Application of planetary ball mill for manufacturing of shielding composite coatings based on polyester powder paints and carbon fillers

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Abstract. Blend polyester powder paint and particulate carbon filler in the form of colloidal graphite and the carbon black product were investigated. Powder paint and carbon materials were treated together in a planetary ball mill. The data of the structural analysis and transmission coefficients of electromagnetic waves of terahertz range through the flat shape samples are presented.

1. Introduction

An important condition for the development of radio engineering and electronics is development and study of properties of new composite materials [1]. Due to their combined properties the composite materials based on the metal or carbon-based particles in the polymer matrix are promising for application to problems of electromagnetic compatibility, interference immunity, radio masking and protection of biological objects. Thereby, design materials that absorb or reflect electromagnetic waves (EMW) in the gigahertz and terahertz frequency range it is actual problem [2]. Using of carbon-containing structures for shielding devices by reducing the background level of EMW to safe values was described in the literature [3, 4]. The materials, that actively interact with the EMW (reflecting and absorbing) [5], are used to prevent their harmful effect on the operation of electronic systems, as well as to reduce the radar visibility of aircraft, ships and technological equipment. Using of powder coatings is an effective way for corrosion protection of products. Also, adding the particulate fillers can impart to composites additional functional properties, in particular, the possibility of EMW shielding. The aim of this study is to investigate the ability of electromagnetic waves absorption and reflection of composite coatings based on polyester powder paint and dispersed carbon fillers in the form of graphite and carbon black. [6]

2. Materials and research methods

Flat samples of Mg alloy with a composite coating were used in the studies. Polyester powder paint “Okhteck-1” produced by JSC "Technos-Ohtek", Russia (with mean particle size of 71-50 µm, bulk density of 0.65 g/cm^3) having high corrosion resistance, physical and mechanical characteristics was chosen as the polymer binder. Carbon black "P-267E" (with average particle size of 70 µm, bulk density – 0.23 g/cm^3, specific volume resistivity at the density of 0.5 g/cm^3 – less than 0.002 Ohm/meter) and the colloidal- graphite powder "C-1" (hereinafter CGP) (with average particle size – of 4 µm, bulk density – 0.14 g/cm^3, the specific volume resistivity at a density of 0.5 g/cm^3 – 1.59 ± 0.06 Ohm/meter) (Fig. 1) were used as fillers. The objects of the study were a coating film formed by spraying powder composition onto substrate made of a fluoroplastic with their subsequent separation.

Powder mixture was prepared in a planetary ball mill MF 4/ 0.5 ("Tekhnotsentr" ltd., Rybinsk) at a total frequency of metal bowls rotation 800 rev./min. The weight ratio of the bearing steel balls to the powder made 40:1. Carbon fillers and powder paint were placed in the required quantities in the planetary ball mill where they were subjected to mechanical treatment (MT) during 40 min [7]. The effect of the MT time on the mechanical properties of the powder mixture was evaluated by the data of bulk density measurement. Vibrating sieve with a net size of 160 µm for dispersing large agglomerates of the powder mixture particles to form during the MT processing was used. The fraction of mixture with dispersity less than 50 µm were separated by sieve and then used for electrostatic spraying. Thus, the filler particles in the composition to be sprayed also had the same level of dispersity.

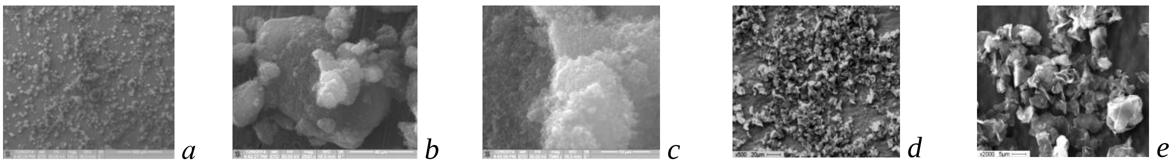


Figure 1. SEM-micrographs of carbon black particles P-267E (*a, b, c*) and colloidal- graphite powder C-1 (d, *e*).

Prepared powder compositions were deposited on the magnesium alloy substrate with a chromium oxide sublayer by electrostatical method using the "Start-50" gun. Further, fluoroplastic (PTFE) plates were used as substrates for deposition coating films and subsequent measurement of reflection and transmission coefficients, as well as permittivity values. During the following sintering at 180 °C for 15 minutes coatings with the thickness of 50 ... 80 µm were formed, and then coatings were delaminated from polytetrafluorethylene (PTFE) substrates.

3. Research methods

The coatings structure was investigated by scanning electron microscope Quanta 200 3D (FEI, USA) in Tomsk State University (Center of shared use of high-tech equipment). Crosscut split of the coatings was made to analyze the morphology. Corrosion tests were carried out in climatic chambers by the UHL 2 regime (GOST 9.401-91, technique No. 13).

Measurements of reflection and transmission coefficients from a flat material layer and spectra of the complex permittivity in the frequency range of 118 ... 258 GHz carried out by the "free space" method in the terahertz spectrometer STD-21 {C1 - C6} (CCU "Center of radio measurements" of TSU) [8, 9]. Terahertz frequency range was selected to study the electromagnetic response in order to determine the possibility of the developed material to be employed as reflecting or absorbing of electromagnetic waves.

Non-contact method were used to measure spectra of the absolute values of the modules and phase components of electrodynamic response: complex reflection coefficient – $R^*(f) = R(f)e^{i\psi(f)}$, and transmission coefficient – $Tr^*(f) = Tr(f)e^{i\varphi(f)}$ from the samples in real time. Operating range was 0.03 – 1.5 THz. Values of the complex permittivity of the material $\varepsilon^* = \varepsilon' - i\varepsilon''$ were calculated using measured modulus and phases of the transmitted and reflected signals. The value ε* characterizes the formed composite structure, and allows physical mechanisms that determine the electrodynamic properties to be define.

4. Results of the research

The aim of combined treatment of the powder paint and carbon fillers in the planetary ball mill is solving the problem of adding maximum amount of functionalizing filler while ensuring satisfactory mechanical properties of the coating (especially, adhesion). The content of filler particles in the mixture was 12; 15; 17; 20 wt. %; time of the treatment was 40 min [10]. After the MT, change of the bulk density of the powder mixtures was evaluated (Fig. 2). The bulk density has changed from 0.35 to 0.5 g/cm^{3}depending on the filler content, because the bulk density of carbon fillers is smaller than bulk density of the powder paint.

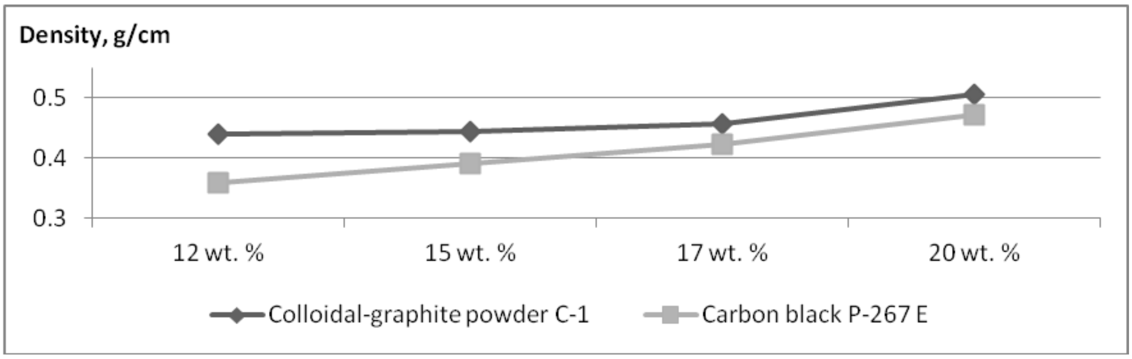


Figure 2. Dependence of the bulk density of "PowderPaint+ CarbonBlack" mixture.

After adding colloidal-graphite powder (CGP) and CB in the powder paint the values of bulk density do not substantially differ. Thus, it is not possible to make far-reaching conclusions by the parameter of bulk density from a point of view of finding the optimal amount of filler to be added into the powder paint. Data of our studies are presented in Fig. 3. The MT is effects on formation of particle fraction with a size more than 100 µm which were absent in the initial components of the mixture. The reason for their occurrence related to agglomerating the paint particles and filler during the MT. An interesting effect was identified after powder mixtures processing. The amount of the fraction suitable for electrostatic spraying is about 65 % for the carbon black being used as the filler and takes about 78% for CGP.

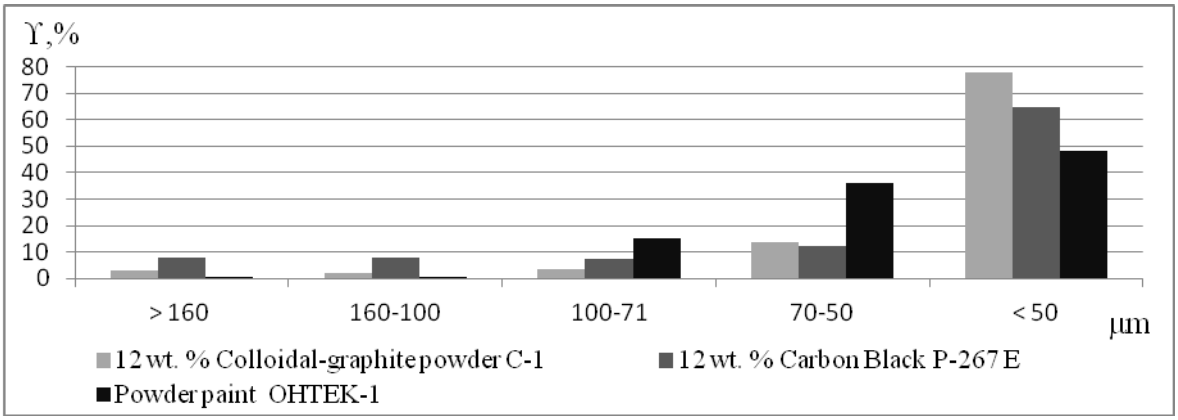


Figure 3. Distribution of powder mixture particles by the size on the basis of sieve analysis.

5. Coating structure and properties

The powder fraction with dispersion less than 50 µm was separated from the powder mixtures processed in the PBM. Then separated fraction was sprayed onto magnesium and fluoroplastic substrates. The degree of functional properties of the coatings was evaluated by measuring the specific volume electric resistance (SVER) (Fig. 5). Analysis of the obtained results shows that SVER of the CGP filled coating is by 15 times less than that of the coating containing carbon black. Most likely, this is due to the fact that the particle size of the CGP is less than 5 μm that is several times smaller than that of carbon black particles (< 70 μm). That is why the content of the particles in the powder fraction used for the spraying (with size less than 50 μm) is greater. This conclusion is also supported by the data presented in Fig. 3. The volume resistivity of CGP is less than volume resistivity of the carbon black powder. That also must affect the SVER of the coatings.

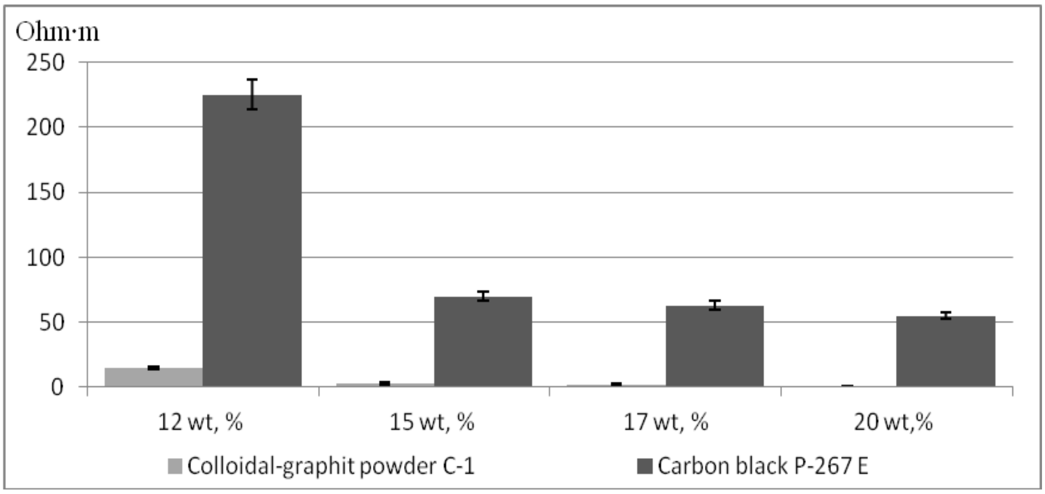


Figure 4. Volume resistance of coatings with various fillers.

Structural investigations carried out for the sprayed coatings with SEM showed that they are substantially non-porous and homogeneous even at the adding 15 wt. % CGP. However, this coating becomes brittle (Fig. 6), so it cannot be used. Adhesion of the coating to the substrate made of magnesium alloy before and after the environmental tests for specimens with filler content of 12 wt. % was performed. The adhesion in relative units is equal to one grade (Fig. 6, a, c).

Climatic tests for the coatings made of the powder mixture with 12 wt. % of the fillers and preliminary treated in the PBM for 40 minutes shown that at coating thickness not less than 70 μm no signs of corrosion are evident. Further increasing of the filler content up to 17 wt. % gave rise to presence of signs of corrosion which is unacceptable from the point of view of operational requirements.

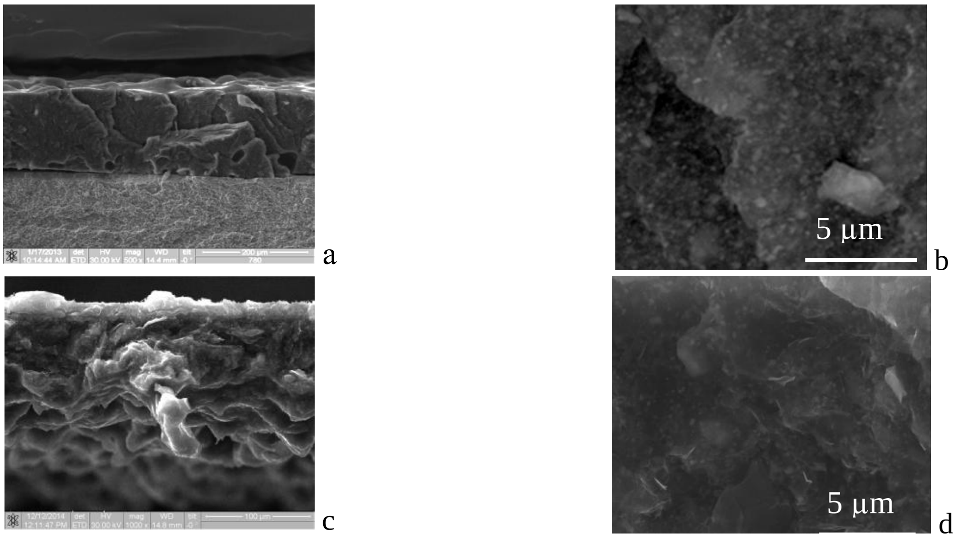
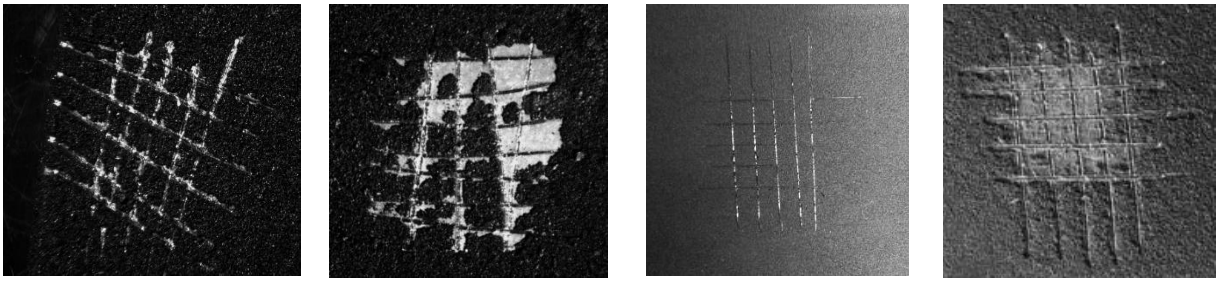


Figure 5. SEM-micrographs of a coating fracture surface at different magnification: *a*, *b*) 12 wt. % carbon black; *c, d*) 15 wt % CGP.



a b c d

Figure 6. Optical micrographs of the coating sprayed onto the substrate of Mg alloy MA-2-1: *a* – 12 wt. % carbon black; *b* – 15 wt. % carbon black; *c* – 12 wt. % CGP; *d* – 15 wt. % CGP.

Spectra of reflection and transmission coefficients and complex permittivity values of three flat shape specimens are in Fig. 7, whose parameters are given in Table 1.

Table 1. Complex permeability values.

Specimen No.	Coating composition	Size of filler particles	Filler content	Coating thickness, mm
1	Powder Paint (PP) OHTEK-1	–	–	0.38
2	PP + BK P-267E	< 71 μm	12 wt. %	0.39
3	PP + BK. P-267E	< 71 μm	12 wt. %	1.33
4	ПК + КГП	< 5 μm	12 wt. %	0.11

The electromagnetic waves is almost completely passed through the paint layer being partially reflected from a smooth surface due to the difference of the electromagnetic characteristics of the sample and the surrounding space (Fig. 7, curve 1). The adding of carbon black powder changes material properties: 45 ... 75 % of the incident power is reflected and partly absorbed by the sample bulk (Fig. 7, curve 2). Increasing the thickness of the layer altered behavior of the spectra of absorbtion and reduce the value of the real component. Particles become more separated by insulating interlayers, than in the thinner layer of the composite. As a consequence, absorptive capacity of the material has increased (Fig. 7, curve 3). This is probably related to the method of coating spraying.

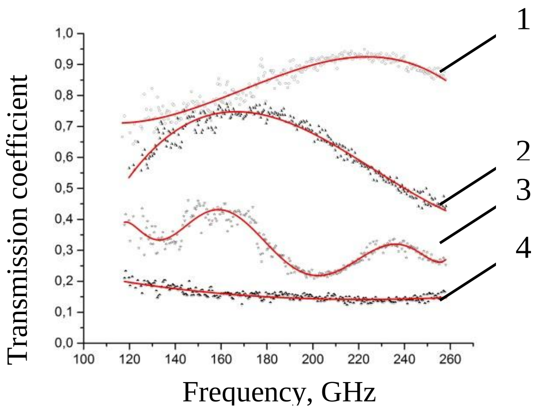


Figure. 7. Electromagnetic response of the “Okhtech” powder paint 1 - specimen № 1, table 1-1; composite «Okhtech + BK P-267E» at different thickness (specimens №2, 3, table 1-2, 3); composite «Okhtech + CGP” (specimen 4 , table 1-4).

Adding of colloidal graphite powder significantly alters properties of the material: 80 % of the incedent power is absorbed by the sample bulk from (Fig. 7). Thus, it is shown that adding of carbon black and CGP into the powder paint changed electrical and physical characteristics of the material. The specimen composed of powder paint with the adding of colloidal graphite with their combined treatment in the PBM can effectively absorb electromagnetic radiation of the terahertz range.

6. Conclusions

1. The results of complex testing simulating various atmospheric and mechanical influences have shown that the developed coating with the content of the carbon black of 12.5 wt. % and the MT time of 40 minutes ensures the formation of the coating film with thickness of 70 μm which exhibits satisfactory functional and protective characteristics.

2. The offered method of forming coatings on parts made of magnesium alloys, combining adding of electrically conductive filler, the treatment of the powder mixture in the planetary ball mill, and electrostatic spraying can be used to remove static electricity from the parts of spacecraft equipment operating in open space.

Acknowledgements

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