Thermal Stability of WB_2 and W–B–N Films Deposited by Magnetron Sputtering

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Abstract

The work is mainly to study the thermal stability including the phase stability, microstructure and tribo-mechanical properties of the AlB_2 -type WB_2 and W–B–N (5.6 at.% N) films annealed in vacuum at various temperatures, which are deposited on Si and GY8 substrates by magnetron sputtering. For the WB_2 and W–B–N films deposited on Si wafers, as the annealing temperature increases from 700 to 1000 °C, α -WB (700 °C) and Mo_2B_5 -type WB_2 (1000 °C) are successively observed in the AlB_2 -type WB_2 films, which show many cracks at the temperature ≥ 800 °C resulting in the performance failure; by contrast, only slight α -WB is observed at 1000 °C in the W–B–N films due to the stabilization effect of a-BN phase, and the hardness increases to 34.1 GPa first due to the improved crystallinity and then decreases to 31.5 GPa ascribed to the formation of α -WB. For the WB_2 and the W–B–N films deposited on WC–Co substrates, both the WB_2 and W–B–N films react with the YG8 (WC–Co) substrates leading to the formation of CoWB, CoW_2B_2 and CoW_3B_3 with the annealing temperature increasing to 900 °C; a large number of linear cracks occur on the surface of these two films annealed at ≥ 800 °C leading to the film failure; after vacuum annealing at 700 °C, the friction performance of the W–B–N films is higher than that of the deposited W–B–N films, while the wear resistance of the WB_2 films shows a slight decrease compared with that of the deposited WB_2 films.

Keywords AlB_2 -type WB_2 films · W–B–N films · Magnetron sputtering · Thermal stability · Mechanical properties

1 Introduction

Recently, AlB_2 -type WB_2 (No. 191, P6/mmm, $a, b = 3.02$ Å, $c = 3.05$ Å) has been suggested as a highly desirable candidate as coating materials and abrasive tools due to its high hardness, outstanding chemical inertness, good thermal and electrical conductivity and excellent wear-resistance property [1–4], and the incorporation of other elements and microstructure control have been investigated to further improve the tribo-mechanical properties of AlB_2 -type WB_2 films by the nanocomposite or multilayered structure [5–7]. As an incorporation element for the transition metal

borides (TmB_x), light element of N is expected to improve the application-related properties of the films with proper N concentration [5, 8]. For instance, the hardness of the $TiB_2(N)$ films can be enhanced greatly from 35 to 40 GPa by N-doping due to the solution strengthening [9]; the formation of BN is generally believed to improve the lubricating properties of the films because of its graphite-like layered structure [10–12]; the high-temperature stability of Me–B–N films can be enhanced due to the boron nitrogen compounds (h-BN, c-BN) which exhibit good thermal stability at elevated temperatures [13, 14]. In our previous study [5], it had also been confirmed that slight N-doping (5.6 at.%) could improve the wear resistance and corrosion resistance of the AlB_2 -type WB_2 films greatly due to the formation of nc- WB_2/a -BN nanocomposite structure, though the film hardness decreased slightly caused by the soft a-BN phase.

It is well known that a variety of tools for dry and fast machining, such as turning, milling and drilling, are presently being coated with different hard coatings in the industry [15–19]; thus, during application, thermal stability in microstructure and mechanical performance is an important

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factor to be considered for coating materials to be used at high temperatures except for their high hardness and low wear rates. In addition, AlB₂-type WB₂ is a metastable phase stable only above about 65 GPa [20, 21] that is absent in the equilibrium phase diagram [22–24], and its high-temperature stability and properties strongly affected by phase composition and microstructure have been seldom studied up to now. Therefore, in this study, the optimized WB₂ and W–B–N films based on our previous works are annealed in vacuum at various temperatures to study their thermal stability including the phase stability, microstructure and mechanical properties and the corresponding strengthening/degenerating mechanism. Moreover, the thermal stability of the WB₂ and W–B–N films deposited on different substrates (Si and WC–Co) is comparatively investigated. This study will be helpful to develop the W–B phase diagram and serve as guide for the further applications of AlB₂-type WB₂ and W–B–N films.

2 Experimental

2.1 Film Preparation

The WB₂ and W–B–N films (1.8 μm) were deposited on Si (100) wafers (10 mm $\times$ 10 mm $\times$ 0.4 mm) and YG8 (WC–Co, 20 mm $\times$ 20 mm $\times$ 2.5 mm) substrates using a direct-current magnetron sputtering equipment. Details of the deposition apparatus had been published in our previous work [4]. The commercial WB₂-type WB₂ (No. 194, P63/mmc, a , b = 2.9831 Å, c = 13.8790 Å) compound was used as target (99.9%, 270 mm $\times$ 70 mm $\times$ 7 mm). Before the deposition, the polished substrates were ultrasonically cleaned in acetone and ethanol in succession and dried with a blower. Then, the substrates were mounted on a stainless steel sample holder placed at a distance of 70 mm from the target. When the base pressure reached 7×10^{-3} Pa, the substrates were heated to 400 °C by a resistive heater, and the temperature was monitored by a thermocouple attached to the surface of the sample holder. When the base pressure was pumped down to be lower than 2.5×10^{-3} Pa, Ar gas of 0.8 Pa was introduced into the chamber, and the substrate surface was pre-sputtered with Ar⁺ bombardment at a direct-current bias voltage of –180 V for 10 min to remove any residual pollution or surface oxides. Subsequently, WB₂ films were deposited at P_{Ar} = 0.5 Pa, and W–B–N films were deposited at P_{N_2} = 0.006 Pa with a total working pressure of 0.5 Pa controlled by a mass flow control system. During the whole deposition process for both films, a pulsed bias voltage of –50 V was used, and the target current was fixed at 0.5 A. More details for the film deposition conditions are listed in Table 1.

Table 1 Summary of deposition conditions for the optimized WB₂ and W–B–N films

Parameters	Values
Substrate temperature (°C)	400
Target-to-substrate distance (mm)	70
Pulsed bias voltage (V)	–50
Target power (W)	172–176
Working pressure (Pa)	0.5
N ₂ partial pressure (Pa)	0 (WB ₂), 0.006 (W–B–N)
Deposition time (min)	80

After the preparation of the WB₂ and W–B–N films, the samples were annealed at temperatures of 700, 800, 900 and 1000 °C for 2 h conducted in a vacuum annealing furnace with a heating rate of 15–20 K/min. The base pressure of the furnace was 3.0×10^{-4} Pa. After annealing, the samples were cooled down to room temperature in vacuum before they were taken out from the furnace to prevent oxidation.

2.2 Characterization

The surface morphology of the samples was observed by optical microscopy and scanning electron microscopy (SEM; –3400 N, Hitachi, Japan). The crystal structure and phase composition of the sample films were detected by X-ray diffraction (XRD; D/Max-2500PC, Rigaku, Japan). The chemical composition and bonding state of the samples were analyzed by X-ray photoelectron spectroscopy (XPS; ESCALAB250 of Thermo VG, USA). The XPS spectra were obtained after plasma cleaning by in situ sputtering with Ar⁺ ions for 120 s and calibrated by the C1s peak at 284.6 eV.

The hardness H and elastic modulus E of the sample films were determined using a nano-indentation tester (Nano indenter G200, Agilent Technologies, USA) with a diamond Berkovich tip under the continuous stiffness mode (CSM). The hardness H and elastic modulus E of the films were calculated based on the Oliver–Pharr model from the load–displacement curves [25]. In the hardness–displacement curves, the mean hardness value at plateau regions that are less than 10% of the film thickness was taken as the hardness of the sample films to avoid the influence of the substrate according to the earlier work [1], and the value of E was obtained using the same method, and ten indentations were made for each sample.

The wear behavior of the sample films was evaluated by a ball-on-disk tribometer (MS-T3000) with an Al₂O₃ ball ($\varnothing$ = 4 mm) in a laboratory environment (RT and 30% RH). The applied load, sliding speed and sliding distance were set to 1.96 N, 0.106 m/s and 380 m, respectively. The wear volume of the film (V) can be acquired based on the wear track depth profiles detected by a surface profiler (Alpha-Step IQ;

KLA Tencor). Then, the wear rate W can be calculated by the Archard's equation [26]:

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

where V is the wear volume, S is the sliding distance and L is the normal load applied.

3 Results and Discussion

3.1 Microstructure and Composition

The pure WB_2 films and the W–B–N films deposited on Si wafers were investigated by annealing in vacuum at different temperatures (700, 800, 900, 1000 °C) for 2 h, and the structural phase transformations were followed by XRD analysis, as shown in Fig. 1. In Fig. 1a, the as-deposited WB_2 films show the (001) preferred orientation centered at 29.358°. As the annealing temperature increases to 700 and 800 °C, two main orientations of (001) plane and (101) plane centered at 45.658° are observed in the WB_2 films due to the enhanced thermal energy stimulating the growth of other planes. In addition, it is clear that the phase transition of the AlB_2 -type WB_2 (P6/mmm) phase has occurred at 700 °C with the formation of the α -WB (I41/amd) phase that remains stable up to 800 °C. Afterward, they begin to decompose into a large amount of α -WB phase and a small amount of Mo_2B_5 -type WB_2 (R-3m) phase at 900 °C and 1000 °C. In general, the phase transition process of materials can be explained using the phase diagram, and Fig. 2a, b shows the calculated [22] and the experimental [23, 24] W–B phase diagram to investigate the phase transformation results discussed above. Unfortunately, our experimental results disagree with both W–B phase diagrams, which do not show the AlB_2 -type WB_2 phase and Mo_2B_5 -type WB_2 phase and their corresponding phase transformation process in the low-temperature region (<2000 K). The absence of AlB_2 -type WB_2 in the W–B phase diagram is probably because the metastable AlB_2 -type WB_2 phase stable only above about 65 GPa cannot be acquired in thermodynamic equilibrium [20, 21]. In recent years, many phases like W_2B , WB, WB_2 , W_2B_5 , WB_3 and WB_4 have been reported in some theoretical and experimental works [1, 2, 4, 20–22, 27–33], and some inconsistencies about the crystal structure of WB_2 , WB_3 and WB_4 still exist in the W–B system, most of which are absent in the present W–B phase diagram. Therefore, it is believed that the W–B system and its corresponding phase diagram need to be further investigated and developed in the future work.

Figure 1b also presents the XRD patterns of the W–B–N films annealed at different temperatures. For the deposited W–B–N films, AlB_2 -type WB_2 phase and a-BN phase were detected by means of XRD and XPS referring to our

Fig. 1 XRD patterns of the sample films annealed at different temperatures for 2 h, **a** WB_2 films, **b** W–B–N films with 5.6 at.% nitrogen on Si wafers

previous work [5]. As the annealing temperature increases, it can be seen that the peak intensity of the W–B–N films increases greatly indicating the improved crystallinity of the films, which is 69.0, 87.0, 90.6, 95.4 and 98.1%, respectively, calculated by the MDI Jade 6 software based on the XRD patterns of the sample films. In addition, the samples do not change up to a temperature of 1000 °C. At 1000 °C, only a weak peak centered at 42.337° corresponding to the α -WB phase is obtained in the XRD patterns. Obviously, the transformation temperature of the pure AlB_2 -type WB_2 phase has been improved greatly from 700 to 1000 °C by slight N-doping (5.6 at.%), and the reason will be discussed in the following part.

To study the phase composition of the sample films and the mechanism for the improved phase stability, the XPS spectra of W 4f, B 1s and N 1s of the WB_2 and W–B–N films annealed at 900 °C are shown in Fig. 3. Figure 3a shows the W 4f spectra of the sample films. The existence of the

Fig. 2 **a** W–B phase diagram calculated from the Gibbs energy functions [22], **b** experimental W–B phase diagram [23, 24]

Fig. 3 XPS spectra of W 4f **a**, B 1s **b**, N 1s **c** peaks of the WB₂ and W–B–N films annealed at 900 °C

AlB₂-type WB₂ compound in the annealed W–B–N films is proved by double peaks centered at 31.24 eV (W 4f 7/2) and 33.42 eV (W 4f 5/2) [4], which, however, tend to shift toward the lower binding energies centered at 31.16 eV (W 4f 7/2) and 33.34 eV (W 4f 5/2) corresponding to the WB phase in the annealed WB₂ films [34]. Figure 3b shows the B 1s spectra of the sample films. For the annealed WB₂ films,

B 1s only has a peak centered at 188.05 eV corresponding to that of WB [34]. For the annealed W–B–N films, two peaks centered at 188.13 eV and 190.23 eV are observed, which can be assigned to AlB₂-type WB₂ phase [4] and BN phase [34], respectively. From Fig. 3c, it can be observed that the N 1s spectrum of the annealed W–B–N films shows only one peak centered at 397.6 eV, further confirming the existence

of BN phase in the annealed W–B–N films [34]. Based on the XRD and XPS results, we can conclude that the amorphous BN must exist in the W–B–N films annealed at 900 °C and no other phases are formed during the annealing process, and the annealed W–B–N films have the same phase composition compared with that of the deposited W–B–N films referring to our previous work [5]. Therefore, it is believed that the annealed W–B–N films still have the crystalline/amorphous (WB₂/a-BN) structure, which contributes to the very high phase stability of the W–B–N films with less N-doping [5]. The presence of the a-BN amorphous matrix with strong covalent bonds helps the stabilization of the WB₂ phase by forming a strong interface that hinders the atom diffusion during the phase transition process [13, 14], which is similar to the results of C-doping into the AlB₂-type WB₂ films [6] with the formation of a-C.

XPS depth scanning method was also used to get the relative content of each element in the WB₂ and W–B–N films before and after annealing at 900 °C. It is worth noting that the oxygen impurity exists inevitably in the films due to the relatively high base pressure. The content of the oxygen impurity is about 3.2–3.6 at.% in both the as-deposited and the annealed WB₂ and W–B–N films, and only the relative contents of B, W and N elements are listed in Table 2. It can be seen that there is almost no difference for the contents of W, B and N elements between the as-deposited and the annealed W–B–N films. When the WB₂ film was annealed

at 900 °C, the relative contents of W and B elements in the films change greatly, and the B/W atomic ratio varies from 61.1%:38.9% $\approx$ 1.6 to 52.8%:47.2% $\approx$ 1.1, which is mainly attributed to the formation of a-WB phase in the annealed WB₂ films and the possible diffusion of B atoms out from the WB₂ films during the annealing process at 900 °C.

Figure 4 presents the surface morphologies of both the WB₂ and W–B–N films deposited on Si wafers after vacuum annealing at different temperatures. In Fig. 4a, the WB₂ film annealed at 700 °C still shows the relative smooth surface. In Fig. 4b–d, it is obvious that some linear cracks occur on the surface of the WB₂ films, and the number of the cracks gradually increases with increasing annealing temperature, leading to the film failure. In Fig. 4e–h, it is found that the surfaces of the W–B–N films annealed at 700, 800, 900 °C are relatively smooth and no cracks occur on the film surface, and only some micro-cracks are observed on the W–B–N films annealed at 1000 °C, as shown in the inset of Fig. 4h. The above results indicate that the thermal stability of the WB₂ films is relatively poor accompanied with a number of linear cracks, which, however, can be eliminated by adding small amount of nitrogen. In addition, the linear cracks demonstrate that the film has the obvious tensile stress during the annealing process [5], which mainly results from (1) the transformation stress; (2) the thermal stress caused by the difference of the thermal expansion coefficient between the substrates and films; (3) the tensile stress (263.6 MPa) of

Table 2 Element compositions of the WB₂ and W–B–N films deposited on Si wafers before and after vacuum annealing at 900 °C

Element	WB ₂ films		W–B–N films		
	W (at.%)	B (at.%)	W (at.%)	B (at.%)	N (at.%)
As-deposited samples	38.9	61.1	33.7	60.7	5.6
Annealed samples (900 °C)	47.2	52.8	33.5	61.0	5.5

Fig. 4 Surface morphology of a–d WB₂ films, e–h W–B–N films deposited on Si wafers annealed at different temperatures

the deposited WB₂ films according to our previous work [5] causing the linear cracks easily during annealing. Since no obvious phase transition is found for the W–B–N films, only the thermal stress occurs in the W–B–N films during the annealing process, which cannot be large enough to destroy the film. Moreover, the compressive stress in the deposited W–B–N films (−657.8 MPa) [5] can be released by annealing, resulting in the difficulty in crack generation.

Because the WB₂ and W–B–N films deposited on YG8 substrates annealed at 700 and 800 °C present the same phase evolution (not shown here) compared with that of the films deposited on Si wafers in our experiment, only the XRD patterns of these two films deposited on YG8 substrates after annealing at 900 °C are given in Fig. 5. It is clear that CoWB, CoW₂B₂ and CoW₃B₃ are detected in the annealed films, which indicate that Co element in the substrates reacts with the films during the annealing process at above 800 °C. The results indicate that slight N-doping cannot play a major role in improving the thermal stability of the WB₂ films deposited on WC–Co substrates. In addition, the thermal stability of both films deposited on Si wafers

is higher as compared with the films deposited on WC–Co substrates because silicon element does not diffuse noticeably into the films [13].

Figure 6 presents the surface morphologies of the WB₂ and W–B–N films deposited on YG8 substrates after vacuum annealing at different temperatures. The very smooth surfaces are obtained for both WB₂ and W–B–N films annealed at 700 °C shown in Fig. 6a, c, and the annealed WB₂ films show the relatively larger particle size as compared with the annealed W–B–N films, which further confirms that N-doping can lead to the refinement of grain size [5]. As the annealing temperature increases to 800 °C, many linear cracks and small bumps containing substrate elements evidenced by EDS analysis occur on the surface of these two films. The above results declare that the diffusion of Co from the YG8 substrate into the film during annealing is limiting the thermal stability of the WB₂ and W–B–N films, which, therefore, cannot be used on YG8 substrates above 800 °C in vacuum for a long time. Combined with the results about the films deposited on Si wafers, three methods can be tried to improve the thermal stability of the WB₂ and W–B–N films deposited on WC–Co substrates: (1) adding Si or other stable transition layers like Si₃N₄ or BN between the films and the WC–Co substrates to hinder the diffusion of substrate elements into the films, but the adhesive strength of the films should be a concern; (2) depositing the nc-WB₂/a-Si₃N₄ or nc-WB₂/a-BN composite films and adjusting the ratio of nanocrystalline to amorphous phase (a-Si₃N₄ and a-BN) which plays an enormous hindrance role to the diffusion of substrate elements based on Karvanková's works [13]; (3) removing Co element in the WC–Co substrates before the film deposition, which, however, will loosen the WC–Co substrate and then deteriorate its properties. Therefore, this will be our next research focus to improve the thermal stability of the WB₂-based films deposited on WC–Co substrates.

Fig. 5 XRD patterns of **a** WB₂ films, **b** W–B–N films annealed at 900 °C deposited on YG8 substrates

3.2 Mechanical Properties

Since many cracks are acquired on the WB₂ films annealed at ≥ 800 °C, Fig. 7 only shows the hardness and the elastic modulus of the W–B–N films deposited on Si wafers before and after vacuum annealing as a function of temperature. It is clear that the hardness of the deposited W–B–N films can be improved by vacuum annealing, and the W–B–N films annealed at 900 °C have the highest hardness about 34.1 GPa, which mainly benefits from its high crystallinity. The W–B–N films annealed at 1000 °C present the relatively lower hardness about 31.9 GPa, which is because the hardness of the WB phase with less B–B covalent bond formed in the annealed W–B–N films is lower than that of the WB₂ phase. From Fig. 7, it also can be seen that the elastic modulus of the W–B–N films decreases from 490.4 to 390.9 GPa with the increase in the annealing temperature. It is well

Fig. 6 Surface morphology of **a, b** WB_2 films, **c, d** W-B-N films deposited on YG8 substrates annealed at different temperatures

Fig. 7 Hardness and elastic modulus of the W-B-N films deposited on Si wafers annealed at different temperatures

known that elastic modulus for the bulk material is usually insensitive to structure, which is less affected by the heat treatment. However, elastic modulus of the film is usually different from that of the respective bulk material due to several common features affected by the heat treatment obviously in the film, such as defects, grain size, residual

stress and preferred orientation. Since as the annealing temperature increases, the crystallinity, phase composition and residual stress of the W-B-N films change markedly, inducing the variation of the film's elastic modulus. In detail, as the annealing temperature increases, the formation of WB phase with less B-B bond and the increased stress (including the tensile thermal stress and the transformation stress) allow small load to be distributed over a given area, resulting in the reduction in the W-B-N film's elastic modulus.

The hardness of the WB_2 and W-B-N films deposited on YG8 substrates before and after vacuum annealing at 700 °C is listed in Table 3. It can be seen that the hardness of the annealed WB_2 films is slightly lower than that of the deposited WB_2 films, which is mainly attributed to two factors: (1) the increased grain size for the annealed WB_2 films according to the Hall-Petch theory; (2) more (101) planes with lower hardness compared with (001) plane in the annealed WB_2 films with the hexagonal crystal structure based on some other works [1, 2, 18]; (3) the release of residual stress in the films during annealing. On the contrary, the hardness of the annealed W-B-N films is higher than that of the deposited W-B-N films, which mainly benefits

Table 3 Hardness, friction coefficient and wear rate of the WB₂ and W–B–N films deposited on YG8 substrates before and after vacuum annealing at 700 °C

	As-deposited films		Annealed films	
	WB ₂	W–B–N	WB ₂	W–B–N
Hardness (GPa)	36.0	32.8	34.7	35.6
Friction coefficient	0.39	0.34	0.41	0.32
Wear rate (10 ^{−7} mm ³ /mN)	4.05	2.20	6.36	1.7

from its improved crystallinity caused by the high annealing temperature.

Table 3 also provides the friction coefficient and the wear rate of the WB₂ and W–B–N films deposited on YG8 substrates before and after vacuum annealing at 700 °C. The effective friction coefficient was obtained by calculating the average values at the steady state of the friction curve. It can be seen that the friction performance of the deposited WB₂ films can be improved with an initial incorporation of a small amount of nitrogen, and the deposited W–B–N films present outstanding capability of wear resistance with low friction coefficient 0.34 and wear rate 2.20×10^{-7} mm³/mN, which has been discussed in detail in our previous work [5]. After vacuum annealing, the friction performance of the WB₂ films is reduced with friction coefficient 0.41 and wear rate 6.36×10^{-7} mm³/mN, which mainly results from the decreased hardness and the increased tensile stress making cracks occur easily during the wear process. In Table 3, it also reveals that the friction performance of the W–B–N films is slightly improved by vacuum annealing at 700 °C with friction coefficient 0.32 and wear rate 1.7×10^{-7} mm³/mN due to the enhanced hardness and the nc-WB₂/a-BN structure, which can inhibit the crack initiation and propagation due to the strong interfaces between nanocrystallite and amorphous phases [35, 36].

4 Conclusions

AlB₂-type WB₂ films and W–B–N films with 5.6 at.% N have been deposited on Si wafers and YG8 substrates by reactive magnetron sputtering, and the prepared films are treated by vacuum annealing at different temperatures (700–1000 °C). The phase structure, element composition, microstructure and tribo-mechanical properties of both the deposited and the annealed films have been investigated systematically, and the results can be drawn as follows:

1. For the WB₂ and W–B–N films deposited on Si wafers, the transformation temperature of the AlB₂-type WB₂ phase has been improved greatly from 700 to 1000 °C by N-doping (5.6 at.%) due to the stabilization effect

of a-BN. As the annealing temperature increases from 700 to 1000 °C, a-WB (700 °C) and Mo₂B₅-type WB₂ (1000 °C) are successively observed in the AlB₂-type WB₂ films, which show many cracks at the temperature ≥ 800 °C resulting in the performance failure; by contrast, only slight α -WB is observed at 1000 °C in the W–B–N films with a small quantity of micro-cracks.

2. Compared with the deposited WB₂ and W–B–N films, the contents of W, B and N in the W–B–N films annealed at 900 °C almost keep the same and a-BN phase still exists in the film, while the B/W atomic ratio of the WB₂ films changes from 1.5 to 1.1 with the annealing temperature increasing to 900 °C.
3. As the annealing temperature increases to 900 °C, both the WB₂ and W–B–N films react with the Co element in YG8 (WC–Co) substrates leading to the formation of CoWB, CoW₂B₂ and CoW₃B₃, and a large number of linear cracks occur on the surface of these two films annealed at ≥ 800 °C leading to film failure.
4. As the annealing temperature increases, the hardness of the W–B–N films deposited on Si wafers increases to 34.1 GPa (900 °C) first due to the improved crystallinity and then decreases to 31.5 GPa ascribed to the formation of a-WB phase.
5. After vacuum annealing at 700 °C, the friction performance of the W–B–N films deposited on YG8 substrates is higher than that of the deposited W–B–N films, while the friction performance of the WB₂ films shows a slight decrease compared with that of the deposited WB₂ films.

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References

- [1] Y.M. Liu, C.L. Jiang, Z.L. Pei, H. Lei, J. Gong, C. Sun, *Surf. Coat. Technol.* **108**, 245 (2014)
- [2] Y.M. Liu, R.Q. Han, F. Liu, Z.L. Pei, C. Sun, *J. Alloys Compd.* **188**, 703 (2017)
- [3] C.L. Jiang, Z.L. Pei, Y.M. Liu, H. Lei, J. Gong, C. Sun, *Appl. Surf. Sci.* **324**, 288 (2014)
- [4] C. Jiang, Z. Pei, Y. Liu, J. Xiao, J. Gong, C. Sun, *Phys. Status Solidi A* **1221**, 210 (2013)
- [5] Y. Liu, D. Deng, H. Lei, Z. Pei, C. Jiang, C. Sun, J. Gong, *J. Mater. Sci. Technol.* **1217**, 31 (2015)
- [6] Y.M. Liu, Z.L. Pei, J. Gong, C. Sun, *Surf. Coat. Technol.* **276**, 291 (2016)
- [7] D. Fan, H. Lei, C.Q. Guo, J. Gong, C. Sun, *Surf. Technol.* **156**, 46 (2017). (in Chinese)
- [8] Q. Wang, F. Zhou, Z. Zhou, K.Y. Li, J. Yan, *Vacuum* **186**, 145 (2017)
- [9] H. Deng, J. Chen, R.B. Inturi, J.A. Barnard, *Surf. Coat. Technol.* **609**, 76 (1995)

- [10] Q. Wang, F. Zhou, Q. Ma, M. Callisti, T. Polcar, J. Yan, Appl. Surf. Sci. **635**, 443 (2018)
- [11] A. Kovalčíková, J. Balko, C. Balázsi, P. Hvizdoš, J. Dusza, J. Eur. Ceram. Soc. **3319**, 34 (2014)
- [12] X.G. Xu, C.H. Xu, B. Fang, C.L. Wang, M.D. Yi, Key Eng. Mater. **307**, 589 (2014)
- [13] P. Karvankova, M.G.J. Veprek-Heijman, M.F. Zawrah, S. Veprek, Thin Solid Films **133**, 467 (2004)
- [14] Y.H. Lu, Y.G. Shen, K.Y. Li, H. Chen, Surf. Coat. Technol. **1228**, 201 (2006)
- [15] J. Musil, M. Jaroš, R. Čerstvý, S. Haviar, J. Vac. Sci. Technol. A **020601**, 35 (2017)
- [16] M. Danek, F. Fernandes, A. Cavaleiro, T. Polcar, Surf. Coat. Technol. **158**, 313 (2017)
- [17] T.G. Wang, Y. Dong, B.A. Gebrekidan, Y.M. Liu, Q.X. Fan, K.H. Kim, Acta Metall. Sin. (Engl. Lett.) **688**, 30 (2017)
- [18] S. Zhang, Z. Wang, P. Guo, P. Ke, M. Odén, A. Wang, Surf. Coat. Technol. **134**, 322 (2017)
- [19] Q.X. Fan, J.J. Zhang, Z.H. Wu, Y.M. Liu, T. Zhang, B. Yan, T.G. Wang, Acta Metall. Sin. (Engl. Lett.) **1**, 30 (2017)
- [20] E. Zhao, J. Meng, Y. Ma, Z. Wu, Phys. Chem. Chem. Phys. **13158**, 12 (2010)
- [21] X.-Q. Chen, C. Fu, M. Krčmar, G. Painter, Phys. Rev. Lett. **196403**, 100 (2008)
- [22] H. Duschaneck, P. Rogl, J. Phase Equilib. **150**, 16 (1995)
- [23] E. Rudy, AFML-TR-65-2, Part V (Air Force Materials Lab, Wright-Patterson AFB, 1969), p. 214
- [24] W.G. Moffatt, *Binary Phase Diagram Handbook* (Schenectady, New York, 1983)
- [25] W.C. Oliver, G.M. Pharr, J. Mater. Res. **1564**, 7 (1992)
- [26] J.F. Archard, J. Appl. Phys. **981**, 24 (1953)
- [27] X. Li, Y. Tao, F. Peng, J. Alloys Compd. **579**, 687 (2016)
- [28] Y. Liang, Z. Fu, X. Yuan, S. Wang, Z. Zhong, W. Zhang, Europhys. Lett. **66004**, 98 (2012)
- [29] T. Moscicki, J. Radziejewska, J. Hoffman, J. Chrzanowska, N. Levintant-Zayonts, D. Garbiec, Z. Szymanski, Ceram. Int. **8273**, 41 (2015)
- [30] H.P. Woods, F.E. Wawner, B.G. Fox, Science **75**, 151 (1966)
- [31] M. Frotscher, W. Klein, J. Bauer, C.M. Fang, J.F. Halet, A. Senyshyn, C. Baetz, B. Albert, Z. Anorg. Allg. Chem. **2626**, 633 (2007)
- [32] M. Maździarz, T. Mościcki, Mater. Chem. Phys. **92**, 179 (2016)
- [33] Y. Liang, Y. Gou, X. Yuan, Z. Zhong, W. Zhang, Chem. Phys. Lett. **48**, 580 (2013)
- [34] <http://srdata.nist.gov/xps/ElmSpectralSrch.aspx?selEnergy=PE>
- [35] S. Veprek, S. Reiprich, Thin Solid Films **64**, 268 (1995)
- [36] S. Veprek, J. Vac. Sci. Technol. A **2401**, 17 (1999)