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Improving the mechanical and tribological properties of TiB_2/a-C nanomultilayers by structural optimization

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ABSTRACT

A novel nanomultilayered architecture was developed through magnetron sputtering to simultaneously achieve excellent mechanical and tribological properties in TiB_2/a-C film. Structural optimization was conducted by adjusting the modulation period from 1 to 10.5 nm. Film hardness and toughness were significantly improved and reached the optimal value at $\Lambda = 6.6$ nm. Combination of a sufficient number of heterointerfaces and appropriate individual layer thickness played a key role in hardening and toughening. The internal stress increased linearly with the increase in modulation period, which may be related to the reduction in the number of interfaces. Furthermore, a low friction coefficient of about 0.1 was achieved in the steady state at $\Lambda \leq 6.6$ nm due to the formation of a uniform and compact transfer film on the worn ball surface. The improved mechanical performance and the presence of an effective transfer film resulted in an outstanding anti-wear performance at $\Lambda = 6.6$ nm.

1. Introduction

Titanium diboride (TiB_2) is a transition metal based ceramic material with a hexagonal structure, in which the boron atoms form a two-dimensional covalently bonded network within the titanium matrix. This structure confers a series of fascinating characteristics, such as high hardness, high Young's modulus, good corrosion resistance, chemical stability, and high melting point [1–3]. Owing to the unique combination of these excellent properties, many studies have been conducted concerning the industrial application of TiB_2, such as in the fields of hard coating and wear-resistant coating and as a protective film for corrosion and thermal oxidation [4–7]. While the inherent brittle nature and poor lubricity of TiB_2 generally restrict its widespread industrial applications. Currently, Diamond-like carbon (DLC) films have been widely recognized as a superior wear-resistant solid lubricant material with a low friction coefficient [8–11]. Therefore, an appropriate combination of TiB_2 with DLC in multilayer structure could provide an effective route to create films that offer high hardness provided by TiB_2 and low friction coefficients provided by DLC. In addition, multilayering effectively restricts crack propagation and results in high toughness, which is critical to achieve good anti-wear performance [12–14].

To date, only few recent studies have focused on creating high-performance TiB_2/a-C multilayer films. Gilmore and Rao et al. [15–18] investigated the effect of film composition and structure on the mechanical and tribological properties of TiB_2/a-C multilayer films. It was found that friction could be reduced by controlling the content of lubricating carbon phase to a suitable value. However, film hardness decreases with the increase in the fraction of carbon due to its relatively lower hardness than that of TiB_2. Namely, an irreconcilable conflict exists between high hardness and low friction coefficients in TiB_2/a-C multilayer films. To the best of our knowledge, no remarkably enhanced toughness was reported by building such multilayered architecture. In light of superlattice hardening model [19–21], a proper modulation period in ultrathin range (approximately 10 nm or less) can remarkably enhance the hardness by restraining the dislocations within and between individual layers. Thus, incorporating sufficient lubricating phase of carbon with hard TiB_2 phase by synthesizing nanoscale multilayer films with ultrathin modulation thickness is a promising way to simultaneously achieve high hardness and low friction.

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Furthermore, a great number of interfaces in nanomultilayers not only contribute to toughening but also to internal stress reduction [22–24].

In this study, TiB_2/a-C nanomultilayers with ultrathin modulation thickness was synthesized through magnetron sputtering, and structural optimization was conducted by adjusting the modulation period from 1 to 10.5 nm. The mechanical and tribological performance of the TiB_2/a-C nanomultilayers were simultaneously improved at an optimized modulation period. The hardening and toughening in the nanomultilayers can be attributed to the excellent combination of sufficient heterointerfaces and appropriate individual layer thickness. The enhanced mechanical properties together with the formation of an effective transfer film between the sliding interfaces are responsible for the low friction coefficients and high wear resistance.

2. Experimental details

2.1. Film deposition

Nanomultilayers of TiB_2/a-C were prepared using a closed field unbalanced magnetron sputtering (CFUBMS) system. The (100) silicon wafers and 304 L stainless steel sheets were utilized as the substrate. Prior to film deposition, the substrates were ultrasonically degreased in acetone and methanol for 5 min and then sputter-cleaned with high energy Ar^+ for 20 min to remove the surface oxide and to achieve surface activation. A Cr adhesion layer (~200 nm) and a Cr/TiB_2/C graded interlayer (~100 nm) were deposited between the substrates and nanomultilayers to enhance the adhesion strength of the films. The TiB_2 and graphite targets were placed opposite to each other to prevent cross-contamination of the target material. Thus, the multilayer structure was formed from the rotation of the specimen holder. The TiB_2 layer was deposited when the substrates passed through the TiB_2 target region, whereas the amorphous carbon layer was deposited when the substrates passed through the graphite target region. Therefore, various TiB_2/a-C nanomultilayers with different modulation periods were obtained by controlling the rotate speed of the specimen holder. The power supplied to each target was selected according to our previous work to create an optimized modulation ratio ($T_{a\text{-}C}$:T_{TiB2} = 1.7:1). The presupposed film structures in this study are summarized in Table 1. The chamber pressure during deposition was maintained at 0.6 Pa, and the temperature of the substrate was between 160 °C and 200 °C depending on the target materials, power density, and sputtering time.

2.2. Film characterization

Crystallographic investigation of the films was conducted by X-ray diffraction (XRD) on a D/Max-2400X diffractometer with a glancing angle of 1°. Focused ion beam (FIB) technology was used to prepare the transmission electron microscopy (TEM) sample. The microstructure of the nanomultilayers was investigated on a JEOL 3010 TEM instrument. Hardness and elastic modulus were measured by Anton Paar TTX-NHT3 Nanoindenter. Raman spectroscopy was performed on a JY-HR800 Raman spectrometer with an aperture hole of 100 μm at an excitation wavelength of 532 nm. Film toughness was evaluated by Vickers indentation method, and the effective fracture toughness (K_{IC}) was given by [25]:

$$K_{\mathrm{Ic}} = \alpha\left(\frac{E}{H}\right)^{0.5}\left(\frac{P}{C^{1.5}}\right)$$

where α is the empirical constant based on the indentation shape (Berkovich indenters: 0.016); E and H are the elastic modulus and hardness of the films, respectively; P is the applied load; and C is the radial crack length measured from the indentation center. An effective crack is defined by $C \geq 2a$, where a is the indentation half-diagonal length. For each sample, five different regions were randomly selected for the indentation test, and three individual indents were made in each region. Thus, the final crack length was obtained by averaging the results of the 15 indents created under every load. The curvature radii of the thin silicon wafer substrates before and after film deposition were measured on an interferometric surface profile, and the internal stress was calculated by the Stoney equation [26]. Tribological behavior of the nanomultilayers was investigated on a reciprocating ball-on-disk CSM tribometer in ambient air with relative humidity of 40% ± 5% at room temperature. The friction tests were applied with a normal load of 10 N, amplitude of 5 mm and frequency of 5 Hz. A steel bearing ball (AISI52100, 6 mm in diameter) was used as static friction partner. The 3D and 2D morphologies of the wear tracks were acquired using a micro-XAM 3D non-contact optical profiler to calculate the wear rates of the films. The worn ball surfaces and wear tracks were observed by an optical microscope.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of the TiB_2/a-C nanomultilayers are presented in Fig. 1. All the diffractograms revealed only one peak at about 44°, which was assigned to the (101) plane in the TiB_2 [27]. The peak intensity increased with the period thickness. These results indicated that even in an ultrathin individual layer, the deposited TiB_2 phase still crystallized in a typical hexagonal structure and preferred a strong (101) crystallographic orientation. Furthermore, the increase in thickness indicates good crystallinity of each individual layer. The crystallization of magnetron sputtered TiB_2 films strongly depends on the negative bias voltage applied to the substrates. The TiB_2 films showed poor crystallinity even in an amorphous stage when deposited without a negative substrate bias voltage [28]. Therefore, a normal negative bias voltage of −70 V in this study should be a key factor to make the TiB_2 films to crystallize well in such thin individual layer.

To obtain more detailed structural information, cross-sectional TEM micrographs of the TiB_2/a-C nanomultilayers with an expected modulation period of 4.7 nm are presented in Fig. 2. Following the Cr/TiB_2/C graded interlayer is a distinct multilayer structure with alternating TiB_2 and a-C layers as shown in Fig. 2a. The deposited TiB_2/a-C nanomultilayers showed typical columnar structure with clear columnar boundaries. The formation of columnar structure in magnetron sputtered films with a graded interlayer can be attributed to the development of cumulative interface waves in the graded region, which has been deeply investigated in our previous work [22]. Fig. 2b presents the

Table 1
Applied modulation ratio and periods, film thickness as well as the individual layer thickness of TiB_2/a-C nanomultilayers.

Modulation period (Λ)/nm	Modulation ratio a-C: TiB_2	Thickness/μm	Interlayer thickness /nm	Rotate speed/ rpm	Number of period	a-C layer thickness /nm	TiB_2 layer thickness /nm
1	1.7	2.30	300	5	2040	0.6	0.4
3	1.7	2.41	300	1.7	694	1.9	1.1
4.7	1.7	2.43	300	1.1	449	3	1.7
6.6	1.7	2.44	300	0.8	326	4.2	2.4
8.7	1.7	2.42	300	0.6	245	5.5	3.2
10.5	1.7	2.45	300	0.5	204	6.6	3.9