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Composition and structure of Ti-C/DLC graded composite films①

SUN Ming-ren(孙明仁), XIA Li-fang(夏立芳)
(School of Materials Science and Engineering, Harbin Institute of Technology,
Harbin 150001, China)

[Abstract] The Ti-C $\rightarrow$ DLC gradient composite films were characterized systematically. The elemental depth profile and elemental chemical state evolution were determined by X-ray photoelectron spectroscopy (XPS). The transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to study the structure of interfacial zone between DLC film and Ti-C layers. Results show that there are composition transition zone between DLC film and either Ti-C layer or steel substrate on condition that pre-deposited Ti layers on the steel substrate then plasma based bias deposited DLC films. In Ti-C graded layer, the chemical state of titanium and carbon are changed gradually. The structures of zone in Ti-C layer near the DLC film is consisted of random oriented nanocrystallines TiC dispersed in amorphous DLC matrix. The structure of the zone between DLC film and Ti-C graded layer is gradually changed too.

[Key words] gradient composite films; DLC films; composition; structure
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1 INTRODUCTION

Diamond-like carbon (DLC) films have many superior properties in terms of optics transparency, hardness, chemical inertness to strong acid and alcali and hydrofluoric acid, low friction and wear resistance in atmosphere and cosmos-like environment, and so on. Hence, DLC films have extremely potential for application in precision mechanisms, optics parts, space navigation etc[1~5]. A plasma based deposition technique for fabricating DLC films has been developed, which possesses the characteristic of low deposition temperature, and large scale[6, 7]. At the same time, considering the poor adhesion of DLC films to most of metals substrates, especially to steel substrates[8~10], the Ti-C graded transition layers have been constructed between DLC film and GCr15 bearing steel substrate based on the ion implantation effects by negative high voltage pulses. Thereby, the Ti-C $\rightarrow$ DLC graded composite films were deposited[11]. In this paper, the elemental depth profile of Ti-C/DLC graded composite films and elemental chemical state evolution of Ti-C layer were characterized by X-ray photoelectron spectroscopy (XPS). The structure of transition zone between DLC film and Ti-C graded layers were also investigated by TEM and HRTEM characterization.

2 EXPERIMENTAL

A commercial GCr15 bearing steel was used as the substrate material. The size and heat treatment conditions were the same as Refs. [7, 11, 12]. The preparation of Ti-C/DLC graded composite films were carried out on type DLZ-01 plasma based ion implanter which has been described in detail elsewhere[12]. Firstly the titanium layers were deposited on substrates by unbalanced magnetron sputtering to different thickness, then these substrates were implanted and deposited with carbon in situ as follows: the substrates were surrounded with plasma generated by electron impact, and a negative pulse bias voltage (− 50 kV, and/or primary − 50 kV then − 30 kV) is applied to the substrate. As the bias voltage is − 50 kV or − 30 kV, the working gas (used for generating plasma) is acetylene or acetylene plus hydrogen, respectively. The flow ratio of acetylene to hydrogen was 1∶1. The plasma density was about 10^8/cm^3. The detail processing are listed in Table 1.

Table 1 Preparation processing of specimens

Specimen	Ti layers thickness/nm	Treating time/h (bias − 50 kV; C_2H_2)	Treating time/h (bias − 30 kV; $C_2H_2/H_2 = 1$)
T1	80	3	No
T2	240	3	No
T3	180	3	2
T4	300	3	2

The elemental depth profile of Ti-C/DLC graded composite films and elemental chemical state evolution of Ti-C layer were analyzed by XPS with a PHI5700 ESCA multi-system, Mg K$_\alpha$ radiation. XPS data were obtained in retarding potential mode. For depth profile analysis, a 3 kV Ar ion beam with a raster size of 4 mm × 4 mm was used for sputtering, the sputtering current density was about 30 μA/cm^2, analysis

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and sputtering were performed in alternating mode, and an area of analysis, d0.4mm, was used. The plan-view TEM (and/or HRTEM) observations of the Ti-C layer structures and cross-section transmission electron microscopy (XTEM) observations of the transition layer structures were carried out with a JEM 200 CX TEM operating at 120keV, and an H-9000 NAR HRTEM operating at 300keV, respectively.

3 RESULTS AND DISCUSSION

3.1 Composition of Ti-C/DLC graded composite films

XPS composition depth profiles for four groups of specimens are shown in Fig. 1. It can be seen that surface layer on the specimen are homogeneous DLC deposited layer. Furthermore, a Ti-C layer between DLC film and substrate steel GCr15 has the character of graded transition layer in both composition and structure. This layer may be formed by that the effect of ion implantation and the implantation mixing for pre-deposited Ti layers caused by negative pulsed bias of − 50kV at primary stages of DLC film forming. Thus, the Ti-C layer was combined with DLC film gradually. The DLC film deposition rate of second stage was about 4~ 5 times greater than that of first stage. The composition, structure and properties of the DLC films formed at first stage are different from second stage. Compared with first DLC layer, the second DLC layer contained more sp^3 bond and exhibited higher resistance and hardness[7,11], therefor, two DLC layers that deposited by two stages were also combined gradually.

Compared Figs. 1(a), (b) with Figs. 1(c), (d), it is apparent that compositional grads of titanium and carbon in Ti-C layers side where near the DLC films are slower for Figs. 1(c) and (d). It seems that the ions implanted maximum range in initial stages of second step deposition was near or greater than the thickness of DLC films deposited by first step, so the compositional grads of titanium and carbon in Ti-C layers are slowed down. In regard to the compositional depth profiles, the different Ti-C layers can be formed between DLC films and GCr15 steel substrates by controlling the thickness of pre-deposited Ti layers. A Ti layer existed obviously in Ti-C layers where near the side of GCr15 steel substrate when the pre-deposited Ti layer was thicker (Fig. 1(c)), and the implanted carbon ions had no effect on the primary Ti/Fe interface for the DLC film forming. Thereby the depth profiles were rapid for titanium and iron. As the pre-deposited titanium layer was about 240nm, the primary Ti/Fe interface was broadened owing to the diffusion acceleration by ions collision cascade (Fig. 1(a))[13]. Moreover, as the pre-deposited titanium layer was less than the range of ions implantation in the stage of DLC forming, the primary Ti/Fe interface was broadened, and there was a lack of pure titanium tier in the Ti-C layer. Since many of ions and/or particles impenetrate the primary Ti/Fe interface, a C-Ti-Fe mixing interfacial layer was formed. In a critical condition, C and Ti compositional grads impenetrate Ti-C layer even, and the primary Ti/Fe interface changed into a interfacial mixing layer consisted of Ti and Fe mainly (Fig. 1(d)).

3.2 Evolution of elemental chemical states in Ti-C layer

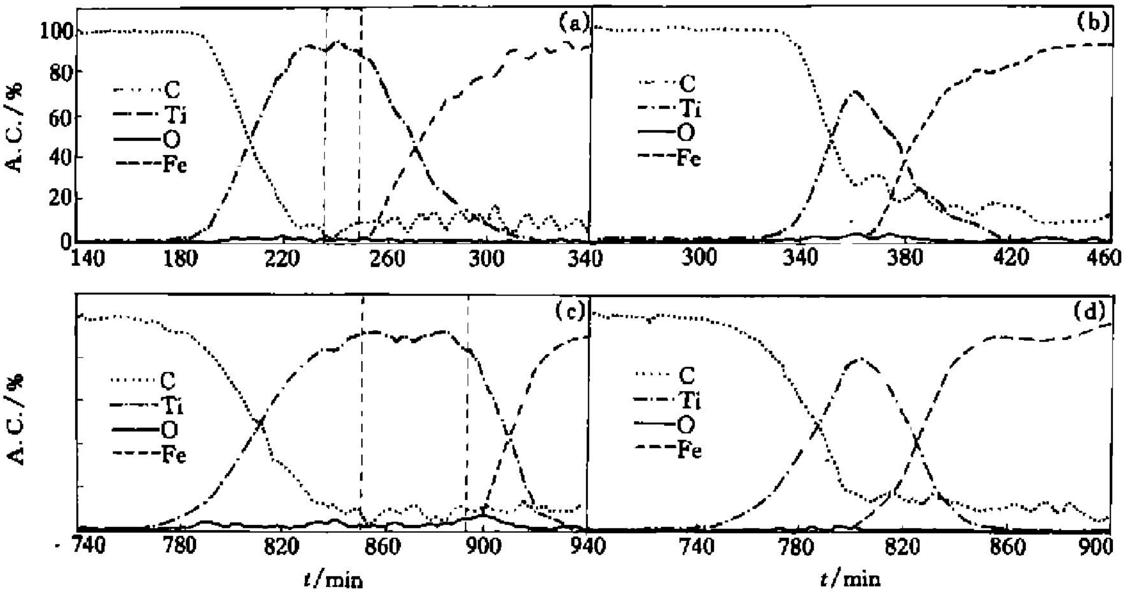

Fig. 1 XPS depth profile of Ti-C/DLC graded composite films
(a) —T2; (b) —T1; (c) —T4; (d) —T3

The evolution of C1s and Ti2p spectra for T2 group specimen is shown in Fig. 2 as a function of sputtering time. It can be seen from Fig. 2 that the chemical states of carbon and titanium evolved with the Ti-C layer depth. In the zone bordered on the DLC film (189.5 min sputtered), the basis is carbon, the C 1s binding energy is 284.30 eV, that is in agreement with the value of diamond-like carbon after Ar ion bombardment essentially[12]. Furthermore, in the C 1s spectrum, a new peak with low binding energy seems to be appeared, which implied the new chemical state forming for carbon. Here, the peaks of Ti2p were located at 454.88 eV and 460.75 eV, for Ti2p$_{3/2}$ and Ti2p$_{1/2}$ respectively, which are in agreement with the Ti2p binding energy for TiC[14~16]. As sputtering time is 204 min, a double peak feature was appeared distinctly for the C1s spectrum, as a result of a peak positioned at 281.75 eV developed markedly which corresponds to the C 1s for TiC essentially. Again, the peak positioned at the high binding energy side of C 1s transition was shifted to low binding energy slightly attributed to increasing of the solid-solved carbon. The Ti2p spectrum located between the chemical state of α-Ti and TiC is corresponding with the C 1s spectrum. The fitted results for C 1s and Ti2p are illustrated in Fig. 3. The concentration of carbon and titanium for this depth are about 59% (mole fraction) and 39% (mole fraction) respectively from the depth profile analysis (Fig. 1(a)). The components with TiC state for carbon and titanium are 17.60% (mole fraction) and 22.62% (mole fraction) respectively calculated by the area of fitted peak that represented a certain elemental chemical state in proportion of the area of C 1s and/or Ti2p spectra, so the Ti component with α-Ti elemental chemical state is about 16.38% (mole fraction). As 234 min sputtered, in the C 1s spectrum, a peak positioned at the low binding energy side grew to be a basis, and the peak positioned at the high binding energy side grew to be an obscure. Here, the carbon content in Ti-C layer is low and exists with TiC chemical state mainly and a small amount of residual carbon is solid-solved in titanium lattice. The peaks of Ti2p located at 454.00 eV and 460.10 eV for Ti2p$_{3/2}$ and Ti2p$_{1/2}$ respectively, which were near 2p binding energy of α-Ti, because the TiC quantity is less, and the Ti2p spectrum is dominated by α-Ti mainly. Compared with the montage display of Fig. 1, it can be considered that from the side bordered DLC film to the side bordered on substrate, primary, the basis is carbon and the diamond-like carbon is dominant, a small quantity of Ti existed with the TiC state essentially in Ti-C layers. With increasing the Ti content and decreasing the C content, the proportion of α-Ti phase was increased, as well as, it was increased continuously that the proportion of carbon existed with TiC chemical state in total carbon content for different depth. A small quantity of carbon was existed with TiC chemical state mainly, as the titanium is basis in Ti-C layer.

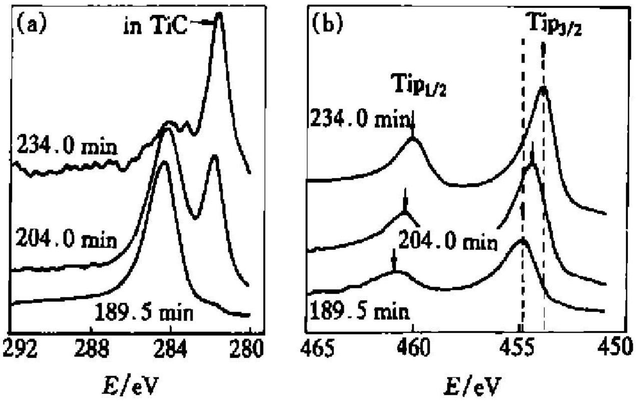

Fig. 2 Evolution of C 1s and Ti2p spectra as function of sputtering time
(a) —C 1s spectra; (b) —Ti2p spectra

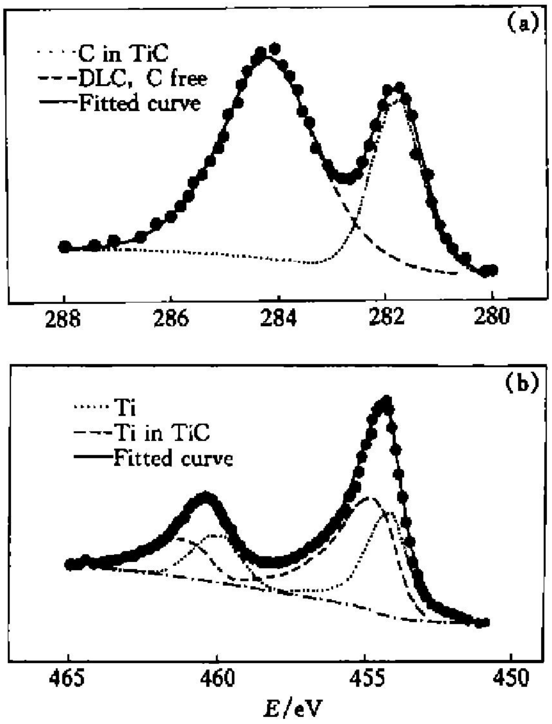

Fig. 3 Fitting results for C 1s and Ti2p spectra
(a) —C 1s spectrum; (b) —Ti2p spectrum

3.3 TEM and HRTEM characterization for Ti-C/DLC interface

The structure of interfacial zone was investigated by TEM and HRTEM characterization for Ti-C/DLC graded composite film. The TEM micrograph and selected area electron diffraction patterns (SADP) are shown in Fig. 4. The granular second phase was dispersed on a characterless matrix, moreover the SADP appeared a halo feature, which implicates that the matrix is amorphous structure. A HRTEM image for a same sample is shown in Fig. 5. It is clear that from the HRTEM image the granular second phase revealed in Fig. 4 is nanocrystalline region (as arrowhead denoted). By reason of a small quantity of

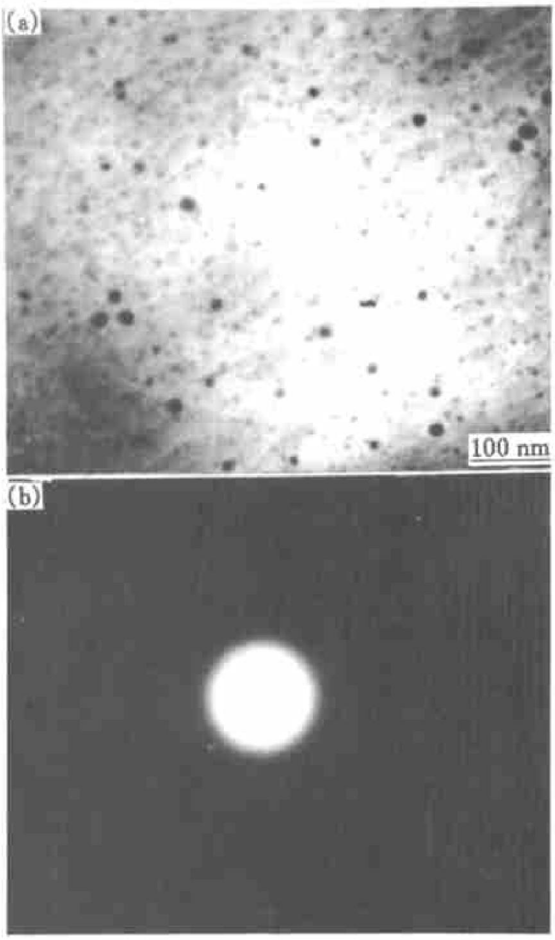

Fig. 4 TEM micrograph and selected area electron diffraction patterns (SADP) of Ti-C layer
(a) —TEM micrograph; (b) —SADP

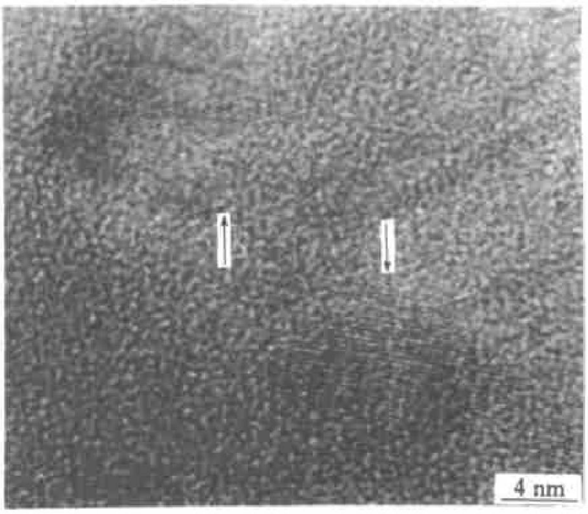

Fig. 5 HRTEM image of Ti-C layer

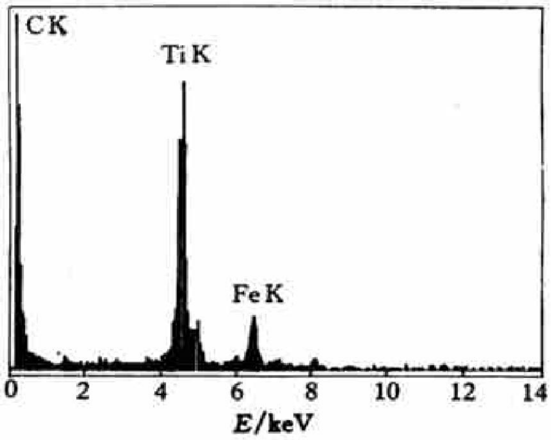

Fig. 6 EDX analysis of TEM viewing area

nanocrystalline, it is difficult to diffract into a pattern. An EDX analysis of TEM viewing area is shown in Fig. 6. It is indicated that thinning area of sample is true located at a area closed with DLC film in Ti-C layer, since, the TiK peak is a dominating signal. The minor FeK signal is excited from edge of thinning area possibly. A cross-view HRTEM image of Ti-C → DLC graded composite film is shown in Fig. 7. It has been revealed that random oriented

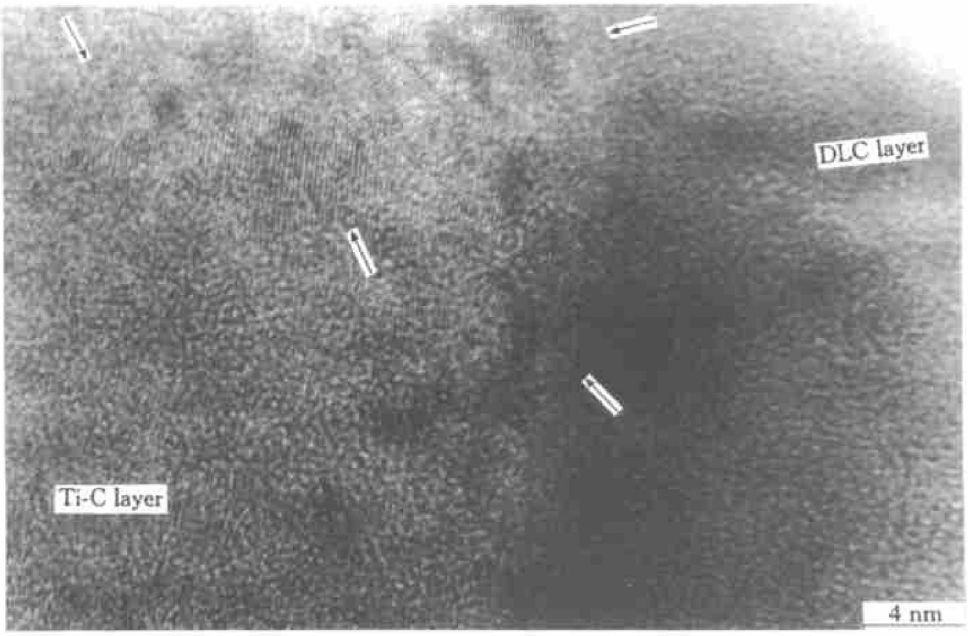

Fig. 7 Cross-view HRTEM image of Ti-C/DLC graded composite film

nanocrystalline dispersed in the zone of Ti-C layer near the DLC film (as arrowhead denoted) as well as, and that, the matrix is the same as DLC film essentially. From the results mentioned in 3.2, it is known that the carbon is a basis and existed with amorphous DLC structure, and a small quantity of Ti existed with TiC structure. Therefore, the nanocrystalline region is the TiC nanocrystalline, which dispersed in the zone of Ti-C layer near the DLC film, and the matrix is the diamond-like carbon. The structure for this zone is the typical Ti-contained DLC (Ti-DLC) film structure[17]. The transition between DLC film and Ti-C graded layer is continuous in structure without a distinct interface.

4 CONCLUSIONS

1) The transitional effects in composition between Ti-C layer and either DLC film or steel substrate can be obtained with unbalanced magnetron sputtering depositing Ti layers and followed by plasma based bias depositing DLC films.

2) In Ti-C graded layer, the chemical state transition of titanium and carbon are continuous and gradual changing, the basis is carbon in the zone bordered on the DLC film, a small quantity of Ti exist with TiC state essentially. With increasing the Ti content and decreasing the C content, the proportion of pure Ti is increased, the chemical state of carbon is changed gradually from diamond-like carbon to TiC essentially and companies with a small quantity solid-solved carbon.

3) It is proved that the zone near the DLC film in Ti-C layer is the typical Ti-contained DLC film which randomly orientates nanocrystalline TiC dispersed in amorphous DLC matrix observed by TEM and HRTEM. The transition between DLC film and Ti-C graded layer is continuous in structure without a distinct interface.

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