Thermoelectric Properties of Compacted Micro- and Nanodisperse Graphite Materials

I.M. Golev¹, V.N. Sanin²

¹ Voronezh Branch of G.V. Plekhanov Russian University of Economics, 67a, Karl Marx Str., 394030 Voronezh, Russia

² Military Training and Scientific Center of Air Forces "Air Force Academy", 54a, Stary Bolsheviks Str.,

394064 Voronezh, Russia

(Received 19 May 2014; published online 15 July 2014)

The experimental results of measuring the Seebeck coefficient *S* for carbon deposits containing multiwalled carbon nanotubes, compacted nanofibers, nano- and ultradisperse amorphous carbon are presented. The value of *S* for such kind of materials lies in the range of 7 to 60 μ V/K. It is indicated that a hopping conduction mechanism is typical of the compacted materials.

Keywords: Thermo EMF, Carbon deposit, Nanodisperse carbon, Hopping conduction mechanism.

PACS numbers: 72.15.Jf, 73.63.Fg, 68.37.Yz

1. INTRODUCTION

The researches of transport phenomena with the availability of electric and thermo gradient in the micro- and nanostructural objects are currently of great theoretical and practical interest. It is determined by the prospect of application of the similar objects both as elements of functional electronics and when creating new composite materials with predetermined properties.

2. EXPERIMENTAL PROCEDURE

The paper presents the results of the research of thermoelectric properties of graphite materials with structural elements from 4 to 2000 nm in size. The objects of the research were:

1. Carbon deposit obtained by sputtering high purity-7-3 type graphite electrode in the arc discharge plasma in a helium atmosphere at a pressure of 500 Torr, electric current density up to 75 A/cm². The structure of the deposit includes bonds of multi-walled carbon nanotubes 10-16 nm in diameter. The bonds are 50-90 nm in diameter, the space between them is filled with amorphous carbon [1, 2].

2. A fractal nanotube structure constituting flocculent formations (granules) 15-20 μ m in size, consisting of bonds 50-60 nm in diameter and 0.5-2 μ m in length, coated with an amorphous carbon layer 20-30 nm in thickness. Each bond contains up to hundreds of parallel longitudinal multilayer nanotubes 2.5-4 nm in diameter [2].

3. The structures obtained by compaction of microand nanodisperse carbon materials:

- nanodisperse amorphous carbon having an average particle size of 30-50 nm, and ultradisperse one having particles 80-120 nm in size, respectively;

- nanofibers 10-80 nm in diameter and 500-2000 nm in length;

- disrupted nanographite, which is a porous mass, consisting of thin layers 30-100 nm in thickness, randomly oriented relative to each other [3].

It should be pointed out that nanodisperse carbon materials differ from confined or enclosed systems, which are, for example, fullerenes and nanotubes, in chemical and physical properties. They are characterized by a significant number of carbon atoms located at the surface and at the edges having unlinked bonds, which makes them more reactive, and facilitates active adsorption and absorption of gas molecules.

3. RESULTS AND DISCUSSION

Fig. 1 shows the results of measurements of dependence Seebeck coefficient S on temperature. The researches were conducted by the procedure described in paper [4].

Curves 1 and 2 are the temperature dependence of S coefficient for mono-and polycrystalline (average grain size ~ 20 µm) graphite, respectively. One can see that the value of S for the polycrystalline graphite is about twice the value of S for the monocrystalline graphite.



Fig. 1 – Temperature dependence of the Seebeck coefficient (S) for different structural states of carbon: (1) – mono- and (2) – polycrystalline graphite; (3) – ultradisperse graphite; (4) – compacted nanofibers; (5) – disrupted graphite; (6) – amorphous nanocarbon; (7) – nanotube deposit; (8) – compacted carbon nanotubes; (9) – bonds of nanotubes with the fractal structure

The article was reported at the International Conference (The Advanced Technology, Equipment and Analytical Systems for Materials), Kursk, 13-14 May, 2014

The highest values of the Seebeck coefficient are typical of compacted nanotubes -33μ V/K, and of nanotube bonds with the fractal structure $-55-60 \mu$ V/K [1, 2].

For nanodisperse carbon S value increases as the size of the structural elements is reduced, so the reduction of particles from 80-120 nm to 30 nm, thermo EMF increases from 7 to 16 μ V/K [4].

Let us focus our attention on the characteristic properties of the temperature dependencies of thermo EMF for the compacted samples. An analysis of the functional dependencies of $S(T^{1/2})$ and $S(T^{1})$ type was carried out for the results presented by the dependencies S(T) (see fig. 1, curves 3, 4, 5 and 6). For example, fig. 2 shows the dependence of $S(T^{1/2})$ for compacted particles of nanocarbon in the amorphous state, similar both to the compacted nanofibers and amorphous ultradisperse nanocarbon.



Fig. 2 – Dependence of $S(T^{1/2})$ for compacted nanocarbon particles in the amorphous state

In order to explain the temperature dependence of thermo EMF in the studied disordered structures we apply percolation theory.

According to the percolation theory, in the scope of application of the Mott law [5] for the hopping conductivity with a variable hopping length, thermo EMF should be described by Zvyagin's formula [6]:

$$S_h(T) = \frac{k}{e} \xi k \left(T_0 T\right)^{1/2} \frac{\partial (\ln g(E_F))}{\partial E}$$
(2)

where k – is the Boltzmann's constant; T_0 – is a characteristic temperature; ξ – is a numerical coefficient; $g(E_F)$ – is density of states at Fermi level.

It was determined that the deviation from the root dependence constitutes 345 K for the samples of nanofibers, 360 K for the samples of ultradisperse carbon in the amorphous state, 335 K

REFERENCES

- I.V. Zolotukhin, I.M. Golev, E.K. Belonogov, V.P. Ievlev, D.A. Derzhnev, A.E. Markova, *Tech. Phys. Lett.* 29 No 12, 1006 (2003).
- I.V. Zolotukhin, I.M. Golev, A.V. Nefodov, A.V. Uskov, S.A. Soldatenko, *Nanotekhnika* No 4 (20), 21 (2009) [in Russian].
- A.V Uskov, I.M. Golev, I.V. Zolotukhin, Vestnik VGTU 7 № 11.1, 62 (2011) [in Russian].



Fig. 3 – Dependence of $S(T^{-1})$ for destructured carbon

in the case of the samples of carbon nanoparticles in the amorphous state. A linear asymptotic behavior $S \sim T$ described by formula (3) which can be linked with Mott's formula for thermo EMF [5] is typical if the temperature is beyond the given values:

$$S(T) = \frac{\pi^2}{3} \frac{k}{e} kT \frac{\partial (\ln g(E_F))}{\partial E}$$
(3)

In the temperature range where the electrical conductivity σ varies according to the activation law, the temperature dependence of S(T) in the disordered systems is generally described by the same expression as that for the crystalline semiconductors:

$$S = -\frac{k}{e} \left(\frac{E_S}{kT} + A \right) \tag{4}$$

where e – is a module of the electric charge; A – is a kinetic coefficient that is independent of the temperature; E_S – is a parameter having the dimension of the energy. This kind of functional dependence is typical for destructured graphite (see fig. 3).

4. CONCLUSIONS

Thus, the conducted researches of the temperature dependence of thermo EMF indicates the availability of the hopping conductivity mechanism in the compacted materials of nanocarbon in an amorphous state, carbon nanofibers, carbon nanotubes, and ultradisperse amorphous nanocarbon. Size reduction of the structural elements of these materials increases the value of the Seebeck coefficient.

- I.V. Zolotukhin, I.M. Golev, A. A. Popov, V. P. Ievlev, *Tech. Phys. Lett.* 28 No 8, 678 (2002).
- N. Mott, E. Devis, *Elektronnyye protsessy v nekri-stallicheskikh veshchestvakh* (Moskva: Mir: 1982) [in Russian].
- I.P. Zvyagin, Kineticheskiye yavleniya v neuporyadochen-nykh poluprovodnikakh (Moskva: MGU: 1984) [in Russian].