УДК 539.1.

USING PIGE FOR ANALYSIS OF BORON CARBIDE OF RECEIVED BY CVD METHOD

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The method PIGE was used for determination of stoichiometry and isotopic content of boron carbide in one measurement. The optimal conditions of experimental measurement were determined. The possibility was shown of obtaining of boron carbide enriched according to boron using CVD-method.

INTRODUCTION

The boron carbide is semiconductor with high temperature of melting. This substance is of interest for development of materials for high-temperature thermoelectric converters. The variation of concentrations of impurities and also stoichiometry out of the way increasing of boron content sufficiently influence on main thermoelectric features of boron carbide. This material consist of atoms of four stable isotopes which have in natural mixture the such concentrations: ^{10}B-19.9 %; ^{11}B-80.1 %, ^{12}C-98.9 %, ^{13}C-1.1 %. The cross-sections of capture of thermal neutrons by nuclear of atoms of isotope ^{11}B is equal 0.005 b, carbon – 0.0035 b, and by isotope ^{10}B is equal 3837 b. Because of this the increasing of content isotope of boron with low cross-section of the absorbing of neutrons influences on radioactive resistance of material, if thermoconverter made from boron carbide is used to convert the thermal energy to electrical in nuclear reactors or isotopic sources.

It is possible to obtain the ceramics on base of boron carbide by means of agglomeration or hot-pressing of powdered boron carbide in vacuum. Nevertheless, materials made with application of these techniques do not have necessary densities. It is known, that thermoelectrical features of boron carbide depend on its porosity sufficiently. The possibilities were studied to obtain boron carbide using gas-phase deposition. During of it production the stoichiometry and isotopic content was checked.

Boron uses extensively in nuclear energetic, medicine, geology, ecology, where namely its isotopic content is important. Carbon from this point of view is interesting for the studying of chains of feeding and it cyclicity in ecosystems and the age dating using isotope ^{14}C. However, despite wide application, the determination of isotopic content these elements are difficult analytical problem. It gives much more articles to analysis of isotopic content of boron in comparison with determination of isotopic content of carbon.

A number of analytical methods of isotopic content boron determination are presented in review [1]. The various ways of analysis and problem arising at they realization were discussed. The cross-sections of capture of thermal neutrons for ^{10}B and ^{11}B are different on six orders of magnitude, that makes difficult the application of neutron activation analysis to determination of isotopic content. In work [2] the neutron flux was optimized by the using of cadmium foil and analytical technique was applied on base studying of tracks of α-particles from reaction (n, α) for determination of enrichment relative to isotope ^{10}B. Mass-spectrometry is one of main methods of determination of isotopic content of boron. The various ways of exiting of sample and obtaining of plasma may be used. The laser exiting of analyzed sample was used in ref. [3] at determination boron isotopes in boron carbide. In ref. [4] it was obtained sufficiently low limits of detection (less then 5 ppm) for boron isotopes using method resonant laser secondary neutral mass spectrometry (r-laser-SNMS). In this case a system of tunable dye-lasers for resonantly ionizing the neutral atoms and time-of-flight mass-spectrometer was use for registration of emission. The high sensitivity at measurement ratio of content of boron isotopes was reached in [5] with the using of mass-spectrometry with inductive connected plasma. The distribution of boron isotopes in absorbing rods was determined by method of second ions mass-spectrometry in [6].

The most general method of determination of stable isotopes of carbon based on transfer of carbon to carbon dioxide and consequent application of mass-spectrometry (Gas Source Isotope Ratio Mass Spectrometry (IRMS). The accelerating mass-spectrometry (AMS) applied generally to determine the content of carbon isotope ^{14}C for age dating.

Mass-spectrometric methods require long and laborious previous sample preparation. Therefore it is naturally to develop simple, suitable and sensitive method of isotopic content determination of boron and carbon. Nuclear reactions induced by charged particles have the wide possibility for these purposes. They have high selectivity, the matrix influence is rather weak, and their limits of detection are low and practically do not need previous sampling. In work [7] the typical application was shown of analytical methods based on particles beams. The film from boron carbide on the mirror for X-rays emission made from Mo/Si was studied. Stoichiometry and surface density of film were determined using Rutherford back scattering and nuclear reactions ^{11}B(p,α)^{8}Be, ^{11}B(d,α$_0$)^{9}Be, ^{12}C(d,p)^{13}C. But in example given and in a number another er ones the reactions chosen require the execution some measurements on one sample with variation of particles type or registration system.

After studying of available literary data the proton induced nuclear reaction were selected which made it possible to determine simultaneously the stoichiometry and isotopic content of boron carbide in one measurement, without previous sampling.

EXPERIMENTAL

THE STUDYING AND STANDARD SAMPLES

Samples of boron carbide were prepared using techniques of gas-phase and plasma-chemical hydrogen reduction of tree-chloride boron in vapors of toluene under streamline flow of the surface of backing by laminar non-skid stream without convection.

The deposition of boron carbide was made in cylindrical flowing-type reactor on graphite substrate. The unit was described in detail, previously [8]. The graphite substrate was previously saturated with pyrolytic carbon for the better separation of deposited boron carbide from the substrate. In reaction volume the substrate was placed in zone of inductor of rf generator at the ohmic heater made from tungsten. The pumping of reaction volume was made by the vacuum pump using the freezing nitrogen trap. After the pumping of reaction chamber up to pressure 1.33 Pa hydrogen was conducted to chamber up to required pressure, and, after warming up the substrate up to given temperature, thee-chloride boron and vapors of toluene were conducted in various relationships. The hydrogen reduction of thee-chloride boron was realized using the reaction

$$28BCl_3 + C_6H_5CH_3 + 38H_2 \Leftrightarrow 7B_4C + 84\ HCl$$
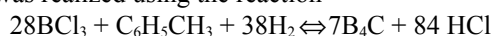
both gas-phase and plasma-chemical methods, exiting high-frequency charge in vapor-gaseous mixture. The thicknesses of deposited films vary from 30 μm to 2 mm. The diameter of samples prepared for analysis was equal 20 mm.

To make quantitative analysis samples of interest were placed in irradiated chamber together with standard samples. Carbon (99.99 %), boron (99.99 %) and boron carbide powder were used as standards.

FEATURES OF NUCLEAR REACTIONS USED FOR ANALYSIS

It was determined, after previous research, that it is appropriate to use for elemental and isotopic analysis of binary compounds on base of carbon and boron, the protons induced nuclear reactions with registration of γ-quanta. The features of proton induced nuclear reactions of radiative capture which were used to determine the isotopes ^{11}B, ^{12}C, ^{13}C are shown in table 1. The isotope ^{10}B was determined using reaction $^{10}B(p,\alpha\gamma)^7Be$.

The γ-lynes with energy 429 keV from reaction $^{10}B(p,\alpha\gamma)^7Be$, 2.36 MeV - $^{12}C(p,\gamma)^{13}N$; 4.43 MeV - $^{11}B(p,\gamma)^{12}C$; 8 – 8.7 MeV- $^{13}C(p,\gamma)^{14}N$ were chosen for analysis.

EXPERIMENTAL SET

The experimental measurements were made on analytical complex "Sokol" NSC KIPT [9]. Experimental set includes electrostatic accelerator with outputting facilities; experimental chambers for fulfillment of set of nuclear-physical methods of analysis; spectrometric and computing devices designed for the handling of operation of experimental set and automation of processing of experimental results. The general form of complex is viewed in Fig.1.

The accelerator provides to obtain the beam of one-charged ions with energy up to 2 MeV and energy reso-

lution up to 0.04 %. The measurements were executed in channel number trees. The all studying samples were placed in irradiated chamber simultaneously. The protons beam was oriented at normal to surface of target. The size of beam on a target was about 3 mm.

Table I

Features of nuclear reactions used for determination of content of boron and carbon [10]

Energy of resonance, keV	Reaction	Cross-section, mb	Width of resonance, keV	E_γ, MeV
163	$^{11}B(p,\gamma)^{12}C$	0,157	7	4.43 11.68 16.11
675	$^{11}B(p,\gamma)^{12}C$	0,050	322	4.43 12.15
459	$^{12}C(p,\gamma)$ ^{13}N	0,127	39,5	2,36
550	$^{13}C(p,\gamma)$ ^{14}N	1,44	32,5	8,06
1160	$^{13}C(p,\gamma)$ ^{14}N	0,56	6	2,39 3,07 4,11 8,62

To register γ-emission scintillation NaI(Tl) detector with volume of crystal 150×100 mm and Ge(Li)-detector with volume of crystal 160 and energy resolution of 2.5 keV at 1332 keV were used. Both detectors were placed outside the chamber. The distances from target to detectors were 5 cm and the angles between beam direction and axes of detectors were 55° for Ge(Li) and 45° - for NaI(Tl). To decrease the natural background and radiation background induced by operating units the sensitive volumes of detectors were shielded by cases made from lead 15 mm in thickness. Ge(Li) detector was used to register γ-emission in range from 200 to 5000 keV. NaI(Tl) detector was applied to register high energy γ-emission with energy 8…10.5 MeV by reason it high efficiency. The standard spectrometric equipment was used. The charge of protons stored on target was measured by current integrator.

THE MEASUREMENTS AND RESULTS

At the development of method of quantitative evaluation of basic components of boron carbide the general efforts were directed on studying of possibility of simultaneous determination carbon and boron in one measurement. The energy and current of beam were changed and absorbers from lead in thickness from 1 to 5 cm in front of Ge(Li) detector for suppressing of high-intensity 429 keV γ-emission were used to find the optimal conditions of analysis. The spectrometric channel including the NaI(Tl) detector was tuned to register γ-emission in energy range 8.0…8.7 MeV in such a way as to except the interferences with emission from other protons induced reactions proceeding on nuclear of atoms isotopes ^{10}B, ^{11}B, ^{12}C.
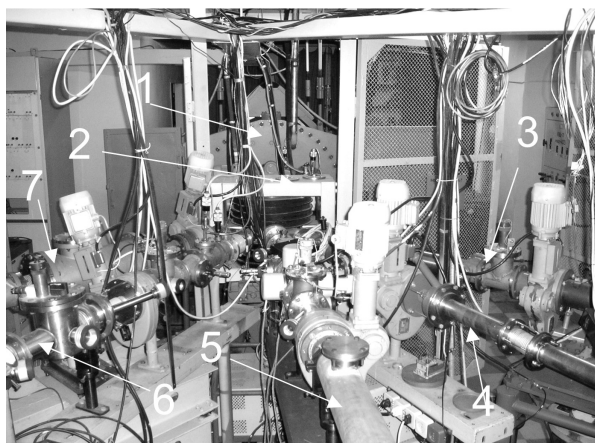
Fig.1. Analytical nuclear-physical complex "Sokol":
1 - electrostatic accelerator; 2 - deflecting magnet;
3 – 7 the channels of outgoing ions beam

For example, in Fig.2 the spectrum was shown of γ-emission from nuclear reactions induced on nuclear of atoms for tree isotopes. This spectrum was measured at energy and current of protons beam 0,57 MeV and 2.7 µA and charge of protons stored on target was 3000 µC. It was possible to increase yields of high-energy γ-emission and decrease the duration of analysis by the increasing of protons energy if the absorber from lead in front of Ge(Li) detector to place.

The range of lower-energy protons used for analysis of samples of boron carbide is rather small. On this basis it can be neglected absorption of γ-rays in a target, and, if atoms of analyzed elements are distributed uniformly in a sample, we can draw on for content determination the formula

$$C_{smpl} = C_{st} \frac{Y_{smpl}}{Y_{st}} \frac{S_{st}}{S_{smpl}}, \qquad (1)$$

where C_{smpl}, C_{st} – contents of in analyzed and standard samples accordingly; Y_{smpl}, Y_{st} - yields of analytical γ-rays from analyzed and standard samples accordingly; S_{smpl}, S_{st} - the stopping power of substance about protons with energy E_p for analyzed and standard.

It was found after determination of elemental content of samples by external standard methods, that the main error of concentration determination was associated with the error of charge measurement. The method of evaluating of content proposed in ref [11] was used to maintain high accuracy of computation. As is shown by authors in case of the sum of contents of determined elements in analyzed samples and standard is equal 100 %, and difference in matrix composition doesn't influence significantly on intensities of analytical lines, the content each of elements may be determined from the formula

$$C_i^{smpl} = \frac{Y_i^{smpl}}{\sum\limits_{j=1}^{n} Y_j^{smpl} \frac{Y_i^{st} C_j^{st}}{Y_j^{st} C_i^{st}}}, \qquad (2)$$

where C_i^{smpl} - content of i-th determining element in analyzed sample; Y_i^{smpl} Y_j^{smpl} - yields of γ-rays, accordingly, i-th и j-th element from analyzed sample. The same symbols with superscript "st" denote according quantities for standard sample. The error contributed by inaccurate measurement of charge is excluded if elemental contents are calculated by some means, as far as ratios of yields depending only on statistical accuracy of definition of sum of counts in analytical peak.
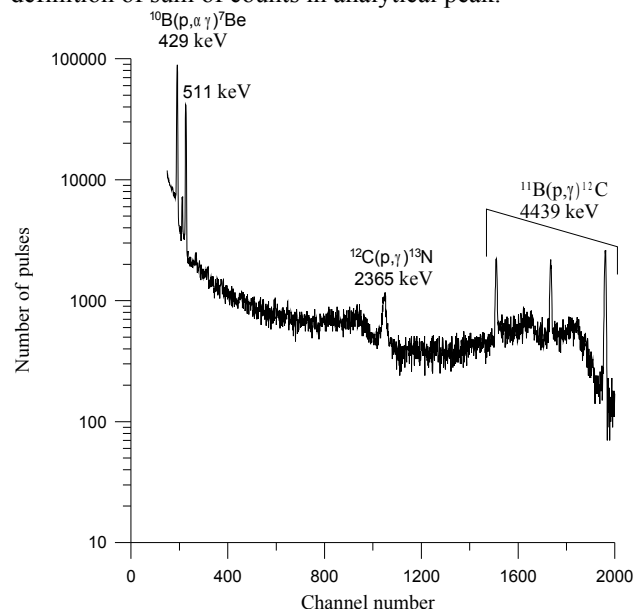

Fig. 2. The spectrum of γ-emission induced in (p,γ) reactions on nuclear of atoms of isotopes ^{10}B, ^{11}B, ^{12}C

The results of analysis a number of samples made in various conditions (temperature, flow, duration) by CVD method are presented in Table 2.

The measurements of isotopic content of boron carbide in various stoichiometry don't reveal of its variation in process of deposition of boron carbide on the backing. The ratio of content of isotopes was 0.24±0.01 for $^{10}B/^{11}B$ and – 0.0111±0.0005 for $^{13}C/^{12}C$.

Table 2

The results of determination of stoichiometry of boron carbide by PIGE

Sample	Concentration, mass %		Stechiomery (per one atom of C)
	B	C	
# 254	0.01	99.99	C
# 235	45.89	54.11	BC
# 221	90.64	9.36	$B_{11,5} C_1$
# 191	94.48	5.52	$B_{20,3} C_1$
# 121	97.48	2.52	$B_{45,8} C_1$
# 113	98.62	1.38	$B_{84,5} C_1$
# 103	99.04	0.96	$B_{122,3} C_1$

CONCLUSIONS

It has been found that CVD method may be used to obtain the boron carbide with given stoichiometry enriched about boron.

The developed technique of boron carbide composition analysis makes it possible on base of nuclear reactions to determine in one measurement the stoichiometry and isotopic content of analyzed product expressively, without previous sampling, with required metrological features.

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ПРИМЕНЕНИЕ ЯДЕРНЫХ РЕАКЦИЙ ДЛЯ АНАЛИЗА КАРБИДА БОРА, ПОЛУЧЕННОГО ГАЗОФАЗНЫМ МЕТОДОМ

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Метод ядерных реакций на протонах с регистрацией гамма-излучения был использован для определения стехиометрии и изотопного состава карбида бора за одно измерение. Определены оптимальные условия проведения измерений. Показана возможность анализа карбида бора с обогащением по боре, полученному газофазным методом

ВИКОРИСТАННЯ ЯДЕРНИХ РЕАКЦІЙ ДЛЯ АНАЛІЗУ КАРБІДУ БОРА, ОТРИМАНОГО ГАЗОФАЗНИМ МЕТОДОМ

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Метод ядерних реакціяй на протонах с реєстрацією гама-випромінювання було використано для визначення стехіометрії і ізотопного складу карбіду бора за одне вимірення. Визначені оптимальні умови проведення вимірювань. Показана можливість аналізу карбіду бора з збагаченням по бору, отриманим газофазним методом.