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Mechanical properties of superhard TiB_2 coatings prepared by DC magnetron sputtering

Marián Mikula[a,*], Branislav Grančič[b], Vilma Buršíková[c], Adrián Csuba[a], Milan Držík[d], Štefan Kavecký[a], Andrej Plecenik[b], Peter Kúš[b]

[a]*Institute of Materials and Machine Mechanics SAS, Račianska 75 Bratislava, Slovakia*
[b]*Department of Experimental Physics FMPI CU, Mlynská dolina Bratislava, Slovakia*
[c]*Department of Physical Electronics MU, Kotlářska 2 Brno, Czech Republic*
[d]*Laboratory of Applied Optics ILC, Ilkovičova 3 Bratislava, Slovakia*

Abstract

Superhard titanium diboride (TiB_2) coatings ($H_v > 40$ GPa) were deposited in Ar atmosphere from stoichiometric TiB_2 target using an unbalanced direct current (d. c.) magnetron. Polished Si (0 0 1), stainless steel, high-speed steel (HSS) and tungsten carbide (WC) substrates were used for deposition. The influence of negative substrate bias, U_s, and substrate temperature, T_s, on mechanical properties of TiB_2 coatings was studied. X-ray diffraction (XRD) analysis showed hexagonal TiB_2 structure with (0 0 0 1) preferred orientation. The texture of TiB_2 coatings was dependent upon the ion bombardment (U_s increased from 0 to -300 V) and the substrate heating (T_s increased from room temperature (RT) to 700 °C). All TiB_2 coatings were measured using microhardness tester Fischerscope H100 equipped with Vickers and Berkovich diamond indenters and exhibited high values of hardness H_v up to 34 GPa, effective Young's modulus $E^* = E/(1-\nu)$ ranging from 450 to 600 GPa; here E and ν are the Young's modulus and Poisson's ratio, respectively, and elastic recovery $W_e \approx 80\%$. TiB_2 coating with a maximum hardness $H_v \approx 73$ GPa and $E^* \approx 580$ GPa was sputtered at $U_s = -200$ V and $T_s =$ RT. Macrostresses of coatings σ were measured by an optical wafer curvature technique and evaluated by Stoney equation. All TiB_2 coatings exhibited compressive macrostresses.

Keywords: Magnetron sputtering; Superhard coatings; Mechanical properties; Residual stresses

1. Introduction

Titanium diboride (TiB_2) is well known as a ceramic compound with high melting point (3226 °C), very high hardness (for bulk ~30 GPa) and high chemical stability at elevated temperature. Accordingly, TiB_2 shows high thermal and electrical conductivities [1]. TiB_2 exhibits a hexagonal ω (C32) structure, in which boron atoms form a covalently bonded network within the titanium matrix. [2]. These excellent properties make TiB_2 a very interesting material for machining application, especially for cutting tools. Different sputtering techniques can be used for deposition of TiB_2 coatings, see Refs. [3–6]. A perspective deposition technique is magnetron sputtering. An advantage of magnetron sputtering is the ability to control the microstructure (growth and orientation) of TiB_2 coatings during deposition by deposition parameters substrate bias U_s and substrate heating T_s. Mechanical properties (hardness and effective Young's modulus) of TiB_2 coatings can be evaluated from loading/unloading curves measured by indentation. The drawback of magnetron sputtering is the formation of compressive macrostresses σ in TiB_2 coatings caused by ion bombardment during deposition. This article reports on (a) the influence of sputtering conditions (substrate negative bias U_s and substrate temperature T_s) on the microstructure and mechanical properties of TiB_2 coatings and (b) the reducting of compressive macrostresses generated in TiB_2 coatings during growth.

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*Corresponding author. Tel.: +421 2 4926 8228; fax: +421 2 4425 3301.
E-mail address: ummsmiku@savba.sk (M. Mikula).

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2. Experimental details

TiB_2 coatings were prepared by d. c. magnetron sputtering in inert Ar (99,999%) glow discharge. The unbalanced magnetron was equipped with sintered stoichiometric TiB_2 target (99.5%, dia. 100 mm). Used substrates: Si (0 0 1), stainless steel (STN 17 249), high-speed steel (HSS, CSN 19 810) and tungsten carbide (WC, Sandvik Coromant) were mirror-polished (average roughness $Ra \approx 0.08\,\mu m$) and ultrasonically cleaned in acetone and isopropyl alcohol. The deposition chamber was evacuated to a pressure of 2×10^{-3} Pa. and the substrates were heated to 400 °C for 30 min to remove adsorbed water molecules. The following step was ion–cleaning using magnetron discharge in Ar atmosphere at pressure 0.2 Pa and applied substrate bias voltage −1000 V for 10 min. Sputtering conditions were fixed at 900 W for power control, 0.5 Pa for working Ar pressure, 7 cm for target-to-substrate distance and 15 min for deposition time. The substrate bias U_s was applied in the range 0−300 V and the substrate temperature T_s ranging from room temperature (RT) to 700 °C in four steps (RT, 300, 500 and 700 °C). A morphology and thickness of TiB_2 coatings were examined by scanning electron microscopy (SEM) (Tescan VEGA) and by transmission electron microscopy (TEM) (Jeol, 200 kV). The microstructure of the deposited films was studied using X–ray diffraction (XRD) analysis in Bragg–Brentano geometry, equipped with CuKα monochromator (wavelength—0.15418 nm). Mechanical properties were characterised using a computer-controlled Fisherscope H100 microhardness tester equipped with Vickers and Berkovich diamond indenters. The residual macrostresses σ in TiB_2 coatings were determined by an optical wafer curvature measurement based on an autocollimation principle. The curvature of the Si (0 0 1) substrates was measured before and after deposition, and the macrostress can be calculated according to Stoney as follows:

$$\sigma = \frac{E_s}{1-\upsilon_s} \cdot \frac{t_s^2}{6\,t_f} \cdot \left(\frac{1}{r_a} - \frac{1}{r_b}\right), \tag{1}$$

where $E_s/(1–\nu_s)$ is the biaxial modulus of the substrate, t_s and t_f are the substrate and coating thickness, r_a is the radius of curvature after deposition and r_b is the radius of curvature for the uncoated substrate.

3. Results and discussion

SEM analysis of all TiB_2 coatings deposited by d. c. magnetron sputtering showed very smooth surface topography. The fracture cross-section exhibited very dense and featureless microstructure (Fig. 1a). This microstructure is typical for the transition zone structure according to Thornton's structural zone model [7]. Bright-field cross-sectional TEM (XTEM) detail of TiB_2 coating confirms this type of structure (Fig. 1b). All TiB_2 coatings had a thickness close to approx. 1.3 μm. Fig. 2 shows XRD patterns for TiB_2 coatings deposited at different deposition parameters (U_s, T_s). The microstructure of TiB_2 coatings exhibited a preferred (0 0 0 1) orientation of TiB_2 crystallines, and was strongly dependent on a negative substrate bias U_s and substrate temperature T_s. An amorphous or a random-oriented nanocrystalline microstructure was formed when the negative substrate bias U_s is less than −26 V. XRD analysis also detected a weak reflection of (1 0 1) TiB_2 phase at $T_s > 500$ °C. No crystalline boron phase was detected. The mechanical properties of TiB_2 coatings are characterized by microhardness H_v, effective Young's modulus $E^* = E/(1–\nu)$; here E and ν are the Young's modulus and Poisson's ratio, respectively, and elastic recovery W_e. These properties were evaluated from loading/unloading curves measured by Vickers and Berkovich indenters. The following testing conditions were used to study the mechanical properties of the given samples:

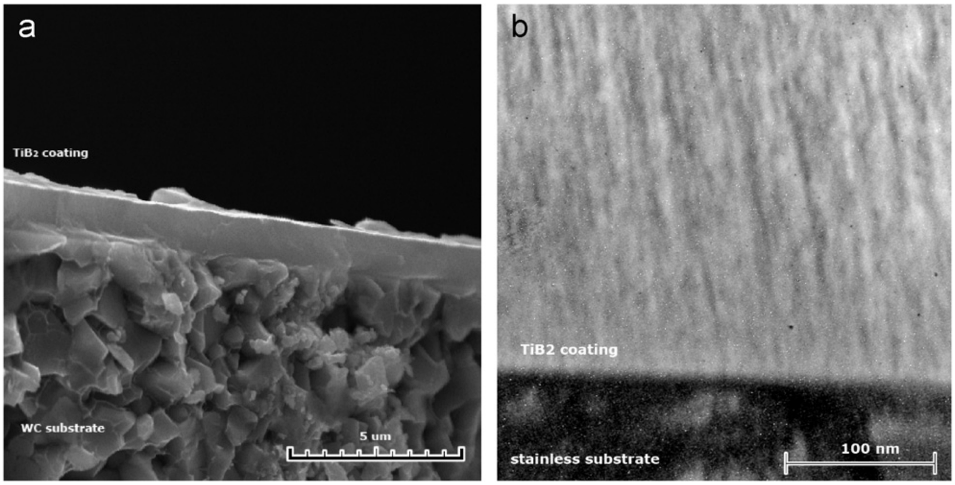

Fig. 1. (a) The fracture cross-section SEM micrograph of TiB_2 coating deposited on WC substrate at $U_s = -150$ V and T_s = RT; (b) Bright-field XTEM detail of TiB_2 coating deposited on stainless steel substrate at $U_s = -150$ V and T_s = RT.