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STUDY OF DISTRIBUTION OF TRANSPORT PORES IN STRUCTURE OF COMPACTED CARBON-FILLED PLASTICS

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Abstract. *The technological features of obtaining of composites on the basis of carbon are described. The transfer of carbon dioxide on length of pores in carbon-filled plastic at gasification is considered. Mechanism of distribution for transport pores in the structure of compacted carbon-filled plastics at its gasification in the medium of carbon dioxide is studied.*

Key words: *composites on base carbon, transport pores, structure, compacted carbon-filled plastic, gasification, carbon dioxide.*

Introduction

The obtaining of high-density carbon fiber reinforces plastic (CFRP) is provided by filling of porous structure of CFRP by a pyrocarbon deposited from a gas phase at decomposition of natural gas [1]. On the stage of making CFRP the total coating carbon fibers by liquid binding material is performed. After the binding material hardens and carbonization process completes, the layer of glasscarbon on the surface of carbon fiber is formed, and a pyrocarbon partly fills porous space of carbonized binder. At the subsequent gasphase deposition of pyrocarbon on the surface and in the volume of porous structure of CFRP the technical carbon is formed which fill large transport pores of material.

The deposition of pyrocarbon in the transport pores provide qualitative compaction, both at conditions of method of radially moving area of pyrolysis and in isothermal method [1,2].

High efficiency of pyrolytic compaction methods supposes the presence of a profiled porosity in CFRP, which is provided by the calculation parameters of gasification process.

The main technological parameters of this process are the initial porosity of CFRP that is formed on the stages of its making and subsequent carbonization, the total duration of process, and also temperature and concentration of gas reagent (carbon dioxide).

Problem formulation.

The task of researches is a study of the distribution of transport pores in the structure of CFRPs at its gasification.

Mathematical model of process.

The process is realized in the medium of carbon dioxide on samples CFRP placed in the thermo-chemical reactors of running type.

Transfer of carbon dioxide by diffusion on length of pore CFRP is described by differential equation with boundary conditions:

$$\frac{d^2C}{d\ell^2} = \frac{2k}{D \cdot r} \cdot f(C) \quad ; \tag{1}$$

$$C\big|_{\ell=0} = C_0^S \quad ; \tag{2}$$

$$\left.\frac{dC}{d\ell}\right|_{\ell=h} = 0 \quad , \tag{3}$$

where C, α are a concentration and decomposition degree of carbon dioxide, respectively; ℓ is a coordinate on length of pore; k is a rate constant of carbon gasification; D is a diffusion coefficient of carbon dioxide; r is a radius of pore; $f(C)$ is a concentration function; C_0^S is a concentration of carbon dioxide on a surface CFRP; h is a half of thickness of wall sample.

Solution of the system of equation (1)-(3) defines the concentration distribution of carbon dioxide on length of pore:

$$C = \frac{C_0^S \cdot \left\langle \exp(-z \cdot \ell) + \exp[z \cdot (\ell - 2h)] \right\rangle}{1 + \exp(-2z \cdot h)} \quad , \tag{4}$$

where z is a root of characteristic equation $z = (2k / r \cdot D)^{0,5}$,

Equation (4) is applicable for pores which belong to any of four local groups of CFRP [3]. The first group of pores is characterized by effective radiuses of 0.001-0.03 μm; second group - 0.03-2.50 μm; third group - 2.50-10.0 μm, and fourth group - 10-200 μm. A part of pores for the first, second, third and fourth groups are 38 %, 32 %, 19 %, 11 %, respectively.

For every group of pores their distribution density on sizes can be approximated by parabolic dependence:

$$f(r_i) = a_i \cdot r_i^2 \quad , \tag{5}$$

where a_i is a parameter of distribution; $a_i = 3q_i / (r_{2i}^3 - r_{1i}^3)$, q_i is a part of pores within i-th local group; r_{1i}, r_{2i} are a minimum and maximal size of pore radiuses within i-th CFRP group, respectively.

Then size of middle radius of pores $\bar{r}_i$ within i-th group may be calculated as

$$\bar{r}_i = \frac{0.75\, q_i \cdot (r_{2i}^4 - r_{1i}^4)}{r_{2i}^3 - r_{1i}^3} \quad , \tag{6}$$

Differential equation of transfer of reaction gas on length of running reactor, taking into account its decomposition on the heated surfaces of porous structure of CFRP samples, has a form [4]:

$$\frac{d(C \cdot U)}{dx} = -2k \cdot \beta \cdot \theta \cdot C \quad , \tag{7}$$

where U is rate of reaction gas flow on length of reactor; β is a coefficient of mass

transfer; $\theta = [\beta + k \cdot (1 - q_n) + q_n \cdot \pi \cdot \sum_{i=1}^{N} \Omega_i] \cdot 1/R$; R is a radius of reactor; $\Omega_i = r_i^2 \cdot D_i \cdot k_i \cdot p_i \cdot [\exp(-2k_i \cdot h) - \exp(2k_i \cdot h]/[2 + \exp(2k_i \cdot h) + \exp(-2k_i \cdot h)]$, r_i, p_i are an effective middle radius and relative part of i-th local group of porous structure CFRP, respectively; N is a quantity of local groups of pores.

The reaction of gasification is written as:

$$C + CO_2 \Leftrightarrow 2CO \quad . \tag{8}$$

For a reaction (8) distribution of reaction gas on length of reactor according to its decomposition degree may be written as

$$C_{CO_2} = C_{CO_2}^{ent} \cdot (1 - \alpha) \quad ; \tag{9}$$

$$C_{CO_2} = C_{CO_2}^{ent} \cdot (1 + 2\alpha) \quad ; \tag{10}$$

$$U = U_{ent} \cdot (1 + \alpha) \quad , \tag{11}$$

where $C_{CO_2}^{ent}$ is a concentration of carbon dioxide at entry of reactor; U_{ent}, U are a rated of gas serve at entry and on length of reactor, respectively.

Equation (7) taking into account correlations (9)-(11) will look like:

$$\frac{3\alpha}{1-\alpha} \cdot \frac{d\alpha}{dx} + \frac{k \cdot \beta \cdot \theta}{U_{int}} = 0 \quad . \tag{12}$$

From the solution of equation (12) the decomposition degree of carbon dioxide is determined as

$$\alpha(x) = (2\theta \cdot x)^{0,5} \quad . \tag{13}$$

Use of solutions (4) and (13) supposes that values of rate constants of gasification for glasscarbon, pyrocarbon and technical carbon are known. These materials are use as components of matrix material at its profiling in the carbon dioxide medium.

Kinetic parameters of gasification process for the mentioned forms of carbon were determinate in the work [5]. It was found that glasscarbon has a maximum value (6000.0 kJ/kg), and technical carbon has a minimum value (266.8 kJ/kg) activating energy.

These differences for mentioned parameter for the studied materials are related to their structure. So, glasscarbon is characterized by a globular structure consisting of ribbon-like formations of carbon atoms. A technical carbon is micropowder with the particles of effective size from a few carbon atoms to a few hundred micrometers. A pyrocarbon obtained by deposition on the heated surface in the medium of natural gas has a well-organized crystalline structure consisting of atomic planes disposed in parallel to surfaces of deposition substrate and at the carbon atoms located in the tops of regular hexagons.

Practical non-porosity of pyrocarbon and particles of technical carbon, high ordering of their structure provide the values of linear rate of gasification two orders below than for glasscarbon.

Determination of kinetic parameters of gasification process for glasscarbon, pyrocarbon and technical carbon which are components of matrix CFRP was made in work [5]. The quantitative values of kinetic parameters of these materials are given in a table. 1.

Table 1

Kinetic parameters of gasification rate constants

Kinetic parameters	Pyrocarbon	Glasscarbon	Technical carbon
Activating energy E, kJ/kg	3656.0	6000.0	266.8
Preexpotential factor k_0, m^2/kg·s	0.96	4484.9	0.00036

Results of tests

Dependences of carbon dioxide concentration distribution (C/C_0) along pores from pores length and changes of initial-to-current pore radiuses ratio (r/r_0) from thickness of wall CFRP in four local maximums of mean radiuses are got on fig. 1 and fig. 2 respectively.

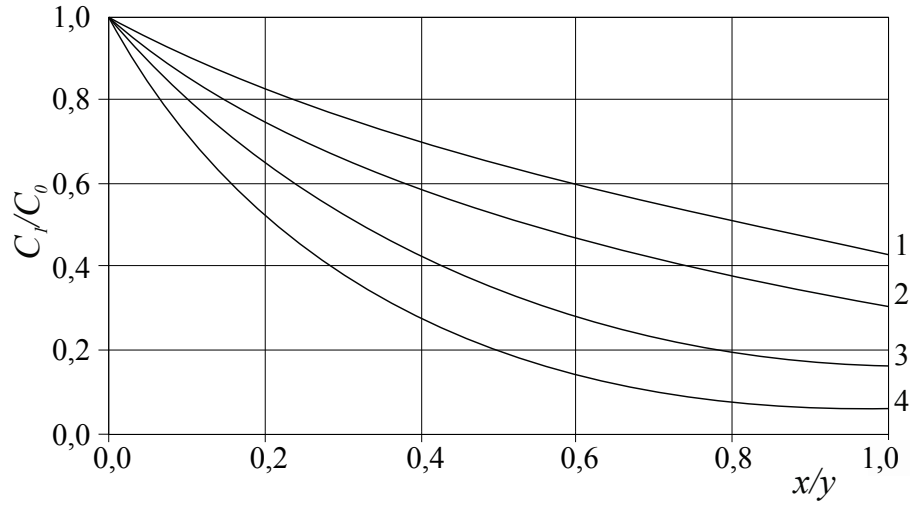

Fig. 1. Charge of carbon dioxide concentration distribution from pores length for mean values of radiuses, μm: 1 - 16.5; 2 - 2.85; 3 - 0.713; 4 - 0.0085

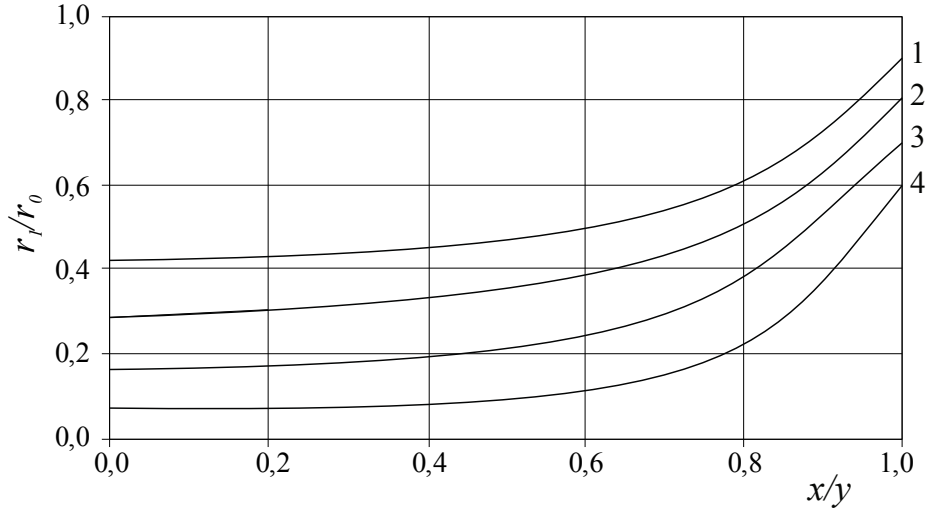

Fig. 2. Charge of initial-to- current pore radiuses ratio from thickness of wall CFRP for mean values of radiuses, μm: 1 – 16.5; 2 – 2.85; 3 – 0.713; 4 – 0.0085

The analysis of fig. 1 and 2 shows that for transport pores of all local size groups of radius increases from the middle of thickness CFRP to its surface.

Conclusion.

1. The mathematical model of transport pores distribution with cone-shaped form in the porous structure of CFRP is worked out.

2. Eventual correlations for the estimation of porosity of CFRP at their gasification in the medium of carbon dioxide are offered.

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Аннотация. *Описаны технологические особенности получения композитов на основе углерода. Изучены закономерности формирования системы транспортных пор в структуре уплотняемых углепластиков при газификации в среде диоксида углерода. Решена задача переноса диоксида углерода по длине пор углепластика, обеспечивающего заданное профилирование его структуры при газификации. Определены кинетические параметры процесса газификации в среде диоксида углерода для трех составляющих углеродных композитов: пироуглерода, стеклоуглерода и технического углерода. Предложены конечные соотношения для оценки пористости уплотняемых углепластиков при газификации в среде диоксида углерода.*

Ключевые слова: *композиты на основе углерода, транспортные поры, структура уплотняемого углепластика, газификация, среда диоксида углерода*

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