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DETERMINATION OF CONTENT AND DISTRIBUTION OF CARBON IN HIGH-TECHNOLOGIC MATERIALS USING NRA

A.O. Shchur, V.V. Levenets, O.P. Omelnyk, O.Yu. Lonin, M.F. Kozhevnikova
National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine
E-mail: shchur@kipt.kharkov.ua

This article is devoted to a review of physical and nuclear-physical methods of analysis, which are used for the determination of the stoichiometry, isotopic content and structure of carbon-based materials, as well as for the determination of the content and distribution of carbon in various matrices. The examples are given of the authors' application of nuclear-physical methods of analysis to study the properties of synthetic-diamond coatings on a silicon substrate and the distribution of carbon in depth in a sample of a high-entropy alloy based on Ti-Zr-Hf-V-Nb-Ta. The options for analyzing the elemental and isotopic content of carbon considered in the work indicate the great possibilities of using resonant nuclear reactions $^{12}C(p,\gamma)^{13}N$ and $^{13}C(p,\gamma)^{14}N$ in scientific and technical research.

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INTRODUCTION

The researches related to the creation of nanoscale structures based on carbon have the increasing importance for the creating high-tech materials. Now carbon, as a base material, is in great demand in many areas of industry. Carbon has a variety of forms and physical and chemical properties in its various states. It used, as before, in the form of graphite in electrical engineering, as anodes for lithium-ion batteries and other current sources and as a diamagnetic with one of the highest susceptibilities per unit mass. Graphite-based materials are used so in rocket nozzle bodies.

Carbon in the form of diamonds is used in metalworking – grinding and cutting tools with diamond coating and in the jewelry industry.

In recent years, new forms of carbon have been discovered that have a complex of unique physical and chemical properties. Among them are graphene and carbon nanotubes – promising materials for microelectronic circuits of the future. Now nanotube transistors are superior in their properties to existing silicon devices.

Another of the recently discovered forms of carbon is carbynes, which are linear chains of carbon atoms with an expected unique specific strength. Different types of carbine – cumulene and polyyne have opposite electrical conductive properties: polyyne is a conductor, but cumulene is a dielectric.

Separate classes of carbon materials, fullerenes, according to their molecular structure, represent a regular pentagon of carbon atoms. Among them are fullerides - fullerene crystals. In these materials some of the cavities between adjacent polyhedra are occupied by metals. It turns this material into a molecular superconductor with a record high transition temperature for similar materials – 18 K.

Another of the new carbon-based materials is Q-carbon, which, unlike diamond, graphite and other forms of carbon, is a ferromagnetic, that loses its magnetic properties when heated to 220 °C. Q-carbon with embedded boron atoms is a superconductor, with a transition temperature of about 58 K.

1. METODS FOR CARBON DETERMINING IN VARIOUS CARBON-CONTAINING MATERIALS

The variety of materials, in which carbon is present, causes a large number of methods for its determination. Thus, for the analysis of carbon in steels, the coulometric method, infrared spectroscopy, gas-volume, X-ray spectral method, electrochemical identification, and lithium intercalation are used. These methods require large financial costs for equipment and consumables.

Thus, for analysis by coulometry, infrared spectroscopy, and gas-volume method, it is necessary to burn the sample in an O_2 flow, at temperatures above 1200 °C – convert carbon into CO_2, use chemical reagents.

Unfortunately, the widely used AES methods, as a rule, do not allow carbon analysis in the normal operation of serial analyzers, as well as when using XRF analyzers. To carry out the analysis by these methods, additional studies and the creation of original methods of analysis are required.

The authors of [1, 2] note that due to the fundamental difficulties in performing XRF, the determination of the mass fraction of carbon in ferro-silico-manganese is usually carried out using carbon analyzers based on coulonometric or infrared [3] absorption cells. As a more budgetary alternative, atomic emission spectral analysis (AESA) is proposed n the variant of blowing powders into a spectrum excitation source (SIS), which is suitable for determining the determination of carbon in the range from 1 to 3 wt.% in ferromanganese [3]. A similar approach was used in the determination of carbon in steels and cast irons, which required the use of a "hard mode" of a low-voltage spark with a sharp focusing of the source image on the slit, fine tuning of the steeloscope slit in the center of the spark [4]

The authors of [5] used XRF to analyze light elements without evacuating the working volume of the spectrometer. For low-alloy steels, the possibility of express analysis of carbon by structural reflections of cementite with an accuracy of 0.025 wt.% was proved.

There are portable laser analyzers LIBS [6] on the market for determining the carbon content in carbon stainless steels and cast irons – SciAps Laser Z-200C/C+. The method requires preliminary stripping of the sample and subsequent 9…12 s test with pre-firing and blowing with argon. For high alloy steels, the carbon detection limit is 0.008%.

It should be noted that almost all of the above methods require the destruction of the analyzed sample, are aimed at solving routine problems of everyday control and do not allow the analysis of carbon structures in the nano and micro ranges. Namely, such tasks are priority for the creation of technologies for the production of new materials based on carbon.

2. NUCLEAR-PHYSICAL METHODS OF DETERMINATION OF CARBON

There are some possibilities to determine of elemental, isotopic content and distribution of carbon in volume of probe. It may be made using Rutherford Backscattering Analysis (RBS), charged particles from nuclear reactions and momentum γ-ray emission from nuclear reaction induced by charged particles (PIGE). The target is eradiated by a beam of protons, deuterons, ^{3}He or α-particles and the charged particles or γ-quanta are registered, which originated in nuclear reaction or backscattered on target surface. The application of these methods to determination of carbon is shown below.

In work [7] simultaneous depth profiling of the ^{12}C and ^{13}C isotopes in different samples using ^{12}C(d,p)^{13}C and ^{13}C(d,p)^{14}C reactions were done. The samples were obtained by implantation of 400 keV ^{13}C ions into polished copper substrates at different temperatures and implanted doses. Tandem accelerator with energy 2 MeV was used for implantation. The study was made of the evolution of ^{13}C depth profile as a function of implanted doses and temperature.

Authors of article [8] have been used deuteron ion beams for the high sensitivity studying of profiles of ions of nitrogen and carbon implanted in zinc oxide and silicon single crystals.

The reaction ^{12}C(d,p)^{13}C was used for the determination of the carbon impurity/dose on the surface and in bulk of ion implanted silicon. Simultaneous detection of ppm-level concentrations and more of ^{12}C, ^{16}O was possible.

As stated in paper [9], carbon in the presence of other light elements, in particular oxygen, can be determined using the ^{12}C(^{3}He,P)^{14}N reaction, since the large cross section of the reaction allows registering the analytical signal even under the conditions of a low value of the beam current – about 0.5 nA.

In paper [10] the samples obtained by simultaneous implantations of ^{12}C and ^{15}N into copper were studied using reaction ^{12}C(d,p0)^{13}C at 1.05 MeV deuteron beam energy. The authors determined depth profiles of both elements and estimated the relative contribution of multiply charged ions ^{12}C and ^{15}N to the distribution of carbon and nitrogen. It was shown that profiles of both elements may be measured simultaneously.

In the article [11] the methods was presented of non-destructive analysis of near surface layers of binary samples of diamonds films obtained by CVD deposition on Si-backing, using PIXE and PIGE. The thicknesses and depth profiles of carbon were determined in synthetic diamonds films using resonance of 457 keV from nuclear reaction ^{12}C(p,γ)^{13}N. The content of ^{12}C and ^{13}C in samples was detected using γ-ray 2365 and 8062 keV from nuclear reactions ^{12}C(p,γ)^{13}N and ^{13}C(p,γ)^{14}N respectively. The differences were founded for isotopic contents of carbon in studying samples. The conclusions were made about possibilities of application of such analytical methods to study physical processes, which take a place at the manufacturing of synthetic diamonds by CVD and determination of parameters, which influence on features of such production.

PIGE was used in [12] for determination of elemental and isotopic content of samples of B_4C. The distribution profiles of boron and carbon are determined using resonance nuclear reaction. Boron isotope content was studied using nuclear reactions ^{10}B(p,αγ)^{7}Be and ^{11}B(p,γ)^{12}C, the best depth resolution was about 400 Å. Nuclear reactions ^{12}C(p,γ)^{13}N and ^{13}C(p,γ)^{14}N with the best resolution equal to 470 Å were used, for the studying of the distribution of carbon

The nuclear reaction ^{13}C(p,γ)^{14}N was used to determine the depth distribution of the ^{13}C atoms implanted into natural type IIa diamond at temperatures ranging between that of liquid nitrogen and 670 K [13]. It was be used the ^{13}C(p,γ)^{14}N reaction to trace the development of the diffusion profiles of the self-interstitials by implanting ^{13}C in diamond implanted previously by ions of F and preimplanted by a fractional monolayer of tungsten between the surface and the fluorine ions' range [14].

3. EXPERIMENTAL SETUP

We used the 2 MeV Van de Graff "Sokol" of the NSC KIPT, which can generate protons with the energy range between 200 keV and 2 MeV. A magnetometer previously was calibrated by means of the 992 keV resonance on ^{27}Al(p,γ)^{28}Si reaction. The target chamber was isolated from the rest of the beam line and served as a Faraday cup for the beam current integration. The γ-rays were detected by Ge(li) with efficiency equivalent of 40% that one for 10.2 x 10.2 cm NaI(Tl). Detector was placed at 0° to the direction of the incident beam and at a distance about 1.5 cm from target surface. The 8192-channel ADC analyzer was used to record the γ-spectra.

4. APPLICATION γ-EMISSION FROM RESONANCE NUCLEAR REACTIONS TO STUDY OF CARBON DISTRIBUTION

High-entropy alloys (HEA) are a new type of materials that began to develop in the last years

According to the formal definition, high-entropy alloys are alloys that have 5 or more metal elements in their composition, while the concentration of each varies in the range of 5…35 at.% These materials are in the center of attention of researchers all over the world, because potentially due to the inclusion of certain types of metals in the composition of such alloys, it is possible to create a specific set of properties for a specific type of product. We are studied the samples of

HEA on base of Ti-Zr-Hf-V-Nb-Ta which were coating of steel substrates. In matter of samples carbon is present and we use resonance from nuclear reaction $^{12}C(p,\gamma)^{13}N$ at energy of protons 457 keV to determine the thickness of covering and profile of concentration of carbon. The result is shown on Fig. 1.

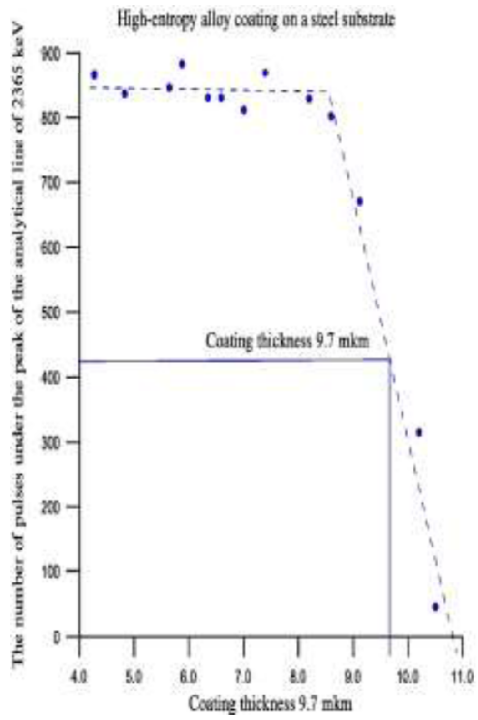

Fig. 1. Profile of concentration of carbon in the sample of HEA on base of Ti-Zr-Hf-V-Nb-Ta

On Fig. 2 the result is presented of determination of thickness of diamond films on silicon substrate and profile of carbon concentration in samples.

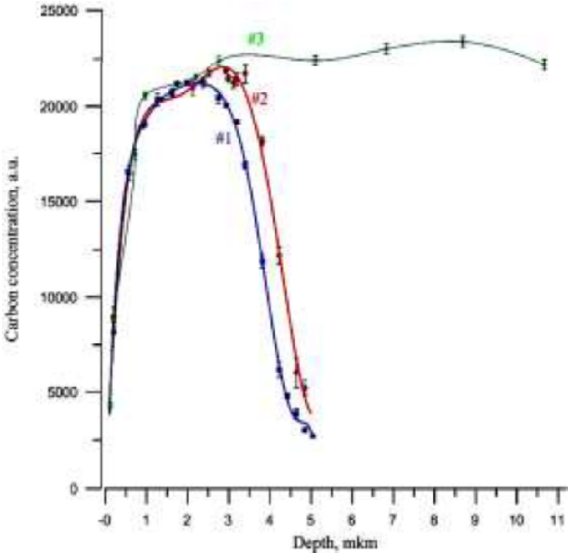

Fig. 2. Profiles of carbon in diamond coatings deposited on a silicon substrate. Symbols – experimental values, lines – fitting of the data set with a 9-degree polynomial for #.1, 2, with splines for #.3

The thickness of covering and profile of concentration of carbon were determined as in previous example. The isotopic content of diamond was determined using $^{12}C(p,\gamma)^{13}N$, $^{13}C(p,\gamma)^{14}N$ reactions.

5. CONSIDERATION OF THEPOSSIBILITY OF DETERMINING CARBON WITH HIGH SPATIAL RESOLUTION USING THE 1747 keV RESONANCE FROM A NUCLEAR REACTION $^{13}C(p,\gamma)^{14}N$

Table shows the characteristics of nuclear reactions on carbon isotopes, which are used to analyze the distribution of this element along the depth of the studied sample

In the above examples of determination of carbon concentration profiles by the authors, resonances at proton energies of 457 and 550 keV from the reactions $^{12}C(p,\gamma)^{13}N$ and $^{13}C(p,\gamma)^{14}N$ were used, respectively. The evaluations performed using the STRIM 2008 code show that depth resolution, due purely to the width of the resonance, of carbon profiles for Si, C, B_4C or steel-based samples are 0.45, 0.35, and 0,17 μm, respectively, which is too much for technologies using nanoscale objects. On the other hand, for resonance 1747 keV, the corresponding values for the same matrices are 2.5, 2.2, and 1 nm. Therefore, the using of resonance at 1747 keV will allow to determine the distribution of carbon in layers with a thickness of tens or several hundreds of nanometers with resolution of some tens of nanometers.

There are some publication which illustrate the possibility of application of NRA with resonance at 1747 keV from $^{13}C(p,\gamma)$ ^{14}N to the depth profiling in nano-dimensions diapason.

The structure of $Si_1{}^{12}C_x{}^{13}C_y$ layers were studied in [18]. The sample was obtained by implantation of the carbon isotopes ^{12}C and ^{13}C into c-Si (1 1 1). The ^{13}C depth profile was measured using the nuclear resonance at the proton energy of 1747 keV. The depth resolution of the method on the surface of the target was 21 nm due to the inclination of the sample normal at an angle of 70° to the direction of the incident proton beam. Due to the energy straggling of the proton beam at a depth of 100 nm, the depth resolution deteriorated to 70 nm. The same way was used in [19] to study the SiC sample prepared by implantation of 40 keV ^{13}C ions into crystalline S (1 0 0) samples. The implanted dose were $(3…8)\cdot10^{17}$ ions/cm^2. The depth resolution in the near-surface region was improved from 31 to 10 nm using the tilting of angle between the surface of target and proton beam directions as previos work [18]. High fluence (10^{16} to $3\cdot10^{17}$ ions/cm^2) carbon (^{13}C or ^{12}C) ion-implantations were performed into silver substrates held at high temperature (400…700 °C) to produce carbon onions [20]. The carbon concentration profiles were determined by using the same resonance and reaction as [18, 19]. The surface depth resolution 10…20 nm can be obtained. In such way ^{13}C concentration profiles were studied at different doses of implanted ions in the depth ranges from 4…25 to 100…400 nm.

The characteristics of the resonance reactions for the carbon depth distribution studying [15–17]

Resonance energy, keV	Nuclear reaction	Cross-section, mb	Resonance width Γ, keV	Energy of E_γ rays MeV	Relative line intensities	Reference
457	$^{12}C(p,\gamma)^{13}N$	0.126	36.0	2.36	100	[15]
550	$^{13}C(p,\gamma)^{14}N$	1.44	32.5	8.06	100	[16]
1747	$^{13}C(p,\gamma)^{14}N$	340	0.075	9.17 6.45 2.74	100 18.05 17.64	[15–17]

In work [21] non-resonant $^{13}C(d,p)^{14}C$ and resonant $^{13}C(p,\gamma)^{14}N$ NRA were used to determinate the content and formation of SiC nanoboulders on silicon. The target was prepared directly from ^{13}C embedded into silicon (1 0 0) by ion implantation and followed by electron beam rapid thermal annealing at 1100 ºC for 15 s. Nanoboulders have the size from 150 to 390 nm. Thanks to the use of 1747 keV resonance, the effect of heat treatment on the content of ^{13}C in the implanted layer was evaluated, the dimensions of SiC nanoboulders were estimated – thickness (-180±97) nm and width 300…500 nm. It is shown that the content of ^{13}C on the surface is approximately 20 at.% increases to a maximum at about 30 nm, and then decreases to 7 at.% at a depth of 100…150 nm.

CONCLUSIONS

The options for the analysis of the elemental and isotopic content of carbon considered in the work indicate the great potential of using resonant nuclear reactions under the action of protons on the nuclei of carbon isotopes ^{12}C and ^{13}C in scientific and technological researches. The $^{13}C(p,\gamma)^{14}N$ reaction is characterized by unique opportunities for studying carbon distribution in the depth range from 10 nm to several micrometers. Due to the presence of two isolated resonances at proton energies of 550 and 1747 keV, this reaction can be used to solve a wide range of problems, including the study of structures that are of interest in the development of nanotechnology.

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ВИЗНАЧЕННЯ ВМІСТУ ТА РОЗПОДІЛУ ВУГЛЕЦЮ У ВИСОКОТЕХНОЛОГІЧНИХ МАТЕРІАЛАХ ЗА ДОПОМОГОЮ ЯДЕРНИХ РЕАКЦІЙ

А.О. Щур, В.В. Левенець, О.П. Омельник, О.Ю. Лонін, М.Ф. Кожевнікова

Дано огляд фізичних та ядерно-фізичних методів аналізу, які використовуються для визначення стехіометрії, ізотопного вмісту та структури матеріалів на основі вуглецю, а також для визначення вмісту та розподілу вуглецю у різних матрицях. Наведені приклади застосування авторами ядерно-фізичних методів аналізу для вивчення властивостей штучних діамантових покриттів на підкладці з кремнію та розподілу вуглецю по глибині у зразку високоентропійного сплаву на основі Ti-Zr-Hf-V-Nb-Ta. Розглянуті у роботі варіанти аналізу елементного та ізотопного вмісту вуглецю свідчать про великі можливості використання резонансних ядерних реакцій $^{12}C(p,\gamma)^{13}N$ і $^{13}C(p,\gamma)^{14}N$ у науково-технічних дослідженнях.