

EFFECT OF BORON ON MICROSTRUCTURE AND PROPERTIES OF Ti-N FILM^①

Yang Qiaoqin, Zhao Lihua, Xiao Hanning

Material Test and Research Center, Hunan University, Changsha 410082

Zhao Nanfang, Huang Qizhong

Central South University of Technology, Changsha 410083

ABSTRACT By adding boron to the Ti-N film, a nanocrystalline multiphase composite Ti-B-N film was deposited using activation ion plating under different negative bias voltages. It is found that the mechanical properties of the Ti-B-N film are much better than that of the Ti-N film. Diffraction measurements show that the composite film consists mainly of TiN with dispersed TiB, cubic BN and Ti-B-N phases. SEM and TEM micrographs indicate that the Ti-B-N film has a dense fine nanocrystalline structure and also a dense close interfacial bonding of the film to substrate. The results of AES and EPMA show that a diffusion zone exists at the film/ substrate interface and the higher the negative bias voltage, the wider the diffusion zone.

Key words boron Ti-N film nanocrystalline multiphase composite

1 INTRODUCTION

Through increasing the tool life by several to several dozens times, the Ti-N film brought about 'the revolution of tools' in the 1970s. And now the commercial film market, especially for tools, continues to be dominated by the Ti-N film due to its high hardness, toughness and chemical stability. However, many uses such as abrasive resistance of the Ti-N film are limited by its intermediate hardness (generally lower than 25 GPa). Recent research efforts on super-hard films have been directed to find better alternatives to this material. In recent years, a variety of hard films have been studied, ranging from diamond, β -C₃N₄, cubic BN to composite films including multiphase and multilayer containing such forms as

Ti(N, C)^[1], (Ti, Al)N^[2], W₂N/Si₃N₄^[3], TiN/Si₃N₄^[4], Ti-B-N^[5-7], Ti-B-C-N^[8], TiC and TiB^[9], Ti-B-N and Al₂O₃^[7].

In order to increase the hardness of the Ti-N film and retain its good properties at the same time, we tried to modify the Ti-N film by the addition of a small amount of boron. The results

suggest that boron has an important effect on the microstructure and properties of the Ti-N film.

2 EXPERIMENTAL METHODS

Sheets of 1W18Cr4V high speed steels were ground, polished and cleaned chemically, and then bombarded by Ar ions in the plating system. A Ti-B-N film with low boron content was then deposited on them using an activation ion plating equipment (type DLM-500A made in China). The reactant gas was nitrogen, and the Ti-B alloy was evaporated by an EB gun. A positive bias voltage was applied to the activation electrode to activate the reactant gas. A negative bias voltage was applied to the substrate to accelerate the ions which bombard on the substrate. The deposition conditions are summarized in Table 1. And the negative bias voltage was 0, -600, -900, -1200 and -1500 V, respectively. In order to compare the Ti-B-N film with the Ti-N film, a Ti-N film was deposited on the same substrate under almost the same conditions (Table 1).

The X-ray diffraction(XRD) measurements were made using Siemens D5000 to analyse the

① Supported by the Natural Science Foundation of Hunan Province

Received Nov. 4, 1996; accepted Apr. 25, 1997

phase composition of the film. The morphology and the film-substrate interface were observed with a JSM-T200 scanning electron microscope (SEM) and a H800 transmission electron microscope (TEM). The chemical composition distribution of the film and interface was obtained by electron probe microanalysis (EPMA), nuclear reaction analysis and Auger electron spectroscopy (AES).

The Vickers microhardness (HV) was measured with Buehler Micromet and an indenter load of 0.098 N was chosen. The sliding friction coefficient and the film-to-substrate adhesion were measured using a BF-1 film adhesion tester made in China.

3 RESULTS AND DISCUSSION

The mechanical properties of the TiB-N film and the TiN film are shown in Table 2. The hardness of the TiB-N film is found to be two even three times that of the TiN film. With the increase of the bias voltage, the hardness increases. When testing with a high load of 9.8 N using Micromet, no cracking appears in the TiB-N film, but some cracks are observed in the TiN film. This fact shows that the TiB-N film is tougher than the TiN film. The sliding friction coefficient of the TiB-N film is a little smaller than that of the TiN film. The value of the critical load shows that the adhesion of the TiB-N film-to-substrate is a little higher than

that of the TiN film, and increases with increasing negative bias voltage.

Fig. 1 shows the horizontal TEM morphologies of the TiN film and the TiB-N film. It can be seen that the TiB-N film is dense, with very fine grain size ranging from several to tens of nanometers, which is much smaller than that of the TiN film. Fig. 2 shows the SEM and TEM longitudinal morphologies of the cross-sectional microstructure of the TiB-N film. From the figure, we can see that the film is found to have a dense and fine fibrous nanocrystalline structure and a dense close interface bonding exists between the film and the substrate. The AES results of the chemical composition analysis of the TiB-N film show that the film is composed mainly of Ti, N and B. Fig. 3 shows the results of nuclear reaction analysis for sample 3 and the standard hBN sample, which gives the boron content of the film. The boron content of the sample is 12.5% (mole fraction). The ratio of the atomic N/Ti of the film determined by EPMA is about 1.01. Therefore, the composition of the film is B:N:Ti = 12.5:44.0:43.5 (mole ratio). Fig. 4 shows the EPMA cross-section scanning curve of TiK_{α} and FeK_{α} of sample 3. From the figure, we can see that there is an obvious diffusion zone at the interface. AES depth profile analysis of the samples (Fig. 5) shows that the width of interfacial diffusion zone increase with increasing negative bias voltage. As the results obtained at different points of

Table 1 Deposition parameters of films

Residual pressure/ Pa	N ₂ operating pressure/ Pa	Deposition rate/ nm·s ⁻¹	Substrate temperature/ °C	Film thickness/ μm	Activation voltage/ V	B/Ti in TiB alloy/ %
6.6×10^{-3}	1.2×10^{-1}	1.5	300	2.5	50	35 (mole fraction)

Table 2 Properties of films

Parameter	TiN			TiB-N film		
Sample number	0	1	2	3	4	5
Negative bias voltage/ V	900	0	600	900	1 200	1 500
Microhardness (HV) / GPa	18	13	51	52	55	57
Critical load/ N	12	6	13	15	16	17
Friction coefficient (load 8.8 N)	0.14		0.088	0.086	0.089	0.091

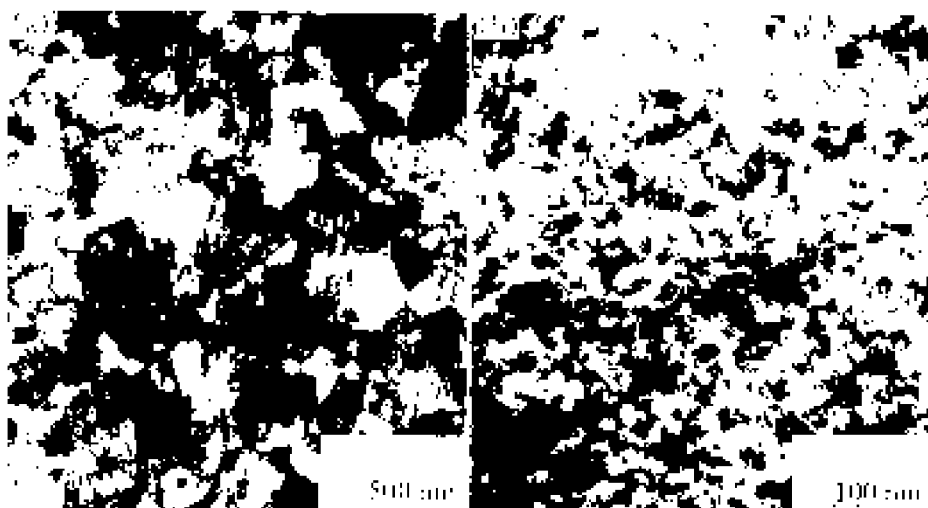


Fig. 1 Horizontal TEM morphologies of films

(a) —Ti-N film; (b) — Ti-B-N film



Fig. 2 Longitudinal morphologies of cross-sectional microstructure of Ti-B-N film

(a) —SEM; (b) —TEM



Fig. 3 Nuclear reaction analyses of Ti-B-N film and standard sample (hBN)

the samples under different negative bias voltages are almost the same, we then conclude that the

chemical composition is homogeneous in the film and the negative bias voltage has little effect on the chemical composition of the film. However, near the film/substrate interface, the content of Fe in the substrate increases and the contents of Ti, B and N decrease slowly, which means that there exists a diffusion zone at the interface and the width of the interfacial diffusion zone increases with increasing negative bias voltage.

X-ray diffraction results of the samples (Fig. 6) show that the negative bias voltage has a great effect on the phase composition of the Ti-B-N films. The higher the value of the negative bias voltage, the more phases are formed. When the bias voltage is 0 (sample 1), the film consists of only TiN phase and the boron is solved in it, which results in the displacement of the diffraction peak of the TiN phase. When the bias voltage is - 600 V and - 900 V (sample 2 and 3), the films are composed of fcc TiN, sim-

ple orthorhombic TiB, cubic BN and simple hexagonal Ti-B-N phases. With further increasing of the bias voltage (sample 4 and 5), TiN, TiB, BN and Ti-B-N still exist and more new diffraction peaks appear. The new diffraction peaks can not be identified by the powder

diffraction card. We think these peaks are caused by the diffraction of some new metastable phases. Further studies by TEM and electron diffraction to determine the phases remains to be carried on. X-ray diffraction further gives the diffraction patterns of the fcc TiN, the simple hexagonal Ti-B-N, simple orthorhombic TiB and the cubic BN phases^[10].

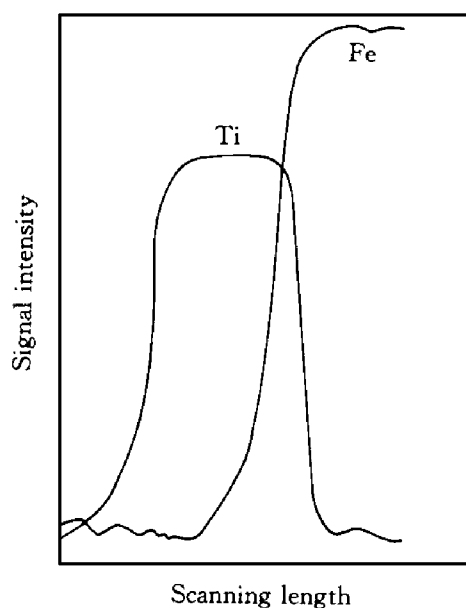


Fig. 4 EPMA cross section scanning curve of TiK α and FeK α of Ti-B-N film (sample 3)

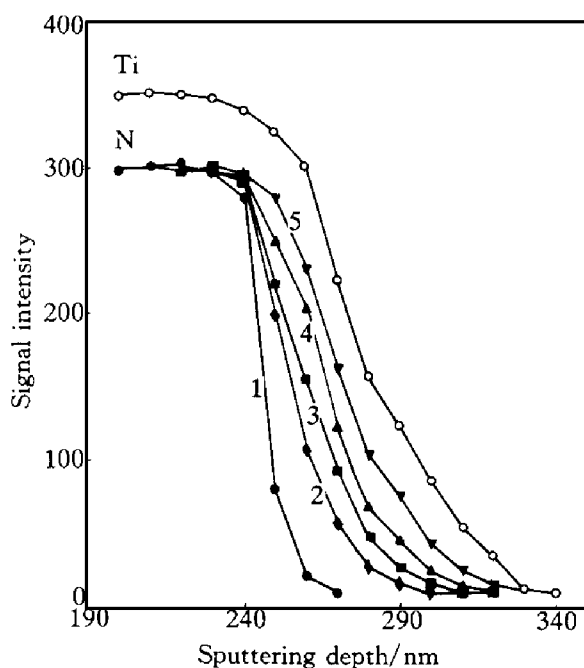


Fig. 5 AES depth profile analyses of samples of Ti-B-N film

1 — 0; 2 — 600 V; 3 — 900 V;
4 — 1 200 V; 5 — 1 500 V

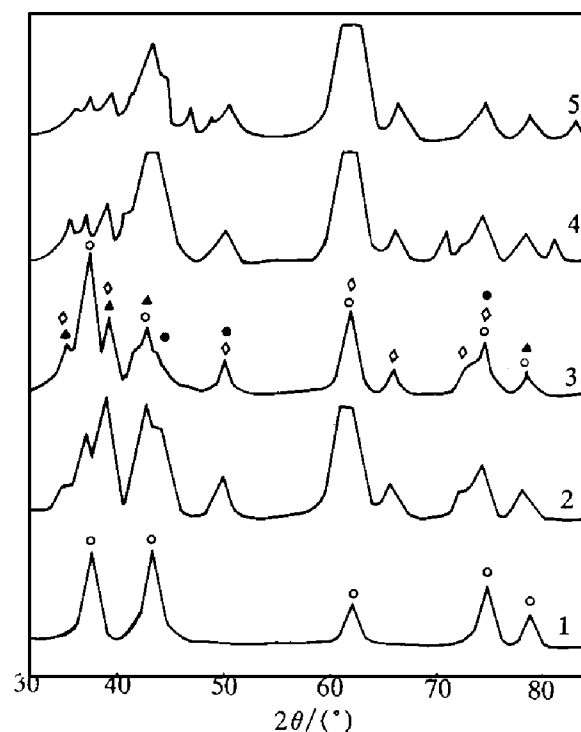


Fig. 6 X-ray diffraction patterns of samples of Ti-B-N film

○ — Peak of TiN phase diffraction;
▲ — Peak of TiB phase diffraction;
◇ — Peak of Ti-B-N phase diffraction;
● — Peak of BN phase diffraction;
1 — 0; 2 — 600 V; 3 — 900 V;
4 — 1 200 V; 5 — 1 500 V

By adding boron to the Ti-N film, a nanocrystalline multiphase composite film consisting of TiN, TiB, cubic BN and Ti-B-N phases was obtained. Cubic BN is a non-equilibrium phase, which was also obtained by Ingawa *et al.*^[11] with the same method. The Ti-B-N film has a dense nanocrystalline structure, and its grain size is dozens of times finer than that of the Ti-N film. It is well known that TiN has the usable toughness but does not have the very high hardness, and cubic BN has the very high hardness but is brittle. The Ti-B-N phase is a solu-

tion consisting of 17% ~ 27% nitrogen and 10% boron in α -Ti. Combination of these phases with the dense nanocrystalline composite structure of the Ti-B-N film is undoubtedly the origin of its extremely good mechanical properties. Even if the boron content is low and only a little of the superhard phase is observed in the film, the film has much better properties than those of the Ti-N film. It is then concluded that the dense nanocrystalline composite structure has a great effect on the properties of the films. We think that the Ti-B-N phase plays a role in increasing the toughness and lowering the friction coefficient, and the dispersed cubic BN and TiB have the effect of strengthening the film slightly but reducing the toughness and the adhesion a little. The analyses above indicate that the addition of B to the Ti-N film improves the mechanical properties of the films through refining the grain size, strengthening the grain boundary and forming dispersed phases in the film. On the other hand, the negative bias voltage applied to the substrate to accelerate the ions which bombard on the substrate has great effect on the phase composition of the film and the width of the interfacial diffusion zone. With increasing negative bias voltage, more superhard phases are formed and the width of the interfacial diffusion zone increases. So the hardness of the film and the adhesion of the film-to-substrate increase with increasing negative bias voltage. These results show that the N ion bombardment has the effect of stimulating chemical reaction, enhancing interfacial mixing and increases the hardness of the film and the adhesion of the film-to-substrate.

4 CONCLUSIONS

(1) By the addition of boron to the Ti-N film, a nanocrystalline multiphase composite Ti-B-N film consisting mainly of TiN with dispersed TiB, cubic BN and Ti-B-N phases was deposited on steels using activation ion plating

under different negative bias voltages. The microhardness(HV), the toughness and the adhesion of the Ti-B-N film are much higher than those of the Ti-N film. And the hardness and the adhesion increase with increasing negative bias voltage.

(2) The Ti-B-N film has a dense fine nanocrystalline structure and a dense close interfacial bonding of the film to the substrate. Ti, B and N in the film are homogeneous, but there exists a diffusion zone at the film/substrate interface. And the higher the negative bias voltage, the wider the diffusion zone, the more phases are formed in the film.

(3) The results indicate that adding B to the Ti-N film improves the mechanical properties of the films through refining the grain size, strengthening the grain boundary and forming dispersed phases in the film. And the N ion bombardment has an effect of stimulating chemical reaction and enhancing interfacial mixing.

REFERENCES

- 1 Kajioka H, Higuchi K and Kawashimo Y. *Thin Solid Films*, 1993, 228: 280.
- 2 Efeoglu I, Arnell R D and Tinston S F *et al.* *Surf Coat Technol*, 1993, 57: 1.
- 3 Veprtek S, Haussmann M and Reiprich S. *J Vac Sci Technol*, 1996, A14: 46.
- 4 Veprtek S, Reiprich S and Shizhi L. *Appl Phys Lett*, 1995, 66: 2640.
- 5 Broszeit E, Matthes B and Kloos K H. *Surf Coat Technol*, 1993, 58: 29.
- 6 Matthes B, Broszeit E and Kloos K H. *Surf Coat Technol*, 1993, 57: 97.
- 7 Tamura M and Kubo H. *Surf Coat Technol*, 1993, 54/55: 29.
- 8 Knotek O, Breidenbach R and Jungblut F *et al.* *Surf Coat Technol*, 1990, 43/44: 107.
- 9 Holleck H, Kuhl Ch and Schulz H. *J Vac Sci Technol*, 1985, A3: 2345.
- 10 Yang Q Q, Wen L S and Chen X Z *et al.* *Vacuum*, 1995, 46: 181.
- 11 Inagawa K, Watanabe K and Ohson H *et al.* *J Vac Sci Technol*, 1987, A5: 2696.

(Edited by Pen Chaoqun)