

Formation of Copper-Containing Fiber Composite Materials for Microwave Radiation Screens

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Abstract—A new method is proposed for the synthesis of radio-wave-absorbing metal-containing composite materials based on polyacrylonitrile fibers. The interaction of electromagnetic radiation with samples of machine-knitted fabric made of copper-containing fibers has been studied in an 8–12 GHz frequency range. The chemical composition of the synthesized materials has been determined. The possible applications of new materials and related structures for the screening of stray electromagnetic radiation of data-processing devices and electronic components and suppressing negative effects of high-frequency electromagnetic fields are considered.

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Humans and animals have always subjected to the action of natural electromagnetic radiation, to which their organisms have adapted during the evolution. The appearance of an additional background related to the development of radio communications and various systems for the transmission and remote processing of data, including television, mobile phone communications, radio sensing and positioning, also significantly influences the functioning of both living organisms and technical systems. Long-term exposure to microwave radiation can lead to changes in the blood characteristics, neural and psychic disorders, and malfunction of mechanisms and electronic equipment [1].

Electromagnetic radiation in the microwave range, which is generated by radioelectronic equipment, differs from the natural background in the frequency and power characteristics and contributes to changes in the response of biological objects. Sometimes this modified response is hardly predictable and exhibits a complex character [1, 2].

It is especially necessary to develop highly effective materials capable of broadband screening and absorbing of radiation in the microwave range. The main characteristics of electromagnetic screens, such as their cost of production, weight, air permeability, heat conductivity, and some other, are determined both by features of the electromagnetic field action on biological objects and by high need in these materials for the creation and development of radioelectronic equipment, data security systems, and military techniques.

The widely used approach to obtaining materials with preset electromagnetic characteristics is to form

composites, which combine the necessary mechanical and dielectric properties of the base structure (matrix) and the magnetic and conducting properties of a filler material. By varying the dimensions and concentration of the filler particles, it is possible to control the characteristic of the composition.

Important advantages of fiber-based composites are their good technological properties and low cost of production. This makes these composites promising materials for flexible screens and absorbers of electromagnetic radiation, which exhibit increased strength, wear resistance, air permeability, and other useful technological and working characteristics.

In this Letter, we propose to incorporate nanodimensional metal-containing elements into the structure of an organic fiber-based material. The elements are formed by a method based on the chemical reduction of metals from aqueous salt solutions, which makes possible a control of the metal deposition process and the synthesis of coatings with preset characteristics. This method is among the most promising approaches to the formation of nanodimensional structures. In selecting metals for deposition, it is necessary to take into account the chemical and physical properties of small-size crystals, including their corrosion resistance and stability of the structure and the electrical and magnetic characteristics). Copper is a metal that possesses high corrosion resistance and is capable of forming numerous alloys with a broad range of useful properties. The wide use of copper in industry is explained by a number of valuable properties, primarily by high electric conductivity, plasticity, and heat conduction [3].

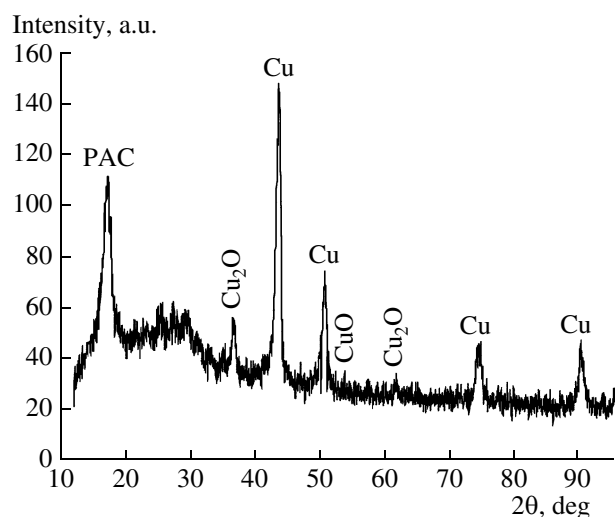


Fig. 1. Typical X-ray diffractogram of PAN fibers upon copper deposition.

Solutions for the chemical copper plating are prepared using formaldehyde, which is the only reducing agent capable of catalyzing the reaction of Cu^{2+} ion reduction at room temperature. Since formaldehyde ensures effective Cu^{2+} ion reduction only in alkaline media, the copper plating in practice is carried out in alkaline solutions and the undesired precipitation of copper hydroxide is prevented by introducing ligands capable of binding Cu^{2+} ions in strong complexes. The possible ligands are oxalates, ammonia, and glycerol, but most frequently used are the salt of tartaric acid (potassium sodium tartrate) and disodium salt of ethylenediaminetetraacetic acid (Trilon B) [4].

For the chemical deposition of metals, the surface of a base material should be prepared and rendered catalytically active so as to ensure the reaction of metal reduction from solution and the adhesion of metal clusters to the substrate rather than to the walls of a vessel in which the reduction process is carried out. We propose using polyacrylonitrile (PAN) fibers as a base material, which are advantageous in being readily available, relatively cheap, and capable of modification [5]. Disadvantages of the PAN fibers are low hygroscopicity, relatively high stiffness, and low resistance to wear.

The modification of PAN fibers consists in carrying out polymer-analogous reactions with amino groups, which render PAN macromolecules capable of chemically adsorbing metal ions. The modification is also necessary because PAN fibers exhibit highly hydrophobicity and poor wettability, which hinder metal deposition reactions. The hydrophobicity and low hygroscopicity are caused by the presence of $\text{C}\equiv\text{N}$ groups in the polymer chain unit. These groups can be modified using oxyamination reaction, by which some triple bonds in the nitrile groups are broken and converted into double bonds [6].

Under laboratory conditions, we have modified 5 g PAN fibers in a $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ solution, which was prepared using 41.3 g hydroxylamine hydrosulfate and 300 ml tap water. Insufficient concentration of hydroxylamine hydrosulfate and improper pH (corrected by sodium hydroxide) reduce the degree of modification, thus decreasing the adsorption properties of fibers.

The chemical copper plating of PAN fibers was performed using a three-stage procedure. At the first stage, the modified PAN fibers were treated in a mixed solution of copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (30 g/l) and nickel sulfate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (4 g/l) for the adsorption of Cu^{2+} ions. At the same time, another solution was prepared using potassium sodium tartrate $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (60 g/l), sodium carbonate (Na_2CO_3 (1.5 g/l), sodium hydroxide NaOH (20 g/l) and Trilon B (1 g/l). At the second stage, the second solution was added to the first solution with PAN fibers and sodium hyposulfite $\text{Ha}_2\text{S}_2\text{O}_3$ (0.005 g/l) was added to the mixture. At the third stage, a 40% aqueous solution of formaldehyde CH_2O (25 ml/l) was added and the reaction of Cu cluster reduction was carried out at 20–25°C.

The electromagnetic properties of obtained fibers with radio-wave-absorbing coatings were studied in a frequency range of 8–12 GHz. These measurements were performed using a panoramic standing-wave-ratio and attenuation meter (Ya2R-67). The efficiency of absorption of the electromagnetic radiation was evaluated by comparing the reflection (S_{11}) and transmission (S_{12}) coefficients measured for a sample arranged between flanges of two waveguides.

The chemical composition of the synthesized material was determined using X-ray diffraction (XRD). The XRD measurements were performed on a DRON-3 diffractometer using filtered CuK_α radiation ($\lambda = 1.5417737 \text{ \AA}$). The diffraction patterns were recorded at a pulse count rate of 1000 cps in an angular interval of 12°–95°. The XRD diffractograms were interpreted using a powder diffraction database (PCPDFWIN) of the International Center for Diffraction Data (ICDD).

The results of XRD measurements showed that PAN fibers upon modification and metal ion adsorption possessed an X-ray-amorphous structure. The diffractograms (Fig. 1) displayed, in addition to a peak due to the modified PAN (interplanar spacing, 5.069 Å), peaks corresponding to metallic copper and its compounds with oxygen (Cu_2O and CuO). The peak at $\sim 17.5^\circ$ is due to spatial bonds between PAN macromolecules. The noisy background and an increased intensity of X-ray scattering in the region of small diffraction angles are explained by the influence of the organic fiber base [7].

The results of our investigation showed that the synthesized copper-containing fiber composite materials exhibit radiation screening properties. The efficiency of microwave screening increases with the signal frequency. An analysis of the interaction of cop-

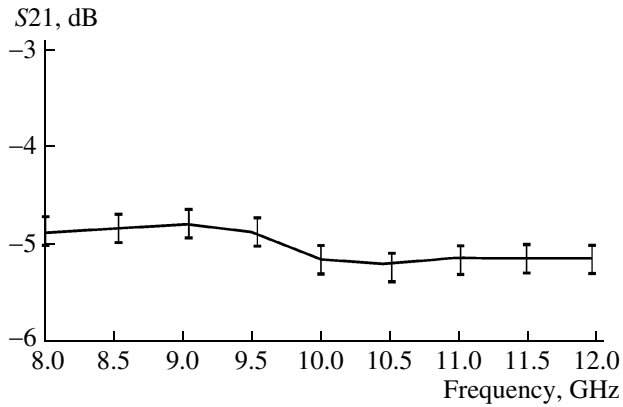


Fig. 2. Spectrum of the transmission coefficient S_{21} of a copper-containing PAN fabric.

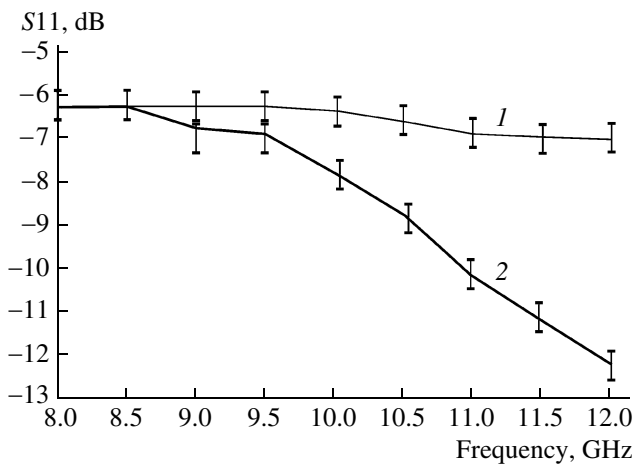


Fig. 3. Spectrum of the reflection coefficient S_{11} of a copper-containing PAN fabric measured (1) without and (2) with a metal reflector positioned behind the sample.

per-containing fiber composite materials with electromagnetic radiation in the microwave range showed that the amplitude–frequency characteristics of the reflection and transmission coefficients of coated fibers in the 8–12 GHz interval exhibited a

nonresonant character. In this frequency range, the transmission coefficient of composite materials studied was on the average about -5 dB (Fig. 2). The reflection coefficient of these materials without a reflector was about -7 dB. In the presence of a metal reflector, the reflection coefficient decreased from -6 to -12 dB with increasing frequency in the interval studied (Fig. 3). Thus, the screening efficiency of copper-containing fiber composite materials varied within 2–5 dB and increased with the radiation frequency.

The characteristics of obtained copper-containing fiber composite materials show evidence for good prospects in using these fabrics as flexible absorbers and screens of electromagnetic radiation and as matching layers in multilayer structures of radiation absorbers in the radio frequency range.

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