Possible nature of electrical conductivity of the corund-graphene composite

A G Zholnin and R S Hafizov
The State University of Land Use Planning SULUP, Kazakova str., 105064, Moscow, Russia
E-mail: azholnin@list.ru

Abstract. The effect of sintering modes on the electrical conductivity of the corundum-graphene composite is investigated. The assumption about the nature of the electrically conductive structure and the conditions of its formation is substantiated.

Graphene, which is a two-dimensional allotrope modification of graphite, was obtained by Novoselov and Geim in 2005 [1]. It possesses a number of unique electrophysical, mechanical and thermal properties. Previous studies have shown 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 with electrical resistance independent of temperature [2–6]. The work [7] shows the promising use of graphene as a hardening additive in ceramic multifaceted cutting inserts for turning tools. In the case of appreciable conductivity of the composite, it becomes possible to electrospark treatment and shape semi-finished products from the graphene / Al2O3 composite. The good electrical conductivity of carbon-ceramic crucibles also makes it possible to use them for heat treatment and electric melting of a number of materials in high-frequency furnaces [8].

The aim of this work is to deepen knowledge about the nature of the formation of a conducting structure when obtaining a corundum-graphene composite, by continuing the research carried out earlier in this direction [9–11].

The corundum-graphene composite was obtained by ultrasonic mixing of graphene powder and aluminum oxide nanopowder in a liquid, followed by their spark-plasma sintering (SPS) or high-temperature pressing (HCP). In the process of compaction, graphene particles are embedded in corundum grains or are located at their boundaries, providing a hardening effect. Under certain compaction modes, it is possible to increase the electrical conductivity of the resulting composite by several orders of magnitude. The electrical resistance was measured at a graphene content of 2 wt. %.

It was found that when sintering a mixture of powders by the HPS method with a pressure of 50 MPa applied during sintering, the presence of graphene had practically no effect on the electrical resistance of the resulting composite. In both cases, a classic insulator was obtained. Its resistance dropped by four orders of magnitude upon heating to the sintering temperature and restored upon subsequent cooling to room temperature.

High electrical conductivity was obtained when sintering was carried out at low pressure (1 MPa). At room temperature, the conductivity of the obtained composite was close to the conductivity of metals (7 orders of magnitude lower than that of corundum without graphene)[9]. At the same time, in the process of reheating and subsequent cooling, the electrical resistance was practically independent...
of temperature and amounted to 0.25 Ω * m. It is assumed that the electrical conductivity is provided by the formation in the bulk of the composite of a conducting network consisting of graphene cells in electrical contact with each other.

The use of an ECP unit for sintering, where heating is carried out by an external heater, without the use of pulse currents, made it possible to measure the electrical resistance directly during the sintering process (1600 ° C, holding for an hour at this temperature and subsequent cooling). During the heating of the mixture, the electrical resistance dropped, during holding it stabilized, but upon subsequent cooling to room temperature, it dropped by another 3 orders of magnitude and amounted to 0.09 Ω * m, i.e. became 7 orders of magnitude less than that of corundum and composites sintered in ATP under pressure. External examination of the resulting compact revealed the presence of two zones: a dark one in the middle of the sample and a light one in its peripheral area. A point resistance measurement revealed a high conductivity in the central regions and a complete absence of electrical conductivity in the periphery.

It was found that during exposure at a temperature of 1600 ° C, a chemical interaction occurs in the composite between graphene carbon and aluminum oxide with the formation of aluminum carbide and carbon monoxide \cite{10}. The result of this reaction is the formation of a porous coarse-grained structure from corundum grains and aluminum carbide flakes (figure 1). This temperature can be considered as the temperature limit of stability of the corundum-graphene composite.

In figure 2 shows a photograph of the cleavage of the central section of the composite, taken on an SEM without applying a conductive coating, is shown. Electrically conductive areas are darker in color. It can be seen that they form a grid that permeates the bulk of the composite and ensures the electrical conductivity of the entire sample. Dark areas at higher magnification have a columnar structure, which is not typical for corundum (figure 3).

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure1.png}
\caption{An example of a flocculent formation at the peripheral portion of the sample.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure2.png}
\caption{Microstructure of the cleavage of the electrically conductive part of the corundum-graphene composite.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure3.png}
\caption{Columnar structure of dark blotches.}
\end{figure}
The question of the nature of the conductivity of the corundum-graphene composite remains unclear. The electrical conductivity of the composite is caused by the formation of a network consisting of graphene flakes in contact with each other, or graphene forms electrically conductive chemical compounds with corundum, and from them an electrically conductive network is formed, observed in figure 1. The latter is supported by the presence of structures in the conduction zones that are not characteristic of corundum (figure 2), and traces of phases of the complex compound Al₄O₄C detected in X-ray spectra [10].

Thus, previous studies have established:
1. The formation of an electrically conductive structure in the corundum-graphene composite takes place only during sintering at low pressure on the powder.
2. The temperature limit for the existence of an electrically conductive structure in a composite is a temperature of about 1600 °C, when graphene chemically interacts with aluminum oxide with the formation of aluminum carbide and carbon monoxide.

To clarify the question of at what stage of the formation of a compact the formation of a conducting structure takes place, 5 samples with a diameter of 15 mm and a thickness of 1-1.5 mm were compacted by the SPE method in various modes. In all cases, the graphene content was 2% by weight; heating and subsequent holding were carried out at 1550 °C. The sintering modes are listed in more detail in the table 1.

Table 1. Sintering modes.

| Sample no. | Heating pressure, MPa | Holding pressure, MPa | Holding time, min | Electrical resistance, Ω |
|------------|-----------------------|-----------------------|-------------------|-------------------------|
| 1          | 50                    | 50                    | 10                | 215                     |
| 2          | 0,6                   | 50                    | 10                | 210                     |
| 3          | 0,6                   | 0,6                   | 0,5               | 220                     |
| 4          | 0,6                   | 0,6                   | 10                | 21                      |
| 5          | 0,6                   | 0,6                   | 20                | 2,8                     |

After sintering, the electrical resistance of the samples was measured at room temperature along their axis. The results are also shown in the table.

From the results obtained it follows:
1. The conductive structure is formed during holding at the maximum temperature only at a pressure of 0.6 MPa in the presence of holding at the maximum temperature. With increasing exposure time, the electrical resistance decreases exponentially (figure 4).

2. Applying a pressure of 50 MPa both at the beginning of heating and during holding blocks the formation of a conductive structure.

From the foregoing, it can be assumed that the conducting structure is formed as a result of a chemical reaction between graphene and aluminum oxide at its initial stage, when compounds of the $\text{Al}_4\text{O}_4\text{C}$ type are formed. For the reaction to proceed, it is necessary to remove carbon monoxide from the reaction zone. At a pressure of 50 MPa, there is no open porosity, carbon monoxide is not removed, and the reaction is blocked. At low sintering pressure, open porosity is present, which ensures the removal of carbon monoxide from the reaction zone. At a temperature of 1600 °C and an hour exposure, the reaction ends with the formation of aluminum carbide. The conducting structure is destroyed, which we observed in [10].

References

[1] Stankovich S, DiKin D A, Dommet G H et al. 2006 Nature 442 282–6
[2] Reimanis I E 1997 Mater. Sci. Eng. A 237 159–67
[3] Centeno A, Rocha V G, Alonso B et al. 2013 Journal of the European Ceramic Society 33 3201–10
[4] Wan Jiang, Yuchi Fan and Akira Kawasaki 2012 Adv. Funct. Mater. 1–7 DOI: 10.1002/adfm.201200632
[5] Yuchi Fan, Lianjun Wang, Jianlin Li et al. 2010 Carbon 48 1743–9
[6] Ting He, Jianlin Li and Lianjun Wang 2009 Materials Transactions 50 749–51
[7] Peretyagin P Yu 2017 Doct. Diss., Moscow, MGTU Stankin 184 http://stankin.ru/science/dissertatsionnye-sovet/212-142-01
[8] Popov V A 1969 Non-metal materials Handbook 5 Machinebuilding 621.002.33 010727 544
[9] Zholnin A G, Tenishev A V and Stolyarov V V 2019 Deformatsiya i razrusheniye materialov 2 20–7
[10] Zholnin A G, Stolyarov V V, Savel’yev M D and Shornikov D P 2019 Poroshkovaya metallurgiya: Inzheneriya poverkhnosti, novyye poroshkovyye kompozitsionnyye materialy. Svarka. Minsk 460–9
[11] Bolinches A S, Klyatskina E F, López S A et al. 2018 Sintez i konsolidatsiya poroshkovykh materialov: (23–26 oktyabrya 2018 g., Chernogolovka) 21