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APPLICATION OF ELECTROLESS METAL DEPOSITION FOR ADVANCED COMPOSITE SHIELDING MATERIALS

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This paper presents the principles of formation and properties of new fibre composite materials for electromagnetic shields. Composite fibres consist of organic basis and metallic particles formed on surface and in the volume of fibre using electroless deposition technology. Polyacrylonitrile was the main type of fibres material that employed for modification and creation of composite structure. Polymer-like transformation of polyacrylonitrile was used to increase chemisorption properties. Clusters of magnetic and highly conductive metals embedded into fibre volume have sub micron size as derived from microstructure investigation. It was found that nanometre size particles of nickel, cobalt and their alloys can be formed from metal ions bounded to fibre with following electroless deposition using either sodium hydrosulphite or sodium hypophosphite as a reducing agent. As deposited materials were shown to have very low stability in air so the principles of protection with surfactants were proposed. Electrical conductivity, magnetic properties of fibre materials and shielding efficiency of electromagnetic wave absorbers in wide frequency range were studied. Special attention was given to application of knitting technology for electromagnetic wave absorbers and shields fabrication. The modular broadband electromagnetic absorbers and shields were developed and tested. It was shown that using multilayer combination of linen composites based on Ni and Co provides increase of shielding efficiency module up to 70 dB with decrease the reflection coefficient down to – 25 dB in the frequency range 1-118 GHz. Possible applications of new materials and structures for reducing harmful electromagnetic radiation effects and unwanted radiation of electronic devices were discussed.

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1. Introduction

Increasing number of radio-electronic devices, intensive using of electromagnetic resource, application of complex signals cause electromagnetic compatibility and radioecology problems. Development of mobile communication, radio navigation, television and different signal processing and transmission systems leads to increasing electromagnetic background that effects adjacent systems and operators. Electromagnetic radiations (EMR) of wide frequency range form informative, control or energetic channels separated by time, frequency and direction using radioengineering and antenna systems. This radiation differs from natural electromagnetic background and introduces complex influence on biological object reactions. Thought human organism, which is complex adaptive system, has its own protection mechanisms that were developed for thousand years, it's requested to provide additional protection in some cases when operator has to be close to electromagnetic radiation source [1]. Development of high-effective, wide band and easy to install means reducing the electromagnetic radiation is perspective not only for protection of human body but also for advanced radioelectronic systems and protection of information.

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The main problem is to decrease the level of unwanted electromagnetic radiations and electromagnetic interference (EMI) of radioelectronic devices arising from imperfections of unit design. Ability of materials to reflect or absorb electromagnetic radiation energy in given frequency range is used for development of electromagnetic shields and radio wave absorbers that is one of the most effective means for EMR suppression. Modern shields and electromagnetic wave absorbing structures employ different kind of materials from simplest metallic shields to complex composite structures or conductive polymers [2].Taking into account that there is neither ideal reflecting no absorbing EMR materials, broad band and high efficiency are usually achieved by both processes [3]. Since absorption of electromagnetic energy happens due to magnetic, dielectric and conductive loss the shielding properties are defined by complex dielectric constant, magnetic permeability and conductivity of material that has to be maximized for maximum shielding efficiency. Reflection of radio waves occurs at any non uniformity in material and interfaces while reflection coefficient is proportional to difference between wave resistance of free space and shield material. In some cases a non-uniformity of absorber surface is employed for scattering of plane wave to reduce level of the reflected signal [4].

Complex mechanism of electromagnetic wave propagation in different media arises problems of shielding optimisation and application, broadening the frequency range, development of universal shielding materials. High reflective properties of metals, which are well known and common shielding materials, influence the shielded devices introducing additional internal interference and change of element parameters that require additional adjustment. Moreover, efficiency of such shields is strongly dependent from quality and reliability of assembly parts and electrical contacts between them [5]. Generally effectiveness of the air penetrable metal or conductive structures reduces with frequency increase.

Composite materials, that usually are dielectric matrix with conductive or magnetic filler of different shape and size, become a new approach for shielding that combines extended frequency range, high efficiency and proper construction. Application of composite material technology allowing selection of base matrix and filler improves properties of shielding and EMR absorbing structures because of combination of several materials properties and introducing a big number of interfaces. Ferromagnetic materials, ferroelectrics, ferrites [6], metals and conductive carbon particles or films [7] are used for electromagnetic wave absorbers design. Main disadvantages of ferrite based structures are resonant absorption of EMR and hence limited frequency range.

Composites may be prepared by mixing of different components with following fixation using powder metallurgy methods, annealing, polymerisation etc. Electroless metal deposition is one of the attractive technologies that provide low-cost and low-temperature process for formation of metal containing structures in dielectric matrix [8]. Formation of metal structures using electroless method is based on reducing of metal ions that receive electrons generated as a result of reducing agent oxidation reaction. Oxidation-reduction reactions occur at catalytic surface of substrate that typically contains nucleation cites of metals. Since the majority of electroless solutions are aqueous the deposition temperature does not exceed 100 ºC, there is no limitation on shape and size of plated substrate, and deposition is performed from soluble metal salts. Reaction rate is controlled by bath composition and it runs enough fast to provide high throughput of industrial systems.

Using of polymers with developed surface allows creation of numerous metallic clusters with different size and shape in nanosize porous of material that forms complex spatial conductive and magnetic structure. Application of high-volume fibres such polyacrylonitrile as a base for metallic composite material combines mechanical properties and high flexibility of fibre with high EMR absorption typical for dispersed metal structures [9]. In this case synthesis of material can be realised on stage either fibre fabrication or entire linen using textile industry tools. Magnetic and high conductive metals such as nickel, cobalt or silver were selected for deposition due to their high stability and relative simple deposition procedure [10]. Metallic clusters are formed from ions attached to fibre by chemisorption with reducing in aqueous solution. Such clusters serve as catalytic cites for following electroless growth or ion-molecular layering [11]. Special type of polymer-like transformations was applied to increase chemisorption properties of polyacrylonitrile [12].

This paper presents method for synthesis of metal containing composite fibres using electroless technology. We studied electrical and magnetic properties of materials synthesized on the basis of polyacrylonitrile using electroless deposition of nickel and cobalt. The material properties were investigated as a function of activation and deposition method. Study of microwave characteristics of the shielding constructions were carried out in wide frequency range.

2. Experimental details

Synthesis of composite fibres was carried out on the basis of modified polyacrylonitrile (PAN) after polymer-like transformation as described in [13]. Initial fibres had a thickness of about 31 × 2 tex. Catalytic cites on the surface of fibre were formed by treatment in 0.01 M $PdCl_2$ aqueous solution for 2 minutes or by sorption of nickel ions from 1 M $NiSO_4$ water solution for 3-4 hours at room temperature or for 1 hour at 60 ºC with following processing by reducing agent.

Electroless deposition of metals was preformed from solutions containing soluble metal salts (nickel or cobalt sulphate, silver nitrate), stabilizer, surfactant and reducing agent. It was found that sodium hypophosphite or sodium dithionite [14] may be employed as reducing agents in the case of formation of cluster structure from nickel, cobalt or alloys, hydrazine hydrate is applied for reducing of silver from strong complexes [15]. Using of sodium hypophosphite requires deposition temperature above 90 ºC while application of sodium dithionite allows decrease of it to 50-60ºC level. Reduction with hydrazine hydrate occurs at room temperature. Growth of metal structures was conducted using either autocatalytic deposition or ion-molecular layering with stirring and correction of main solution components: metal ions and reducing agent. Amount of deposited metal was measured via gravimetric technique. High activity of metal particles and its oxidation by air oxygen in the presence of residual water from plating solution requires additional protection that was created using low molecular weight surfactants such as iso-butanol. PAN treatment was carried out in form of separated fibres as well as complete knitted linen. Structure investigation was performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods.

Electrical and magnetic properties of composite fibre materials were measured. Electrical resistivity was determined at constant current by applying of two contacts scheme to sample of specified volume and shape. The magnetic properties were measured with a Quantum Design SQUID MPMS XL5 magnetometer.

Composite fibres were employed for fabrication of knitted linen used in multilayer flexible electromagnetic wave absorbers. Parameters of developed multilayer knitted structures for electromagnetic shield and microwave absorbers were tested in the frequency range from 1,5 to 118 GHz by vector network analysers VNA 1,5-18, VNA 18-25, VNA 25-37, VNA 78-118 and measuring cell containing two horn antennas. Frequency dependence of reflection coefficient magnitude |S11| and transmission coefficient magnitude |S21|, which is very close to shielding efficiency value E, was studied as a function of construction design.

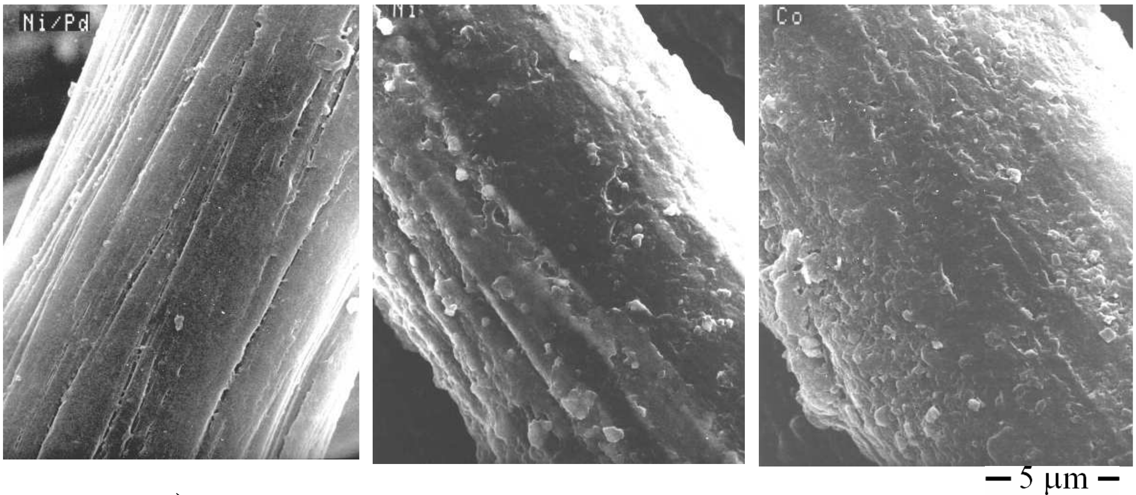
3. Results and discussion

Study of composite fibre properties included several main parts: microstructure characterization, electrical and magnetic properties investigation and finally research of microwave properties of flexible linen of different constructions.

Synthesis of metal particles happens according to similar schemes based on accepting by metal ions missing electrons from reducing agent and transformation of metal atoms into intermediate simplest clusters. Such structures contain several combinations of atoms corresponding to favorable energetic parameters. Particularity of nickel and cobalt clusters formation is ability to form relative stable intermediate metalo-organic compounds.

Microstructure. Changing of PAN chemical structure during modification process that appears as transformation of ternary bond C≡N into binary C=N with generation of free active bond for chemical sorption of metal ions was studied recently [16]. XRD study shown amorphous structure of fibres before, after modification and after sorption of metal ions as well. Exception is formation of the ordered structure with interplanar spacing about 0.507 nm that occurs during PAN modification through creation of three-dimensional intermolecular bonds. When reduction of metal was completed XRD spectra demonstrated peaks that were attributed to presence of highly dispersive polycrystalline metal particles and sulphur-containing metal compounds [12, 13, 16]. The size of crystallites was found to be in the range from 3 to 5 nm depending on deposition time. Total amount of metal was up to 17 % wt.

SEM study (Fig. 1) shown that depending on activation method electroless deposited metal forms continues cover or clusters embedded into fibre volume. In the case of Pd activation the catalytic sites forms at fibre surface and metal growth occurs mainly as a continuous layer localized around fibre. When clusters are formed by chemical sorption in the porous of fibre they are distributed as particles of different size and shape in whole volume of material.



a) b) c)

Fig. 1. SEM images of PAN fibres: a) - after electroless deposition of Ni by sodium hypophosphite using Pd activation, b) – after electroless deposition of Ni using chemical sorption with following reduction by $Na_2S_2O_4$, c) - after electroless deposition of Co using chemical sorption with following reduction by $Na_2S_2O_4$.

Electrical properties. Electrical properties of composite fibre are determined by amount, shape, size and distribution of metal inclusions. As a result of deposition the fibre changes colour and electrical conductivity that increases with deposition time (Fig. 2).

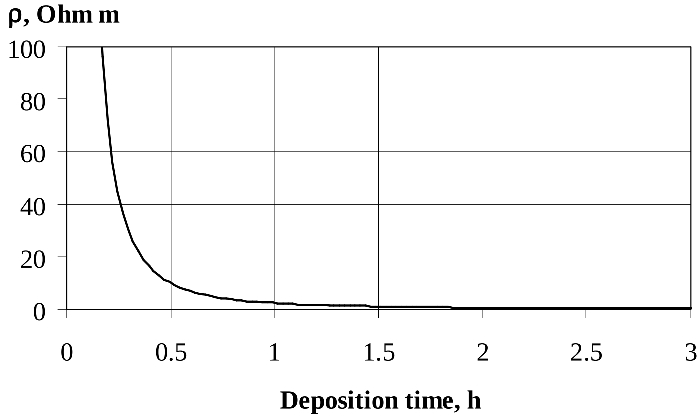


Fig. 2. Resistivity of composite fibres fabricated by electroless Ni deposition using Pd activation as a function of deposition time.

Fast oxidation of metal clusters by air oxygen after finish of synthesis and washing requires development of protection method. We proposed encapsulation of particles by creation around object a protective cover using treatment in surfactant containing liquids. The main idea of stabilization is exchange of active oxygen by part of a surfactant molecule and isolation of reaction zone from environment. Method of metal cluster structure stabilization includes wet and gaseous drying with following treatment by aqueous and nonaqueous solutions with high-molecular surfactants. One of the best stabilization procedures with shortest transient time is based on butanol and oil.

Specific resistivity of fiber composite linen with 15 mg/cm^2 of Ni that correspond to 17 % wt. was about 2.5×10^{-3} Ohm m and then increased according to logarithmic law due to interaction of particles with environment. Initial resistivity of Co containing materials did not exceed 50×10^{-3} Ohm m. Difference between electrical properties of materials with different metals is determined mainly by degree of dispersion but not by metal nature. Only in case of continuous layer formation the bulk metal properties are decisive factors. It was shown that electroless Co deposition using chemisorption method provides less conductive and more disperse deposits than that for Ni deposition (Fig. 3).

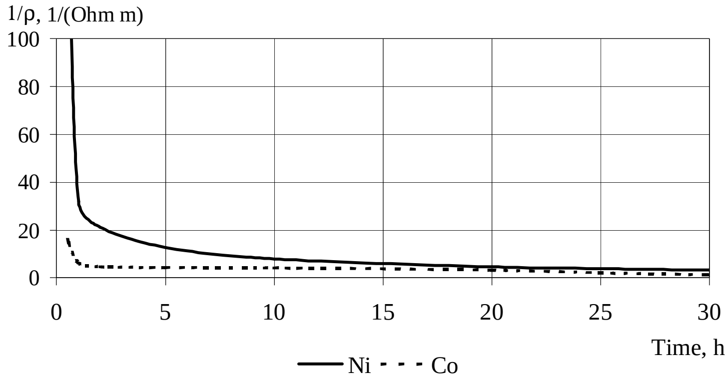


Fig. 3. Conductivity of composite fibres with as-deposited Co and Ni particles formed by chemisorption method as a function of time.

Magnetic properties. Composite fibres demonstrated weak magnetic properties and low magnetic permeability (Fig. 4) due to very low amount of particles with size enabling creation of magnetic structure from total number of clusters. Nickel containing material shown diamagnetic properties while cobalt containing fibres had ferromagnetic behaviour that is, probably, attributed to size effect. Taking into account ability of transition metals to form metalo-organic compounds the magnetic cluster cover also may response for the composite properties.

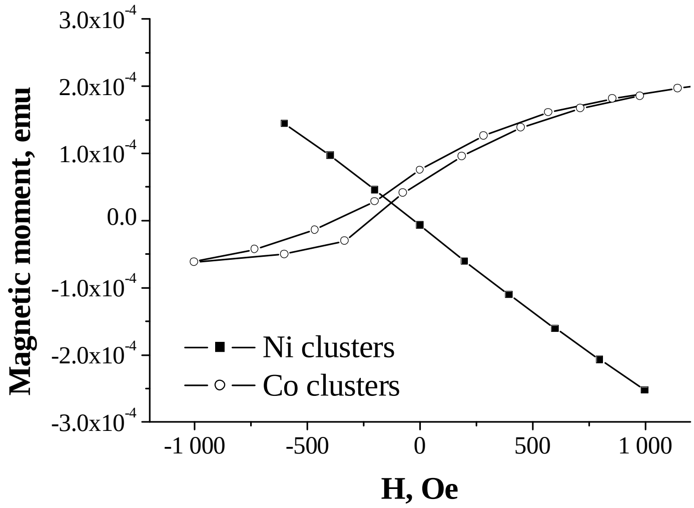


Fig. 4. Magnetic moment of composite fibres with Co and Ni particles as a function of external field.

Knitted shielding structures and their properties. Dependence of reflection and transmission coefficients of devices fabricated from composite fibres was measured as a function of electromagnetic radiation frequency. We studied characteristics of knitted linen shields from Ni containing fibres synthesized using Pd activation or chemisorption method (Fig. 5), Co containing materials (Fig. 6) and EMR absorbing multilayer structure (Fig. 7) where matching layer was fabricated from Co containing fibres, absorbing layer was Ni containing material deposited by chemisorption method, and reflective layer was developed from Ni composite prepared using Pd activation.

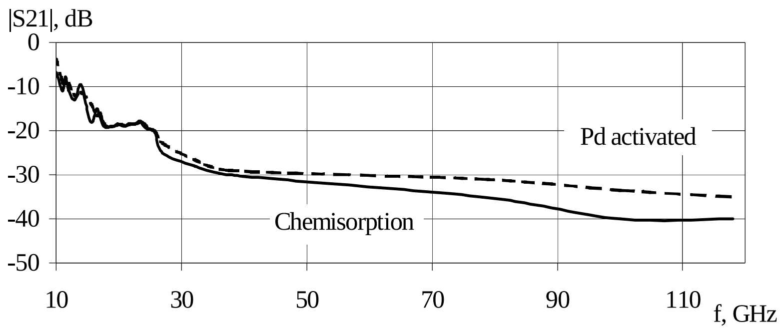


Fig. 5. Transmission coefficient of linen fabricated from composite fibres with electroless Ni clusters deposited using Pd activation or chemisorption method as a function of EMR Frequency.

Shielding properties of fibre composites were investigated in wide band range. Knitted linens were formed using combined satin weave. It was determined that shielding efficiency of metal containing fibre composites increases with electromagnetic radiation frequency. Ni containing materials demonstrated higher suppression of EMR due to reflection of electrical component of wave. Suppression of magnetic component is poor because of low magnetic permeability of materials. High reflection ability of conductive composite is controlled by difference of wave resistances of free space and shielding device.

Ni containing materials fabricated using Pd activation method shown higher reflection coefficient than composite prepared by chemisorption. In first case deposited metal forms more uniform cover on the fibre surface and provides lower resistivity of material that results in decrease of shield wave resistance. Shielding efficiency of Ni containing materials is typically above 20 dB (it corresponds to more than 100 times) in frequency range 20-118 GHz. Co containing materials demonstrated lower shielding efficiency (Fig. 6), but such linens had better matching to free space (lower reflection coefficient) than that for Ni containing ones. Reflection coefficient of Co containing linen did not exceed – 10 dB and shown nonresonance behaviour in microwave range. It was shown that using of the cobalt containing fibres as a matching layer in EMR absorbing structures decreases the reflection coefficient of structures together with increased efficiency up to 70 dB (Fig. 8).

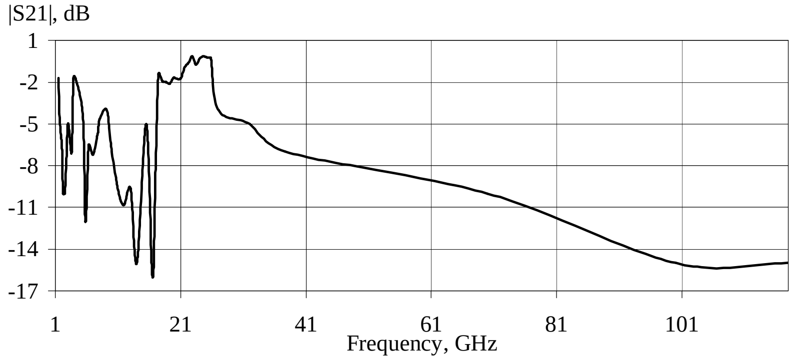


Fig. 6. Transmission coefficient of linen fabricated from composite fibres with electroless Co clusters as a function of EMR frequency.

The modular flexible broadband electromagnetic absorbers and shields were developed and tested (Fig. 7). Amplitude-frequency characteristics for magnitude of reflection and transmission coefficients in frequency range 20-118 GHz demonstrated nonresonance behaviour. The reflection coefficient level does not exceed –17 dB level. Transmission coefficient level increases up to 70 dB. Improvement of shielding and EMR absorption characteristics of multilayer construction was achieved by using of low reflective layer of Co composite in combination with absorbing and reflective layers fabricated from Ni containing fibres. In this case wave resistance gradient is formed and reflected electromagnetic wave is reduced. Absorption and reflection of electromagnetic wave energy by layers were controlled via amount of deposited metal and activation method.

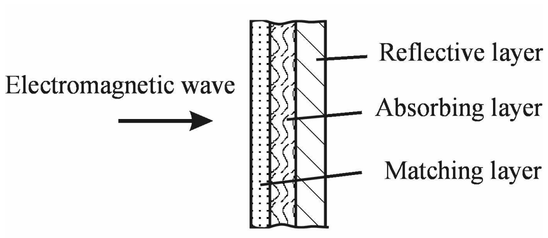


Fig. 7. Schematic design of flexible electromagnetic shield based on knitted linen composite materials.

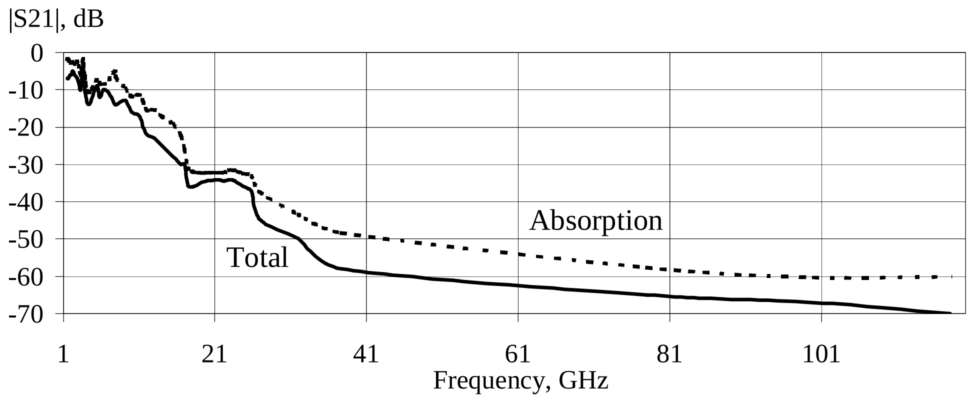


Fig. 8. Transmission coefficient of multi layer flexible electromagnetic shield as a function of EMR frequency.

Composite fibres obtained using electroless metal deposition maintain their properties for relative long period exceeding 5 years. Application of fibre composites for biological protection and radioelectronic devices updating is proposed.

4. Conclusions

The principles of formation of new fibre composite materials for electromagnetic shields were discussed. Electroless metal deposition was considered as a perspective method for nano particle formation. We proposed formation of the composite fibres that consist of organic basis and metallic particles on surface and in the volume of fibre using electroless deposition technology. Polyacrylonitrile after polymer like transformation was the main type of fibres material that employed for modification and creation of composite structure. Clusters of magnetic and highly conductive metals embedded into fibre volume have sub micron size as derived from microstructure investigation. Nickel, cobalt and their alloys can be formed from metal ions bounded to fibre with following electroless deposition using either sodium hydrosulphite or sodium hypophosphite as a reducing agent. As deposited materials shown very low stability in air so the principles of protection with surfactants were proposed. Electrical conductivity, magnetic properties of fibre materials and shielding efficiency of electromagnetic wave absorbers in wide frequency range were studied. It was shown that using multilayer combination of linen composites based on Ni and Co provides increase of module shielding efficiency up to 70 dB with decrease the reflection coefficient down to –25 dB in the frequency range 1-118 GHz. Possible applications of new materials and structures for reducing harmful electromagnetic radiation effects and unwanted radiation of electronic devices were discussed.

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