

ELECTRONIC STRUCTURE AND PROPERTIES

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Low-Temperature Thermionic Converters Based on Metal–Nanostructured Carbon Composites

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The present work is devoted to the search for new electrode materials for low-temperature thermionic energy converters (TECs). As shown, the carbon nanostructures (CNS) adding to pure powdered titanium in an amount of 3–9% wt. and their subsequent mechanical mixing leads to the formation of composites that acquire new qualities that were not present in any of their original pure constituents. Thus, the significant changes in the mechanical and electrical characteristics of composites are observed. For example, the electrical conductivity is changed up to 2 orders in initial state of composites as well as its maximum values after samples' compaction are increased (1.6–5 times) in comparison with both the pure Ti powder and the pure thermally extended graphite (TEG) in corresponding compression states. Such changes are caused by the presence of contacts between the metal particles and the CNS in the metal–nanocarbon composites and, accordingly, the possibility of the transition of free charges, including hot charges, from the metal to the CNS. This allows the use of such composites as cathode materials for low-

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temperature thermionic energy converters (TECs). For such TECs the high nonequilibrium state of electronic subsystem as well as the electronic structure and surface geometry are important, for example, a significant aspect ratio for separately located surface elements, *i.e.* the thin needles of carbon nanotubes and thin blades of graphene planes of TEG, protruded from composite surface. The electron emission properties of the Ti-TEG composite materials under the conditions of their illumination by concentrated sunlight are investigated. Thus, at temperatures of 170–350°C, which are 3–5 times lower than the operating temperatures of traditional TECs made with refractory metals, a voltage and, for the first time, a constant current in a closed electric circuit are observed without applying an additional external difference of potentials. As found, in addition to decreasing of contribution of thermal electron emission mechanism for benefit of autoelectronic one, the influence of ionized residual gases in the vacuum chamber, especially caesium ions, plays a significant role in reducing the electron work function from such composite nanostructures and compensating space charge. As revealed, under the influence of concentrated solar radiation a change in the morphology of the composite surface is occurred, *i.e.* on the Ti particles a large number of new CNS with a diameter of 20–80 nm are formed. This new type of CNS also acts as sources of electronic emission and increases the cathode emission efficiency and decreases its operating temperature due to their small thickness and the negative electron affinity of carbon in the sp^3 -hybridized state.

Key words: concentrated solar energy, low-temperature thermionic converters, caesium ions, metal–nanostructured carbon composites.

Роботу присвячено пошуку нових електродних матеріалів для низькотемпературних термоемісійних перетворювачів. Показано, що додавання до чистого порошкового титану вуглецевих наноструктур (ВНС) у кількості від 3 до 9% мас. та наступне їх механічне перемішування призводять до утворення композитів, які набувають нових якостей, не притаманних жодній з їх вихідних чистих складових. Так, спостерігаються суттєві зміни механічних та електричних характеристик композитів, наприклад, значні зміни (до 2 порядків величини) в їх електропровідності у вихідному стані та суттєве зростання (у 1,6–5 разів) максимальних значень електропровідності композитів за умов їх стискання у порівнянні з чистими порошком Ti та терморозпущеним графітом (ТРГ). Металеві частки виступають для провідної мережі з ВНС переважно у ролі постачальника вільних носіїв заряду, у тому числі «гарячих». Це дозволяє використовувати такі композити при створенні катодних матеріалів для низькотемпературних термоемісійних перетворювачів (ТЕП). Для таких ТЕПів важливими є як високі показники нерівноважності електронної підсистеми, так і електронна структура й геометрія поверхні, наприклад, значне аспектне співвідношення для окремо розташованих елементів поверхні, що забезпечується виходом на поверхню композиту тонких голок вуглецевих нанотрубок та тонких лез графенових площин ТРГ. В роботі проведено дослідження емісійних властивостей таких композитних матеріалів в умовах їх освітлення концентрованим сонячним промінням. Так, на зразках Ti-ТРГ за температур 170–350°C, що у 3–5 разів нижчі за робочі те-

мператури традиційних ТЕП з тугоплавких металів, спостерігалися напруга та, вперше, постійний струм у замкненому електричному колі без прикладання додаткової зовнішньої різниці потенціалів. Встановлено, що, окрім зменшення внеску термічного механізму електронної емісії на користь автоелектронного, суттєву роль відіграє вплив йонізованих залишкових газів у форвакуумній камері, особливо йонів Цезію, які забезпечують зменшення роботи виходу електронів з поверхні композитних наноструктур та компенсують просторовий заряд. Виявлено, що під впливом концентрованого сонячного випромінювання відбувається зміна морфології поверхні композитного зразка за рахунок утворення на частинках Ti великої кількості нових ВНС діаметром 20–80 нм, що також виступають в якості джерел електронної емісії, підвищуючи емісійну ефективність катоду та зменшуючи його робочу температуру через їх малу товщину та від’ємну спорідненість вуглецю в sp^3 -гібридизованому стані до електронів.

Ключові слова: концентрована сонячна енергія, низькотемпературні термоелектричні перетворювачі, йони Цезію, композити метал–наноструктурований вуглець.

Работа посвящена поиску новых электродных материалов для низкотемпературных термоэмиссионных преобразователей. Показано, что добавление к чистому порошковому титану углеродных наноструктур (УНС) в количестве от 3 до 9% масс. и последующее их механическое перемешивание приводят к образованию композитов, которые приобретают новые качества, не присущие ни одному из их исходных чистых составляющих. Так, наблюдаются существенные изменения механических и электрических характеристик композитов, например, значительные изменения (до 2 порядков величины) их электропроводности в исходном состоянии и существенный рост (в 1,6–5 раз) максимальных значений электропроводности композитов в условиях их сжатия по сравнению с чистыми порошком Ti и терморасширенным графитом (ТРГ). Металлические частицы выступают для проводящей сети из УНС преимущественно в роли поставщика свободных носителей заряда, в том числе «горячих». Это позволяет использовать такие композиты при создании катодных материалов для низкотемпературных термоэмиссионных преобразователей (ТЭП). Для таких ТЭПов важны как высокие показатели неравновесности электронной подсистемы, так и электронная структура и геометрия поверхности, например, значительное аспектное соотношение для отдельно расположенных элементов поверхности, которое обеспечивается выходом на поверхность композита тонких игл углеродных нанотрубок и тонких лезвий графеновых плоскостей ТРГ. В работе проведено исследование эмиссионных свойств таких композитных материалов в условиях их освещения концентрированным солнечным светом. Так, на образцах Ti–ТРГ при температурах 170–350°C, что в 3–5 раз ниже рабочих температур традиционных ТЭП из тугоплавких металлов, наблюдались напряжение и, впервые, постоянный ток в замкнутой электрической цепи без приложения дополнительной внешней разности потенциалов. Установлено, что, кроме уменьшения вклада термического механизма электронной эмиссии в пользу автоэлектронного, существенную роль играет влияние

ионизированных остаточных газов в форвакуумной камере, особенно ионов цезия, которые обеспечивают уменьшение работы выхода электронов с поверхности композитных наноструктур и компенсируют пространственный заряд. Обнаружено, что под воздействием концентрированного солнечного излучения происходит изменение морфологии поверхности композитного образца за счёт образования на частицах Ti большого количества новых УНС диаметром 20–80 нм, которые также выступают в качестве источников электронной эмиссии, повышая эмиссионную эффективность катода и понижая его рабочую температуру благодаря их малой толщине и отрицательному сродству углерода в sp^3 -гибридизированном состоянии к электронам.

Ключевые слова: концентрированная солнечная энергия, низкотемпературные термоэлектрические преобразователи, ионы цезия, композиты металл–наноструктурированный углерод.

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1. INTRODUCTION

The realization of the idea of direct conversion of solar energy into an electrical one stimulated a progress in the photovoltaic [1, 2], thermoelectric [3, 4], and corresponding hybrid systems [5–10] as well as in thermionic converters [11–15] and their hybrids [16–19]. Herewith, a thermionic energy converter (TEC) can provide higher current and power densities as compared with thermoelectric and photoelectric converters, and the efficiency of a non-hybrid TEC in high- and medium-temperature modes can reach 63.8% and 45%, respectively [15].

Low-temperature thermal sources, in contrast to high-temperature ones, are more readily available to use, so it seems relevant to consider the direct conversion of thermal energy into electrical one at the temperatures less than 600°C. Such and more bigger temperatures can be easily achieved by heating the materials with concentrated solar radiation [20]. However, the need for simultaneous monitoring of many system parameters does not yet allow moving from a theoretical consideration of low-temperature energy conversion to a wide practical implementation of such TECs [14]. The most promising in this direction are ideas for the combination of pre-thermoemission excitation of electrons, for example, directly by light quanta (implementing primarily in semiconductors) [12, 13, 21] or immediately by plasmons (in metals) [22, 23]. The creation of subpopulations of electrons (that are ‘hotter’ than ordinary charge carriers) in materials using various external influences is, although not a new, but very promising and actively developing research area [22–26].

Electron emission methods [27] in the specified low temperature range can become a reality if metal–nanostructured carbon composites

are used as cathodes [28]. It is known [29, 30] that metals have a high concentration of charge carriers but their mobility is relatively low. And the exact opposite situation occurs in conductive carbon nanostructures (CNSs), where a low concentration of charge carriers is combined with their very high mobility along graphene planes, which is 3–4 orders of magnitude higher than in metals [30, 31]. The metal particles act for the CNS network mainly as a provider of free electrons including non-equilibrium hot electrons. The nonconducting CNSs with wide band gaps can have a negative electron affinity simplified autoelectronic emission [32–34]. This allows the use of such composites when creating cathode materials for low-temperature thermal emission converters, for which high nonequilibrium state of electronic subsystem as well as the electronic structure and surface geometry are important. Thus, the electric field intensity around objects with high aspect ratio increases by several orders, which significantly reduces the potential barrier for electrons [30]. Therefore, the part of electrons leaving the cathode mainly by tunnelling mechanism through reduced potential barriers at the edge of cathode is increased.

In addition, the creation of metal–carbon compositions opens up the prospect of combining the advantages of both these types of materials, as well as the appearance in them of qualitatively new characteristics, that are not inherent in the original systems. All of the above is a confirmation of the possibility of creating ‘cold’ cathodes for thermophotoemission converters of energy on the basis of the proposed ‘metal–CNS’ composites.

2. EXPERIMENTAL DETAILS

In this work, on solar energy concentrators we tested the samples obtained by mechanical mixing of thermally expanded graphite (TEG) and industrial titanium powder with particle sizes from 0.1 to 100 μm , followed by cold (at room temperature) pressing with a pressure of 1 ton/cm². Thus, the Ti–TEG composite systems were created in which bonds are formed at the quantum level between metal particles and TEG plates. The creation of such composites can lead to an increase in the concentration of free charge carriers in carbon nanostructures, where they move faster, and an increase in the electrical conductivity of the whole system by a factor of tens [28]. The electrical conductivity of composites and their initial components in powder form during their loading and unloading was measured by the two-contact method in a cylindrical chamber with a conductive base and force plunger. Measurements were carried out prior to pressing samples into moulds.

The obtained samples of the Ti–TEG composites, compacted into washers with a diameter of 30 mm and a thickness of 2 mm, were used as a cathode of a photo-thermionic converter of solar energy (concen-

trated by a parabolic mirror of 2.5 m in diameter) into electrical one. The distance between the cathode and the anode was 1 mm. The special design of the molybdenum anode allowed the sun's rays to reach through it the cathode with minimal obstructions and heat the last one to a certain temperature, which was regulated by the degree of opening of the metal blinds in front of the mirror. The massive copper radiator that was connected to the anode provided efficient heat exchange with the environment and the necessary temperature difference between the electrodes of the proposed energy converter. Concentrated sunlight enters the working vacuum chamber through ultraviolet-transparent quartz glass. Under the cathode material it can be placed an insulated by foil cavity with caesium-contained salts which at T between 200–400°C were decomposed, and Cs atoms can diffuse to the cathode material thereby reducing its work function and in the space of vacuum camera where they partially compensated a space charge near cathode. The initial pressure of the residual gases in the chamber was not more than 0.1 Pa.

Electron microscopy of the pressed samples before and after heating by concentrated sunlight was provided using scanning electron microscope Jeol JSM-6700F.

3. RESULTS AND DISCUSSION

Electron microscopic studies of the obtained after 8 h of mixing Ti–TEG samples (with 9% wt. TEG) in the initial state showed (Fig. 1, *a*) that along with metal particles with sizes from 100 nm to 50 μm , nanostructured carbon is also present in the composite, which tightly fills all the cavities in the metal matrix (pores and cracks with linear dimensions of about 10–15 μm). Such areas are interconnected either directly or through metal bridges. This creates favourable conditions for the continuous supply of free charge carriers to all possible elements of the surface which emit electrons by different mechanisms.

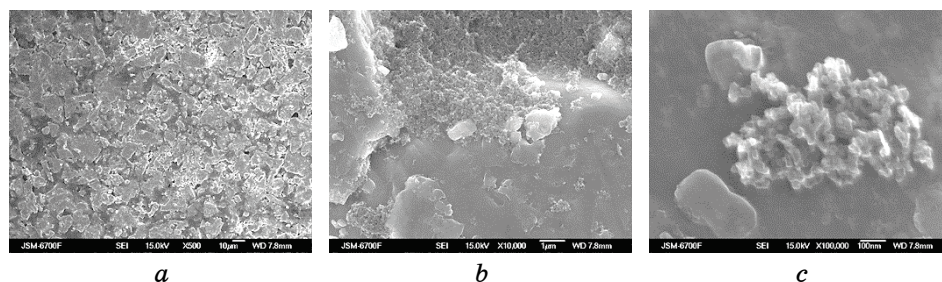


Fig. 1. Multiscale SEM images of the Ti–TEG (with 9% wt. TEG) composite sample before annealing by concentrated solar radiation.

Therein, as Fig. 1, *b* shows, the surface of the metallic particles is quite smooth, and the TEG particles (in the areas filled with them) lose their normal view of separate layered tubes. Due to machining the TEG particles take the form of continuous coral-like structure with sizes of small elements at ranges of 30–50 nm (Fig. 1, *c*).

Investigation of the cold emission effect requires a more careful study of the used metal–nanocarbon composites, in particular their electrical properties. As can be seen from Figs. 2, 3 and Table 1, as the volume of the mixtures obtained in the cylinder under the piston decreased, their electrical conductivity increased from the initial value σ_0 , which for various mixtures varied up to 2 orders of magnitude, to the maximum value of σ_{\max} , which lies in the range $\approx 5\text{--}24\text{ (Ohm}\cdot\text{cm)}^{-1}$. Note, that for a pure TEG array (Fig. 2, *b*) the value of σ_{\max} is realized by the relative deformation ε of the material less than the maximum values of this value, which was reached during the experiment and given in Table 1, and for the other substances, the maximum of achieved deformation coincides with the deformation at which it is reached σ_{\max} .

The compaction of pure Ti powder (Fig. 2, *a*) increases the contact area between the Ti particles and between them and the electrodes and, consequently, increases the electrical conductivity of the compacted material. In this case, the reverse of the dependence $\sigma(\rho)$ indicates the almost complete absence of the elastic component in the deformation of this powder—the restoration of the form practically does not occur, unlike to pure TEG, for which a relatively elastic relaxation is observed after a load is removed.

Addition to the Ti powder of equal in weight (1.5% wt.) portions of TEG and multi-walled carbon nanotubes (CNTs) does not significantly increase (Fig. 3, *b*) the elastic characteristics of the composite, but

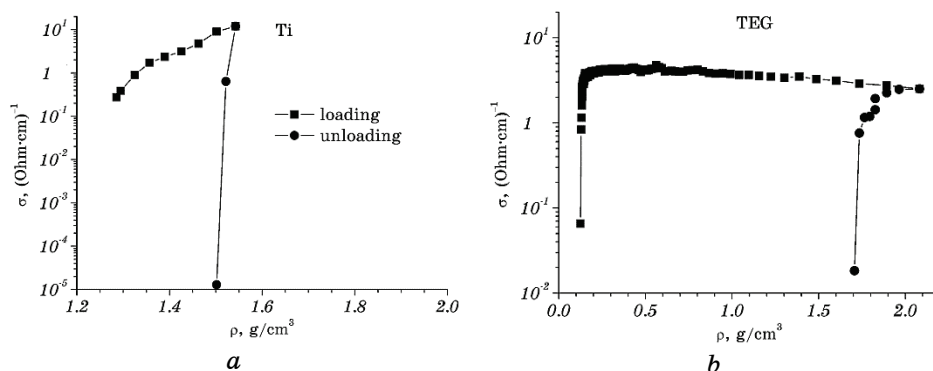


Fig. 2. Multiscale SEM images of the Ti–TEG (with 9% wt. TEG) composite sample before annealing by concentrated solar radiation.

TABLE 1. Initial values σ_0 of electrical conductivity on the dependences $\sigma(\rho)$ and corresponding values of the initial density ρ_0 of the powdered composites and their pure components, as well as the maximal values of both the electrical conductivity σ_{\max} and the relative deformation ε .

Sample composition (% wt.)	σ_0 , (Ohm·cm) ⁻¹	ρ_0 , g/cm ³	σ_{\max} , (Ohm·cm) ⁻¹	ε , %
Ti	0.2754	1.29	11.94	2.0
TEG	0.0661	0.13	4.72	18.0
Ti + 9% TEG	0.5495	1.58	23.70	7.3
Ti + 1.5% CNT + 1.5% TEG	0.0016	1.53	19.75	5.8

more than two orders of magnitude reduces the electrical conductivity of the starting material. This is due to the low conductivity of the CNT arrays without their compression. The formation of numerous contacts between TEG and Ti particles leads to an increase in the number of free electrons in the CNT, which are practically absent in pure defect-free CNTs. The maximum value of electrical conductivity of composite 1.5% wt. CNT after sample compaction is increased 1.6 and 4.2 times in comparison with the pure Ti powder and the pure TEG in corresponding compression states. In the Ti composite with a fraction of 9% wt. TEG, the highest value of σ_{\max} is realized (Fig. 3, *a*), it is 2 times higher than the corresponding value for pure Ti powder and 5 times more than that of pure TEG.

It should be expected that in the presence of numerous tunnel contacts between the metal particles and the relatively transparent for electrons TEG plates or CNTs, the increase in the electrical conductivity

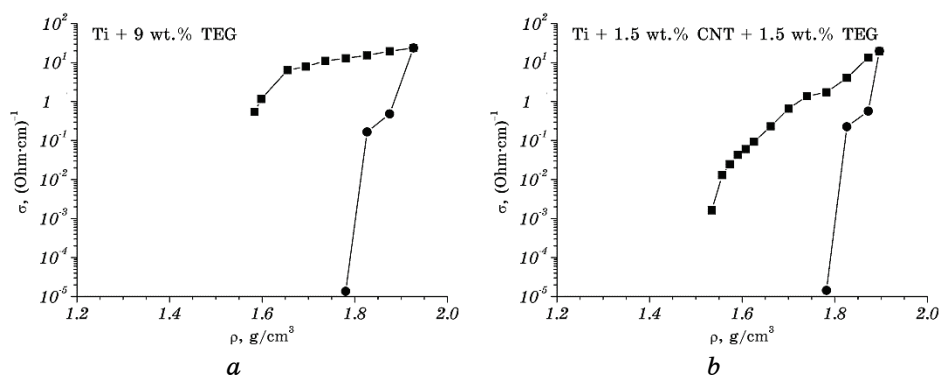


Fig. 3. Dependences of electrical conductivity σ of metal-carbon composites with different content of carbon nanostructures (TEG and CNTs) on the density ρ of the material in the process of loading-unloading.

ty of the system will not be accompanied by an increase in its thermal conductivity (this is explained by the inability of phonons to pass the spatial (tunnelling) barriers), that will allow to increase thermoelectric figure of merit $ZT = T\alpha^2\sigma/\lambda$ of such nanostructures (where T is the temperature, α is Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity).

Thus, metal–CNS composites acquire new features that were not found in any of their original pure components. This allows using such composites for solving new problems, in particular for creating low-temperature thermal emission converters cathode materials, which high conductivity and surface geometry are important.

For experiments on a solar concentrator in this work a Ti–TEG composite with 9% wt. TEG was chosen as the cathode material in the presence and absence caesium salt in the cavity under the sample. At the first heating of the sample with Cs in the sun concentrator, the voltage U and current I (solid lines in Fig. 4, *a* and *b*, respectively) in the closed electrical circuit, to which the TEC was included as a source of EMF, appeared at rather low temperatures (when a small amount of concentrated sunlight hits a sample). The values of quantities slowly increased with increasing temperature to about 220°C, and then reached saturation (with $U \cong 1.5$ mV, $I \cong 0.4$ mA). After heating the sample to temperatures above 300°C, the voltage and current values dropped with the simultaneous loss of vacuum in the working chamber (see Fig. 4, *c*).

For previously studied composites based on metals with multilayer carbon nanotubes and with TEG, EMF values were obtained at near 1.5 V [2, 3], which is an estimation of maximal value of EMF also for new metal-containing composites with carbon nanostructures that were studied in this work.

After the first experiment, the sample was outdoors for several

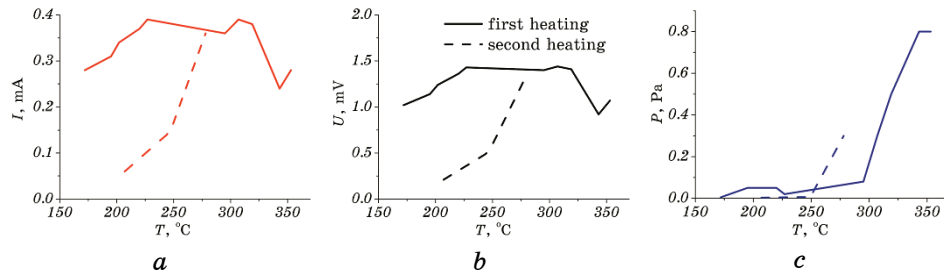


Fig. 4. Dependences of the voltage U (*a*) and the current I (*b*) in a closed electrical circuit with thermionic converter containing a Ti–TEG (with 9% wt. TEG) composite cathode on the temperature T of the test sample, which was twice heated by concentrated solar radiation in a vacuum chamber with the pressure of residual gases P (*c*).

days.

At the second heating of the sample by sunlight (dashed lines in Fig. 4), one can notice a significant change in the appearance of the voltage and emission current in the electric circuit, namely, a sharp increase in both of these quantities after the temperature rises above 200°C. Moreover, the same values of voltage and current that were observed at saturation during the first heating, are achieved at the second heating at higher temperatures (about 280°C), but in a much smaller temperature interval. The most rapid increase in U and I values (after 250°C) is accompanied by a significant vacuum fall (Fig. 4, c).

Primarily the difference between the first and second annealing of the sample by concentrated solar radiation is that the first annealing was accompanied by intensive degassing of the sample and a corresponding degradation of vacuum characteristics (Fig. 4, c) starting with the lowest temperatures. At the beginning of the second heating, despite the prolonged stay of the sample in the air after the first test, the effect of degassing is practically imperceptible, and the vacuum remains almost maximal for a long time (the pressure in the chamber is about an order of magnitude lower than at the same temperatures in the previous test, but stay in the range of pre-vacuum).

As can be seen from the comparison of temperature dependences for U and I with similar dependences for the residual gas pressure P , the presence of these gases in the chamber causes higher values of U , I . However, during the first heating at $T > 300^\circ\text{C}$, vacuum begins to deteriorate especially intensively, and during the second test a similar effect is observed at temperatures $T > 250^\circ\text{C}$. However, at pressures higher than 0.5 Pa (see solid curves in Fig. 4) there is a sharp deterioration of the emission characteristics of the studied system (*i.e.*, sample + gas in the chamber). The above data prove that the working body of the device under consideration is not only a sample of the Ti-TEG composite, but also residual gas, to which the voltage and the emission current are very sensitive. Note that the caesium ions play a particularly important role, without them (for sample without Cs) electron emission is not observed.

It should also be noted that during the first annealing at $T > 300^\circ\text{C}$ not only degassing took place, but also occurs the process of burning of TEG in the pores and its transferring to titanium particles with a change in the type (possibly, the predominant type of chemical bond of carbon atoms) and shape of the carbon nanostructures. A similar process occurs with the second annealing. It indicates that temperatures between 150 and 310°C are critical for initiating the structural change of composite specimens of the investigated type. Given the fact that at such low temperatures only amorphous carbon can be formed [35, 36], the newly formed particles are most likely composed of it and can contain a large number of diamond-like sp^3 -hybridized bonds.

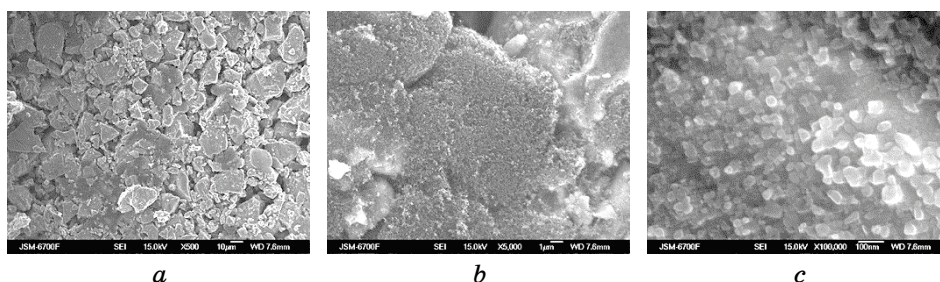


Fig. 5. Multiscale SEM images of the central part of the sample of the Ti-TEG (with 9% wt. TEG) composite, which was most exposed to concentrated solar radiation.

Figures 5 and 6 confirm the progress of such restructuring. As can be seen from these figures, after the second treatment of the sample with concentrated sunlight, its surface becomes more developed both due to the TEG release of some small cavities (gaps) between Ti particles and the formation of new carbon nanostructures on the surface of these particles. The new nanostructures have a look of separately spaced ‘pimple-like’ growths with diameters of 20–80 nm. Definitely the appearance and growing of such structures ensure, with the operation of the cathode, a significant increase in contribution from autoelectronic emission because of working surface (with carbon emission centres) extension. At the same time, only the most dense conglomerates modified by machining and subsequent annealing of the TEG remain in the cavities.

In addition, the tested sample demonstrates the appearance of a texture on the surface of titanium particles that looks like a pavement with structural block sizes of 10–20 nm (Fig. 6, *c*). Such block-stones, more probably, are the nucleation centres of new carbon nanostructures. The surface of titanium particles was clean and smooth before a

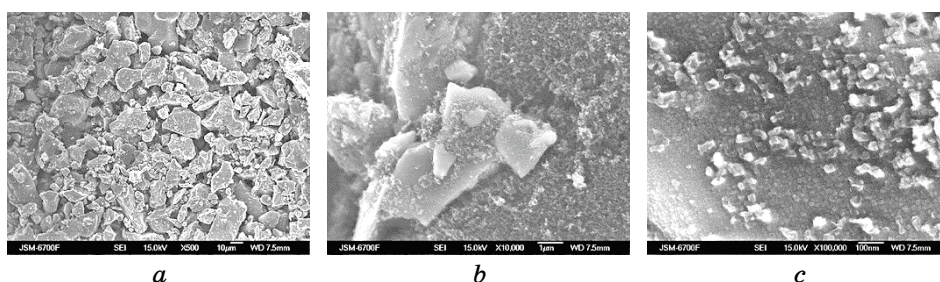


Fig. 6. Multiscale SEM images of the sample (Ti-TEG composite with 9% wt. TEG) surface boundary, which was slightly less exposed to concentrated solar radiation (less burned).

heating in the sun.

The results obtained in the paper also testify to the dependence of the low-temperature emission process not only on the residual atmosphere pressure in the chamber, but also on its composition, namely, on the caesium concentration in it. At the absence of caesium in the sample no electron emission is observed. In the case of packing the under-electrode space with a caesium-containing salt having a decomposition temperature of about 400°C, which is almost twice the same temperature as for the salt used in sample, the results of which are presented in Figs. 4–6, the appreciable electron emission is observed at temperatures higher than 500°C.

The creation of effective and easy to use and maintain low-temperature TECs during a long time had been impossible. Only due to development of nanotechnology and intensive creation of new nanomaterials the interest to this field of research has been revived. Today, fast progress in this area is inhibited mainly by the complexity of the task itself, which involves the need to take into account many factors: the chemical composition and atomic structure of the used heterostructures, their electronic structure and the spectra of other quasiparticle excitations in them, charge and heat transport in various components of the electrodes, their spatial characteristics (thicknesses, periodicity of location, aspect ratios), the presence and composition of adsorbates on the electrodes surfaces, the density and composition of the residual gases and their participation in reducing the work function, density and length of the space charge between the electrodes, construction of the TECs (number and the shape of the electrodes, the distance between them and the differences in their temperatures and work functions, the presence of external voltage and control magnetic fields), as well as a detailed description of the external sources of converted energy (flux of heat, flux and spectral composition of light, the presence of ionizing radiation) and environmental conditions. In addition, there are unsolved physical problems, for example, about how many simultaneous different influences will affect the work of emission centres, depending on their structure. As can be seen from the results presented in this paper, the observed effect is the result of the influence of many of the above factors.

It is known [37–40] that an electron can leave the cathode material only by two ways: by receiving from the outside an energy sufficient to overcome the work function, or by tunnelling through a holding potential barrier. In the first case, it can acquire the missing energy either through thermal excitation (absorbing phonon energy) (thermionic emission) [37] or by absorbing a quantum of electromagnetic radiation (photoemission) [38]. The energy of the electron outside the crystal in this case will be equal to the difference of its energy in the crystal, measured from the Fermi level and supplemented by the energy of the

absorbed quantum, and the work function. In the second case, field emission occurs and the electron get outside the material while maintaining the same energy that it had inside the solid [39, 40]. Each of the mentioned emission options requires energy costs and technically difficult implementation conditions: achieving high temperatures, exposure to high-energy radiation, and application of high voltage. Nevertheless, these effects were the basis of many modern electronic devices, including direct energy converters [15–20, 27]. At the same time, the continuous search for new materials and methods for extracting electrons from cathode without cumbersome and/or complicated equipment use [14, 32–34]. In addition, the fact that a combination of the above emission options significantly facilitates the electron yield from the material has long been revealed and actively used [12, 13, 21–23]. For example, in an external electric field that bents the potential barrier, the probability of electron tunnelling, which exponentially increases with increasing electron energy, provides emission at much lower temperatures or light quanta energies than in the absence of a field [32–34, 40]. The applied field may be also substantially smaller.

Auxiliary mechanisms stimulating emission have also been widely studied. Among them, it is the effect of strengthening the electric field around thin (needle-shaped) or flat (blade-like) elements on the cathode surface. The greater aspect ratio of such emission centre corresponds to its greater efficiency. Recently, the possibility of using CNTs with a large aspect ratio as emitters has been investigated [30, 41]. The effect of the negative affinity of the emitter material for the electron is also important [32, 33, 36]. This is achieved by using a semiconductor layer with a large energy gap as the emitting surface, such that its conduction band is higher than the vacuum level, for example, as in diamond (nanocrystalline or amorphous, but with a predominance of sp^3 -hybridized bonds between atoms), especially activated by hydrogen or alkali metals atoms adsorbed on its surface. The combination of these methods also reduces the energy costs of emission and is promising to efficient cold cathodes creating [35, 42, 43].

In recent years, research has been carried out on other auxiliary mechanisms for the creation and emission of hot electrons. These mechanisms are associated with plasmon excitations in small metal particles on the emitter surface [22, 23], as well as with the polarization by external electric field of non-metallic nanoparticles located near the surface. In the last case, the nanoparticles increase the field in the vacuum gap and electrons can tunnelling from the metal part of the cathode through this gap into such particles, where they turn out to be hot [34].

Residual gases in the vacuum chamber in which the emission of electrons occurs, *i.e.* their ionization and interaction with the cathode and anode, also have a significant effect [15, 27, 35, 43–45]. Thus, the ad-

sorption of some types of atoms can significantly change the electronic structure of the surface, including the formation of emission centres with a reduced work function. The positively charged ions of the residual gases promote the compensation of the space charge which generated near the cathode from the electrons that have left it and preventing their further exit from surface. In this regard, it is worth noting the extremely important role of caesium in the atmosphere of residual gases and in the composition of the electrodes surface layers.

The results of present work were obtained under the influence of not only the above physical features of the TEC, but also the features of its construction. We will try to separate them into components and determine their roles.

To begin with, the experiment demonstrated the possibility of obtaining an emission current without applying an external electric field and heating the cathode to high temperatures. In this case, it confirms the fundamental possibility of low-temperature heat utilization by TECs, for example, as in our case, concentrated sunlight concentration.

As already noted, a composite material combining the advantages of a metal (Ti) and a conductive nanostructured carbon material (TEG) was chosen to create the cathode. In the initial state (before heating), the electrons could free move to the cathode surface and redistribute along it depending on its local and, importantly, inhomogeneous structure. This led to the appearance of inhomogeneous electric fields around individual nanoscale (with discrete energy levels) or chemically different (Ti and TEG; the adsorbates are also locally change the electronic structure of surface) surface elements, significantly enhanced due to large aspect ratios in the case of elements protruding above the average surface level. A vacuum was generated between the cathode and the cellular anode from polycrystalline molybdenum with a residual gas pressure not more than 0.1 Pa and with a free path length of molecules comparable to the size of the vacuum chamber.

At the first stage, during the opening of the barn door in front of the concentrating mirror, the flow of sunlight and the temperature of the main elements of the TEC increased. The temperature difference between the cathode and the anode was provided by efficient heat removal from the anode using a massive copper radiator. The materials of the anode and cathode were selected so that in the initial state the work function from the cathode (composite) was in excess of work function from the anode (molybdenum). Solar light containing ultraviolet component, which led to the ionization of residual gases in the chamber and to photoemission of electrons from the heated cathode, entered to the chamber through a quartz window. The listed processes already at the initial stage set a larger concentration of negative charges at the cathode, the direction of their movement to the anode and the movement of positive charges in the opposite direction, which is important

for compensating the space charge of electrons near the cathode. The last also helps to create (due to the accumulation of positively charged ions in the near-cathode space) an additional electric field that lowers and narrows the potential barrier for electrons according to Schottky effects. However, the number of electrons emitted under such conditions is too small for reliable recording of the voltage and emission current between the electrodes.

At the second stage, when the cathode was heated to temperatures of $\cong 150^{\circ}\text{C}$ and higher, the process of active degassing of the porous composite material, the decay of the least stable carbon structures emerging on surface, and their deposition on metal particles (less heated due to a higher reflectivity than the TEG) as thermally more stable amorphous carbon nuclei was began. In the cavity under the sample, the process of thermal dissociation of caesium salt began, as a result of which caesium began to diffuse into the cathode material, and then into the interelectrode space.

All these process led to several significant changes. Firstly, during the heating of the sample and the appearance of first nuclei and then amorphous carbon nanoparticles on the surface of titanium particles, the electron affinity on most of the surface of the composite tended to zero or to negative values. This was also facilitated by caesium, which appeared on the surface of the cathode and in its surface layers. Degassing of the sample led to an increase in the residual pressure in the chamber and, accordingly, to an increase in the density of the positive charge at the cathode surface. This, together with an increase in the average aspect ratio of the elements of the cathode surface, provided the necessary electric field for the start of field emission. In this case, the electronic structure of the surface of the metal particles probably also changed due to the appearance of carbon on them and its diffusion into the surface layers. Under such conditions, the absorption of light by metal particles can not only heat them and release photoelectrons, but also excite surface plasmon vibrations in them. The appearance of plasmons can be an additional mechanism of electron heating and formation for their subpopulation participating in plasma oscillations an additional statistical temperature distribution, bringing the electron energy in the metal even closer to the vacuum level.

If the layer of carbon covering the metal turns out to be sufficiently thin, as in our case, then hot electrons from the metal, getting into this layer, do not have time to thermalize during the time which they cross it. In this case, electrons energetically fall into in the conduction band of sp^3 -hybridized carbon, from where they easily go beyond the crystal mainly due to the tunnelling process. As already mentioned, an increase in the relative contribution of field emission is also facilitated by the presence on the cathode surface of many protruding relief elements with a large aspect ratio and a significant electric field generat-

ed by the near-cathode layer of charged ions (the Schottky effect is manifested). Residual gas atoms can also participate in charge transport between the electrodes: giving the anode an electron after ultraviolet ionization, positive ions are attracted to the cathode surface and, recombining there, replenish the residual atmosphere as neutral atoms.

It should be noted that even though the thermophotoelectric energy conversion is based on the well-studied thermo- and photo-excitations of nonequilibrium charge carriers in a solid, the nonlocality of these processes in time and space is important for the case of 'cold' emission without application of an external electric potential. Thus, the lifetimes of all important excitations of the electronic subsystem, for example, the lifetimes of plasmons, should be sufficient to move them from the nucleation place to the interface with the semiconductor emitter. In nanoscale semiconductor emitting centres, the length over which the thermalization of hot electrons that have fallen into them from the metal takes place should be the same order with a size of the system itself. This leads to the need to consider thermophotoelectric effects as distributed in time and throughout the depth of the heterostructured emitter involved in the emission process. As one can see, the complexity of the technical support of traditional emission can be significantly reduced only by increasing the structural complexity of the nanostructured emitter itself and the complexity of the physical processes leading to the emission of electrons from it.

Reducing the operating temperature of the emitter to $\cong 300^{\circ}\text{C}$ expands the range of energy sources available for TECs, including low-temperature heat sources. This helps to miniaturize and reduce the cost of TEC (and related equipment). It is important to remember that the initial voltage and power of the TEC depend on the difference in the work functions between the cathode and anode materials. The larger difference leads to the higher values of these parameters at a fixed current density. Thus, a decrease in the work function of the cathode (decrease in operating temperature) should be accompanied by a decrease in the work function of the anode. At the same time, acceptable values of the voltage taken from the TEC cell should be maintained. However, such a parallel decrease in the work functions of the cathode and anode has a natural limit due to the binding energy of electrons with the anode material.

In our experiment, caesium, getting into the interelectrode space, not only got the ability to participate in the compensation of the space charge, but also adsorbed on the surface of the anode, significantly reducing its work function. In addition, carbon nanostructures apparently deposited not only on the cathode, but also on the anode, as was previously observed with laser-stimulated emission from a continuous 'forest' of CNTs on a nickel substrate [46], reducing electron affinity

of anode surface. A contemporaneous decrease of the work functions of the cathode and anode most likely led to a decrease in the difference between these work functions and, accordingly, to a decrease in the potential difference provided by the TEC, which, for a given density of emission centres and a common small working surface of the cathode and anode, could not provide large currents. This can explain the low output power of our TEC.

It has long been known that the presence of caesium on the surface of refractory metal anodes affects their work function. An experiment closer to ours was described in [45]. For a nickel anode with a nanocarbon coating (at its operating temperature of 900 K), it was found that adsorption of Cs can reduce the work function from 4.5 to 1.5 eV, and intercalation with caesium of the upper carbon layer (due to defects in it) with the formation of complexes Cs–O–Cs rising above the surface can reduce the work function to 0.95 eV at a sufficient their density on the anode surface. This occurs due to the dipole moment of these complexes. Naturally, this mechanism of lowering the work function can also work on the surface of ‘cold’ cathodes.

Thus, for ‘low-temperature’ TECs, it is necessary to take additional steps to ensure the optimal difference between the work functions of the cathode and anode. For example, applying to the anode all of the above methods of decreasing its work function (making it nano- and heterostructured with minimal work function), it is possible for the cathode to limit itself to the use of metal nanostructures that support resonant plasmon absorption [22, 23]. In such structures, it is possible (with a sufficiently large work function) to maintain the high temperatures necessary for effective vacuum emission only in a population of hot electrons photo-excited by stationary solar illumination with photon energies in the range of $\cong 1\text{--}4$ eV, while maintaining the lattice temperature of the cathode metal in the temperature range up to 300–350°C.

4. CONCLUSION

New nanomaterials were created by mechanical mixing of carbon nanostructures (CNS) and titanium powders in an amount of 3–9% wt. CNS. The significant changes in their mechanical and electrical characteristics indicate of composites formation with new qualities that were not present in any of their original pure components. Thus, the electrical conductivity is changed up to 2 orders in initial state of composites and its maximum values after compaction of samples are increased 1.6 times in comparison with the pure Ti powder and 5 times in comparison with the pure TEG.

The Ti–TEG composite with 9% wt. TEG was studied at a solar light concentrator in the presence and absence of caesium in the samples. On

this samples were observed voltage and, at first, permanent direct current at temperatures 170–350°C, that is 3–5 times lower than the operating temperatures of traditional TECs made from refractory metals. Direct current was observed in a closed electric circuit without application of additional external potential difference. It is confirms the possibility of creating of ‘cold’ cathodes for thermophotoemission converters based on the proposed composite.

The TEC’s vacuum chamber of the original design was created and it was shown that the working body in it is not only a sample of the Ti–TEG composite, but also residual gas, to which the voltage and emission current are very sensitive. The caesium ions play a particularly important role, without them electron emission is not observed.

Changes in the surface morphology and chemical composition of the composite sample under the influence of concentrated solar radiation and the temperatures caused by it have been revealed. Temperatures above 150°C are critical for the processes of structural reconstruction of the composite surface. Thus, after the heating of the sample in the sun, its surface became more developed due to both the TEG release of some small cavities between Ti particles and the formation of new carbon, probably sp^3 , nanostructures on these particles. The new carbon nanostructures on the cathode have the form of separately spaced ‘pimple-like’ growths with diameters of tens nanometres, which provide a significant increase in the contribution from electron field emission. Possible mechanisms determined the low temperature of electron emission without adding an external electric field are analysed. Among them, those that can reduce the work function of both the cathode and the anode are distinguished. The ways to ensure the necessary difference in the work functions of the anode and cathode are determined while maintaining the emitter low temperature due to the ‘heating’ of only its electronic subsystem, when various collective electronic excitations, for example, plasmons, are generated by external action in a solid.

It is shown that for the case of ‘cold’ emission without an external electric field, the nonlocality in time and space of the totality of the processes causing it and the use of nanostructured homogeneous and heterogeneous materials are important. Hereby, the experiment, which clearly demonstrated the possibility of obtaining voltage and direct current with such emission, confirms the fundamental possibility of thermionic utilization of low-temperature heat, including concentrated solar light.

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