Current state of the technology of obtaining and research of properties of the corundum-graphene composite

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Abstract. The aim of the work is to review publications on a narrow circle of composites, namely corundum graphene. Quite a lot of research has been devoted to this composite to conduct generalizations and identify patterns.

Graphene, which is a two-dimensional allotropic modification of graphite, was obtained by Novoselov and Geim in 2005 [1]. It has a number of unique electrophysical, mechanical, thermal properties. Graphene is produced on an industrial scale by ultrasonic exfoliation of microcrystalline graphite crystals, SEM image of graphene produced by the method is shown in figure 1.

![Figure 1. Image of graphene particles in a scanning electron microscope.](image)

The corundum-graphene composite is derived by ultrasonic mixing of graphene powder and Al2O3 nanopowder in a liquid followed by their spark plasma sintering (SPS). In the sintering process, graphene particles are embedded in corundum grains or located at their boundaries, exerting a
reinforcing effect. The presence of graphene in the sintered composite is appeared both in a slight decrease in the density of the compact and in an increase in its microhardness [2]. The abrasion test results of the composite during circular motion of a sapphire ball over its surface at room temperature are also presented. In figure 2 the profilogram of the wear track and its image for pure corundum is shown. Torn grains and nanosized particles are visible (the result of abrasion of grains).

![Profilogram of the wear track and its image in a corundum sample without graphene.](image1)

**Figure 2.** Profilogram of the wear track and its image in a corundum sample without graphene.

With a graphene content of 1 and 2%, the wear path is almost absent. The amount of wear in both cases is lower than that of pure corundum by 2 orders of magnitude. The friction coefficient decreases by 40% in a composite with 1% graphene and by 20% in a composite with 2% graphene [3]. The surface view of the wear paths is shown in figure 3.

![The surface of the wear paths for a composite with 1 wt.% graphene (left) and 2 wt.% graphene (right).](image2)

**Figure 3.** The surface of the wear paths for a composite with 1 wt.% graphene (left) and 2 wt.% graphene (right).

At a content of 1% graphene, a manifestation of the reinforcing effect of graphene is visible: the grains hardly knock out from the rubbing surface. At a content of 2% graphene, the wear surface is almost completely covered by a viscous mass, acting as a layer between the abrasion surfaces. It is assumed that the viscous mass is formed from corundum nanoparticles with juvenile surfaces formed at the initial stage of wear and graphene particles leaching from the composite during friction.

If graphene flakes are evenly distributed in the volume of the composite, if they are sufficient, they can line up in chains or nets with the formation of electrical contacts between the flakes. With high electrical conductivity inherent to graphene and a non-conductive filler, the composite becomes conductive [4–6], and it works with graphene produced by different methods. In the work [4], oxidized graphene was used. A mixture of powders was obtained in a colloidal manner. In [5, 6], graphene was
obtained from graphite powder, grinding it in a mixture with alumina in a ball mill according to the method proposed in [7].

Most measurements of the conductivity of the corundum-graphene composite were carried out at room temperature and below. However, in a series of works [3, 8–11], the electrical resistance was measured with uniform heating up to a temperature of 1600 °C. It was shown that when the composite was prepared by the SPS method at a pressure of 40 MPa, the resistance decreased exponentially with temperature by 4 orders of magnitude, which is characteristic of pure alumina, in which the ionic conductivity after 450 °C becomes electronic. The presence of graphene up to its concentration in the composite up to 2 wt.% practically did not affect the electrical resistance [3]. An important feature of the temperature dependence of the electrical resistivity is its reversibility upon cooling.

When sintering a mixture of powders with a graphene content of 2 wt.% was carried out without applying pressure to the punches (only the weight of the current-supplying plunger of the apparatus affected the powder), the electrical resistance of the obtained tablet after cooling to room temperature was 6 orders of magnitude lower than usual. Subsequent heating-cooling with simultaneous measurement of electrical resistance, the resistance practically did not change and amounted to 0.25 Ω * m.

Even lower values of electrical resistance were obtained by sintering a mixture of alumina with 2 wt.% graphene in a hot pressing unit during radiation heating [8]. During heating and an hour exposure at 1600 °C, the resistance approached the values characteristic of composites sintered in the SPS upon application of pressure, but upon subsequent cooling to room temperature it dropped by 3 orders of magnitude and amounted to 0.09 Ω * m, i.e. it became 7 orders of magnitude lower than that of corundum and composites sintered in the SPS upon application of a pressure of 40 MPa. A photograph of the cleavage of such a composite taken on a SEM without applying a conductive coating is shown in figure 4. Electrically conductive areas have a warmer color. It can be seen that they form a network penetrating the bulk of the composite and providing the electrical conductivity of the entire sample. Dark areas at a higher magnification have a columnar structure, which is not characteristic of corundum.

![Figure 4. A photograph of the composite cleavage taken on a SEM.](image)

It was established in [9] that at a temperature of about 1600 °C, a chemical interaction occurs between the carbon of graphene and aluminum oxide with the formation of aluminum carbide and carbon monoxide. The result of this reaction is the formation of a porous coarse-grained structure from corundum grains and flakes of aluminum carbide. The indicated temperature can be considered as the temperature limit of stability of the corundum-graphene composite.

The review showed that the corundum-graphene composite is a promising material both from the point of view of reducing wear during friction, and from the point of view of obtaining conductive ceramics having an electrical resistance independent of temperature.
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