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Electroconductivity of Al_2O_3/graphene nanocomposite processed by SPS technique

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Abstract. Electrical conductivity (σ), relative dielectric permittivity (ε_r) and dissipation factor (*D*) measured in graphene-alumina composites. Samples obtained by plasma spark sintering (SPS) from a mixture of raw powders: δ-alumina (36 nm average particle size) and graphene flakes (3 nm thickness and 2–3 μm length). Graphene content in samples was 0, 1 and 2% by weight. The study carried out for frequencies from 50 Hz to 100 kHz. Both σ and ε_r were higher for Al_2O_3–2% graphene: up to 90 μS/m and 19 respectively; while alumina with 1% graphene showed similar values to the pure alumina samples: 50 μS/m to electrical conductivity and 16 to relative permittivity. The dissipation factor was similar in the three materials tested. *D* increased with the frequency, reaching high values (0.7) at 100 kHz. Composites with 1 and 2% graphene content showed a dissimilar dielectric behavior with the frequency. Alumina reflected a classical behavior of the permittivity dependence with the frequency. Graphene composites also show the same behavior at frequencies above 100 Hz. Below this frequency, the presence of graphene increases the relative permittivity to exceed that from pure alumina. The graphene content leads to rise of relative permittivity, which means easier polarizability.

1. Introduction

The study of the properties of ceramic composite materials is one of the priority trends in the development of modern materials science. Of particular interest is the introduction of a two-dimensional structure in the graphene composite. This chemically inert material has unique properties: very high electronic conductivity, thermal conductivity above 5000 W/mK and an elastic modulus close to 1 TPa, due to the large specific surface area of graphene plates [1–3].

The method of plasma spark-sintering (SPS) is one of the most used for the production of composite ceramic materials with a nanostructure, since it significantly reduces the sintering time. This makes it possible to avoid thermally activated structure-phase transformations in the nanopowder and to obtain a non-porous material [4, 5].

Al_2O_3 ceramics is the most studied material for a matrix of composites with graphene due to its wide use as a structural material in the automotive, aerospace and biomedical fields.

The present study of Al_2O_3/graphene composites is associated with the problem of increasing the electrical conductivity of aluminum oxide. It is assumed that the mechanism of the occurrence of conductivity can be associated with overlapping of the surfaces of graphene plates, which form a more efficient network than graphene nanotubes, in which the contact is point like and leads to a higher resistance. When a sufficiently high electrical conductivity of 1 S/m is reached, this material can be used for the manufacture of complex ceramic parts by the methods of electric spark machining [6]. The authors of this paper investigated the dependence of the electrical conductivity measured on alternating current on the content of graphene and showed that when graphene is added above 8 wt %, the required electrical conductivity is achieved. With a graphene content below the percolation limit the electrical conductivity did not exceed 10^{-9} S/m. The authors of another work carried out similar studies of the electrical conductivity at a direct current of a composite with 2 wt % graphene and showed that the electrical conductivity was 10^{-2} S/m [7]. Such a large difference in the results may be due to different methods of measuring electrical conductivity. The goal of this paper is to investigate the effect of graphene additives in the range from 0 to 2 wt % on the electrical properties of the Al_2O_3/graphene nanocomposite in the alternating current measurement process.

2. Experimental method and materials

Nanopowders δ-Al_2O_3 and graphene were used in the work. The starting powder δ-Al_2O_3 was obtained by oxidizing disperse aluminum in air plasma (IMET RAS). The average particle size was 36 nm, the surface area was 35–40 m^2/g. The particles of the original powders are rounded, but most of the particles are collected in agglomerates. Graphene was produced by the method of ultrasonic exfoliation by the firm Graphene-tech (Spain) and was not oxidized flakes whose thickness and length were 3 nm and 2–3 μm, respectively. A mixture of the components of the composite was ultrasonically dispersed in dimethyl formamide using a Sonicator Q500 ultrasound disperser at a power of 250 W. The optimum dispersion time was determined experimentally and was 40 min. The resulting suspension was air-dried by heating and constant stirring for 1 h, and then triturated in a mortar.

SPS powder mixtures were conducted in a vacuum on a Labox-625 SinterLand in a graphite matrix with an internal diameter of 15 mm. To reduce heat losses due to radiation and to reduce the temperature difference between the matrix surface and the sintered object, the matrix was enveloped by a graphite felt 6 mm thick with a hole for the pyrometer. Thus, the pyrometer measured the temperature of the lateral outer surface of the matrix at the level of location of the sintered object. The sintering regime was chosen empirically for pure alumina from the condition of obtaining a high homogeneity of compacts with a maximum average microhardness of their surface [8]. The heating rate was 100°C/min; the maximum heating temperature measured by the pyrometer on the surface of the matrix was 1550°C; holding at maximum temperature was 10 min. To the punches a pressure of 50 MPa was applied. To prevent welding to the mold, the sintered powder is isolated from it by graphite paper. The thickness of the sample disk after sintering was 2 mm. The same sintering regime was also used in the preparation of composites with a content of graphene by mass of 0, 1, and 2%. The electrical properties, the relative permittivity (ε_r) and the loss tangent (*D*), in the thickness direction of sintered tablets, were measured in an alternating electric field from 50 Hz to 100 kHz using precision Hameg 8118 and Agilent 4294A devices with an accuracy of 0.05%.

3. Experimental results

Figure 1 shows the frequency dependences of the electrical properties of ε_r and *D* of a sintered composite with various graphene contents. In the absence of graphene (0%), these dependences reflect the classical behavior of the dielectric - a decrease in the dielectric constant (figure 1a) due to the disconnection of one of the polarization mechanisms (electronic or ionic) and an increase in dielectric losses (figure 1b). The samples with graphene show the same dielectric behavior for frequencies above 100 Hz.

The increase in the graphene content is manifested in two ways. At low frequencies, up to 100 Hz (figure 1a), the presence of graphene leads to dielectric constant values less than one of the pure alumina which indicates the appearance of conductivity. For higher frequencies the increasing in graphene content leads to the rise of the relative permittivity which means an easy sample polarizability.

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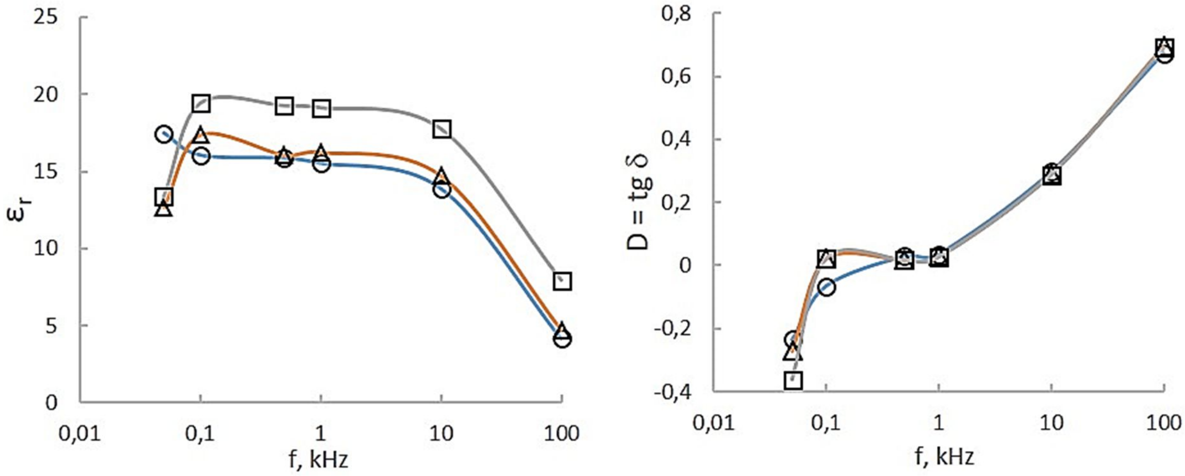

(a) (b)

Figure 1. Dependence of the (a) relative permittivity and (b) dielectric loss of the composite on the field frequency and graphene content. ◯ 0%; △ 1%; □ 2%

The curves for *D* (figure 1b) reflect an almost monotonic increase with frequency, and are very similar for more than 700 Hz in all samples. The coincidence of all three curves for frequencies above 700 Hz and their consistency with the curves of the relative permittivity indicates the prevalence of dielectric losses in aluminum oxide. The curves from the samples with graphene indicate the existence of ohmic conductivity below 700 Hz.

The composites conductivity (σ) was calculated as the real part of their admittance: $\sigma = (2\pi f \varepsilon_r \varepsilon_0)/D$. Its dependence on the frequency and graphene content (figure 2) show that from the 0% of graphene the value of σ is quite high. It can be explained by the presence of traces of carbon due to the details of the SPS method. The growths of the conductance with the frequency is a quite general trend for the composite dielectrics [9].

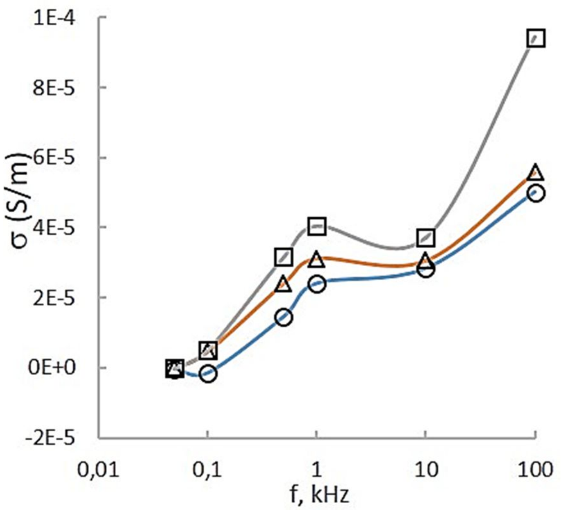

Figure 2. Dependence of the composite relative conductivity on the field frequency and graphene content. ◯ 0%; △ 1%; □ 2%.

4. Conclusions

The effect of the additive graphene and the frequency of alternating current on the electrical properties of SPS composites is established. It is shown that at frequencies up to 70 Hz, the addition of graphene up to 2% to the nanopowder of aluminum oxide can increase the electrical conductivity of the sintered composite in comparison with the value for pure corundum. This is manifested in a decrease in the dielectric constant and an increase in the dielectric loss. An increase in the frequency of the current in the region up to 100 kHz promotes a stronger increase in electrical conductivity, with the effect of graphene weakening or even absent.

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