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Microstructure Development in Multilayer $TiB_x/TiSi_yC_z$ Coatings during Post-Deposition Heat Treatment

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Multilayer amorphous $TiB_x/TiSi_yC_z$ coatings were formed by duplex treatment: dual beam ion beam assisted deposition and pulsed laser deposition. Post-deposition heating was applied to activate crystallization in the coating. *In situ* transmission electron microscopy heating experiments were conducted in the temperature range 20–600 °C. Crystallization of TiB_2 phase in TiB_x layers begun at 450 °C, while $TiSi_yC_z$ layers retained nearly amorphous up to 600 °C.

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1. Introduction

Titanium diboride TiB_2 is characterized by high melting point of 3225 °C, high hardness (30–35 GPa) and resistance to wear, high thermal stability, low specific resistivity of 5×10^{-6} Ωm^{-2}, which make it attractive for different applications such as hard, wear-resistant coatings, diffusion barriers [1]. Thin films and coatings of titanium diboride are produced by different methods, mainly by chemical vapor deposition (CVD) and physical vapor deposition (PVD). Magnetron sputtering (MS) is mostly researched but produced non-stoichiometric coatings of TiB_x type with $x < 2$, or polycrystalline with columnar grains grown perpendicular to the substrate surface, with preferred [001] or [101] orientation [2, 3], characterized by low toughness, so are still not applied. Useful coatings containing titanium diboride are multiphase (mono- or multilayered), designed usually with a second, softer and more resistant to cracking phase: Ti, Cu, amorphous C (a-C), diamond-like carbon (DLC), SiC, TiC [4–6]. In each case the volume fraction of TiB_2 phase has to be determined with a great care, as a reasonable compromise between high hardness and toughness of produced material [3, 4]. Nanostructured coatings containing amorphous TiB_2 (a-TiB_2) were produced by plasma-enhanced CVD in Ti–B–N system [5]. However, coatings containing nanocrystalline TiB_2 phase were produced by PVD methods using bombardment of high-energy ions [7], a negative bias voltage applied to substrates [8] or by crystallization from amorphous phase. Depending on chemical composition of TiB_x coating, deposition method, heat-treatment parameters, different temperatures of crystallization of TiB_2 phase are reported: in the range 900–1100 °C [9], or 500 °C — for coatings produced by dynamic ion mixing. Recently, to determine the temperature of crystallization of amorphous phase, *in situ* heating experiments are usually applied. In this paper *in situ* transmission electron microscopy (TEM) heating experiment was realized, to activate crystallization in amorphous $TiB_x/TiSi_yC_z$ multilayer coatings and to study the microstructure development in it and stability when heated up to 600 °C in vacuum.

2. Experimental

$TiB_x/TiSi_yC_z$ coatings were formed in vacuum (10^{-2} Pa), at room temperature, by duplex treatment: dual beam ion beam assisted deposition (DB IBAD) and subsequent pulsed laser deposition (PLD). Two separate targets were used: TiB_2 (Goodfellow, UK) and stoichiometric Ti_3SiC_2 target (Institute of Advanced Manufacturing Technology, Poland), prepared in form of discs of 50 mm in diameter and 5 mm in thickness. One-side polished, Si (100) square sections (10 mm × 10 mm) of 0.28 mm in thickness (Institute of Electronic Materials Technology, Poland) were used as substrates. Prior deposition substrates were cleaned in acetone, then in ultrasonic cleaner in distilled water bath, degreased in isopropyl alcohol and dried in warm air. First two thin layers (i.e. TiB_x and $TiSi_yC_z$) were deposited by DB IBAD method, with grounded substrate. In the process, two Ar^+ ion beams of the same energy of 15 keV were applied. First Ar^+ ions beam was directed at 67 °C to the normal to the target and used for sputtering. The second one was perpendicular to the surface of Si (100) substrate and used for densification of growing films, as we reported in detail previously [10]. The deposition rate in DB IBAD process was 2 nm/min, time of deposition was 1 h. Pulsed laser deposition in standard geometry [11], was performed in vacuum 10^{-4} Pa, with the Nd:YAG

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laser beam of the wavelength of $\lambda = 266$ nm, operating at the energy density of 4 J/cm^2, at frequency 10 Hz. The deposition rate in PLD process was close to 12 nm/min.

The phase composition of produced coating was studied by X-ray diffraction spectroscopy in grazing incident geometry (GI XRD) at $\alpha = 0.5$, 1, 1.5, and 2 °C. PANalytical Empyrean X-ray spectrometer was applied, equipped with the Anton Paar HTK 1200 temperature camera (AGH University of Sciences and Technologies, Krakow). Spectra were collected with Cu K_{α_1} X-ray radiation of $\lambda = 1.5417$ Å($U = 40$ kV, $I = 30$ mA) at 2θ angle range 5–60° (as the main reflexes of phases of both Ti–B and Ti–Si–C are recorded in this area and to avoid strong diffraction reflection from monocrystalline Si substrate, recorded in a preliminary measurement), with a step size of 0.2° 2θ and time counts for a step of 1000 s. For phase identification PANalytical High Score Plus program was used, integrated with a crystallographic database ICDD PDF4+ 2014. The microstructure development of $TiB_x/TiSi_yC_z$ coatings was studied at temperature range 20–600 °C during *in situ* TEM heating with the rate of 50 °C/min, with 5 min stop each 50 °C, for stabilization of the temperature of the sample. TEM, scanning-transmission microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM) observations were realized on thin foil prepared by focused ion beam (FIB) method using Ga^+ ions (FEI Dual Beam), cut perpendicularly to the coating surface. The microstructure examinations were realized on Tecnai G^2 (200 kV).

3. Results

The surface of the coating was uniform and flat. Single droplets were rarely observed on the coating surface, as shown in Fig. 1. Recorded GI XRD spectra do not contain diffraction effects from the coating, probably because of low degree of ordering of it and low atomic numbers of its components. Strong reflexes of titanium and silicon oxides (TiO_2 and SiO_2) were identified in grazing incidents angles $\alpha > 0.5°$, indicating oxidation of the coating.

In as-deposited state $TiB_x/TiSi_yC_z$ coating was amorphous, as shown in Fig. 2a. The thickness of the coating was ≃600 nm, the thickness of a single layer deposited

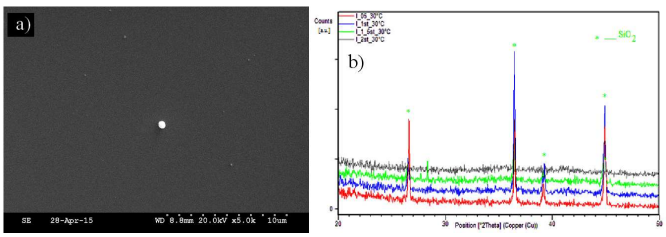

Fig. 1. (a) SEM image of the surface of $TiB_x/TiSi_yC_z$ coating in as-deposited state. (b) GI XRD spectra registered for Si (100) substrate coated by $TiB_x/TiSi_yC_z$ multilayer at $\alpha = 0.5$, 1, 1.5, and 2°.

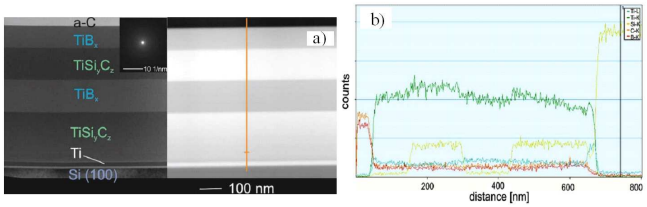

Fig. 2. (a) TEM bright field (BF) image with inserted selected area electron diffraction (SAED) pattern and STEM high angle annular dark field (HAADF) image of the cross-section of $TiB_x/TiSi_yC_z$ coating deposited on Si (100) substrate with marked line for EDS analysis, (b) Ti, Si, B, and C profiles registered by EDS along the line on the coating cross-section.

by DB IBAD was 30 nm, while the thickness of layers deposited by PLD were 100–120 nm. Boundaries between layers were clear, continuous, and free of voids and pores. Energy-dispersive spectroscopy (EDS) profiles of Ti, Si, C, and B, presented in Fig. 2b, do not indicate any diffusion of elements between layers nor implantation of them to Si substrate. Ordering in TiB_x layers begun at 450 °C and at 600 °C was finished, resulting in nanocrystalline TiB_2 phase. During crystallization, the size of crystallites has grown to 5–15 nm. Some ordering in $TiSi_yC_z$ layers was observed up to 600 °C. Single, highly defected nanocrystallites of 3–5 nm in size, were observed in amorphous $TiSi_yC_z$ matrix, as presented in Fig. 3. Reported temperature of TiB_2 phase crystallization of amorphous TiB_x coating differ in several hundred degrees, depending on chemical composition of the coating, deposition method and its parameters as well as parameters of heat-treatment. Typically, reported temperatures for crystallization in PVD coatings are in the range 800–1100 °C [6, 7]. During post-deposition *in situ* TEM heating up to 600 °C, crystallization in TiB_x layers was activated (Fig. 4). Post-deposition annealing at 800 °C of amorphous overstoichiometric TiB_x coatings (of B/Ti ratio value in the range 2–2.45), formed by MS at room temperature condition, resulted in crystallization of equilibrium hexagonal TiB_2 phase as columnar grains of 5–10 nm in diameter, oriented along [001] direction [7, 8], while excess boron formed thin layer (a tissue layer) separating TiB_2 grains. It was shown that this orientation was unchanged during annealing of the coating up to 800 °C. Reported temperature required for crystallization of TiB_2 is high, but not surprising as it is related to the melting point of that boride. In the case of the TiB_x layer deposited by us in duplex treatment, thermal activated crystallization in TiB_x thin film started at 450 °C, i.e. at 350 °C lower temperature in comparison to MS coatings, and 50 °C lower to the temperature reported for TiB_x coatings produced by dynamic ion mixing. Ion beam mixing and ion sputtering deposition methods are known to operate at much more higher energies of species than PVD methods, the energy accumulated in the coating during ion bombardment allow lower temperature to activate the crystallization.

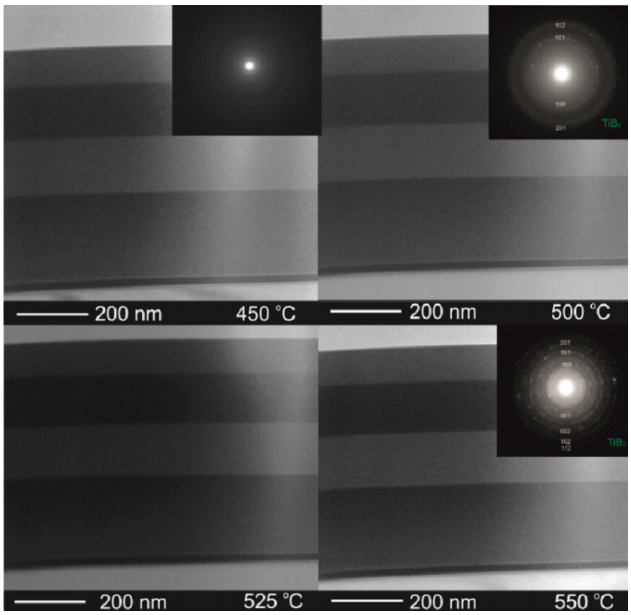

Fig. 3. TEM BF images of the cross-section of $TiB_x/TiSi_yC_z$ coating during *in situ* TEM heating at temperature 450–550 °C, with corresponding SAED patterns, taken from the coating area.

4. Summary

- Crystallization process in amorphous $TiB_x/TiSi_yC_z$ multilayer, produced by duplex treatment DB IBAD/PLD, could be activated thermally during heating from 450 °C.
- Post-deposition heating in vacuum up to 600 °C results in randomly oriented nanocrystallites of TiB_2 embedded in amorphous matrix in TiB_x layers, while $TiSi_yC_z$ layers retain nearly amorphous.

Acknowledgments

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