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Microstructure and properties of AlB_2-type WB_2 thin films deposited by direct-current magnetron sputtering

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ABSTRACT

In this study, AlB_2-type WB_2 films are deposited on YG8 (WC–Co) substrates by DC magnetron sputtering at different substrate bias voltages and temperatures. Their effects on the film microstructure, elemental composition, mechanical and tribological properties are investigated systematically by various analysis methods, including X-ray diffraction (XRD), electron probe X-ray microanalyzer (EPMA), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), nano-indentation, ball-on-disk tribometer and micro scratch tester. The as-deposited films show an under-stoichiometric composition with rich tungsten concentration and have an obvious columnar structure. With the substrate bias voltage increasing (from 0 V to −150 V), the orientation of the films changes from (0 0 1) to (1 0 1). And films obtained at −50 V show superior mechanical and tribological properties. By increasing the substrate temperature to 500 °C, the maximum hardness about 40.5 GPa and the best adhesive strength of 60 N are detected. The films with the fine-grain amorphous structure, produced at 300 °C and −50 V, exhibit the minimum friction coefficient of 0.28. And the minimum wear rate of 2.3×10^{-7} mm^3/mN is obtained for the films deposited at −50 V and 400 °C. The properties described above are attributed to the variations of microstructure and morphologies in the films. Furthermore, the wear track and debris are also discussed by virtue of FESEM/EDS to explore the self-lubricating behavior of the AlB_2-type WB_2 film.

1. Introduction

Recently, a growing interest has been focused on the synthesis and characterization in borides of transition metals such as WB_2, OsB_2, ReB_2 and RuB_2 [1–3], which usually possess high hardness, outstanding chemical inertness, good thermal and electrical conductivity. Among these borides, WB_2 has been taken as a new research hotspot theoretically and experimentally. And it is also expected to be used as a self-lubricating material due to the formation of tungsten and boric oxides at elevated temperature under atmospheric conditions [4–6]. Two different crystal structures have been found experimentally for WB_2 phase: AlB_2-type (No. 191, P6/mmm, a, b = 3.02 Å, c = 3.05 Å) and WB_2-type (No. 194, $P6_3$/mmc, a, b = 2.9831 Å, c = 13.8790 Å) [7,8]. There has been a lot of research on WB_2-type WB_2. While for AlB_2-type WB_2 films, although it had been fabricated for the first time by hot-filament CVD as early as in 1966 [7], the process was not environmentally-friendly and also the films were porous and too difficult to be further practically applied. Since then, however, there are few successful cases to produce the AlB_2-type WB_2 bulk even film because it is pointed out to be a high pressure phase stable only above about 65 GPa according to the reports [9–11]. Recently, it is found that the AlB_2-type WB_2 film has been prepared by DC magnetron sputtering in our previous work [12]. And the deposited films exhibit high hardness (43.2 ± 5 GPa), low friction coefficient (0.23) and low wear rate (6.5×10^{-6} mm^3/mN), indicating its high potential application as superhard and low wear films. However, the effect of the deposition parameters on the microstructure and properties of AlB_2-type WB_2 films, which is very important to promote the industrial applications, has never been investigated systemically before.

It is well known that the excellent performance of a film significantly depends on the dense microstructure by adjusting the energy delivered to the growing film, particularly substrate heating and conversion of the kinetic energy of bombarding ions and/or the fast neutrals [13–15]. And various microstructures of sputtered thin films, including grain size, preferred orientation, lattice defects, phase composition, and surface morphology, can be modified by changing the sputtering parameters to obtain the desirable properties [16–19].

Therefore, the present work is focused on comprehensively studying the relationship between the microstructure (including preferred orientation, grain size, film thickness, elemental composition, surface and cross-section morphology) and the mechanical and tribological properties of the DC-magnetron-sputtered AlB_2-type WB_2 films, as a function of substrate bias voltage and temperature. In addition, the wear track and debris are also discussed to explore the friction behavior of the AlB_2-type WB_2 film.

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2. Experimental

2.1. Film deposition

WB_2 films were deposited on YG8 (WC–Co) substrates of 20 mm × 20 mm × 3 mm and glasses (for composition characterization) by DC magnetron sputtering. The schematic diagram of the experimental setup had been depicted in detail in our previous study [12]. The commercial WB_2-type WB_2 (99.9%) with the B/W atomic ratio of 2:1 was used as target (270 mm × 70 mm × 7 mm). Prior to deposition, the polished YG8 substrates and glass substrates were degreased ultrasonically in acetone and ethanol successively. Then they were mounted on the resistive heater. And the substrate heating was measured by a thermocouple placed on the substrate holder surface. After the base pressure of the chamber was evacuated to less than 3×10^{-3} Pa, Ar gas was introduced to get an etching pressure about 0.8 Pa. Subsequently, the substrates were sputter-etched by Ar^+ ion bombardment with a substrate bias of −180 V for 10 min to remove contaminations for good adhesion of the deposited films. During the whole deposition process, the sputtering power, argon pressure, target-to-substrate distance and deposition time were kept constant, while only the substrate bias voltage and temperature were changed. And the typical thickness of the deposited films is about 2 μm. The detailed deposition parameters are summarized in Table 1.

2.2. Characterization

To minimize the effect of the high peak intensity of the YG8 substrates, the glancing XRD (X'Pert PRD, PANalytical, Holland) was utilized to detect the phase structure of the as-deposited films. According to the XRD results, the film crystallinity was calculated by means of MDI jade 6. The compositional analysis of the WB_2 films was performed using EPMA (EPMA-1600, Shimadzu, Japan). The surface roughness and morphology were measured by AFM (Pico Scan 2500, Agilent Technologies, USA) under the non-contact mode. Three 2 × 2 μm^2 images were taken at different positions of each sample to get the corresponding average Root Mean Square (RMS) roughness. The microstructure of the film was observed by FESEM (S-3400N, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM; JEM-2010F, JEOL, Japan), respectively.

The nano-indentation tester (Nano indenter G200, Agilent Technologies, USA) with a Berkovich indenter tip under the continuous stiffness mode (CSM) was performed to estimate the mechanical properties of the films according to the method proposed by Oliver and Pharr [20]. To avoid the effect of the substrate and more exactly get hardness H and the effective elastic modulus E* of the samples, a commonly used rule of thumb is to limit the indentation depth to less than 10% of the film thickness. Here E* is given directly by the nano-indentation tester based on the formula $E^* = E / (1 - \nu^2)$, where E is the elastic modulus, and ν is the Poisson's ratio.

Ball-on-disk tribometer (MS-T3000) was applied to obtain the tribological properties of the films with an Al_2O_3 ball (Ø = 4 mm) in a laboratory environment (RT and 30% RH). The applied load, the sliding speed and the sliding distance were set to 1.96 N, 0.106 m/s and 380 m, respectively. Moreover, the wear rate *W* of the samples can be calculated by the Archard's classical wear equation [21]:

$$W = V / (S \times L) \quad (1)$$

where *V* is the wear volume measured using a surface profiler (Alpha-Step IQ; KLA Tencor), *S* is the sliding distance and *L* is the normal load applied. In addition, the morphology and chemical composition of the worn surfaces both on the ball and on the film were also analyzed by FESEM/EDS.

The film-substrate adhesive strength was monitored by MFT-4000 multifunction material surface tester with a Rockwell diamond indenter. The critical load Lc for film failure was determined by combining the change of friction and acoustic emission signal and the corresponding scratch image obtained by optical microscope. The normal load was applied linearly from 0 N to 100 N with a loading rate of 100 N/min.

Table 1
Summary of deposition conditions for AlB_2-type WB_2 films.

Parameters	Value
Sputtering power (W)	175
Argon pressure (Pa)	0.5
Target-to-substrate distance (cm)	7.0
Deposition time (min)	80
Substrate bias voltage (V)	0, −50, −100, −150
Substrate temperature (°C)	300, 400, 500

3. Results and discussion

3.1. Effect of substrate bias voltage

Fig. 1 illustrates the XRD patterns of the WB_2 films obtained by changing the substrate bias voltage. The patterns clearly present that the as-deposited films are AlB_2-type WB_2 according to the analysis in our previous work [12]. By increasing the substrate bias, the preferred orientation of the WB_2 films is found to change from (0 0 1) to (1 0 1), which is in good accordance with the result of AlB_2-type TiB_2 obtained by Sricharoenchai et al. [17]. The model proposed by Lee describes in great detail that the atom or ion concentration adjacent to the deposit plays a very pivotal role in texture evolution [22]; namely, the texture of vapor deposits changes from the orientation that places the lowest energy crystal facets under the condition of low atom or ion concentration adjacent to the deposit, to the orientation that places the higher energy crystal facets as the atom or ion concentration adjacent to the deposit

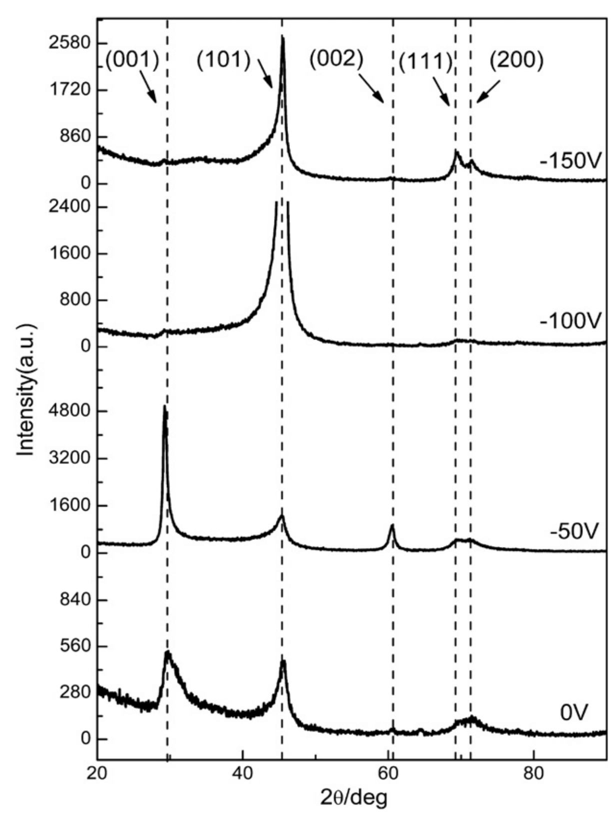

Fig. 1. XRD patterns of the WB_2 films deposited at 400 °C with different substrate biases.