Vol 16 No 4, April 2007
1009-1963/2007/16(04)/1105-06
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Nanocomposite TiC/a-C:H film prepared on titanium aluminium alloy substrates by PSII assistant MW-ECRCVD*

Ma Guo-Jia(马国佳)[a)†], Liu Xi-Liang(刘喜亮)[b)], Zhang Hua-Fang(张华芳)[a)], Wu Hong-Chen(武洪臣)[a)], and Peng Li-Ping(彭丽平)[a)]

[a)] *Beijing Aeronautical Manufacturing Technology Research Institute, Beijing* 100024, *China*

[b)] *Harbin Engineering University, Harbin* 150001, *China*

(Received 3 June 2006; revised manuscript received 20 October 2006)

Thin films of titanium carbide and amorphous hydrogenated carbon have been synthesized on titanium aluminium alloy substrates by PSII assisted MW-ECRCVD with a mirror field. The microstructure, chemical composition and mechanical property were investigated. Using XPS and TEM, the films were identified to be a-C:H film containing TiC nanometre grains (namely, the so-called nanocomposite structure). The size of TiC grains of nanocomposite TiC/DLC film is about 5 nm. The nanocomposite structure has obvious improvement in the mechanical properties of DLC film. The hardness of a-C:H film with Ti is enhanced to 34 G Pa, while that of a-C:H film without Ti is about 12 G Pa, and the coherent strength is also obviously enhanced at the critical load of about 35N.

Keywords: nanocomposite, TiC/a-C:H, diamond like carbon film, PSII
PACC: 5275R, 8115C, 8115H, 6855

1. Introduction

Diamond-like carbon (DLC) film as an effective protective coating that offers protection against wear, friction and corrosion is used in many fields, ranging from engineering tools to electronic devices, due to its excellent properties, such as high hardness, high elasticity, low wear and low friction in contact with several materials and optical transparency in IR region. However, the high intrinsic compressive stress between the film and substrate results in a serious problem that limits the adhesion, and the sp^3 bond of DLC film would be graphitized when the ambient temperature increases to 350 °C,[1] in addition, the hardness of the a-C:H film is lower than other hard carbon films. A limited number of industrial applications of DLC coating are practiced due to the above problems. In recent years, many methods have been used to solve the problem, for example the incorporation of some elements (silicon, nitrogen and some metals).[2−6]

In this study, the a-C:H films containing Ti were formed by combined ECR-CVD and PSII. The PSII technology was used to form a transitive layer for enhancing its coherent strength. The properties, such as chemical structure and mechanical properties of the DLC films with or without Ti were investigated.

2. Experimental details

The schematic drawing of the experimental equipment is illustrated in Fig.1. Working gases were fed into the discharge chambers through a concentric gas ring. The basic pressure of 3×10^{-4} Pa in the reactor was attained using a turbo-molecular vacuum pumping system. Microwave was introduced into the discharge chambers through waveguide tubes. All the experiments were carried out with 360 W microwave power and 64 A current in the magnetic coil. Polished titanium aluminium alloy samples were used as the substrates. Because there is normally some contamination on the surface, the substrates were ultrasonically pre-cleaned and rinsed in an ethanol bath. In this work, the DLC films were synthesized using the processing parameters listed in Table 1.

*Project supported by the National Defence Key Laboratory Foundation of China (Grant No 51461070905ZS5003).
†E-mail: mgjm7678@yahoo.com.cn

Table 1. Parameters for preparing the nanocomposite DLC film.

	Cleaning	TiC transitive layer (Implantation)	TiC/DLC (Deposition)
Gas flow rate/sccm	$Q_{Ar} = 5$	$Q_{Ar} = 4$ $Q_{C2H2} = 20$	$Q_{C2H2} = 40$
Working pressure/GPa	0.06	0.065	0.065
Substrate bias/V	−600	−20k (pulse)	−500
Target voltage/V	0	−550	−500
Preparation time/min	30	10	50

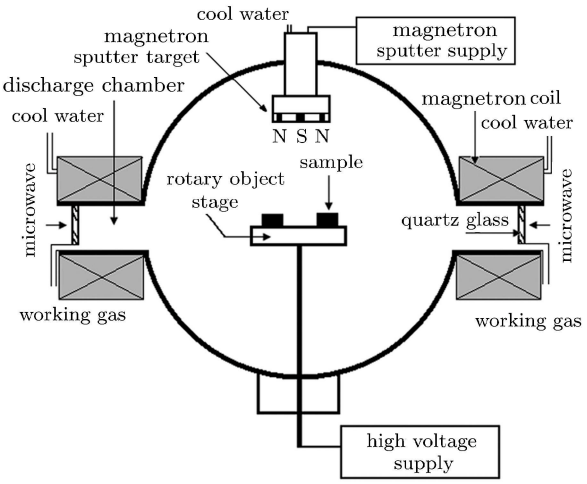


Fig.1. Schematic view of ECR-MWPSII system.

3. Results and discussion

3.1. Chemical composition and bonding

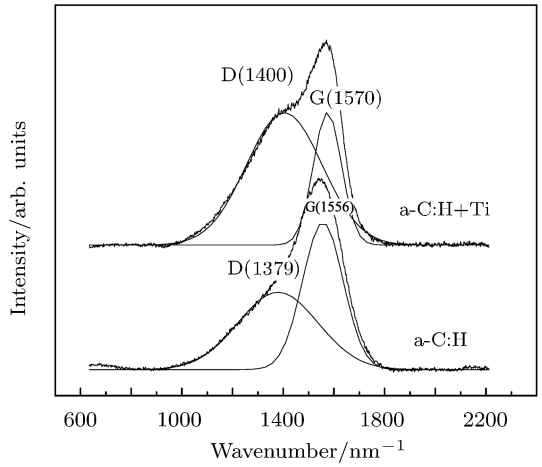


Fig.2. Raman spectra of the a-C:H films.

The Raman spectra of the films with or without Ti are shown in Fig.2. The Raman spectrum is the best way to obtain the detailed bonding structure of DLC, and it proved the presence of the amorphous phase in these coatings. More generally, the bonding nature of carbon in the film can be clarified using the Raman peaks. In room-temperature deposited hydrogenated amorphous carbon (a-C:H), the sp^2 cluster size and the sp^3 content are identified by the following two parameters:[6,7] 1) the I_D/I_G area ratio of the two peaks (the smaller the I_D/I_G value of the film, the higher the sp^3 content in the film); 2) the centre position ω_G of the G peak (G peak will shift to low wavenumber with the sp^3 content increasing). As shown in Fig.2, the G peak position of the Ti doped a-C:H film moved up to high wavenumber and the I_D/I_G value of this film was estimated to be increasing using the Gaussian-curve function, so it is believed that the sp^3 content of Ti doped a-C:H film was decreased.

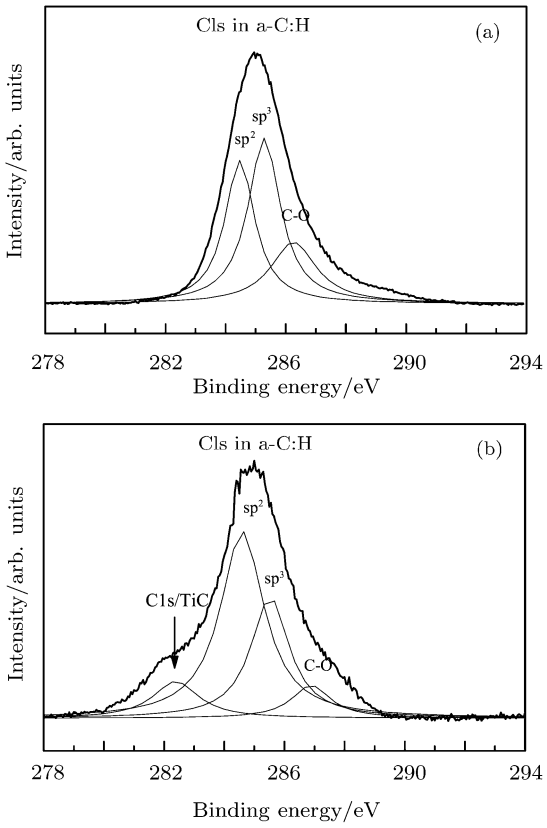


Fig.3. XPS and its decomposition spectra. (a) a-C:H; (b) a-C:H containing Ti.

Figure 3 shows the C1s XPS peak of the a-C:H films with or without Ti. Some researchers reported that the C1s binding energies of graphite (sp^2) and the diamond (sp^3) were 284.3eV and 285.2eV,[8,9] respectively. For discrimination between the Ti-free carbon film and the Ti-containing carbon film, the C1s peaks in Fig.3 were fitted using Gaussian-curve function. The film without Ti was fitted to three peaks including sp^2 bond (284.4eV), sp^3 bond (285.3eV) and C-O bond (286.3eV). The film with Ti was fitted to four peaks including sp^2 bond (284.6eV), sp^3 bond (285.5eV), C-O bond (286.6eV) and C1s/TiC(282eV). Both C1s peak positions in Fig.3 lie between 284.3 eV and 285.2 eV, which suggests that the film is a typical DLC film. In the light of the area ratio of sp^3C1s peak and whole C1s peak, the sp^3 fraction of the a-C:H films without or with Ti is about 40.2% and 33%, respectively.

3.2. Microstructure and grain size

The typical x-ray diffractogram of the a-C:H film with Ti is given in Fig.4. For avoiding the influence of Ti diffraction peaks of the TiAl alloy substrate on TiC diffraction peaks of the DLC film doped with Ti, silicon substrate is used in XRD analysis. Three broad peaks are observed to exist in the XRD patterns of Ti-containing a-C:H films, including TiC(111), TiC(200) and TiC(220) reflections, which can also be observed in the SAD pattern (Fig5). The XRD information can also be used for estimating the grain size in the film. If grain size is assumed to be solely responsible for the observed peak broadening, an upper limit of TiC grain size can be estimated using the Scherrer equation[10]

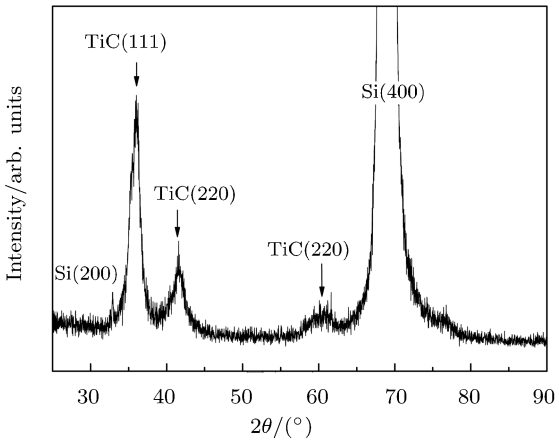


Fig.4. The XRD spectrum of a-C:H containing Ti film.

$$D = \frac{0.9 \times \lambda}{\omega \times \cos\theta}, \tag{1}$$

where D is the grain size, λ is the wavelength, ω is the full width at half maximum of the peak, θ is the Bragg diffraction angle. The value of estimated TiC grain size is about 5.7 nm, which is confirmed by Fig.6.

Figure 5 shows a selected area electron diffraction (SAD) pattern of the a-C: H film with Ti. Crystalline diffraction rings are clearly visible, which can be indexed as TiC(111), TiC(200) and TiC(220) reflections. These crystalline diffraction rings are very sharp. Various diffraction rings corresponding to different crystallographic planes show that the crystalline precipitates exist randomly in the matrix without any preferred crystallographic texture.

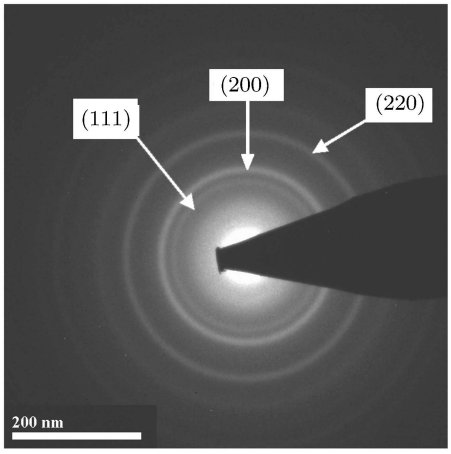


Fig.5. A selected area electron diffraction pattern of a-C:H containing Ti film.

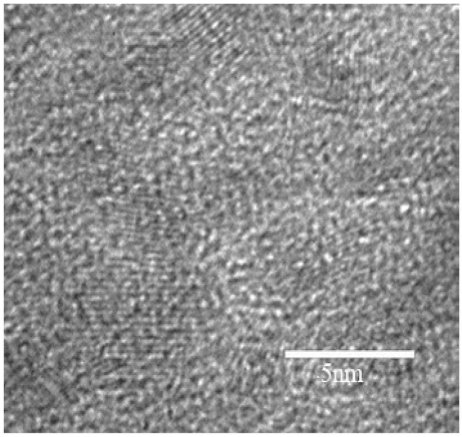


Fig.6. TEM micrograph of Ti-containing DLC film.

Figure 6 shows TEM micrograph of the Ti-containing DLC film. The crystalline precipitates

are uniformly distributed in the amorphous matrix. The size of crystalline precipitates is less than 5nm. The XRD and TEM observations reveal that TiC nanocrystalline clusters are embedded in the amorphous hydrocarbon matrix and the cubic crystallites are surrounded by the amorphous phase.

3.3. Mechanical properties

Nanohardness and elastic modulus versus displacement of a-C:H film with or without Ti are plotted in Fig.7 and Fig.8, respectively. The continuous stiffness method is used in this study to determine the coating hardness and the elastic modulus.[11]

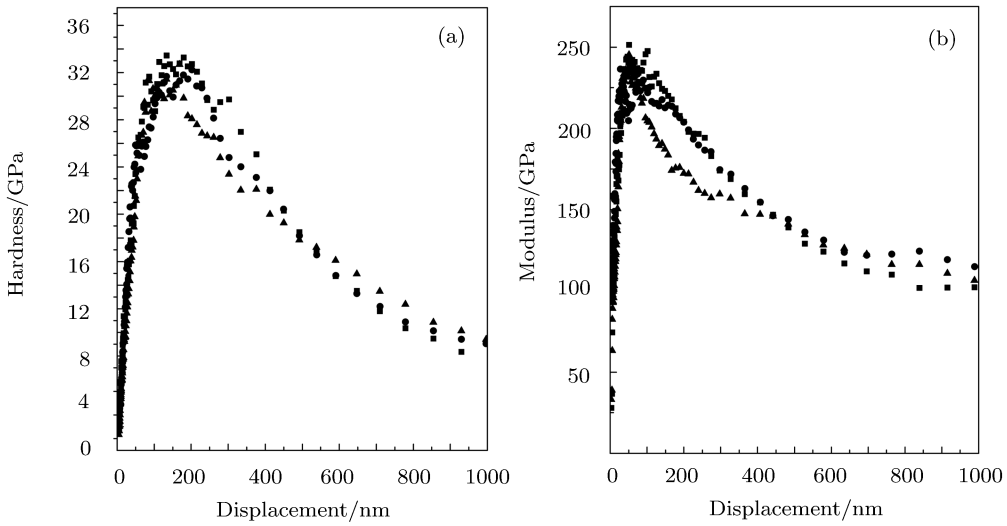


Fig.7. Hardness and modulus versus displacement of Ti-containing a-C:H film.

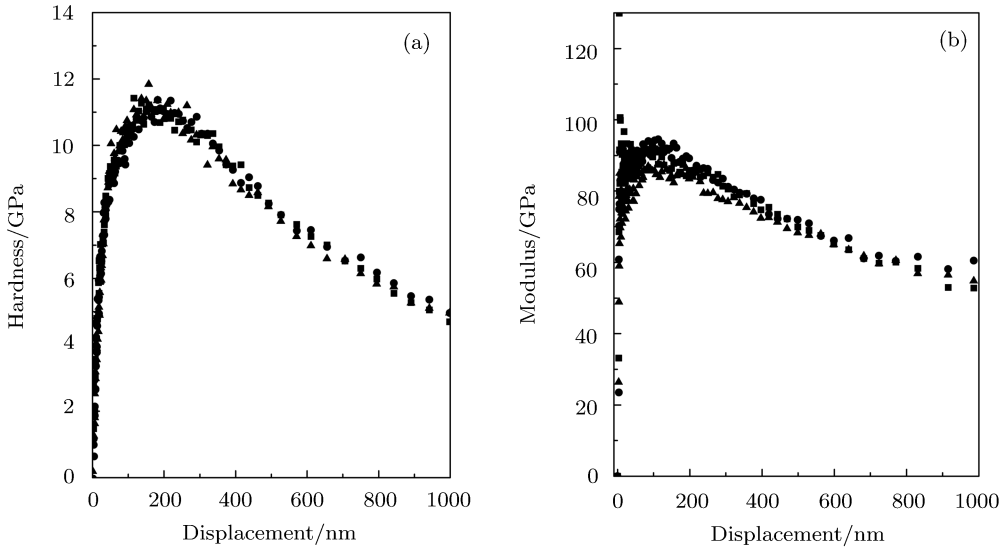


Fig.8. Hardness and modulus versus displacement of a-C:H film.

Nanoindentation tests with a maximum depth of 1000nm were performed on the Ti doped a-C:H film. When the indentation depth is small, the hardness value of the film increases with the indentation depth increasing, and the highest hardness is 34 GPa. Then, the hardness value gradually decreases to the hardness value of the TiAl alloy substrate (about 5 GPa) as indentation depth increases. The elastic modulus curve behaves similarly as does the hardness curve. The highest elastic modulus obtained was 250 GPa. As shown in Fig.8, the highest value for a-C:H film without Ti is 12 GPa, and the highest elastic modulus

value is 98 GPa. Compared with a-C:H film without Ti, the hardness and elastic modulus are distinctly enhanced. The presence of TiC phase in amorphous carbon film and complex grain boundaries must have caused the hardness enhancement.[12]

Figure 9 shows the coefficient of friction as a function of the scratch distance under various ramping normal loads. The biggest ramping normal load is 300mN. When the scratch distance is between 100 and 250 μm, the friction coefficient curve is comparatively stable, which corresponds to the friction coefficient of Ti-containing a-C:H film (about 0.09). The friction coefficient begin to increase when the scratch pin scratches into the interface between the film and the substrate, then the friction coefficient gradually increases to the substrate coefficient as the scratch distance increases.

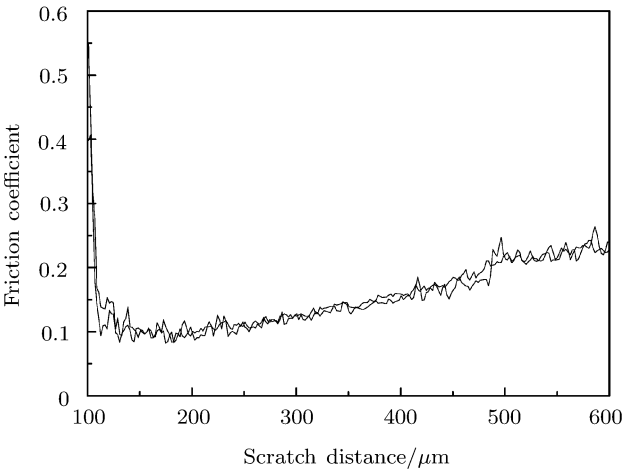


Fig.9. Friction coefficient versus scratch distance of Ti-containing a-C:H film.

The microscratch curves of the a-C:H films with or without Ti on TiAl alloy substrates are shown in Fig.10. The maximal load is 50 N and the scratch distance is 5mm. Due to using friction force sensor in the experiment, the ordinate is friction force intensity of the samples. The curve shows strong fluctuation when the load is greater than the critical load, which indicates that the film on the substrate has suffered fracture. As evidenced in Fig.10, the critical load of the a-C:H with Ti, which is about 35 N, is higher than that of the a-C:H without Ti (about 7.5 N). The improvement in adhesion strength is a result of the Ti doping and the application of PSII technology.[13] Detailed reasons are as follows: firstly, the component gradient variable interface is formed on the substrate surface by Ti and C ions implantation; secondly, deposition process during Ti and C ions implantation creates a transitive layer, which is in favour of releasing internal residual stress; and thirdly, Ti doping mitigates the influence of mismatch of the coefficients of thermal expansion of the DLC film and Ti alloy substrate.

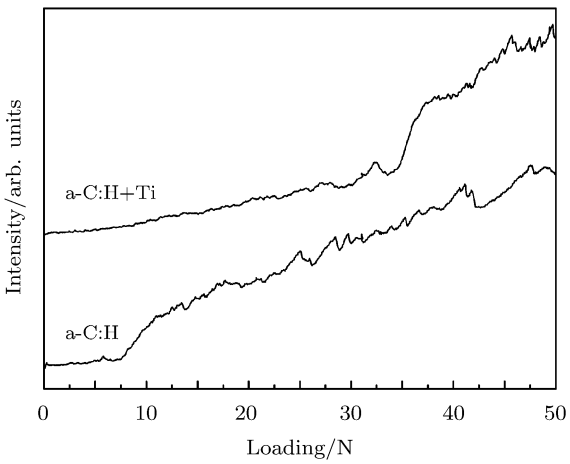


Fig.10. Microscratch cure obtained from a-C:H film and Ti-containing a-C:H.

4. Conclusion

The characterization by Raman spectroscopy confirmed the DLC characteristics of the films. XPS, XRD and TEM analyses showed that TiC nanocrystalline cluster were embedded in an amorphous hydrocarbon matrix, which indicated the film is nanocomposite TiC/a-C:H film.

PSII assisted MW-ECRCVD with a mirror field could be used to prepare nanocomposite TiC/a-C:H film on titanium alloy substrate.

The highest hardness of nanocomposite TiC/ a-C:H film obtained by nanoindentation measurement is 34 GPa and the friction coefficient of nanocomposite TiC/ a-C:H film obtained by nanoscratch measurement is 0.09. The nanohardness of the metal free a-C:H film is about 12 GPa, the critical load of the a-C:H with Ti, which is about 35 N, is significantly higher than that of the a-C:H without Ti (about 7.5 N), so it could be concluded that the mechanical properties of the a-C:H film are enhanced by Ti doping.

References

[1] Zhang S, Bui X L, Jiang J R and Li X M 2005 *Surf. Coat. Technol.* **198** 206

[2] Won Jae Yang, Yong Ho Choa, Kwang Bo Shim, Koichi Niihara and Keun Ho Auh 2003 *Thin Solid Films* **434** 49

[3] Ju J H, Xia Y B, Zhang W L, Wan L J, Shi W M, Huang Z M, Li Z F, Zhang G Z and Tang D Y 2000 *Acta Phys. Sin.* **49** 2310 (in Chinese)

[4] Feng B, Cao D M, Meng W J,J Xu, Tittsworth R C, Rehn L E, Baldo P M and Doll G L 2001 *Thin Solid Films* **398** 210

[5] Ikeyama M, Nakao S, Miyagawa Y and Miyagawa S 2005 *Surf. Coat. Technol.* **191** 38

[6] Tuinstra F and Koening J L 1970 *J. Chem. Phys.* **53** 1126

[7] Yang W B, Fan S H, Zhang G L, Ma P N, Zhang H Z and Du J 2005 *Acta Phys. Sin.* **54** 4944 (in Chinese)

[8] Diaz J, Paolicelli G and Ferrer S 1996 *Phys. Rev.* B **54** 8064

[9] Mei X X, Xu J and Ma T C 2002 *Acta Phys. Sin.* **51** 1875 (in Chinese)

[10] Voevodin A A and Zabinski J S 1998 *J. Mater. Sci.* **33** 319

[11] Li X, Tang Z A, Ma G J, Wu G M and Deng X L 2003 *Chin. Phys.* **20** 692

[12] Zehnder T and Patscheider J 2000 *Surf. Coat. Technol.* **133** 138

[13] Klages C P and Memming R 1989 *Mater. Sci. Forum* **52** 609