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Mechanical properties and thermal stability of tungsten boride films deposited by radio frequency magnetron sputtering

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ABSTRACT

Tungsten and boron compounds belong to the group of superhard materials since their hardness could exceed 40 GPa. In this study, the properties of the tungsten boride WB_x coatings deposited by radio frequency magnetron sputtering were investigated. The sputtering was performed from specially prepared targets that were composed of boron and tungsten mixed in a molar ratio of 2.5 and sintered in Spark Plasma Sintering (SPS) process. WB films were deposited on silicon (100) and stainless steel 304 substrates at temperatures of 23 ÷ 770 °C. Microstructure, chemical and phase composition were investigated by using Scanning Electron Microscope (SEM), X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD), respectively. The mechanical properties like Vickers hardness and Young's modulus were obtained by using nanoindentation test at a load of 5 ÷ 100 mN. The friction coefficient and wear resistance of αWB coatings were investigated in scratch test and reciprocal sliding wear instrumentation. Moreover, in order to investigate thermal properties, the αWB films were annealed at 1000 °C in argon/air for 1 h and at 250 °C for 2 h in air atmosphere. Results of our research confirm that αWB coatings can be considered as an alternative to superhard materials in the production of wear resistant, long-lasting tools.

1. Introduction

The constantly growing interest in efficient machining techniques requires materials with high hardness, good chemical stability and thermal firmness. The hardest materials which are currently used include diamond and cubic boron nitrides. However, their direct application has some drawbacks. For example, diamond reacts with ferrous materials causing the formation of brittle carbides while synthesis of cubic boron nitride requires high-pressure high-temperature conditions. For this reason, investigation of new superhard materials is still in the interest of many researchers, manufacturers and machine tools industry.

Verpek [1] and Solozhenko et al. [2] indicate that new superhard materials can be obtained by designing the microstructure, synthesizing compounds of light elements, or by synthesizing compounds of metals from the transition group with light elements. In this work we decided to analyze thin films (about 1 μm thick) of tungsten borides deposited by radio frequency (rf) magnetron sputtering technique.

Theoretical calculations indicate that hardness of tungsten borides results mainly from the strong covalent bonds introduced by boron (B-B bonds). Therefore, depending on the chemical and phase composition, recorded hardness of W_xB_y can be from about 12.9 GPa in the case of W_2B [3] to 46.2 GPa in the case of WB_3 [4] and 41.1 GPa in the case of WB_4 [5]. Nevertheless, recently published study on the fabrication and characterization of tungsten monoborides (WB) [6,7] showed that tungsten borides with lower boron concentration could have very high hardness 31–35.5 GPa [8] or exceed 40 GPa [7] for bulk materials and thin films, respectively. Reported findings encouraged us to further investigate the properties of WB materials. Motivation behind this research is the possibility of using this material in the production of superhard tools and wear resistant films. In our study, we focused on the homogeneity of the deposited films, their thermal stability, and mechanical properties.

2. Materials and methods

2.1. Magnetron deposition

The sputtering target was produced by Spark Plasma Sintering process from boron powder (1 cm crystals, 99.7% purity, Sigma Aldrich, milled to a particle size of ~ 550 mesh) and tungsten powder (~ 625 mesh, 99.9% purity, Sigma Aldrich) mixed with a 2.5:1 M ratio.

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The target consists of two phases WB (57%) and WB_2 (47%). Detailed information about the manufacturing process can be found in Ref. [9] while the information about both the chemical structure and mechanical properties are described in Ref. [7].

The one-inch diameter target was mounted in the water-cooled magnetron sputtering cathode (Kurt J. Lesker). The deposition process occurred in a vacuum chamber initially pumped to $2{\cdot}10^{-5}$ mbar and then filled with an argon to working pressure $9{\cdot}10^{-3}$ mbar. The gas flow of argon was 19 mL/min. Prior to each deposition, the target was sputtered for 5 min in order to ensure its clean surface and stable sputtering conditions. During all experiments, power supplied to the magnetron cathode was maintained at 60 W. Films were deposited for 45 min on silicon (100) substrates (Institute of Electronic Materials Technology, Poland) positioned 40 mm in front of the target. Several substrate temperatures were investigated: room temperature, 320, 420, 520, 600 and 770 °C.

2.2. Annealing

The annealing proceeded inside the furnace with pressure and atmosphere composition control (Czylok), in three ways. In the first case we wanted to investigate the thermal stability of WB films in high temperature-protective atmosphere conditions. The quartz tube was pumped to a pressure of 0.01 at and then filled with argon to atmospheric pressure. The furnace reached the temperature of 1000 °C in 40 min and the annealing process lasted for 1 h. After the annealing, the furnace was cooled down for 90 min to a temperature of 250 °C. A positive test result would mean the possibility of using the investigated films as a substitute of diamond in processes that cause graphitization of the diamond. In the case of second annealing type, the oxidation at elevated temperature was investigated, therefore sample was annealed as described above but in air. In the case of third annealing type we investigated the ability to perform sterilization of tools coated with WB films and for that purpose, samples were annealed at 250 °C for 2 h in normal air atmosphere.

2.3. Characterization

The roughness was measured using scanning profilometer (Hommel Etamic T8000) and the surface morphology was measured using atomic force microscope (NT-MDT NTEGRA). The surface's microstructure and chemical composition were investigated using Scanning Electron Microscope – SEM (Hitachi SU-8000) equipped with Energy Dispersive X-Ray Spectroscope (EDS). In the case of EDS the accelerating voltage was 5 kV, according to the suggestion presented in Ref. [10]. For more precise chemical composition determination, especially boron detection, selected samples were investigated using X-Ray Photoelectron Spectroscope – XPS (ULVAC-PHI Quantera SXM). The power of X-radiation (Al Kα mono) was 100 W (20 kV, 5 mA) and the area of investigated surface was 1.4 mm × 0.1 mm. Prior to each measurement, any area was cleaned for 3 min (~ 6 nm film was removed). The crystal structure and phase composition of deposited layers were characterized by X-Ray Diffractometer (Bruker D8 Discover, λ = 1.5418 Å). Measurements were taken in 2θ scan mode, with source fixed at 8° position. In this configuration, it was possible to avoid signal from the substrate while maintaining high intensity of the signal originating primarily from the coating.

2.4. Mechanical properties

Mechanical properties of the deposited films were measured by using Vickers nanohardness tester (Micro Materials Laboratory NanoTest Vantage) in two ways. The multiple load cycle tests were performed to investigate changes in mechanical properties as a function of depth into the sample. This provides a reliable and accurate method for obtaining coating-only properties. The indentation was applied in 40 cycles up to the maximum load of 100 mN (see Fig. 1).

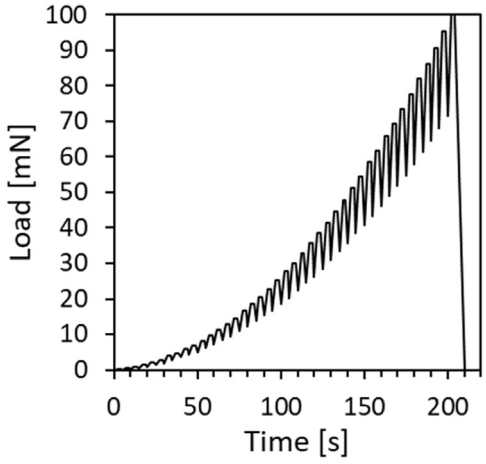

Fig. 1. Load-time profile for the multiple load cycle test.

After each cycle, before increasing again to a higher value, the load was partially reduced. For each indentation, the load time, unload time and dwell at maximum load were set as 2, 1 and 2 s, respectively. The multiple load cycle test was repeated 4 times. For as defined optimal depth of indentation the nanoindentation test was performed. Such configuration allows one to analyze load-displacement curves and determine when coating starts to crack. The nanoindentation hardness was calculated by using Oliver-Pharr method and Young modulus was calculated according to the Eq. (1)

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (1)$$

where E_i and ν_i are the Young modulus and the Poisson's ratio of the indenter, respectively.

Friction and wear resistance were investigated at room temperature in ambient air at relative humidity of 60%. Scratch test was performed in three pass scan technique (profile, scratch, profile) in both single scratch and multi-pass mode. In the single-scratch mode, the diamond conical indenter with 5 μm tip radius was used. During the test 1000 μm scratch up to 500 mN maximum load (at 15 mN/s) was performed.

In multi-pass wear test mode, the Al_2O_3 ball (φ = 6 mm) was used with a constant normal load of 0.39 N. The ball moved with a mean reciprocating speed of 0.08 m s^{-1} for 60 min. The 3D scan of the wear track was measured by using scanning profilometer (T8000, Hommel Etamic). The wear resistance was calculated according to the Eq. (2)

$$K = \frac{V}{D \bullet F} \quad (2)$$

where V is the wear volume, D is length of the wear track, and F is the normal load.

3. Results and discussion

3.1. The effect of substrate temperature

The influence of substrate temperature was investigated in the range from 23 to 770 °C. Films deposited at room temperature (23 °C) appears to have cracks and very rough surface which finally leads to the delaminating problems. Raising the temperature resulted in adhesion increase which is confirmed by the fact that the films deposited at substrates heated above 320 °C have a smooth surface with a mean roughness R_a = 0.002 μm and good adhesion. Further increase of the temperature caused the formation of the coating with preferred directions of growth and therefore roughness increase (in the case of coating deposited at 770 °C R_a = 0.016 μm). In Fig. 2, the comparison of films' surface morphology and in Table 1 the films' roughness are presented,