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Carbon with tubelene-like nearest atomic order in inclusions of iron-nickel-carbon alloys

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Abstract

The presence of skeleton carbon with tubelene-like nearest atomic order in inclusions of Fe-Ni-C alloys of a specially found composition has been found by the X-ray emission spectroscopy (CK α line) method. Such a carbon has been synthesized in the specific environment of the closed space of micropores in the alloys.

1. Introduction

New allotropic forms of carbon that consist of sphere-like (fullerenes) or tube-like (nanotubes or tubelenes) molecules excite the keen interest of investigators by their unique properties (see e.g. reviews [1,2]). It is known that such molecules can be found in products of laser beam evaporation of carbon [3], electric arc discharge between carbon electrodes [4,5], and pyrolysis at temperatures $\sim 1000^{\circ}$ C [6]. Electron beam [7–9] and thermal [10] evaporation are also used to produce such molecules. All these processes occur either in vacuum, or in gases at low pressures (~ 500 Torr), where nothing can hinder the synthesis of the great voluminous molecules of fullerenes and tubelenes and their skeleton structures that consist of tens or hundreds of C atoms.

The question, the answer to which we want to give in the present work, arose, whether there could be found conditions in solids or liquids under which structures made of fullerenes or tubelenes could be synthesized in a dense environment of matrix atoms. In a continuous uniform matrix such processes seem to be impossible. We supposed, however, that such conditions could arise in an inhomogeneous matrix when at the places of carbon segregation (which is necessary for the accumulation of C atoms for the construction of great molecules) inside the matrix discontinuities such as micropores or/and crevices appear. Micropores usually appear in liquids at outgassing (at the reduction of temperature or pressure) of dissolved gases. Microcrevices can appear at the shrinking of a solid material and/or its slide deformations.

As basic materials for internal production of tubelene or fullerene-like forms of carbon we took Fe-Ni-C alloys. The reasons for this were as follows. (1) It is known that inside Fe and Ni based systems inclusions of various carbon forms could be produced – amorphous carbon and sometimes diamond (see Fig. 8 in the review [11]). (2) According to Ref. [12] particles of a Fe-Ni alloy promoted the production of nanotube carbon structures in an arc. (3) Ni is known to push carbon away at elevated temperatures (~1000°C) and to form stable Fe–Ni alloys in which synthesis of iron carbides is suppressed [13]. Thus the presence of Ni had to promote the segregation of carbon along the grain borders during crystallization of the melt. (4) In foundry processes and powder metallurgy of Fe–Ni alloys their ability to absorb gases (especially H₂) has been stressed. Gas saturated nickel alloys at solidification are subject to defect formation such as gas bubbles and friable borders of primary grains formed by outgassing at supercooling [13,14]. (5) There are crisps in such alloys, the appearance of which along the borders of grains can be connected with the ability of such alloys to shrink at cooling and crystallization [15].

When choosing the three-component system, we took into consideration that such a system should be formed from the two-component system with an infinite solubility of the two basic components in the solid state. Systems of these two components with a third one (C) should be characterized by two binary diagrams with a eutectic discontinuity of the solubility. Carbon as the third component should not form when cooling stable phases or compounds with two other components.

The principal idea of the work on the synthesis of tubelene-like forms of carbon in Fe–Ni–C alloys was to create conditions for ousting carbon from the alloy melt at cooling. That was done by searching for the carbon concentration and melt cooling mode when micropore production and the formation of carbon nanoelements and skeleton structures in them would be possible under the influence of walls of micropores with a high surface curvature made of catalysts – Fe and Ni.

2. Experimental

2.1. Sample synthesis

Samples on the basis of Fe–Ni–C alloys were synthesized of chemically clean iron, nickel and graphite powders in the proportions: Ni: 10%-20%, graphite: 1%-4%, Fe: 76%-89%. The blend was thoroughly mixed and placed into a carbon crucible. The fusion process took place in a muffler at $1250-1300^{\circ}$ C during one hour, then the ingot was cooled in air.

The alloy samples prepared by subsequent mechanical sawing, grinding and polishing were prior to their analysis chemomechanically cleaned by polish paste Pikal (Nihon Maryo-Kogyo Co., Japan) containing a thin fraction of whitewash, and washed in acetone. Such a treatment removed the excess hydrocarbon contaminations and carbon fractions spread over the surface of the sample in the process of grinding and polishing.

2.2. Identification of carbon inclusions in alloys

2.2.1. Methods of experimental analysis

The manufactured samples were separated first of all as regards the presence of characteristic inclusions formed mainly of pure carbon. This was done with the help of optical and scanning electron microscopy (JSM-840) accompanied by electron beam microanalysis (JXA-5A, JEOL).

For identification of the allotropic forms of carbon the emission X-ray spectroscopy method was chosen. It was applied in the spectral region corresponding to the CK α line of carbon. We considered that this spectroscopic method like related methods of electron spectroscopy (see Ref. [16]) should be sensitive to differences in the distributions of electron states of the valence bands of carbon in its different allotropic forms: fullerenes, tubelenes, etc.

We consider the electron beam induced X-ray emission spectroscopy analysis of the CK α line to be the method most adequate to the problem posed in the present work. The advantages of this method in our case are as follows: (1) the high localization in the surface plane of the sample (down to ~3 μ m) necessary for the spectral analysis of inhomogeneous alloy samples; the possibility to decrease the space resolution when necessary to reduce the local dose of the electron beam irradiation; (2) the rather high depth of information extraction (~ 3×10^{-4} g/cm^2), which makes this method (as opposed to photoelectron and Auger spectroscopy with corresponding depth ~ 10^{-7} - 10^{-6} g/cm²) insensitive to possible surface hydrocarbon contaminations (the common thickness of such contaminations without special cleaning is ~ $(3-30) \times 10^{-7}$ g/cm³).

In spite of the fact that Auger spectroscopy [16] and electron energy loss spectroscopy (EELS) data [17] indicated the distinct differences in the densities of states of valence bands of tubelenes and graphite, the few works [18,19] on X-ray emission spectroscopy of fullerenes and graphite gave either no [19], or specific [18] distinctions in the corresponding CK α spectra. Thus to solve the problem we had first of all to find out whether there could be found stable differences between the CK α spectra of fullerenes, tubelenes and graphite. To improve the reliability of our comparative analysis we used an approach quite different from that in Ref. [18,19] to register and treat the spectra. Contrary to Refs. [18,19], where the spectra were recorded with the highest possible resolution (in Ref. [18] 1.5, in Ref. [19] 0.4 eV) either at poor signal to noise ratio (SNR) Ref. [18], or (according to our estimations) at high electron beam doses [19] (all this could distort the results), we decided to use for comparative analysis smoothed spectra with poorer resolution but recorded at high SNR ($\sim 10-30$) and low (see later) doses of irradiation. Such spectra should reflect the most stable reproducible features of the valence band state distribution of the investigated forms of material almost undistorted by the electron beam. According to this we obtained spectra with an energy resolution ~ 1.5 eV accompanied by a subsequent smoothing procedure executed by the fast Fourier transform (FFT) method (see e.g. Ref. [20]).

The described approach gives the possibility to work with substantially lower doses of electron irradiation than necessary for the high resolution spectra. This is very important for, as our investigations have shown, at doses of electron beam irradiation $> 7 \times 10^{-1}$ C/cm² (at 10 keV) the spectra of the tubelene-like carbon become distorted and take the form of the graphite spectra. The results of the published works [16,21] also indicate the destruction of tubelene-like carbon under the electron beam.

In the present work CK α spectra were recorded in the spectral region 250–300 eV with the help of the electron probe microanalyser JXA-5A (JEOL, Japan). The parameters of the electron beam were as follows: primary energy: 10 keV; current: 5×10^{-8} A, the diameter: 10–30 μ m, the X-ray take-off angle: 40° off the surface, doses of radiation: $\leq 5 \times$ 10^{-1} C/cm². A STE pseudo crystal was used in the crystal diffraction X-ray spectrometer. The SNR was improved in the input electronic circuit by the height selection of pulses from an X-ray quantum detector (proportional counter); the differential mode was used. The energy resolution of the CK α spectra



Fig. 1. Typical cross-section of Fe-Ni-C alloy sample with elongated carbon inclusions (secondary electron emission picture).

I, arbitrary units

after smoothing (estimated with the help of the third order of the sharp Ni L $\alpha_{1,2}$ line, registered in the same spectral region) was ~ 2.5 eV.

To decrease the contamination of the investigated samples in the vacuum chamber of the microanalyser the partial pressure of hydrocarbons was lowered ~ 10 times with the help of a liquid nitrogen trap. Thus in many cases we did not notice the influence of hydrocarbon contaminations on spectra at all.

2.2.2. Comparison of the forms of $CK\alpha$ lines to standard forms

The spectra of samples of the following materials were taken as different standards for comparative analysis: (1) crystalline graphite and amorphous carbon made by pyrolysis; (2) powders of tubelenesnanotubes (Allied Signal Inc., USA, R. Baughman); (3) purified powder of fullerenes made by the arc method (Research Center of Chemical Technology, Moscow State University, A. Dityat'ev); (4) carbon multilayered nanotube films produced by Z.Ya. Kosakovskaja [9]; (5) samples of hydrocarbon contaminations on an Au substrate polymerized by the electron beam irradiation at various doses; (6) samples of carbon rich steels U8, U13 and Cr doped Cr12V1. Samples (5) and (6) were made in the course of the present work. The identification of the carbon nanotubes with diameters $\sim 100-300$ Å was done by the high resolution electron microscopy method at the Institute of Crystallography, RAS, Russia (A.N. Kiselev) (see Ref. [9]).

All the registered spectra were subjected to standard computer-aided processing: smoothing (FFT method), background subtraction, normalization with respect to maximum, drawing in the same scale. To improve the sensitivity of the spectral form comparison, the first and second derivatives of the smoothed spectra were calculated.

2.2.3. Results and discussions

The inclusions of carbon which are found by the X-ray emission spectroscopy to consist mainly of the skeleton tubelene-like forms of carbon (see later), have the characteristic elongated appearance of their cross sections (see Fig. 1). All inclusions are practically insoluble in benzene. This proves the absence of ball shaped fullerenes like C_{60} [1] in them.

Both the standard CK α X-ray emission spectra



Fig. 2. Smoothed standard CK α spectra of: (----) fullerenes (powder); (---) tubelenes (powder); graphite single crystal, (----) amorphous pyrocarbon. (For details (....) see text.)

of graphite and pyrocarbon and those of tubelene and fullerene type carbon are shown in Fig. 2. The differences between these spectra are clearly seen. The spectra of graphite and pyrocarbon are sharper and more symmetric at their peaks than those of tubelenes and fullerenes but at their base they have (especially in the case of graphite) pronounced tails in the low energy region, which should be connected with the high semimetallic conductivity of graphite (see Ref. [22]). The spectra of fullerenes and tubelenes being close to each other are asymmetric near the peaks, are convex on the high energy side and concave on the low energy side, their maxima are displaced ($\sim 1 \text{ eV}$) towards higher energies with respect to the spectra of graphite and pyrocarbon. The spectra of tubelenes are situated between the spectra of graphite and fullerenes. As for our smoothed spectra of fullerenes and graphite, they are similar to the general forms of the corresponding spectra registered in Ref. [18] at low radiation doses.

The comparative analysis of the CK α spectral forms for various parts of the grown alloy samples shows that a form of carbon with spectra quite close to those of tubelenes is reproducibly detected only in the elongated carbon inclusions in the Fe–Ni–C alloys represented in Fig. 1. The spectra of such inclusions are very close to those of tubelene powders and nanotube films, similar to the spectra of

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I, arbitrary units
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Fig. 3. Smoothed CK α spectrum of elongated carbon inclusions $(\cdots \cdots)$ compared to standard CK α spectra: (---) fullerenes (powder); (---) tubelenes (powder).

fullerenes and different from those of graphite, pyrocarbon (see Figs. 2, 3), Fe-C steels (Fig. 4) and polymerized hydrocarbons. This result is confirmed by numerous spectra of inclusions in five samples of alloys prepared according to the close technological processes described above.

Thus we can claim that we have obtained the carbon form inside the elongated inclusions in Fe-



Fig. 4. Smoothed CK α spectra of different steel samples without Ni, characterized by different densities of small ($\leq 1 \ \mu$ m) oval inclusions of carbon. Besides CK α the third order of the Fe L $\beta_{3,4}$ line and the second order of the Cr L $\alpha_{1,2}$ line (at ~284 eV) are present in the spectra. (-----) U8, (---) U13, (...) Cr doped Cr12V1.

Ni-C alloys that is characterized by the nearest atomic order (reflected in CK α) close to the order in tubelenes. In this respect we speak of the tubelene-like form of carbon.

As for the uniform alloy regions without inclusions revealed by SEM, optical microscope and microanalyser, their CK α lines resembled not the lines of tubelenes, but that of graphite with some hydrocarbon contamination.

3. Conclusions

The results of the present work show that the tubelene-like form of carbon characterized by the nearest atomic order close to the order in tubelenes can be produced not only in vacuum or in the low pressure atmosphere of inert gases but also inside inclusions of a metal system such as Fe–Ni–C alloy prepared in a specific way.

This has been realized in a system with components that give the monovariant system with the eutectic transformation. One can imagine other combinations of components in such systems, that might possess the ability to produce inside them the inclusions of similar carbon forms. However, it can turn out that, as happens with Fe–Ni particles on free surfaces [23], the specific catalytic action of the combination of Fe and Ni atoms on pore surface convexities is of vital importance for the formation of multilayered tubelene-like carbon structures in pores at elevated temperatures.

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