Composite tin/carbon material synthesis by arc discharge at different helium pressures

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Abstract. Composite Sn + C electrodes were sputtered using an electric arc method. As a result, materials representing spherical tin nanoparticles packed in a carbon matrix were synthesized. The carbon matrix reliably separates the nanoparticles, preventing them from contacting and coagulating, which preserves their size. The structure of the material was studied in detail by transmission electron microscopy. The sizes of tin nanoparticles were described by a log-normal distribution, and the average size depended on the pressure of the buffer gas. The carbon structure was studied by Raman spectroscopy. It is established that tin and carbon structures are related to each other, and the processes of condensation of tin vapor and agglomeration of the carbon structure affect each other.

1. Introduction
Electric arc discharge is actively used in the field of nanoparticle synthesis. In 1990, Kratschmer published an article on the experimental detection of a fullerene carbon structure in soot produced by the electric arc method [1]. After that, this method has been developed and now it can be used to produce up to 15% of fullerenes in the products of synthesis [2]. The electric arc method also received several branches of development in the direction of synthesis of carbon nanotubes [3], graphene structures [4], and composite materials [5-7], which are metallic or carbide nanoparticles packed in a carbon matrix. This carbon matrix prevents particles from contacting each other, coagulating and increasing the size of nanoparticles. Saito collected similar material from the produced cathode deposit [5]. In his works, he concluded that this material structure is formed due to saturation of hot metal particles with carbon, which exude on the surface during cooling. Scott and Madzhetich found similar structures in the material deposited on the cold walls of the reactor [6]. Seraphin, on the other hand, proposed a mechanism for the formation of such structures through the stage of formation of a quasi-liquid metal-carbon cluster [7]. Earlier tin nanoparticles packed in a carbon matrix have already been obtained by arc discharge at Pt/CeSnOx catalyst synthesis [8]. But the mechanisms of Saito and Seraphin cannot explain the formation of tin particles packed in the carbon matrix, since the solubility of carbon in tin is less than 2*10⁻²%, which would result in a carbon shell around 10nm tin particles with a thickness less than an atom as a result of cooling [9]. On the other hand, the wettability of graphite with liquid tin is very small [10], which makes it impossible to form a single quasi-liquid carbon-tin cluster. Thus, in order to understand the processes of formation of a nanomaterial consisting of tin particles closed by a carbon shell, additional research is needed.
This work reveals new experimental data on the processes occurring during heterogeneous condensation of tin and carbon vapor, which leads to formation of the structure of ball-shaped tin nanoparticles packed in a carbon matrix.

2. Experimental setup
Electro arc synthesis was carried out using the reactor described in detail in [11]. The reactor consisted of a sealed chamber in which there are two electrodes. The cathode having a cylindrical shape with a diameter of 20 mm could move along its axis and the axis of discharge, respectively. The anode was rigidly fixed to the construction of the reactor; it was a cylindrical graphite rod with a diameter of 8 mm with a coaxial cylindrical cavity with a diameter of 6 mm, which was tightly filled with a mixture of powders of graphite and tin. This mixture had the composition Sn/C = 1/2. The reactor chamber was pre-evacuated to a pressure of $10^{-2}$ Torr, purging with helium twice, and then filled with helium to a predetermined pressure. The determined pressures of the buffer gas were $10^{-2}$, 3, 6, 12, 25, 50, 100, 200 Torr. The electrodes were connected to a DC source. An electrical discharge was ignited by contacting the electrodes. Next, the electrodes were separated by a distance providing a voltage of 25V. Spraying anode material led to anode consumption. At the same time, the distance between the electrodes was maintained at the same value by controlling the arc voltage and the movement of the cathode. The sprayed material of the anode in the gas phase flew into the interelectrode gap, partially deposited on the cathode, and the remaining part flew out from the interelectrode gap in the form of a turbulent fan-shaped jet. This jet expanded and mixed with the buffer gas, which led to its cooling. The processes of condensation, agglomeration and crystallization occurred, which led to the formation of nanostructured material, which was deposited on a water-cooled screen. The deposited material was then collected from the screen for structural analyzes.

3. Results and discussions
As shown by TEM study, the material consists of spherical tin nanoparticles surrounded by a carbon matrix (Figure 1(a)). The carbon matrix prevents the contact of tin particles with ambient air, protecting them from oxidation, and prevents the contact of particles with each other, thereby preventing coagulation and growth of the size of tin nanoparticles. The particle size distribution is well described by a log-normal distribution (Figure 1(b)), while the average size depends on the pressure of the buffer gas at which the synthesis was carried out. So, at pressure less than 12 Torr, particles are synthesized with an average size of about 20-25 nm. At pressures from 12 to 200 Torr, the average size increases linearly from 16 to 32 nm (Figure 2).

![TEM-image](image1.png)  
![Size distribution](image2.png)

**Figure 1.** TEM-image (a) and size distribution (b) of the Sn nanoparticles encapsulated in the carbon matrix in the material synthesized at 12 Torr.
Figure 2. (a) Lognormal distributions of the tin nanoparticles in the materials synthesized at different buffer gas pressure, (b) tin nanoparticle average size dependence on buffer gas pressure.

Raman spectra of synthesized materials have characteristic peaks corresponding to the carbon structure: D-peak in the region of 1340 cm⁻¹, G - peak in the region of 1580 cm⁻¹, 2D-peak in the region of 2680 cm⁻¹ (Figure 3(a)). Also, some spectra contain peaks corresponding to vibrations of air molecules (1128 cm⁻¹, 2103 cm⁻¹, 2170 cm⁻¹, 2332 cm⁻¹). The G-peak corresponds to the vibrations of the bonds of sp²-hybridized carbon atoms. D-peak corresponds to respiratory modes of hexagonal carbon rings, and appears only at the edges and defects of a graphite structure. The 2D peak is an overtone of the D peak for graphitic materials and it can be referred to the features of graphene due to D peak is forbidden for ideal graphene structure that has only 2D peak. The intensity ratio of the peaks D to G (ID / IG) characterizes the defectivity of the carbon structure. The value of this coefficient varies in the range from 1.6 to 2.8 for materials synthesized at different pressures of the buffer gas, which characterizes the carbon structure as highly disordered. Nevertheless, it can be concluded from dependence of ID/IG on the pressure of the buffer gas (Figure 3(b)) that with an increase in the pressure of the buffer gas from 25 to 200 Torr, the order of carbon structure worsens. At pressures less than 12 Torr, the carbon structure has the worst order.

Comparing the results of the structural analysis of tin and carbon structures, it can be noted that there is some correlation between the dependences of the size of tin nanoparticles and the order of the carbon structure, which implies that the process of condensation of tin vapor and formation of tin nanoparticles, and the process of rearrangement and ordering of the carbon structure are interrelated.
Conclusion
As a result of electric arc sputtering of a composite Sn/C electrode in a helium medium, nanomaterials consisting of spherical tin nanoparticles packed in a carbon matrix were synthesized. The distribution of tin nanoparticles in size is well described by a lognormal distribution. The average size of nanoparticles depends on the pressure of the buffer gas. Up to 12 Torr, the average size of nanoparticles lies in the range of 19–23 nm, with an increase in pressure from 12 to 200 Torr, the average size of nanoparticles increases linearly with the pressure of the buffer gas from 16 to 32 nm. The carbon structure in the synthesized materials has an ID/IG ratio in the Raman spectra in the range from 1.6 to 2.7, which indicates a strong disordering of the carbon structure. The ordering of the carbon structure also depends on the pressure of the buffer gas. It has been established that an increase in pressure from 25 to 200 Torr leads to deterioration in the order of the carbon structure. The dependence of the average size of the synthesized tin nanoparticles correlates with the dependence of the intensity ratio of the peaks ID/IG on the Raman spectra. Thus, it has been established that the processes of formation of tin nanoparticles and carbon structure are related to each other.

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