VISUALIZATION OF NANOSIZE HETEROGENEITIES OF MEDIA AND A HYDRODYNAMIC MODEL OF FORMATION OF TUBULAR NANOSTRUCTURES.

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ABSTRACT

The method of visualization of nanosize heterogeneities of a two-phase medium is proposed and a new point of view on the mechanism of formation of tubular structures is advanced in this work.

Keywords: visualization, hydrodynamic, fluctuations, nanoparticles, Kolmogorov scale.

INTRODUCTION.

The problems of visualization of formation processes of morphological structures of carbon, silicon and different metal-silicon-carbon containing composites in different thermodyinamically heterogeneous (turbulent) media are well known. One of such problems is related to the presence of a smoll range turbulence of the carrying medium. So, formation of a condensation aerosol of the given substance in the field of a hydrodynamic flow is accompanied by all possible fluctuations (pulsation) of gas- and thermodynamic values /1/. It is this circumstance that impedes not only the process of visualization itself but also understanding the problems of mathematical modelling of aerosol condensation process /2/. The same is true for the process of formation of some coherent structures in the form of carbon-silicon nanoparticles in the flow of a two-phase medium, including tubular structures. For example, nucleation, i. e. formation, in the volume of a metastable phase, of a stable phase nucleidue to heterophase fluctuations, plays a key role at phase transitions, including the process of volume condensation of supersaturated vapor. The fact that disturfances in thermodynamic values significantly effect the process of volume condensation was exemplified by condensation relaxation in the work /3/.

On the other hand, in order to construct adequate models of the processes of effective heat evolution in high rate reacting flows, it is necessary to know the structure of combustion zones and the dynamics of their development. A significant heterogeneity of the flow, the determining factor of which is the presence of shock waves and expansion shock waves, exerts a significant effect on the structure of mixing areas, ignition parameters and development of combustion zones. Characteristic spatial and time scales of the proceeding processes may differ in strands, that makes experimental registration and physical interpretation of the observed phenomena difficult /4/. Large power containing vortexes being observed in the experiments include smaller ones, finally dissipative vortexes. The increase in the scales of vortexes (< 1mm) accelerates the processes of mixing and intensifies the process of combustion /5/. It is difficult to visualize these vortexes as it is technically complicated to reach the registration rate of the order 10^{-8} s which is necessary for fluctuations of a millimeter range. At the same time, it is these vortexes that form vortex filaments which are so important in formation of morphological structures in case of a two-phase medium flow.

VISUALIZATION OF NANOSIZE HETEROGENEITIES OF THE MEDIUM.

Practically the obtained "visual" registration of the processes under study is not the cause of "direct observation". In this connection, we propose to use electron-microscopic pictures as possible graphic demonstration of registration of nanosize changes in thermodynamic conditions of the system, in particular, those existing when particles of nanosize range grow. The morphological structure of particles which are formed in different processes fix hydrodynamic conditions accompanying its formation. These may be local changes of temperature, pressure (density), the rate of gas flows, formation of vortexes, the existence time of heterogeneities and others.

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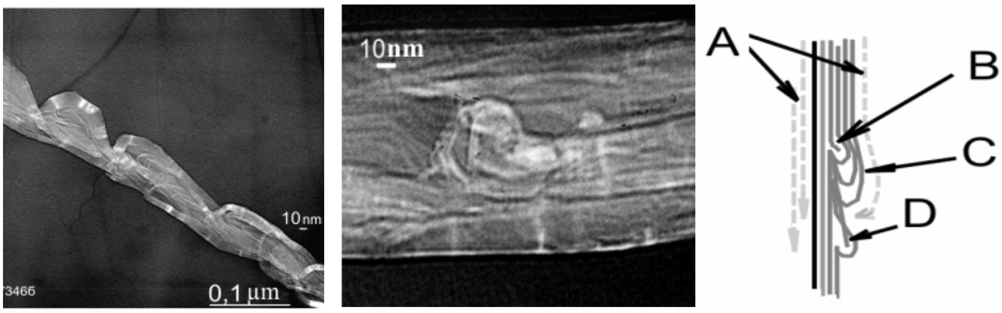
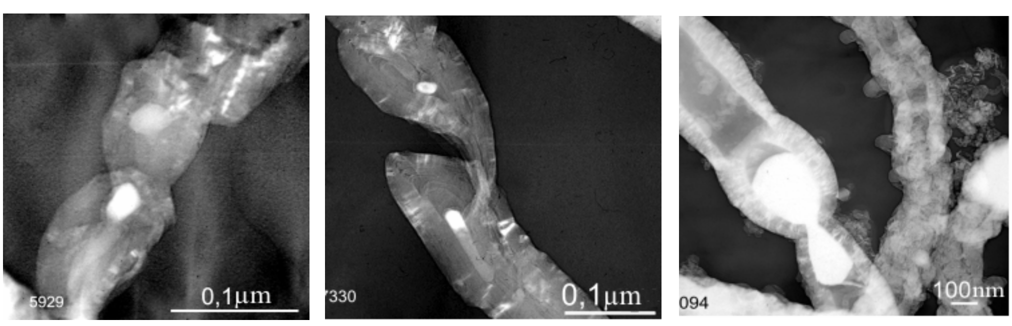
For example, when investigating nanosize particles of carbon, silicon and different metal-silicon-carbon containing composites which are formed in gas continuous thermostatted reactor /6/, periodically repeated elements of structure were stated (Fig. 1-3) and possible mechanisms of their growth were proposed /7-9/. Both the periodicity of appearance of separate details and their structure may serve as an illustration of the presence of instability regions in the reaction zone – local heterogeneities of the particle growth medium. We suggest a possible evaluation of the time interval of one structural element formation or the existence time of thermodynamic conditions for formation of a structural packing of a definite type. For example, fibrous particles formed by nanosize bands rolled up into loops (Fig. 1a). The thickness of the cross-section layer which forms a loop makes up 1.3nm. The loops, as a rule, consist of two layers and a space (or a more transparent substance) between then (of about 5-8nm), more rarely occur packings consisting of three and more layers. Multilayer (3 and more layers) loops usually have strongly expressed external layers and feebly marked internal layers, but it is internal layers that more often originate formation of new loops. The outlying part of particles composed of densely packed loop formations is usually multilayer and its structural degree of order is close to a graphic one. Such balls of carbon loops are likely to represent loop "octopuses".



a b c

Fig. 1. Electron-microscopic pictures of loop structures: in the space – a, on the surface – b. The scheme of formation of loop structures – c: A – a flow of hydrocarbon gas, B – the defect of the layer, C – loop carbon layers getting formed, D – a carbon layer bending (a secondary defect).

Formation of loops can by explained by the presence of vortex heterogeneities in the field of hydrocarbon gas flow around the growing tube and supplying it with «a construction material». Also, heterogeneities may appear due to the presence of defects on the surface. Further – according to Ostvald's law: pressure over the convex part of the sample is always higher than over the even surface. The formed instability creates vortex pressure differentials of vapors resulting in appearance of loop structures. The condensation rate of the substance in the wave of hightened pressure is higher than that in the defectless part of the lamillar particle surface (tubes, fibres). The process of uptake of carbon material by the particle determines the sizes of forming bands or steps.

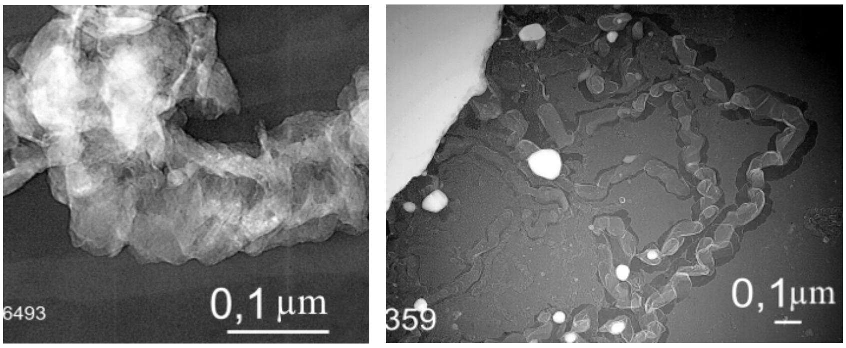


a b c

Fig. 2. Electron-microscopic pictures: a fragment of the fibre formed by "petal" particles - a, opening of metal containing multilayered carbon buds - b, c.

Another variety of nanosize formations is encapsulated structures. Fig. 2a presents a tube fragment - a fibre formed by petal particles. In Fig. 2b one can see the principle of growth of these fibrous structures. Inside each "petal" there is a tube a chanael along which a mobile metal containing phase travels. According to VLC (vapor-liquid-crystalline) and carbide mechanism, when metal carbide inside a carbon bud gets cooled, there takes place seizure of carbon, probably, with a different structural packing, and a dense capsulating layer is formed. Formation of a lamillar capsule is explained, first of all, by gradients of temperature and phase concentrations in eutectic liquid.

The heating up of a nanosize metal phase (carbonization temperature 500-1000ºC) results in the rupture of a carbon capsule and charge of part of the material. The controlled flow of carbon containing gas in the reactor stimulates continuation of the growth of a tubular - fibrous particle and direction of formation of a new capsule around a metal phase. The morphological structures shown in Fig. 2b, are, in our opinion, a good illustration of the suggested "explosive" mechanism. It can explain similarly the obtaining of other particles, for example, large surfaces from tubular - fibrous formations at cyclic change of a phase composition and the rate of hydrocarbon gas supply. The process of encapsulation is not likely to be completed and constructions of «explosion cones» are formed (Fig. 3a).



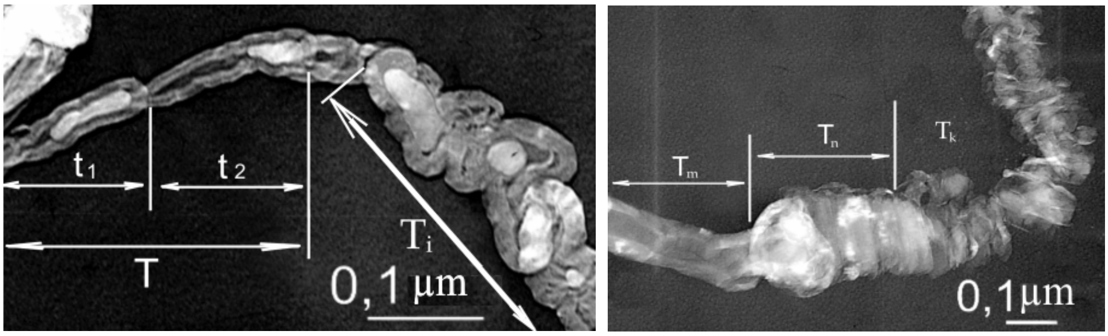
a b

Fig. 3. Electron-microscopic pictures: a fibre fragment from isometric cone particles growing in the space - a, tubular-petal structures being formed on the plane - b.

Similar processes are likely to take place on the surface where there is no enough amount of "construction" carbon in the volume (Fig. 3b).

The metal containing phase reacts with the surface layer of the carbon film and, at cyclic traveling, forms periodically closed tubular - fibrous structures. The size of separate chains of structurized carbon left by a catalytic particle (according to the VLC mechanism) is proportional to its size. The travel of an active part is only probably along the amorphized carbon of the support. This process takes place and is registered in the column of the electron microscope. The traveling rate of the particle – catalyst is controlled by the electron beam intensity (by the change of the specific quantity of electrons and the temperature gradient).

The change in the morphological structure of the particles during its growth, probably, reflect the existence time of definite thermodynamic conditions and their periodicity. That is registers (in general and in time) the emerging local heterogeneities of the medium of the particle growth and, correspondingly, the time of their existence (Fig. 4a, b).



a b

Fig. 4. Electron-microscopic pictures of nanosize particles (a,b). Determination of time of formation of one cycle (t) and the existence time of definite thermodynamic conditions of the particle growth (T).

For example, from the vapor phase of mercury at supersaturation coefficient ≈ 20, Hg filaments grow with the average rate of about $1.5 \cdot 10^{-4}$ sm /s (1500nm/s) /10/. Conseguently, having the designed parameters of the system, one can approximately evaluate the time interval of formation of one "petal" (t ≈ 1.5 s, Fig. 1a) or the existence time of thermodynamic conditions for formation of a definite type of packing (Tn ≈ 2.5s). Formation of encapsulated – petal structures can be considered as a "cold" stage of selfpropagating synthesis, i.e. the time between two separate waves of combustion. The rate of formation, amount or ratio of the kinds of carbon nanopaticles depend on the time of the process procedure.

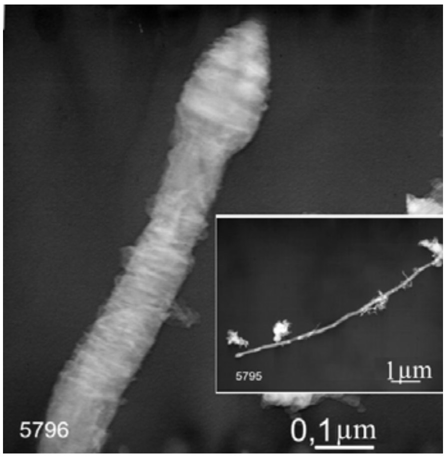


Fig. 5. The electron-microscopic picture of a tubular nanostructure. The moment of the structure formation is accompanied by energy conversion and change in the volume of the system being considered.

When investigating formation of nanosize particles of carbon, silicon and different metal-silicon-carbon containing composites, we registered periodically repeated elements making the morphological structure of tubular - fibrous particles complex. Investigations of the details of such complication can serve as a good illustration of both the proposed mechanisms of particles growth of different kinds and the presence of instability ranges in the reaction zone - local heterogeneitics of the particle growth medium. Here comes the possibility to evaluate the time interval of formation of structural elements and the existence time of thermodynamic conditions for formation of morphological structures of a definite type.

HYDRODYNAMIC MODEL OF FORMATION OF TUBULAR NANOSTRUCTURES.

The quantitative analysis of nanostructures formation processes has shown that in the cases under study the effect of hydrodynamics in the regime of a turbulent flow can be guite significant. The existence of vortex dissipative hydrodynamic structures in the form of vortex tubes indicate the possibility of formation of our nanotubes in the field of high temperatures.

Indeed, the field of the geterogeneons two-phase medium flow is, as a rule, turbulent. The effect of turbulence is particularly great around solid surfaces. There emerge a whole number of specific and still little studied phenomena. One of them is formation of length-wise vortexes near the solid surface. A well known scheme of such vortexes is presented in Fig. 6.

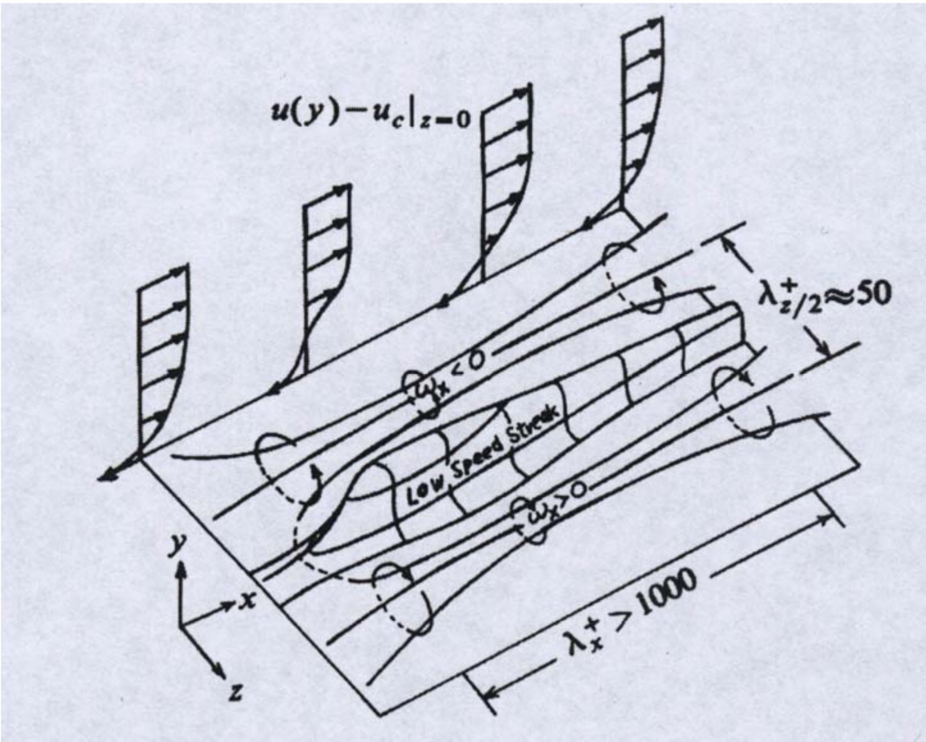


Fig. 6. Formation of length-wise vortexes near a solid surface.

A similar pattern can take place in case of a "free" flow with a strong shift of a cross-section rate. The following mechanism of nanostructures formation is possible: in a two-phase medium, an "initial" diameter of small scale vortex tubes, on the surface of which nanoparticles are concentrated, has an order of Kolmogorov scale μ ≈10-4inch. The further "compression" of these tubes under the effect, for example, electromagnetic forces results in packing of the surface layer from nanparticles and gives them the "final" diameter of the order 10micron. Under the effect of temperature these tubes acguire a "stable" state and can be visualized by the above proposed method with the result presented in the pictures.

Thus, regulation of formation of vortex dissipative structures by varying the parameters of the flow hydrodynamics and its temperature will allow creating nanparticles of the required morphological structures.

As far as creation of the mathematical theory of this process is concerned, it is necessary, first of all, to develop further Kolmogorov's theory which would take into account the processes of "internal" alternation of both dynamic and scalar fields of the turbulent flow.

In conclusion it should be noted that purposeful synthesis of materials with the designed structure will allow obtaining materials with new characteristics. For example, substances with the high specific surface, hightened chemical and physical sorption, unusual electric and magnetic properties. Electron -microscopic pictures are proposed to be used for registration of nanosize changes of thermodynamic conditions of the system existing during growth of the particles of nanosize range. These may be local changes of temperature, pressure (density), rate of gas flows, formation of vortexes, time of heterogeneities existence and others.

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