

PACS numbers: 72.80.Tm, 73.30.+y, 73.40.-c, 79.60.Jv, 79.70.+q, 81.05.U-, 81.40.Rs

Structure and Electronic Properties of Composite Hydrogenated Titanium–Thermally Expanded Graphite Before and After Vacuum Furnace Annealing

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Previous studies have shown that mixture of hydrogenated Ti and thermally expanded graphite (TEG) can be used as a material for cathodes of thermophotoemission energy converters and allows reducing significantly the temperature of the start of electron emission. In the present work, the changes in the structural state and electronic properties of nanostructured material based on hydrogenated Ti with 0.53 wt.% TEG during the vacuum annealings of it at different temperatures in a furnace are studied. By comparing the experimental and theoretical values of electrical conductivity for different densities of the powder material, it is shown that the hydrogenated Ti–TEG mixture can form a composite. The reason for this is the important role of interfaces between the components of the composite as well as the charge transfer through these interfaces. As found, the short-term increase of temperature changes significantly and irreversibly the structure of each component of the composite and its electrical conductivity, but the composite does

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Citation: M. M. Yakymchuk, H. Yu. Mykhailova, I. Ye. Galstian, O. Yu. Gerasymov, T. D. Shatnii, M. O. Rud, and E. G. Len, Structure and Electronic Properties of Composite Hydrogenated Titanium–Thermally Expanded Graphite Before and After Vacuum Furnace Annealing, *Metallofiz. Noveishie Tekhnol.*, **45**, No. 9: 1041–1066 (2023). DOI: [10.15407/mfint.45.09.1041](https://doi.org/10.15407/mfint.45.09.1041)

not show significant irreversible changes during such heating. As shown, the long-term (1.5 h) annealing of the material in a vacuum furnace at $\cong 700$ K and 900 K leads to the loss of above-mentioned thermal stability of composite. As established, the specific electroconductivity of the composite is increased after long-term vacuum annealing at a temperature of 700 K, and, when the annealing temperature is near 900 K, it is decreased compared to the previous case. According to the results of the specific electroconductivity temperature dependences' analysis, activation energies of electrokinetic phenomena in the studied material are established and, for the first time, the important role of electronic subsystem in investigated composite formation and in changes of its properties under various thermal influences is proved experimentally that is important to create 'cold' emitters of electrons.

Key words: composite material, thermally expanded graphite, hydrogenated titanium, electrical conductivity, thermal treatment, thermophotoemission energy conversion.

Попередні дослідження показали, що суміш гідрогенізованого Ті та терморозширеного графіту (ТРГ) як матеріал для катод термофотоемісійних перетворювачів енергії уможливорює істотно понизити температуру початку емісії електронів. В даній роботі досліджено зміну структурного стану й електронних властивостей наноструктурного матеріалу на основі гідрогенізованого титану з 0,53 ваг.% ТРГ за його відпалів за різних температур у вакуумній печі. Шляхом порівняння експериментальних і теоретичних значень електропровідності за різних густин порошкового матеріалу показано, що суміш гідрогенізований Ті–ТРГ може утворювати композит. Причиною цього є вагома роль інтерфейсів між складовими частинами композиту, а також перенесення заряду крізь ці інтерфейси. Встановлено, що короткочасне підвищення температури істотно та необоротньо змінює структуру кожної окремої складової композиту та її електропровідність; проте композит під час такого нагрівання не демонструє значних необоротніх змін, оскільки його структура й електрофізичні властивості є результатом одночасної дії багатьох стимульованих підвищеною температурою процесів. Показано, що тривалий відпал (упродовж 1,5 год.) матеріалу у вакуумній печі за $\cong 700$ K і 900 K позбавляє даний композит вищеприписаної термічної стабільності. Встановлено, що питома електропровідність композиту зростає після тривалого відпалу у вакуумі за температури у 700 K, а зі збільшенням температури відпалу до 900 K зменшується порівняно з попереднім випадком. За результатами аналізу температурних залежностей питомої електропровідності встановлено енергії активації електрокінетичних явищ у досліджуваному матеріалі та вперше експериментально доведено важливу роль електронної підсистеми в утворенні композиту та зміні його властивостей за різних термічних впливів, що важливо для створення «холодних» емітерів електронів.

Ключові слова: композитний матеріал, терморозширений графіт, гідрогенізований титан, електропровідність, термооброблення, термофотоемісійний перетворювач енергії.

(Received 11 October, 2022; in final version, 21 September, 2023)

1. INTRODUCTION

Today, the problem of alternative renewable and mobile energy sources is very acute. New challenges arising from the change of the next economic setup (already on the 6th), as well as large-scale plans for the development of space far beyond the limits of the Earth's orbits, require the development of ecological, easy-to-use and efficient energy sources. One of the ways to reduce losses and pollution in power generation is the use of direct energy converters, especially, of solar energy. Among such converters, thermionic converters (TECs), which use the thermo- and photo-stimulated effects of electron emission from cathode material (into the vacuum gap between the cathode and the anode), are still the most powerful. Less powerful thermo- and photovoltaic devices are based on the similar but internal (in the absence of a vacuum gap) effects. Until now, the main disadvantage of TECs is still the high temperature of electron emission, which entailed many technical problems that have gained prospects for solving due to the development of nanomaterials and nanotechnologies only [1–4].

The use of metal–nanocarbon composite materials for the fabrication of cathodes of thermophotoemission converters (TPECs) of radiation and thermal energy has made it possible to the significantly lower temperature, at which electron emission begins. The use of a mixture of hydrogenated titanium powder and thermally expanded graphite (TEG) for these purposes showed that under the influence of concentrated solar radiation, the TPEC becomes a source of direct current when its cathode is heated up to 170°C [5]. Similar effects have also been observed in composites of LaNi₅ + carbon nanotubes (CNTs) [6], in which laser-stimulated emission was realized at laser pulse energies much lower than for other types of materials.

The study of the initial mixtures of metal powders with carbon nanostructures (CNS) made it possible to establish that, for example, at low concentrations of CNTs in the hydrogenated titanium matrix, composites are formed. It has mechanical and electrical properties different from similar properties of the origin materials and their simple mixtures [7, 8]. Similar composites are also formed when thermally expanded graphite is added to hydrogenated titanium powder, but over a wider range of filler concentrations [9]. The nature of such composites is associated with the transfer of charges between their components, which can significantly affect the emission properties of the materials [3].

However, it would be incorrect to explain the decrease of the emission's start temperature by the properties of the composites in their initial state only, because, as shown by electron-microscopy studies [5, 6], under the action of concentrated solar and laser radiation, the surface of the cathodes changes significantly—mainly the carbon component of

the composite is restructured. Thus, a thin transparent carbon layers with numerous bubble-like overgrowths were formed on the surface of the metal particles of the Ti-TEG composite in the sunlight concentrator. This means that in addition to the changes in the concentrations of free electrons in the components of the composite, the 'hot' electrons in the metal particles (excited by light and heat fluxes) and the near-zero electron affinity of the mainly sp^3 -hybridized carbon thin film can also contribute to the decrease of emission temperature. All of the above-mentioned factors, as well as the presence on the surface of small elements of relief with significant aspect ratio, are important for creating electron emitters with a structure and properties that will change the contributions from different emission mechanisms, for example, increase the contribution from autoelectronic emission. It should also be considered that, as the temperature increases in hydrogenated titanium, hydrogen diffusion processes are activated and the reduction of oxide film on the surface of the metal particles is began, and, on the other hand, the rate of the rate of oxidation of titanium increases in the presence of oxygen in the residual atmosphere. The emission of electrons may also depend on the number and density of contacts between the components of the composite of the same and different types, which are determined by the concentration of CNS and the degree of homogeneity and compaction of powder samples. The influence of the peculiarities of carrier transfer through numerous interfaces, both between individual components of the composite and through a thin carbon layer formed on the surface of metal particles under the influence of light and/or temperature, may also be significant.

It should be noted that the study of the influence of elevated temperatures on hydrogenated titanium powders has a separate importance for metal science, since on the air the particles of titanium powder are very quickly covered by oxide shells, which significantly change the electrophysical properties of the material. The studies of both the mentioned changes and the process of partial recovery of metal particles' properties due to thermal activation of hydrogen diffusion in the material are an important physical metallurgy task as well as the study of the addition of different types of nanostructured carbon influence on the properties of corresponding composite systems.

The diversity and competitive complexity of the processes described above require additional research, in particular, the study of changes in the structural and electronic properties of this type of composite under the influence of thermal energy fluxes. For this purpose, two series of hydrogenated Ti-TEG samples have been prepared with a concentration of 0.53 wt.% TEG, which corresponds to the filler concentration that demonstrated a low emission temperature in experiments on a solar energy concentrator [5]. The samples were annealed in a vacuum furnace at two fixed temperatures. Part of the samples was pre-compressed be-

fore annealing in the furnace, and the rest remained in the powder state. The electron-microscopy and resistometric studies were carried out on the initial and annealed samples, as well as the dependences of their specific electrical conductivity on temperature are measured.

2. OBJECTS AND EXPERIMENTAL METHODS

The composite Ti+0.53 wt.% TEG was obtained by mechanically mixing powders of hydrogenated Ti (with a hydrogen content of 2.74 wt.% (1.32 at.%)) and TEG in a 'drunk barrel' type mixer for 8 hours. A portion of the material was pressed at room temperature under a pressure of approximately 0.8 tonne/cm² into steel cuvettes, in which the annealing of the material took place. Powder and pressed samples were subjected to vacuum annealing in a furnace for about 1.5 h at temperatures of $\cong 700$ K and 900 K.

Resistometric studies of powder materials were performed using the following setup. The powder sample was placed in a cylindrical capsule with the dielectric side face and compressed with a copper piston. The copper bottom of the capsule and the piston played the role of electrical contacts through which current was applied to the powder materials under study. The dependences of the electrical conductivity (σ) on the sample density (ρ) were obtained during the powder compressing by piston (loading) and further unloading.

The study of the temperature dependence of the specific electrical conductivity was carried out with the same equipment, but the powder was placed in a ceramic capsule surrounded by a heating element.

Electron microscopic studies of compacted samples were performed on a JEOL JSM-6700F SEM electron microscope with a JED-2300 energy dispersive analyser.

3. RESULTS AND DISCUSSION

3.1. Resistometric studies

The results of resistometric studies of the initial (before heat treatment) pure components and the composite based on them are presented in Fig. 1. It can be seen (Fig. 1, *a*) that the initial density of TEG is very small— $\rho = 0.198$ g/cm³ ($\sigma = 5.1 \cdot 10^{-6}$ ($\Omega \cdot \text{cm}$)⁻¹), and, even after reaching the maximum of compression achievable on this equipment, it remains smaller ($\rho = 2.041$ g/cm³, $\sigma = 0.895$ ($\Omega \cdot \text{cm}$)⁻¹) than for the initial hydrogenated Ti powder ($\rho = 2.872$ g/cm³; Fig. 1, *b*). After reaching the maximum value of the specific electrical conductivity $\sigma = 0.950$ ($\Omega \cdot \text{cm}$)⁻¹ at $\rho = 0.955$ g/cm³, the values of the σ reach saturation ($\cong 0.90$ ($\Omega \cdot \text{cm}$)⁻¹) and almost do not change even when the density is increased by two

times (from 0.955 to 2.041 g/cm³). At the unloading stage, there is almost no relaxation of the compressed TEG body. Subsequent loading–unloading cycles are practically not accompanied by changes in the material density and conductivity: the values of the corresponding quantities fluctuate slightly around the values recorded in the saturation region. Note that the growth of the function $\sigma(\rho)$ in the compression stage is due to an increase in the total area of contacts between particles and the number of conductive channels during the compaction of the powder material. Usually, as the piston is raised and the volume filled with the powder sample increases, a relaxation of the composite occurs, which continues up to a certain density value, at which the rapid decrease in the number and area of contacts between particles ends and a sharp drop in σ occurs due to the breakdown of the electrical circuit. In the case of pure TEG, the material is compressed and remains in this state.

The initial hydrogenated titanium (below often simply denoted as Ti) powder during the first loading (Fig. 1, *b*) is significantly compacted—from $\rho = 2.161$ g/cm³ to $\rho = 3.535$ g/cm³, and its specific electrical conductivity changes from the value $\sigma = 9.38 \cdot 10^{-3}$ (Ω·cm)⁻¹ to the maximum of 3.58 (Ω·cm)⁻¹ at $\rho = 3.122$ g/cm³, and then reaches saturation at the level of $\cong 3.03$ (Ω·cm)⁻¹ at the maximum value of $\rho = 3.535$ g/cm³. The stress relaxation range during unloading of Ti powder is very narrow. Subsequent load–unload cycles leave the Ti powder density almost unchanged ($\cong 3.68$ g/cm³), but lead to a slight decrease in conductivity (to $\cong 2.2$ (Ω·cm)⁻¹). The decrease in conductivity in the saturation region and during cycling can be explained by the deformation of Ti particles and an increase in the number of defects (dislocations) in them. The obtained maximum values of specific conductivity are in full agreement with the corresponding literature values for titanium hydride powder with an oxide film on its particles [10].

For the composite sample (Fig. 1, *c*) with 0.53 wt.% TEG (33 vol.%

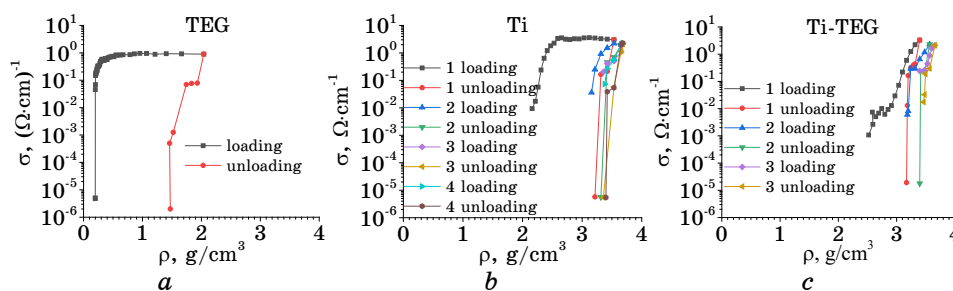


Fig. 1. Dependences of the specific electrical conductivity of pure components (*a*, *b*) and composite Ti+0.53 wt.% TEG (*c*) on the materials' density before heat treatment (for several load–unload cycles).

TEG), the density of the material before compression was $\rho = 2.521 \text{ g/cm}^3$, and the specific electrical conductivity was $\sigma = 1.07 \cdot 10^{-3} (\Omega \cdot \text{cm})^{-1}$. The composite conductivity reaches the level of non-compacted Ti powder ($\cong 1 \cdot 10^{-2} (\Omega \cdot \text{cm})^{-1}$) at composite density value of $\cong 2.8 \text{ g/cm}^3$. Further compression of the sample leads to an increase in electrical conductivity by 2 orders of magnitude, while the maximum value of conductivity $\sigma = 3.28 (\Omega \cdot \text{cm})^{-1}$ is observed at the maximum value of density $\rho = 3.397 \text{ g/cm}^3$ obtained in this experiment. Starting from the second load-unload cycles, the behaviour of the composite during deformation is similar to that of pure hydrogenated Ti (Fig. 1, b), and the value of the specific electrical conductivity after several such cycles approaches the value $\sigma = 2.11 (\Omega \cdot \text{cm})^{-1}$ at maximum compression, when $\rho = 3.66 \text{ g/cm}^3$.

Note that the calculated average values of the density of the mixture $\rho = \rho_{\text{TEG}}\vartheta_{\text{TEG}} + \rho_{\text{Ti}}\vartheta_{\text{Ti}}$ (ϑ is the volume fraction of a given component of the mixture), both before ($\cong 1.51 \text{ g/cm}^3$) and after ($\cong 3.04 \text{ g/cm}^3$) partial densification that takes place during the resistometric studies, are smaller than the corresponding experimental values of the density: 2.521 and 3.397 g/cm^3 . On the other hand, the conductivity of the mixture at maximum compression is greater than the corresponding conductivity values of the two pure components. This indicates both the significant influence of long-term mechanical processing (mixing) on the structure of the composite material and certain changes in the electronic structure of the composite. As a result of such processing, a decrease in the volume fraction of the carbon component of the composite is observed in the initial state, while its mass fraction remains constant (the TEG becomes less crumbly and more homogeneous). As shown the estimations based on the mass fraction of each component of the mixture unchanged during the mixing process and assumed that the density of Ti particles does not change during mixing, at the maximum compaction of the composite the density of TEG in it reaches a value of 0.41 g/cm^3 , which is only $\cong 2$ times exceeds the density of pure TEG without compaction (and mixing). Thus, after compaction of the composite, TEG remains in a state far from the maximum compaction obtained during resistometric studies of pure TEG.

The above analysis of the mixing density is not enough to make any assumptions about the mixing model that would explain the electro-physical properties of the material. Next, we will limit ourselves to comparing the specific electrical conductivity data of only the first load-unload cycles of powder materials. Since the maximum conductivity of the composite is $\cong 10\%$ higher than the maximum conductivity of titanium powder, and more than 3.6 times higher than the electrical conductivity of TEG at its maximum compaction, and 5.75 times higher than the conductivity of TEG at a density of 0.41 g/cm^3 , which it has in composites, it can be concluded that the material studied is

really a composite, whose properties differ both from the properties of the pure components and from the values of the corresponding values averaged for the mixture.

For further analysis, let us decide on the model of the heterogeneous system we are studying. Its natural model (see Fig. 2) is one, in which the space between Ti particles, which are compacted and provide a relatively deformation-resistant conductive skeleton of the composite, is filled by the partially compacted and conductive TEG powder, which was modified during mechanical processing. Within the framework of such a model, the decrease in the maximum value of the specific electrical conductivity of the composite during the second and subsequent load–unload cycles can be explained not only by the decrease in the conductivity of the titanium particles themselves due to the deformation-stimulated increase in the number of defects in them, but also by the additional effect of the decrease in the number of direct contacts

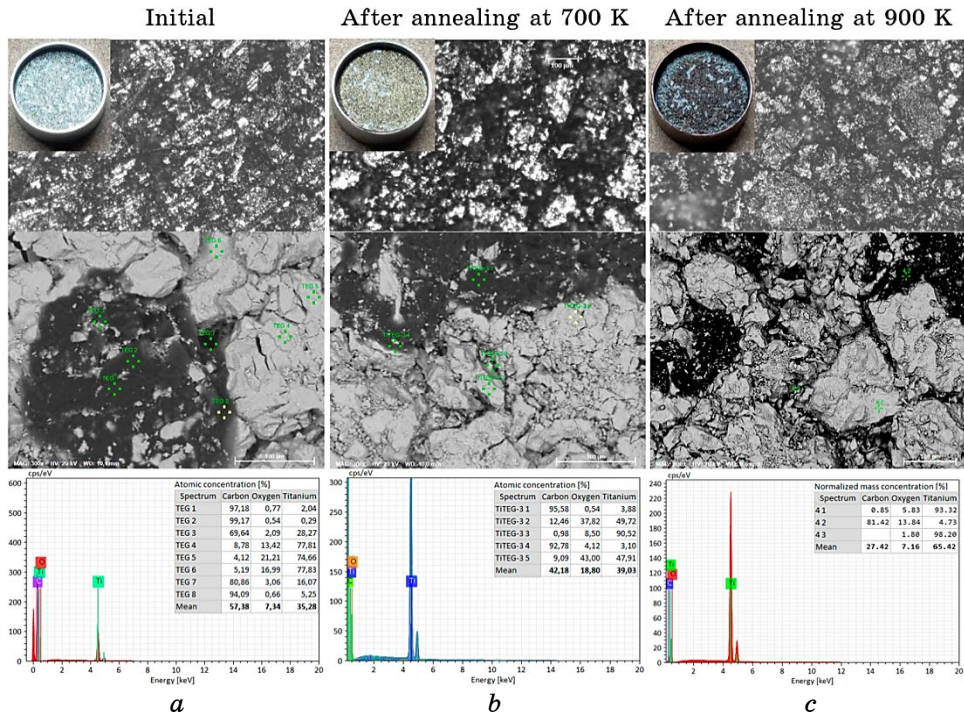


Fig. 2. Optical (top row) and SEM (middle row) images of the surface of the composite Ti+0.53 wt. % TEG after pressing under a pressure of about 0.8 tonne/cm² in the initial state (a) and after annealing at 700 K (b) and 900 K (c) for 1.5 h, as well as the corresponding results of EDX analysis (see the tables in the bottom row, the EDX spectra are shown for the points with the largest numbers).

between metal particles during cycling, which is accompanied by the destruction of some current flow channels through the relatively highly conductive titanium skeleton, as well as by the decrease in the conductivity of this channel due to the flow of free charge carriers between metal particles and carbon component of the composite.

Therefore, the material obtained is a weakly porous heterosystem, one part of whose volume is occupied by the matrix component and the other by isolated from each other particles of the second component, which, in a certain approximation, can be considered as equidistant inclusions. Since the volume fractions of the components of the mixture are comparable in values and Fig. 2 shows only the surface of the sample, from which most of the TEG was removed by the press mould during pressing, it remains undefined which material plays the role of matrix and which inclusions. Let us consider both possible options: if in the bulk of the sample, inclusions in the form of hydrogenated titanium particles (with oxide shells) are surrounded by TEG layers, and, *vice versa*, if areas filled with TEG are surrounded by a metal matrix.

In any case, within the framework of used theoretical model [11], we will replace the real approximately equidistant inclusions with different shapes by similar inclusions of cubic shape with corresponding effective mean sizes, whose centres form a simple cubic lattice in a continuous matrix phase. The work [11] also substantiates the legality of replacing a wide range of real matrix systems by the idealized one described above. Such replacing is correct if the 'piecewise-homogeneous' electrical field approximation within structural parts of the composite is satisfied. This supposition is equivalent to the Lorentz's assumption concerning the approximate compensation of reactive fields acting on the selected particle of inclusion from other particles from the Lorentz's sphere, when the dielectric permeability of the composite is calculated as one of the type of generalized conductivity of the heterogeneous environment. Then, for such material, it is possible to calculate the generalized conductivity (in our case specific electrical conductivity) according to the formulas of the work [11]. In the case of a three-dimensional isotropic matrix heterostructure, we have:

$$\sigma = \sigma_0 \left(1 + \frac{\vartheta_1}{\vartheta_0 / 3 + \sigma_0 / (\sigma_1 - \sigma_0)} \right), \quad (1)$$

where $\vartheta_0 = 1 - \vartheta_1$ is the volume fraction of the matrix, ϑ_1 is the volume concentration of the inclusions, σ is the specific electrical conductivity of the system, the index 0 denotes the properties of the matrix material and the index 1 denotes the properties of the inclusions' material.

Since formula (1) is only suitable for materials with negligible porosity, in our case, it can only be used for samples that have already been subjected to maximum densification during resistometric stud-

ies. If TEG is chosen as the matrix, three calculation options are possible: 1— $\vartheta_0 = 0.33$ (initial value) and, as values of $\sigma_{0,1}$, the values for the maximally compacted pure components of the composite are taken from Figs. 1, *a* and *b*, respectively; 2— $\vartheta_0 = 0.041$ (estimate of TEG volume fraction after mixing) and $\sigma_{0,1}$ remain the same; 3— $\vartheta_0 = 0.041$, but the value of σ_1 for the most compacted pure Ti powder is taken from Fig. 1, *b*, and $\sigma_0 = 0.57 (\Omega \cdot \text{cm})^{-1}$ is taken from Fig. 1, *a* and for the value of density of TEG (0.408 g/cm^3), which corresponds to the selected value of ϑ_0 . In the case, when the role of the matrix is played by titanium, the indices 0 and 1 in the given values are changed places.

The specific electrical conductivity of the composite under maximum compression is, as noted earlier, $3.28 (\Omega \cdot \text{cm})^{-1}$. In the three cases mentioned above, the values of σ more closest to this value are given by calculations with a matrix of titanium particles: 1—2.2, 2—2.91, 3—2.88 $(\Omega \cdot \text{cm})^{-1}$ (for comparison, for a matrix with TEG: 1—2.02, 2—2.87, 3—2.78 $(\Omega \cdot \text{cm})^{-1}$). Firstly, this indicates that the matrix material in such heterosystem is most likely to be hydrogenated Ti and the TEG particles play a role of inclusions (which is also correlated with Fig. 2). Secondly, the assumptions [11], which underpin Eq. (1), regarding the insignificance of the influence of contact phenomena and linear and point defects on the specific electrical conductivity of the heterosystem, are violated in the case of the studied mixture, and therefore, it does not fall under the definition of a simple mixture. Thus, this is another argument in favour of the fact that the studied material is a composite.

In the studied heterosystem, the effects caused by the interfaces between particles of the same and different components of the composite, the deformation of these particles (their defect state), as well as the sizes of conducting clusters form particles of the same and different types, which determine the paths of current flow through such systems, become governing. If we assume that the dominant effect is the flow of free charge carriers across the interfaces between components with different chemical potentials, then, using formula (1), it is possible to estimate what conductivity, for example, the carbon component of the composite would have, assuming that the conductivity of the metal component would not change: $\sigma_1 \cong 17 (\Omega \cdot \text{cm})^{-1}$. Depending on value of σ_1 , which is being compared—cases 3 or 1, 2—the flow of charges between the components corresponds to an increase in the conductivity of TEG (at $\vartheta_1 = 0.041$) of 19 or 30 times. Of course, in a real system, there is more than one factor. However, the tens-fold change in the conductivity of TEG mechanically processed to the state of multilayer graphene (see Fig. 2, *c*) can be easily explained within the framework of a simplified model. It is known that, in such quasi-two-dimensional system, the Fermi level lies in the region of the quasi-gap on the density of electronic states, and even a small change in the electron concentration can lead to a significant change in the density of

electronic states at the Fermi level, which also determines the electrical conductivity of the system. In addition, the high mobility due to the Dirac-like character of such carriers also contributes to the rapid growth of the electrical conductivity of the graphene-like system.

It should be noted that a change in the electrical conductivity of the composite due to its metal component can be significant, for which a decrease in the electron concentration (due to the flow of charges on the TEG) can be accompanied by a significant shift of the Fermi level in the energy spectrum of electrons. The latter can lead to a change in the value of the density of electronic states at the Fermi level, and thus to a change in the electrical conductivity of the metal component and the composite as a whole. This problem is also discussed in the Ref. [14].

The previous studies [5] have shown that the effect of low-temperature thermophotovoltaic emission is observed on a sample of hydrogenated Ti with 0.53 wt.% TEG previously treated during a long-term annealing in a solar energy concentrator. Therefore, one of the goals of this study was to investigate the changes in the structure and electronic properties of the same composite material during different heat treatments, in our case, in a vacuum furnace.

The studied material was annealed in a vacuum furnace at temperatures of ≈ 700 K and 900 K for 1.5 hours. After annealing at ≈ 700 K in the first load–unload cycle, a decrease in the density of the transition to the conductive state is observed (Fig. 3, *a*): at $\rho = 1.68$ g/cm³ with the value of the specific electrical conductivity $\sigma = 1.44 \cdot 10^{-2}$ ($\Omega \cdot \text{cm}$)⁻¹, which is almost 15 times higher than that of the unannealed sample (Fig. 1, *c*). During further densification (up to $\rho = 2.732$ g/cm³), a relatively smooth increase in electrical conductivity is observed up to the maximum value of $\sigma = 13.35$ ($\Omega \cdot \text{cm}$)⁻¹, which is 4 times greater than

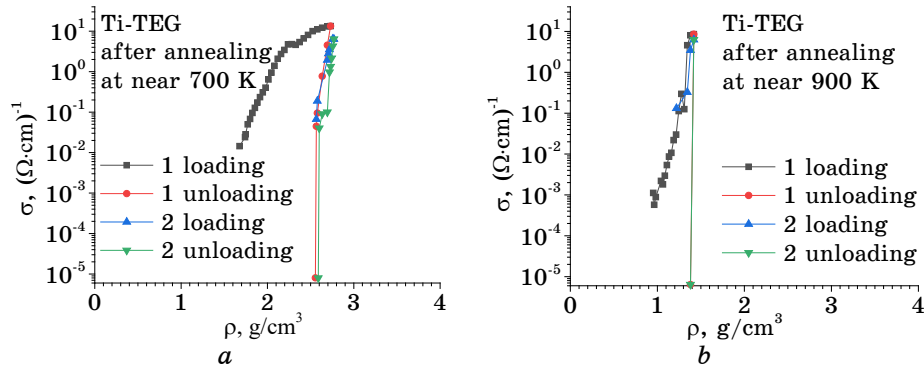


Fig. 3. Dependences of the specific electrical conductivity of the Ti+0.53 wt.% TEG composite on the density after annealing in a vacuum furnace for 1.5 h at temperatures around 700 K (*a*) and 900 K (*b*) for two loading–unloading cycles.

that of the initial sample.

After annealing at $\cong 900$ K (Fig. 3, *b*), the density of the transition to the conductive state also decreases: to 0.96 g/cm³ with the value of the specific electrical conductivity $\sigma = 5.75 \cdot 10^{-4}$ ($\Omega \cdot \text{cm}$)⁻¹. Subsequent loading (up to $\rho = 1.42$ g/cm³) leads to a sharp increase in electrical conductivity to a maximum value of $\sigma = 8.56$ ($\Omega \cdot \text{cm}$)⁻¹, which is 2.6 times higher than that of the initial sample, but 36% lower than that of the sample annealed in a vacuum furnace at $\cong 700$ K. The last indicates some degradation of the composite material during long-term high temperature vacuum annealing (higher than the temperature at which TEG destruction begins). In addition, as can be seen in Fig. 2, as the vacuum annealing temperature increases, sintering of the hydrogenated titanium particles occurs, but without a significant change in the morphology of the surface of the sample, as happened during concentrated sunlight annealing, when a thin carbon layer with icicle-like growths formed on the surface of the titanium particles [5]. Therefore, vacuum annealing does not provide the surface properties of the composite necessary for use in TECs, but it does allow a better understanding of the processes that occur during the formation of the composite and under various thermal influences on it.

For the annealed samples in powder state, as for the initial sample, starting from the first loading–unloading cycle, the almost complete absence of the elastic component in the dependence of the specific electrical conductivity on the density is characteristic (see Fig. 1, *c* and Fig. 3), *i.e.*, after the first compaction of the powder material, the shape of the sample is practically not restored. The resulting weakly compressed material begins to behave during the next load–unload cycle as an elastic, almost incompressible medium, which reaches slightly lower maximum values of specific electrical conductivity: for annealing at 700 K, 6.36 ($\Omega \cdot \text{cm}$)⁻¹, and for annealing at 900 K, 6.26 ($\Omega \cdot \text{cm}$)⁻¹. For a case of annealing at 700 K, corresponding value is obtained at a slightly higher density of 2.77 g/cm³ compared to the first cycle of loading–unloading, and for a case of annealing at 900 K—with the same density value of 1.42 g/cm³ as on the first cycle. As the annealing temperature increases from room temperature (no annealing) to 900 K, the same values of electrical conductivity are obtained at lower densities of the powder composite and in a smaller range of ρ values. The decrease in the density of the composites after annealing (Table 1) and the range of its change in Fig. 3 can be explained by the processes of destruction of TEG, sintering of metal particles, as well as partial stratification of the powder material during the vacuum annealing, which leads to an increase in the volume fraction of TEG (due to its loosening) in the composite. The decrease in the maximum values of the specific electrical conductivity of the annealed powder samples during the second loading–unloading cycle can be explained by a better

TABLE 1. Electrophysical characteristics of composite samples Ti+0.53 wt.% TEG before and after annealing for 1.5 h at different temperatures in a vacuum furnace (resistometric data are given for the first load–unload cycle).

Annealing temperature, K	ρ_{cr} , g/cm ³	$\sigma_{\rho_{cr}}$, ($\Omega \cdot \text{cm}$) ⁻¹	$\rho_{\sigma_{max}}$, g/cm ³	σ_{max} , ($\Omega \cdot \text{cm}$) ⁻¹
Without annealing	2.52	0.001	3.39	3.28
700	1.67	0.014	2.73	13.35
900	0.95	0.001	1.41	8.56

filling of the cavities between the titanium particles with thermally expanded graphite during the material compaction at both loading–unloading cycles, *i.e.*, by a decrease in the number of contacts between the metal particles.

The higher, in comparison with the initial (unannealed) state, values of σ in Fig. 3 (see also the values of σ_{max} in Table 1) are, probably, due to the annealing of gas impurities and a change in the chemical composition of the surface of the metal particles. The last changes in hydrogenated titanium during long-term vacuum annealing are associated with the release of hydrogen to the metal particles' surface and partial reduction of titanium oxide in the oxide shells of the metal particles. A decrease in the thickness of the oxide layer is reflected in the EDX analysis data as a decrease in the oxygen concentration on the surface of the metal particles with increasing annealing temperature (see the tables in Fig. 2 for the points of maximum titanium content). It should be noted that, for a more wide range of annealing temperatures, resistometric studies also could provide information on the thickness of the oxide layer and the diffusion coefficient of impurities in metal particles [12]. In addition, it can be seen from Table 1 that, at annealing temperature of 900 K, the value of σ_{max} decreases compared to the case of annealing at 700 K, which is also caused by the additional destruction of the TEG and the composite material in whole. The decrease in its density associated with the destruction of the composite is also confirmed by the changes depending on the vacuum annealing temperature in the values of the density ρ_{cr} of the powder material and the electrical conductivity $\sigma_{\rho_{cr}}$ (Table 1), which correspond to the points of beginning of the current flow through the composite. The transfer of charge between TEG and metal particles can also lead to additional loosening of the TEG due to Coulomb repulsion between similarly charged particles.

3.2. Temperature Dependence of Specific Electrical Conductivity

Additional information about the composite material can be obtained

by analysing the temperature dependence of the specific electrical conductivity of the composite itself and its pure components. The previously unannealed samples were heated and cooled twice; the range of temperatures investigated was approximately 280–835 K. It can be seen in Fig. 4 that all the dependences presented show an increase in the specific electrical conductivity with increasing temperature in almost all parts of corresponding curves. Thus, both the pure components and the composite itself mainly exhibit the semiconductor temperature dependence of the specific electrical conductivity, which has an activation character (see also Ref. [13]). There may be several types of charge carriers simultaneously in the material, which can be activated during the temperature growing. Each of them is characterized by its own activation energy E_g . For each temperature range, where $k_B T \cong E_g$, the activation energy determines the exponential dependence of the specific electrical conductivity:

$$\sigma(T) = \sigma_0 \exp(-E_g / (k_B T)). \quad (2)$$

For a semiconductor $E_g = E_b / 2$, where E_b is the width of the energy gap separating the corresponding electronic (hole) states from the conduction (valence) band. In particular, this type of $\sigma(T)$ dependence confirms the oxide shell model of hydrogenated titanium particles (see also [14]) and the semi-metallic character of the carbon component.

From the dependences of the specific electrical conductivity in a logarithmic scale on the inverse temperature for the unannealed composite in a vacuum furnace, one can see (Fig. 5) that the processes of thermal activation of each type of charge carriers correspond to their own linear section of the function $\sigma(1/T)$. The tangent of the inclination angle of this function is directly proportional to the activation energy E_g . At the same time, at relatively low temperatures, small slopes of the linear sections of the function $\sigma(1/T)$ are observed in all dependences, and at higher temperatures the slopes increase, which indicates

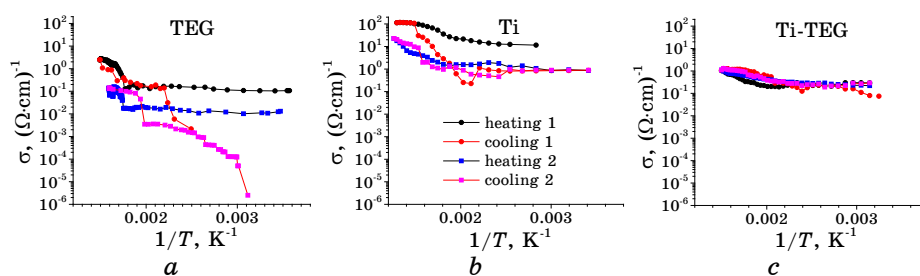


Fig. 4. Temperature dependences of the specific electrical conductivity of the initial powders of the pure components (*a*, *b*) and their mixture (*c*) during two heating–cooling cycles.

the thermal excitation firstly of carriers from low energy levels, and then of carriers that have to overcome some higher energy barriers (see Table 2). With a further increase in temperature, carriers from most of the impurity energy levels are excited and replenish the population of band ones. For the last, the role of thermal dissipation of charge carriers begins to grow, which determines the output of specific electrical conductivity values at saturation with a tendency to transition to metallic temperature dependence.

In the initial components, charge carriers with low (< 0.1 eV) activation energy are most likely associated with their excitation from impurity levels in the oxide shell of titanium particles (for example, oxygen vacancies can be donors [15]) and from the lower part of the π zone of the graphene layers of TEG to the upper one (*i.e.*, in the energy region above the Fermi level, the position of which in TEG particles is determined by the thickness and degree of deformation of their graphene layers, the type and number of adsorbates on them, *etc.*). The nature of these carriers remains the same in the composite. Although, due to the differences in the processes taking place in the composite during heating and cooling, for both heating-cooling cycles, in the cooling sections at low temperatures, a transition from the semiconductor type of temperature dependence of the specific electrical conductivity of the composite to the metallic one is observed when the temperature decreases. Moreover, at higher temperatures, the rather larger activation energy values (up to 0.19 eV) are observed, which probably correspond to the excitation of low-energy polaron states in the oxide shells of titanium particles [15]. There is practically no activation of the intrinsic carriers in titanium oxide, since the band gap for them is in-

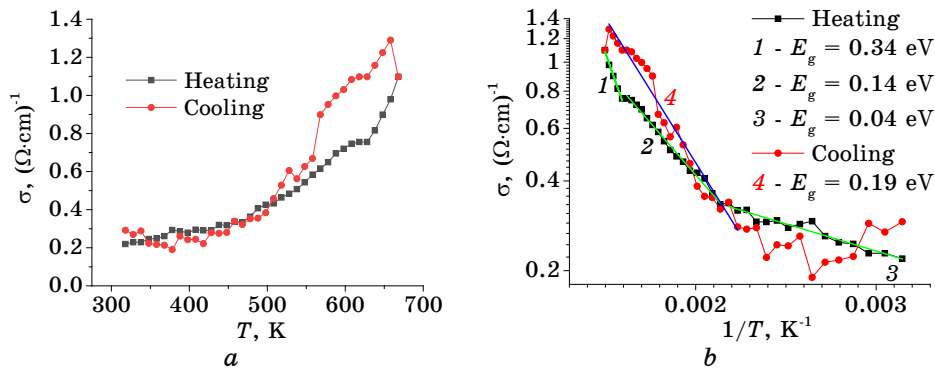


Fig. 5. Temperature dependences of the specific electrical conductivity of the initial composite Ti+0.53 wt.% TEG on the second heating-cooling cycle in linear (as a function of T) (a) and logarithmic (as a function of $1/T$) (b) scales. The activation energies of the charge carriers are given for the numbered parts of the temperature dependences.

TABLE 2. Activation energies E_g of charge carriers in the initial samples (before vacuum annealing) of the pure powder components and the Ti+0.53 wt.% composite itself. % TEG, determined from the temperature dependence of the specific electrical conductivity on two heating–cooling cycles (see Fig. 5).

Material		Activation energy, eV								
		TEG			Ti			Ti-TEG		
Type of carriers		1	2	3	1	2	3	1	2	3
Cycle 1	Heating	0.44	–	0.04	0.47	–	0.08	0.32	–	0.06
	Cooling	0.42	0.28	–	0.64	–	0.09	–	0.19	–
Cycle 2	Heating	0.4	–	0.03	0.57	–	0.04	0.34	0.14	0.04
	Cooling	–	0.23	–	0.41	–	0.07	–	0.19	–

surmountable (3.05 eV).

Mechanical processing of the mixture increases the number of defects and leads to a decrease in the activation energy. It should be noted that the α -phase of titanium is characterized by features of the electronic structure, thanks to which this metal is included in the list of potential topological materials [16]. At even higher temperatures, even ‘pure’ titanium can exhibit an increase in electrical conductivity with increasing temperature, which is explained in [13] by the presence in it, as a transition metal, of several energy zones with significantly different effective masses (s - p and d) of electrons and the possibility of their band-to-band transitions. At the same time, for strongly localized d -electrons, the semiconducting temperature dependence of their concentration near the Fermi level with a certain value of the activation energy ($E_g \cong 0.2$ – 0.5 eV) of electron transitions from d -band states to s - p -band states (in terms of Ref. [13] from the states of the second Brillouin zone to the conduction band) (Table 2).

In Figure 4, all graphs are on the same scale, and one can directly see the differences in the absolute values of the specific electrical conductivity of the pure components and of the composite before their vacuum annealing. The characteristic slopes of individual parts of the dependence $\sigma(1/T)$ can be seen in Fig. 5, *b* on a logarithmic scale. In Figure 5, it is also given the activation energies of certain charge carriers connected with the widths of the corresponding band gaps or the energies of the interband transitions.

A significant decrease in the absolute values of the electrical conductivity of the pure initial components of the composite during the second heating–cooling cycle, compared to the first cycle, draws attention. It can be explained by the rather high temperatures of our research and the changes in the chemical composition and defects of the materials at these temperatures. Thus, during the first heating–cooling cycle, a significant amount of adsorbed gases is removed from

the TEG, which decreases the number of free charge carriers and shifts the Fermi level closer to the minimum value of the energy dependence of the density of electronic states of graphite, leading to a decrease in the number of electrons around the Fermi level and, therefore, in the electrical conductivity. Even the presence of such quasi-gap in the energy spectrum of graphite is the reason for its relatively low conductivity in the temperature range from room temperature to 1300 K. The first heating of hydrogenated titanium powder in air to temperatures of about 500 K leads to the beginning of decomposition of titanium hydride and partial recovery of the oxide shells of metal particles by hydrogen (due to hydrogen diffusion from bulk to surface). This is manifested in a faster growth of electrical conductivity at the corresponding temperatures. However, with the oxide reduction process, the reverse process—oxidation—also accelerates with increasing temperature. When they compensate each other at temperatures ≥ 700 K, the dependence $\sigma(1/T)$ almost reaches saturation.

When the powder is cooled to temperatures ≤ 700 K, the release of hydrogen in the sample slows down significantly, and the oxidation process remains quite intense (the concentration of oxygen in the air does not decrease with time), so, the thickness of the oxide shell of the metal particles increases, and the conductivity of the sample decreases to values at which the second heating-cooling cycle begins. At the same time, the hydrogen-depleted sample does not return to the previous high values of electrical conductivity—the new maximum value of its conductivity will be several times lower. During the second cycle, hydrogen atoms do not have time to reach the surface and leave the particle through a thicker oxide shell (taking oxygen atoms with them) during a relatively short stay at high temperatures, and therefore, no sharp change in conductivity is observed during cooling.

At the same time, the nature of both impurity and 'band' free carriers remains unchanged in the pure materials considered. Therefore, the slopes of the dependences $\sigma(1/T)$ for different heating-cooling cycles remain unchanged, as well as the values of the activation energies. From heating-cooling cycle to next one, only the occupation of impurity levels decreases and/or the thickness of the semiconductor layer increases, which leads to the shifting of the $\sigma(1/T)$ curves to the region of lower values of electrical conductivity.

The dependences of the specific electrical conductivity of the initial powder of the hydrogenated Ti+0.53 wt.% TEG composite on the inverse temperature (Fig. 4, c) demonstrate mainly an increase in $\sigma(1/T)$ with increasing T , except the first heating and the second cooling, when at low temperatures a decrease in electrical conductivity is observed with increasing of values of T . Note that, for samples annealed in a vacuum furnace, a metallic type of conductivity can be observed even at low temperatures (Figs. 7 and 9). In such parts of the $\sigma(1/T)$

dependence, the determination of the activation energy E_g values loses a sense. The samples were heated from room temperature to ≤ 670 K.

Compared to the similar dependences of $\sigma(1/T)$ (on a logarithmic scale) for the initial pure components, the dependence of $\sigma(1/T)$ for the unannealed composite sample is almost independent of the number of cycles and the heating or cooling stages. This can mean that in the composite, the processes that determined the behaviour of its pure components at different heating and cooling stages are either suppressed or compensated. One probably scenario is that TEG degassing begins in the composite upon heating, but the Fermi level shift due to the change in electron concentration leads to the flow of free charge carriers across the interfaces between TEG and Ti. If, at the same time, the electron concentration changes in hydrogenated Ti, then, this can complicate the process of hydrogen reduction of the oxide shells of metal particles.

Thus, the change of electron concentration in TEG because of desorption of gases compensates due to charges' transfer from the titanium particles, which blocks significant changes in the chemical composition of surface of the grains of powder. Therefore, when the studied composite is heated and cooled, the structural changes of the interfaces between its individual components and changes in the electronic structure of last will not be sharply effect on composites' kinetic properties. Such thermal stability of the composite (before annealing in a vacuum furnace) allows tracing the mechanisms of activation of charge carriers in it in a more or less pure form based on the dependences of $\sigma(1/T)$.

During heating and cooling of the initial composite Ti+0.53 wt.% TEG, the temperature dependence of the specific electrical conductivity in the range of its semiconducting behaviour has an exponential character with a break at 620 K (see Fig. 4, *c* and Fig. 5). At the same time, the $\sigma(1/T)$ curves show a slight difference between the heating and cooling regions compared to similar curves for pure components: at high temperatures, the dependence of $\sigma(1/T)$ is some higher in the cooling region than in the heating one. In addition, it can be seen that during the second heating, $\sigma(1/T)$ is mostly some higher than during the first one, and the opposite behaviour is observed during the cooling.

In Figure 5, *a*, the dependences of $\sigma(T)$ of the composite on the second heating-cooling cycle are shown, and Fig. 5, *b* shows the corresponding plots of the $\sigma(1/T)$ dependences. The activation of new excitation processes of charge-carrying quasi-particles is indicated by breaks in the $\sigma(1/T)$ dependence. It can be seen that the thermal energy $k_B T$ in section 3 is sufficient to activate only charge carriers with a small energy $E_g = 0.04$ eV, which can correspond to the excitation of electrons into free states of the π zone of the TEG through a point (or

an energy quasi-gap of very small width) with almost zero density of electronic states in the energy spectrum of electrons of the semi metallic TEG. At higher temperatures (sections 2 and 4), the quasi-particles from impurity levels with $E_g = 0.14\text{--}0.19$ eV start to be excited (for example, the binding energy of the donor electron is $E = 13.6(m^*/m_0)/\varepsilon^2 \cong \cong 0.02\text{--}0.09$ eV, effective electron mass $m^* = 1.1\text{--}4.3m_0$, relative permittivity $\varepsilon \cong 80$, m_0 is electron rest mass [15, 17, 18]). Higher temperatures involve ‘intrinsic’ charge carriers in the kinetic phenomena. However, their energy, which is of $\cong 0.34$ eV (section 1), corresponds only to the excitation of *d*-electrons in Ti [13], and for the activation of the intrinsic electronic states of Ti oxide, it would be necessary to overcome an order of magnitude higher energy gap.

The temperature dependences of the specific electrical conductivity was also studied for the composite Ti+0.53 wt.% TEG with initial hydrogen content in titanium of 2.74 wt.%, when the sample was previously annealed for 1.5 h in a vacuum furnace at temperatures of $\cong 700$ K and 900 K. Plots of the electrical conductivity versus temperature are presented in Figs. 6–9 and Table 3 for 3 degrees of compression of each of the powder samples.

As for the unannealed Ti+0.53 wt.% TEG composite, the temperature dependences of the specific electrical conductivity during heating and cooling for samples annealed at $\cong 700$ K and 900 K are mainly semiconducting (exponential) in nature with the breaks of the curves around 500 K (Fig. 7) and 550 K (Fig. 9), respectively. At the same time, the $\sigma(T)$ curves (Fig. 6) show a certain difference between the heating and cooling stages, namely, the $\sigma(T)$ dependences in the cooling stages are mostly higher than in the heating ones, but their slope (see Fig. 7, *a*) changes very little. It can also be seen that with each consecutive (second and third) heating–cooling cycle, which is also accompanied by subsequent compression of the material, the $\sigma(T)$ dependencies pass higher and higher.

The effects described above are similar to those observed on the unannealed composite sample, but now they are significantly enhanced by both the additional compression and the previous annealing. The last removed more impurities from the carbon component and a certain amount of hydrogen from the titanium particles. During the Ti-particles’ dehydration, the average thickness of their oxide layers is decreased. Thus, in the annealed sample, the effect of compensating the change in conductivity of different components of the composite is much less pronounced. At the same time, the least compacted powder after annealing in a vacuum furnace (this is the first heating when taking $\sigma(T)$ dependence) showed conductivity values $\cong 2$ times lower than that of the unannealed sample, and the most compact powder (this is the third heating, when obtaining $\sigma(T)$) showed conductivity values $\cong 2$ times higher than that of the unannealed sample.

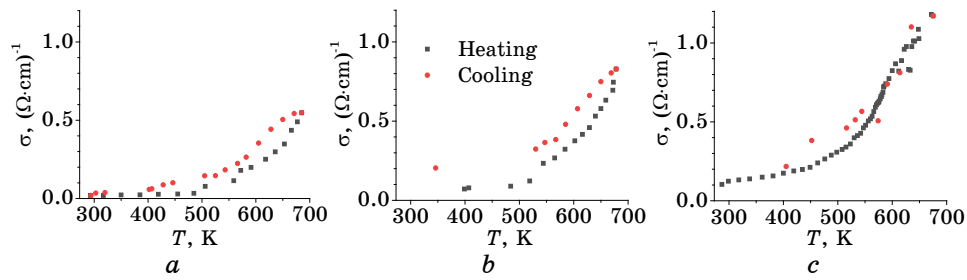


Fig. 6. Temperature dependences of the specific electrical conductivity of the composite material Ti+0.53 wt.% TEG after pre-annealing in vacuum at a temperature of $\cong 700$ K for different compressions determined by the material density ρ : 1.60 g/cm³ (a), 1.63 g/cm³ (b), 1.65 g/cm³ (c).

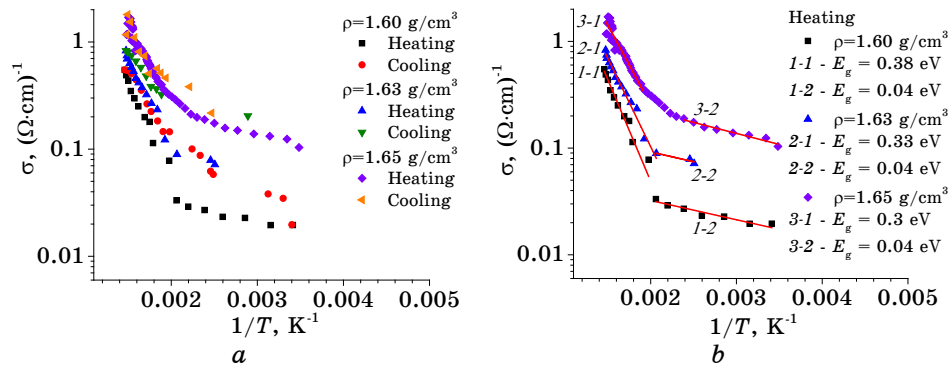


Fig. 7. Temperature dependences of the specific electrical conductivity of the composite material Ti+0.53 wt.% TEG after pre-annealing in vacuum at a temperature of $\cong 700$ K in the logarithmic scale and as a function of $1/T$ for different densities: *a*—heating and cooling stages, *b*—activation energies of the free charge carriers during the heating stage.

The electronic properties of the composite material of the sample annealed in a vacuum furnace, which are determined by the temperature dependence of the electrical conductivity, remain the same as for the unannealed sample. Thus, the values of the activation energies of the free carriers are practically the same in both cases, as shown by the fitting of the curves of the dependences of the electrical conductivity on the temperature (see Figs. 5 and 7). However, Figure 7 also allows us to follow the growth patterns of the specific electrical conductivity with increasing material density at all the temperatures studied, which is in full agreement with the resistometric studies described above (Figs. 1 and 3).

At the same time, a decrease in the activation energy of the inter-band transitions in titanium is clearly observed during densification

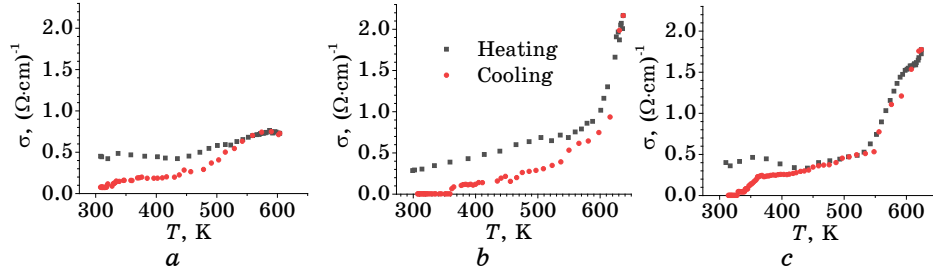


Fig. 8. Temperature dependences of the specific electrical conductivity of the composite material Ti+0.53 wt.% TEG after pre-annealing in vacuum at a temperature of $\cong 900$ K for different compressions determined by the material density ρ : 1.47 g/cm³ (a), 1.50 g/cm³ (b), 1.58 g/cm³ (c).

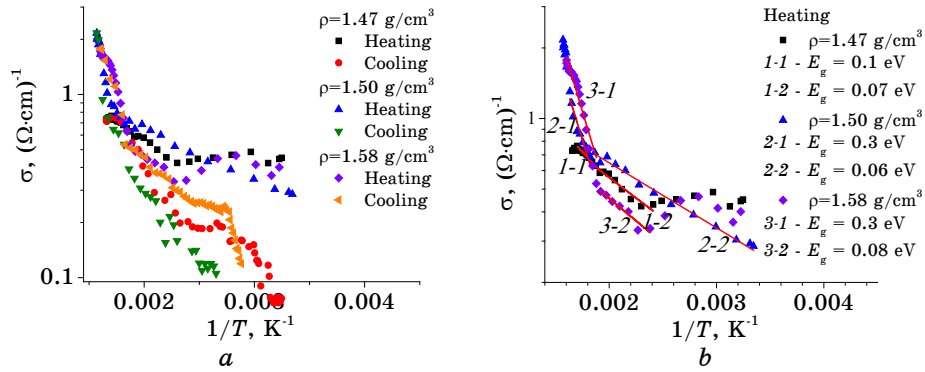


Fig. 9. Temperature dependences of the specific electrical conductivity of the composite material Ti+0.53 wt.% TEG after pre-annealing in vacuum at a temperature of $\cong 900$ K in the logarithmic scale and as a function of $1/T$ for different degrees of compression: *a*—heating and cooling stages, *b*—activation energies of the free charge carriers during the heating stage.

(see the value of E_g for the sections 1-1, 2-1, 3-1 of the dependences $\sigma(1/T)$ in Fig. 7, *b*) and the practical invariance of the energy gaps for impurity levels (see the value of E_g for the sections 1-2, 2-2, 3-2 of the dependences $\sigma(1/T)$). This indicates, on the one hand, the different nature of the corresponding activation energies and, on the other hand, it proves that when the composite is compressed, not only its structural properties (which we tried to consider with Eq. (1)) but also its electronic structure (mainly the filling of different zones of both components of the composite) change. Therefore, the above-described mechanisms of influence of the corresponding interfaces between the components of the composite material, in particular, the charge transfer through them, receive experimental confirmation.

The electron microscopy and EDX studies of samples before and af-

TABLE 3. Activation energies E_g of charge carriers in composite samples Ti+0.53 wt.% TEG after annealing in vacuum for 1.5 h at different temperatures, determined from the temperature dependences of the specific electrical conductivity (Figs. 7 and 9) for three heating–cooling cycles at three different densities.

Ti-TEG		Activation energy, eV			
		Annealing at 700 K		Annealing at 900 K	
Type of carriers		1	2	1	2
Cycle 1	Heating	0.38	0.04	0.1	0.07
	Cooling	0.25	0.06	0.2	0.04
Cycle 2	Heating	0.33	0.04	0.3	0.06
	Cooling	0.21	0.04	0.26	0.11
Cycle 3	Heating	0.3	0.04	0.3	0.08
	Cooling	0.27	0.1	0.39	0.09

ter annealing at 700 K and 900 K show (Fig. 2) that annealing in a vacuum furnace leads to a change in both the surface morphology and its chemical composition. Unfortunately, annealing in a vacuum furnace does not provide the formation of the nanostructures necessary to reduce the temperature of emission onset [5]. However, it allows a better understanding of the behaviour of composite systems under conditions of elevated temperature and a determination of the upper limit of the last. Since during vacuum annealing at 700 K, the electrophysical properties (*i.e.*, specific conductivity) of the composite are improved, but, when the annealing temperature is increased to 900 K, they are deteriorated (see Table 1).

Significant changes in the structure and electronic properties of both components of the composite during annealing at 900 K are also confirmed by the data on the activation energies of band-to-band transitions in titanium and energy gaps for impurity levels (Table 3). The both mentioned characteristics begin to increase when the powder is compressed, in contrast with the annealing at 700 K, when the first characteristic is significantly larger and decreases during compression, and the second one is smaller and remains almost unchanged during compression. The reason for this is not only the destruction of the carbon component at 900 K, but also the desorption of hydrogen from hydrogenated titanium and a change in the conditions for the transfer of charge carriers between the components of the composite.

4. CONCLUSIONS

The comparison of experimental (resistometric) and theoretical values

of electrical conductivity shows that the mixture of powders of hydrogenated Ti +0.53 wt.% TEG, in which low-temperature thermophotoelectronic emission was previously observed, is a composite whose electrophysical properties differ significantly from those of an ordinary mixture and its pure components.

For the first time, it was experimentally confirmed that the reason for the formation of a composite is the significant role of the interfaces between its components. The probable mechanism of their influence through the redistribution of free charge carriers between the components was proposed.

1. It has been found that preliminary mechanical processing of the Ti-TEG mixture significantly changes the structural state of the carbon component of the composite, which becomes more homogeneous and less crumbly compared to pure TEG. It is shown that, at the maximum compression of the composite used in the experiment, its carbon component is compacted only 2 times compared to the initial (before mechanical processing) state of TEG, while pure TEG can be compacted more than 10 times.

2. It is shown that such a composite can be represented as a heterogeneous matrix system in which the particles of hydrogenated Ti plays the role of matrix and TEG particles play the role of inclusions. At the same time, it was found that for an adequate description of the experimental data, one should go beyond the limits of the used theory of the generalized conductivity of such systems and assume an increase of the specific electrical conductivity of the carbon component of the composite by 19–30 times as compared to pure TEG, which can occur due to the transfer of charges between the components and the peculiarities of the electronic structures of graphene-like materials.

3. It is shown that short-term heating in the range of 280–835 K leads to significant and irreversible changes in the structure and electronic properties of each individual component of the composite. However, in the composite, these properties do not show significant irreversible changes during such heating, since the structure and electrophysical properties of the composite are the result of the simultaneous action of many processes stimulated by elevated temperature, namely, desorption of impurities from TEG, decomposition of Ti hydride, diffusion of hydrogen throws metal particles to the surface with reduction of their oxide shells, those rapid oxidation during experiments in air, transfer of charges between components of the composite, *etc.* The result of their joint action is the stabilization of the electrophysical properties of the composite material under the influence of temperature.

4. It was found that the preliminary annealing of the composite material for 1.5 hours in a vacuum furnace at a temperature of about 700 K leads to the removal of impurities from the TEG and the release of hydrogen from the Ti particles, due to which the thickness of the oxide

layer in the last is decreased. All this disrupts the balance of the above-mentioned processes and leads to the loss of thermal stability of the composite electrophysical properties. A similar annealing at $\cong 900$ K leads to the degradation of the composite material due to the onset of destruction of TEG, which is reflected in a decrease in the specific electrical conductivity of the sample. In addition, as the vacuum annealing temperature increases, sintering of the hydrogenated titanium particles occurs, but without a significant change in the surface morphology of the sample, as was the case during concentrated sunlight annealing, when a thin layer of carbon with icicle-like growths formed on the surface of the titanium particles. Therefore, vacuum annealing does not provide the surface properties of the composite required for use in TPECs, but it does provide a better understanding of the processes that occur during composite formation and under various thermal influences on it.

5. Based on the results of the analysis of the temperature dependence of the specific electrical conductivity, its semiconducting nature was established, as well as the activation energy of electrokinetic phenomena in the studied material before and after its long-term annealing in vacuum at temperatures around 700 K, which have a dual nature: at low temperatures, the excitation of free charge carriers from impurity levels prevails, and at higher temperatures, band-to-band transitions in the titanium are activated.

6. Analysis of the dependence of the activation energies on the degree of compression of the material under study after long-term annealing in vacuum at a temperature of about 700 K demonstrated, for the first time, the electronic nature of the formation of the composite and provided indirect experimental confirmation of the importance of the role of the interfaces between the different components of the composite and the transfer of charges through them, which is important for the creation of electrons' emitters with a structure and electronic properties that can change the contributions from different emission mechanisms, for example, increase the contribution from autoelectronic emission.

7. It was found that the electrophysical properties of the composite improve after annealing in vacuum at a temperature of about 700 K, and, when the annealing temperature is increased to 900 K, they deteriorate compared to the case of annealing at 700 K due to the degradation and removal of the carbon component at a higher annealing temperature, dehydration of hydrogenated titanium and changes in the conditions of transfer of charge carriers between the components of the composite.

8. It is shown that the Ti-TEG mechanical mixture demonstrates a significant transformation of the electronic structure during the formation of the composite material and its following thermal treat-

ments, which opens the way to lower the operating temperature of thermal emission devices and expand their scope of application.

ACKNOWLEDGMENTS

This work was supported by projects Nos. 0118U000416 and 0123U102275 of the National Academy of Sciences of Ukraine, and partially by UKRAPRO scholarship program for Ukrainian researchers (Volkswagen Foundation).

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