

## Electrical and thermal conductivity of graphite-metal composites

*O.I.Stelmakh, L.L.Vovchenko, V.I.Matzui\**

T.Shevchenko National Kyiv University,  
64 Volodymyrska St., 01033 Kyiv, Ukraine

\*G.Kurdyumov Institute of Metal Physics, National Academy of Sciences  
of Ukraine, 36 Vernadsky Boulvd., 03142 Kyiv, Ukraine

Electrical and thermal conductivity of graphite-Co(Ni) composites on the basis of two different types of thermoexfoliated graphite, TEG(1) and TEG(2) have been studied. The distinctions in electric resistivity ( $\rho_a$ ) between compacted TEG(1) and TEG(2) can be explained by a better compressibility of TEG(2) powders resulting in lowered contact resistance  $R_k$  between the TEG(2) particles. Co or Ni deposition onto TEG surface (up to metal content of 30 to 50 % mass.) has been found to result in an increased electric resistivity of compacted TEG-metal samples and weakened temperature dependence  $\rho(T)$ . These  $\rho$  changes are associated likely to increased  $R_k$  between TEG particles due to introduced metal. The fixation of metal (Co, Ni) particles on the TEG(2) surface does not influence essentially the thermal conductivity ( $\lambda_c$ ) of compacted TEG(2)-Co(Ni) samples. In TEG(2) and TEG(2)-Co(Ni) samples, thermal conductivity exhibits a complex temperature dependence:  $\lambda_c$  increases slowly under heating in 300 to 700 K temperature range while a sharp  $\lambda_c$  rise is observed under cooling from 250 to 150 K.

Исследованы электро- и теплопроводность композиционных материалов графит-Со(Ni) на основе различных типов терморасширенного графита — ТРГ(1) и ТРГ(2). Различия в величине удельного электросопротивления  $\rho_a$  компактированных образцов ТРГ(1) и ТРГ(2) могут быть объяснены лучшей прессуемостью ТРГ(2), что приводит к уменьшению контактного электросопротивления  $R_k$  между частицами ТРГ(2). Обнаружено, что нанесение частиц Со или Ni на поверхность ТРГ (содержание металла — 30–50 масс %) приводит к увеличению электросопротивления компактированных образцов ТРГ-металл и ослаблению температурной зависимости  $\rho(T)$ . Эти изменения  $\rho$  могут быть связаны с увеличением контактного электросопротивления  $R_k$  между частицами ТРГ за счет внесенного металла. Закрепление частиц металла (Со, Ni) на поверхности ТРГ(2) не влияет существенно на величину теплопроводности  $\lambda_c$  компактированных образцов ТРГ(2)-Со(Ni). В образцах ТРГ(2) и ТРГ(2)-Со(Ni) теплопроводность сложным образом зависит от температуры:  $\lambda_c$  медленно возрастает при нагревании в интервале температур 300–700 К и наблюдается резкое увеличение теплопроводности при охлаждении образцов от 250 до 150 К.

Recently, a strong trend is observed to apply carbon materials and carbon-carbon composites in various industry fields, because these materials exhibit a unique combination of characteristics such as low density, high electric conductivity, thermal and corrosion stability as well as electrocatalytic activity. Besides, the highly developed surface of carbon materials makes it possible to

fix readily different chemical substances thereon. The development of metal-graphite composite materials (CM) showing unique physical and chemical properties or unique combinations thereof is due to several reasons. First, the coating of graphite materials by refractory metals or their carbides and nitrides makes it possible to extend essentially the temperature range in which

the materials can be used. Second, the employment of metal-carbon composites as catalysts in different chemical reactions provides numerous advantages as compared to other catalyst types due to chemical inertness, recoverability of metal after removing the support, low cost, and possibility to increase catalytic activity due to interaction between the metal and support [1, 2]. Third, the employment of metal-graphite composites as electrodes in lithium batteries and accumulators seems to be extremely promising, since those will allow a substantial increase of capacity and number of recharges [3, 4].

Thermoexfoliated graphite (TEG) is the most promising support for development of graphite-metal CM due to its high specific surface (50 to 60 m<sup>2</sup>/g), and porous structure. The use of TEG as a matrix allows to produce the compacted materials by cold pressing without binder with density of 0.2 to 2.0 g/cm<sup>3</sup>. TEG-based materials are ecologically pure, thermally and chemically stable, possess high antifriction and mechanical properties. The aim of this paper is to investigate electrical and thermal conductivity of composite materials graphite-metal (Co, Ni) as functions of structural state of TEG and metal type.

In order to determine the influence of graphite matrix on physical properties of compacted graphite-metal materials, the following types of graphite were used: thermoexfoliated graphite obtained by thermal shock of oxidized natural graphite (TEG(1)) [5]; thermoexfoliated graphite obtained by re-oxidizing of TEG(1) with sulfuric acid

and repeated thermal shock at 900°C (TEG<sub>s</sub>(2)); and thermoexfoliated graphite obtained by re-oxidizing of TEG(1) with nitric acid and repeated thermal shock at 900°C (TEG<sub>n</sub>(2)). The bulk density of TEG powders was 5 to 6 kg/m<sup>3</sup>, and specific surface was about 30 to 50 m<sup>2</sup>/g. The chemical deposition of salt from an aqueous solution following by thermal decomposition of the salt to metal has been applied to prepare the graphite-metal CM [6]. The samples of compacted CM TEG and TEG-metal were prepared in press moulds using a hydraulic press and had the density of 1.7 to 2.7 g/cm<sup>3</sup>. The electric resistance ( $\rho_a$ ) in direction perpendicular to the compaction one was measured using the four-probe method. The thermal conductivity ( $\lambda_c$ ) in CM along the compaction direction was measured using a dynamic  $\lambda$ -calorimeter, i.e. with the heater and cooler temperature increasing continuously due to the constant increase of heating power. The temperature interval of investigation was ranged from 150 to 673 K. The heating rate was 3 K/min.

As electron microscopy studies had shown [7], the repeated oxidation and thermoexfoliation of TEG(1) result in an additional structural disintegration of graphite particles. The size of macro-pores in TEG(2) was 1.5 to 2  $\mu$ m, being essentially smaller than that in initial TEG(1). Besides, the facet surface of graphite macro-planes becomes "wavelike" and "rough" due to intensive exhausting of oxidant at thermal shock. High porosity of TEG(1) and TEG(2), their high imperfection and chemical activity result in an effective impregnation of

Table. Characteristics of compacted composite materials TEG(1), TEG(2) and TEG-metal

Sample	Metal content, mass %	Density $d$ , g/cm <sup>3</sup>	$P$ , porosity	$\rho_a$ , $\Omega\cdot\text{m}$ $T = 293 \text{ K}$	$\rho_{77}/\rho_{293}$	$\lambda_c$ , W/m·K $T = 323 \text{ K}$
TEG(1)	–	1.87	0.20	$5.5 \cdot 10^{-6}$	1.60	6.0
TEG <sub>s</sub> (2)	–	1.98	0.11	$1.47 \cdot 10^{-6}$	1.67	–
TEG <sub>n</sub> (2)	–	2.05	0.08	$1.45 \cdot 10^{-6}$	1.48	–
TEG <sub>s</sub> (2)	–	1.68	0.25	–	–	1.34
TEG <sub>n</sub> (2)	–	1.74	0.22	–	–	1.17
TEG(1)-Co	25	2.01	0.27	$1.13 \cdot 10^{-5}$	1.26	–
TEG(1)-Ni	30	1.99	0.31	$7.44 \cdot 10^{-6}$	1.36	–
TEG <sub>n</sub> (2)-Co	45	2.42	0.24	$2.17 \cdot 10^{-5}$	1.28	–
TEG <sub>s</sub> (2)-Ni	40	2.71	0.20	$1.56 \cdot 10^{-5}$	1.24	–
TEG <sub>n</sub> (2)-Co	45	2.15	0.32	–	–	0.73
TEG <sub>s</sub> (2)-Ni	40	2.35	0.31	–	–	1.07

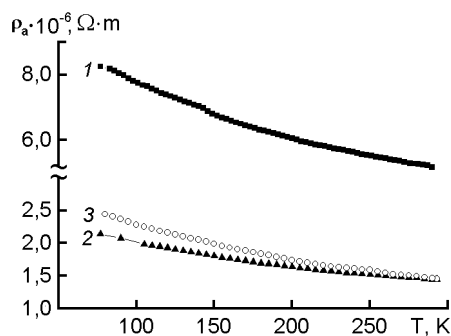


Fig. 1. Temperature dependence of electrical resistivity  $\rho_a$  for compacted TEG samples: TEG(1) (1), TEG<sub>n</sub>(2) (2), TEG<sub>s</sub>(2) (3).

these materials with the salt solutions and preparation of TEG-metal CM with high content (30 to 50 mass %) of metal particles. According to electron microscopy studies [7], the sizes of metal particles are as follows: 150 nm in TEG(1)-Co, 250 nm in TEG<sub>n</sub>(2)-Co, 100 nm in TEG(1)-Ni, and 500 nm in TEG<sub>s</sub>(2).

In order to reveal the influence of repeated oxidation and thermoexfoliation of TEG(1) on electrical properties of TEG-metal CM, we have studied the temperature dependence of electrical resistivity  $\rho_a$  for compacted samples of pure TEG(1), TEG<sub>n</sub>(2), and TEG<sub>s</sub>(2) and the electrical resistivity of CM with Co, Ni based on these TEG. Table presents the characteristics (composition, density, and porosity) of the samples studied. The porosity of compacted samples was determined as described in [8]. The results of electrical resistivity examinations are presented in Figs. 1, 2 and in Table. As it is seen from Fig. 1, the electrical resistivity decreases as temperature rises for all compacted samples of TEG(1), TEG<sub>n</sub>(2) and TEG<sub>s</sub>(2). The  $\rho_{77}/\rho_{300}$  ratio for TEG(1) amounts 1.6, for TEG<sub>n</sub>(2), 1.48, and for compacted TEG<sub>s</sub>(2), 1.67. However, the electrical resistivity values for compacted TEG(2) is in 3 to 4 times lower in comparison with compacted TEG(1).

For compacted samples, the contact resistance of particles  $R_k$  plays an important part. In general, the electrical resistivity of compacted TEG sample,  $R$ , can be presented as

$$R = R_k + r, \quad (1)$$

where contact resistance  $R_k$  depends on the contact area, pressure on the contact, and quality of contacting surfaces;  $r$  is the resistance of material the particles are made.

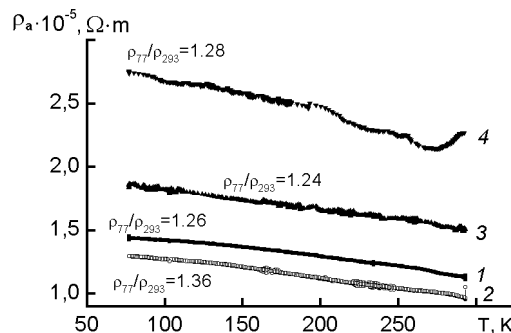


Fig. 2. Temperature dependence of electrical resistivity  $\rho_a$  for compacted TEG-metal samples of different densities ( $d$ , g/cm<sup>3</sup>): TEG(1)-Co,  $d=2.26$  (1), TEG(1)-Ni,  $d=1.99$  (2); TEG<sub>s</sub>(2)-Ni,  $d=2.70$  (3), TEG<sub>n</sub>(2)-Co,  $d=2.43$  (4).

The temperature dependence of compacted sample resistivity is defined by increase of the true contact area between the particles under heating due to thermal expansion of graphite particles and by temperature dependence of  $r$ . The resistivity  $r$  is defined by the electric resistance of individual TEG particles and depends on concentration of charge carriers ( $n + p$ ) and mean free path of charge carriers  $L_{ef}$  at scattering on phonons, defects, boundaries of crystallites, etc:

$$r \sim \frac{m^* V_F}{e^2 \cdot (n + p)} \cdot \frac{1}{L_{ef}}, \quad (2)$$

where  $m^*$  is the effective mass of charge carriers,  $V_F$  is the charge carrier speed at Fermi level. The charge carrier concentration in TEG increases as the temperature rises and at the prevailing scattering of charge carriers on crystallite boundaries,  $r$  decreases under heating.

The differences in electrical resistivity for compacted TEG(1) and TEG(2) can be explained by a better compressibility of TEG(2) powders that results in lowered contact resistance  $R_k$ .

Fig. 2 presents the temperature dependence of electrical resistivity  $\rho_a$  for compacted samples TEG-Co and TEG-Ni. The metal fixing on TEG particles results in an increased electrical resistivity of compacted TEG-metal samples. As it is seen, the temperature dependences of TEG-metal electrical resistivity are similar to temperature dependence  $\rho_a(T)$  for pure compacted TEG(1), TEG(2), but there are differences

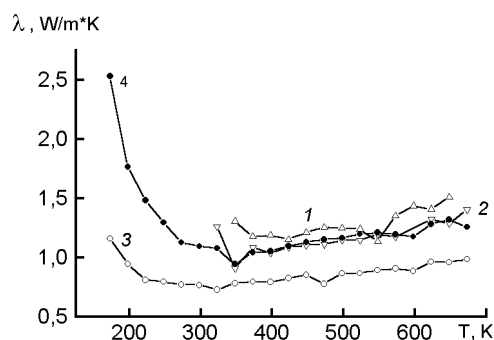


Fig. 3. Temperature dependence of thermal conductivity  $\lambda_c$  for compacted TEG(2) and TEG(2)-metal samples: TEG<sub>s</sub>(2) (1); TEG<sub>n</sub>(2) (2); TEG<sub>n</sub>(2)-Co (3) TEG<sub>s</sub>(2)-Ni (4).

in the electrical resistivity values. In contrast to pure compacted TEG(1) and TEG(2), compacted TEG(1)-Co(Ni) samples are characterized by lower electrical resistivity as compared to compacted TEG(2)-Co(Ni). In our opinion, the increase of electrical resistivity and changes in temperature dependence  $\rho(T)$  are caused by increasing contact resistance  $R_k$  due to influence of metal particles.

Table and Figs. 3, 4 present the results of thermal conductivity investigations for compacted TEG(1), TEG(2) and TEG(2)-Co(Ni) materials. As it is seen from the Figures, the repeated oxidation and thermoexfoliation of TEG(1) result in an increased thermal conductivity in compacted samples TEG(2) as compared to TEG(1) ones. The fixation of metal particles on TEG(2) does not influence the  $\lambda_c$  for compacted TEG(2)-Co(Ni) samples. Both TEG(2) and TEG(2)-Co(Ni) exhibit a complicated temperature dependence of thermal conductivity:  $\lambda_c$  increases slowly under heating in the temperature range 300 to 700 K while a sharp  $\lambda_c$  increase is observed under cooling from 250 to 150 K.

To describe thermal conductivity of compacted TEG and TEG-metal composite materials and its temperature dependence, we must take into account many factors. First, since the compacted samples were used for measurements, one should take into account the contact thermal resistance influence on the total thermal conductivity:

$$\lambda \sim \lambda_{TEG} \cdot \frac{1}{R_{ct}}, \quad (3)$$

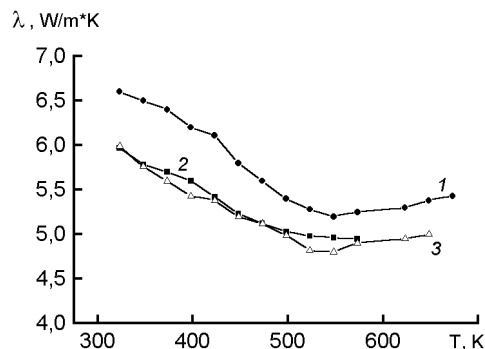


Fig. 4. Temperature dependence of thermal conductivity  $\lambda$  for compacted TEG(1) samples of different densities ( $d$ , g/cm<sup>3</sup>): 2.01 (1), 1.87 (2), 1.6 (3).

where  $\lambda_{TEG}$  is the thermal conductivity of TEG particles,  $R_{ct}$  is thermal resistance between particles. Second, in composite TEG-metal materials, metal particles also influence the total thermal conductivity of composite. At last, as the all investigated samples are the compacted and porous materials, it is necessary to consider the thermal conductivity of CM in the frame of Maxwell theory [9]:

$$\lambda_{ef} = \lambda(1 - P)/(1 + P/2), \quad (4)$$

where  $\lambda_{ef}$  is the effective thermal conductivity;  $\lambda$ , thermal conductivity of solid skeleton;  $P$ , porosity of the compacted sample. The lower thermal conductivity of compacted TEG(2) and TEG(2)-Co(Ni) samples (1–2 W/m·K) as compared to compacted TEG(1) may be explained by smaller TEG(2) particles and larger number of contacts between TEG-TEG and TEG-metal particles. Thus, it has been found that fixation of Co or Ni particles on TEG particle surface (metal content 30 to 50 % mass) results in an increased electrical resistivity  $\rho_a$  of compacted TEG-metal samples and weakens its temperature dependence  $\rho_a(T)$ . These changes in electrical resistivity are likely to be caused by increased contact resistance due to decrease in the contacting area of particles in TEG-metal composites. It has been shown that the thermal conductivity of compacted TEG(2)-Co(Ni) samples is 1 to 2 W/m·K in the temperature range 250–700 K and increases sharply under cooling below 250 K.

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## Електро- та теплопровідність композиційних матеріалів графіт-метал

*О.І.Стельмах, Л.Л.Вовченко, В.І.Мацуї*

Досліджені електро- та теплопровідність композиційних матеріалів графіт-Со(Ni) на основі різних типів терморозширеного графіту — ТРГ(1) та ТРГ(2). Відмінності у величині питомого електроопору  $\rho_a$  компактованих зразків ТРГ(1) та ТРГ(2) пояснено кращою здатністю ТРГ(2) до пресування, що призводить до зменшення контактного електроопору  $R_k$  між частками ТРГ(2). Знайдено, що нанесення часток Со або Ni на поверхню ТРГ (вміст металу — 30–50 мас %) призводить до збільшення електроопору компактованих зразків ТРГ-метал і послабленню температурної залежності  $\rho(T)$ . Ці зміни  $\rho$  можуть бути пов'язані із збільшенням контактного електроопору  $R_k$  між частками ТРГ за рахунок внесеного металу. Закріплення часток металу (Со, Ni) на поверхні ТРГ(2) не впливає суттєво на величину теплопровідності  $\lambda_c$  компактованих зразків ТРГ(2)-Со(Ni). У зразках ТРГ(2) та ТРГ(2)-Со(Ni) теплопровідність складним чином залежить від температури:  $\lambda_c$  повільно зростає при нагріванні в інтервалі температур 300–700К і спостерігається різке збільшення теплопровідності при охолодженні зразків з 250 до 150 К.