

THERMAL STABILITY OF FILM NANOSTRUCTURE OF HIGH-MELTING COMPOUNDS

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Basic researches of films nanostructures and coverings of phases of introduction (nitrides, carbides and borides transitive metals) are one of the basic perspective directions of development of nanotechnologies. As it is known, the given compounds concern the category of superhard materials, i.e. possessing high thermodynamic stability.

This materials received in nanostructure a condition, in a kind of films, leads to increase of their physics-mechanical characteristics, i.e. to hardness increase in 1,5-2 times and thus to decrease in the module of elasticity on (20-40 %) in comparison with a polycrystalline condition. However, as show the researches, the given film materials are in a metastable condition, their thermodynamic stability therefore is of great importance.

The most investigated is thermal stability thin of nitrides [1-6], and to a lesser degree carbides films [7-8]. Thermal stability nanostructure on a basis borides and nitride of borides transitive metals was studied now in not enough degree. Thus, as show researches [1-6], thermodynamic stability nitrides films is limited by temperatures 1000-1100°C. In work [8], it is possible to see that the size of crystalline particles and hardness stably to 1100°C for coverings nc-TiN/a-Si₃N₄.

Films of borides or nitrides of borides transitive metals are investigated in very limited quantity, basically on a basis diboride of titan [9-12].

Research of thermal stability of films TiB_{2,4} [10] with fine columned (columnar) structure show that the synthesized films keep the structure and superhardness 48,5 GPa at temperature up to 900°C. In one of the first works C. Mitterer, etc. [12] it is shown that after higher vacuum annealing at temperature 1200°C throughout 1 hour primary orientation practically disappears.

For films synthesized in system Ti-B-N after higher vacuum annealing under the same conditions observed formation of sharp peaks TiB₂ and TiN. Besides, authors observed "peaks" boride molybdenum, as result of interaction between molybdenum substrate and a covering.

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Composites received in system Ti-B-N showed streamlining process that led accordingly to growth of hardness of synthesized coverings. For example composite $\text{TiB}_{0,8}\text{N}_{0,83}$ having cluster structure, consisting of 2-3 nanometres grains TiN and TiB_2 , encapsulated in 50 % unrank areas at rise in temperature of annealing to 900°C was exposed to crystallization process that as a result led accordingly to growth of hardness from 36,7 GPa to 43 GPa. The similar effect of structure streamlining for quasibinary system $\text{TiB}_2\text{-W}_2\text{B}_5$ was observed by authors in work [12].

Comparison of the structural data to results of research of hardness and the module of elasticity of condensates a method nanoindentation has shown that in system $(\text{W,Ti})\text{B}_2$ – a covering – «the silicon substrate» at increase of structural streamlining of a covering which is observed in the range of temperatures $300\text{-}700^\circ\text{C}$, occurs continuous growth of hardness and the module of elasticity from $H=28,6$ GPa and $E=290$ GPa at $\text{TS}=300^\circ\text{C}$ to $H=34,6$ GPa and $E=323$ GPa at $\text{TS}=700^\circ\text{C}$. The further increase TS to 950°C doesn't result in essential changes ($H=35,6$ GPa, $E=300$ GPa) that completely correlates with earlier resulted results [10].

That is, for films put in "inadequate" conditions [14] the increase in hardness connected with process of streamlining, i.e. film crystallization is characteristic.

Thus, one of the major factors which have affected an urgency of given research is feature nanostructure films to pass, under the influence of high temperatures, from one structural condition in another. And, in the course of transition, under the influence of the high temperatures arising in the field of contact «the tool - preparation» in the course of processing physics-mechanical characteristics of a sheeting change. It is connected by that there is a chemical reaction of a covering to the air environment at high temperatures. It is shown [6] that annealing on air nitrides coverings in comparison with vacuum is characterized by fall of temperature stability to $500\text{-}600^\circ\text{C}$ above which formation of oxides in a condensate, leading to its destruction is observed. Similar researches of stability doridaes films in the vacuum environment at high temperatures, except for work [15], practically it was not spent.

Therefore, researches of phase structure of films are conducted in the given work диборида a hafnium in the course of high-temperature annealing on air within one hour on substrates T15K6 and a steel 12X18H9T.

On *fig. 1.*, are presented diffractogram films диборида a hafnium with a structure of growth (00.1), i.e. in an initial condition (a) and after annealing on air at temperature $T=600^\circ\text{C}$ within 1 hour. As a substrate the plate of mark T15K6 is used hard-alloy. It is possible to see that in the course of film annealing, the structure of growth by a plane (00.1) practically disappears, new lines which are identified as phase HfO_2 are thus formed, i.e. there is a formation of oxides on which earlier it was informed in works [6,15].

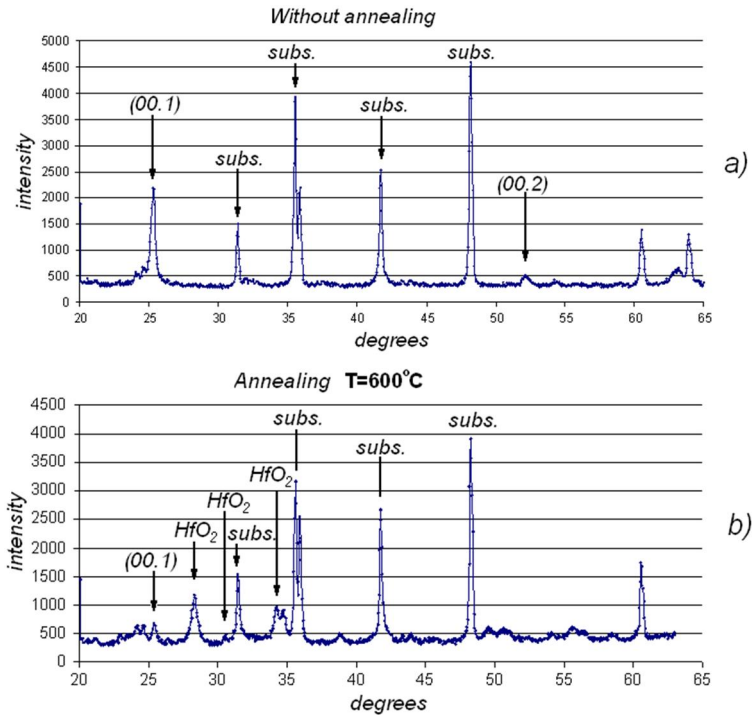


Fig. 1 – Diffractograms of system films of HfB₂ – substrate T15K6, in an initial condition (a) and after high-temperature annealing on air (b).

Thus, from the point of view of practical application has interest of research kinetics of process of high-temperature annealing on air depending on temperature and annealing time. The given process represents a great interest from the point of view: to use the given coverings in processing of metals cutting since cutting process occurs in the air environment and knowing kinetics covering destructions, it will be possible to predict without special work period firmness and time before full breakage of the cutting tool.

REFERENCES

- [1] L. Hultman. Vacuum 2000. V. 57, Issue 1, P. 1-30.
- [2] H. Zeman, J. Musil, J. Vlaek, P. H. Mayrhofer and C. Mitterer. Vacuum. 2003. V. 72, Issue 1, P. 21-28.
- [3] R. Daniel, J. Musil, P. Zeman and C. Mitterer. Surf. and Coat. Technol. 2006. V. 201, Issue 6, P. 3368-3376.
- [4] H. Willmann, P.H. Mayrhofer, P.O.Å. Persson, et al. Scripta Materialia. 2006. V. 54, Issue 11, P. 1847-1851.
- [5] H. D. Männling, D. S. Patil, K. Moto et al. Surf. and Coat. Technol. 2001. V. 146-

- 147, P. 263-267.
- [6] V. Beresnev, O. Sobol', A. Pogrebnjak et al. *Technical Physics*, Vol. 55, No. 6. p. 871-873.
- [7] P. Zeman, J. Čapek, R. Čerstvý and J. Vlček. *Thin Solid Films*. 2010. V. 519, Issue 1, P. 306-311.
- [8] G. Gassner, P.H. Mayrhofer, J. Patscheider and C. Mitterer. *Thin Solid Films*. 2007. V. 515, Issue 13, P. 5411-5417.
- [9] C. Mitterer, P. H. Mayrhofer and J. Musil. *Vacuum*. 2003. V. 71, Issues 1-2, P. 279-284.
- [10] P. H. Mayrhofer, C. Mitterer, J. G. Wen et al. *Journal of Applied Physics*. 2006. V. 100 (4).
- [11] P.H. Mayrhofer and M. Stoiber. *Surf. and Coat. Technol.* 2007. V. 201, Issue 13, P. 6148-6153.
- [12] C. Mitterer, M. Rauter and P. Rödhammer. *Surf. and Coat. Technol.* 1990. V. 41, Issue 3, P. 351-363.
- [13] O. V. Sobol'. 2007. *Phys. Solid State*. V. 49. P. 1161–1167.
- [14] A. D. Pogrebnjak, A. P. Shpak, N. A. Azarenkov, and V. M. Beresnev. *Usp. Fiz. Nauk*. 2009. V. 179. Issue. 52 (1), P. 29–54.
- [15] Kiryukhantsev-Korneev F.V., Shtansky D.V., Petrzhik M.I. et al *Surface and Coatings Technology*. 2007. V. 201 pp. 6143-6147.