

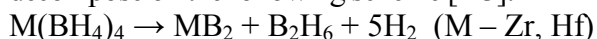
FEATURES OF THERMOLYSIS OF BOROHYDRIDE OF ZIRCONIUM

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Introduction

Lately interest grew to the use of borohydrides of transitional metals or their derivatives as precursors for the preparation of nanocrystalline hydrides, borides, nitrides or their mixtures. So, for example, the volatile borohydrides of zirconium and hafnium at heating decompose on the following scheme [1-3]:



In this connection the study of processes of metals borohydrides thermolysis is an actual task. As a model object $Zr(BH_4)_4$ was used. Unlike works [3,4] in which heating was carried out by the laser irradiation and another terms of synthesis of initial matters were realized, in present work the ordinary methods of heating were used in isothermal and polythermal modes.

Results and discussions

Thermolysis of $Zr(BH_4)_4$ steams was produced in the interval of temperatures 523 – 623 K in a vacuum during 5 hours in the laboratory setting supplied by special devices for the selection of gaseous probes for the spectral and chromatographic analyses. Completion of thermolysis was determined on disappearance of $Zr(BH_4)_4$ in a source and on absence of volatile products of reaction in a gas phase. The product of thermolysis – amorphous powder of zirconium diboride – settled in the extended part of reactor, and directly in the area of heating brilliant dense film of ZrB_2 was appeared.

In a table 1 presented the results of thermolysis of $Zr(BH_4)_4$ steams in the interval of temperatures 523-623 K. In accordance with the resulted information, thermolysis of $Zr(BH_4)_4$ at 523 K does not take place. Based on electron microscopy data powders of ZrB_2 which were produced at $573 \div 623$ K consist

of the rounded particles measuring about 40 nm. This value are in agreement with the results of measuring of specific surface of powders, which for the theoretical density of ZrB_2 (6.1 g/cm^3) give the value of particles diameter approximately 37 nm. The contents of oxygen in such powders was about $1.0 \div 1.5$ mass %.

According the results of XPS analysis the basic component of powders is ZrB_2 . Energy of electrons link on $3d_{3/2}$ –level of Zr was equal 179.0 eV and on 1s- level – 187.7 eV that corresponds to energy of electrons link in metals borides. Except the typical lines for ZrB_2 in XPS spectrums were detected the lines of boron oxides, zirconium oxides and the elementary boron.

During the heating from 293 to 1273 K in the atmosphere of argon the amorphous powder of ZrB_2 are crystallized in hexagonal phase with the lattice periods $a=0.3157 \text{ nm}$ and $b=0.3525 \text{ nm}$ without noticeable calorification or absorption of heat and loss of mass. For more detailed research of crystallizations process the powder of amorphous ZrB_2 were annealed during 1 hour in vacuum $1.33 \cdot 10^{-1} \text{ Pa}$ in the isothermal mode at temperatures 623, 773 and 1273 K. The beginning of crystallization of amorphous zirconium diboride was observed already at 623 K and at 1273 K the crystallization process was completed. Periods of crystalline lattice of ZrB_2 after annealing ($a=0.3160 \text{ nm}$ and $b=0.3521 \text{ nm}$) are in close agreement with previous results [5] and literature data [6]; crystallite size was about 14 nm.

Conclusions

Thus, at thermolysis of steams of $Zr(BH_4)_4$ the nanocrystalline ZrB_2 can be got both as a powders and as a films.

Table 1. Products of thermolysis of $Zr(BH_4)_4$ steams (523-623 K, weight - 0.5 g, 5 hours)

T, K	Type of ZrB_2	a , nm	c , nm	S , m ² /g
523	-	-	-	-
573	Powder Film	Amorphous		27.7
		0.3167	0.3528	-
623	Powder Film	Amorphous		26.2
		0.3165	0.3524	-

References

1. Jensen J.A., Gozum J.E., Pollina D.M., Girolami G.S. Titanium, Zirconium and Hafnium Tetrahydroborates as "tailored" CVD Precursors for Metal Diboride Thin Films // J.Am.Chem.Soc. 1988. V.110 N 5. P.1643-1644.
2. Wayda A.L., Schneemeyer L.F., Opila R.L. A Low-Temperature Film Deposition of Zirconium and Hafnium Borides for the Thermal Decomposition of the Borohydrides, $M(BH_4)_4$ // Appl.Phys.Lett. 1988. V.53. N5. P.361-363.
3. Rice G.W., Woodin R.L. Zirconium Borohydride as a Zirconium Boride Precursor. // J.Am.Chem.Soc. 1988. V.71. N4. P.C-181 – C183.
4. Axelbaum R.L., Bates S.E., Buhro W.E. et al. Wet Chemistry and Combustion Synthesis of Nanoparticles of TiB_2 . // Nanostruct. Mater. 1993. V.2. P.139-147.
5. Andrievski R.A., Kravchenko S.E., Shilkin S.P. Some Properties of Ultrafine Zirconium Boride Powders and Films. // Proc. XI Int. Symp. Boron, Borides and Related Compounds (Tsucuba, 1993) // Jpn.J.Appl.Phys. 1994. V.10. P.198-199.
6. Andrievski R.A., Spivak I.I. Strength of high melting point compounds and corresponding materials. Chelyabinsk. Челябинск: Metallurgy. 1989. 368 p.