MICROSTRUCTURES AND MECHANICAL PROPERTIES OF Ti(C, N) FILMS DEPOSITED BY PEMSIP①

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ABSTRACT Ti(C, N) films were deposited by Plasma Enhanced Magnetron Sputtering Ion Plating (PEMSIP), and their microstructures and properties were investigated by means of XRD, AES, TEM and scratch test. The results showed that an interlayer about 80 nm thickness was formed between the high speed steel (HSS) substrate and Ti(C, N) films. In addition, crystalline orientation relationships were found among the substrate, interlayer and Ti(C, N) films. Therefore, the Ti(C, N) films combine high hardness and excellent adhesion strength.

Key words PEMSIP interlayer adhesion strength crystalline orientation relationship

1 INTRODUCTION

Plasma Enhanced Magnetron Sputtering Ion Plating (PEMSIP) is a new kind of Physical Vapor Deposition(PVD), which based on traditional technique of Magnetron Sputtering Ion Plating (MSIP), but a thermal electron-emission device, plasmatron, is constructed to emit a large quantity of electrons to activate the reacting gases under the high bias and enssure the full synthesis of the films. Using this method, stable sputtering in large-area substrates can be realized and the corresponding films are dense and homogeneous[1]. PEMSIPed-TiN films have been put into application successfully. However, this film has a relatively low hardness and tends to spall after a certain period of service[2]. Therefore, it is necessary to develop a new film to substitute the TiN film. In this work, Ti(C, N) was chosen as the film being studied because this film contains TiC phase which has a higher hardness than TiN phase, whereas TiC film has a low plasticity and poor adhesion strength[3,4]. Ti(C, N) films were deposited by means of PEMSIP, and their microstructures and properties were studied. Mechanisms to improve the film's hardness and adhesion strength were investigated to find effective ways to produce high-quality films.

2 EXPERIMENTAL PROCEDURE

Ti(C, N) films were deposited by PEMSIP using a cylindrical titanium target. Argon was used as the medium gas to clean the surface of HSS substrate and sputter the target to activate titanium atom. N_2 and CH_4 were chosen as reacting gases. The average N_2: CH_4 ratio (gas flow) was 0.45, and the substrate negative bias was -600 V. Hardness of as-prepared films was measured by DMH-ZLS durometer and adhesion strength was measured using CSR-01 scratch tester. XD-3A diffractometer was used to analyze the phase composition of the films. Investigation on the microstructures was carried out on SIA 100 surface/interface analysis system and JEM-2000Fx transmission electron microscope.

3 RESULTS AND DISCUSSION

3.1 Mechanical properties of as-prepared

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films

The hardness and adhesion strength of Ti(C,N) film are listed in table 1 and Fig.1, respectively.

Table 1 Hardness and adhesion strength of TiN, Ti(C, N) films

Reacting gas	As-prepared films	Depth of films/nm	Load /mN	HV /GPa
N_2	TiN	500	50	22.10
N_2/CH_4 = 0.45	Ti(C,N)	500	50	26.80

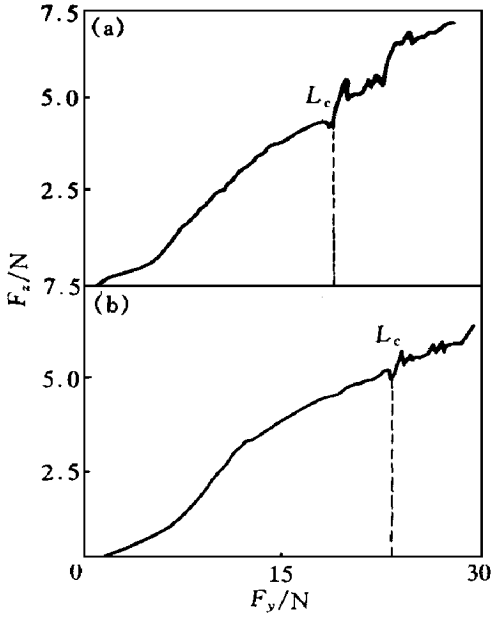

Fig.1 Scratch curves of as-prepared films(film depth: 500 nm; load: 40 N)
(a) —TiN film; (b) —Ti(C, N) film

In Fig.1, F_z represents the frictional force while F_y stands for vertical pressure. When the tested film begins to spall, the friction coefficient changes accordingly, causing intensive vibration of F_z and F_y. Consequently, inflection point appears in the scratch curves, and the corresponding F_z is called critical load L_c, which is admittedly regarded as an effective index to appraise the adhesion strength of as-prepared films[5].

According to the above results, Ti(C, N) film has superior mechanical properties to TiN film.

3.2 **Microstructures of Ti(C,N) film**

Fig.2 shows the XRD patterns of as-prepared Ti(C, N) films deposited when the N_2/CH_4 flow ratios are 0.25, 0.45 and 0.60.

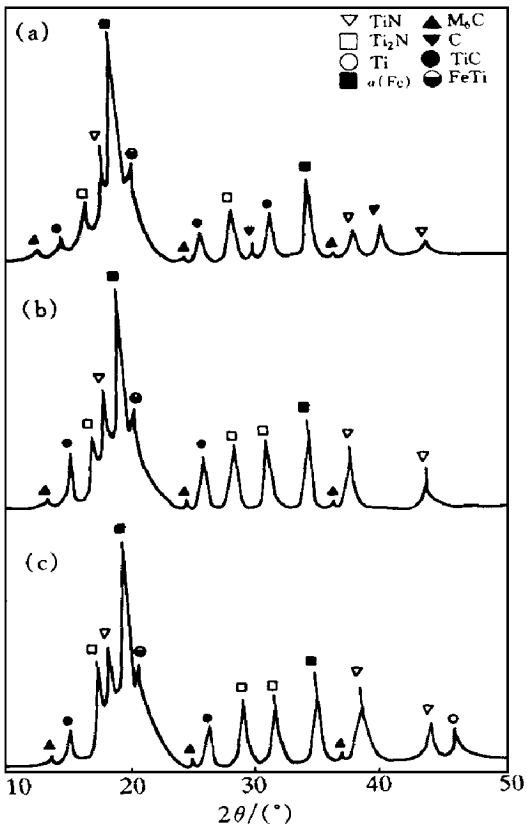

Fig.2 XRD patterns of Ti(C, N) film with different N_2/CH_4 flow ratios
(a) —0.25; (b) —0.45; (c) —0.60

The film is mainly composed of TiN, Ti_2N and TiC. Both Ti_2N and TiC phase have higher hardness than TiN phase[3], and contribute to the increase of the hardness of Ti(C, N) film. Meanwhile, the N_2/CH_4 flow ratio plays a key role to control the amount of α(Ti) and free graphite which cause the remarkable decrease of the hardness.

Fig.3 shows the result of Auger Electron Spectroscopy (AES) of the surface of Ti(C, N) film. The film is mainly made up of Ti, C and N. Such contamination elements as O, S, Cl were also detected because AES is very sensitive.

It can be seen from Fig.4(a) that the dis-

tributions of Ti, N and C in the film are homogeneous. With the spallation of the film, the carbon content near the film/substrate interface decreases, shown as Fig.4(b). The reason is that a thin Ti layer was first deposited on the substrate to strengthen the adhesion of the Ti(C, N) film[3]. Near the interface, the contents of Ti and N decrease gradually, and Fe doesn't vanish and extends into the film for a relative long distance, shown as Fig.4(b). So, it can be concluded that a pseudodiffusive interlayer was formed by the sputtering-redeposition resulted from the bombardment of particles with high energy under the high substrate negative bias[6]. According to the average spallation rate, the depth of the interlayer was about 80 nm. It is obvious that the interlayer can greatly improve the adhesion strength of the Ti(C, N) film.

In order to investigate the microstructures of the film and the film/substrate interface, transverse section TEM samples were prepared because an electron transparent area containing the film and the substrate can be gained[7].

It can be seen from Fig.5(a) that along the growth direction of the film, the transverse section sample is made up of substrate, interface and film. And Fig.5(b) shows that the films are divided into two distinct layers: F_1 and F_2, according to their morphologies. F_1, the inner layer, consists of fine equiaxed grains while F_2, the outer layer, is composed of columnar crystals which are perpendicular to the interface.

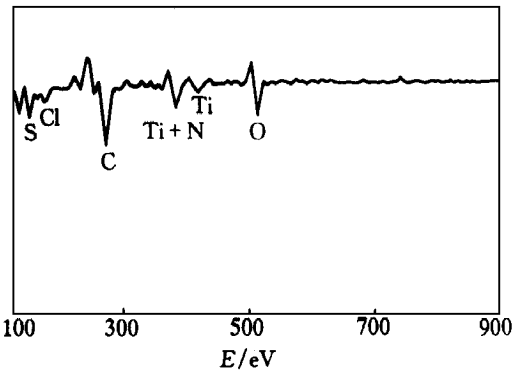

Fig.3 Result of auger electron spectroscopy of surface of Ti(C, N) film

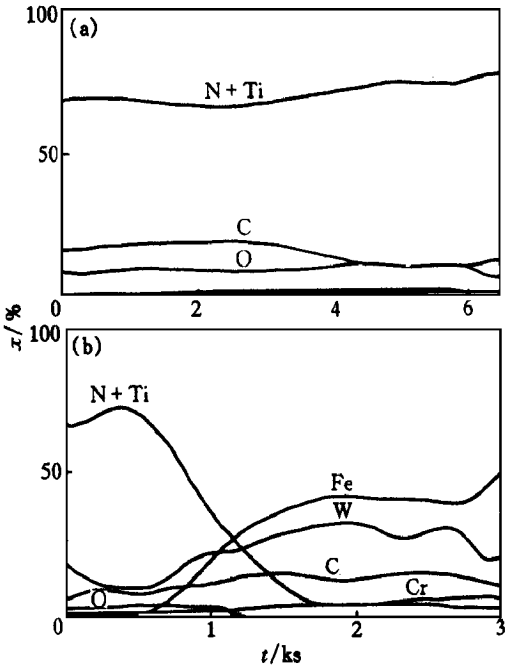

Fig.4 Auger depth profiles of Ti(C, N) film
(a) —Near surface of film;
(b) —Adjacent to substrate

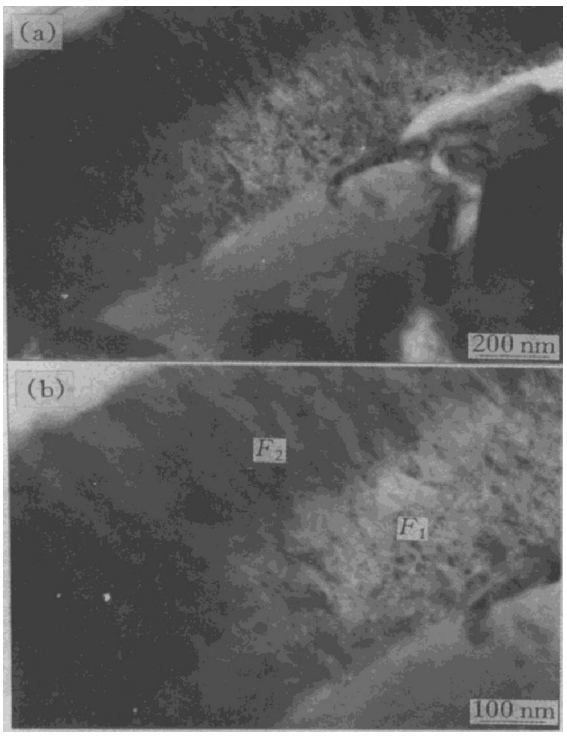

Fig.5 Transmission electron micrographs showing a BF image of film/substrate(a) and a BF image of Ti(C, N) film(b)

Fig.6(a) is the substrate electron diffraction pattern indexed as α(Fe)[011]. Fig.6(b) shows the electron diffraction patterns of the interface. It can be found that they contain two

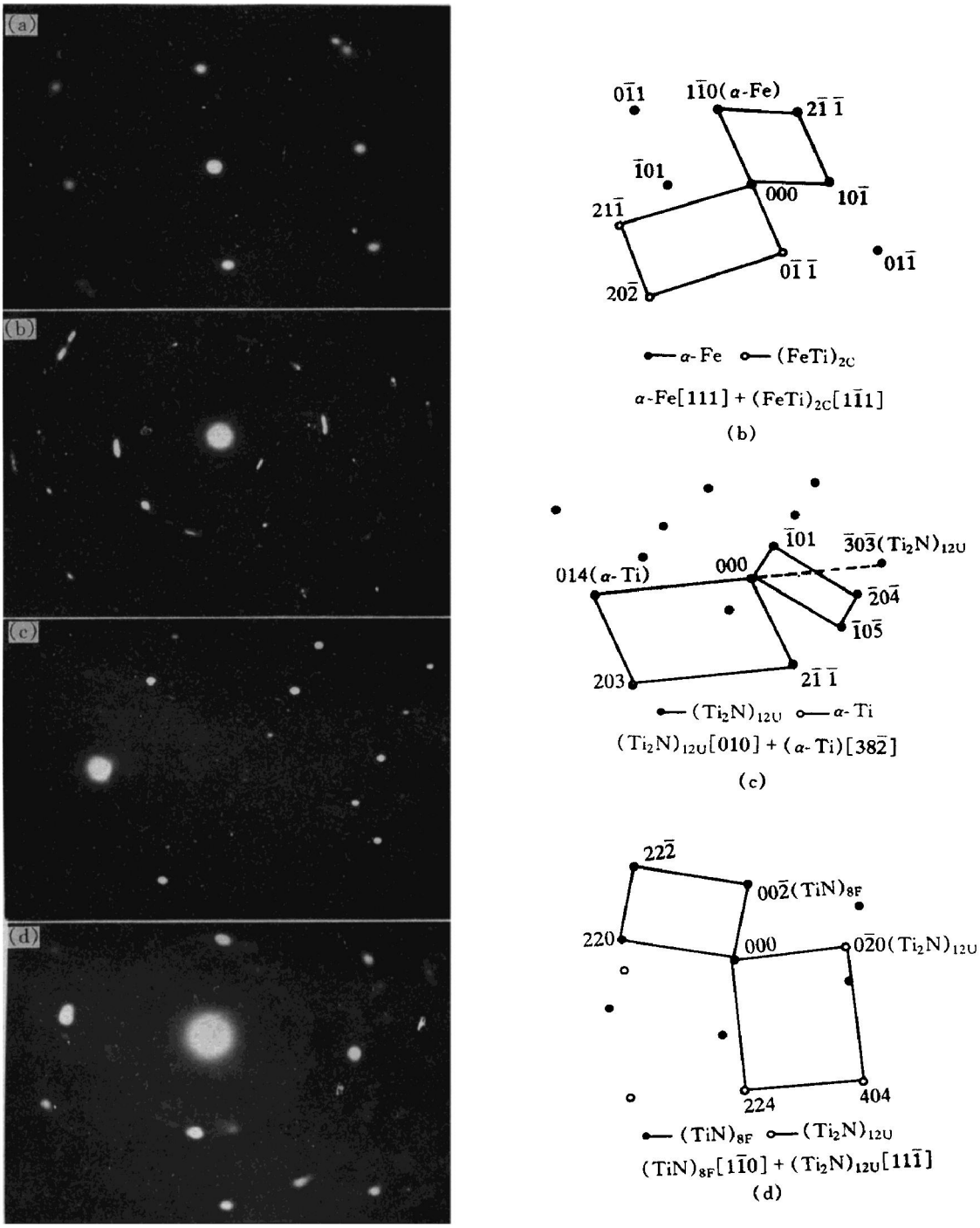

Fig.6 Electron diffraction patterns and their indexes in different positions
(a) —Substrate; (b) —Interface; (c) — F_1 layer; (d) — F_2 layer

independent patterns: α(Fe)[111] and FeTi [1 $\bar{1}$ 1], their crystalline orientation relationships are

$$[111]_{\alpha(Fe)} \parallel [1\,\bar{1}\,1]_{FeTi}$$

$$(1\,\bar{1}\,0)_{\alpha(Fe)} \parallel (011)_{FeTi}$$

The results indicate that the alloy phase FeTi formed when a thin Ti layer was deposited first on the substrate, because Fe was sputtered from the substrate by Ti and Ar ion with high energy up to several hundred eV. Then, Fe was ionized, and deposited again with Ti ion on the substrate[7]. The anti-sputtering and redeposition led to the mixing of Fe and Ti. Under the effect of plasma under high bias, solid reaction between Fe and Ti took place far below their equilibrium temperature[2]. It can be concluded that excellent metallurgical cohesion formed[8] and the adhesion strength of the film was greatly improved.

Electron diffraction patterns of F_1 layer, as shown in Fig.6(c), reveal that there is a crystalline orientation relationship between F_1 layer and the thin Ti layer

$$[010]_{Ti_2N} \parallel [38\,\bar{2}]_{\alpha(Ti)}$$

Such relationship does improve the cohesion between the film and the Ti interlayer.

From Fig.6(d) and Fig.5(b), it can be found that F_2 layer mainly consists of TiC, Ti_2N and TiN columnar grains. TiN and Ti_2N have such a crystalline orientation relationship as

$$[1\,\bar{1}\,1]_{TiN} \parallel [11\,\bar{1}]_{Ti_2N}$$

Because the PEMSIP process is of one-dimensional characteristic, heat diffuses fastest along the direction perpendicular to the substrate, and green grains also grow most quickly in this direction[9]. So, columnar grains formed vertically to the substrate, and as-prepared films have typical directional growing characteristics[10].

4 CONCLUSIONS

(1) Ti(C, N) films deposited by PEMSIP possess high hardness and excellent adhesion strength.

(2) A thin Ti layer was deposited first on the substrate to improve the cohesion of the Ti(C, N) films. Alloy phase FeTi formed in the course of deposition, and there are crystalline orientation relationships between FeTi phase and the substrate.

(3) A pseudodiffusive interlayer, about 80 nm thickness, was formed by the sputtering-redeposition resulted from the bombardment of particles with high energy under the substrate negative bias.

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