Nanocarbon mesh in the flame of aromatic compounds

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Abstract. The soot in the flame of the pyrotechnic composition is presented in a variety of shapes and structures. Part of the dispersed particles consists entirely of carbon. The sizes of such particles are in the submicron range. Another part of the particles contains carbon in the form of nanostructures - needles and tubes. A detailed study of the morphology and chemical composition of dispersed particles on optical and scanning electron microscopes showed the existence of yet another unidentified species of particles - tuba. The resulting formations are micron-sized and retain the properties of nanostructures.

1. Introduction
Various ordered carbon nanostructures - linear-chain carbon, fullerenes, single-walled nanotubes - are formed depending on the physicochemical conditions of the experiment. A film of two-dimensionally ordered linear-chain carbon is obtained by sputtering by the method of pulse-plasma evaporation of a graphite cathode. The resulting films have a thickness of up to several microns, high anisotropy of electrophysical and physicochemical characteristics [1]. Fullerenes or sphere-like carbon molecules are closed spherical networks consisting of a combination of 6- and 5-membered carbon rings. They can be obtained by evaporation in an inert atmosphere of a graphite rod in a volt arc [2, 3]. Nanotubes are extended structures consisting of graphite-like layers rolled into single or multilayer tubes with a cavity diameter of up to 6 nm. The distance between the layers is 340 pm, which is close to the interplanar distance in graphite. The length of nanotubes reaches tens of micrometers. The end of such a tube can be open or closed by a fullerene-like hemisphere [3]. Carbon nanotubes can also be produced by arc discharge, laser ablation, or chemical vapor deposition.

Carbon nanostructures obtained during the combustion of magnesium in carbon dioxide at a pressure of 2000 atm are shown in Figure 1. The phases of the formation of nanostructures are clearly visible. First, this is the formation of round or spherical clusters of amorphous carbon (Figure 1a). Then, structuring of these nanoclusters into a “zigzag” system with rather extended linear regions of a loose nanocluster structure (Figure 1b). Further, the compaction of this structure with the almost complete disappearance of round or spherical clusters and the formation of linear or zigzag bamboo-like carbon nanofibers of considerable length (1 - 5 μm), with an outer diameter of up to 40 nm and an inner diameter of up to 20 nm (Figure 1c) [4].
The introduction of solids into the pyrolysis gas medium of hydrocarbons leads to the formation of fibrous carbon on the surface of solids with catalytic activity (SiO$_2$, Al$_2$O$_3$, MgO) [5].

Figure 1. Combustion products of magnesium in CO$_2$. Formation of carbon clusters of various shapes: (a) circular; (b) spherical; (c) bamboo.

2. Research object
Combustion products in a flame of pyrotechnic compositions based on magnesium powder, inorganic oxidant and aromatic compounds. Powders of the components were thoroughly mixed and pressed into cardboard casings. The combustion of the samples was carried out under room conditions.

3. Research methods
a) sampling of condensed dispersed particles from the flame of pyrotechnic compositions by the method of carrying glass plates; b) examination of samples by methods of optical and scanning electron microscopy to study the morphology of dispersed particles; c) IR – spectrometry for the analysis of organic carbon compounds.

4. Experimental results and their discussion
A high temperature (3100 K) in the flame is achieved by burning a pyrotechnic composition based on magnesium powder, inorganic oxidant. The presence of diphenyl in the composition, as a combustion phlegmatizer, helps to reduce the maximum flame temperature. An excess of the mass concentration of diphenyl of 30% can cause an unstable combustion regime, and subsequently, the cessation of the combustion itself. The oxygen of the oxidizing agent, first of all, is spent on the reaction with the metal, and only then on the reaction with hydrogen and carbon. At the same time, an insignificant part of oxygen goes to the combustion of carbon, as a result of which, compounds with a negative oxygen balance form flames with a large amount of smoke.

The selection of condensed combustion products was carried out by passing a quartz plate through the flame. The particles deposited on the plates were “frozen” and subjected to microscopic studies, IR – spectrometry.

Soot in the flame of a pyrotechnic composition can be represented in different ways [6, 7]. Part of the dispersed particles consists entirely of carbon. The sizes of such particles are in the submicron range. Another part of the particles contains carbon in the form of nanostructures - needles and tubes. A detailed study of the morphology and chemical composition of dispersed particles on optical and scanning electron microscopes showed the existence of yet another unidentified species of particles - tube. The resulting formations have micron sizes, retaining the properties of nanostructures [8, 9].

The tube is a woven mesh with a diameter of 30 - 40 microns and a length of more than a millimeter (Figure 2). It begins on the surface of a particle that reacts by a heterophase mechanism. The enveloping mass of diphenyl is a supplier of material for the formation of nanotubes. The resulting mesh of a certain length is a pipeline of combustion products. The two-phase medium of combustion products moves along the tube. The gas component freely passes through the tube grid, dispersed particles settle on the inner surface of the tube. The settled particles of micron size deform...
the surface of the tube and form bulges. Submicron sized particles settle on the inner surface of the tube and plug the tube mesh. In this case, the hydrodynamic resistance increases greatly, and this contributes to the formation of new cells of the tube.

Figure 2. Fragments of carbon tubes. Magnification (a) 200x; (b) 500x.

A model of a tube with dispersed particles moving inside it is shown in figure 3. The growth process of the tube ends with the cessation of combustion. The formation of parallel branches or a change in the directions of growth of the tube itself is possible when the tube is clogged.

Figure 3. Model of the formation of a carbon tube: 1 - metal, 2 - oxidizer, 3 - diphenyl shell, 4 - two-phase flow of combustion products, 5 - tube, 6, 7 - dispersed particles.

The carbon mesh of the tube burns out during combustion, and a dense layer of metal oxide particles remains, preserving the appearance of the tube. The micrographs show tubes with a partially burnt out carbon mesh (Figure 4).

Figure 4. Micrograph of the sample area.

The section of the tube was studied by X-ray spectral analysis. Below are maps of the distribution of individual chemical elements from the analyzed area of the sample (Figure 5). The distribution of carbon, magnesium and oxygen is discrete and coincides with the contours of the tube.
Figure 5. Results of high-quality energy microanalysis: (a) electron microscopic image; (b – d) distribution map of chemical elements.

The IR absorption spectrum indicates the presence of various organic compounds in condensed combustion products (Figure 6). The absorption bands due to stretching vibrations of the OH– group are located in the frequency range 3500 – 3300 cm\(^{-1}\) in the form of a broad intense absorption band. Absorption bands related to stretching vibrations of –CH\(_2\) and –CH\(_3\) – groups are observed in the range of 2980 – 2820 cm\(^{-1}\) and 2985 – 2850 cm\(^{-1}\), respectively, bending vibrations of –CH = CH\(_2\) groups – 1410 – 1420 cm\(^{-1}\) appear as peaks against the background of intense absorption. Stretching vibrations of groups with multiple bonds –C = C– appear in the frequency range of 2167 cm\(^{-1}\). The absorption bands at 1460 cm\(^{-1}\) are skeletal vibrations of the benzene ring.

Figure 6. IR - absorption spectrum of combustion products.
5. Conclusion

Thus, in the flame of pyrotechnic compositions, many structures containing carbon are formed. Some structures are identified as nanosized carbon tubes and needles, while other structures are micron-sized tubes in diameter and several millimeters in length. However, there is no description of the mechanism, the rate of formation of submicron carbon tubes, and methods for determining their size factor in the literature.

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