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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 (C_2F_4). 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 C_2F_4 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 (C_2F_4) 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 C_2F_4 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 C_2F_4 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.

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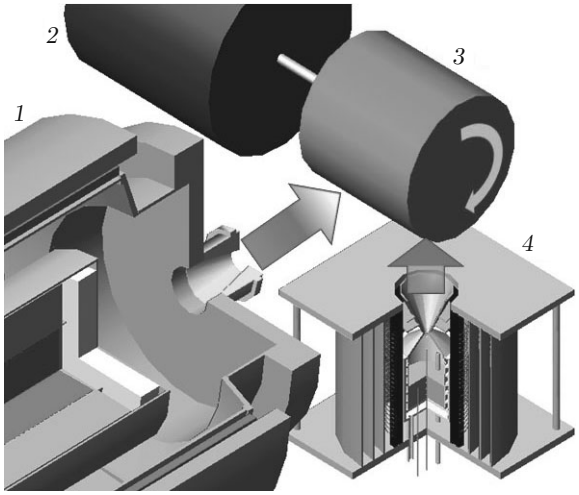

Fig. 1. Setup for deposition of the silver–polymer film: 1) PTFE reactor; 2) electric motor; 3) rotating drum; 4) Ar–Ag reactor.

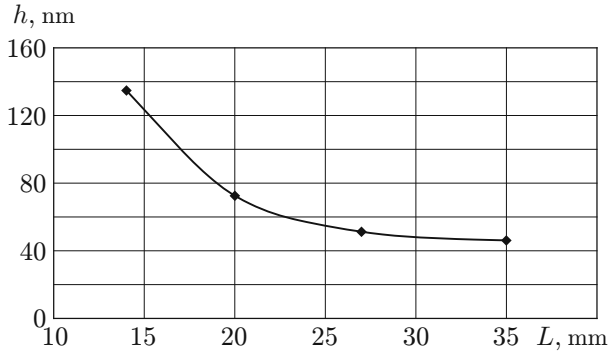

Fig. 2. Thickness of the deposited silver film versus the distance between the nozzle and the target at $T = 950^{\circ}$C, $P = 333.3$ Pa, and $t = 15$ min.

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. Two

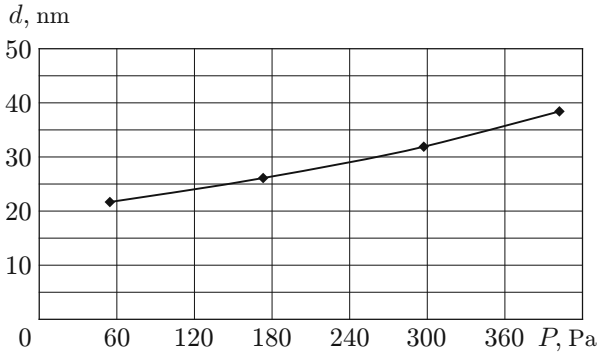

Fig. 3. Cluster size versus pressure in the Ar–Ag mixture at $L = 17$ mm and $T = 940^{\circ}$C.

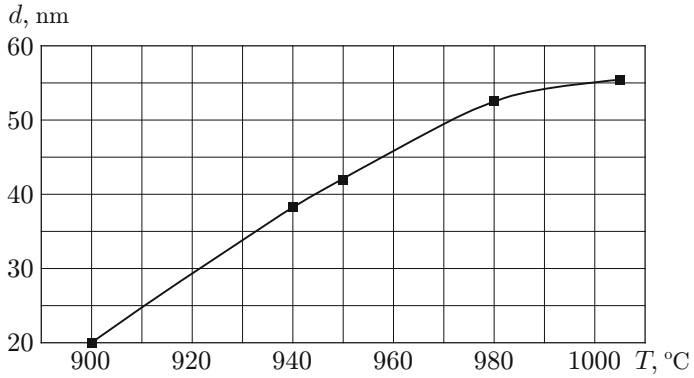

Fig. 4. Cluster size versus stagnation temperature at $L = 19$ mm and $P = 333.3$ Pa.

small-size (4×4 mm) copper grids covered with a thin carbon film were introduced into the supersonic part of the jet. The carbon film prevents migration of silver nanoparticles and clusters over the target surface, thus, almost eliminating growth of nanoparticles on the surface due to migration.

The main idea of the experimental study was as follows. If silver nanoparticles are formed in the supersonic part of the jet, then nanoparticles with different distribution functions in terms of the particle size are deposited onto the surface of each copper grid, because the grids are located at different distances from the nozzle. If silver nanoparticles are formed from the vapor on the target surface, we obtain a thin silver film, which is continuous or consists of several islands. If clusters are formed in the settling chamber or on the nozzle surface, they are incident onto the target with an identical size distribution on each of them. The coating on the copper grids was analyzed by means of transmission electron microscopy (TEM). The TEM photographs of the grid surfaces are shown in Fig. 5. An analysis of these photographs shows that the size distributions of nanoparticles deposited on different targets are similar to each other. Therefore, we can conclude that the clusters are formed in the settling chamber or on the nozzle surface.

Silver–fluoropolymer films were obtained in the setup shown in Fig. 1. The structure of the resultant film is shown in Fig. 6 for the case of the concentration of silver atoms in PTFE equal to 74%.

Specific features of the atomic composition and structure of metal–polymer films and the states of silver atoms were studied with the use of infrared (IR) spectroscopy and x-ray photoelectron spectroscopy (XPS). IR spectra were obtained in the frequency range $\nu = 400$–2000 cm^{-1} with the Scimitar FTS 2000 Fourier spectrometer and in the frequency range $\nu = 100$–600 cm^{-1} with the Vertex 80 Fourier spectrometer. The samples were prepared in the form of pellets (for the range $\nu = 400$–2000 cm^{-1}) or in the form of a polyethylene powder (for the range $\nu = 100$–400 cm^{-1}). IR spectra of silicon-based films were obtained with the signal from the silicon surface being ignored. Figure 7 shows the IR spectra of the initial PTFE and PTFE-based fluoropolymers in the form of the absorption intensity I (in arbitrary units) in different ranges of the spectrum of ν.

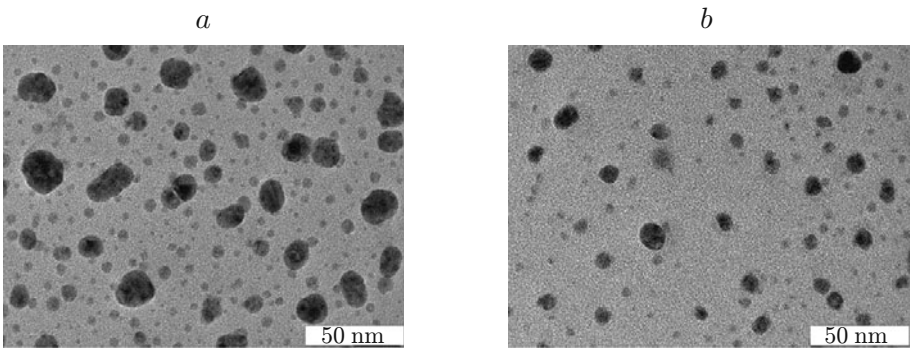

Fig. 5. TEM photographs of the copper grid surface with deposited silver nanoparticles: (a) surface of the grid located closer to the nozzle exit; (b) surface of the grid located farther from the nozzle exit.

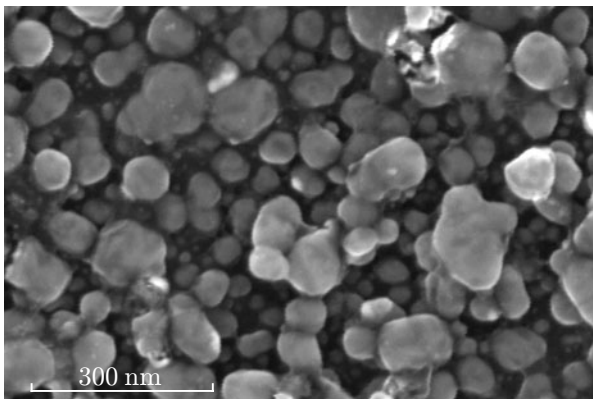

Fig. 6. Structure of the silver–fluoropolymer film with the silver concentration equal to 74%.

The most intense bands in the spectrum in the range $\nu = 1100$–1300 cm^{-1} refer to symmetric and antisymmetric stretching vibrations of —CF_2 groups and —C—C—PTFE chains; the bands in the range $\nu = 500$–700 cm^{-1} correspond to deformation vibrations of —CF_2 groups; finally, the band at $\nu = 203$ cm^{-1} refers to out-of-plane vibrations of these groups [5]. At $\nu = 1785$ cm^{-1} and $\nu = 293$ cm^{-1}, the IR spectra of the powder and the film display additional weak bands, which are not observed in the spectrum of the initial PTFE material. Similar bands are observed in the spectrum of fine-grain PTFE [5]. It was demonstrated by the method of magnetic resonance [5] and quantum-chemical calculations [6] that the first band corresponds to the olefin end groups —CF═CF_2, and the second band corresponds to rocking vibrations —CF_3 groups. The presence of these bands confirms depolymerization of PTFE chains and formation of oligomers. IR spectra of metal-based composites do not contain bands of olefin groups and —CF_3 groups, which can be explained by the weak intensity of the spectra of these samples or by possible interaction of the metal with the polymer matrix.

The x-ray electron spectra were measured by the Specs spectrometer (Germany) with excitation of the AlKα line of the x-ray tube by monochromatic radiation. To eliminate the effects of inhomogeneous charging of the samples, they were subjected to irradiation of low-energy electrons from a special source. The line C1s on the surface of the hydrocarbon film is observed at the photoelectron energy $E = 285$ eV, the lines C1s and F1s of the polymer matrix are observed at $E = 292.5$ and 687.9 eV, which corresponds to signals of carbon and fluorine in the initial PTFE sample.

The spectrum of Ag3$d_{5/2}$ shows that silver particles on the silicon substrate in the absence of PTFE are only in the metal state ($E = 368.3$ eV).

It is rather difficult to study the state of silver particles in the polymer matrix because of inhomogeneous charging of the samples; for this reason, the lines of Ag3$d_{5/2}$ have abnormally large positive shifts ($E = 370.2$–371.5 eV). This effect is caused by the absence of the electric contact between the silver particles on the surface and testifies that the silver particles are encapsulated in the polymer matrix.

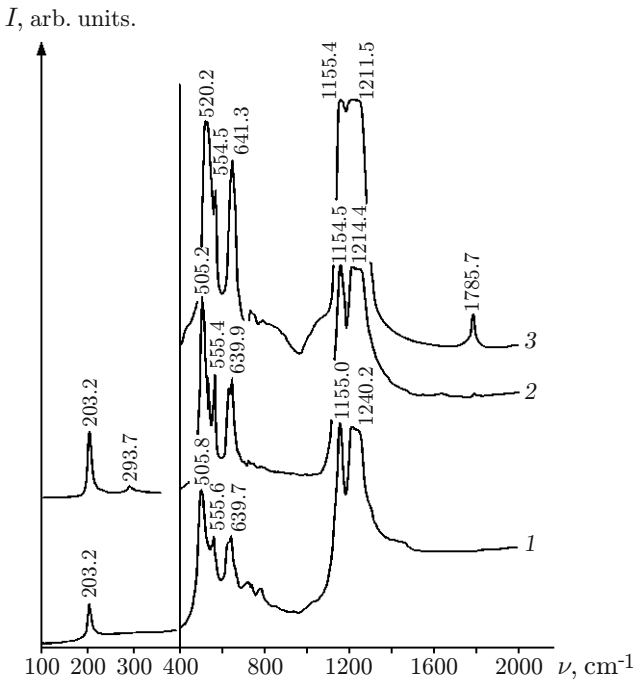

Fig. 7. Infrared spectra: 1) initial PTFE; 2) deposited PTFE (powder); 3) PTFE film on the silicon surface.

TABLE 1

Results of an Experimental Study of the Effect of the Materials Obtained on the Growth of Several Pathologic Bacteria

Microorganisms	Titres of microorganisms after processing (CFU/ml)			
	Ag–fluoropolymer 1	Ag–fluoropolymer 2	Ag	Reference group
Escherichia coli	$1.7 \cdot 10^6$	$2.6 \cdot 10^6$	$2.3 \cdot 10^8$	$3.0 \cdot 10^8$
Pseudomonas aeruginosa	$4.6 \cdot 10^6$	$4.7 \cdot 10^6$	$6.0 \cdot 10^8$	$7.4 \cdot 10^8$
Salmonella typhimurium	$4.4 \cdot 10^8$	$2.8 \cdot 10^8$	$3.3 \cdot 10^8$	$1.0 \cdot 10^9$

After elimination of inhomogeneous charging of the samples by means of their irradiation by an electron beam, it was found that the line of Ag$3d_{5/2}$ is a superposition of the lines of several phases: particles of metal silver and products of its interaction with polymer matrix atoms, presumably in the form of silver oxides and fluorides ($E = 367.6$ eV) where the concentration of silver ions is approximately 15%.

We studied the antibacterial effect of the materials obtained on pathogenic bacteria *Escherichia coli, Pseudomonas aeruginosa*, and *Salmonella typhimurium*. Suppression of the growth of microorganisms was estimated on the basis of the optical density and biological titer in a liquid medium in the presence of samples containing silver clusters, and comparisons with a reference group were made. The results obtained are summarized in Table 1 (CFU means colony-forming units).

The experimental study showed that Ag–fluoropolymer samples obtained at different times ensure a more significant bacteriostatic effect than the use of silver without the polymer. The stock-culture-based dependence of this effect of silver-containing samples was observed. The bactericide effect of the samples containing silver clusters in the polymer matrix was found to be much more pronounced than that of the samples containing pure silver.

The results of studying various properties (including bactericide properties) of silver nanocomposites and fluoropolymers testify that the use of the gas-dynamic method of obtaining metal–polymer materials is fairly promising and offers prospects of using these materials in various applications, in particular, in medicine.

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