

# STRUCTURE, CHEMICAL AND RADIATION RESISTANCE OF METAL CARBON NANOCOMPOSITES - PYROLYZED DERIVATIVES OF BIS-PHTHALOCYANINES OF RARE-EARTH ELEMENTS AND ACTINIDES

V.Yu. Bairamukov<sup>1</sup>, M.Yu. Presniakov<sup>2</sup>, V.T. Lebedev<sup>1</sup>, V.K. Kapustin<sup>1</sup>, V.I. Tikhonov<sup>1</sup>

<sup>1</sup>Petersburg Nuclear Physics Institute named by B.P. Konstantinov of National Research Centre «Kurchatov Institute»

<sup>2</sup>National Research Centre «Kurchatov Institute»

E-mail: [ybayramukov@gmail.com](mailto:ybayramukov@gmail.com)

## Abstract

Multi-level carbon structures, matrices encapsulating atoms of rare-earth elements and actinides as a result of temperature transformations in bis-phthalocyanines during pyrolysis in an inert atmosphere, were studied by atomic force microscopy, transmission electron microscopy, X-ray diffraction and small-angle neutron scattering. Varying annealing temperature (800-1600°C) lead to transform the crystalline phase of the metal bis-phthalocyanine to the amorphous phase of pyrolyzed derivatives to form a branched network of carbon nanoclusters with an incorporated atom.

Tests for thermal, radiation resistance and leaching at different pH values showed that the incorporated radionuclide is held by in such type of matrix that can be used for long-term storage of radioactive waste and their transmutation.

## Introduction

To solve the problems of the processing and disposal of radioactive waste, chemically and thermally stable matrices resistant to ionizing radiation capable of reliably binding (encapsulating) long-lived isotopes, including minor actinides, should be created. At present matrices on the basis of borosilicate and phosphate glasses and materials of the SYNROC type are used on an industrial scale for the immobilization of highly active waste. Mineral-like composites are also being developed. Carbon-based matrices are not inferior to traditional materials as concerns their functional properties. Carbon is chemically stable, capable of withstanding high temperatures and both of its isotopes (<sup>12</sup>C and <sup>13</sup>C) have a low neutron capture cross section (3.4 and 1.3 mbarn, respectively).

The method of manufacturing matrices for the storage and transmutation of radioactive waste based on the pyrolysis of carbon structures, e.g., bis-phthalocyanines developed at the Petersburg Nuclear Physics Institute, National Research Centre Kurchatov Institute, has shown promising positive results in a series of tests on the chemical, thermal and radiation stability of pyrolysate matrices [1]. The precursors, i.e., phthalocyanines, selected for the preparation of matrices are synthetic structural analogs of porphyrins. It is important that these compounds form mono- and dicomplexes with all transition, rare-earth elements and actinides, the radioactive isotopes of which represent the greatest problem in the processing of radioactive waste.

As concerns their structure, monophthalocyanines are planar molecules  $[\text{C}_{32}\text{H}_{16}\text{N}_8]\text{-Me}$ , while di-complexes possess a sandwich structure, i.e., two planar molecules connected by a metal atom  $[\text{C}_{32}\text{H}_{16}\text{N}_8]\text{-Me-}[\text{C}_{32}\text{H}_{16}\text{N}_8]$ . Upon the pyrolysis of bis-phthalocyanines ( $\text{Pc}_2\text{Me}$ ) in an argon atmosphere ( $800^\circ\text{C}$ ) the almost complete removal of nitrogen and hydrogen takes place. Due to free bonds in the  $\text{Pc}_2\text{Me}$  molecule conditions arise for binding the upper and lower planes through the outermost carbon atoms. In this manner cells are formed, i.e., a sort of “mousetrap for atoms”. The size of the “windows” in them is such that only atoms having a Van-der-Waals radius of 0.13-0.14 nm can exit them. In the course of pyrolysis, monomolecular carbon cells are connected with each other creating an ultraporous carbon matrix  $\text{MeC}_x$  ( $x = 30\text{-}40$ ) with a set of intramolecular and intermolecular voids and metal atoms enclosed in them.

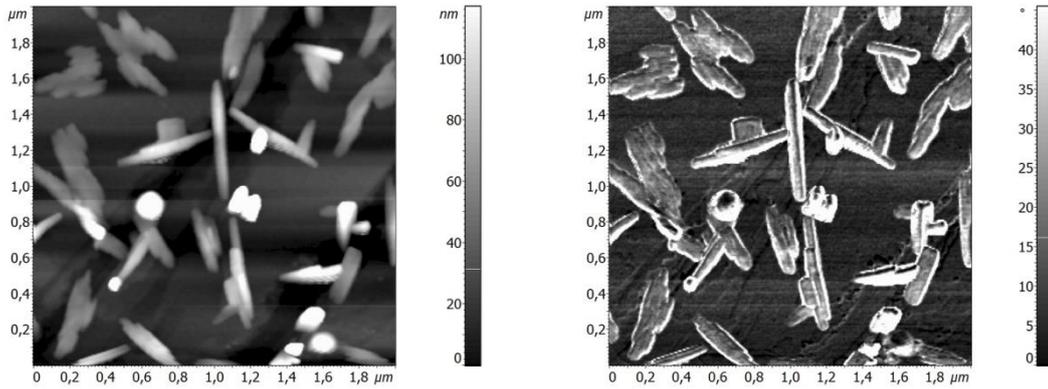
Determination of the structure of bis-phthalocyanines is especially important in the fundamental aspect and for understanding how such a structure can create barriers for the retention of radionuclides which in the end determines their diffusion rate.

### **Structural transformations revealed by atomic-force microscopy**

It is known [13] that metal diphthalocyanines have a crystalline structure which is confirmed by experimental data. Figure 1 shows the AFM image of uranium bis-phthalocyanine crystals deposited onto a substrate at  $500^\circ\text{C}$ .

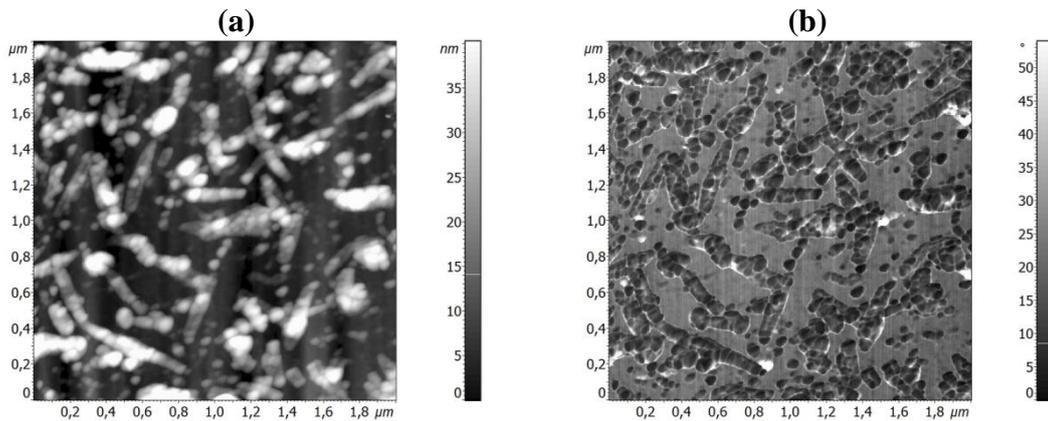
(a)

(b)



**Fig. 1.** AFM image of the  $Pc_2U$  crystal deposited at  $500^\circ C$ : (a) height; (b) phase contrast. Scan field of  $2 \times 2 \mu m$ .

The noticeable destruction of  $Pc_2U$  with the formation of the amorphous phase begins at temperatures on the order of  $800^\circ C$ . The destruction manifests itself in the AFM images as the transition of the crystalline phase into the amorphous one (Fig. 2a). The boundaries of the crystals are still distinguishable; however, different types

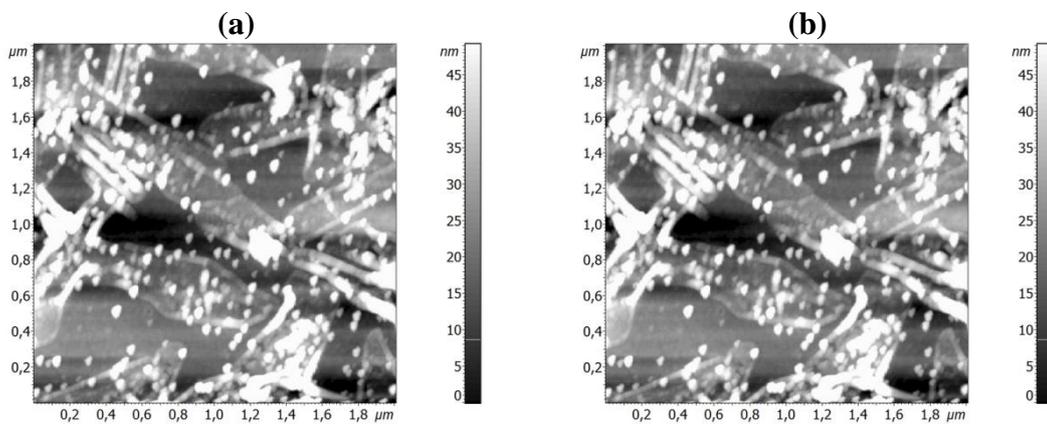


**Fig. 2.** AFM image of the  $UC_x$  sample pyrolysed at  $800^\circ C$ : (a) height; (b) phase contrast. Scan field of  $2 \times 2 \mu m$ .

of spherical particles are formed. The particle sizes are inhomogeneous and vary within 10-40 nm in diameter and 10-20 nm in height. It is seen in the image with phase contrast (Fig. 2b) that crystals do not exist and they have turned into tightly fitting aggregates of spherical particles. Such contrast is achieved by the fact that the probe tip in the process of vibrations touches the sample surface experiencing not only repulsive but also adhesive, capillary and a number of other forces. As a result of interaction with the surface of the sample, a shift in the frequency and in the phase of the vibrations occurs. If the sample is not homogeneous in its properties, the phase

shift is also inhomogeneous. The distribution of the phase shift along the surface will reflect the distribution of characteristics of the sample material.

Figure 3 shows the further destruction of  $UC_x$  at a temperature of  $880^\circ\text{C}$ . There is almost no crystalline phase, the scan field is filled with individual spherical particles of approximately the same size (diameter of 40-50 nm and height of 15-20 nm). In the phase pattern, these particles are clearly distinguishable against the background of the substrate. There are also large aggregates of particles (diameter of  $\sim 150$  nm and height of 50 nm), although this trend is not strongly pronounced for a single layer.

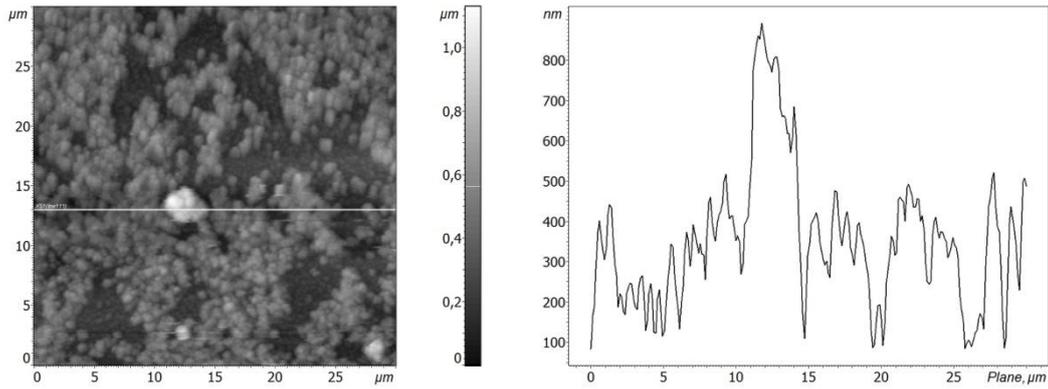


**Fig. 3.** AFM image of the  $UC_x$  sample pyrolysed at  $880^\circ\text{C}$ : (a) height; (b) phase contrast. Scan field of  $2 \times 2 \mu\text{m}$ .

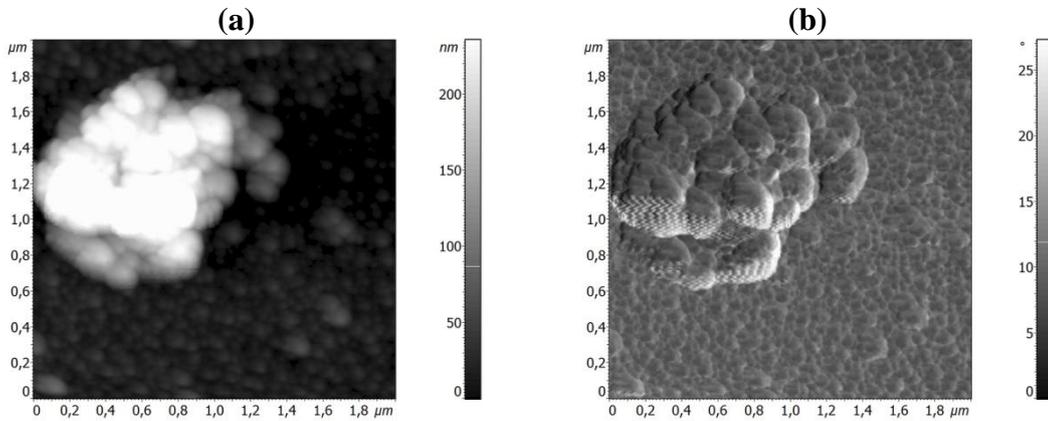
A highly porous structure is formed upon the deposition and subsequent pyrolysis of the bulk deposited layer of diphthalocyanine on the substrate. Figure 4a shows the large-scale ( $30 \times 30 \mu\text{m}$ ) AFM image of  $UC_x$  pyrolysed at  $1300^\circ\text{C}$ . Several layers of large aggregates  $\sim 50$ - $200$  nm in size filling the scan field 100% were formed, and larger particles with a scale of  $\sim 1000$  nm consisting of 200 nm conglomerates were formed (Fig. 5).

(a)

(b)



**Fig. 4.** AFM image of the UC<sub>x</sub> sample pyrolysed at 1300°C: (a) height; (b) cross section. Scan field of 30 × 30 μm.



**Fig. 5.** AFM image of the UC<sub>x</sub> sample pyrolysed at 1300°C: (a) height; (b) phase contrast. Scan field of 2 × 2 μm.

In fact, the cross-sectional construction for large scale images (Fig. 4b) reveals distances between carbon aggregates of 100 to 1500 nm. The superposition of layers of such particles onto each other inevitably creates pores of different sizes between them – closed and open, constituting a complex network of diffusion channels. Finally, additional isolating barriers are formed for the incorporated radionuclide preventing its release from the matrix (1).

### Small-angle neutron scattering

Detailed analysis of the neutron scattering on pyrolyzate samples has shown that, irrespective of the kind of the base element (metal), the behavior of the cross sections follows the general scattering law:

$$\sigma(q) = \sigma_r/[1 + (qr_c)^2]^2 + \sigma_R/[1 + (qR_c)^2]^{D/2}$$

Here, the first term describes fine globular particles (agglomerates) whose correlation radius  $r_C$  is only several times larger than the size of the bis-phthalocyanine molecule (cells in the pyrolyzate matrix), and the second term describes coarse aggregates of size  $R_C \gg r_C$ . The cross sections  $\sigma_r$  and  $\sigma_R$  characterize the scattering power of these objects at  $q \rightarrow 0$ , and the exponent  $D$  characterizes the fractal dimension of the aggregates.

The observed globular agglomerates (correlation radius  $r_C$ ) result from combination of the cells in the course of pyrolysis within the limits of several first coordination spheres. The size of such formations strongly depends on the base element, as illustrated by the example of a series of samples with three elements (Y, Sm, U) strongly differing in the atomic number and weight.

For the lightest element (Y), the correlation radius is  $r_C = 2.45 \pm 0.02$  nm; for the heavier Sm atom, a larger value was obtained,  $r_C = 3.74 \pm 0.07$  nm; and for the heaviest atom in this series, U, the correlation radius is almost two times larger,  $r_C = 6.65 \pm 0.16$  nm. Notably, an increase in the agglomeration scale is accompanied by an increase in the cross sections of the system of such objects:  $\sigma_r = 93 \pm 2, 119 \pm 11, 957 \pm 50$  cm<sup>-1</sup> for the samples with Y, Sm, and U, respectively. The scattering cross section  $\sigma_r$  of the revealed particles increases by an order of magnitude, approximately proportionally to the cube of the radius. The dependence  $\sigma_r \sim r_{cor}^3$  suggests the globular character of the revealed agglomerates. As shown by analysis of the scattering data, small agglomerates in yttrium and samarium pyrolyzates are organized in coarse aggregates of size  $R_C \geq 100$  nm. In the case of yttrium, these are virtually continuous formations, as indicated by the parameter  $D_Y = 3.00 \pm 0.02$ . In the Sm containing pyrolyzates, aggregates in the form of strongly branched bulky fractals with the dimension  $D_{Sm} = 2.64 \pm 0.06$  are formed under the same conditions. The sample with uranium demonstrates a different type of ordering. The agglomerates in this sample form relatively compact globular aggregates with the correlation radius  $R_C = 56 \pm 4$  nm, which is larger by an order of magnitude than the size of the separate agglomerate. The ratio of the cross sections gives the number of agglomerates in the aggregate  $(\sigma_R/\sigma_r) \approx 380$ , in reasonable agreement with the estimation based on the particle size,  $\alpha(R_C/r_C)^3 \approx 430$  (coefficient  $\alpha = 0.74$  for close packing of spheres). As shown by the value of the parameter  $D = 3.26 \pm 0.04$ , the aggregate boundaries are not smooth and are very defective surfaces with the fractal dimension  $D_S = 6 - D \approx 2.7$ . In

interpretation of the neutron scattering data, we considered the forms of organization of carbon particles in the matrix, which, as already noted, is a very loose material with the density two times lower than that of graphite. This means that the void volume in such material is comparable with the total volume of the carbon and metal atoms. The constituents of the carbon matrix (agglomerates, aggregates) include this void volume, i.e., the ultraporous structure of the pyrolyzates with the same characteristic size ( $r_C$ ,  $R_C$ ) of the void volume fragments is realized (2).

## Conclusions

At temperature pyrolysis above 1000°C the aggregation of clusters occurs in conglomerates of a size of ~150-200 nm and ~1000 nm. Thus, the multi-level and multiply-connected ultra-porous carbon matrix of pyrolyzate is consistently formed for different metal-complexing agents (Y (3), U).

Analysis of the neutron scattering data in multiply bonded carbon matrices incorporating metal atoms allowed determination of the main structural elements and their ratio in the size range from units to tens of nanometers. In the structure of pyrolyzed bis-phthalocyanines, there are several (at least two) isolation barriers preventing the release of the incorporated atoms from the host material, which accounts for efficient retention of the radionuclides and their decay products in voids of the carbon framework of the host material.

## References

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