Synthesis and characterization of amorphous Al–Mg–B prepared by various deposition temperatures

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Abstract Amorphous Al–Mg–B thin films were synthesized via a combinatorial sputtering approach. The properties of Al–Mg–B films with the varying deposition temperature was investigated. The deposition temperature was found to dominate the hardness of the amorphous as-deposited film. The hardness increases with increasing deposition temperature and may even exceed that of crystalline $AlMgB_{14}$ material. The high hardness may be attributed to the existence of randomly distributed B_{12} icosahedra structure. Therefore, the thin film that was deposited on cemented carbide shows well-cutting performances in turning Ti alloy bar. At the same time, an appropriate method of pretreatment is the key to ensure the coating tool with the excellent adhesion by impact fracture test.

Keywords Amorphous Al–Mg–B; Deposition temperature; Properties; Coated cutting tool

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1 Introduction

There has been considerable interest in boron and boron-rich compounds because boron can form the basis of several important materials, each with a variety of intriguing structural phases. These boride materials usually compose phases that are boron rich, with the main building block, B_{12} icosahedra, interdispersed between several types of chemical impurities. A typical example is $AlMgB_{14}$, a class of superhard material [1, 2]. In this orthorhombic intermetallic compound, the regular boron polyhedrons are arranged as the major skeleton with a forbidden morphology [3]. This special crystal texture contributes to the excellent hardness. Moreover, $AlMgB_{14}$ material has low friction coefficient [2, 4]. Therefore, it is widely used as material on cutting tools.

$AlMgB_{14}$ material used previously was crystalline and in bulk form [5–7]. However, it is well known that thin film materials have advantage that it can be attached to the surface of complex tools and endue the substrate with new property. Moreover, amorphous film usually exhibits unique mechanical properties [8]. Therefore, it is expected that amorphous Al–Mg–B thin films possess higher hardness and lower friction coefficient. In fact, many researchers from Ames laboratory have finished lots of work about $AlMgB_{14}$ material and Al–Mg–B thin film synthesis and deposition [2, 4–7, 9, 10], and the sintered crystal $AlMgB_{14}$ was the major original material as sputtering source to prepare thin film. The metal-rich Al–Mg–B film was easily obtained by bulk $AlMgB_{14}$ material sputtering, which does not correspond to the $AlMgB_{14}$ stoichiometry [11].

The effect of elements concentration on the structural and mechanical properties has been investigated in Ref. [12]. Based on the results of the above study, and to obtain

better performances, the sputtering parameter was fixed at a constant that is according to the best state in previous study. Therefore, Al–Mg–B film with different deposition temperature was prepared by magnetron sputtering method. The surface morphology, hardness, and friction coefficient of the films were examined. Then, the effects of deposition temperature on these properties are discussed. Then again, the cutting performance of Al–Mg–B coating tools was also investigated.

2 Experimental

Al–Mg–B thin films were deposited on Si (100) wafers and cemented carbide (WC-6 % Co) cutting tools by magnetron sputtering method. Elementary substance materials, Al (purity 99.99 %, Φ75 mm × 4 mm), Mg (99.95 %, Φ75 mm × 4 mm), and boron (99.9 %, Φ75 mm × 4 mm), were used as the sputtering targets. High-purity argon (99.999 %) was used as the sputtering gas. To get rid of the surface contamination, the Si wafers were cleaned with acetone, alcohol, and deionized water in an ultrasonic bath. WC-Co (YG6X) sample was submitted to a two-step chemical etching with Caro's acid solution of hydrogen peroxide (3 ml 96 wt% H_2SO + 88 ml 40 % m v^{-1} H_2O_2, 30 min etching time) and then with a Murakami's reagent (10 g $K_3[Fe(CN)_6]$ + 10 g KOH + 100 ml water, 30 s etching time) [13, 14]. During deposition, the chamber was evacuated to a base pressure of 7.0×10^{-4} Pa and then Ar plasma sputtering was conducted to clean substrates for 15 min at a negative bias voltage of 650 V before deposition of the Al–Mg–B films. The deposition pressure, sputtering distance, Ar flow ratio, Al/Mg target (at an area ratio of 5:3), and boron target power were kept at 0.5 Pa, 110 mm, 8 ml·min^{-1}, 20 and 400 W, respectively. Deposition temperature, as a unique variable, increases from 300 to 600 °C, and the detailed conditions of deposition are shown in Table 1.

The film chemical composition was investigated by electron probe microanalysis (EPMA; Shimadzu EPMA-1600). The material structure was identified by X-ray diffraction (XRD; Bruker Discover 8) using Cu Kα radiation (λ = 0.15418 nm) and by transmission electron microscopy (TEM; FEI Tecnai 20). The TEM specimens were prepared by depositing films on carbon-coated copper grids. Fourier transform infrared (FTIR) spectrometer was employed to extract local bonding information. The surface morphology was observed by optical microscopy and atomic force microscopy (AFM; Being Nano-Instruments CSPM-5000). The hardness was measured by nanoindentation with the continuous stiffness measurement technique using a Vickers diamond indenter (MTS, Nanoindenter XP). The chemical composition was analyzed by a VG ESCALAB 250 X-ray photoelectron spectroscope (XPS) equipped with a monochromatic Al Kα (1486.6 eV) X-ray source. Hardness measurement was constrained by the maximal indentation depth to <15 %–20 % of the as-deposited film thickness to avoid substrate effects arising from the underlying Si wafer substrate. The friction coefficient of the films was measured against Si_3N_4 balls in air to evaluate the friction behavior.

3 Results and discussion

Samples deposited with different deposition temperatures are listed in Table 1. Sample Nos. 1–4 were deposited using deposition temperature from 300 to 600 °C. A deposition temperature <300 °C may result in a cracked film. First, the concentrations of Sample Nos. 1–4 were investigated. Generally, the adsorption rate of deposition decreases with increasing temperature [15]. This effect is more significant on magnesium because the magnesium concentration slightly decreases with increasing deposition temperature. Corresponding to the decrease in the magnesium concentration, the aluminum concentration increases. The effect of deposition temperature on boron concentration is slight. The structure of as-deposited films is amorphous, which was determined by XRD. As an example, the XRD profile and TEM images of Sample No. 4 are given in Fig. 1. In the XRD profile (Fig. 1a), no crystalline peak can be seen. Correspondingly, amorphous features can be readily seen in TEM image and the selected area diffraction pattern (Fig. 1b and inset).

The surface topographies of the films with different deposition temperature were investigated by AFM. The images of Sample Nos. 1–4 corresponding to Fig. 2a–d display a smooth surface profile dominated by domed features, whereas the deposition temperature increased. The root mean square (RMS) roughness measured over the scan area of 3 mm × 3 mm is 2.25, 2.01, 1.48, and 1.15 nm, respectively. With increasing deposition temperature, the higher substrate temperature will enhance the surface particle migration, which could explain the evolution of surface roughness.

Table 1 Deposition parameters of amorphous Al–Mg–B thin films

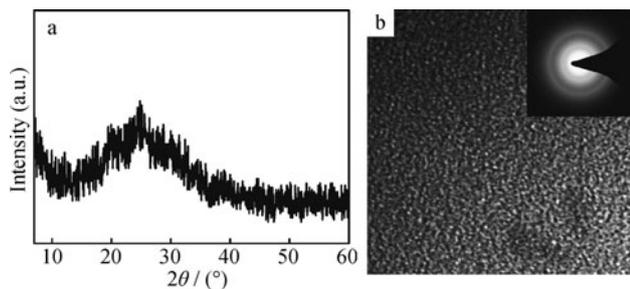| Sample Nos.	Sputtering power/W		Deposition temperature/°C	Substrate
	Al/Mg	B		
1	20	400	300	Si
2	20	400	400	Si
3	20	400	500	Si
4	20	400	600	Si, YG6X cutting tool

Fig. 1 Microstructure analysis of Sample No. 4: **a** XRD profile of sample, and **b** TEM images (inset being the corresponding selected area diffraction pattern)

The Vickers hardness of the Al–Mg–B thin film as a function of deposition temperature is shown in Fig. 3. The hardness of the as-deposited film increases with increasing deposition temperature and reaches a maximum value of 43 GPa. The detailed hardness value as a function of displacement into surface is shown in the inset. It was suggested that the increase in the hardness of amorphous Al–Mg–B with increasing deposition temperature is possibly related to the formation of B_{12} icosahedron unit [16]. This suggestion can be supported by the fact that the relatively high hardness of pure boron materials, such as α-boron or β-boron, is due to the formation of stable B_{12} icosahedron structure [17]. The B_{12} icosahedron unit also exists in the amorphous Al–Mg–B films, which can be confirmed by FTIR analysis. As shown in Fig. 4, the spectrum of the silicon substrate is shown here for comparison. In substrate, the broad absorption peak at a wave number of 1,100 cm^{-1} originates in the Si–O compounds on the surface. However, the strong absorption peaks at 1,100 cm^{-1} from the as-deposited thin films can be attributed to B_{12} icosahedron vibrations [17], which could be assigned to an overlapping of A2u and Eu vibrational modes of a single B_{12} icosahedron [18]. However, further research will be aimed toward the characterization of B_{12} by different testing methods. With increasing deposition temperature, the intensity of absorption peak become stronger, indicating an increase in the concentration of B_{12} icosahedron in the films, which results in an increase in the hardness. Moreover, the higher deposition temperature could improve the film density by enhancing the migration effect, that is, the thermal motion of deposition atoms. The absorption peak at 610 cm^{-1} could be attributed to Si–Si bond of the substrate and the Al–O and Mg–O bonds of the as-deposited thin film. This result can be confirmed by XPS analysis.

High-resolution XPS core level spectra Al 2p, Mg 1s, and B 1s were collected from all the samples. The B 1s spectrum in Fig. 5a was acquired from Sample No. 4. The deconvoluted spectrum shows at least three chemical states. The peak at a binding energy of 187.62 eV is
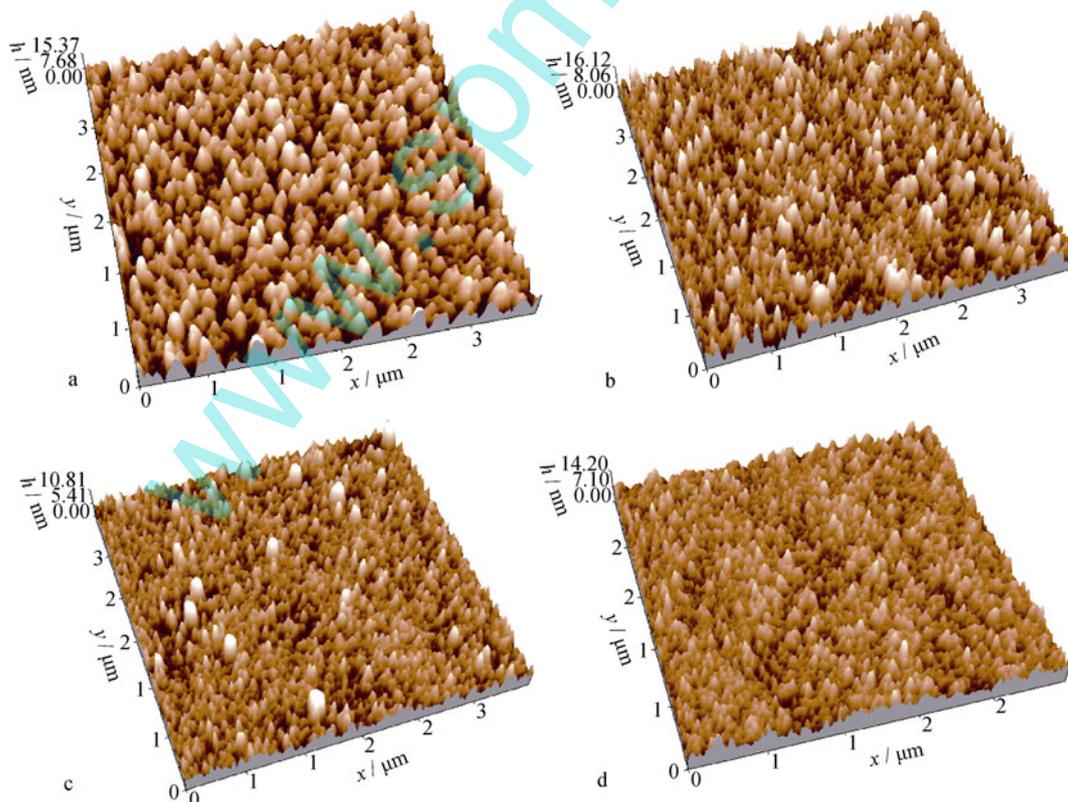

Fig. 2 AFM surface morphology of Al–Mg–B thin films as a function of deposition temperature: **a** 300 °C, **b** 400 °C, **c** 500 °C, and **d** 600 °C

assigned to B–B bonding and the broad peak at 188.61 eV corresponds to borides. The Al 2p accumulated from the same analysis spot, in Fig. 5b, shows three deconvoluted peaks. The peak at a binding energy of 74.02 eV reveals Al–Al and the peak at a binding energy of 75.01 eV denotes Al-borides. The higher binding energy of 75.53 eV arises from some Al–O bonds, which are abundant in the surface region due to adventitious adsorption of water and oxygen species during sample exposure to air. However, the Mg 1s core level, in Fig. 5c, is deconvoluted to two peaks at binding energies of 1,304 and 1,303.8 eV that are associated with the presence of Mg–Mg state and magnesium oxides [19].

The friction properties of these samples were then studied. The average friction coefficients decrease gradually from 0.25 to 0.15 with increasing deposition temperature. It is possibly due to self-lubricating by the formation of a thin boric acid boundary film. In previous studies of Al–

Mg–B film and boron-rich compounds [20, 21], it was suggested that the surface oxidation might form a glassy B_2O_3 layer. This layer spontaneously reacts with ambient water vapor to form a thin boric acid boundary film. This impure thin film has a low friction coefficient of ~ 0.15 and hence causes an excellent self-lubricant performance [22].

Coated cutting tool with amorphous Al–Mg–B thin film was prepared at the highest deposition temperature. Figure 6 shows the rake face wear data of uncoated and coated
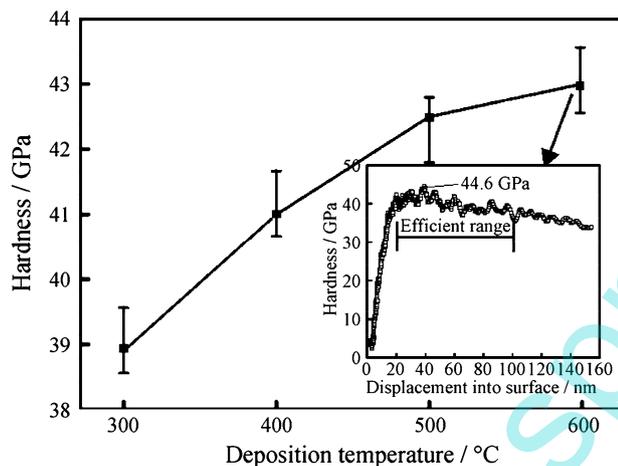

Fig. 3 Hardness of Al–Mg–B films as a function of deposition temperature
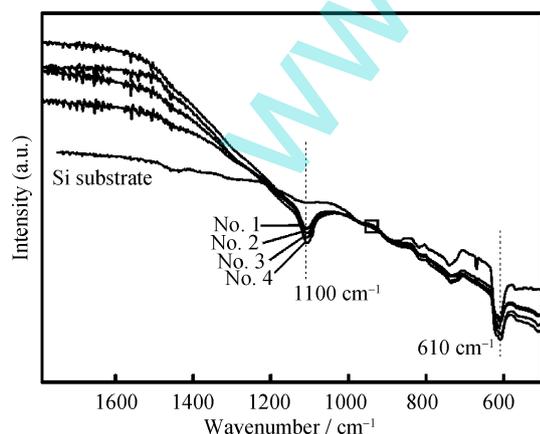

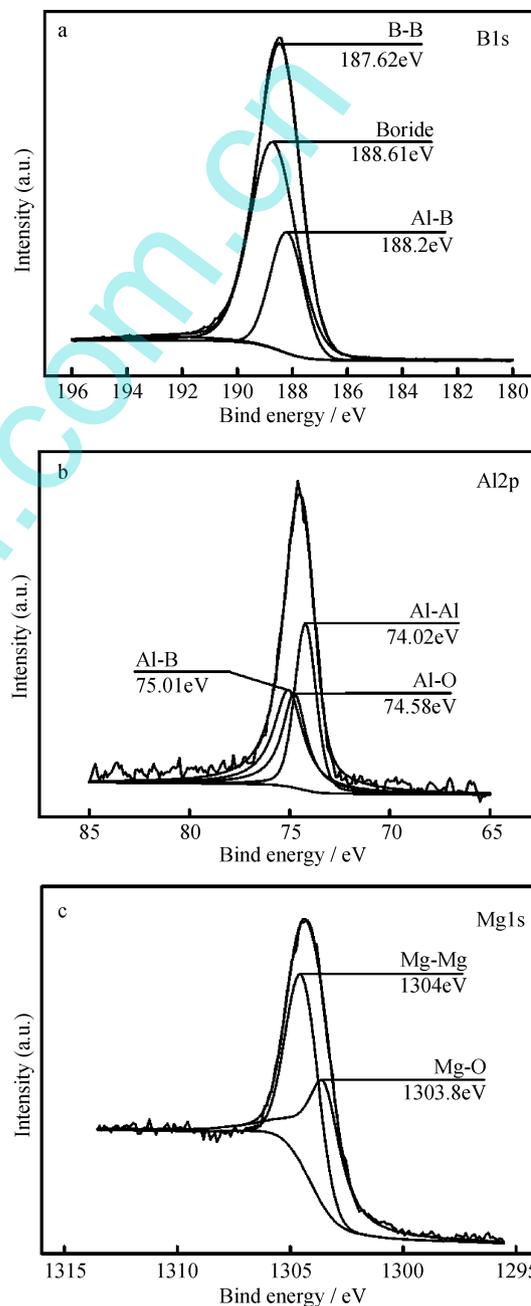Fig. 4 FTIR spectra of Al–Mg–B thin films as a function of deposition temperature

Fig. 5 High-resolution XPS core level spectra of Sample No. 4: **a** B 1s core level spectrum, **b** Al 2p core level spectrum, and **c** Mg 1s core level spectrum
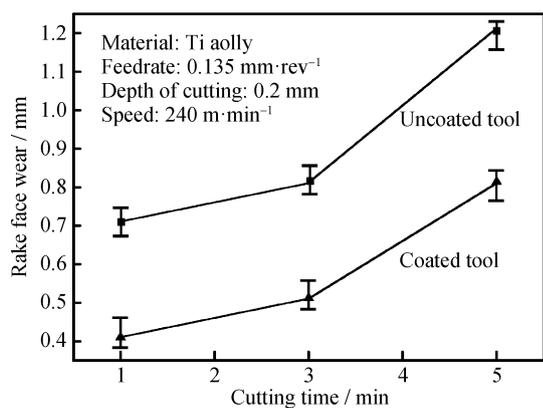
Fig. 6 Rake face wear versus cutting time for uncoated and coated YG6X cutting tools in dry machining
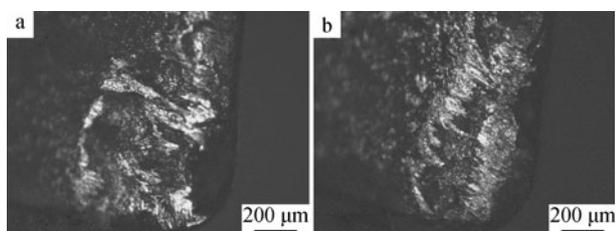

Fig. 7 Optical micrographs showing rake face wear patterns of **a** uncoated, **b** coated YG6X cutting tools

YG6X carbide inserts in turning Ti alloy bars. The coated tools provided consistent reductions in wear with cutting time, although the length of rake face wear craters with an increase in cutting time. An increase in coating hard and thickness is expected to further increase the wear performance for two reasons: (1) more volume is available for wear and (2) plastic deformation of the corner radius, responsible for cracking and spallation of the flank face, decreases [23, 24]. Hence, coated cutting tool possesses good abrasion-resistant properties than uncoated.

The optical micrographs in Fig. 7 is showing the wear pattern of rake face. Uncoated tools (Fig. 7a) exhibited significant cratering. However, the improved wear resistance of coated tools (Fig. 7b) is due to higher hardness, adherence of coating to the sharp edges because of the coating's thinness ($\sim$500 nm), and appropriate method of pretreatment. On the other hand, the performance of coated cutting tool was directly relevant to the quality of thin film and preparation method [24].

4 Conclusion

In conclusion, amorphous Al–Mg–B films with high hardness and low friction coefficient were fabricated on silicon wafer using magnetron sputtering method. It was observed that the increase in deposition temperature can improve the hardness and decrease the friction coefficient. The increase in the hardness is related to the formation of B_{12} icosahedron unit. Moreover, coated cutting tool with amorphous Al–Mg–B exhibits well-cutting performance. Because of these excellent properties, the amorphous Al–Mg–B films prepared by magnetron sputtering method are good candidates as protective coating for cutting tools.

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