REGULARITIES OF NANOFORMS OXIDATION IN CARBON MATRIX

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Introduction

During nanotechnology development the carbon nanostructure materials (CNM) as a subject of investigations represent fixed scientific interest. The physicochemical aspect of studying of CNM oxidation-reduction properties has fundamental character. Studying of processes of CNM formation and destruction is immediately referable to optimization of obtaining technologies, attestation and exploitation of constructional and functional materials on their basis.

The urgency of these questions is caused by a critical mass of the inconsistent physicochemical CNM properties obtained by different authors [1].

The purpose of the current work - to obtain regularities of an oxidation of carbon matrices (CM) of problem CNM samples at the composition control of impurities without structural change of carbon nanoforms (CNM) making its basis.

The present contribution demonstrates experimental data of examination of an oxidation of two samples: Co-CNM obtained by disproportionation CO [1] and a product of refractory fibers technology – ACFM [2].

Experiment

Extraction of probes were carried out with and without decomposition of CM. The most efficient appeared selective extraction of the catalytic agent in solution HCl 1:1 with addition of HNO_3 in hydrothermal conditions (an analytical autoclave) at 180-230 °C and pressure 2,0-10,0 MPa during 0,5-2,0 hours [3]. A cobalt and SiO_2 have been determined with the help of arbitration methods of chemical analysis [4].

Temperatures of the reduction extraction maximums and fractions of total mass (χ, %) of O, N, H have determined with the help of a method of pulsing reduction extraction in a helium flow with chromatographic fractionation and determination of gaseous reaction products as CO, N_2, H_2. Equipment was in accordance with GOST 27417. The reduction extraction of samples is carried out in a helium flow at 1350-1400 °C within 1-2 hours.

Chrono-temperature oxidation performances of CNM up to CO_2 (with after-burning of low-temperature branch by CuO+5%La_2O_3 at 700 °C) in a flow of purified oxygen have been obtained with the help of the graduated temperature coulombocarboxymetry [5].

Results and discussion

Oxidation of Co-CNM sample, where χ_{Co} = 12,5 % (mass), occurs in one stage at temperature 450 °C. Decreasing of the cobalt content down to 0,66 % (mass) results in an increase of oxidation temperature and split on a doublet at 500 °C and 550 °C (fig. 1, a). Extraction of oxygen O – 1,84 % (mass) (N < 0,001 % (mass) and H < 0,001 % (mass)) has given in split of CNM thermal-oxidative spectrum as a triplet (fig. 1, b). Where at temperature 650 °C 72,2 % (mass) of platelet-type graphite nanofibers (GNF) were oxidated, at 700 °C - 20,0 % (mass) of herring-bone GNF, and at 760 °C - 5,3 % (mass) of carbon multiwall nanotubes (MWCNT) (tables 1, 2).

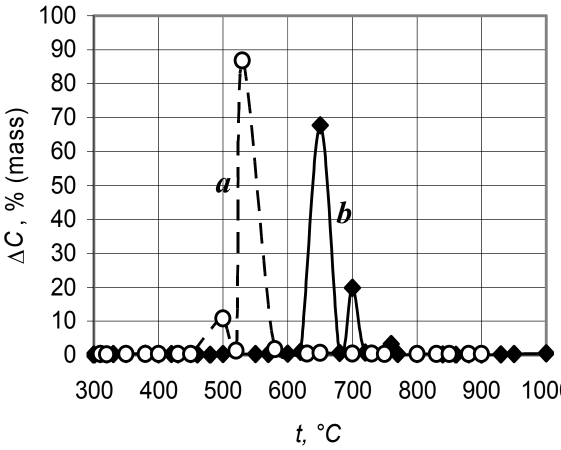

Fig. 1. Oxidative performances of Co-CNM sample: before (***a***) and after (***b***) the reduction extraction

Table 1. Componential characteristics*

Sample	Fraction of total mass χ, %				
	Co	SiO_2	O	N	H
Co-CNM	0,66	—	1,84	0,001	0,001
ACFM	—	3,31	4,00	0,14	0,001

* the rest – carbon.

The obtained data are well compounded with a phenomenon of temperature discreteness of the RED/OX identity of CNF [5], and also with the data known in the literature [1].

Purified in a similar way CM of other origin (nanoonions, carbon black, pyrolitic graphite, thermal expanded graphite, glass-graphite, carbon deposits, high-temperature fibrous materials) acidify analogously according to presence of CNF included in their composition.

Oxidative performances after both purification and the reduction extraction of ACFM sample obtained on technologies of high-temperature carbon materials presented on fig. 2 [2]. Componential composition of this sample presented in tab. 1. Integrated statistical composition carbon nanoforms included in CM ACFM presented in tab. 2, and also illustrated on fig. 2, where 600 °C – an oxidation of 7,4 % (mass) graphite nanoparticles, 740 °C - 19,8 % (mass) twisted-layered GNF.

Table 2. Content of CNF in CM

Sample	Fraction of total mass χ, %				
	600°C	650°C	700°C	740°C	760°C
Co-CNM	—	72,2	20,0	—	5,3
ACFM	7,4	38,8	26,4	19,8	—

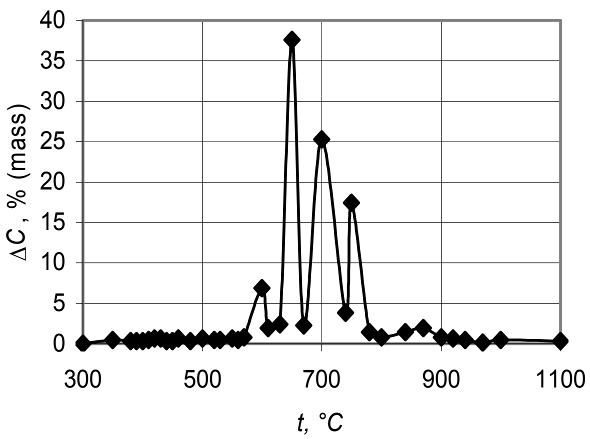

Fig. 2. Oxidative performances of ACFM sample after the reduction extraction

Character of CNM oxidation reminds effects of a volumetric and surface oxidation of porous nickel explored by A.P.Lyapunov [7]. Presence of the catalytic agent, a functional overlying strata (oxy-, keto-, aldehydic, carboxylic, nitroso-, nitro-, etc. groups), and also cumulene (C=C=C=C) and polyyne (C≡C–C≡C) chains [2] results in volumetric CNM oxidation. Heat of reaction essentially rises the sample temperature that results in pseudo-low-temperature destruction of a sample. Elimination of these factors statistically localizes process of an oxidation on a surface of the least resistant CNF. Allocated heat (as has shown experiment) does not play an essential role.

Conclusions

Regularities of CNM oxidation are systematically investigated.

Character of CNM oxidation is influenced with the catalytic agent, and also fixed gas-forming elements preferentially generated a functional overlying strata [6] on a free surface of the unit «a solid body – gas» [7].

The reduction extraction of gas-forming elements (O, N, H) results in sequential CNF oxidation that there corresponds to integrated statistical composition of local allocation of base units CM.

Obtained results confirm unity of material system of carbon materials.

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