GAS-JET SYNTHESIS OF SILVER–POLYMER FILMS


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A new method of gas-jet deposition of metal-polymer composites with simultaneous deposition of polymer matrices and silver clusters from two gas-dynamic sources is presented. Specific features of cluster deposition and the properties of composite films are described. Results on the antibacterial effect of silver–polymer composites on stock cultures of various bacteria are reported.

Key words: gas-jet deposition, metal-polymer composites, clusters, x-ray photoelectron spectroscopy, infrared spectra.

Antibacterial activity of silver has been known since ancient times. The recent interest in silver agents is caused by the necessity of solving problems of antibiotic applications (habituation of microorganisms to antibiotics, deletion of useful bacterial populations, etc.). The use of media containing ions and nano-sized clusters of silver turned out to be extremely effective. Most methods of cluster synthesis are based on chemical transformation of silver nitrites to the final product containing silver clusters 5–20 nm in size. These clusters are deposited onto surfaces by various methods. Environmentally friendly “dry” vacuum technologies based on re-condensation of the initial products in vacuum are available [1, 2].

The present paper describes a new method: deposition of silver clusters onto a polymer matrix from supersonic jets, as it was realized in [3, 4]. One variant of this method is deposition of silver and polytetrafluoroethylene (PTFE) as a polymer matrix whose precursor is tetrafluoroethylene (C₂F₄). PTFE is chosen as a matrix material owing to its high stability to thermal and chemical effects and by its biological compatibility. Implementation of the method required creation of two high-temperature sources: for formation of a high-temperature C₂F₄ flow and for evaporation of silver in the argon environment. Simultaneous deposition of the polymer and silver clusters onto a target placed alternatively under one flow and the other was performed (Fig. 1).

The precursor gas (C₂F₄) acquires the initial state (stagnation parameters) in a reactor where PTFE decomposition occurs at a pressure of several millimeters of the mercury column and at a stagnation temperature T = 500–700°C. The flow of PTFE decomposition products becomes expanded in a sonic nozzle (nozzles 3 and 10 mm in diameter were used). Deposition of the metal–polymer film is performed on the target placed into supersonic jets of C₂F₄ and argon with silver vapors.

A steady flow of a mixture of argon and silver vapors is formed by a high-temperature source at a stagnation temperature T = 900–1000°C. The jet is formed behind a conical supersonic nozzle with a total apex angle of 54°, throat diameter of 3 mm, and geometric Mach number M = 10.5; the distance between the nozzle and the target is L = 15–20 mm. Typical mass flows of C₂F₄ and argon are approximately 0.1 g/sec; the mass flow of silver vapors in the argon flow is approximately 10⁻⁴ g/sec.

To find the specific features of cluster formation, we studied the influence of the distance between the nozzle and the target on the character of silver deposition with the polymer being absent.
Fig. 1. Setup for deposition of the silver-polymer film: 1) PTFE reactor; 2) electric motor; 3) rotating drum; 4) Ar–Ag reactor.

Fig. 2. Thickness of the deposited silver film versus the distance between the nozzle and the target at $T = 950^\circ C$, $P = 333.3$ Pa, and $t = 15$ min.

Figure 2 shows the film thickness $h$ as a function of the distance $L$ at the deposition time $t = 15$ min. This figure reflects the complicated dependence of the deposition rate on the configuration of the jet flowing around the target in the presence of peripheral jet zones formed owing to the influence of the boundary layer in the nozzle. It follows from Fig. 2 that the film thickness decreases with distance from the nozzle because of the decrease in the specific mass flow of silver.

Let us consider the process of obtaining silver clusters, which form the structure of the resultant film. It is important to find the effect of the deposition conditions on cluster characteristics. For a constant stagnation temperature $T = 940^\circ C$ and the distance $L = 17$ mm, Fig. 3 shows the cluster size averaged over the entire spectrum of clusters as a function of the total stagnation pressure of the mixture of argon and silver vapors. The dependence of the cluster size on stagnation temperature for $L = 19$ mm and $P = 333.3$ Pa is plotted in Fig. 4. Important information needed to solve various application problems is not only the cluster size, but also the effect of flow parameters on the clusters.

Under the conditions considered, the range of cluster sizes is fairly wide: from 10 to 130 nm. To shift the distribution function toward smaller mean cluster sizes (down to 5–20 nm), it is necessary to optimize the deposition conditions by changing the stagnation parameters and the working area geometry.

Additional studies were performed to determine the mechanism of formation of silver nanosize particles (nanoparticles) during gas-jet deposition. It was assumed that five places of silver nanoparticle formation are possible: 1) in the settling chamber ahead of the nozzle throat; 2) on the surfaces ahead of the nozzle throat; 3) on the surfaces of the supersonic nozzle; 4) in the expanding supersonic flow; 5) directly on the target surface.