard carbon film. Furthermore, the slight decrease of thickness occurs above 800 °C, which may be due to the dehydrogenation of the carbon films.

Raman spectroscopy is one of the most widely used techniques to investigate the state of carbon in detail, because of its sensitivity to changes in translation symmetry. Fig. 1(a) shows the evolution of the Raman spectra of the polymer films on steel substrates heat-treated with increasing temperature. The spectrum of the polymer film heat-treated at a temperature of 400 °C is similar to that of the original polymer film. There is no detectable feature to be observed in the original polymer film. This result indicates that little change in the polymer occurs for a temperature below 400 °C. A weak shoulder appears at about 1588  $\text{cm}^{-1}$  in the spectrum of the polymer film heat-treated at

Table 1  
The thickness of the polymer films on steel substrates heat-treated with increasing temperature

Temperature/°C	25	200	400	500	600	700	800	900	1000
Thickness/nm	3240	3200	2450	1490	1180	1000	930	910	900