

STRUCTURAL FEATURES OF FORMING OF FILMS OF DIBORIDES OF TRANSITIONAL METALS

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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. The compounds of this type have high melting temperature, therefore their synthesis in the film state is performed by magnetron sputtering methods (PVD). The features of synthesis of film materials are shown up depending on the formed structure and accordingly properties from energy of falling ions and substrate temperature. Differences in the power parameters of forming result in formation of film condensates in the size structural states – amorphous, cluster or nanocrystalline. 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) [1-5].

The purpose of the present work is determination of conformities of forming of structure, substructure and properties of transitional metals diborides films.

As shown in works [1-6] the most characteristic morphological feature of forming structure films of diborides of transitional metals by synthesized PVD-methods is a columnar structure with texture of plane growth a (00.1). In *Fig. 1 a, b* and *Fig. 2 a, b* are shown diffractograms of films of diboride tantalum (*Fig. 1*) and hafnium (*Fig. 2*) 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 $\text{MeB}_{2,4}$.

It gives every reason to suppose that the process of their forming took place on a mechanism, offered in work [11], i.e that formations of additional donor-type-acceptor-type connection B-B.

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.

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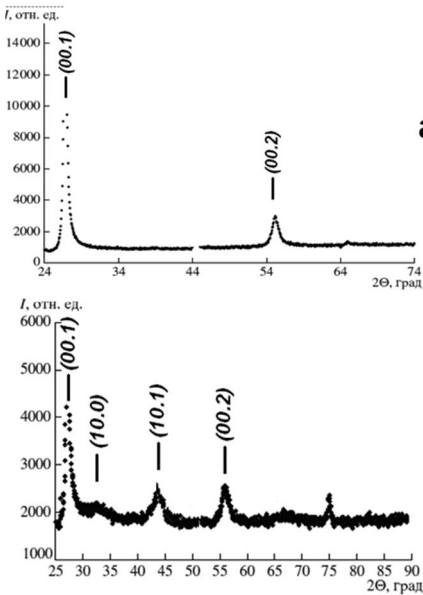


Fig. 1 – Diffractograms of films of diboride tantalum (a,b) with texture of growth (00.1)

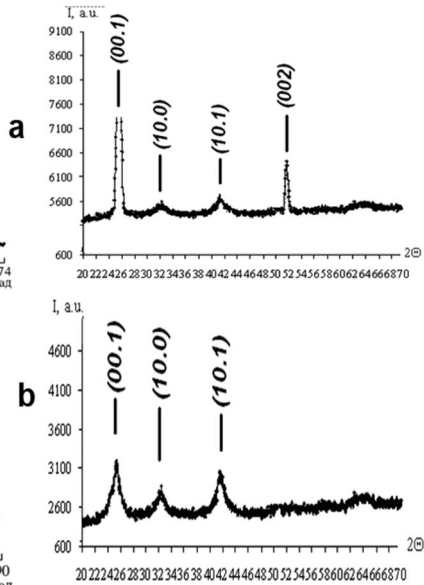


Fig. 2 – Diffractograms of films of diboride hafnium (a,b) with texture of growth (00.1)

An anisotropy of sizes of OKR (table. 1) 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).

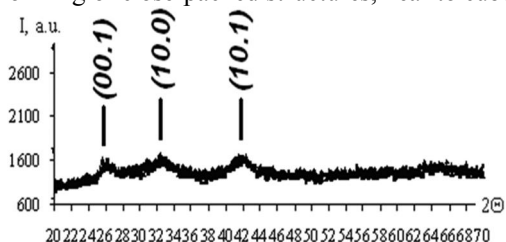
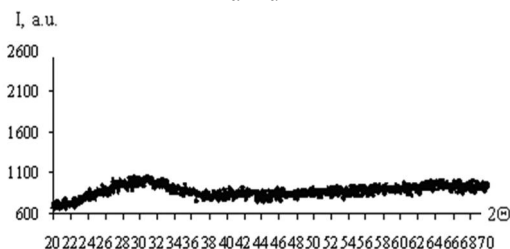
There is the increased hardness of films of transitional metals diborides: 44 GPa (TaB_2), 44 GPa (HfB_2), 49 GPa (CrB_2) [6], 48,5 GPa (TiB_2) [2,3]. Moreover, as shown in work [1] the hardest films were those ones which had the increased concentration and maximum parameters «c» increase.

Texture degree decrease resulted in parameter «c» decrease and parameter «a» increase (Fig.1 b and Fig.2 b). The estimation of OKR on «a» and «c» showed, that their sizes become comparable and are in limits $\sim 15\div 20$ 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]. While forming of clustering films, with the sizes of grains $\sim 5\div 10$ nm large broadening of diffraction planes with the simultaneous decline of their intensity is observed (Fig.3).

Table 1 – Structure, composition, substructural, and physics and mechanical characteristics of superstoichiometrical, нанокристаллических 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		40,6	397
4.	CrB ₂							20-50	44,8	–
5.	TaB ₂	3.098	3.127	3.226	3.271	1.046	2,4	20-40	44	348

There is yet more substantial change of parameters of lattice; the parameter of «a» is increased, and the parameter of «c» decreased. The values of hardness even more decreased to 26 GPa for HfB₂ and 29 GPa for TaB₂. These results for TiB₂ films were before marked in works [9,10]. Size effect in nanocrystalline films is possible to explain that at the sizes of grains ~ 20 nm and less, influencing of superficial energy becomes determining, that is shown up in forming of close-packed structures, near to cube.

**Fig. 3** – Diffractogram of cluster films of diboride hafnium**Fig. 4** – Diffractogram of amorphously films

At the size of grain ~ 5 nm forming of amorphously-films takes place (Fig. 4) with a «quasi-cubic» structure ($a \approx c$), here surplus atoms, stimulating forming of more difficult structures are in intergrain-space which can make at such sizes of grains ~50% of all the volume of the film. Transition of the film to the amorphously state results in even more substantial decreasing of values of hardness and elasticity module to 11,5 GPa (TaB₂) and 13 GPa (HfB₂) and (157 and 187 GPa).

Thus, the level of physics-mechanical characteristics of the examined nano-composite coverages is largely conditioned by nanodimensions of their grain structure.

REFERENCES

- [1] Kunc F., Musil J., Mayrhofer P.H., Mitterer C. Surf. And Coat. Techn. 2003 V. 174-175. P. 744-753.
- [2] Mayrhofer P.H., Mitterer C., Wen J.G., et al. Appl. Phys. Lett. 86 (2005) 131909.
- [3] Mayrhofer P.H., Mitterer C., Hultman L., Clements H. Progress in Materials Science. 51 (2006) 1032-1114.
- [4] Zhou M., Noseb M., Makinoa Y. and Nogi K. Thin Solid Films. 2000, Vol 359, Issue2, P. 165-170.
- [5] Herr W., Broszeit E. Surf. and Coat. Tech. 1997. V. 97. P. 335–340.
- [6] Dahm K.L., Jordan L.R., Huase J. and Dearuley P.A. Surf. And Coat. Techn.1998 Vol. 108-109, Issues 1-3, P. 413-418.
- [7] Goncharov A.A., Kononov V.A., Dub S.N. et al. PMM.2009. V.107. №3– P. 303-308.
- [8] Goncharov A.A., Dub S.N., Agulov A.B. PMM – 2011. – in press.
- [9] Andrievskii R.A., Glezer A.M. PMM. 2000. Vol. 89. №1. P. 91-112.
- [10] Andrievskii R.A., Kalinnikov G.V., Kobelev N.P. and others. Physics of the Solid State. 1997. Vol. 39. №10. P. 1661-1666.
- [11] Goncharov A.A. Physics of the Solid State. 2008 Vol. 50. №1. P. 168-172.