Electrophysical Properties of Composites Based on Hydrogenated Titanium with Different Contents of Thermally Expanded Graphite

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The formation of carbon-containing composites based on metals opens the prospect of combining the advantages of their components and manifesting new electrophysical properties, which are not characteristic of the original materials. Mechanical synthesis of hydrogenated titanium (TiH) and thermally expanded graphite (TEG) powders leads to such composites formation. As shown, the increase by 1.65 and 6.3 times in their electrical conductivity is observed in comparison with original TiH and TEG components, respectively. It is due to an increase of free electrons in the TEG because of their transport from the metal component.

Key words: powder materials, composite, thermally expanded graphite, hydrogenated titanium, mechanical properties, electrical conductivity.

Формування вуглецевмісних композитів на основі металів відкриває перспективу поєднання переваг кожної з компонент і прояву в створених композитах нових електрофізичних властивостей, які не властиві вихідним матеріялам. Показано, що поєднання порошку гідроґенізованого ти-

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тану (TiH) з терморозширеним графітом (ТРГ) за допомогою механосинтези сприяє утворенню такого роду композитів. Спостерігається зростання їхньої електропровідности у 1,65 і 6,3 разів порівняно з вихідними компонентами TiH та ТРГ відповідно, що зумовлено збільшенням концентрації вільних електронів у ТРГ за рахунок металічної складової композиту.

Ключові слова: порошкові матеріяли, композит, терморозширений графіт, гідроґенізований титан, механічні властивості, електропровідність.

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1. INTRODUCTION

Specific electrophysical properties of carbon nanostructures determine their extensive research and use in various fields of science and technology. The electronic properties of individual particles of carbon nanostructures and composites or materials containing such structures differ significantly. The properties of heterostructures based on nanostructured carbon depend not only on the characteristics of the original components, but also on the number and type of contacts between neighbouring particles, and the presence and type of defects and impurities in them. Contact phenomena play a significant role in determining specific properties in such structures and composites.

The synthesis of metal−nanocarbon composites is interesting because they combine components that have completely different mechanical, electronic, and thermal properties, which, in turn, contributes to the emergence of composites with properties and characteristics that are not inherent to the original components [1, 2].

The optimizing of materials' properties is widespread in materials science because it permits to improve the properties in the desired direction. Adding of carbon component (carbon nanotubes, graphene, carbon fibbers, *etc.*) to matrices of various types (ceramic, metal, polymer, *etc.*) makes possible a significant mechanical strengthening and a significant change in other properties of such heterosystems [3, 4, 5].

It is known that graphite has a wide range of applications, for example, it can be a sealing material, an admixture for lubricants and heat insulating materials, to use in gas sensors [6−9]. Today, its modifications in the form of thermally expanded graphite (TEG) are widely used and studied as electrode materials for power sources [10, 11, 12]. Thermally expanded graphite is a plastic, chemically inert material that almost does not change its properties under the influences of high temperatures. It occupies a special place among dispersed forms of carbon. In this state, carbon can be pressed without bonding agent into a continuous material, which makes it possible to use it in many fields [13, 14], in particular, in microelectronics and current sources [15, 16]. The addition of TEG to the composite materials opens up more

possibilities for creating composites with unusual physicochemical properties, for example, it makes it possible to synthesize a conductive polymer matrix being dielectric in its initial state.

Metals have a high concentration of charge carriers with low mobility ($n_M \cong 10^{25}$ cm^{-3}, $\mu_M = 10^{-3}$ m^2/V·c). Conducting carbon nanostructures (CNS), on the contrary, have a low concentration of charge carriers with high mobility along the graphene area ($n_{CNS} \cong 1.3 \cdot 10^{19}$ cm^{-3}, $\mu_{CNS} = 10$ m^2/V·c) [17]. The last is higher by 3−4 orders compared to metals. Specific conductivity is directly proportional to these quantities ($\sigma = en\mu$).

The metal particles have mainly less value of the work function (φ) then carbon nanostructures with graphene-like electron structure. Therefore, when the carbon component of the nanocomposite is in contact with metal, some part of free electrons pass from metal to carbon (for the opposite ratio of work functions there is analogously moving of holes). In addition, after certain heat treatments [18], new carbon nanostructures can be formed on the surface of metal−carbon composites. They have a wide band-gap and a negative affinity to electrons, which are simplified autoelectronic emission from the surface of such systems. That makes it possible to use such composites as cathode materials for low-temperature thermionic converters (TECs). At the same time, not only electronic structure, and morphology of surface but the ability to transfer electronic subsystem of composite to a very nonequilibrium state due to many types of external excitations of electrons are important. Thus, for the possibility of emission at temperatures lower than the working temperatures (~2000°C) of traditional TECs based on refractory metals, the carbon nanostructures are added to a cathode metal. They play a role of electron emitters on the surface. It is possible to control the structure, orientation, and aspect ratio of carbon nanostructures, which allows determining the optimal technological conditions for synthesis new materials for thermal and solar energy.

For mass use of thermionic conversion of energy from traditional and alternative sources, it is necessary, on the one hand, to try to maintain the high values of electrons emission currents characteristic as for high-temperature TEC, and, on the other hand, to significantly reduce the operating temperature of the cathode. Today, the lowest temperature (<200°C) of the electrons emission has been achieved when we use for cathode a composite material of the Ti−TEG system [18]. That determines our interest in this system.

In the present work, the features of the formation and change of mechanical and electrophysical properties of composite materials of the Ti−TEG system at different content of carbon (TEG) component are considered.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The composites of Ti−TEG are obtained by mechanical mixing of original components in the agate mortar during 2 hours. As original materials, there are used titanium hydride powder with particles up to 200 μm in size and thermally expanded graphite powder.

Electrophysical properties are study by the method described in [19]. The powder samples are placed in a dielectric cylinder under a well-conductive piston, which also plays a role of upper electrode; the metallic bottom of the cylinder is the second electrode. The density of the sample increases by reducing the distance between the electrodes. It promotes the establishment of electrical contacts between the particles of the investigated material and creates conditions for measuring electrical characteristics during the loading (compression) of the system. After reaching the maximum compression (on the used equipment) of the powder sample, the system is unloaded. In this case, the piston gradually rises, and the material can elastically relax while it maintains contacts with the electrodes. The termination of the relaxation process is accompanied by a sharp fall in electrical conductivity and the rupture of the electrical circuit.

The coefficient of relative mechanical deformation is calculated as $\varepsilon = \Delta L / L$, where L is a sample length in the cylinder after unloading, ΔL is a magnitude of sample elastic relaxation.

3. RESULTS AND DISCUSSION

Figure 1 presents the results of studies of the electromechanical properties of TiH−TEG composites for different concentrations of TEG depending on the density of the composites. The powder samples placed in the dielectric cylinder under the piston (Fig. 2) are compressed until the electrical circuit is closed. Therefore, the samples show the transition to a conductive state at a certain critical value of density ρ_{cr} (see Fig. 3). At the higher values of density ρ, there is a sharp increase in the specific electrical conductivity σ, with the subsequent release of its values on saturation.

For the studied sample of the disordered pure TEG array (Fig. 1, *a*) under load, the transition to the conductive state is at a density of $\rho_{cr} = 0.19$ g/cm^3, and a corresponding value of the specific electrical conductivity is $\sigma = 5,1 \cdot 10^{-6}$ (Ohm·cm)$^{-1}$. The subsequent compression to the density of $\rho = 0.20$ g/cm^3 is accompanied by an increase in electrical conductivity by five orders of magnitude. At density $\rho = 0.95$ g/cm^3, the electrical conductivity reaches its maximum value $\sigma = 0.95$ (Ohm·cm)$^{-1}$. Further increase in density up to $\rho \cong 2.04$ g/cm^3, on the contrary, leads to a decrease in the specific electrical conductivity by 7%. The last phenomenon can be explained by the partial destruction

of graphene-like layers in TEG under compression.

For powder of pure titanium hydride, the maximal value of the specific electrical conductivity during compression is $\sigma = 3.62$ (Ohm·cm)$^{-1}$ at density $\rho = 3{,}10$ g/cm^3. With a further increasing in density up to $\rho \cong 3.52$ g/cm^3, there is also a fall in electrical conductivity to 3.01 (Ohm·cm)$^{-1}$ (by $\cong 17\%$, Fig. 4). The obtained values of electrical conductivity of hydrogenated titanium powder differ significantly from the known in literature values of electrical conductivity of massive pure titanium [20–22] due to the presence of an oxide film on the surface of metal particles and their leaky contacts with each other.

The mixing of hydrogenated titanium particles with TEG powder leads to a decrease in the critical density of the transition in conductive state with an increase in the carbon component concentration c (Fig. 3). Therefore, the main influence on the transport properties of the composite under its minimal compression and $c \geq 15$ wt.% TEG is mainly due to the peculiarity of the structure and electronic properties of TEG.

At the same time, for samples of nanocomposite TiH+ c wt.% TEG, the character of the curve $\sigma(\rho)$ is changed when the content of the carbon component increases (Fig. 1, b, c). At low concentrations of TEG (up to 30 wt.%) at the initial compression stage, it is observed an increase in electrical conductivity without a sharp jump. When $c \geq 30$ wt.%, as well as for pure TEG, there is a sharp increasing in electrical conductivity at the initial stage of compression, due to the peculiarities of the structure of TEG particles.

Significant deformation of the composite causes mechanical stresses, which contribute to the appearance of additional potentials for the scattering of conduction electrons, which is accompanied by a drop in specific electrical conductivity. Note, that at high deformation, a solid sample (see Fig. 2) is formed due to coupling of the metal particles with each other by squeezing the graphite interlayers. Therefore, in addi-
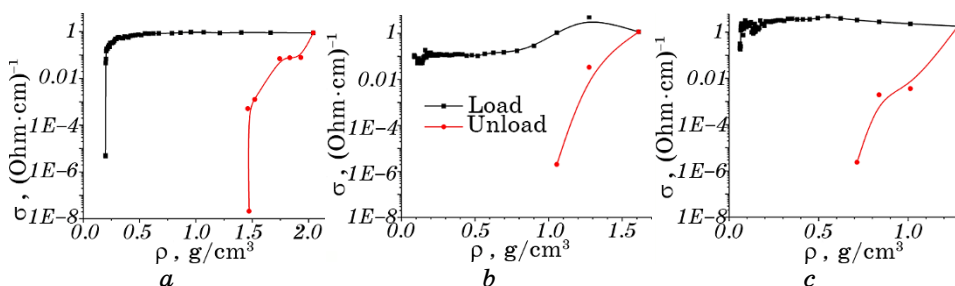

Fig. 1. Dependences of the specific electrical conductivity σ on the materials density ρ in the loading and subsequent unloading process: a—pure powder of TEG, b, c—nanocomposites TiH with 20 and 49.4 wt.% TEG, respectively.
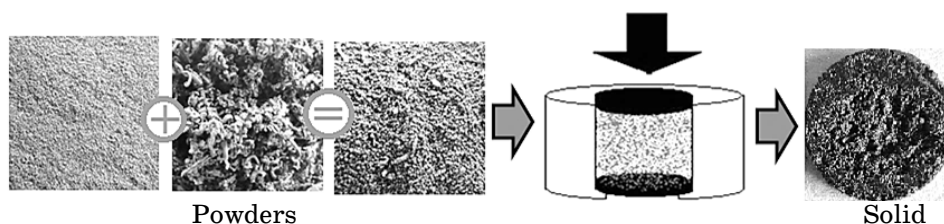
Fig. 2. The structure of the original components and the nanocomposite TiH + TEG, as well as the scheme of resistometric studies.

tion to increasing the defects (deformation) of both components, there is also an increase in the number of contacts between the metal particles with the simultaneously reducing the number of contacts between them and TEG. Since the contacts between metal particles with oxide shells have a higher electrical resistance compared to other contacts in this two-component heterosystem, this also contributes to a decrease in the specific electrical conductivity of the composites under high loads (Fig. 1, *b*, *c*).

The electrical conductivity of studied samples for the values of the density near the transition to the conducting state has an exponential dependence, *i.e.*, the curve $\sigma(\rho)$ (Fig. 1) in the logarithmic scale has a linear law of increase at low values of the density. This is a consequence of the fact that such objects are actually two-component systems, which, in addition to the solid component (in our case it is a com-
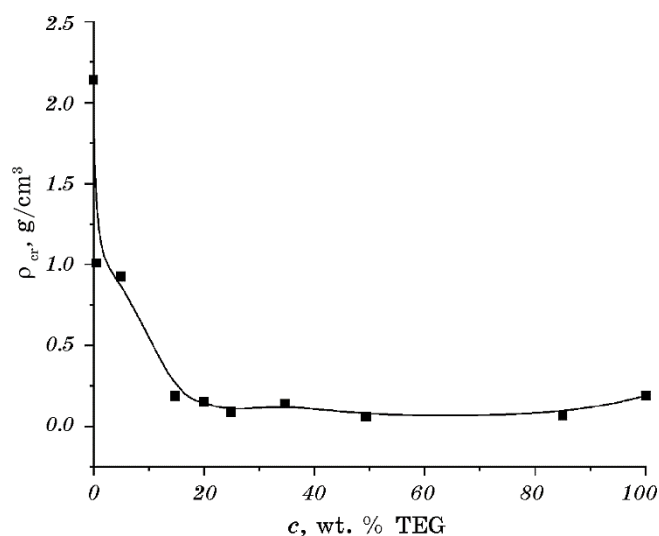

Fig. 3. The dependence of critical density ρ_{cr} corresponded to transition of composite into conductive state on the TEG concentration.

posite), contain cavities filled with air. After reaching the compression at which the maximum values of specific electrical conductivity σ_{max} is observed (all the more at the maximal compression ρ_{max} available on our equipment, which corresponds to the value of electrical conductivity $\sigma_{\rho_{max}}$), the composite is compacted and its porosity is significantly reduced. Therefore, investigated material practically becomes a two-component system of the TEG + metal type.

After reaching the maximum possible compression, the unloading process is carried out, and the specific electrical conductivity is measured during the piston return stripping. The end of the elastic relaxation process is accompanied by a sharp drop in electrical conductivity; a decrease in the contact area between the composite components and electrodes leads to a breakdown of the electrical circuit.

The coefficient of relative mechanical deformation ε is calculated based on the value of elastic relaxation ΔL (Table 1). The metal component of the composite is characterized by the absence of an elastic component, so its shape recovery practically does not occur (Fig. 1). The addition of TEG to hydrogenated titanium powder does not significantly affect the elastic characteristics of the obtained composite (Table 1), but a significant change in its electrical conductivity is observed (Figs. 1, 4).

As already mentioned, at the initial stages of samples compressing, the porosity of the composite decreases and TEG particles fill the cavi-
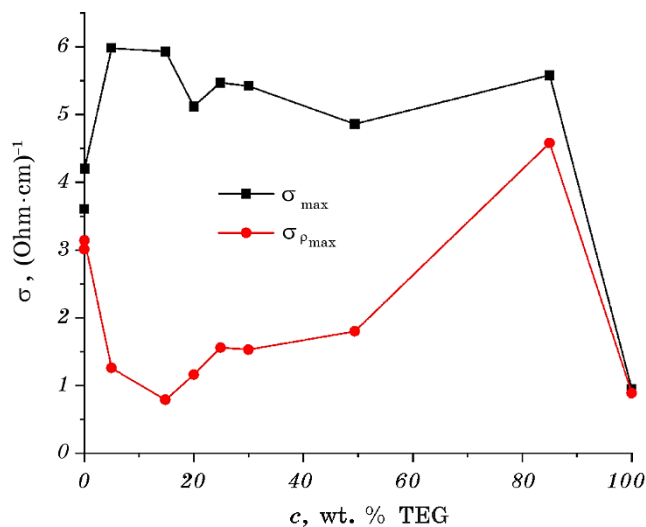

Fig. 4. Dependences of the maximum value of specific electrical conductivity σ_{max} and the specific electrical conductivity $\sigma_{\rho_{max}}$ at maximal compression of the powder nanocomposites TiH−TEG on the TEG concentration.

TABLE 1. Coefficient of relative mechanical deformation ε of nanocomposites TiH + c wt.% TEG and their density $\rho_{\sigma_{max}}$ at which the maximum values of specific electrical conductivity are reached.

c, wt.% TEG	0	0.53	4.96	14.83	20	25	34.66	49.4	85	100
ε, %	9	6	9	37	9	29.5	12	44	9.7	14.6
$\rho_{\sigma_{max}}$, g/cm³	3.10	1.88	1.24	0.45	1.27	0.42	0.90	0.55	0.29	0.95

ties between the metal particles of hydrogenated titanium, which contributes to the appearance of conductive bridges between the composite components during compression. The TEG is characterized by the possibility of creating solid bodies without a binding material [23]. In the obtained samples, TEG particles do not have a specific orientation: they are randomly oriented. It can also assume that in the process of mechanosynthesis, a thin layer of TEG is formed around the hydrogenated titanium particles (this was observed in work [24]). The TEG wraps the metal particles when an amount of the carbon component is sufficient and the required loads are enough to the formation of a continuous sample. In this case, during the lowering of the piston and compaction of the sample, the contribution to the specific electrical conductivity is made by the effects on the boundaries between the components of the composite of different types. The influence of these interfacial effects determines the behaviour of the dependences $\sigma(\rho)$ in Fig. 1.

An increase in specific electrical conductivity by orders of magnitude is characteristic of all samples when they are compressed under a piston (Fig. 1). At the same time, the maximum value of the specific electrical conductivity $\sigma_{max} = 5.98$ (Ohm·cm)$^{-1}$ is observed in the composite with 4.96 wt.% TEG for its density value of 1.24 g/cm³. It is 1.65 and 6.3 times bigger than the similar values for the initial TiH and TEG components, respectively (Fig. 4). As can be seen from the Table 1, for various samples, the values of σ_{max} are observed at densities in the range of $\rho_{\sigma_{max}} \cong 0.3-3.1$ g/cm³. After adding TEG to Ti, the values of $\rho_{\sigma_{max}}$ decrease significantly (<1.27 g/cm³).

For all studied samples, further compression is accompanied by a decrease in electrical conductivity relative to its maximum values: from 6.3% (for pure TEG) to 86.7% (for a composite with $\cong 15$ wt.% TEG) (Fig. 4). This dependence of the specific electrical conductivity on the degree of loading is conditioned by a change in the dominant mechanism of formation of the transport properties of the system: in the beginning, an increase in the contact area between the particles of the powder sample leads to an increase in the electrical conductivity, and then the deformation of the TEG and metal particles as well as the

increasing of number of contacts between metal particles contribute to a decrease in the electrical conductivity.

When particles of hydrogenated titanium have contacts with TEG, electrons begin to pass from the metal particles to the carbon component due to $\varphi_{Ti} < \varphi_{TEG}$, and the electron concentration in TEG increases (with a slight change in their mobility) [25]. Thus, higher values of σ_{max} in all composites (Fig. 4) compared to the original components are associated with the main role of metal−TEG interfaces, through which a redistribution of charges occurs between the composite components. Since the density of electronic states of TEG remain graphene-like and the Fermi level must lie in the region of the (quasi)gap in the energy spectrum, even small changes in the electron concentration can lead to a significant increase in the value of the density of electronic states at the Fermi level, which determines the electrical conductivity of carbon component of the composite.

The transfer of charges also leads to the opposite charging of TEG and metal particles, as a result, a Coulomb attraction between them occurs, which causes an additional bond strength in the studied samples at low concentrations of TEG and probably the above-discussed absence of a sharp jump on $\sigma(\rho)$ curve at the initial stage of compression (Fig. 1, *b*, *c*) for TEG concentrations up to 30 wt.%. Therefore, this effect is an additional evidence of charge transfer through the interfaces in the composites of the Ti−TEG system.

Note, that the electrons transferred from Ti particles are distributed overall volume of the carbon component of composite, which is increased with an increase in the concentration of TEG. This leads to a decrease in the average electron concentration and corresponding decrease in the specific electrical conductivity (Fig. 4) at $c \geq 15$ wt.% TEG (in comparison with the maximal value of σ_{max} of the composite with 4.96 wt.% TEG).

4. CONCLUSIONS

1. In the hydrogenated titanium−TEG composite, there is an increase in the maximum values of electrical conductivity compared to the initial TiH and TEG components by 1.65 and 6.3 times, respectively, which is associated with the transport of electrons from metal particles to TEG through the corresponding interfaces. This effect indicates that the current in the studied systems flows mainly through their carbon component.
2. For all investigated powder samples, the maximum values of specific electrical conductivity are observed in the range of the density values $\cong 0.3–3.1$ g/cm^3, which corresponds to the maximum contact area between powder particles. Subsequent compression of the materials is accompanied by a decrease in electrical conductivity relative to its

maximum values from **6.3**% (for pure TEG) to **86.7**% (for a composite with $\cong 15$ wt.% TEG). Such charges of transport properties are due to deformation of TEG and metal particles as well as increasing of number of contacts between metal particles with oxide shells.

3. The transfer of charges through the interfaces also leads to the appearance of the Coulomb component of the bond force between the TEG and the metal particles that mostly manifests itself at the initial stages of compression of samples with low TEG concentrations (up to 30 wt.%).

4. An increase in the concentration of TEG in the composite (≥ 15 wt.%) leads to a decrease in the average electron concentration and a corresponding decrease in its specific electrical conductivity.

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