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Composites materials with applications in electromagnetic protection

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The increasing use of technology in our everyday environment has led to the ubiquitous presence of electromagnetic fields. Example of electromagnetic sources range from domestic electricity cables and high frequency sources such as radio and television transmitters or cellular phone network stations to visible and ultraviolet light. From this unprecedented situation arise at least two main problems which are waiting to be solved: the safety of information transmissions and electronic devices proper working one a side and on the other hand the biological protection against the increasing level of electromagnetic fields radiated from such a large variety of sources. The paper presents the different composite materials, produced in rigid or flexible form, with potential applications as electromagnetic shields, in range of 0.8 – 3 GHz, with a medium attenuation of ca. 20 dB. The materials are prepared through Powder Metallurgy ways as carbon/ceramic, recycled pyrite ashes/polymeric composites.

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Keywords: Electromagnetic protection, Composite material, Powder metallurgy route

1. Introduction

With the rapid advances and broad implementation of computer and telecommunication technologies there is increased interest in shielding of electromagnetic radiation, especially in the radio and microwave frequency ranges.

The usual shielding techniques focus on the use of standard metals and their composites, which have disadvantage due to limited mechanical flexibility, heavy weight, corrosion, and difficulty of tuning the shielding efficiency. Carbon-ceramic composites are promising materials for shielding electromagnetic radiation and reducing or elimination of electromagnetic interference (EMI) because of their conductivity and dielectric constant and ease of control of these properties through chemical processing [1,2].

Electrical conductivity of such systems is strongly dependent on the concentration of conductive phase [3]. When weight ratio of conductive phase achieve a specific critical value, named percolation threshold, appears a dielectric-conductive microstructural phase transition.

In the last years were started projects for the valorisation of the pyrite ashes resulted from the processes of sulphuric acid fabrication at the Chemical Plants from Romania. Narrow of these plants exist pyrite ashes dump, which contains of about 20 millions tones [4]. The valorisation of these ashes is imposed by economically and ecologic criteria [5]. For an iron amount of 49 - 53 %, which is present in the pyrite ashes, result an iron reserve of about 2 millions tones.

2. Experimental

2.1 Carbon/ceramic composites

The raw materials used for carbon/ceramic composite materials are presented in Table 1.

Table 1. The raw materials used for carbon/ceramic composites preparation.

Graphite	Alumina	Kaolin	Sodium silicate
< 63 μm	< 80 μm	< 250 μm	Water solution with a density 2g/cm^3

The filler materials (graphite, alumina, kaolin) were homogenised in a double-con mixer for 30 min. with small speed. The mixed powder are homogenised with sodium silicate as binder and then dry in free air, one day. After that the composite granules are crushed and sorted to a granulation of 63 μm. The carbon/ceramic composites samples are obtained by forming the powder in a metal die to a pressure of about 60 – 80 MPa. The green samples are dried 24 h to a constant temperature of about 55 ± 5^{o}C and then composites are thermal treated at about 900^{o}C. The compositional map for designed C-ceramic composites, ceramic-matrix for electromagnetic shielding applications is presented in the Table 2.

Table 2. Compositional map for designed C-ceramic composites.

Mixture samples	Compositions (wt. %)			
	P4	**P5**	**P6**	**P7**
	41	**51**	**61**	**71**
Kaolin / Graphite / Al_2O_3	55 / 40 / 5	45 / 50 / 5	35 / 60 / 5	25 / 70 / 5
	42	**52**	**62**	**72**
Kaolin / Graphite / Al_2O_3	50 / 40 / 10	40 / 50 / 10	30 / 60 / 10	20 / 70 / 10
	43	**53**	**63**	**73**
Kaolin / Graphite / Al_2O_3	45 / 40 / 15	35 / 50 / 15	25 / 60 / 15	15 / 70 / 15
	44	**54**	**64**	**74**
Kaolin / Graphite / Al_2O_3	40 / 40 / 20	30 / 50 / 20	20 / 60 / 20	10 / 70 / 20
	45	**55**	**65**	**75**
Kaolin / Graphite / Al_2O_3	35 / 40 / 25	25 / 50 / 25	15 / 60 / 25	5 / 70 / 25

2.2 Recycled pyrite ashes/polymeric composites

The medium chemical composition of the studied pyrite is presented in Table 3. The amount of precious metals: Au and Ag is 1.2 - 1.6 g/to, respectively 22 - 30 g/to and the humidity is around 25 - 30%. The main amount of elements/oxides of the pyrite ashes wastes are, in wt. %: 5.07% SiO_2, 2.75% S, 0.62% Zn, 0.39% Pb, 0.07% As, 1.96% Cu, 59.35 % Fe, 0.6% MnO, 0.8% Al_2O_3. In order to eliminate As, the pyrite ashes must processed as pellets with coal powders and treated in rotative furnace at temperatures in the range 700 - 900^{o}C. The constitutive iron is present in the pyrite ashes as different compounds: α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, FeS, $CuFeS_2$.

In order to mark out the separation methods which can be used for the recovering of a significant part of the constitutive iron from the pyrite ashes, the wastes was thermal treated in different conditions (see Table 3) [7]. After the thermal treatments, it was observed the changes produced by these on the powders: the weight losses (due to the water elimination), the powders aspect.

Table 3. The thermal treatments performed on the pyrite ashes.

Sample	Thermal treatment
1	Oven drying at 150^{o}C, for 5 hours, in air
2	Furnace calcinations at 800 – 850^{o}C, for 2 – 3 hours, in air
3	Reduction at 800 – 850^{o}C, for 2 – 3 hours, in hydrogen

The magnetic characterization of the obtained powders was performed with vibrating sample magnetometer type Lakeshore 7300, using powder samples.

For investigation the EMI shielding properties, the composite samples were exposed to different frequencies electromagnetic fields (100 kHz – 12 GHz).

3. Results and discussion

3.1 Carbon/ceramic composite

The carbon-ceramic composites developed are ceramic-matrix composites having dielectric components (kaolin and Al_2O_3) with inclusion of a conducting phase (natural graphite) [7]. These composites were designed to display a combination of characteristics of components as micro-electrical networks, micro-resistors (carbon) and micro-capacitors (insulators), randomly disposed in space. The electrical behaviour of this type of composites is confirmed by XRD investigations (see Figs. 1 - 3).

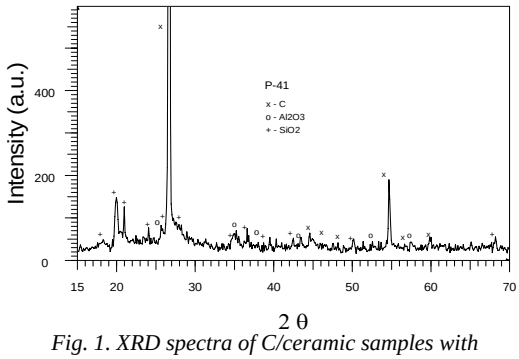


Fig. 1. XRD spectra of C/ceramic samples with composition: 55% caolin-40% graphite-5% Al_2O_3.

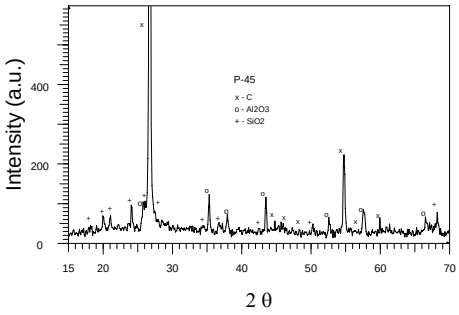


Fig. 2. XRD spectra of C/ceramic samples with composition: 35% caolin-40% graphite-25% Al_2O_3.

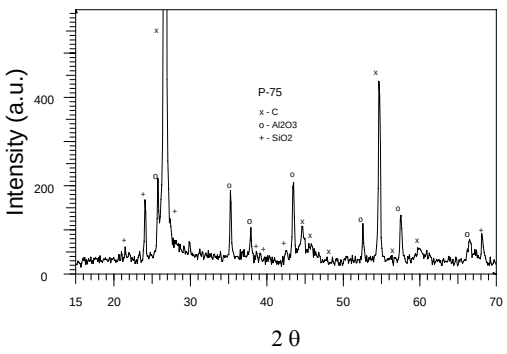


Fig. 3. XRD spectra of C/ceramic samples with composition: 5% caolin-70% graphite-25% Al_2O_3.

Electrical characterization of the obtained materials were done by V-A method. It was established the electrical resistivity behaviour function of the caolin/alumina ratio (wt. %) between 55:5 and 2:25. In the Fig. 4 is presented the variation of electrical resistivity function of the alumina content (wt. %) for all series of designed composites: with 40% graphite (P4), with 50 % graphite (P5), with 60 % graphite (P6), and with 70 % graphite (P7).

It was observed an accentuated variation of resistivity in the case of samples with 40 % graphite (P4) and with 50 % graphite (P5). The electrical resistivity is decreasing in these case with the increasing of alumina content. In the case of samples having 60 % or 70 % wt., graphite (P6 and P7), the alumina content variation does not influence the electrical resistivity.

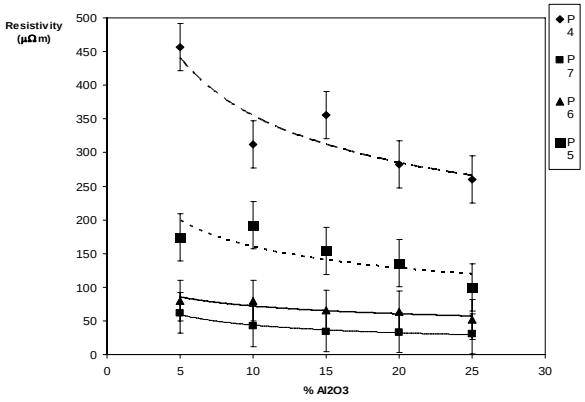


Fig. 4. Electrical resistivity versus alumina content for the studied C/ceramic composites.

It is known that in general a material to be considered as EM shielding should be placed over the limit of 20 dB. The obtained results for the shielding tests are plotted as absorption, in dB, *versus* frequencies (Figs. 5 – 8). The studied C/ceramic composites are investigated, from the point of view of the shielding properties, in in the frequency range between 100 kHz – 20MHz. The all 20 samples shown electromagnetic shielding properties in the frequency range between 1-10 MHz, with the highest registered values for shielding effectivenes of 60 - 70dB. There was a slight difference of 5 - 6 dB between tested samples. In the range of 20 - 300 MHz could be seen sharp modifications of shielding effectiveness, between 25 and 60 dB.

In the range of 300 - 1000 MHz, the samples shown the same behaviour regarding the shielding properties for the all tested samples, with a large difference of 18 to 42 dB.

The tests between 1 - 12 GHz shown large differences between the values of shielding effectiveness.

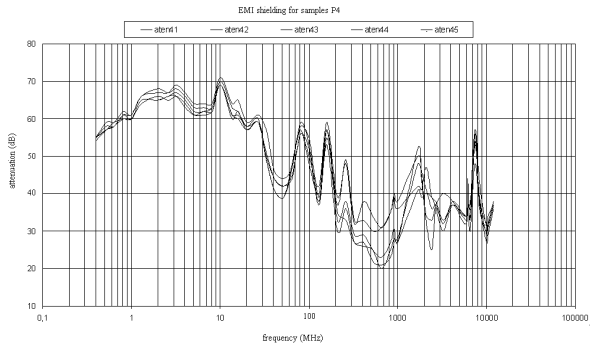


Fig. 5. Attenuation versus frequency for C/ceramic composites with 40 % graphite (P4 samples).

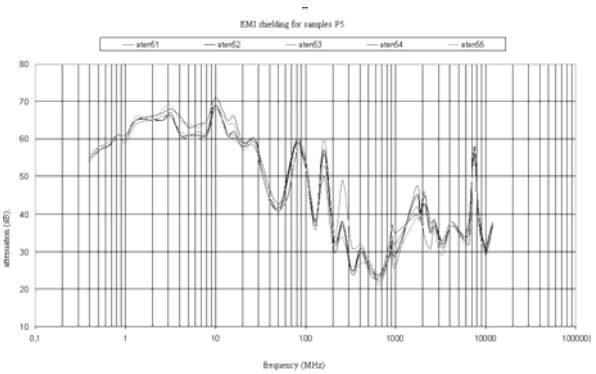


Fig. 6. Attenuation versus frequency for C/ceramic composites with 50 % graphite (P5 samples).

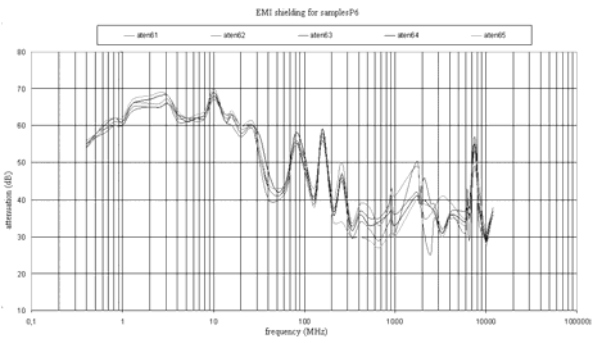


Fig. 7. Attenuation versus frequency for C/ceramic composites with 60 % graphite (P6 samples).

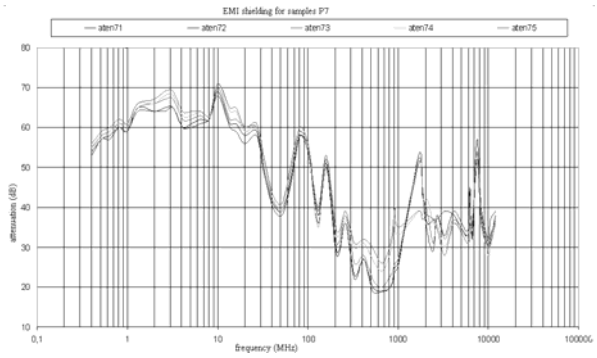
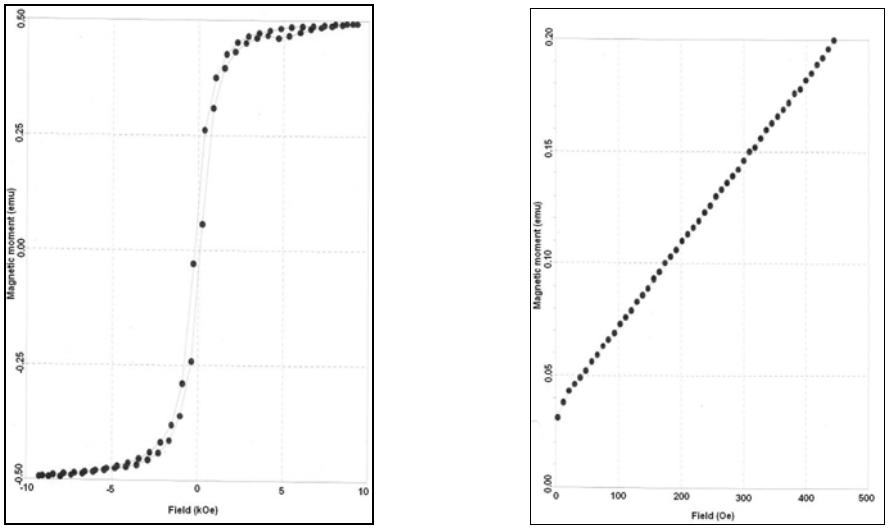


Fig. 8. Attenuation versus frequency for C/ceramic composites with 70 % graphite (P7 samples).

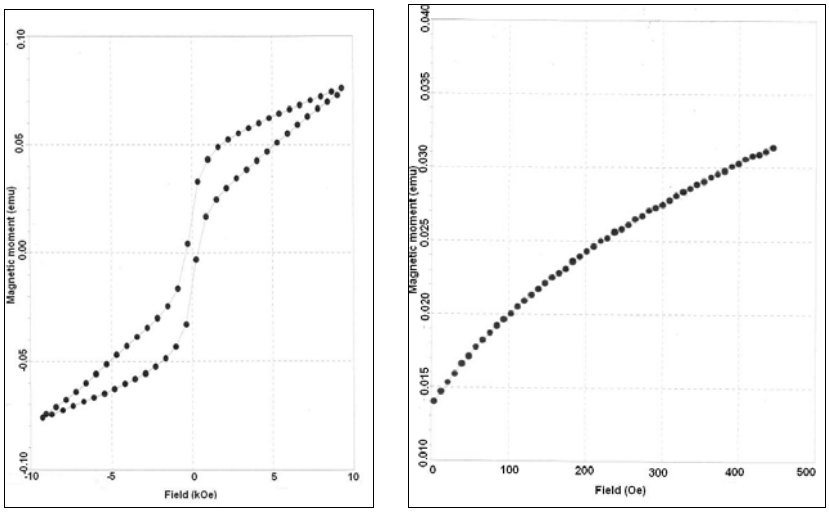
3.2 Recycled pyrite ashes/polymeric composites

The specific magnetization of the pyrite ashes, after oven drying at 150°C, for 5 hours, in air is very low, σ = 3.65 emu/g (see Fig. 9 (a). The hysteresis curve show that the analyzed ashes is a ferromagnetic material (or ferromagnetic), having in composition iron oxides: α-Fe_2O_3 (antiferromagnetic) and γ-Fe_2O_3 (ferromagnetic) and Fe_3O_4 (ferrimagnetic). Because the specific magnetisations for γ-Fe_2O_3 and Fe_3O_4 at room temperature were 74 emu/g, respectively 84 emu/g, results, from the very low values of the sample specific magnetization, that the dried pyrite ashes sample contains a great quantity of α-Fe_2O_3. The magnetic measurements at low field intensities (see Fig. 9 (b), the initial magnetization curve) for this sample were in accordance with the value from the Fig. 9 (a).



(a) (b)

Fig. 9. Hysteresis (a) and initial magnetization (b) curves for the pyrite ashes samples, dried at 150°C for 5 h.



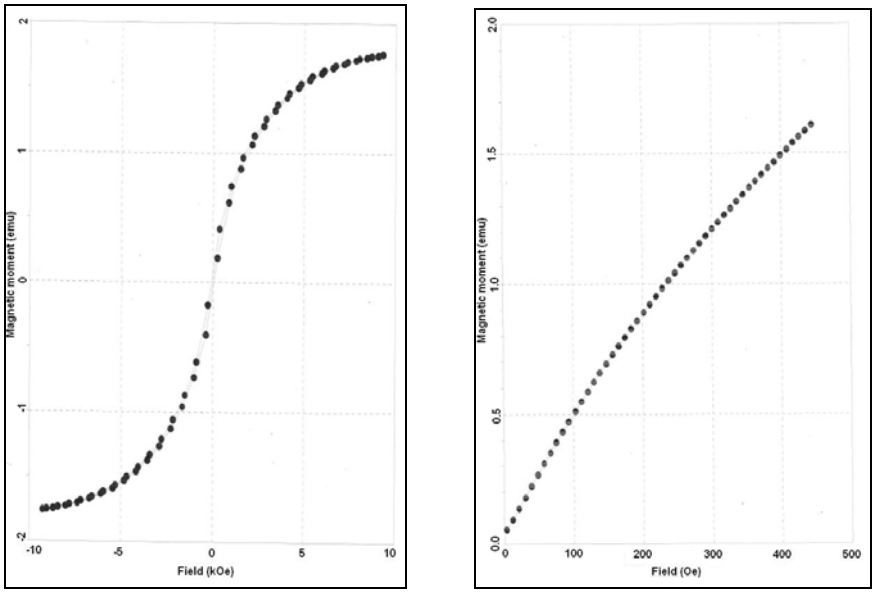
(a) (b)

Fig. 10. Hysteresis (a) and initial magnetization (b) curves for the pyrite ashes samples, heat-treated in air at 800°C for 2h.

After calcinations in air at temperatures in the range 800 – 850 ^oC for 2 – 3 hours, the α-Fe_2O_3 amount has increased and the specific magnetization of this powder is only 0.672 emu/g (see Fig. 10a). The high coercivity of this samples (due to the ferro- and ferromagnetic components, γ-Fe_2O_3 respectively Fe_3O_4) is a proof that these ferro- and ferromagnetic constituents were magnetically isolated in the magnetic matrix of the ashes and have a preferential elongated shape. The low values of the magnetizations were confirmed by the measurements at low magnetic fields – the initial magnetisation curve, presented in Fig. 10b.

Fig. 11 (a) presents the hysteresis curves for the pyrite ashes samples, heat-treated in hydrogen at 850^{o}C/2 h. We can observe that the Fe oxides were almost reduced and the specific magnetization, σ = 128 emu/g is very close to the value specific magnetization of Fe, σ = 222 emu/g. Because $\sigma > \sigma(Fe_2O_3) = \sigma_\gamma$ and $\sigma = \sigma\ (Fe_3O_4) = \sigma_m$, that means that in the heat-treated pyrite mixture we have also free iron. So, can be estimated the weight concentration of this free iron. The σ values at low magnetic fields is according to the values obtained from the initial magnetization curve (Fig. 11 (b)).

The VSM measurements were in accordance with the d.c. hysteresisgraph measurements. The great inequality between the specific magnetizations of the samples heat-treated at 850^{o}C/2 h in hydrogen and the calcinated (800^{o}C/2 h) samples maintain. However, for these measurements we have not attained to the samples saturation because of the high internal demagnetizing fields due to the interstices between the ferromagnetic particles.



(a) (b)

Fig. 11. Hysteresis (a) and initial magnetization (b) curves for the pyrite ashes samples, heat-treated in hydrogen at 850^{o}C for 2 h.

We consider that the total magnetic moment, M of the samples, after H_2 reducing treatment, is a sum of the moments for γ-Fe_2O_3, M_γ, for Fe_3O_4, M_m and for Fe, M_{Fe}:

$$M_\gamma + M_m + M_{Fe} = M \tag{1}$$

If we share relation (1) to the sample mass, m and $m = m_i / c_i$, where *i* can be γ or Fe, than we can obtain:

$$\frac{\mathcal{M}_\gamma}{\frac{m_\gamma}{c_\gamma}} + \frac{\mathcal{M}_m}{\frac{m_m}{c_m}} + \frac{\mathcal{M}_{Fe}}{\frac{m_{Fe}}{c_{Fe}}} = \frac{\mathcal{M}}{m} \tag{2a}$$

$$\sigma_\gamma c_\gamma + \sigma_m c_m + \sigma_{Fe} c_{Fe} = \sigma \tag{2b}$$

Because σ_γ and σ_m not differ very much, we can change σ_γ and σ_m with their arithmetical average $(\sigma_\gamma + \sigma_m)/2$, and $c_\gamma + c_m = 1 - c_{Fe}$, from (2) results:

$$\frac{\sigma_\gamma + \sigma_m}{2}\left(1 - c_{Fe}\right) + \sigma_{Fe} c_{Fe} = \sigma\,, \tag{3}$$

and results the iron amount, C_{Fe}:

$$c_{Fe} = \frac{\sigma - \frac{\sigma_\gamma + \sigma_m}{2}}{\sigma_{Fe} - \frac{\sigma_\gamma + \sigma_m}{2}} \tag{4}$$

With our data, results that $c_{Fe} \simeq 34$ %, namely in the reduced ashes exist an amount of ~ 34 % metallic iron.

Because not all the oxides were reduced, we can suppose that these are intergranular compounds, which cannot be reduced in the presence of hydrogen, at temperatures in the range of 800 – 850 ^{o}C.

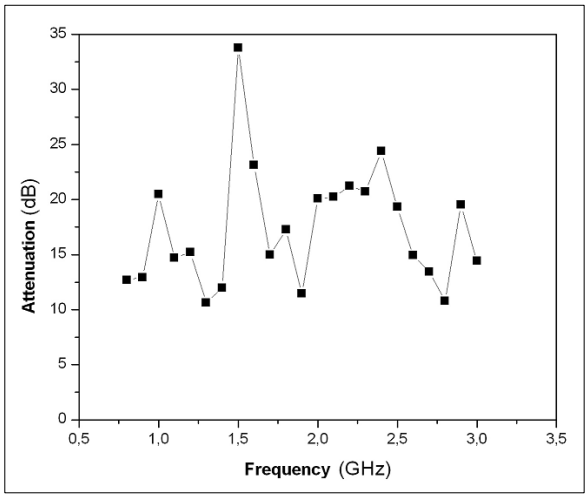


Fig. 12. Attenuation dependence on frequency for the composites materials prepared from the reduced pyrite ashes.

By testing and evaluation of sample behavior in the frequency range between 0.8 – 3 GHz (see Fig. 12) can be observe that the composites prepared by reduced pyrite ashes and epoxy resin as binder shown electromagnetic shielding properties, with the highest registered values for shielding effectiveness of 30 - 35 dB. For this type of shielding composite materials, in all ranges of frequency could be seen sharp modification of shielding effectiveness, between 5 and 35 dB. The modification was expected due to resonant phenomena.

4. Conclusions

The carbon-ceramic composites developed in this stage are ceramic-matrix composites having dielectric components (kaolin and Al_2O_3) with inclusion of a conducting phase (natural graphite).

The dielectric phases show strong responses where they became active and hence giving a corresponding specific range of frequencies. This representation corresponds to a texture of dielectric networks with conductive inclusions, which is confirmed by XRD investigations. Considering the obtained results, we recomand the utilization of carbon/ceramic composites in applications regarding EMI shielding in the frequency range of 1 to 10 GHz. There is possibily for realization of a shielding system with extended utilization between 100 kHz - 12 GHz, for attenuation in large areas.

The useful metallic elements i.e. iron, can be recovered from the pyrite ashes, by an appropriate reducing thermal treatment. The resulted powders can be processed, by embedding in an epoxy resin matrix, in order to obtain composite materials, with can be used, as electromagnetic shields, due to their magnetic properties.

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