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Full Length Article

# Microstructure, properties and thermal stability of W/$B_4C$ multilayer coating synthesized by ion beam sputtering

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A B S T R A C T

Microstructure, hardness and toughness as well as the thermal stability of W/$B_4C$ multilayer coating synthesized by ion beam sputtering were investigated. The results show well-defined layered structure and uniform monolayers can be found in the as-deposited multilayer coatings with various period thickness at fixed period ratio (W:$B_4C$ = 1:1.5). The crystallinity of W layer and the roughness of W/$B_4C$ interfaces are changed as the period thickness increasing. It can be concluded that the nano multilayer coatings have superior strengthening and toughening effects. The hardness of as-deposited $(W_{5.2nm}/B_4C_{7.6nm})_{20}$, $(W_{10.5nm}/B_4C_{15.8nm})_{10}$ and $(W_{14.5nm}/B_4C_{21.5nm})_7$ coatings is greatly enhanced and higher than that of pure $B_4C$ coating, and the toughness of W/$B_4C$ multilayer coating is significantly higher than that of pure $B_4C$ coating. Subsequently, the investigations about thermal stability of $(W_{10.5nm}/B_4C_{15.8nm})_{10}$ multilayer coatings indicate that the layered structural is stable when the heat treatment temperature is lower than 500 °C. With increasing of heat treatment temperature, the oxidation of W layer and the formation of $WO_3$ compounds were found. The nano layered structure was dramatically destroyed accompanying severe oxidation and slight carbonization when the temperature increase up to 600 °C. The hardness of $(W_{10.5nm}/B_4C_{15.8nm})_{10}$ multilayer coating increases up to 37 GPa when the coating is heat treated below 500 °C, while it declined sharply when the coating is heat treated at 600 °C due to the a degradation of layered structure. In addition, the toughness of the multilayer coatings monotonously decreases with the increase of heat treatment temperature.

## 1. Introduction

Hard coatings, such as TiN, $TiB_2$, VC, $B_4C$, and so on, are wildly used as the protective coatings in the aeroengine, moulds fabrication, medical science and tools areas due to the high hardness, excellent anti-oxidation, good corrosion resistance, low coefficient of friction, high temperature stability and good conductivity [1,2]. With the development of hard coating fabrication technology and the innovation of the nanotechnology, much efforts have been focused on the nano hard coating even the hardness of some nano ceramics coating is over 40 GPa [3–5]. Unfortunately, there is an inverse relationship between hardness and toughness. The harder the material, the lower the plasticity. Moreover, because of low toughness and poor deformation compatibility, the hard coatings are susceptible to be damage during the service process and then, their lifetimes will be reduced. Therefore, toughening the nano hard coatings meanwhile retaining their hardness is remarkably important to the development and application of nano hard coatings. For coatings with nanometer layer thicknesses, the grain size is generally on the same order. Therefore, by having metal nanolayer alternating with ceramic nanolayer much thinner than the metal, one should obtain coatings that are both hard and tough, since metals are generally tougher than ceramics [6]. For instance, studies have shown that hardness increases with decreasing bilayer thickness to go beyond the rule-of-mixture value for Ti/TiN [7], TiN/NbN [8] and TiN/VNbN [9] multilayer. Generally, the Hall-Petch hardening law ($\sigma \propto h^{1/2}$) is valid by dislocations piling up against the interface when the individual layer thickness (h) is at submicron length scales [10]. At the few to a few tens of nanometers length scales, where the single dislocation is confined and bowing between the interfaces, confined layer slip of single dislocations is treated as the operative mechanism [11]. In addition, as reported in Ref. [12], the much difference in shear moduli between two components, the higher hardness of multilayer. And, as emphasized by Sobol [13], for multilayer coating with nanometer size of layers it is very important to take into account interlayer mixing during the deposition.

As mentioned above, however, all these theories are based on dislocation motion, which means they can only be effective in crystalline multilayer. Generally, multilayer coatings produced by vapor

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deposited, such as magnetron sputtering (MS) or Ion Beam Sputtering (IBS), usually exhibit homogenous and amorphous layers. Especially, IBS is the bottom-up approach, enables the production of nanostructures in only one step on a wide variety of materials. Unfortunately, little research has been focused on the amorphous multilayer coating in recent years. Furthermore, the multilayer coatings fabricated by MS or IBS usually are in a state of metastability resulting in its temperature sensitivity. Some research showed that layer-structured degradation, changes in period thickness and compounds formation are observed in multilayer upon annealing [14–17]. Jankowski et al. [17] have performed a comparative study on structural stability between W/C and W/$B_4C$ multilayer by heat treatment at 500 °C for 4 h. They observed that crystallization and compound formation were detected in the W/C multilayer while none of those effects occurred in W/$B_4C$ system.

Furthermore, the thermal stability of multilayer used as hard coatings which contain carbides, borides and nitrides, is very important to their longevity application at high temperature. For hard coatings, the layered structure and the interdiffusion between layers are dominant influence factors for the properties of coatings. For example, TiAlN/$Al_2O_3$ multilayer synthesized by magnetron sputtering after vacuum heat-treatment at 700 °C showed hardness enhancement from 36 GPa for as-deposited coating to 39 GPa for annealed multilayer due to their sharp interface restrained the dislocation motion [18].

In this paper, we choose W as the metallic layer and $B_4C$ as the ceramic layer to synthesize W/$B_4C$ multilayer coatings via ion beam sputtering because elastic modulus of W is very high even to 411 GPa, and furthermore Boron carbide ($B_4C$) is the hardest material at temperature over 1100 °C. The influence of bilayer thickness on the mechanical properties, i.e. hardness and toughness, of W/$B_4C$ multilayer was studied. And then, the thermal stability of W/$B_4C$ multilayer coating also will be investigated.

## 2. Materials and experimental

### 2.1. Preparation of multilayer coatings

W/$B_4C$ multilayers were deposited on Si(1 0 0) wafer at room temperature employing a 682 Precision etching coating system from Gatan Company. This apparatus is equipped with two Penning ion guns and four targets, which can be easily switched at vacuum conditions. The base pressure of the chamber was below $1.0 \times 10^{-4}$ Pa, and the working pressure was about $5 \times 10^{-3}$ Pa as the chamber is filled with high pure argon (99.999%) atmosphere. The W and $B_4C$ layers are deposited by $Ar^+$ ion beam irradiating to the W(99.99%) and sintered $B_4C$ targets at an incident angle of 45°, respectively. Before the W and $B_4C$ layers were alternately deposited, Si substrates were ultrasonically cleaned in acetone and alcohol for 15 min successively. In order to reduce the residual stress and improve adhesion, a 20 nm thick $B_4C$ buffer was first deposited onto the Si wafer. The energy and current of ion-beam were set at 7 keV and 300 μA, respectively. The deposition rate for W was about 0.4 Å/S, while for $B_4C$ was about 0.2 Å/S, which were measured by a 681 thickness monitor from Gatan Company.

In this paper, $(W_x/B_4C_y)_n$ was used to illustrate the architecture of W/$B_4C$ multilayer coatings, as described in Fig. 1, where x and y denote the each layer thickness of W and $B_4C$ respectively within a period thickness, and n is the number of bilayer. Six kinds of $(W_x/B_4C_y)_n$ multilayer coatings with different period thickness (Λ = 6.5, 12.8, 26.3, 36, 52.2, and 63.45 nm) were subsequently deposited at fixed period ratio x:y = 1:1.5. In order to investigated the influence of period ratio on the microstructure and properties of multilayer coatings, a set of W/$B_4C$ multilayer coatings with different period ratios, such as 2:1, 1.5:1, 1:1, 1:1.5, 1:2, etc., have been prepared and analyzed. Concerning the space of this manuscript, only the W/$B_4C$ multilayer coating with 1:1.5 period ratio was concentrated on. For the sake of reducing the thermal residual stress resulted from the difference in Coefficient of Thermal Expansion (CTE) between the substrate and the deposit sediments, Ti-6Al-4V Titanium alloy was coated onto the substrate as a transition layer preceding the deposition of W and $B_4C$. Based on the total thickness of films (~260 nm), the bilayer numbers of the multilayer coatings could be deduced as 40, 20, 12, 7, 5, and 4 correspondingly. The heat treatment was carried out at 400 °C, 500 °C, and 600 °C for 30 min in air.

### 2.2. Microstructure characterization

Scanning electron microscopy (SEM, ZEISS Super 55) was used to observe the surface morphology of the coatings. X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15406 nm) was employed to indentify the crystal structure of multilayer coatings at grazing incidence XRD mode (GIXRD) with a 2° incident angle. The layer architecture of W/$B_4C$ multilayer coatings was analyzed by using low-angle X-ray diffraction (LAXRD). Transmission electron microscopy (TEM, Tecnai F30 G2) was performed to confirm the microstructure and bilayer periods of the multilayer coatings at bright field and high-resolution transmission electron microscope (HRTEM).

### 2.3. Hardness and toughness measurement

Hardness of multilayer coating was conducted through nanoindentation (Nano Indenter G200, Agilent Technologies Inc.) with a Berkovich diamond tip at a maximum indentation depth of 40 nm. The toughness of the multilayer coating was measured via modified Vickers indention, reported by Xia et al. [19]. In this method, the substrate was partially covered with multilayer coating to form a sharp boundary between the coated and uncoated areas on the substrate (as shown in Fig. 2). When the experimental of Vickers indention was carried out on the uncoated substrate, the radial cracks were generated, and one of crack oriented toward the multilayer coating propagated and broke the multilayer coating. Conspicuously, there is difference between the length of crack propagating into the multilayer coating (marked by $a$) and the length of crack in the uncoated substrate (marked by $b$) because of the toughness of multilayer coating. Then, the toughness of multilayer coatings can be calculated via the parameters $a$ and $b$. Without delamination, the coating fracture toughness $Kc$ is related to the substrate fracture toughness $Ks$, and it could be calculated using the following equation:

$$K_C = \left\{ K_S^2 \left[ 1 + 0.45\frac{(\varphi b - a)}{t}\sqrt{\frac{E_C^*}{E_S^*}} \right]^2 \pm \left[ 1.9\sigma_r\sqrt{t\frac{E_C^*}{E_S^*}} \right]^2 \right\}^{1/2} \tag{1}$$

where ∅ is the slope of $a$ versus $b$, $t$ is coating thickness, $\sigma_r$ is residual stress, $E_{c,s}{}^*$ is effective elastic modulus given by

$$E_{c,s}^* = E_{c,s}/(1-\vartheta_{c,s}{}^2) \tag{2}$$

subscript $c$ and $s$ describing the coating and substrate respectively, and $\vartheta$is the Poisson ratio. The "+"and "−" signs are for tensile and compressive residual stresses, respectively. The residual stress in the multilayer coatings was determined from the substrate curvature and calculated through Stoney equation [20]:

$$\sigma_r = \frac{E_s t_s{}^2}{6t_c(1-\nu_s)}\left(\frac{1}{R_c} - \frac{1}{R_s}\right)$$

where $E_s$is elastic modulus of substrate and$t_s$, is thickness of substrate and $t_c$, is thickness of coating and $\nu_s$, is Poisson ratio of substrate and $R_c$, is curvature radius of substrate after deposition coating and $R_s$, is curvature radius of substrate before deposition coating.