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Structure and properties of Al_2O_3 / Graphene nanocomposite processed by spark plasma sintering

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Abstract.The ultrasonic dispersion and spark plasma sintering technique have been used to process Al_2O_3 / Graphene nanocomposite (Al_2O_3 /G) with 0-2wt.% graphene. The topography of fracture, microstructure, density, microhardness, Young modulus, electrical and thermal conductivity of Al_2O_3 / G nanocomposite are investigated.

1. Introduction
It is known that the graphene, two-dimensional allotropic modification of carbon, possesses a number of unique physical and mechanical properties and can be used as the reinforcing additive for composite materials [1, 2]. It appeared that properties of such composites depend on material and matrix dispersion, and also an introduction method of a graphene. The composite on the basis of Al_2O_3 nanopowder and small adds of a multilayered graphene is of interest [3, 4]. At present the most successful for processing such composites is the spark plasma sintering (SPS). It is supposed that graphene flakes as the second phase will cause considerable wear reduction because of friction forces reduction on contact of nanometric and submicrometric structure elements [5]. However, data on tribological properties, and also heat conductivity and electrical conductivity are practically absent.

The purpose of work is demonstration of successful processing nanocomposite of Al_2O_3 /G by SPS technique and results of research of its physical and mechanical properties.

2. Experimental procedure

2.1. Materials preparation
To process a ceramic nanocomposite the mixture consisting of the nanopowder δ - Al_2O_3 (45 nm, IMET RAS, Moscow, Russia) and 0.5; 1 and 2 wt. % of graphene nanoflakes (δ = 3 nm, the lateral size of 10x10 μm) prepared by ultrasonic exfoliation method (3 x Graphene-tech, Zaragoza, Spain) has been prepared. After ultrasonic dispersion in solvent and the subsequent drying the samples with size of Ø15x2 mm have been compacted at 1550 °C within 10 min. under pressure of 50 MPa in vacuum SPS set (LABOX-625, SinterLand, Nagaoka city, Japan) as is described in [6].

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2.2. Characterization

The bulk density of samples was measured by Archimedes method. Microhardness (HV) was measured on the FM-800 device along diameter at the load 3H during 10 s. Elastic modulus (E) was measured on the nanotester G200, MTS by a method [7]. Fractography researches and structure certification of graphene distribution are executed, respectively, on the electronic microscopes FESEM, ZEISS ULITRA 55, Oxford Instrument and Hitachi SU8000. Optimization of analytical measurements is performed within the approach described earlier [8, 9]. To evaluate the structural stability analysis of a graphene Raman spectroscopy was used at the room temperature by Renishaw via spectrometer with laser wave length λ=532 nm.

Temperature dependence of specific electroconductivity χ(T) has been determined by resistivity measurement on hot pressing set in Ar atmosphere (6.6 Pa) in the disc thickness direction under heating in the range of 20-1500^{o}C with the speed of 20 °/min. Temperature dependence of heat conductivity of λ (T) was defined on the computer heat conductivity tester KIT-600 along a disk surface in the range of 20-195°C to within ±0.8 W/м*K. Tribological researches are executed on the Tribometer, CSM Instruments at indenter rotation according to the scheme «ball on disk», at load of 20 N and the speed of 10 cm /s during 15 hours. As a counter material the ruby ball of Ø 6 mm and HV 2400 was used. Sample surface was polished down to 1 μm and cleaned before and after the wear test. Wear track surfaces were examined by scanning electron microscopy. Wear rate (V_w) was calculated using the volume of a friction track (mm^3) which sizes were measured on the profilometer.

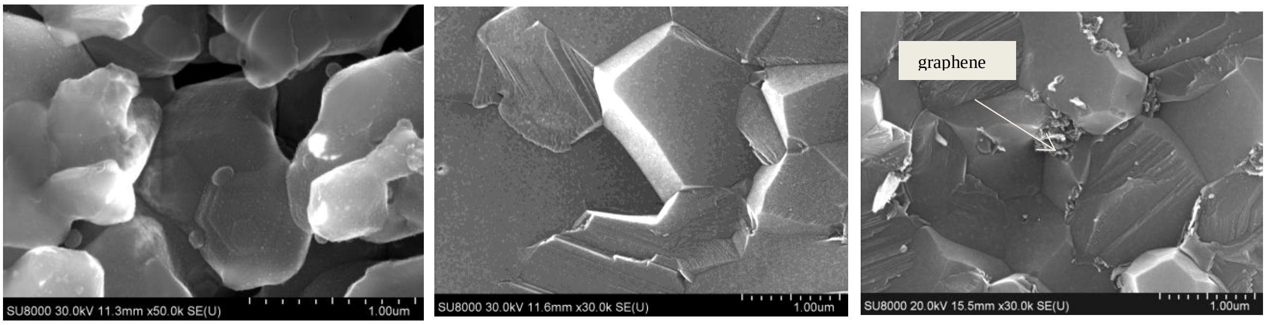
3. Experimental results

Density measurement results, microhardness and the elastic modulus of Al_2O_3/0.5wt.%G nanocomposite are given in the table 1. Density of a composite with graphene is slightly lower than the theoretical density of aluminum oxide. Microhardness and the elastic modulus of the composite with 0.5 wt. % graphene are 20-25% higher ones for the sample without graphene. Note that level of mechanical properties is higher, than for similar researches of micrometer composites [10, 11].

Table 1. Density and mechanical properties of Al_2O_3 sample with and without graphene

Graphene content (wt.%)	ρ (g/sm^3)	HV (GPa)	E (GPa)
0	3.99	20-24	380
0.5	3.95	27.4	456

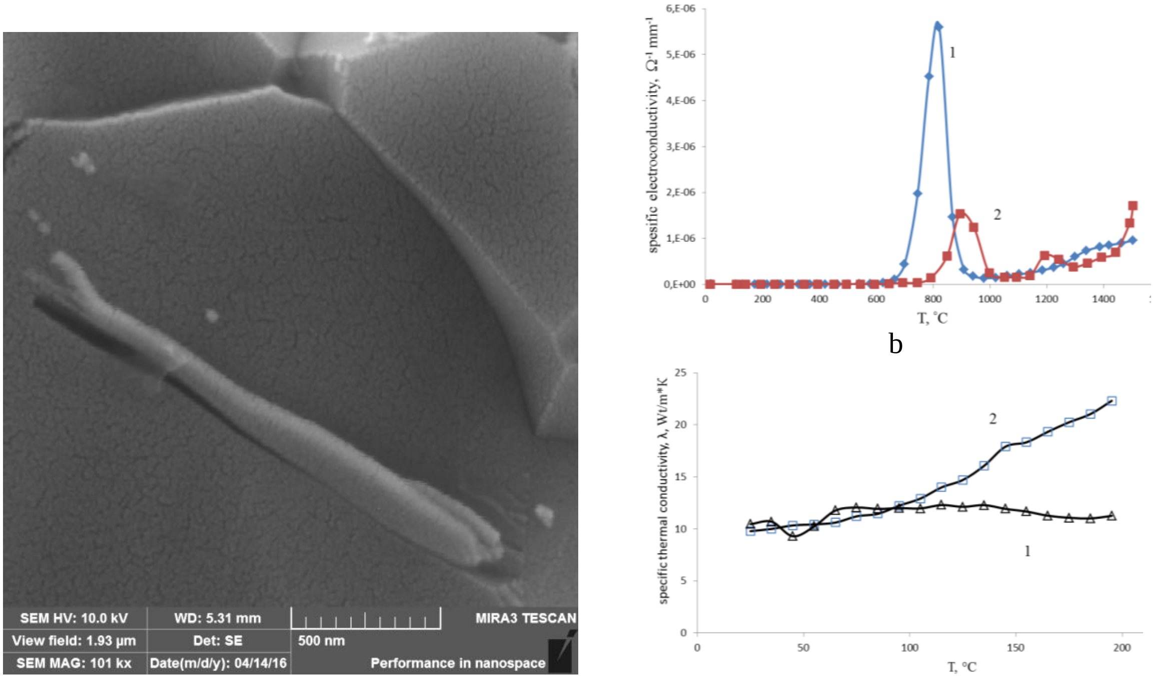
The SEM photographs of nanocomposite fracture surface (fig. 1) show that graphene introduction promotes disappearance of microvoids (fig. 1a, b), at the same time slightly increases the size of matrix grains and leads to heterogeneity in graphene distribution.



a b c

Figure 1. SEM photographs of fracture surface for Al_2O_3/G composite: (a) 0%, (b) 0.5%; (c) 2%.

Increase in graphene contents up to 2% leads to formation of the submicron graphene agglomerates (fig. 1c) that was confirmed with the EDS analysis. It is important to emphasize that the initial graphene flakes during of high-temperature SPS processing didn't degrade and remained stable that has been confirmed with Raman spectroscopy



a c

Figure. 2 SEM photo of graphene flake (a) and temperature dependences of specific electrical conductivity (b) and specific thermal conductivity (c): 1 - Al_2O_3 / 2wt.%G; 2 - Al_2O_3.

It is rather difficult to find and investigate the graphene flakes morphology because of their small sizes and low contents. However it is possible to see that some graphene flakes can be placed inside Al_2O_3 grains in (fig. 2a). Nevertheless, some TEM data demonstrate that graphene particles can be located also on the grains boundaries [12].

The research of physical properties, for instance, electro-and heat conductivity of composites is of special interest (fig. 2b, c). First of all, the behavior of specific electroconductivity with temperature variations is in opposition relation with the one of metals. The same tendency is observed for the Al_2O_3 / 2wt.%G. Another feature for both materials is the manifested peaks of electrical conductivity in the area of 600 – 1000 °C. However samples with a graphene have shown stronger peak than a sample without graphene (fig. 2b). The peak of specific conductivity for a sample without graphene is weaker and is shifted towards high temperatures. The reason of peaks is perhaps connected with phase transformation of Al_2O_3 that demands an additional research. As for specific heat conductivity its value grows with a temperature for a sample without graphene and practically doesn't change for a sample with a graphene (fig. 2c). The last indicates a possibility of increase in heat-insulating properties at graphene introduction to composite material.

It is possible to suppose that tribological properties of Al_2O_3 composite will be depending on the graphene content. In fact, data in the table 2 demonstrate that wear rate V_w for samples with a graphene decreases by two orders in comparison with samples without graphene at insignificant reduction of friction coefficient

Table 2. Friction coefficients (K_f) and wear rate (V_w) of nanocomposite.

Graphene content (wt. %)	V_w (mm^3/h)	K_f
0	$5.4 \cdot 10^{-4}$	0.77
2	$< 2 \cdot 10^{-6}$	0.63

4. Conclusions

1. The method of graphene introduction to ceramics based on ultrasonic dispersion and spark plasma sintering can be successfully used for creation of high density and high-strength on Al_2O_3 composites.
2. Some surface properties as friction coefficient, microhardness, wear resistance are the most sensitive to the graphene content (to 2%), last of which raise to 30% and for 2 orders, respectively.

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