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Influence of Sintering Conditions on Specific Electrical Conductivity in Aluminum-Graphene Composite

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Abstract

Dependence of specific electrical resistance on temperature (20 - 1600 °C) and processing method in an aluminum-graphene (up to 2wt.%) composite is investigated. It is established that spark plasma sintering (SPS) under pressure 40 MPa does not influence on electrical resistance, whereas SPS at low pressure (<10 MPa) reduces electrical resistance at a room temperature on 6 orders. Lower values of electrical resistance (up to 90 Ω *mm) received at sintering in hot pressing set at radiating heating. It is supposed that the reason of sharp decrease in electrical resistance at the lowered pressure is presence of current pulsations during SPS. They induces magnetic fields in graphene flake which lead to their moving and forming of particles to electroconductive chains or their capture in arched cells at applied pressure.

Keywords: composite, aluminum, graphene, electrical resistance, temperature dependence.

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1. INTRODUCTION

It is known that a graphene two-dimensional allotropic modification of carbon having a number of unique physical and mechanical properties is used as the reinforcing additive for composite materials [1-10]. It has turned out that properties of such composites depend on material, dispersion of initial particles, a method of introduction of a graphene and a way of compaction of the powder mix. In this direction it is necessary to refer to recent works [5-10]. The main emphasis in them is placed on influence of a graphene on strength properties and wears at friction. The most popular way of compaction is the spark-plasma sintering (SPA).

In the course of SPS of the aluminum nanopowder close by the sizes to graphene scales, the last fasten the next grains, carrying out a role of the reinforcing element. It positively affects both composite strength, and on wear resistance at friction of

ceramic couples. As a result the wear at the room temperature decreases on two orders [7-10]. Stability of a graphene in aluminum up to the agglomeration temperatures (1500-1550 °C) allows expecting maintaining positive properties of a composite at high temperatures.

At the sufficient graphene content and its uniform distribution in volume of a composite electroconductive chains or grids can be formed. At high conductivity peculiar to a graphene the dielectric ceramics becomes electroconductive material [3, 11, 12], and at different ways of the graphene processing. For instance, the oxidized graphene used in work [3]. Mix of powders was received in the colloidal way. In works [11, 12] the graphene was received from graphite powder, crushing him in mix with aluminum oxide in a spherical mill on the way offered in [14].

The purpose of the work is to study influence of temperature and a processing way of a aluminum-graphene composite on their electrical resistance.

2. EXPERIMENTAL METHODS

Graphene nanoplatelets powders (GNPs), supplied by Graphene-tech (Zaragoza, Spain) were produced in the flake form with an average thickness of 3 nm (about 5 atomic layers) and 10x10m^{2}by the ultrasonic exfoliation method.

Nanosize δ-Al_2O_3 powders and GNPs were dispersed in ethanol and then mixed in an ultrasonic bath Sonicator Q500 at power 250 Wt during 40 min under mechanical stirring. After that, the powder mixture is dried on a heating plate to completely remove all the dispersant.

Finally, Al_2O_3-GNPs mixture was sintered under vacuum using the spark plasma sintering technique (SPS, LABOX-625, SinterLand, Japan), where the powder was placed in a graphite die with an inner diameter of 15 mm. The sintering temperature was established at 1550 °C with a holding time of 10 min at the maximum temperature under an applied pressure of 50 MPa and a heating rate of 100 °C/min. During sintering at 1250°C δ-Al_2O_3has been transformed to aluminum with changing type and decreasing crystal lattice volume [14].

Resistance of a composite was measured in a vacuum in the course of radiation heating at speed 20°/min in a temperature interval 20- 1600 °C. The measuring stand has been mounted on the basis of high-temperature press FR210-30T-A-200-EVC with use of the universal B7-40 voltmeter. The sample in the form of the disk Ø 15x2 mm was clamped between two graphite punches. Punches were isolated from the grounded plungers by alumina disks. Current was brought to a sample through a tungsten wires

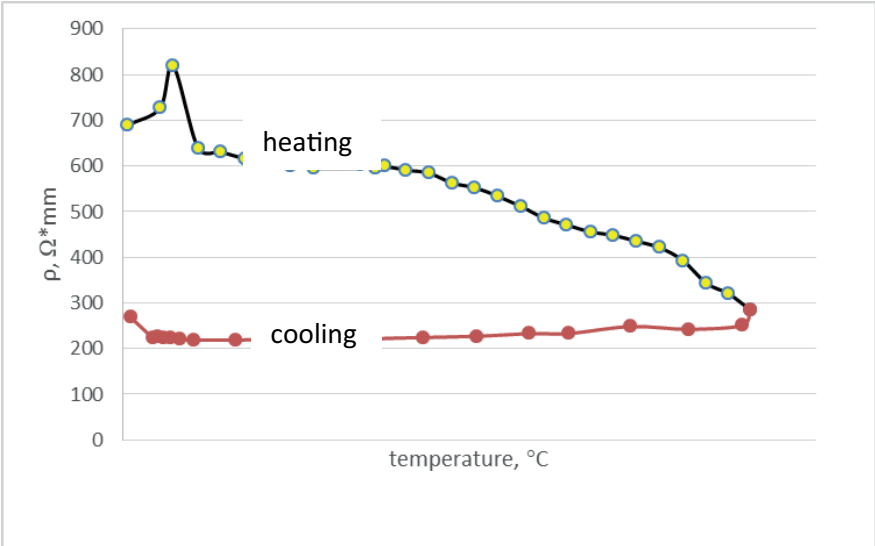

Figure 1: Temperature dependence of specific electrical resistance of Al_2O_3-2wt.% graphene processed without pressure.

from the thermocouples which are mechanically fixed on punches. Intrinsic resistance of a measuring chain didn't exceed 5.5Ω at all temperatures of measurement.

3. EXPERIMENTAL RESULTS

The graphene presence in the range of 0 - 2 wt. % practically doesn't influence on resistance if SPS was carried out with pressure 40-50 MPa [10]. The resistance with temperature increase decreases by 4 orders that is typical for aluminum in which the ionic conductivity after 450 °C passes in electronic [15]. At cooling the resistance was restored to 1 GΩ*mm.

If SPS of a composite Al_2O_3-2wt.% graphene has been performed without pressure, the resistance after cooling to room temperature was 6 orders lower than usually and 2 orders below, than at 1600 °C. During heating the resistance has decreased still twice. At the subsequent cooling the resistance practically didn't change and was equal 250 Ω*mm (Fig. 1). Such high electrical conductivity of the composite is possible only due to forming of the conductive graphene chains (or grids).

Lower values of the resistance are received at hot pressing and radiation heating. Previously cold compacted mix was placed in a ceramic matrix, subjected to heating with a pressure of 10 MPa and measured the resistance of the formed compact in the direction of a tablet axis. In the course of heating and hour holding at 1600 °C the resistance reaches the values typical for the SPS composites sintered with pressure (Fig. 2). At the subsequent cooling to room temperature it has decreased by 3 orders

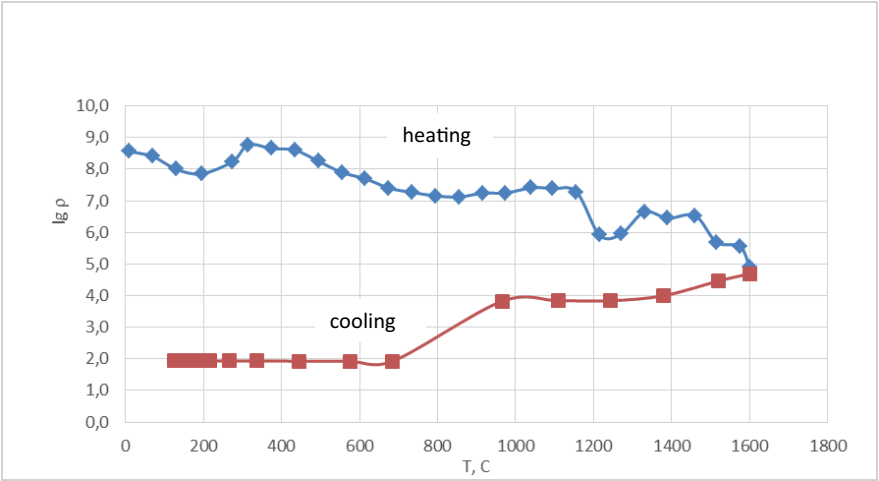

Figure 2: Temperature dependence of specific electrical resistance of Al_2O_3-2wt.% graphene during sintering at radiation heating with the rate 20°C/min, hold at 1600°C, 1 hour and following cooling with pressure 10 MPa.

and reached to 90 Ω*mm, i.e. it became 7 orders less, than for SPS composites at pressure of 40 MPa.

Table 1: Specific electroconductive resistance and density for the various heating and pressure ways.

graphene, %		0	1	2	2*	2**
Relative density, %		99,2	97,4	95,2	89,2	78,7
Specific resistance ρ, Ω*mm	Before heating	1,3 E+9	1,3 E+9	1,2 E+9	2,7 E+2	2,0 E+8
	At 1600°C	2,5 E+5	1,3 E+5	3,2 E+5	2,2 E+2	1,8 E+4
	After cooling	1,4 E+9	1,0 E+9	1,4 E+9	1,2 E+2	1,0 E+2
2* - SPS without pressure						
2** - sintering at radiation heating						

Specific resistance for all studied samples are presented in table 1.

4. DISCUSSION

The composite Al_2O_3-2wt.% graphene has the specific resistance which depends on a way and the mode of sintering. It has properties of the insulator, if carried out by SPS with pressure or has rather high conductivity close to metal conductivity if carried out without pressure (Fig. 1). Composite density at the same time is much lower. It is interesting the composite specific resistance doesn't change practically at cooling. It

demonstrates that in the composite electric properties of aluminum aren't defining. Everything depends on conductivity of the created carrying-out graphene grid. When cooling graphene configuration is almost invariable as there are no phase or structural changes in material.

Similar values of specific resistance are in the works where measurements were performed at the room [3, 11] or below room temperature [12]. Difference between the obtained results and literary data is that the high conductivity of the composite in our experiments is received at SPS without pressure or high-temperature pressing with radiation heating. In all other works SPS carried out with rather high pressure. Other difference is the way of graphene processing. The different graphene processing method can be the cause of differences in the sizes and a shape of graphene flakes.

Fracture images by scanning electron microscopy of Al_2O_3-2wt.% graphene composite processed by SPS with a pressure of 40 MPa have revealed availability of graphene agglomerates [8]. That is only a part of a graphene is distributed among aluminum grains. It means that the graphene content is insufficiently for formation of the carrying-out chains. Apparently, graphene agglomerates were observed also by other researchers, considering that their presence is obliged to insufficiently careful dispergation at ultrasonic mixing of graphene and aluminum powers. That is why sometimes the blender with quickly rotating knives uses for reduction of graphene particles agglomeration in an ultrasonic bathtub with an emulsion [16].

Graphene particles agglomerates, despite rather high porosity of a composite, aren't found at SPS without pressure or at radiation heating. It means all graphene is distributed in volume and can form the carrying-out chains or grids. As for radiation heating it can't influence on graphene configuration. The lack of graphene agglomerates in the sintering composite at radiation heating means the our way of an ultrasonic dispergation provides destruction of agglomerates and uniform flakes distribution in volume.

The hole on a heating curve (Fig. 2) obviously, is caused by phase transformation δ-α in Al_2O_3 [14] which is followed by reorganization of a lattice of oxide and reduction of its volume. Reduction of the specific resistance at cooling is perhaps connected with improvement of mechanical and electric contact between a graphene flakes at thermal stress compression of a composite.

Availability of Al_2O_3-2wt.% graphene agglomeration at SPS with pressure of 40 MPa can be explained by current pulses at heating with duration of 1 ms.

Impulses of current generate the impulses of magnetic field exciting magnetic field of the counter direction in the conductive graphene flakes. The induced magnetic field in graphene flakes interacts with magnetic field of a matrix. Through this interaction

graphene flakes receive the mechanical pulse forcing them to move and rotate in powder. In the presence of mechanical pressure in powder the arch emptiness which are traps for the moving decanter particles are formed. There is no pressure, there are no arch emptiness, the graphene is distributed uniformly and creates the carrying-out chains.

5. CONCLUSIONS

1. SPS processing of alumina-graphene compacts without pressure and at radiation heating has allowed to create the conductive composites with electrical resistance up to 90 Ω*mm.

2. Influence of temperature and sintering conditions on the electrical resistance of composites is investigated. It is shown that in lack of pressure or at radiation heating the non-conducting composite becomes the conductor.

3. The model of graphene flakes agglomeration based on interaction of the magnetic fields of matrix and graphene flakes induced by current pulse due to SPS is offered.

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