Formation of carbon nanostructures in a high-temperature flame

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Abstract. Carbon nanostructures in the form of tubes are formed during the heterophase regime of metal combustion with fluoroplastic. These tubes are filled with condensed particles of combustion products and change the optical properties of the flame.

1. Introduction
High temperature develops in a flame of a pyrotechnic composition, which contains metallic fuel. A high temperature zone is located at the base of the flame. In this zone, as a rule, the metal burns in vapor-phase mode. However, metal burns in a heterophase mode in a flame too. The reaction rate of metal in the heterophase mode is much lower than the vapor phase, and depends on the surface contact of fuel and oxidizer.

2. Object and research methods
The flame of a model pyrotechnic composition based on aluminum-magnesium alloy and fluoroplastic F–3 was studied in this work. The photopyrometric measurement methods developed by the authors [1] allow the measurement of flame temperature. The maximum temperature is reached at the base of the flame. It is 2446 K. At a height of 300 mm above the combustion surface, the temperature decreases to 1715 K. Possible condensed combustion products (fluorides, chlorides and carbides of magnesium and aluminum) at this temperature are in a liquid state or a sublimation process is under way. Fluorides and aluminum chlorides (AlF₃ and AlCl₃) are sublimated. Magnesium and aluminum fluorides (MgF₂ and AlF) and magnesium chloride (MgCl₂) can be in the molten state. Carbon in a flame can be present in a variety of conditions. These can be particles in the form of fine soot or in the form of soot in the composition of complex dispersed particles.

The dispersed particles of the combustion products were selected on glass plates by means of a sampler passing through a flame. Samples were further studied by microscopy. Micrographs of the surface of the sampler obtained using an optical microscope are shown in figure 1.

3. Experimental results and their discussion
An analysis of the obtained images shows that the condensed combustion products consist of particles of fine soot and particles of a filamentary structure. The threads are intertwined and it is difficult to make out individual structures using an optical microscope.
Further study of the combustion products was carried out using a scanning electron microscope. Two types of particles are distinguished among the condensed combustion products.

![Microphotographs of the surface of the sampler](image)

**Figure 1.** Microphotographs of the surface of the sampler: the upper row is the central zone, the lower row is at a distance of 26 mm from the axis of the flame. Height of carrying over the combustion surface $h$, mm: (a) 40; (b) 80; (c) 120; (d) 160. The length of the frame 1 mm.

One of the types of particles is coral-shaped formations. These formations consist of a plurality of particles with sizes $0.2–0.4 \mu m$, which accumulate directly at the reacting particle (figure 2a, b). Particles are composed of fluorides and metal chlorides.

![Micrograph of the sample area](image)

**Figure 2.** Micrograph of the sample area. Magnification (a) 1500x; (b) 6000x.

Another type of particles is threadlike structures originating from the surface of the reacting particle (figure 3a, b). A more detailed study of these particles showed that the threads are a complex structure. The outer surface of the particle is a carbon mesh in the form of a tube. The length of the tube can be several millimeters, the transverse dimensions - several tens of microns. The transverse dimensions of the tube are commensurate with the external dimensions of the reacting particle (figure
3a, b). Dispersed particles with sizes from 1 to 20 microns in diameter are observed on the surface of the sampler too.

![Figure 3. Micrograph of the sample area. Magnification (a) 150x; (b) 2500x.](image)

The tube is a grid woven from carbon nanotubes. Transportation of metal combustion products with fluoroplastic in the form of a two-phase flow takes place inside a hollow tube. Large particles with a size of 10–20 microns are retained on the inner surface of the tube. At this point, the tube is deformed and bulge forms (figure 3). The gas component of the flow freely passes through the carbon mesh of the tube. Dispersed particles of submicron size cannot penetrate the grid and are retained on the inner surface of the tube. A fragment of a tube with high magnification is shown in figure 4a. The micro relief of the surface of the tube is complex. It indicates the unsteady processes existing during its formation.

The sizes of dispersed particles were determined using software [2]. The size distribution function of the settled particles on the tube is such that most particles have a diameter of ~ 0.15 μm (figure 4). It can be assumed that the carbon mesh cells are smaller in size than the transverse dimensions of the settled particles.

![Figure 4. The distribution of dispersed particles by size on the surface of the tube.](image)

The X-ray spectral method, implemented on a scanning electron microscope, allows element-by-element identification of the composition of these particles. Indeed, the elemental composition of the particles and the maps of the arrangement of elements within the tube make it possible to isolate carbon, magnesium, aluminum, and fluorine (figure 5b – e). The brightness of the image on the map of the arrangement of elements is proportional to the concentration of this element in the sample. In those places where there are no particles, silicon is highlighted as the basis of a glass substrate (figure 5e).
Figure 5. Results of high-quality energy microanalysis: electron microscopic image (a), distribution map of chemical elements (b–f). The length of the frame 100 microns.

Carbon formations in the form of a tube, ranging in size from several tens of microns to several millimeters in length, were first discovered in combustion products [8, 9]. The number of particles in the form of a tube decreases with a decrease in the concentration of fluoroplastic. There is no such information in the literature [3–6].

The length of the carbon tube is determined by the hydrodynamic resistance during the movement of a two-phase flow. The tube model is schematically shown in figure 6.

Figure 6. Model of a tube: 1 – metal, 2 – oxidizing agent, 3 – gas, 4 – particle of combustion products, 5 – tube.

Hydrodynamic resistance increases due to the deposition of dispersed particles on the walls of the tube. This leads to the formation of new elements of the tube and, accordingly, to an increase in the length of the tube itself, its branching, or the formation of parallel tubes.

The optical constants of particles consisting of fluorides and metal chlorides are such that the imaginary part of the refractive index does not exceed $10^{-6}$ in the visible and near infrared ranges of the spectrum [10]. The carbon mesh of the tube is an object with a high imaginary part of the
refractive index $k \approx 1.0$. However, the mass of the grid itself, compared to the total mass of dispersed particles in the tube, is small and amounts to no more than one percent. The optical properties of a complex particle are defined as averaged over the volume of each component. The refractive index values measured on an ellipsometer are such that they are determined by the expression:

$$m = 2 + i \cdot 1.73.$$  

4. Conclusion

It should be noted that dispersed particles adsorbed on the surface of the tube have not only physical but also chemical nature of the bonds with the substance of the tube. Responsive combustion products are energy carriers, and the outer surface of a tube with embedded dispersed particles is an emitter of electromagnetic energy in the near infrared range of the spectrum.

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