Thin Solid Films 662 (2018) 137–144

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

The effect of low titanium content on the phase composition, structure, and mechanical properties of magnetron sputtered WB_2-TiB_2 films

O.V. Sobol[a,*], S.N. Dub[b], A.D. Pogrebnjak[c], R.P. Mygushchenko[a], A.A. Postelnyk[a], A.V. Zvyagolsky[a], G.N. Tolmachova[d]

[a] National Technical University "Kharkiv Polytechnic Institute", Kharkiv, Ukraine
[b] Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
[c] Sumy State University, Sumy, Ukraine
[d] National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine

ARTICLE INFO

Keywords:
Tunsten boride
Titanium boride
Magnetron sputtering
Elemental composition
Phase composition
Microstructure
Nanocomposite
Nanoindentation
Hardness
Brittleness

ABSTRACT

The effect of the low Ti content on the phase composition, structure and mechanical properties of magnetron sputtered WB_2 - TiB_2 films was studied. Non-equilibrium conditions during the films deposition cause the difference of their phase composition from the composition of the target. Sputtering of a WB_2 target (hexagonal crystal lattice) results in formation of the β-WB phase with an orthorhombic crystal lattice and a B/W atoms ratio of about 1.19. It was found that even a very low Ti content (about 0.6 at. %) act as a catalyst for the formation of a diboride phase with hexagonal crystal lattice. A nanocomposite β-(W,Ti)B/(Ti,W)B_2 (where (Ti,W)B_2 has a hexagonal crystal lattice) is formed in the range of $0.6 < x < 4.6$ at. % of Ti. At $x = 10.2$ at. % a nanocomposite based on the (Ti,W)B_2 phase is formed, which results in the highest hardness (33 GPa).

1. Introduction

Obtaining nanostructured materials under conditions of strong nonequilibrium in the process of their formation has become in recent years the main technology of creating materials with a unique structure and high mechanical properties [1–3]. The method of ultrafast thermalization (ie, the reduction of particle energy in a very short time [4]) is one of the most used for obtaining materials in highly nonequilibrium conditions. Superfast thermalization determines the structure of materials formed using magnetron sputtering technology in vacuum. In this case, a high-temperature β-phase can be stabilized [5, 6]. The second feature of materials obtained under conditions of ultrafast thermalization is the formation of a nanocrystalline structure. For this state, a significant increase in hardness has been identified.

It is established that the highest hardness is characteristic of composite materials obtained as a result of a phase decomposition (by the type of a spinodal) supersaturated solid solution. Among the first composite materials with unique high mechanical characteristics was the Ti-Si-N ternary system [7]. High hardness is determined by strong adhesion at the boundaries of nanoscale grains. The supersaturated solid solution decomposion cuases formation of nanocomposite which consist of nanocrystalline TiN grains and an amorphous SiN_x interlayers between them [8]. Thus, an ultrahard composite nc-TiN/a-SiN_x was created [9]. The use of quasibinary carbide systems [10, 11] significantly increased the class of materials for which an ultrahard condition was achieved. Such materials are essentially ternary compounds, which consist of 2 types of metallic atoms and carbon atoms (for example, Ti-W-C [10], Ti-Mo-C [12], Ti-Zr-C [13] and others).

In recent years, much attention has been paid to the creation of composite materials based on transition-metal borides. The basic element in these materials is mainly TiB_2. As a second component of the composite boride material, tungsten boride is promising [14]. Tungsten borides have a high hardness and they are chemically inert to iron-based alloys (when used as a materials for cutting tool) [15]. Therefore, in [16, 17], it was proposed to use a composite on the basis of tungsten tetraboride (WB_4) with the addition of transition metals Ti, Zr and Hf to form high-hard materials. As follows from the results of this work, spinodal decomposition can result in the formation of nanoscale grains. A disadvantage of such materials is their low impact strength. In comparison with WB_4, tungsten diboride WB_2 (or its defective modification - W_2B_5 [18]) is much more ductile. In this connection, the quasibinary system TiB_2-WB_2 is investigated both in the massive state

* Corresponding author.
E-mail addresses: soova@ukr.net, sool@kpi.kharkov.ua (O.V. Sobol).

https://doi.org/10.1016/j.tsf.2018.07.042
Received 16 January 2018; Received in revised form 29 July 2018; Accepted 30 July 2018
Available online 31 July 2018
0040-6090/

(hot pressing) [19, 20] and in the form of films obtained by magnetron sputtering [21–24].

The Mayrhofer group is very active in this direction [23, 25, 26]. However, in these papers, the main attention is paid to compositions with the predominant content of the TiB_2 component. This is due to the fact that TiB_2 has a higher hardness (32 GPa) compared to WB_2 (21 GPa) [23, 27, 28]. However, as was shown in [21], nanocomposite can form in the region of high contents of the WB_2 component in the TiB_2-WB_2 system, which is optimal for achieving high strength [1]. The nanocomposite is formed as a result of the decomposition of a supersaturated solid solution of diboride $(Ti,W)B_2$ into WB_2 and (Ti,W)B. The formation of a solid solution $(Ti,W)B_2$ supersaturated by W atoms occurs under nonequilibrium conditions because of the high rate of thermalization of accelerated particles in magnetron sputtering [4, 29].

The aim of this paper was to investigate the effect of low Ti content on phase composition, structure and properties of the TiB_2-WB_2 quasibinary system films obtained by DC (direct current) magnetron sputtering.

2. Experimental methods

The films were deposited by magnetron sputtering of WB_2 - TiB_2 targets with different TiB_2 concentration. The targets were obtained by hot pressing. The targets had a diameter 50 mm and a thickness 4 mm. For the sputtering of the targets a planar magnetron was used (Fig. 1). The magnetron was powered by a direct current power supply (DC power 50 W used and the target power density – 2.7 W/cm^2). This is comparable to the power of the magnetron used by the authors of the article [30]. But this article was used RF (radio frequency) magnetron sputtering with a higher degree of ionization of atoms.

The substrate was located 55 mm above the anode, and the anode target distance was 4–5 mm. The bias potential on the substrate was not fed (floating potential). The substrate ion current density is 0.8 mA/cm^2. During deposition the argon pressure in the vacuum chamber was $6 \cdot 10^{-1}$Pa. Prior to coating, the substrates were held for 1 h in a vacuum of 3×10^{-4} Pa at 950 °C to remove gaseous impurities from the surface. The deposition rate of the coatings was kept close to 0.5 nm/s. The polished plates of single-crystal silicon (111) were used as substrates. A special unit was used to heat the substrate. The temperature of the substrate (T_s) was about 700 °C. The use of T_s = 700 °C was necessary for the process of phase decomposition (by the spinodal type) of the formed supersaturated solid solution [21]. The cooling rate from 700 °C to RT is 12 °C/min.

The thickness of coatings (d) for structural studies was about 2 μm, and for hardness measurement about 3.5 μm.

X-ray diffraction studies of the samples were carried out on D8 Advance diffractometers (Bruker-AXS, Germany) and DRON-4 (Burevesnik, Russia) in Cu-K_α radiation. The scattering was registered in a discrete shooting mode with scanning step $\Delta(2\vartheta)$ = 0.01–0.05° (depending on the half-width and intensity of the diffraction reflections). Exposure time at the point was 40–100 s. The separation of diffraction profiles in the case of their superposition was carried out according to the program "New profile" [31]. The ratio of the phase fraction in the film was calculated by the standard method from the data on the integrated intensity of the diffraction peaks [32, 33]. The Scherrer equation was used to estimate the crystallite sizes from the widths of a diffraction peaks (the values obtained are the lower limit for the crystallite sizes). We used diffraction lines at small angles θ = 13–22°. to reduce the influence of microstrain.

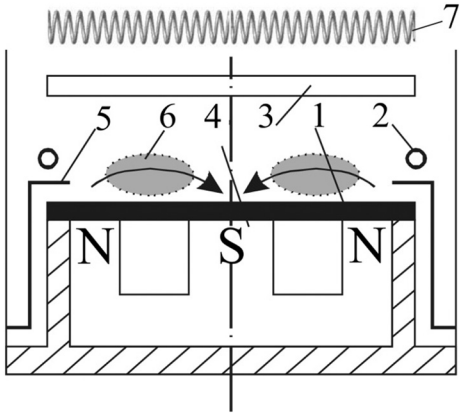

Fig. 1. Magnetron sputtering system: 1 - target (cathode); 2 - anode; 3 - substrate; 4 - magnet, 5 - screen; 6 - plasma; 7 - heating element.

Scanning electron microscopy (SEM) studies in combination with local element analysis were performed on JEOL-JSM-7001F (JEOL, Japan) with an attachment for energy dispersive X-ray spectroscopy (EDS, Oxford Instruments, UK). High-resolution translucent electron microscopy (HR TEM) were performed on an electron microscope PEM-U (Selmi, Ukraine) with an accelerating voltage of 100 kV (magnification of 108.000–270.000). Ionic thinning of samples was carried out by Xe ions with an energy of 5 keV (from two sources, both from the side facing the substrate and from the side of the condensation surface). The angle between the ion beam and the surface of the sample when thinning was 12°.

The mechanical properties of the WB_2-TiB_2 films deposited on Si substrates were studied by nanoindentation using a Nano Indenter-G200 system (Agilent Technologies, USA) equipped with a continuous stiffness measurement (CSM) attachment. This attachment offers a continuous measurement of the contact stiffness via a superimposed alternating current signal during loading, which in turn provides a continuous measurement of the elastic modulus E and average contact pressure (ACP) - Meyer's hardness H as function of the penetration depth during a single loading segment [34]. Ten indentations were made on each sample. A diamond Berkovich tip with some tip blunting was used. Atomic force microscopy measurements of the tip shape showed that the Berkovich tip can be described as a sphere with an effective radius R of 340 nm when the indentation depth is < 35 nm. Load P and displacement h were continuously recorded up to a maximum displacement of 400 nm at a constant indentation strain rate of 0.05 s^{-1}. The frequency of the CSM signal was 45 Hz, the amplitude of the oscillations was 2 nm.

3. Result and discussion

3.1. Elemental and phase compositions and structure of films

Elemental composition of the films was determined by EDS. The generalized results of the elemental composition of the films are given in Table 1. As can be seen from the results presented in Table 1, with an

Table 1
Elemental and phase composition of magnetron sputtered WB_2-TiB_2 films.

№ series	Elemental composition, at.%			C_{Ti}/C_W	Phase composition	Phase state
	Ti	W	B			
1	–	45.7	54.3	0	β-WB	Single-metal boride
2	0.6	36.0	63.4	0.017	β-(W,Ti)B/(Ti,W)B_2	β-(W,Ti)B-based nanocomposite
3	1.2	34.6	64.2	0.035	β-(W,Ti)B/(Ti,W)B_2	
4	1.9	33.1	65.0	0.057	β-(W,Ti)B/(Ti,W)B_2	
5	4.6	30.3	65.1	0.152	β-(W,Ti)B/(Ti,W)B_2	
6	10.2	24.2	65.6	0.421	(Ti,W)B_2/β-(W,Ti)B	(Ti,W)B_2-based nanocomposite