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HIGH-TEMPERATURE TESTS OF FINE-GRAINED HIGH-DENSE GRAPHITE FOR NEUTRON TARGET CONVERTER

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High-temperature tests of fine-grained high-dense graphite for neutron target converter

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Abstract

Tests and investigations of samples of fine-grained high-dense graphite of firm HENSHKE have been performed to predict lifetime at high temperatures (~2000°C). Tests are heating of samples by the electric current up to sample destruction temperature. Investigations include electron microscopic, X-ray, electrophysical and other measurements of samples. Rentgenography has been executed for initial samples, results was compared with X-ray photography for graphite of a domestic production MPG-class. The raster electronic microscopy was executed both for initial and heated samples. The forecast of lifetime was based on application of classical Zhurkov formula. It is shown, graphite of CGD brand has structural characteristics relatives to of MPG graphite, however its durability as well as lifetime at high temperatures are appreciably different.

INTRODUCTION

The circuit of an intense source of high-energy neutrons (with energy up to several MeV) on a basis of a proton accelerator in Budker's INP of the Siberian Branch of the Russian Academy of Science is offered. The basic unit of this source should be the graphite converter [1,2] cooled by thermal irradiation. Feature of the design are both the high operation temperature and the gradient of temperature of the converter up to 1800 – 2200°C and 100° C/mm, respectively. The most perspective material for such converter from the point of view of constructional durability are fine-disperse carbon composites MPG-6/7, however in the present time manufacture of such composites is cancelled. For replacement graphite of MPG trade was examined CGD-graphite of firm HENSHKE, Germany.

For check of efficiency of carbon composites in operationing modes a number of test with fine-dispersed composite of CGD was carried out. Thermal tests were provided by heating of specially prepared samples of graphites by a alternating electric current. As a parameter of degradation a material in a time of heating the electrophysical and structural changes of composites were investigated.

SAMPLES

The graphite of firm HENSCHKE with an optimum ratio price /quality was chosen for tests. The graphite of the CGD trade is delivered by blocks by the size 110×220×220 at the price about 248 euro for the block of weight 9,6 kg. The graphite of the mark CGD has the following specification.

Table 1

Parameters	Unity	CGD	MPG-7
Density	g/cm^3	1.80 –1.84	1.72 – 1.87
Specific resistance	μΩm	9.4 – 10.2	9,5 – 12
Durability on a bend	MPa	35	35 – 52
Durability on compression	MPa	55	65 – 119
Porosity	%	15	
The contents of ashes	%	< 0.01	0.1 – 0.25
The size of a grain	Mkm	<80	30 – 150
The module modulus of elasticity	GPa		10 – 12
Heat conductivity	W/m*K		110 – 120

The samples of fine-dispersed industrial dense graphite 60x5x1mm in size of the grade MPG–7 were heated by alternating current in a vacuum of 10^{-2} Torr; the temperature of the samples was measured by a pyrometer IS12 (Impac Electronics). The temperature and the heating time by now are thought to be the main parameters affecting the converter resource. The tests simulating the heating under the action of a neutron beam were made by transmitting alternating current through the sample 60×5×1 mm in size to investigate the regularities of fracture of a graphite target. The necessity of such testing was confirmed by the fact that the noticeable increase in conductivity of the sample takes place as under the long action (more than 30 hours) by a high-energy electron beam, and on heating of the sample. The higher the temperature or heating time of the sample, the more essential this increase [3].

EXPERIMENTAL PART

Electron microscopy measurements of samples were carried out using a JEM-100C transmission electron microscope (TEM) at an accelerating voltage of 100 keV and a resolution of 0.5 nm. Samples for TEM were prepared using a standard procedure. A carbon material was ground in an agate mortar and dispersed by ultrasound in ethanol solution; the obtained suspension was applied onto a copper grid coated with a carbon film with micrometer holes.

X-ray diffraction studies were conducted on an URD-6 device using monochromatized Cu Kα radiation. X-ray diffraction patterns were measured in a step-bystep mode (the step is 0.05°, the acquisition time is 10 s) in the angular range from 10° to 100°.

The temperature dependences of the conductivity of the samples were measured using the four-probe method. The sample to be measured was a rod 0.5x5x10 mm in size, cut from the source carbon material. Electrical contacts were applied using G3692 Acheson Silver DAG 1415 mit Pinsel silver paste with a resistance of $\cong 1\Omega$. The measurements were carried out in a helium atmosphere and in air in a temperature range of 4.2 – 300 K.

Microphotos of a surface of samples in a mode of reflected electrons are executed on raster electronic scanning microscope LEO 1430 VP with energo-dispersing spectrometer EDX OHFORD.

RESULTS AND DISCUSSION

XRD and electron microscopy results. The XRD pattern for CGD of the samples are shown in Fig. 1,2. X-Ray diagram of CGD graphite is typical for 2H graphite polytype as so for MPG-6 graphite. All reflexes have a place, but broadening degree between them is very big. The narrow ones, *00l* and *hk0* type, can be interpreted as good evidence for the large size of coherently scattering

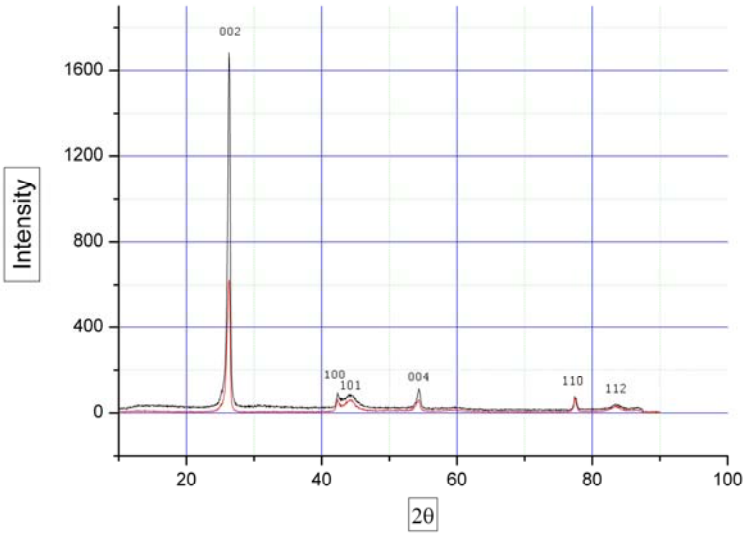


Fig. 1. X-ray diffraction (XRD) measurements of the samples fine-dispersed CGD graphite was carry out from not destroyed plates (black line), and from crumbled sample (red line). Height of peak [*002*] appreciably more in the first case, as so for a plate takes a place texture in direction – [*00l*].

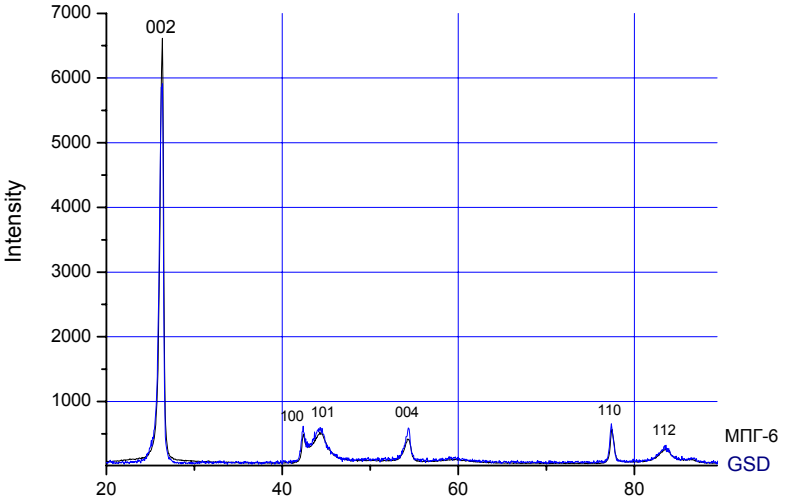


Fig. 2. X-ray diagram of the samples fine-dispersed dense graphite CGD (dark blue line) and MPG (black line) type.

domains (CSD). At domain bounds the periodic structure retains as in normal direction to graphite layers so far as in basal plane direction. At the same time, the essential broadening of peaks of *hkl* type shows that a lot of stacking faults (distortions of the stacking sequence) take a place. It is possible as same as for MPG-samples to estimate interplane distances and size of coherent dispersion domain (CDD).

Diffraction picture of both samples practically closely agree (Fig. 2). But more exacter accounts have shown, that have a place as similarity, so some distinction in these samples (Tab. 2).

Table 2

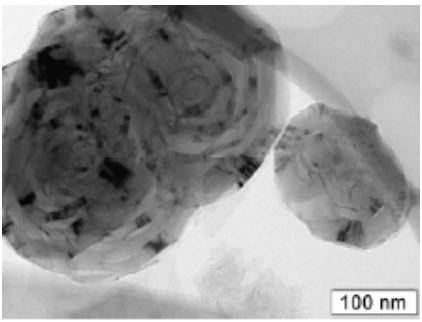
Sample	Lattice parameters		SCD, Å		microdistortion size ε *00l*
	a, Å	*c*, Å	*00l*	*hk0*	
МПГ-6	2.464(1)	6.766(3)>	1500	250	0.0065
CGD	2.465(1)	6.764(4)	300	250	0.0030

The parameters of a lattice of both samples coincide within the limits of estimated errors. The sizes CDD in a plane of a graphene layer also are identical. Some distinctions are available in microstructure of samples in a direction [*001*].

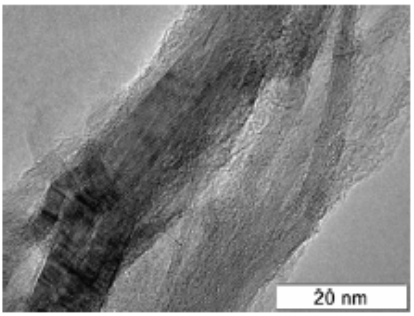
The CSD in a sample of CGD are essentially less, though the size of microdistortions (variations of interlayer's distances) is less too. It testified to presence in these samples more thin, but better ordered packages of graphene grids in comparison with MPG-6. It is only smaller size of variations interlayer distances have a place under the best ordering for CGD graphite. But the concentration of graphene layers defects of imposing by anisotropy and broadening of peaks, is identical in both samples.

The accounts for [*001*] CSD is well correlate with high resolution electronic microscopy (Fig. 3) that height of the ordered packages can be appreciable less than 30 nm.

In Table 2 are listen the lattice parameters and microstructural characteristics of the samples. The uncertainty in lattice parameters is indicated in parentheses, and that in CSD size is about 10%. The magnitude of lattice strain is known to characterize variations in interplanar spacings (interlayer spacing d_{002} in this study).



a)



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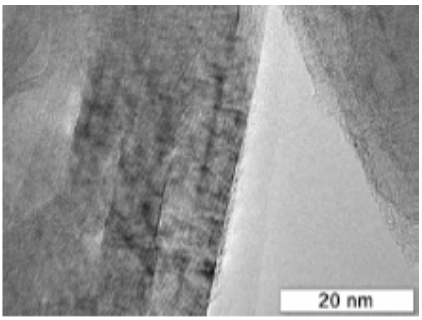

c)

Fig. 3. High resolution transmission electronic microscope for samples of graphite CGD type. Interstitial impurity defects (a), forcipate defects (b) and twinning defects (c) are good visible.

High resolution transmission electronic microscope

Electronic-microscopic shootings of carbon samples were executed by transmission electronic microscope JEM-1020 (Japan) at accelerating voltage 200 кV and the subnanometer resolution in 0.2 нм. The samples for shooting were going from spirit suspensions which drop on the carbon substrates. This substrates was located on fixed copper grids.

The defects in graphite can be divided in agree [4] into two types: the defects concerning derangements between layers, and defects of grid's connection. Defaults of packing of the layers are the first, described by derangements packing parallel graphene layers. The second kind of defaults of structure in graphite are defects in connections of a carbon lattice. Vacancies concern to them and their groups, the atoms of impurity introduced in hexagonal layer, isomeric connections defects, when the part of atoms has hybridization sp^3, and regional defects too.

The basic kinds of defects of the second sort:

1. Regional defects when connection C-C can not be formed, for example, if one macromolecule is not in a plane of the nearest neighbours.

2. "Hole" or "forcipate" defects, when at destruction of connections emptiness or breaks in hexagonal grid of carbon atoms are formed. At forcipate defects there can be screw dislocation or other curvatures hexagonal grids.

3. Twinning defects, when on a twinning line appears the alternating rings consisting of four and eight atoms. It is necessary to mean, that there are two types twinning: such as the accretion named basic, which axis it is parallel to an axis "c" a graphite lattice. Thus crystal formations from two or several identical on structure, but not identical under the form and size of the parts naturally located rather each other are observed. Law is, that the lattice of one part is combined with another turn in twinning axes.

The second kind to twinning - outbasic, is caused by reflection in twinning plane or overlapping of turn and reflection. Outbasic twinning assumes presence of a symmetry plane (the plane of mirror reflection named as a twinning plane). It is shown as a bend of system of graphene planes on the certain corner.

For hexagonal structure of graphite with a sequence of layers packing ABAB exist only two corners (48°18' and 35°12') true twinning. In other cases laws of symmetry are broken, i.e. the sequence of layers at the left and to the right of border of the unit is not kept even at symmetric border of an inclination. From here, the inclined borders of crystals symmetric and especially asymmetrical should be accompanied by numerous breaks of connections and enough the advanced system of regional dislocation.

Besides there are chemical defects (inclusions of alien atoms in a carbon grid) and the defects connected to displacement of atoms from the normal positions in a lattice. That such particles of an impurity exist in the given type of graphite, show results of measurements by method AMS which fixes presence of impurity potassium, and also sulfur and oxygen (Fig. 4). Follows to note, the cooper is not a characteristic impurity for given graphite, the peak cooper in this case is connected to the holder of a sample.

Well-ordered graphite according to reference is characterized fusion enthalpy ΔH equal ~104 кJ /mol, combustions enthalpy ΔH equal ~ 395 кJ / mol. The last approximately corresponds to energy σ-connection for graphite, that according to [4,5] equal 418.7 – 460.6 кJ /mol. At the same time initial energy of activation for destruction which can be received from the data on destruction time of graphite MPG-6 by work [3] have value about 890 кJ /mol. It can corresponds, for example, sublimation enthalpy ΔH ~ 716.7 кJ /mol or so-called energy of activation of self-diffusion of carbon in graphite. This energy can be equal ~ 840 кJ /mol in good agree to the data [5].

According to [4] high-temperature area (2500 – 3000°C) creep of the polycrystalline graphite, explained the majority of authors self-diffusion of carbon in graphite, depends on the phenomenon of sublimation of graphite. As energy of activation of process of creep for these temperatures within the limits of 720 – 1230 кJ/mol, it is commensurable with heat of sublimation of graphite ~715 кJ/mol. Obviously, sublimation is a source of vacancies in crystallites, i.e. an

original cause vacancy diffusions, and consequently, the diffusion mechanism of creep at high temperatures.

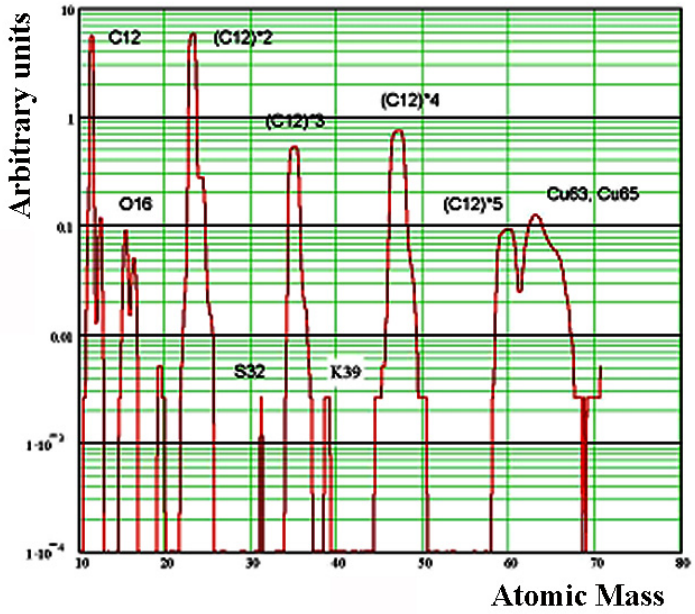

Fig. 4. Measurements of graphite CGD by a method AMS. The impurity of oxygen, sulfur, and also potassium and copper are well visible.

It is necessary to note also, that a number of authors connects the phenomenon of creep in graphite to movement of regional and screw dispositions. In particular, in the field of temperatures up to 2500°C the explanation of creep of the polycrystalline graphite, made Mrozovsky and Green, is quite acceptable. They explain the mechanism of creep break of peripheral C-C connections and sliding crystallites from each other.

The attraction of attention to afterflow is, on our sight quite proved, as so can help to understand destruction mechanism of graphite at high operate temperatures of a graphite target. Nevertheless, high initial energy of destruction ~890 kJ/mol, received from the previous work [3] requires additional check. At the same time this energy well enough corresponds to energy sublimation, equal approximately ~713 kJ/mol.

On our representations, initial energy of activation of destruction in Zhurkov's formula really should be correspond to energy of sublimation, as a minimum. So as substitution in this formula of energy of the activation equal enthalpy of fusion ~120 kJ /mol [5,6] would result to that lifetime of MPG-graphite would not exceed $\sim 10^{-9}$ cek, that does not correspond to the validity.

Electrophysical measurements for graphite CGD, in particular, measurements of temperature dependence of conductivity, magnetoresistance and effect of the Hall have shown full concurrence to results same measurements for graphite MPG-6 [3]. It is necessary to note absence small parcel the negative magnetoresistance, characteristic for graphite MPG-6, connected with defects of packing in graphite, and also predominantly hole character of conductivity.

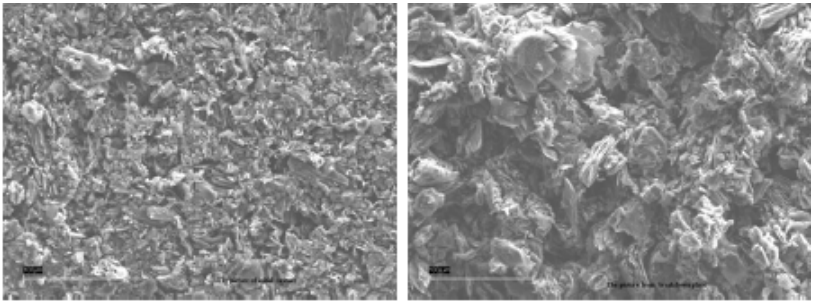

Fig. 5. Electronic raster microphotos of a surface initial sample CGD (left) and warmed an alternating current up to destruction (right) are shown. Pictures of a surface are executed on raster electroncic scanning microscope LEO 1430 VP with energodispersing spectrometer EDX OHFORD.

Electronic raster microphotos of a surface initial sample CGD (left) and warmed an alternating current up to destruction (right) are shown on Fig. 5. It is visible, that a sample of graphite composite CGD, warmed up to destructions temperatures, has much more advanced surface, with big quantity porous and apertures. It is shown on Fig. 6, that the beginning of process of destructions is characterized by fast temperature growth of a sample, that also testifies for the benefit of change a composite mesostructure before destruction. As it was shown earlier [3] for carbon composites of MPG class that do not occur on CSD level of appreciable changes structures of a composite.

Then, following [7, 8], the predictable lifetime of the neutron target converter based on fine-grained dense graphite can be determined in the first approximation by the simple Zhurkov's formula based on the representations of the thermal-fluctuation nature of fracture of solids:

$$\tau = \tau_0 \exp[(U_0 - \gamma\sigma)/kT] \,. \qquad (1)$$

Where k is the Boltzmann constant, τ_0 is the period of atomic thermal vibrations equal to $\sim 10^{-13}$ s, U_0 is the initial activation energy of the fracture process that is reduced by the applied stress σ; $\gamma = qVa$; Va is the activation volume in the elementary act of fracture, q is the coefficient of local overstresses. This coefficient reaches the values of 10 – 100 because of local defects, and the magnitude U_0 is close in many cases to the energy of sublimation.

By using the data of the temperature dependence of lifetime of the sample MPG–6 represented in [2] and constructed by us in the Arrhenius coordinates

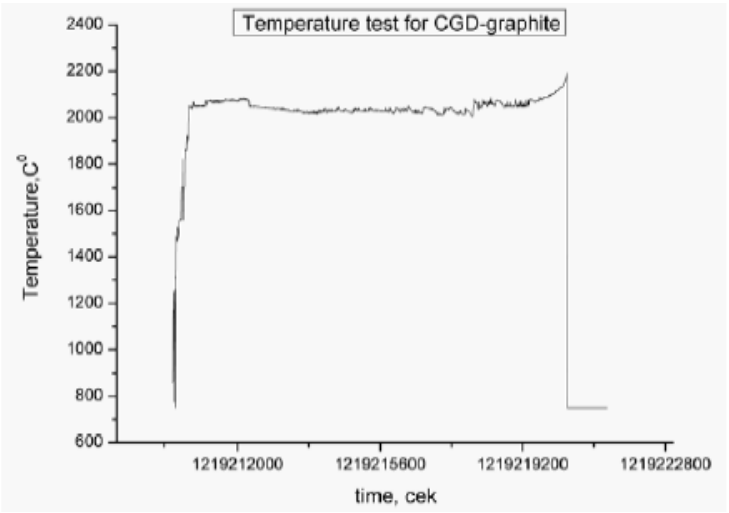

Fig. 6. Character of temperature change of a composite CGD sample in the testing time.

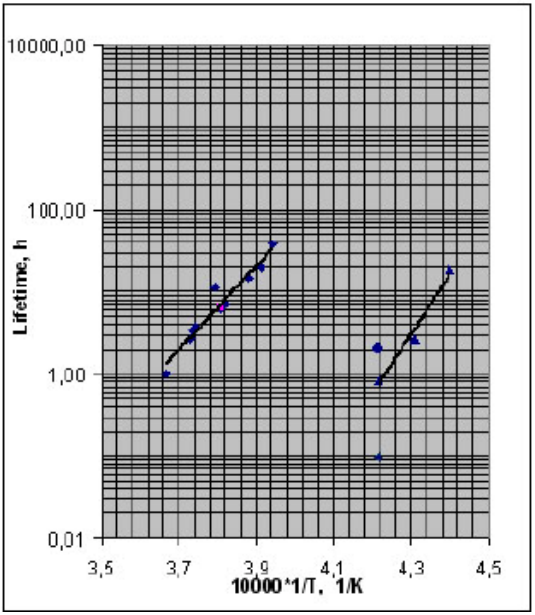

Fig. 7. Lifetime dependence vs return temperature for MPG samples (at the left) and CGD samples (on the right).

(Fig. 7), the predictable lifetime of a neutron target converter was determined and amounted to 10^4 hours at the operating temperature of 2200°C. Same predicted

lifetime for the converter on the basis of graphite CGD will demand decrease of the operating temperatures down to 1800°C.

CONCLUSIONS

According to the data of electrophysical and X-ray measurements [3], the changes of carbon mesostructure composites of MPG–7 is presumably related to the changes in a intercrystalline phase of the fine-dispersed dense graphite samples. It allows us to use the simple Zhurkov's formula [7] to calculate the lifetime of a neutron target converter. The operating temperature for the neutron target converter of 1800°C chosen in [2] as reasonable from the converter lifetime of 10^4 hours is quite valid.

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