STRUCTURAL VARIABILITY OF THE SOOT PARTICLES OF DIFFERENT ORIGIN

T.I. Ryshkevich, E.F. Mikhailov, and S.S. Vlasenko

Institute of Physics at St. Petersburg State University
Received January 26, 1996

Structural parameters of different-origin soot particles are studied. The effect of water vapor on the fractal dimensionality variations and the coefficients of anisotropy of an aggregate shape is considered. The main reasons for restructing of different types of soot are analyzed and its mechanisms are revealed.

The soot is known as one of the most optically active components of the atmospheric aerosol. Among the main sources of soot in the atmosphere are, first of all, forest fires and pyrolysis of hydrocarbon raw materials such as oil and natural gas. Studying the properties of the soot aerosol becomes particularly urgent in view of increasing anthropogenic pollution of the atmosphere.[1]

Smoke particles are aggregates formed due to coagulation of a great number of fine-disperse (size of the order of nanometers) soot monomers. In the modern physical usage they are called the fractal clusters. Peculiar features of such systems are caused by their very rarefied structure that results in a very low density of the order of 0.01–0.02 g/cm^3. Physical properties, especially aerodynamical and optical ones, of soot fractals differ significantly from the corresponding properties of both a uniform particle, equivalent in mass (or size), and a system of independent small particles.[2] This circumstance causes the necessity of in-depth study of aerosols of such a class in order to provide a more correct description of their physical properties in modern numerical models of the atmosphere.

Peculiarities in the structure of soot particles cause its high susceptibility to the external effects. In the atmosphere, one of the governing factors of the external effects is water vapor. However, the character of interaction of soot fractals with the water vapor is very poorly studied. In this connection, it seems to be very urgent to analyze the reasons and to reveal the physical mechanisms responsible for changes in the structure of soot particles. This paper presents some results of the laboratory experiments aimed at solving this problem.

For our research we sampled the soot produced by burning of pine-tree woods, natural gas, west-siberian oil, and carbon generated in the arc discharge plasma from carbon rods. The structure analysis of smoke particles was performed based on the data of computer processing of the electron microscopic images.

For all types of soot we found the fractal dimensionality, the shape anisotropy coefficient, the mean size of monomers and clusters. The monomer mean size is practically the same for all types of soot and equals $d = (40\pm8)$ nm. All structure parameters of fractal aggregates were estimated before and after the exposure to water vapor. Samples were conditioned for 10 min in the atmosphere of saturated water vapor at 40°C.

Table presents the measurement results for the fractal dimensionality and the cluster mean size for all types of soot.

It is seen from the data presented in the table that for the soot samples produced by burning of pine-tree wood and oil about 25% reduction of the mean size and a 10% increase of the fractal dimensionality are observed what reflects the change in density. The fact of the structure change is clearly demonstrated by microphotos recorded before and after the exposure to the water vapor (Fig. 1).

The second important parameter reflecting the structure change of the fractal aggregates is the shape anisotropy coefficient which is the length-to-width ratio of a rectangle enclosing a separate aggregate. The measurement results obtained as a cluster size dependence of the shape anisotropy coefficient are shown in Fig. 2.

A comparative analysis of the plots shows that soot of different types has different susceptibility to the action of water vapor. In all cases clearly seen is the change in the cluster size dependence of the shape anisotropy coefficients after the exposure to water vapor. The only exception is the soot produced by burning pure carbon generated due to evaporation of carbon rods in the arc discharge plasma, for which the change is not so well pronounced. The reason for this difference is the presence of high-molecular substances (resins) sorbed on the surface of primary carbon nuclei. This fact well correlates with the results of absorption measurements. The experimentally obtained isotherms of water vapor absorption on analogous specimen are shown in Fig. 3. It is seen from the figure that the absolute amount of the water vapor absorbed by pure carbon soot differs practically by order of magnitude from that for soot produced by burning corresponding hydrocarbon materials.

Joint analysis of experimental data suggests that the degree of the aggregate restructuring is governed

0235-6880/96/06 542-04 $02.00

mainly by two factors: the character of particle-to-particle contact and the wettability. It is known that in burning of hydrocarbons, in addition to soot, high-molecular organic substances are produced. Resinous products are adsorbed on the particle surface, therefore the coagulation contact between particles is realized via the interphase layer that reduces the bond energy. Fractal aggregates, containing the elements with reduced energy of particle-to-particle interaction, are more likely to be restructured under the action of external factors. On the other hand, the presence of organic substances, including oxygen in the form of hydroxyl and carbonyl groups, on the particle surface significantly increases the system capability to absorb water vapor and, therefore, increases its wettability.

TABLE I. Change of the structure of soot particles under exposure to water vapor.

Origin of soot particles	Fractal dimensionality of particles		Particle mean size (μm)	
	before exposure	after exposure	before exposure	after exposure
Pine-tree wood	1.76	1.88	0.59	0.47
Oil	1.72	1.85	0.53	0.40
Carbon	1.74	1.76	0.45	0.45

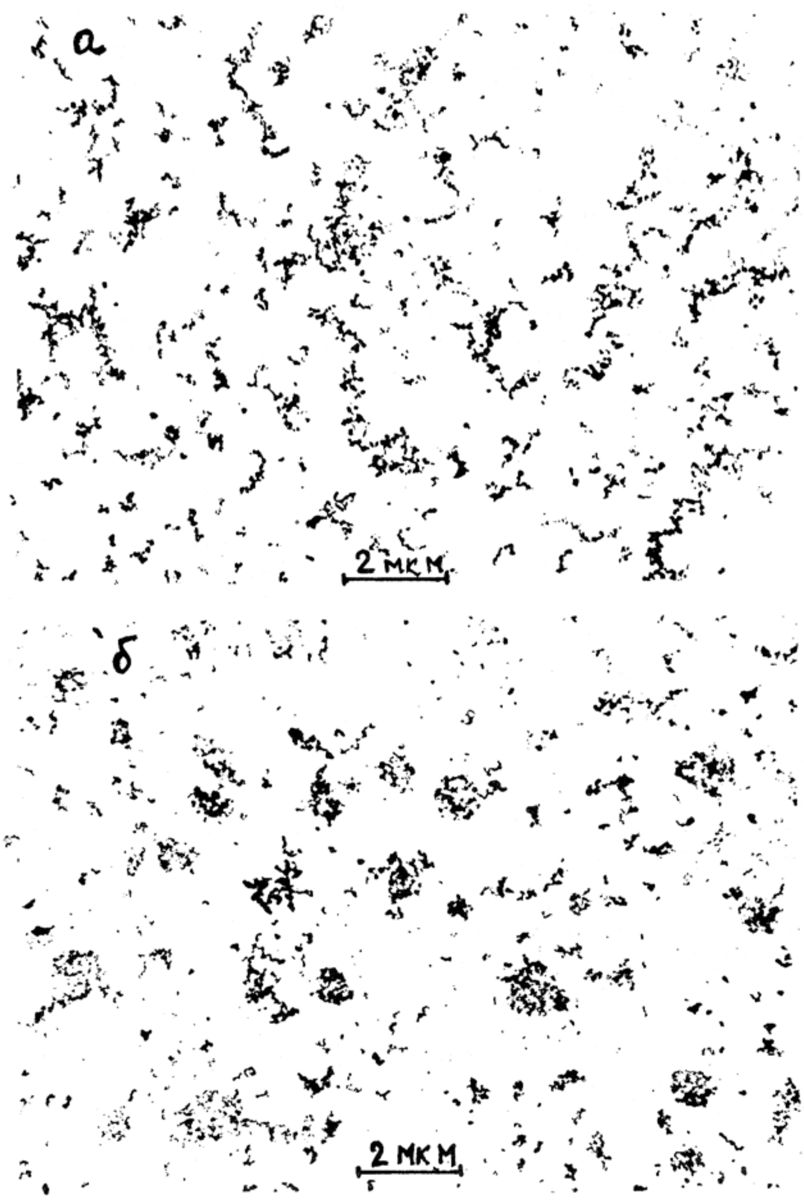

FIG. 1. Microphotograph of clusters of the soot produced by burning of oil: before (1) and after (2) the exposure to water vapor.

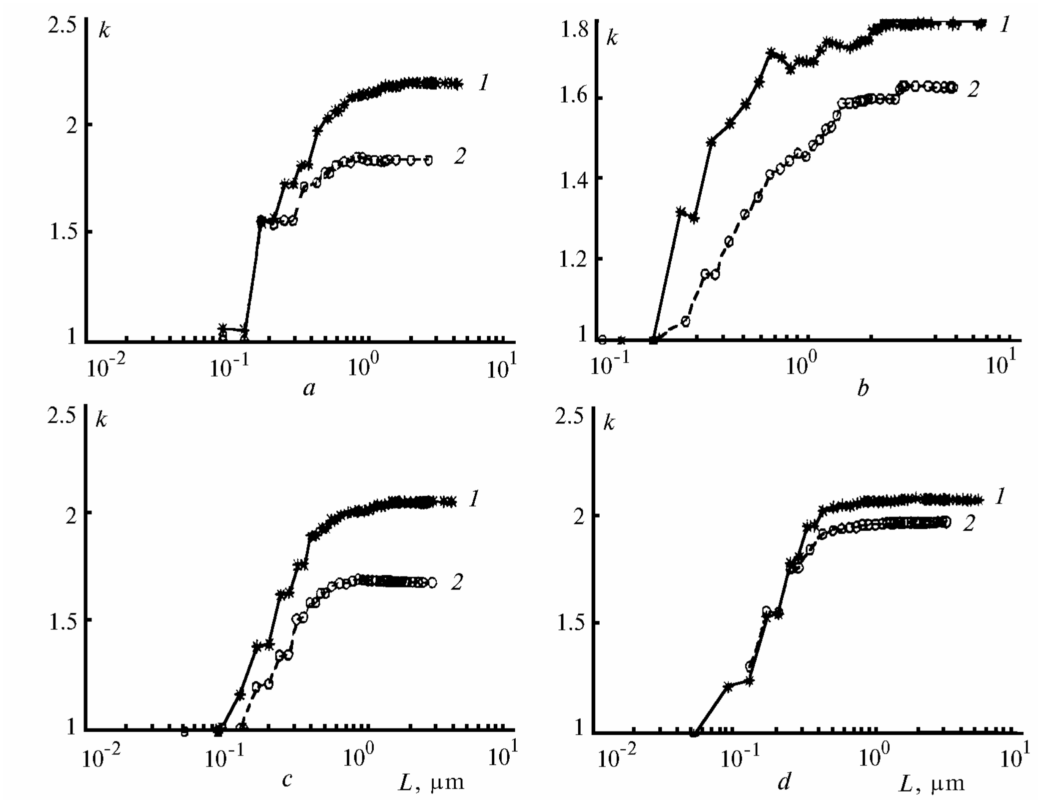

FIG. 2. The cluster size dependence of the shape anisotropy coefficients for the soot produced by burning pine-tree wood (a), natural gas (b), oil (c), and pure carbon generated by evaporation of carbon robs in arc discharge plasma (d): before (1) and after (2) the exposure to water vapor.

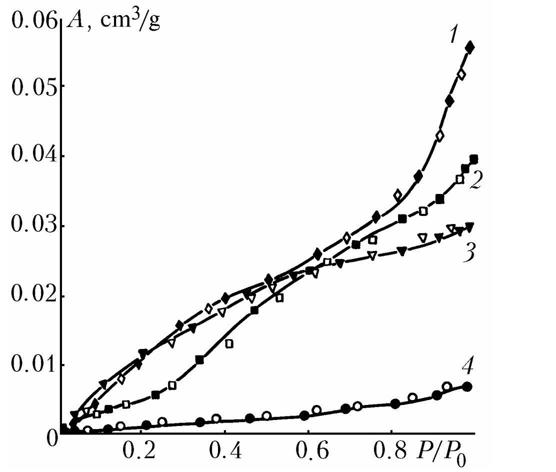

FIG. 3. Experimental isotherms of water vapor adsorption at a specimen temperature of 25°C *for soot produced by burning of pine-tree wood (1), oil (2), natural gas (3), and pure carbon generated by evaporation of carbon rods in the arc discharge plasma (4); the closed symbols correspond to the adsorption branch, while the open ones are for the desorption branch.*

In the general form the mechanism of changing the structure of fractal clusters under the action of water vapor can be presented in the following way. Fractal aggregates, being the condensation nuclei, absorb the vapor. In the places of drop formation, due to the surface tension forces, the structure deforms thus giving rise to more dense globules. And, if the critical size of a drop is greater than the fractal size, the whole object proves to be deformed. Otherwise, separate "ballsB are formed in the fractal matrix. Both variants of the structure change under the exposure to water are clearly seen in the microphotographs of soot clusters; Fig. 1*b* demonstrates the restructing of the first type, whereas Fig. 4 corresponds to that of the second type. The presence of the charge in fractals is of principal importance for the condensation acitivity.[3] In this case globules are formed on even nonwettable carbon particles (pure carbon) in the places of charge concentration. It can be seen from Fig. 4 that this process occurs mainly at the periphery of an aggregate. By virtue of the remote character of Coulomb forces, the periphery is the most probable place for "bindingB of charged particles.

Thus the results obtained show that one of the possible reasons for ambiguous interpretation of the experimental data obtained in optical measurements of aerosols containing the soot component may be due to the structure variability of soot particles under the exposure to external factors, among them water vapor.

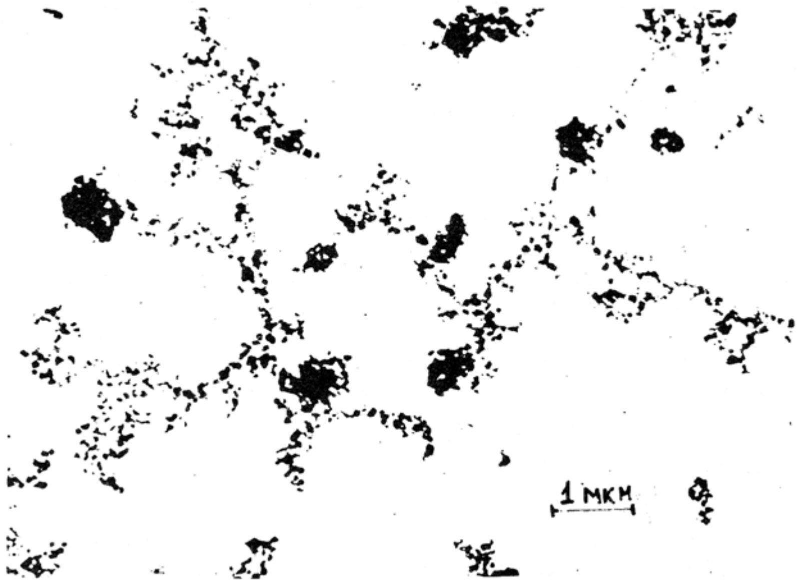

FIG. 4. Microphotographs of clusters for the soot produced by evaporation of carbon in the arc discharge plasma.

REFERENCES

1. I. Colbeck, L. Appleby, E.J. Hardman, and R.M. Harrison, J. Aerosol Sci. **21**, No. 4, 527–538.
2. M.V. Berry and I.C. Percival, Optica Acta **33**, No. 5, 577–591 (1986).
3. E.F. Mikhailov, S.S. Vlasenko, and A.A. Kiselev, Fizika Plazmy **21**, No. 5, 442–448 (1995).