Sn filament formation under arc discharge sputtering of SnO2/C electrode

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Abstract. As a result of electric arc sputtering of a composite SnO2/C electrode in a rarefied helium medium, the formation of tin fibers reaching a length of more than 20 μm was discovered. The length of the formed fibers depends on the distance from the arc discharge to the area of deposition on a graphite substrate. The formation of tin fibers is influenced by such factors as the temperature of the gaseous medium and the partial pressure of tin vapor.

1. Introduction
The electric arc synthesis method is common in the field of various composite nanomaterials. The method has been intensively developed after Kratchmer work on the synthesis of fullerenes [1]. Then this method was studied by the work of Iijima [2], who discovered the formation of carbon nanostubes on catalyst particles, the work of Majetich [3] and Saito [4], who studied the formation of metal and carbide nanoparticles in conjunction with the carbon matrix. Relatively recent works are also known where the structure of graphene is obtained in an arc discharge [5]. Arc spraying of tin-containing electrodes showed that the resulting materials are spherical tin nanoparticles packed in a carbon matrix [6]. However, the collection of synthesis products at various distances showed that elongated tin structures also form near the arc discharge. Other researchers spraying tin oxide in a carbon monoxide environment found that carbon nanofibers also form under certain conditions [7]. Other researchers describe the electric arc synthesis of tin nanofibers during electric arc evaporation of a tin anode in a mixture of argon and methane [8].

It is also known that indium and tin oxide nanofibers grow as a result of vapor-solid and vapor-liquid-solid growth mechanisms on In, Pt, Pd, Au catalysts during the thermal evaporation of precursors in a rarefied argon medium. As a result, nanofibers of more than 2 μm in length are formed [9]. Tin fibers are also grown using electrodeposition from a liquid electrolyte using a nanoporous polycarbonate membrane. The sizes of such fibers reach 2 μm in length and 100 nm in thickness [10].

In this work, we study the formation of tin fibers during electric arc spraying of a composite SnO2/C anode in a rarefied helium medium.

2. Experimental
2.1. Arc discharge synthesis
Plasma-chemical synthesis was carried out using an electric arc reactor presented in Figure 1. Two electrodes are located in the hermetic chamber of the reactor. The cathode is a graphite tablet with a diameter of 20 mm which can move along the axis. The anode is a cylindrical graphite rod with a diameter of 8 mm, in which an axial hole is made, densely filled with tin oxide powder. The reactor
chamber is filled with helium with a pressure of 12 Torr. An electric arc with a current strength of 120A is ignited between the electrodes, which leads to the evaporation of the anode components and the formation of a vapor flow from the interelectrode gap. Moving away from the discharge, the vapor cools, condenses, which leads to the formation of various structures. A substrate in the form of a graphite cylindrical rod is installed perpendicular to the axis of the electrodes in the reactor chamber, which makes it possible to deposit material at various distances from the discharge.

![Figure 1](image1.png)

**Figure 1.** A model of the arc discharge reactor (a) and a photograph of the cathode and the graphite substrate in the reactor chamber.

2.2. **Structural analysis**

After synthesis, the graphite substrate was removed from the reactor and was studied in various areas shown in Figure 2 using scanning electron microscopy (SEM). SEM was carried out in the mode of detection of secondary electrons (SE) and in the detection mode of backscattered electrons (BSE). SE provides a more volumetric picture of the topology of the material, and BSE provides information on the distribution of heavy and light elements in the material. So, heavier elements appear on SEM images as light areas.

![Figure 2](image2.png)

**Figure 2.** Positions of analyzed areas on the graphite substrate.
3. Results and discussions

Figure 3. SEM images in SE and BSE mode of material on various areas of substrate and length distributions of Sn filaments.
The areas of the graphite substrate on which the SEM analysis was performed are shown in Figure 2. SEM images of the material structure are shown in Figure 3. The first area corresponds to the closest region to the arc discharge on a deposit on the graphite substrate. The material is a globular carbon structure. Tin is practically absent in this area. The second area is farther from the arc discharge. Carbon takes on a more branched structure. Tin appears as spherical particles that are clearly visible in BSE mode. In the third and fourth areas, tin structures take the form of fibers growing from a common center. Further, when removed from the discharge in the fifth area, the resulting tin fibers have a shorter length. In the sixth region, only rare embryos of tin fibers are observed. And in the seventh area, the tin structure again takes on a spherical shape. Energy dispersive X-ray analysis of the all areas of the deposited material showed that the composition contains oxygen of around 5wt% independently of presence of tin. It can be explained by air adsorption and the formation of oxygen-containing radical groups on the materials surface. Tin fibers located on edges of the structure allow for measuring the length. 

Figure 4 shows The dependence of the average and maximum length of tin fibers on the distance from the center of the arc discharge is shown in Fig. 4. As it can be seen, at a distance closer than 15 mm from the discharge, no fibers are formed, but through a small step there is a big jump in the growth of tin fibers. Further, when moving away from the discharge, the fiber length decreases smoothly, and tin fiber structures are not observed at distances of more than 30 mm.

![Figure 4](image_url)

**Figure 4.** Dependences of Sn filament average and maximum length on distance from arc discharge axis.

This behavior is explained by physical processes occurring in the reactor chamber. Vapors of the evaporating electrode fly out of the interelectrode gap. When removed from the discharge and mixed with buffer gas, the vapor cools. At the same time, at sufficiently close distances to the discharge, a sufficiently hot temperature provides condensation of carbon, but tin still remains in a gaseous state. When moving away from the discharge, tin begins to condense into liquid droplets, which are deposited on a graphite substrate. Radiation from the discharge and gas temperature provides a liquid state of tin, which merges and combines into large spherical particles. Further, when moving away from the discharge, the gaseous temperature decreases and a graphite substrate with a high heat capacity provides crystallization of tin deposited on its surface. However, tin still exists in a liquid state in helium due to the high gas temperature. In this case, tin is also present in the gaseous state.
according to the dependence of saturated vapors on temperature [11]. The deposition of tin vapor on tin solid particles initiates self-catalytic fiber growth by the VLS mechanism. With farther distance from the discharge, the gas temperature decreases and the pressure of saturated tin vapor decreases, which leads to the formation of tin fibers of a shorter length. At a sufficient distance from the discharge, the processes of condensation of tin in helium medium have been almost completed and as a result tin spherical particles are deposited on a graphite substrate.

Conclusions
An electric arc discharge leads to the evaporation of the anode consisting of graphite and tin oxide. Vapors of materials form a flow from the interelectrode gap, in which the vapors are mixed with a buffer gas, cooled, and where the processes of condensation and formation of the material structure take place. The material deposited in different areas of the graphite substrate located at various distances from the arc discharge has a different structure. Near the arc discharge, the tin structure has the form of spherical particles. When moving away from the discharge on the graphite substrate, tin fibers are detected, the length of which can reach more than 20 μm. The length of the fibers decreases with distance from the arc discharge. And at distances of more than 30 mm, there are practically no tin fibers on the graphite substrate, and the structure takes the form of spherical particles. The formation mechanism of such structures is explained by vapor-liquid-solid growth, the conditions for which change with distance from the arc discharge. So, at distances less than 15 mm, the gas temperature and radiation from the discharge do not allow tin to crystallize on the surface of the graphite substrate. At distances greater than 15 mm, the gas temperature decreases, and the heat-capacitive graphite substrate provides crystallization of the tin deposited on it. Subsequent deposition of tin vapor on crystalline tin particles leads to the appearance of a liquid cap and vapor-liquid-solid growth of the structure of tin fiber. With farther distance from the arc discharge, both the gas temperature and the partial pressure of tin vapor decrease, which leads to the formation of fibers of shorter length. At distances greater than 30 mm, tin fibers on the graphite substrate are practically not observed.

Acknowledgments
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