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Optimal deposition and layer modulation parameters for mechanical property enhancement of TiB_2/Si_3N_4 multilayers using orthogonal experiment

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ABSTRACT

TiB_2/Si_3N_4 multilayers have been synthesized by ion beam assisted deposition (IBAD). SEM, XRD, XP-2 profiler, and Nano indenter were employed to investigate the effect of modulation ratio, modulation period, thickness of buffer layer, and deposition temperature on the microstructure and mechanical properties. Orthogonal experiment found that the TiB_2/Si_3N_4 multilayer with modulation ratio of 15.4:1 and modulation period of 11.8 nm prepared with 38 nm-thick Ti buffer layer at deposition temperature of 225°C displayed optimal mechanical properties. Its hardness and elastic modulus were up to the highest values of 36.2 GPa and 448 GPa. This hardest multilayer also showed the improved residual stress and fracture resistance.

1. Introduction

Titanium boride (TiB_2) multi-phase ceramic has promising applications for protective armors, tool knife materials, shaping moulds and so on, due to high micro-hardness, high performance and thermal stability at high temperatures [1–4]. In comparison, Si_3N_4 also exhibits high fracture toughness, outstanding wear resistance, both impingement and frictional modes, and good thermal shock resistance. They can be used in many severe mechanical, thermal and wear applications [5–9]. However, both available monolithic materials largely limit the properties and performance of hard coatings due to predominant columnar grain growth and compressive stress accumulation with the increase in the film thickness that lead to brittle fracture, delamination, and plastic deformation.

Multilayer coatings made of borides, nitrides, and carbides, exhibiting high hardness, corrosion resistance, wear resistance and adhesion properties, have been developed and applied to various kinds of industries for the past decades [10–14]. In our previous works [15–17], we synthesized ZrN or ZrB_2-based multilayers and revealed superior mechanical properties. In this work, TiB_2/Si_3N_4 nano multilayers were synthesized by ion beam assisted deposition (IBAD) system in order to overcome these problems above. The orthogonal experiment method [18] was used to hunt optimal deposition parameters for microstructure and mechanical property enhancement of TiB_2/Si_3N_4 multilayers. Our purpose is to investigate the significance of buffer layer, deposition temperature, modulation period and ratio on multilayer growth.

2. Experimental

The description of our IBAD system can be found in previous article [17]. The Ti, TiB_2, and Si_3N_4 targets were sputtered alternately by Ar^+ beam (1.1 KeV, 25 mA) from sputtering ion source to deposit TiB_2 or Si_3N_4 and TiB_2/Si_3N_4 coatings. The deposition of TiB_2/Si_3N_4 multilayers started with the deposition of Ti buffer layer to increase coating adhesion. A series of TiB_2/Si_3N_4 multilayers with different modulation ratio were prepared under different deposition conditions. The working pressure was about 1.2×10^{-2} Pa. All thicknesses of the coatings were controlled in 450–500 nm.

In this experiment, deposition parameters were optimized by the orthogonal experiment method. Table 1 lists the schedule of the orthogonal experiment in which four key deposition parameters including (A) deposition temperature, (B) modulation period (Λ), (C) modulation ratio (t_{TiB2}:t_{Si3N4}), and (D) Ti buffer layer thickness were selected. Every parameter had three levels to be optimized. The micro-hardness and elastic modulus of the coatings are taken as the index points to evaluate the coatings performance under different factors and levels.

The cross-section of the coatings was examined by a field-emission scanning electron microscopy (SEM, Hitachi 4800, Japan). The phase structure of the coating was investigated by X-ray diffraction (XRD) on a D/MAX 2500 diffractometer operated at 40 KV and 40 mA, with Cu Kα (40 kV, 20 mA, $\lambda=0.15406$ nm) radiation in steps of 0.02°. The residual stress of the coatings was calculated applying the Stoney formula [19] by curvature measured using an XP-2 profiler. A Nano Indenter XP system was employed to perform hardness and elastic modulus tests. In these tests, the continuous stiffness measurement (CSM) technique was adopted, a technique which allows the continuous measurement of the contact stiffness during loading. The scratch scan recorded the scratch depth during scratching.

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Table 1
Deposition parameters and levels for orthogonal experiment.

Level	Deposition parameters			
	A (°C)	B (nm)	C	D (nm)
1	25	3	9:1	0
2	225	9	6:1	30
3	425	15	3:1	60

3. Results and discussion

Detailed deposition conditions and hardness or elastic modulus values are listed in Table 2. From the mathematical processing of the data, some results can be concluded as follows. First, compared with modulation period (B), the modulation ratio (C) displays the more significant effect on whichever index point. High modulation ratio is good parameter for hardness increase. Second, middle deposition temperature and about 30 nm-thick Ti buffer layer should be considered under multilayer deposition process. Moreover, 32.5 GPa hardness and 356 GPa elastic modulus are achieved under the optimized deposition parameters.

The typical cross-sectional SEM image for TiB_2/Si_3N_4 multilayer synthesized at deposition temperature of 225°C is illustrated in Fig. 1. It gives a direct evidence of the clear multilayered structure. The light and dark colored layers are TiB_2 and Si_3N_4, respectively. The intermixture in interfaces can be observed in this figure. We believe that enhanced mobility of interface species at higher deposition temperature is main reason. The multilayer Λ is about 12 nm and t_{TiB2}:t_{Si3N4} is about 4:1.

In order to further investigate the effect of t_{TiB2}:t_{Si3N4} on multilayer growth, we synthesize another series of TiB_2/Si_3N_4 multilayers with different t_{TiB2}:t_{Si3N4} based on this orthogonal experiment table. In this series, constant Λ of 11.8 nm, Ti buffer layer thickness of 38 nm, and deposition temperature of 225 °C were kept as optimal deposition parameters. Our purpose is to detail investigate the significance of modulation ratio on multilayer growth under other constant deposition parameters.

The low-angle XRD pattern of Fig. 2 gives direct information on t_{TiB2}:t_{Si3N4} = 15.4:1 from the coating prepared at constant Λ. The strong multiple reflections clearly indicate sharp interfaces between TiB_2 and Si_3N_4 layers and distinct layer structure in multilayer. The Λ was calculated to be 11.8 nm using the modified Bragg equation.

Fig. 3 gives the XRD patterns of monolithic and multilayered coatings. Compared with amorphous structure of monolithic TiB_2 coating, a strong hexagonal structure with both Si_3N_4 (110) and (101) orientations is observed in monolithic Si_3N_4 coating. However, the Si_3N_4 (110) peak disappears in the multilayered structures. It is probable that TiB_2 layer introduction suppressed the growth of Si_3N_4 (110) grain. The multilayer at t_{TiB2}:t_{Si3N4} = 6:1 shows only stronger Si_3N_4 (110) textures. With the t_{TiB2}:t_{Si3N4} increasing to 15.4:1, the TiB_2 (100) and (101) textures appear. Their weaker and broader full-width at half-maximum (FWHM) indicates smaller TiB_2 grain sizes. This small grain size or microcrystal structure should lead to a positive effect on mechanical properties of the multilayers.

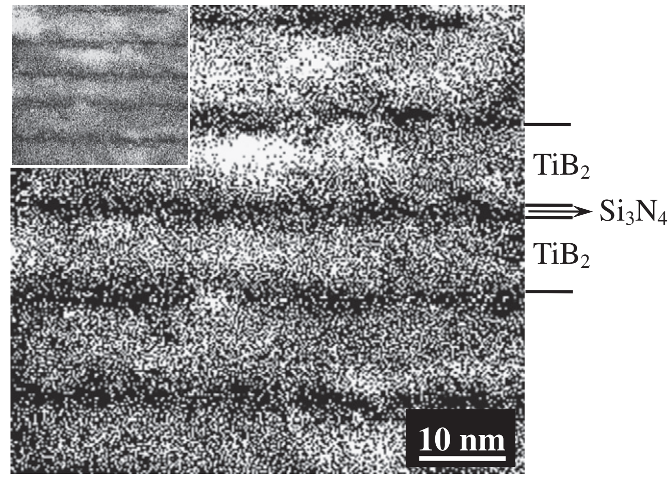

Fig. 1. Cross-sectional SEM image of TiB_2/Si_3N_4 multilayer with Λ = 12 nm and t_{TiB2}:t_{Si3N4} = 4:1.

Residual stress was generated during the coating growth process. Multilayered structure causes a decrease in the residual stress of the coatings, as it can be seen in Fig. 4. High compressive stresses are present in monolithic TiB_2 layers. However, multilayers have lower compressive stress than the value of monolithic TiB_2 layers. It is due to periodically introduction of Si_3N_4 layers into TiB_2 layers that help to relax the stress built in TiB_2 layers. Within constant Λ, the thinner is the Si_3N_4 layer, the larger is the t_{TiB2}:t_{Si3N4}. So, a possible mechanism is that defects in TiB_2 layers are more easily diffuse to or cross the thinner Si_3N_4 layer and relieve their strain fields when t_{TiB2}:t_{Si3N4} is increased. So, larger t_{TiB2}:t_{Si3N4} multilayers show much more obvious decrease in compressive stress than smaller t_{TiB2}:t_{Si3N4} larger coatings.

Fig. 5 shows the effect of t_{TiB2}:t_{Si3N4} on hardness and elastic modulus. The hardness of monolithic TiB_2, Si_3N_4 coatings is 30.6 and 23.2 GPa, respectively. Hardness of the TiB_2/Si_3N_4 coatings increases firstly and then decreases with increasing t_{TiB2}:t_{Si3N4}. All of multilayers possess an obviously higher hardness than the rule-of-mixtures value of monolithic TiB_2 and Si_3N_4 coatings. The maximum hardness and elastic modulus are up to 36.2 GPa and 448 GPa at t_{TiB2}:t_{Si3N4} = 15.4:1. According to hardness $H = \lambda_a H_a/\lambda + \lambda_b H_b/\lambda$ formula (H_a and H_b are hardness of monolithic ZrB_2 and Si_3N_4 coatings, λ_a and λ_b represent thickness of ZrB_2 and Si_3N_4 coatings in a multilayered coating, respectively, λ is total thickness of a multilayered coating), hardness of the multilayer at t_{TiB2}:t_{Si3N4} = 15.4:1 should be 29 GPa. However,

Table 2
Detailed scheme of orthogonal experiment and hardness or elastic modulus values of TiB_2/Si_3N_4 multilayers.

Samples No.	Level of A	Level of B	Level of C	Level of D	Hardness GPa	Elastic modulus GPa
1	25	3	9:1	0	28.3	302
2	25	9	6:1	30	28.0	271
3	25	15	3:1	60	23.3	336
4	225	3	6:1	60	26.2	295
5	225	9	3:1	0	27.6	309
6	225	15	9:1	30	32.5	356
7	425	3	3:1	30	27.4	332
8	425	9	9:1	60	27.2	341
9	425	15	6:1	0	29.4	271

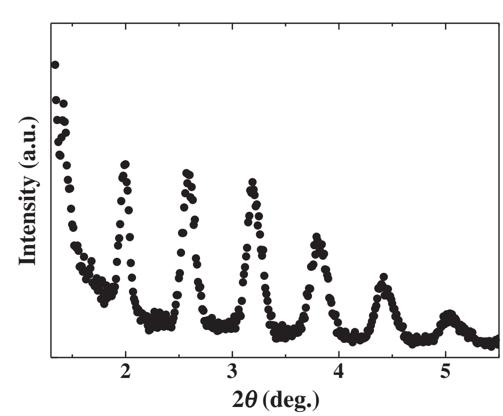

Fig. 2. Low-angle XRD pattern for TiB_2/Si_3N_4 multilayer.