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Electromagnetic loss in carbon based materials

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Paper presents the results of investigation of electromagnetic insertion loss (A) for carbon materials, including thermoexfoliated graphite (TEG), TEG-metal and TEG-epoxy composites (CMs) in temperature ranges 77–300 K at the frequency $f \approx 1.8$ GHz. The performed investigations have shown that TEG-based composite materials are prospective to use them as radio-protective materials in the electromagnetic shields for radio objects and buildings in particular. The microwave insertion loss L for studied TEG and TEG-Me based specimens at the frequency of 1.8 GHz is ranged within (16.2–18.5) dB. TEG-based composites containing polymer binder (epoxy resin) was shown to provide high electromagnetic insertion loss (L = 23.5 dB) as well as high level of elastic-plastic parameters. The increase of microwave insertion loss $A(L)$ is observed for all the studied CMs under decrease of temperature. But the character of $A(T)$ was found to be essentially dependent on the type of CM.

Представлены результаты исследования вносимых потерь электромагнитного излучения (A) в углеродных материалах, в частности, в терморасширенном графите (ТРГ) и в композитах (КМ) ТРГ-металл и ТРГ-эпоксидная смола в температурном интервале 77–300 К при частоте $f \approx 1{,}8$ ГГц. Проведенные исследования показали, что композитные материалы на основе ТРГ являются перспективными для использования их в качестве защитных материалов для экранирования источников электромагнитного излучения и, в частности, для защиты помещений от воздействия излучения. Микроволновые вносимые потери L для исследованных образцов на основе ТРГ и ТРГ-металл составляют (16,2–18,5) дБ при частоте электромагнитного излучения 1,8 ГГц. Обнаружено, что в композитах на основе ТРГ, содержащих полимерное связующее (эпоксидная смола) электромагнитные вносимые потери достаточно высокие (L = 23,5 дБ), кроме того, эти композиты характеризуются высоким уровнем упруго-пластических характеристик. Установлено, что при понижении температуры вносимые электромагнитные потери $A(L)$ возрастают для всех исследованных композитов, но характер температурных зависимостей $A(T)$ существенно зависит от типа КМ.

The peoples in modern cities and suburbs are now under continuous negative action of a set of electromagnetic field sources: radio and TV systems, microwave and cellular telephonic systems, electric power generators and perhaps microwave generators for the directed deleterious effect on technical and alive objects. Besides, the unauthorized access to the confidential information could be realized by remote registration from the outside to computers, radio-phones, wired communication systems, etc. That is why the problem of the alive objects protection against electromagnetic radiation and protection of confidential information against unauthorized access are now especially urgent. One of the most perspective way to solve these problems is the development of special electromagnetic shields. The aim of this paper is to study the characteristics of the electromagnetic radiation absorption in composite materials (CMs) based on thermoexfoliated graphite (TEG) and to determine the influence of TEG modification (the supporting of metal particles (Co, Ni) on TEG surface) on electromagnetic loss in these CMs.

TEG based samples produced under various technological regimes using certainly modified graphite matrices have been studied. TEG(1) samples are the samples of thermoexfoliated graphite produced by the technology described in [1]. Thermoexfoliated graphite TEG$_n$(2) was obtained after re-oxidizing of TEG(1) with nitric acid and repeated thermal shock at 900°C [2]. Metal-graphite composites were prepared by chemical deposition of salt ($Me(CH_3COO)_3$ or $Me(NO_3)_2$) from aqueous solution followed by thermal decomposition of the salt to metal [3].

TEG-epoxy CMs were prepared via several stages: preparation of the solution of epoxy resin in acetone; preparation of the TEG mixture with organic solution and drying the mixture at 20°C for 3–4 days under periodic agitation; adding of plasticizer (dibutyl phthalate, DBF) and hardener (polyethylene polyamine, PEPA); final drying in an oven at 100–110°C for 4 h up to total evaporation of acetone. The TEG content in the prepared TEG-epoxy composite was 11 mass%. The bulk CM samples were prepared by cold compaction of powders. The investigated samples were shaped as tablets of 15 mm diameter and about 2 mm thickness.

The adjustment of experimental procedure, experimental studies of TEG samples and the analysis of the experimental data have been performed using network analyzer P2-52/3 SHF [4]. The operation of the network analyzer is based on the reflectometry principle, i.e. on separate selection of signals proportional to the power of incident wave from generator and of the wave reflected from the measuring load or of the wave passed through the sample. The variable frequency of P2-52/3 is (1.07–2.14) GHz. The presented equipment permits to study the insertion loss conditioned by different TEG samples, to perform the variation analysis of their electrophysical parameters for the subsequent classification. At the same time, it is possible to carry out the measurements compared with reference samples. The microwave investigations of TEG based samples in the temperature range 77–293 K have been carried out in cryogenic arrangement (CA) that was enclosed in cryostat. The CA provides input and pickup of microwave signal from investigated sample and stabilization its temperature during measurement.

The investigation of the insertion loss (A) has been performed for a series of composite materials based on TEG in order to analyze the influence of thermochemical treatment of TEG on the electromagnetic radiation absorption characteristics (see Table). According to the experimental data discussed in [5], the repeated thermochemical treatment of TEG (TEG(2) samples) and an additional surface activation of the TEG particles (TEG$_{extr}$ samples) result in a sig-

Table. Electric, magnetic and electrodynamic characterictics of composite materials based on TEG

No.	Sample composition	Density d, g/cm^3	Electric resistivity ρ_a, $\Omega\cdot$m	ρ_{77}/ρ_{300}	Magnetic suscept. χ, cm^3/g	Insertion loss A (L in dB)	
						Along the compacting axis	Along the compacting axis
1	TEG(1)	1.79	$1.0\cdot10^{-5}$	1.59			77(18.8±0.4)*
2	TEG(1)	1.81				42 – (16.2±0.4)	
3	TEG(1)	1.78				49 – (16.9±0.4)	
4	TEG$_n$(2)	1.74	$6.0\cdot10^{-6}$	1.48		50 – (17.0±0.4)	
5	TEG(1)$_{extr}$	1.60				42 – (16.2±0.4)	
6	TEG$_n$(2) + + C (45 mass %)	2.15	$2.17\cdot10^{-5}$	1.28	$6\cdot10^{-3}$	44 – (16.4±0.4)	
7	TEG(2)-Co	1.64				70 – (18.5±0.4)	
8	TEG(1)-Ni	1.79			$3.5\cdot10^{-3}$	64 – (18.1±0.4)	
9	TEG(1)-epoxy (89 mass %)	1.13	$1.55\cdot10^{-2}$	1.45		225 – (23.5±0.4)	

* — Rod-shaped sample (set of samples 1, 2, 3).

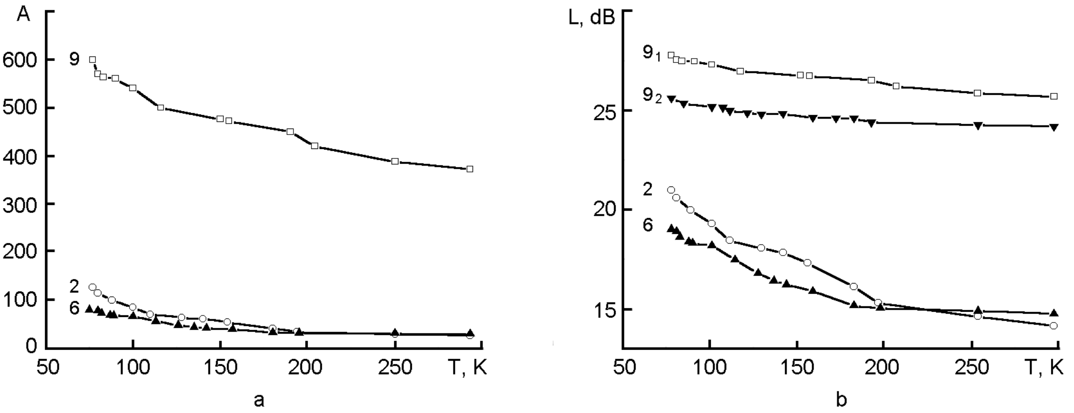

Fig. 1. Temperature dependences of microwave insertion loss for different CM samples: (a) microwave insertion loss A (in times), sample 2 — pure TEG, 6 — TEG–Co, 9_1 and 9_2 — different samples prepared using TEG-epoxy (89 mass %) powder; (b) microwave insertion loss *L* in dB.

nificant fragmentation of particles, to the changes in their structure and phase composition and, correspondingly, to the variation of their electrochemical characteristics.

The electrophysical parameters of TEG samples were analyzed before the investigations. A set of electrodynamic parameters containing the widest information about the TEG CMs under study has been determined. As it is seen from Table, the electrical resistivity for all the investigated samples is not high: ($6.0\cdot10^{-6}$–$2.5\cdot10^{-5}$) Ω·m for the TEG and TEG-Co, Ni and $7.90\cdot10^{-2}$ Ω·m for TEG-epoxy CM, respectively.

The metals are known to be used widely in construction of electromagnetic radiation shields due to high concentration of free carriers therein. The possibility to deposit nanoscaled metallic component on the surface of graphite substrate, i.e., the creation of metal-graphite nanocomposite materials, offers a new challenge to use these materials as radio-protective ones.

Experimental data on the insertion loss A of electromagnetic radiation are presented in Table and in Fig. 1. The Table contains the insertion loss *A* values in the studied TEG samples in comparison with insertion loss in copper analogues. Copper possesses one of the highest conductivity values ($\rho_{Cu} = 1.72\cdot10^{-8}$ Ω·m (*dc* current at 20°C)) and one of the lowest loss in the microwave range. Cooper conductors are used to construct the microwave waveguides, antennas and reflective shields. The majority of the electric parameters for other materials are usually normalized to the appropriate values for copper. Hence, the presented parameters characterize the microwave properties of the studied samples unambiguously and in a full measure. The insertion loss A values measured at frequency $f \approx 1.8$ GHz are tabulated. It is seen that TEG samples are characterized by the insertion loss values over 16 dB (more than 40 times by the power). This indicates good prospects of their application as radio-protective materials.

The Samples 1, 2, 3 produced under the same technological regimes and having almost the same density display almost the same level of the microwave loss. Extruding of TEG particles results in a significant diminution of particles (the particle length decreases by a factor of 5 to 7). As it is seen from the Table, the level of the microwave loss decreases thereby.

According to [6], the main mechanisms of electromagnetic interference (EMI) shielding are reflection of radiation, absorption and multiple reflections which refer to the reflections at various surfaces or interfaces in the shield. The total loss characterizes the shielding efficiency. To provide the radiation reflection by the shield, the latter should contain mobile charge carriers (electrons or holes) which interact with the radiation electromagnetic fields.

All the investigated CMs based on TEG are electric conductors that is a precondition for high electromagnetic shielding. In addition, compacted TEG samples are highly anisotropic, that causes differences in characteristics measured along different directions of sample. It has been found that the average insertion loss in the direction perpendicular to compacting axis (*a*-axis) are 1.5 times higher than the losses measured along the compacting axis (*C*-axis). This fact may be explained by the electrical conductivity anisotropy in compacted TEG: the ratio between electric conductivity in direction perpendicular to compacting axis σ_a and that along *C*-axis σ_c, σ_a/σ_c, is about ~70. For the single crystalline graphite, this value may attain 10^3–10^4.

For sufficient radiation absorption, the shield should include electric or magnetic dipoles which interact with the radiation electromagnetic fields. The presence of magnetic dipoles can be provided by materials with high magnetic permeability. The insertion loss is a function of $\sigma_r \cdot \mu_r$, while the loss due to reflection is a function of σ_r/μ_r, where σ_r is the electrical conductivity relative to copper and μ_r is the relative magnetic permeability [7]. The supporting of metal particles (Co, Ni) on TEG surface provides the ferromagnetic properties of TEG-metal CMs. As it is seen from the Table, magnetic susceptibility χ is $6 \cdot 10^{-3}$ and $3.5 \cdot 10^{-3}$ cm^3/g for TEG–Co and TEG–Ni, respectively.

Unexpectedly, we have not observed any essential increase of insertion loss for the TEG–Me samples (Co or Ni content ~30–40 mass%). This fact may be explained by significant diminution of TEG particles under chemical modification of TEG surface with metal.

Finally, the third mechanism of EMI shielding is based on multiple reflections which refer to the reflections at various surfaces or interfaces in the shield. This mechanism requires the presence of a large surface area or interface area in the shield. The more effective are the composite materials containing electrically conducting filler with a large surface area. In this case, the surface currents are appeared on large surface and loss due to electric resistance is large. In our opinion, the use of TEG with high specific surface (50–60 m^2/g) as the filler is promising for development of the materials for shielding. As it is seen from Table, the insertion loss A is maximal for TEG-epoxy composites: the loss in sample No.9 TEG-epoxy (89 mass %) is 4 times higher than in other investigated samples.

The depth at which the alternating electric field in radiation drops by a factor of $1/e$ of the incident value is called the skin depth (δ), which is determined as

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}},$$

where f is the frequency; $\mu = \mu_0 \mu_r$, the magnetic permeability $\mu_0 = 4\pi \cdot 10^{-7}$ H/m; σ, the electrical conductivity. Hence, the skin depth decreases with increasing frequency and increasing conductivity or permeability. Due to the skin effect, a composite material containing a conductive filler with a small filler particle size is more effective than one having the conductive filler with a large one. For effective use of the entire filler particle cross-section for shielding, the filler particle size should be comparable to or less than the skin depth.

The polymer-matrix composites containing conductive fillers are attractive for shielding [7–9] due to their processability (e.g. moldability).

Temperature dependences of the insertion loss $A(T)$ for different CM samples are presented in Fig. 1. Evidently, the increasing of insertion loss is observed for all the studied CMs at reducing of temperature. But the character of $A(T)$ was found to depend essentially on the CM type. Materials on the basis of pure TEG are characterized by the ratio $A_{77}/A_{300} \approx 5$. Co additive causes a decreasing of A_{77}/A_{300}. As it is seen from Fig. 1, the A value for CM on the basis of TEG and epoxy is 6–7 times higher than for pure TEG and TEG–Co CMs (9_1 and 9_2 are different samples prepared by using TEG-epoxy (89 mass %) powder). The value for those materials, $A_{77}/A_{300} \approx 1.8$.

Thus, for the first time the insertion loss of electromagnetic radiation in compacted TEG samples has been investigated in temperature range 77–300 K and for two directions — along and across the compacting axis. The investigations of insertion loss in TEG based composites (TEG, TEG–Co, TEG–Ni, TEG-epoxy) have shown that the microwave insertion loss for the studied TEG based samples at 1.8 GHz frequency is ranged within 16.2–23.5 dB. These TEG based materials could offer a challenge to use these materials as radio-protective ones in the electromagnetic shields for radio objects and buildings in particular, in order to avoid the unauthorized access to the confidential information. TEG based CMs containing a polymer binder have been shown to provide high electromagnetic radiation insertion loss as well as a high level of elastic-plastic parameters.The microwave insertion loss for TEG based composites increases under cooling, that agrees with increase of electric resistance of these materials under cooling.

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Електромагнітні втрати у матеріалах на основі вуглецю

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Представлено результати досліджень внесених втрат електромагнітного випромінювання (A) у вуглецевих матеріалах, зокрема, у терморозширеному графіті (ТРГ) і у композитах (КМ) ТРГ-метал і ТРГ-епоксидна смола у температурному інтервалі 77-300К при частоті $f \approx 1{,}8$ ГГц. Проведені дослідження показали, що композитні матеріали на основі ТРГ є перспективними для використання їх у якості захисних матеріалів для екранування джерел електромагнітного випромінювання і, зокрема, для захисту будівель від дії випромінювання. Мікрохвильові внесені втрати L для досліджених зразків на основі ТРГ і ТРГ-метал складають (16,2–18,5) дБ при частоті електромагнітного випромінювання 1,8 ГГц. Знайдено, що у композитах на основі ТРГ, що містять полімерне зв'язуюче (епоксидна смола), електромагнітні внесені втрати достатньо високі (L = 23,5 dB); крім того, ці композити характеризуються високим рівнем пружно-пластичних характеристик. Встановлено, що при зниженні температури внесені електромагнітні втрати A (L) зростають для всіх досліджених композитів, але характер температурних залежностей $A(T)$ суттєво залежить від типу КМ.