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Superhardness Effect of the Films of Transition Metals Diborides

A.A. Goncharov*

Donbass State Engineering Academy, 83013, Kramatorsk, Ukraine

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In this work the data of superhardness effect of thin film coatings based on diborides transition metals are presented. The results of substructural characteristics of the synthesized films are discussed. The structure, physicomechanical characteristics of the films are investigated. The formation mechanism sp^2 and sp^3 chemical bonds are described. The measurements of the hardness and the elasticity module of the coating are conducted.

Keywords: Film, Structure, Stoichiometric, Superstoichiometric, Hardness.

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Films of transitional metals diborides (TiB_2, CrB_2, TaB_2, HfB_2, and others), are presently actively probed due to their high physics and mechanical characteristics. Morphology of structure of the films, got on the basis of diborides of transitional metals, is most often characterized as columnar with texture of plane growth (00.1) [1-7].

In Fig. 1 a, b and Fig. 2 a, b are shown difractograms of films of diboride tantalum (Fig. 1) and hafnium (Fig. 2) with texture of growth (00.1).

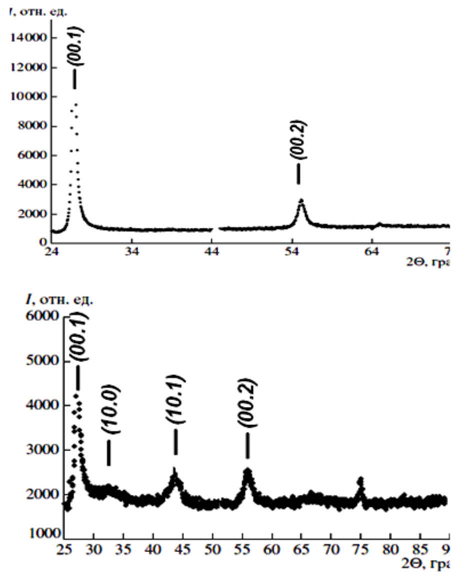

Fig. 1 – Difractograms of films of diboride tantalum (a,b) with texture of growth (00.1)

An analogous picture for other diborides was observed by many authors: for films of TiB_2 in works [1-3], HfB_2 [5], CrB_2 [4 ,6] and others. Moreover, special features of substructural characteristics of the described films and their properties were noticed. The substantial increase of parameter «c» takes a place in a greater degree because of the increased concentration of the dissolved atoms of B in lattice of transitional metals diborides.

There is a substantial increase of parameter of «c» and «a», that testifies to formation of superstoichiometrical tapes of $MeB_{2,4}$ (table. 1). It results in the increase of sizes of elementary cell with growth of values «a» and «c», here the relation of c/a remains close to tabular. An anisotropy of sizes of OKR is one more characteristic feature of forming texturing films of transitional metals diborides. The increase of values OKR [8] is noticed to direction of the axes «c » with growth of perfection of texture of the formed coverages. The features of structure and substructure of films were found while researching their physics and mechanical characteristics (Table. 1).

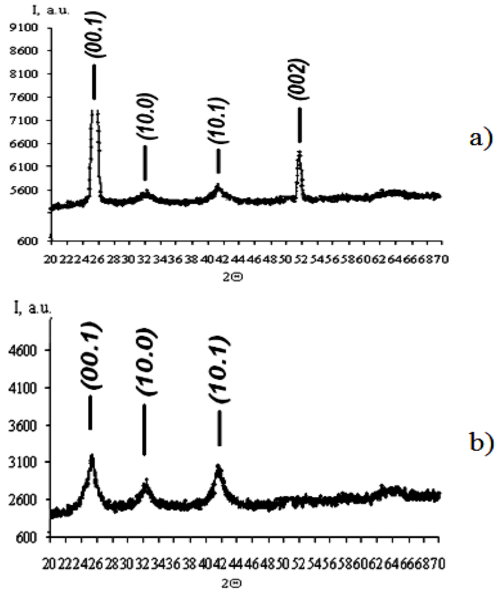

Fig. 2 – Difractograms of films of diboride hafnium (a,b) with texture of growth (00.1)

There is the increased hardness of films of transitional metals diborides: 44 GPa (TaB_2)[7], 44 GPa (HfB_2)[8], 44,8-49 GPa (CrB_2) [6], 48,5 GPa (TiB_2) [2,3]. Moreover, as shown in work [1] the hardest films were those ones which had the increased concentration and maximum parameters «c» increase.

* applmath@dgma.donetsk.ua, algon.61@mail.ru

Table 1 – Structure, composition, substructural, and physics and mechanical characteristics of superstoichiometrical nanocrystalline films

№	Target	Parameter of lattice					Composition B/Me		Hardness films	
		«a» (table)	«a»	«c» (table)	«c»	c/a		Size of graine	Nano-hardness, GPa	Elastic module GPa
1.	TiB_2			3,229	3,258		2,4	20	48,5	400~500
2.	HfB_2	3.14	3.17	3.47	3.51	1.107	2,4	20	44	396
3.	CrB_2						2,4	20-50	44.8	397
4.	TaB_2	3.098	3.127	3.226	3.271	1.046	2,4	20-40	44	348

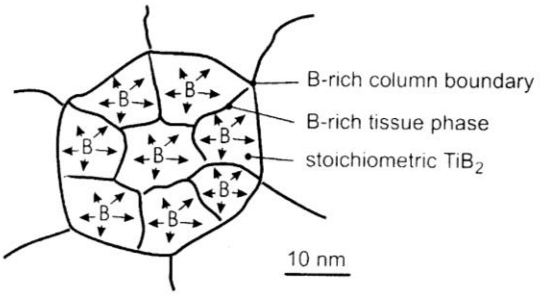

Fig. 3 – Schematie plan-view of the (0001) textured ~20 nm wide columns, indicating the formation process of the B-rich tissure phase by preferred B-diffusion on the (0001) plane

Effect of superhardness was explained of P. H. Mayrhoffer and C. Mitterer [2]. As TiB_2 has a relatively narrow single-phase field (65,6-66,7 at.% B), the excess B in the films segregates to interfacas. Due to the limited diffusivity at the low deposition temperature of 300°C B-atoms that cannot reach the column boundariesaccumulate to form a tissure phase within the columns (see Fig. 3). This process is preferred along the (0001) plane as this is the preferred B-diffusion plane in TiB_2. Consequently, columns are encapsulated in excess B and are themselves composed of smaller stoichiometric TiB_2 subcolumns with an average diameter of ~ 5 nm, separated by a thin B-rich tissue phase exhibiting a thickness of 1-2 ML.

Due to the small dimension across the TiB_2 nanocolumns, i.e., the (0001) plane, nucleation and glide of dislocations is inhibited during hardness indentation measurements (the primary dislocation glide planes in TiB_2 are {0001} planes), while the high cohesive strength of the thin B-rich tissue phase prevents grain boundary sliding. Together, these two effects explain the observed superhardness of B-rich TiB_2 layers.

As MeB_2 has and relatively narrow single-phase field (65,6-66,7 at.% B), therefore in our view effect superstoichiometrical is related to formation of additional chemical connections of B-B. It gives every reason to suppose that the process of their forming took place on a mechanism, offered in work [9], i.e that formations of additional donor-type-acceptor-type connection B-B(see Fig. 4 b).

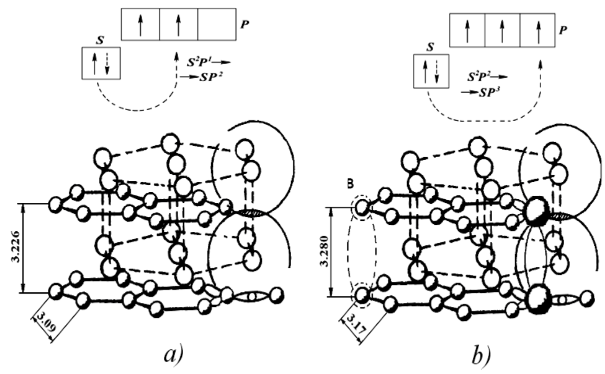

Fig. 4 – Schematie chemical connection stoichiometrical (a) and superstoichiometrical (b)

Texture degree decrease resulted in parameter «c» decrease and parameter «a» increase (Fig.1 b and Fig.2 b), that leads to forming of stoichiometrical films (see Fig. 4 a). The estimation of OKR on «a» and «c» showed, that their sizes become comparable and are in limits ~ 15÷20 nm. Thus, there is decreasing of values of hardness accordingly to 35 GPa for TaB_2 [6], 36 GPa for HfB_2 [5], 36 GPa for TiB_2 [1] and 33 GPa for CrB_2 [4].

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