

The morphology of carbon-metal composite synthesized in arc discharge

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Abstract. The phase state of nanoparticles and function of distribution by size of particles, formed at joint electric arc spraying of metal (Ni/Cu/Ti/Pt/Zr) - carbon electrode, is studied. It is shown that the metal and carbide nanoparticles with the size of 2-9 nm are formed in the carbon matrix at spraying. When annealing the metal-carbon composites, the metal-containing nanoparticles oxidize and coagulate, forming the agglomerates of 100 nm or more.

1. Introduction

The arc discharge is one of the oldest, well-studied and promising methods of obtaining the nanomaterials [1], [2]. In particular, fullerenes were discovered in the arc discharge by Kretschmer in 1990 [3], and the CNT were firstly discovered at carbon deposition in the arc discharge by Iijima in 1991 [4]. Usually, in plasma of an arc discharge gap, the temperature varies from 5000 K in the channel center to 1000 K at the periphery [5]. Under the conditions of arc discharge, metal and carbon atomic spraying, followed by condensation at expansion to the buffer gas, takes place. Currently, when synthesizing nanoparticles in the arc discharges, the experimental efforts are focused on the study of mechanisms related to anode sputtering, deposition of material on the cathode, and current-voltage characteristics of the anode arc discharge [6], [7], [8], [9], [10], [11], and [12].

Due to simplicity of practical implementation of the plasma-arc method, the expansion of its capabilities is important for both scientific research and practical application. Synthesis of nanomaterials in the electric arc occurs under the non-equilibrium conditions. Moreover, the synthesis conditions (electric parameters of the arc, buffer gas and its pressure, geometry and composition of electrodes, etc.) influence kinetics of the synthesis. Therefore, the theoretical approaches to the study of processes occurring at synthesis are hampered, and the experimental studies go top.

In this work, we study the materials, formed in the gas phase at combined electric arc spraying of metal-graphite rods in the arc discharge. The powders of Ni, Cu, Ti, Pt, and Zr metals were used as the additions to the graphite electrode.

2. Experimental setup and methods

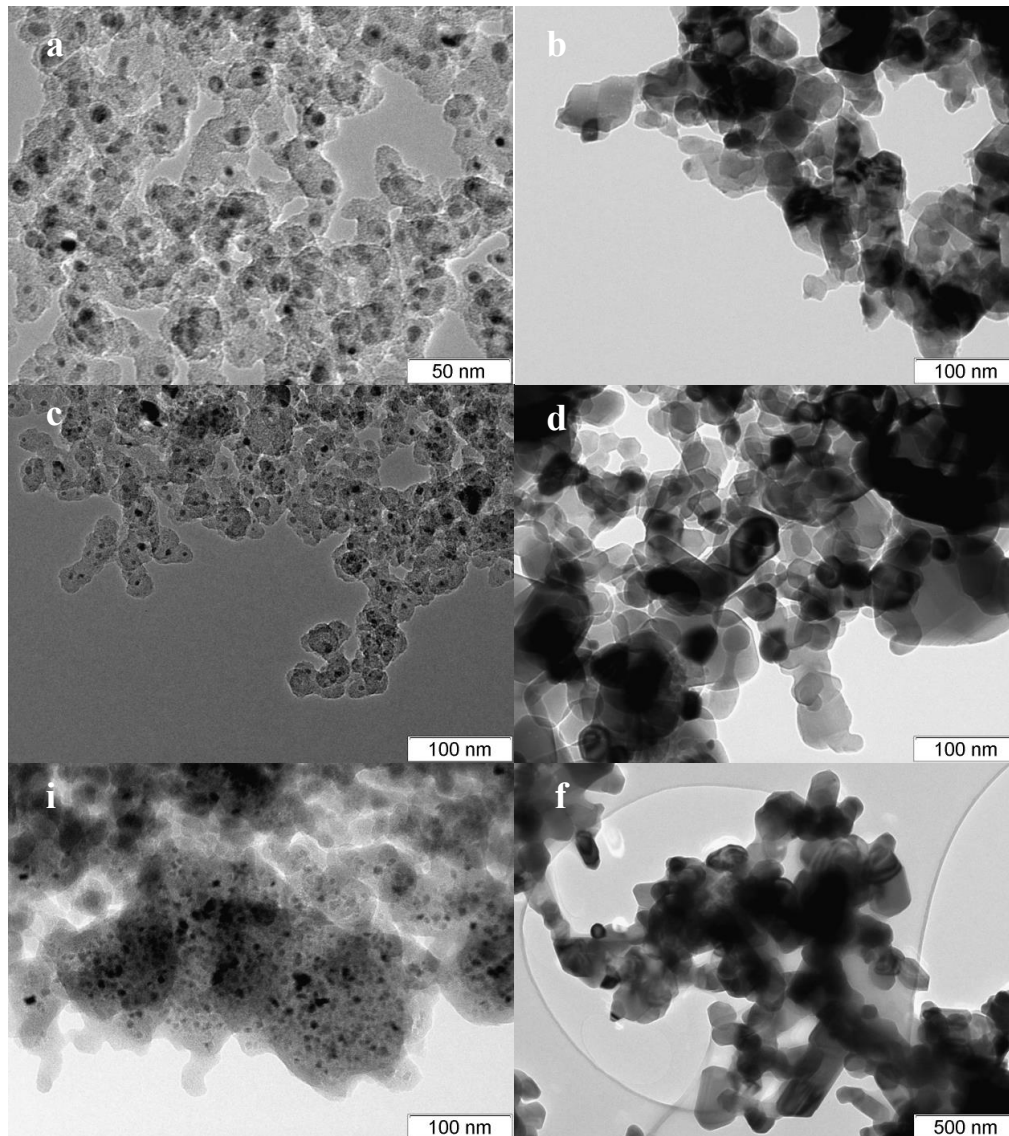
The metal-carbon black was synthesized in helium under the pressure of 25 torr and discharge current of 100 A, using the setup described in detail in [11]. The mole fraction of metal in the sprayed



electrode was the same for all metals and equaled 6.4%. The synthesized material was annealed in air at 950°C during 2 hours. The materials were analyzed by the methods of transmission electron microscopy (JEOL – 2010) and X-ray diffractometry (Siemens D500).

3. Results

The TEM images of synthesized materials are shown in Fig. 1. The nanoparticles of metals integrated into the carbon matrix are obvious for each synthesized material. The images of materials annealed in the oxygen medium are also shown in Fig.1.



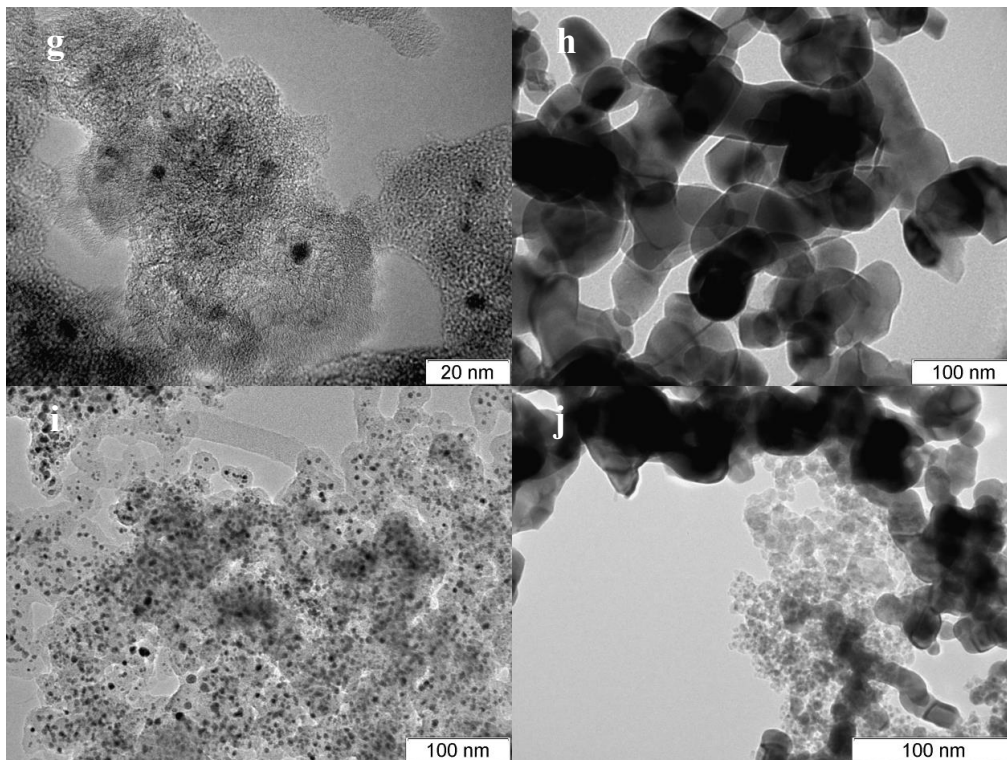


Figure 1. TEM images of Me-C composites. a) Cu-C, b) Annealed (a) at 950°C, c) Ni-C, d) Annealed (c) at 950°C, e) Ti-C, f) Annealed (e) at 950°C, g) Zr-C, h) Annealed (g) at 950°C, i) Pt-C, j) Annealed (i) at 950°C.

The function of size distribution of metal particles was measured by the method of statistical processing of a large array of TEM images. The data were described by lognormal distribution that corresponds to the function of cluster size distribution at agglomeration in the gas phase. After annealing, the nanoparticles fused, forming the agglomerates of the larger particles with the size of about 100 nm and higher; therefore, annealing these composites data does not allow obtaining the nanoparticles of metal oxides.

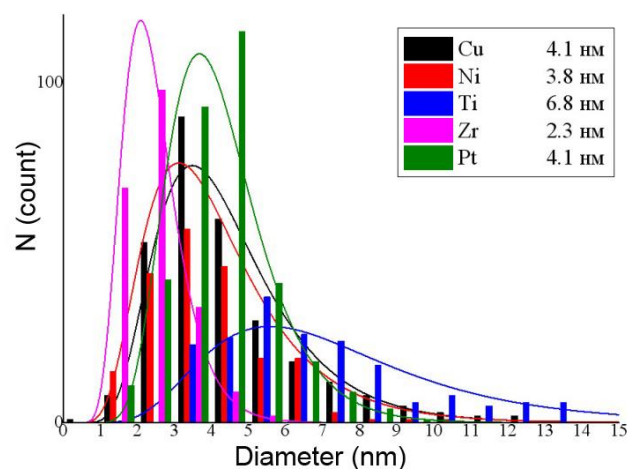


Figure 2. Size distribution of nanoparticles obtaining at sputtering the composite electrodes in the arc. The corresponding approximations by the lognormal distribution are presented with indication of the median.

The phase composition of synthesized samples is presented in Table 1; it can be seen that the crystalline phase is not observed in every sample. Formation of oxides of various stoichiometry and phase composition is characteristic of nanoparticle oxidation.

Table 1. Phase structure of samples.

| Element composition of samples | Crystalline structure | Crystalline structure after annealing |
|--------------------------------|-----------------------|---|
| Cu-C | none | Cu ₂ CO ₅ (P 121/a1) Cu ₄ O ₃ (I 41/amd) |
| Ni-C | none | None Ti ₄ O ₇ (A-1(-1)) |
| Ti-C | TiC (Fm-3m) | TiO ₂ (Pbca) Ti ₆ O ₁₁ (-1(1)) |
| Zr-C | ZrC (Fm-3m) | ZrO ₂ (P 121/c1) ZrO ₂ (P bcm) |
| Pt-C | Pt (Fm-3m) | Pt (Fm-3m) |

5. Conclusions

The method of electric arc spraying allows obtaining the nanoparticles of various metals with a narrow size distribution function. The absence of impurities (except carbon) makes it promising in comparison with the methods of solution chemistry. Additionally, in some applications, such as super capacitors, lithium-ion batteries, and fuel cells, it is necessary to obtain metal nanoparticles on a base matrix with high porosity. Various types of activated carbon are commonly used as these matrices. Thus, the proposed method can be considered as the one-stage synthesis of metal-carbon catalyst. Another important advantage of this technology is the possibility to get the joint composites of several metals.

In these works, the experimental data on the synthesis of metal-carbon composites were obtained. We investigated the size distribution functions for various metals in the carbon matrix. The average size of the formed nanoparticles is in the range of 2-9 nm. It is shown that for all studied metals, when the carbon matrix is removed, nanoparticles sinter and form the larger oxide particles of 100 nm and higher. We studied the phase state of particles; it is shown that when spraying the Pt electrodes, the particles of metal platinum are formed in the carbon matrix. When spraying Zr and Ti, the carbide particles are formed in the carbon matrix. When spraying Ni and Cu, the metal or carbide particles have no crystal structure.

6. Acknowledgements

The reported study was funded by RFBR, according to the research project No. 15-38-20454 mol_a_ved.

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