The effect of chemical interaction on the morphology of metal-carbon composites formed in a graphite arc

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Abstract. This work deals with the analysis of mechanism of nanostructured composite formation at joint electric-arc spraying of graphite electrodes with addition of various elements. It is shown that the morphology of nanoparticles, formed at condensation of carbon vapors with the additive elements that have similar pressures of saturated vapors, can vary significantly. This difference is explained by chemical interaction of an additive element with the carbon matrix.

1. Introduction
To date, a wealth of experimental experience on electric-arc synthesis of carbon nanostructures and composite materials consisting of nanoparticles of various elements in the carbon matrix has been accumulated. It is shown in [1,2] that it is possible to change the size of nanoparticles and morphology of carbon matrix at electric-arc spraying of graphite electrodes with the additives of various elements, varying the spraying conditions. Moreover, when annealing the synthesized composites in an oxygen-containing atmosphere, it is possible to produce nanoparticles of oxide of an additive element. Despite the extensive experimental approbation of technology of electric-arc synthesis, theoretical ideas about the processes of joint condensation of the spraying products and formation of nanoparticles of the additive material and carbon are scarcely presented in literature. The models of condensation in a graphite arc, presented in modern literature, describe mainly the processes occurring with participation of pure carbon materials and condensation of carbon vapors on the surface of a catalytic particle, i.e., formation of fullerenes, onion structures, carbon nanotubes, etc. The development of ideas about the effect of vapors of various elements on condensation processes in a graphite arc can lead to the development of efficient methods for the synthesis of nanoparticles with different morphology of the additive elements and carbon matrix. For example, possibility of obtaining silicon carbide on graphene sheets, when silicon vapors are added to the atmosphere of discharge, is experimentally shown in [3]. It is shown in [4,5] that under the certain conditions the metal particles can form hollow spherical shells, but not bulk nanoparticles. In the present work, the analysis of processes occurring during joint condensation of various metal-carbon composites with similar thermophysical properties has been carried out on the basis of literature data and results of experimental studies.

2. Experiment
Cu-C and Mn-C nanocomposites were synthesized in helium at a pressure of 24 torr and discharge current of 150 A using the setup for electric-arc spraying described in detail in [3], Fig 1. In the reactor there were two electrodes. The cathode was a graphite tablet with a diameter of 20 mm, and the anode...
was a rod with a diameter of 7 mm and a length of 70 mm. Around the electrodes, at a distance of 5 cm, there was a water-cooled removable screen for collecting the products of synthesis. The mixture of additive element powder with carbon was pressed into the sprayed electrode (anode). The molar fraction of the additive element in the sprayed electrodes was 2.5%. Spraying was carried out at a constant voltage, regulated by the rate of sprayed electrode supply. The synthesized material was collected from the cooled walls of the reactor. The materials were analyzed using transmission electron microscopy (JEOL - 2010).

**Figure 1.** Experimental setup. 1 – vacuum chamber, 2 – mobile electrode 3 – immobile electrode (anode), 4 – translation transfer, 5 – hermetic input, 6 – copper water-cooled circuit, 7 – removable stainless steel screen.

### 3. Results and discussion

Studies of synthesized materials by the methods of transmission electron microscopy are presented in [3-8]. In most cases, the material is presented by metal nanoparticles encapsulated in carbon globules. However, as it is shown in [3-5], for a number of metals, such as aluminum, silicon, and magnesium, carbon composites have a nontrivial morphology. Table 1 presents the characteristics of the sprayed materials and nanoparticles formed by spraying.

| Element | Type of carbide | Temperature at saturated vapor pressure of 25 torr, °C | Temperature of melt crystallization, °C | Average size of particles | Link to source |
|---------|-----------------|-----------------------------------------------------|----------------------------------------|---------------------------|----------------|
| Pt      | no              | 3270                                                 | 1768                                   | 4.1                       | [6]            |
| Cu      | no              | 2060                                                 | 1084                                   | 4.1                       | [6]            |
| W       | Metal-like      | 4460                                                 | 3422                                   | 3.9                       | [7]            |
| Zr      | Metal-like      | 3240                                                 | 1855                                   | 2.3                       | [6]            |
| Ti      | Metal-like      | 2490                                                 | 1668                                   | 6.8                       | [6]            |
| TiC     |                | 3260 (TiC)                                           | 3260                                   |                           |                |
| Fe      | Metal-like      | 2372                                                 | 1538                                   | 7                         | [8]            |
| Ni      | Metal-like      | 2250                                                 | 1455                                   | 3.8                       | [6]            |
For all materials presented in the Table, formation of structures other than bulk nanoparticles is typical only of salt-like carbides formed by aluminum and magnesium. During their spraying and subsequent removal of carbon at calcination, the hollow spherical frames are formed [4,5]. The sizes of spherical shells forming for magnesium and aluminum differ significantly, the diameters are 20 and 200 nm, and this is associated in [4,5] with different dynamics of material condensation; the saturated vapor pressure for magnesium is significantly higher (Table 1). Thus, the carbon frame, where deposition of the metal-enriched layer occurs, in the case of magnesium grows to large sizes. When carbon vapors with silicon condense, silicon carbide is formed at the temperatures of 2800°C and lower; according to the concepts of condensation of carbon vapors in an arc, the carbon chains and fullerene-like structures are formed at these temperatures [3]. Based on these facts it can be concluded that the growth of carbon globules (which act as a frame) starts at the temperatures below 2800°C and occurs to the temperature of magnesium condensation of 1090°C. In the case of magnesiu, the material is easily oxidized, and metal spheres are observed in the original composite before annealing in air. Hence, magnesium condensation occurs at the final stage of composite formation and all metal is on the surface of carbon material. In the specified temperature range of 2800-1000°C, vapor condensation of other metals such as iron, nickel, copper and manganese occurs also (Table 1). Copper and manganese have the lowest temperature corresponding to saturation. However, in all the cases mentioned, there occurs condensation of nanoparticles without internal cavities, whose sizes are significantly lower; at that, the metal particles are often located in the geometric center of a soot globule, Fig. 1.

**Figure 2.** The morphology of the synthesized material, manganese is on the left, copper is on the right.

This contradiction can be eliminated by the assumption of the mobility of nanoparticles within the soot globule until liquid-solid phase transition, which occurs for nanoparticles at the temperatures significantly lower than those shown in Table 1 for the bulk material. Diffusion of metal atoms inside the soot globule can lead to formation of nanoparticles in its center. This effect should be most pronounced for metals that do not form chemical bonds with carbon (carbides) and form metal-like
carbides with carbon built-in to the metal lattice. In the case of salt-like and covalent carbides, the chemical bond with the carbon matrix should reduce the mobility of the additive element. Thus, the size and shape of nanoparticles is determined by the type of carbide formed and mobility of the additive component in the soot globule.

The analysis of TEM images in Fig. 2 and [6-8] shows that the size of soot globules differs also. At the same flow of sprayed material, this should lead to a change in their number. The number of soot particles is determined by concentration of nuclei that have reached a critical size at the initial stage of growth; the presence of metal vapors in the system can change the time and probability of formation of a critical nucleus in the system. According to the proposed assumption about the mobility of an additive element in the soot globule, the size of the forming nanoparticle should depend on the size of the soot particle and total content of the additive in it.

**Conclusions**

It has been experimentally shown that kinetics of carbon–metal composites formation during electric-arc spraying differs for metals forming various types of carbides. For carbides forming their own crystal structure, formation of hollow spherical structures is characteristic. For the elements that do not form stable carbides and form metal-like carbides, formation of bulk nanoparticles occurs. The described effect is explained by the ability of nanoparticle to grow inside the soot globule during its cooling due to mobility of the additive element. According to the proposed assumption, the morphological features can be expected in the case of spraying the composites with elements forming salt-like (Li, Na, K, Rb, Cs, Fr, Be, Ca, Sr, Ba, Ra, Sc, Y, La) and covalent (B) carbides.

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