EFFECT OF HEAT TREATMENT TEMPERATURE ON MICROSTRUCTURE AND PROPERTIES OF Ti-B-N FILM①

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ABSTRACT The microstructure and mechanical properties of Ti-B-N film after heat treatment under different temperatures were studied. The adhesion of the heat-treated film increased and the higher the treatment temperture, the higher the adhesion. When the treatment temperature was not higher than 600 ℃, the grain did not grow and no obvious change took place in the microstructure and the hardness of the film. When the treatment temperature reached 700 or 800 ℃, the hardness of the film decreased greatly, the grain was obviously growing, and the supersaturation metastable phase transformed into stable phase to form alternating slice structure within the grain of the film. The thickness of the slice was several dozen nanometres. It was found that some grains were TiN slice alternating with Ti_2N slice, the other grains were Ti_2N slice alternating with Ti-B-N phase slice and certain orientation relationship existed among them.

Key words heat treatment Ti-B-N film slice structure

1 INTRODUCTION

Ti-N films prepared by means of physical vapour deposition (PVD) or chemical vapour deposition (CVD) are widely used on tools for their good composite properties. Through increasing the tool life by serveral to serveral 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. However, many uses of the Ti-N film are limited by its intermediate hardness (generally lower than 25 GPa) and high deposition temperature (generally higher than 550 ℃). An important research direction on the development of hard films is how to increase the hardness of a Ti-N film, decrease its deposition temperature and retain or even improve its good properties at the same time. In recent years, a variety of hard films have been researched, ranging from diamond, β-C_3N_4, cubic BN through to composite films including multiphase and multilayer containing forms such as Ti(N, C)[1], (Ti, Al)N[2], W_2N/Si_3N_4[3], TiN/Si_3N_4[4], TiC and TiB[5]. Taking into account that boron had effect of refining grain size, strengthening grain boundary in many kinds of materials and it is easy to form superhard phases with Ti and N, we tried to modify the Ti-N film by addition of a small amount of boron by means of activation ion plating. The former papers by us[6-11] had reported that the Ti-B-N film formed by activation ion plating consisted mainly of fcc TiN with dispersed simple orthorhombic

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TiB, metastable cubic BN and simple hexagonal Ti-B-N phases. The hardness of the film is two to three times higher than that of the Ti-N film, the other mechanical properties are better than that of the Ti-N film, and its deposition temperature is only 300 ℃, much lower than that of the Ti-N film. It is promising to be an ideal film used on tools instead of Ti-N film. When coated tools is being used, the temperature of the coating surface will go up for the effect of friction. Therefore, we would like to study the microstructure and properties of heat-treated Ti-B-N film. And now in this paper, we present the results.

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)[6]. 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 eletrode 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. The Ti-B-N was then heat treated under nitrogen at temperatures 500, 600, 700 and 800 ℃ for 1 h and cooled down with the furnace.

The Vickers microhardness (Hv) was measured with a Buehler Micromet. An indenter load of 0.25 N was chosen. The adhesion were measured using a scratch tester re-equiped from a micromet. The scratch was observed using a microscope. The load under which a crack starts to occur on the edge of the scratch was defined as critical load. And the microstructure of the samples were observed using a H800 transmission electron microscope(TEM).

3 EXPERIMENTAL RESULTS AND DISCUSSION

The mechanical properties of the heat-treated Ti-B-N film are shown in Table 2. From the table, we can see that the scratch critical load of the treated film increased, and the higher the teatment temperature, the higher the critical load; when treatment temperature lower than 600 ℃, no obvious change was observed in the hardness of the film. However, when treatment temperature reached 700 or 800 ℃, the hardness of the film decreased greatly. The results indicated that the adhesion of the heat-treated film increased, and the higher the teatment temperature, the higher the adhesion; however, the hardness of the film decreased greatly when the heat-treatment temperature was too high.

Table 1 Deposition parameters of the Ti-B-N film

Parameters	Values
Residual pressure/ Pa	6.6×10^{-3}
N_2 operating pressure/ Pa	1.2×10^{-1}
Deposition rate/ ($nm\cdot s^{-1}$)	2.5
Substrate temperature/ ℃	300
Film thickness/ μm	3
Activation voltage/ V	50
B/ Ti in Ti-B alloy/ %	28
Negative bias voltage/ V	600

Table 2 Mechanical properties of the Ti-B-N film

	as-deposited	Treated			
Treatment temperature / ℃		500	600	700	800
Microhardness (HV)/GPa	40	39	39	25	21
Critical load/ N	13	15	16	18	19

Fig. 1 shows the TEM morphologies of the Ti-B-N film as-deposited and heat-treated at different temperatures. It shows that the Ti-B-N film untreated is dense, with very fine grain size ranging from several to tens of nanometers. When the treatment temperature was not higher than 600 ℃, the grain did not grow and no obvious change took place in the film. When the treatment temperature reached 700 or 800 ℃,

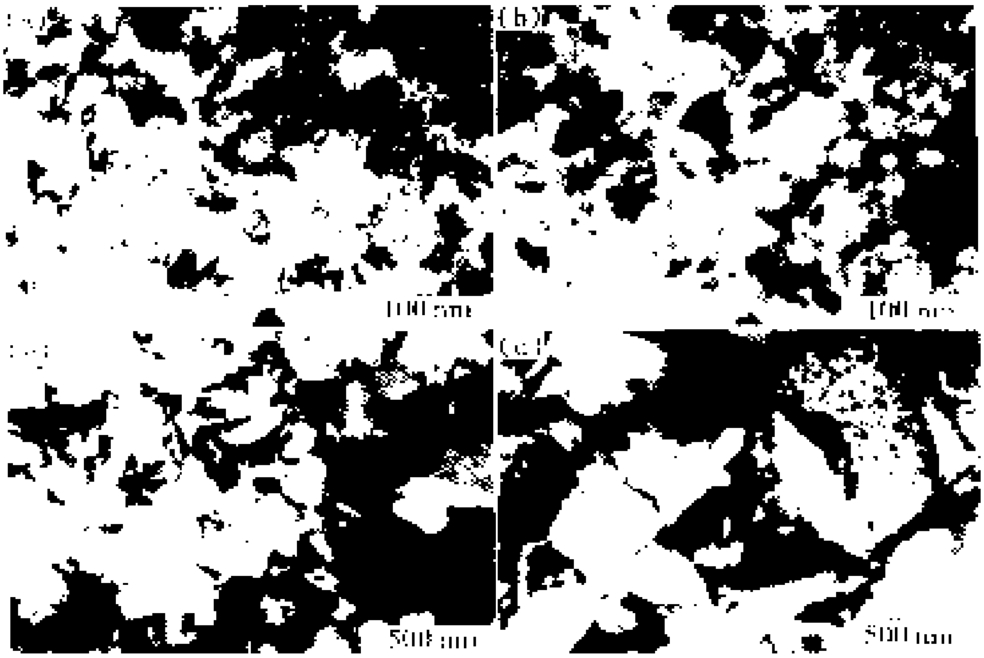

Fig. 1 TEM micrographs of the Ti-B-N film as-deposited (a) and heat-treated at (b) 600 ℃ (c) 700 ℃ (d) 800 ℃

the grain is obviously growing, and the grain size is more than 10 times the size of the film untreated. The higher the treatment temperature, the bigger the grain size. And slice structures existed within the film, which is shown in Fig. 2. It is easy to see that the thickness of the slice is several dozen nanometers. The electron diffraction patterns of the slices are shown in Fig. 3 and Fig. 4. It is found that some grains were TiN slice alternating with Ti_2N slice (Fig. 3), and their orientation relationship is as follows:

[010] Ti_2N // [112] TiN,
(200) Ti_2N // (111) TiN,
(002) Ti_2N // (220) TiN

Fig. 2 Slice structure of the treated Ti-B-N film

The other grains are Ti_2N slice alternating with Ti-B-N phase slice (Fig. 4), and their orientation relationship is as follows: [001] Ti_2N // [111] Ti-B-N, (200) Ti_2N // (110) Ti-B-N, (111) Ti_2N // (011) Ti-B-N. These results indicate that the supersaturation single-phase grain precipitates the second phase and the two phases form slices alternating with each other after heat treatment at 700 or 800 ℃.

In our experiment, because of the low deposition temperature (300 ℃) and the high deposition rate (2.5 $nm \cdot s^{-1}$) of the Ti-B-N film, the diffusion of the atoms was limited during the deposition process, and the supersaturation solution phase with a meta-equilibrium structure was formed. When the samples were heat treated to 700 or 800 ℃, the vibration and diffusion of the atoms were strengthened, the supersaturation single-phase grain precipitates the second phase and the two phases form slices alternating with each other. The same phenomenon was observed

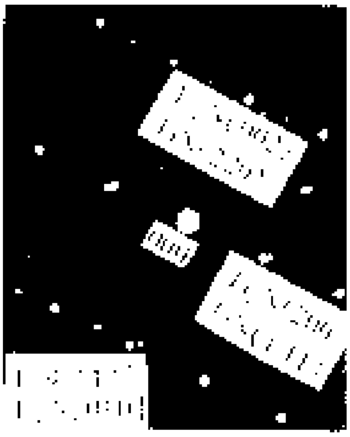

Fig. 3 Diffraction pattern of TiN and Ti_2N alternating slice

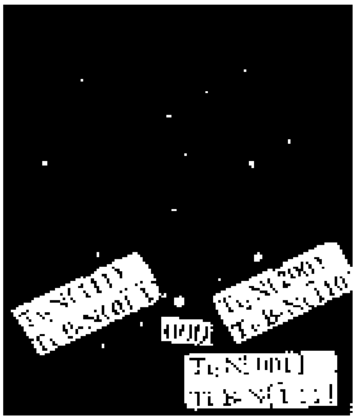

Fig. 4 Diffraction pattern of Ti_2N and Ti-B-N alternating slice

by Hibbs *et al*[12] in the deposition of Ti-N film by high frequency reaction sputtering. Heat treatment of film can stimulate the diffusion of the film and film/substrate interface. Conseqently, a wider interfacial zone could be formed, which would moderate the sudden change of physical properties at the film/substrate interface and lower the stress concentration at the interface, thereby improve the film-to-substrate adhesion. However, when the treatment temperature is too high (reached 700 or 800 ℃), the grain in the film is obviously growing and some metastable phases transform to stable phases, thereby dereases the hardness of the film.

4 CONCLUSIONS

When Ti-B-N film heat treated at temperature not higher than 600 ℃, no obvious changes took place in the microstructure of the film and the mechanical properties of the film improved. However, when the treatment temperature reached 700 or 800 ℃, the supersaturation meta-equilibrium phase precipitated the second phase and the two phases formed slice structure. And certain orientation relationship existed among the slices. The hardness of the film decreased greatly.

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