UDC 621.785.377

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Structural analysis of inclusions detected by X-ray inspection of preforms and parts from fine-grained graphite MPG-7

By X-ray diffraction analysis and Raman spectroscopy, we studied samples of fine-grained graphite MPG-7 with detected chemical and structural defects. We determined the effect of structural and chemical defects on the micro- and macrostructure of graphite. Estimation of graphite crystallinity depending on the type of defects detected was carried out.

Keywords: MPG-7 graphite grade, X-ray analysis, Raman spectroscopy, structure, structural inhomogeneities

Introduction

Graphite of the MPG-7 grade belongs to the class of artificial graphite materials. Due to its resistance under conditions of thermal shock and high temperature gradient, it preserves its performance capacity at temperatures up to 3900 K in the medium of gas flow of erosion-aggressive products of composite propellant combustion [1], as well as gives up excessive heat due to radiation at the infrared and visible-spectrum wavelengths. For these reasons, the MPG-7 graphite is one of the most important construction materials in manufacture of the throat inserts for nozzle clusters of solid-propellant rocket motors (SPRM).

It is known that the mechanical and thermal-physical properties of artificial graphite materials are determined first and foremost by their structural characteristics. The MPG-7 grade graphite, which is used in the articles developed by Novator Design Bureau, is a fine-porous material produced by the method of powder sintering in the form of pressed blocks [2]. The process of graphitisation of semi-manufactured products (pressed-powder blocks) runs at a temperature above 2700 K, therefore graphite, as a rule, shall have good homogeneity and crystallinity. A perfection criterion for such structure can be graphitisation index g, which is determined as follows:

$$g = \frac{0,344 - d_{002}}{0,344 - 0,3354}, \quad (1)$$

where 0.344 nm – interlayer distance in turbostratic carbon [3];

d_{002} – interlayer distance (nm) in graphite;

0.3354 nm – interlayer distance in defect-free graphite monocrystal.

For artificial graphites of the MPG grade with high treatment temperature, the graphitisation index lies within 0.8…0.9 relative units [4, 5]. At the same time, graphite with more ordered structure has higher strength and performance capacity in high-temperature gas flow.

As was established earlier [6], certain regions revealed in an MPG-7 graphite matrix are characterised by high (up to 20 % wt.) content of impurity elements, as well as by macrostructural heterogeneity. Such regions are characterised by inhomogeneity revealed in X-ray images. One can presume that the cause of emergence of such macrostructure are defects in the packing of its layers and lattice bonds when a part of the carbon atoms has sp^3-hybridisation [7]. However, the present-day scientific literature fails to refer to such interrelations between the observed inhomogeneity of graphite macrostructure and its structural defects.

The objective of this paper is to determine the nature of macrostructural inhomogeneities during X-ray inspection of parts made of MPG-7 grade graphite and the effect of such inhomogeneities on the graphite structure and crystallinity.

Experimental part

Based on the study of MPG-7 grade graphite preforms and parts by the methods of electron microscopy and energy dispersive microanalysis, as well as X-ray analysis [5], the following samples were selected for carrying out structural investigations:

1) without determinable impurities and macrostructural inhomogeneities;

2) with chemical impurity elements;

3) with macrostructural inhomogeneities.

A detailed description of samples Nos. 2 and 3 and anomalies observed in them is given in paper [5].

The crystalline structure and phase composition of the samples were studied on diffractometer *Empyrean* (*PANalytical*) in monochromated Cu-Kα radiation (graphite monochromator). Method sensitivity – up to 1% vol. of impurity phase. Determination of the crystalline structure parameters was performed with the use of a software system for X-ray diffraction analysis [8, 9]. The study samples were taken from crushed graphite material. For determining crystallographic texture, a plate cut out from a graphite preform was used.

Raman spectra (RS) were taken at room temperature using a *RENISHAW-1000* spectrometer (λ = 532 nm, P = 7 mW). The samples used were plates cut out from graphite preforms as well.

Results

For all studied X-ray diffractogram samples (Fig. 1), a characteristic feature was the presence of 2H graphite polytype basic reflexes ($P6_3/mmc$). At that, only sample No. 1 (Fig. 1, a) is a single-phase one. Reflex (*) on the diffractogram of sample No. 2 (Fig. 1, b) does not belong to graphite. The results of energy dispersive microanalysis performed for this sample in paper [5] demonstrated the presence of impurity elements Al, Si, and Ti in the composition. The impurity phases can be represented by TiO_2 (orthorhombic) and/or Al_4C_4Si (hexagonal), for which reflex (*) is the most intensive line (100 % relative intensity).

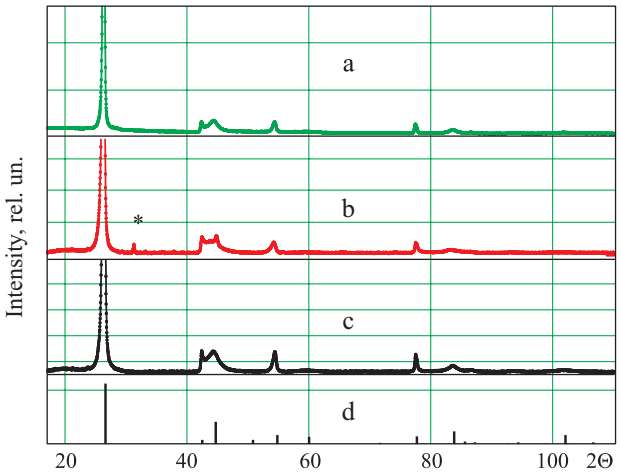

Fig. 1. X-ray diffractograms of samples: a – No. 1; b – No. 2; c – No. 3; d – crystalline phase identifier diagram; (*) – impurity phase reflex

The observed increase of the background level in the diffractogram small-angle region (17–23°) indicates the presence of an amorphous component in the sample along with the impurity phases. In sample No. 3 no impurity phases are observed; however, same as in sample No. 2, there is an amorphous component in it (Fig. 1, c). Broadening of graphite reflexes can be caused by defects in its structure. Characterised by the narrowest reflexes of lines 00l and *hk*0 is sample No. 1, which proves the presence of large-size coherent scattering regions (CSR) as compared with the other samples (see Fig. 1).

The table for graphite samples shows lattice parameters a and c, CSR size $<L>$, and graphitisation index g calculated by equation (1). Given for comparison are also the values of a, c, and g, taken from literature [4, 10] for the MPG-7 grade graphite. As seen from the table, sample No. 1, having the minimum value of lattice parameter c and the maximum graphitisation index g amongst

Lattice parameters a and c, CSR size <L> and graphitisation parameter g for considered samples of MPG-7 graphite

Sample	a, Å (±0.002)	c, Å (±0.002)	<L>, nm (±1)	g, rel. un.
No. 1 (a)	2.466	6.745	15	0.8
No. 2 (b)	2.459	6.775	10	0.6
No. 3 (c)	2.462	6.778	8	0.6
Graphite MPG-7 (data from [4, 10])	2.460	6.716–6.754	29	0.8–0.9

the samples considered, has a more perfect crystalline structure. The obtained parameter values for this sample well correlate with the data of [4, 10], whereas the values of parameter c in samples Nos. 2 and 3 are more characteristic for the turbostratic rather than for the ordered 3D structure of graphite.

Along with determination of lattice parameters, crystallographic texture in the considered samples was analysed. To that end, the diffraction spectra obtained on powders and from plate surface were compared. The intensities and shapes of spectrum lines showed absolute matching in both cases, which testifies to the absence in them of any preferential crystallographic orientation.

For estimation of defect structure and the amount of amorphous phase in the samples, further investigation into their structure was performed with the use of Raman spectroscopy, which enables to make a quantitative evaluation of graphite's crystalline structure perfection degree and get an insight into the nature and amount of structural defects. This method is sensitive to defects in the layers, presence of interstitial atoms, ordering in the packing. Besides, it helps to determine the nature of hybridisation in the layer fragments of graphite.

Fig. 2 shows RS of the graphite samples.

The RS of all samples include lines characteristic of polycrystalline graphite. The line at 1572 cm^{-1} corresponds to its ideal vibrational mode with symmetry E_{2g} (line G) [11]. The position and intensity of line G, by means of which it is possible to determine carbon graphitisation degree, correspond to carbon atoms oscillations in sp^2-hybridisation. The line at 1343 cm^{-1}

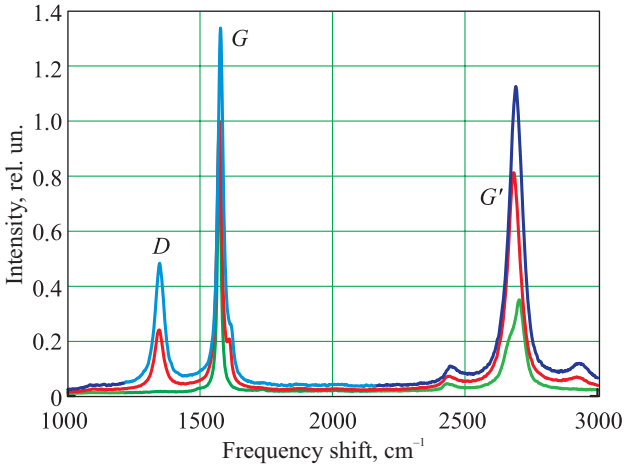

Fig. 2. RS of graphite samples:
— No. 1; — No. 2; — No. 3

is induced by disordered carbon atoms; it relates to lattice oscillations with symmetry A_{1g} (line D). This line is conditioned by C–C bonds with sp^3-type hybridisation. Line D represents a characteristic of carbon material defectiveness degree and is the cause of structural disorder. It is absent in single-crystal graphite, and an increase of its intensity is conventionally regarded as the result of an increase in the amount of disordered carbon in a sample. The line at 2693 cm^{-1} (line G') is an overtone of line D.

All three samples are characterised by well-resolved and intensive line G (see Fig. 2), which means presence of a large number of carbon atoms in sp^2-hybridisation in all the samples. In the spectrum for sample No. 1 line D is not observed. This goes to show that the sample is characterised by good crystallinity. In samples Nos. 2 and 3 line D manifests itself. Its considerable intensity, as compared with line G, indicates the presence of defect regions in the samples' structure.

The known interpretation of the intensity ratio of lines *D* and *G* allows us to estimate at the semi-quantitative level the dimensions of the ordered regions of an amorphocrystalline substance and distinguish graphite, by its RS, from other carbon forms [12]. A high value of the ratios of lines *D*/*G* intensity indicates considerable defectiveness of the samples. The relationships (I_D/I_G) are linked by semi-quantitative expression (2) to the size of graphene crystallites (L_a) [13] present in the base plane:

$$L_a = \left(2{,}4 \cdot 10^{-10}\right) \lambda^4_{\text{лазер}} (I_D/I_G)^{-1}. \qquad (2)$$

Here, λ – excitation laser wavelength in nm (in the considered case – 532 nm).

Sample No. 1, for which line *D* is absent (see Fig. 2), should be categorised as crystalline graphite, whereas samples Nos. 2 and 3 are amorphous graphites, size L_a for which is equal to 5 and 7 nm, respectively.

As a result of structural analysis of macrostructural and chemical inhomogeneities of the scrutinised articles [5], their belonging to objects with poor crystallinity was established [4, 14]. Samples with such defects can be categorised as amorphous graphite because of the minimum size of the ordered regions and the maximum content of amorphous phase with sp^3-type hybridisation.

In that case impurity elements form individual phases, characterised by their symmetry type and lattice parameters, and increase total defectiveness. It can be stated that the observed impurity phases in graphite are conditioned by the quality of initial stock material [15], when its low homogeneity and crystallinity is a consequence of insufficient thermal treatment of preforms. Such structural defects may become the cause of unwanted variability in physical and mechanical properties of the end product [2]. Subsequently, graphite preforms with structural peculiarities (chemical and macrostructural inhomogeneities) detected by the X-ray inspection method, as applied in the R&D activities of "Novator" Design Bureau, require additional evaluation and screening in order to improve their performance capacity as throat inserts of SPRM.

Conclusions

1. Macrostructural inhomogeneities observed during X-ray inspection of parts manufactured from graphite of the MPG-7 grade represent amorphous graphite with the size of ordered carbon regions of the order of 5–10 nm.

2. Impurity elements observed in graphite form their own phases characterised by their individual symmetry type and lattice parameters.

3. The studied graphite samples, with their inherent chemical and structural defects, are characterised by turbostratic rather than the ordered 3D structure, which is characteristic of the MPG-7 grade graphite.

4. Based on the obtained data, to carry out incoming inspection by the X-ray inspection method, quality references for preforms and parts of the throat inserts for nozzle clusters of SPRM were created.

The work was performed under agreement No. 125-2016-HTC, dated December 12, 2016, between "Novator" DB, JSC and the Institute of Solid State Chemistry, Ural Branch of the RAS.

The authors express their gratitude to V. S. Gaviko, leading researcher at the Institute of Metal Physics, Ural Branch of the RAS, for the assistance in carrying out X-ray diffraction analysis.

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Submitted on 05.03.2019

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Структурный анализ включений, выявляемых в процессе рентгеновского контроля заготовок и деталей из мелкозернистого графита марки МПГ-7

Методами рентгеноструктурного анализа, спектроскопии комбинационного рассеяния выполнено исследование образцов мелкозернистого графита марки МПГ-7 с выявленными химическими и структурными дефектами. Установлено влияние структурных и химических дефектов на микро- и макроструктуру графита. Проведена оценка его кристалличности в зависимости от типа обнаруженных дефектов.

Ключевые слова: графит марки МПГ-7, рентгеноструктурный анализ, спектроскопия комбинационного рассеяния, структура, структурные неоднородности.

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