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Investigating Thermoelectric Batteries Based on Nanostructured Materials

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Abstract: This article discusses the characteristics of the design of thermoelectric generators (TEGs) for cold climates. Since the thermocouples of thermoelectric batteries are produced from different materials, their major properties are studied. Particular attention is given to nanostructured materials regarding the modern class of thermoelectric materials. Two-, three-, and four-component alloys (metallic glasses) of the Fe-Ni(Cu)-P-B system are chosen based on the experience of thermoelectric thermometry. The close chemical composition of two thermoelectrodes enables their compatibility in thermocouple production and satisfactory thermoelectric efficiency of batteries during long-term operation. The improvement of the thermoelectric battery characteristics related to a unit of mass is evaluated. The materials studied are distinguished by the absence of toxic components harmful to the environment at the manufacturing and operating stages.

Keywords: thermoelectric generator; thermoelectric battery; thermocouple; nanostructured material; metallic glass

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1. Introduction

Thermoelectric generators seem to be effective as a part of waste heat recovery systems [1]. In creating TEGs, there is a tendency to search for new constructive solutions based on the use of nontraditional materials. This is due to the presence of new operational conditions and environments, and, mainly, the need to improve the operational performance of the designed thermoelectric converters [2]. The relevance of creating TEGs has become undeniable for the production of electricity in remote areas of the North [3], including for the cathodic protection of gas pipelines, their telemetry, etc. In areas without extensive electrical networks, the advantages of their use are indisputable. This requires working out the technological [4], scientific, and technical aspects, in particular the issues related to materials based on modern approaches to their design.

A significant number of thermoelectric materials for different temperature ranges and regimes are known [5–7]. However, there are still ambiguities regarding both the selection of the materials themselves and the formation of methods, means, and methodologies for their optimisation, according to a spectrum of operational and other characteristics. For example, there are problems in the evaluation of thermoelectric efficiency (figure of merit ZT) for enhancing thermoelectric materials. It might be better to estimate the needed materials by other coefficients, for instance by their long-term stability [8]. Thus, it is important to choose the technologies (namely nanotechnologies) to improve the required characteristics [9].

The purpose of this work is the study of nanostructured thermoelectric batteries based on promising thermoelectric materials for TEGs, depending on the conditions, dimensions, manufacturing technology, and characteristics of application.

2. Study of Nanostructured Thermoelectric Materials

Research on nanostructured materials, which are characterised by optimal electrical, physical, and mechanical properties, as well as long-term stability while enhancing thermoelectric efficiency per unit mass, is currently combined with the possibility of modifying structures at the nanolevel.

2.1. Nanostructured Materials as Objects of Study

Nanostructured materials are materials that can form massive samples, and in this state, they are inherent to the unique properties of nanosized samples [10]. On this basis, we evaluate the suitability of such materials for thermoelectric generators. At the same time, these materials can be attributed to the group of high-entropy alloys (HEAs), which are of great interest in materials science [11,12]. Unlike binary alloys, which contain one or two base elements, HEAs comprise multiple principal elements, with the possible number of HEA compositions considerably higher than simpler alloys. The properties of HEAs, such as excellent specific strength, superior mechanical performance at high temperatures, exceptional ductility, and fracture toughness at low temperatures, are the result of their more complex structures.

The choice of the Fe-Ni-P-B system for current research is due to some previous issues, for instance, interest in the thermoelectric thermometry $Ni_{1-x}P_x$ subsystem. Here, by altering the phosphorus content, we receive alloys with electrical resistivity in the range from 100 to 170 μΩ·cm. This covers the value of 150 μΩ·cm, which is a characteristic point in the Mooij correlation [13]. There are trivial ways of operating with the electrical and physical properties of alloys, for example, by enlarging the number of components or by changing their structural state (micro doping, heat treatment, etc.). Thus, we study the well-known groups of particular materials regarding concrete thermoelectric properties conjugated with electric and thermal properties. This ensures the material's best performance for TEGs as the deciding unit of the heat recovery system. We consider below the different groups of parameters inherent to constructive elements of the major determinative design units of thermoelectric generators/batteries for the purpose mentioned [14].

Nanostructured materials include metallic glasses (MGs) [15], the structure of which is determined by the features of their manufacture. The last consists of pouring a melt onto a cold, rotating surface. The material solidifies in a disordered structure of the melt with nanoprecipitations of the second phase fixed in it. It is kept in this state, even at medium-high temperatures, until at a certain moment, a rapid transition to a crystalline state occurs.

2.1.1. Geometric Parameters

Given the specificity of the geometric parameters of MGs by technology (the length is measured in meters and the thickness is no more than 10 . . . 100 μm), thermoelectric batteries are formed by a sequence of thermoelectric thermocouples and are characterised by the presence of a certain plane in which the thermocouple junctions are located. The thermoelectrodes made of nanostructured materials are located perpendicular to it. Except for traditionally integrated thermocouples, various topological configurations of their branches into linear or circular batteries and cascades are considered in [14].

2.1.2. Thermophysical Characteristics

For typical effective areas of application of thermoelectric energetics, sensitivity and inertia are noncritical characteristics. Here, it becomes expedient to use thermoelectrode materials with high specific electrical resistance and small thickness, inherent to the MG samples, with a simultaneous increase in thermal resistance. However, in the case of thermoelectric batteries made of MGs, the temperature range of their use should be considered, which is within the temperature of relaxation annealing T_r and the temperature of the beginning of crystallisation T_{ck}. Usually, the recommended temperature of metallic glass for using metallic glass T_{rec} is 0.75 T_{ck}. But, in practice, it should be less than the temperature of plasticity loss (embrittlement temperature T_{em}). While using MGs in heat radiation converters, the maximum heat flux $Q_{\max}$ absorbed by the converter should not exceed the value [16]:

$$Q_{\max} \leq (0.65 \ldots\ 0.75)(\chi/cd)^{1/2}\varepsilon^{-1}(\tau_1)^{1/2}T_{rec}, \tag{1}$$

where χ is the specific thermal conductivity, c—the specific heat capacity, d—the specific density of the material, ε—an emissivity factor, and τ_1—the duration of irradiation. The thickness of the thermoelectrode should not be less than the permissible value $h_{\min}$ [16]:

$$h_{\min} \geq (0.65 \ldots\ 0.75)(\chi/cd)^{1/2}(\tau_1)^{1/2}\ T_{rec}. \tag{2}$$

2.2. Studying Nanostructured Materials in Thermoelectric Generators

When choosing optimal materials for thermocouples based on MGs, the criterion of thermoelectric quality ZT (figure of merit) [17] may not be sufficiently satisfactory; it makes sense only for massive specimens and does not consider the heat exchange with the environment of the designed thermoelectric battery or the availability of specified chemical elements (Bi, Te, Sb, Se) with their negative impact on natural resources, including water resources.

For MG thermoelectrodes, the impact of electrical-insulating fittings should be considered. These fittings have almost no effect on the electrical parameters but influence the thermal parameters of the studied thermocouples. Therefore, the expression for thermoelectric factor Z_{MG} for thermocouples with MG electrodes is as follows [18]:

$$Z_{MG} = S^2/(\rho\ (\chi_{MG} + \chi_{EIF}\ h_{EIF}/h_{MG})), \tag{3}$$

where ρ is the specific electrical resistance of the MG thermoelectrode; χ_{EIF} is the specific thermal conductivity of electrical insulating fittings; and h_{EIF}/h_{MG} is the ratio of the thicknesses, respectively, of the insulating armature and the MG thermoelectrode. If $\chi_{EIF}\ h_{EIF} >> \chi_{MG}\ h_{MG}$. Then, the choice of MG for the thermoelectrode should be made using the so-called thermoelectric power factor $q = S^2\sigma$ similar to the factor in [19,20].

2.3. Spatially Distributed Thermoelectric Materials

Recently, a direction for improving the thermoelectric characteristics of materials has emerged; progress has provided new research impetus. The approach consists of developing spatially inhomogeneous structures with inclusions [21], the dimensions of which are comparable to the characteristic wavelengths of electrons and phonons; that is, they are in the nanometer range. Reducing the size of the system to the nanometer scale causes sharp differences in the electron density states and creates possibilities for the quasi-independent variation of S, σ, and χ. The nanometer-sized components cause the quantum-size effect, which increases the thermoelectric power factor $S^2\sigma$. The composition of the internal boundaries in the nanostructure facilitates lowering thermal conductivity compared to electrical conductivity, which is based on the differences between the phonon and electronic scattering lengths [20]. On this basis, systems with quantum wells, wires, dots, and various composites with disordered nanosized inclusions are created [22].

In this regard, the studied MGs can be considered as nanostructured materials, suitable for effective use as materials of TEGs that absorb IR radiation in the wavelength range longer than 800 nm, where the photovoltaic effects of generation become ineffective.

Since effective doping allows an increase of the factor $S^2\sigma$ due to the high carrier mobility, in order to increase ZT, the thermal conductivity of the material should be reduced. The so-called “electronic crystal-phonon glass” concept is developed [23]. This means that ideal thermoelectric materials should have excellent electronic properties, but at the same time behave like glass in terms of heat transfer. Therefore, metallic glass with second-phase nanoprecipitations [24] seem to be appropriate objects of TEG study.

The three most well-known groups of thermoelectric materials, bismuth telluride, lead telluride, and alloys based on silicon or germanium, differ significantly in terms of thermoelectric Q-factors for different temperature ranges. Bismuth telluride-based materials are characterised by the highest ZT values at room temperature, and silicon (germanium)-based compounds are inherent to the highest values at 1300 K. For the intermediate temperature range (400 . . . 800 K), lead telluride-based materials are considered the best thermoelectric materials. However, when expressing the efficiency of the materials by the figure of merit ZT, their values are nearly the same. Currently, these values reach two, regardless of the type of material.

Another way to improve the characteristics of TEGs for the needs of energetics is the formation of heterogeneity in materials. Moreover, the object of optimisation is the function that describes changes in thermo-electromotive force (thermo-EMF), electrical conductivity, and thermal conductivity along the direction of the electric current and heat flow vectors. Such changes can be achieved both by the appropriate distribution of the concentration of impurities or the composition of the material, and by the effect on the material of the external physical fields (magnetic, force or others) during production and/or operation. The materials obtained in this way are functional gradient [25]. We create these materials to achieve maximum stability of thermoelectric characteristics in time [26].

A special place among thermoelectric materials is occupied by composites [25,27]. This is due to the formation of periodic structures not always being necessary. The introduction of many surfaces into the host material significantly reduces thermal conductivity and increases S and finally ZT by carrier filtering. Nanoparticles with a size of ~10 nm significantly reduce the thermal conductivity of the material in SiGe superlattices. The decisive factor here is that short-wave phonons in nanocomposites are scattered on point defects, while medium and long-wave phonons are scattered on nanoparticles [28]. The original method to increase ZT was developed for PbS-metal composites [29], in which the output energy allows injecting electrons into the intrinsic PbS host.

3. Principles of Research of Thermoelectric Materials in Thermometry

Another field of application of thermoelectricity is thermoelectric thermometry, where one of the most important and exact parameters is the stability of readings over time. Since the mechanisms and conditions of the use of thermometers correspond to the predicted conditions of TEGs, let us consider how the achievements of thermometry can be transferred to the thermoelectric materials science of generators.

Nanomaterials, with rare exceptions, can be considered quasi-equilibrium substances. Thus, it is quite legitimate to apply the fluctuation-dissipation theorem to them. The latter connects equilibrium and nonequilibrium thermodynamics. According to the approach of I. Prigozhin considered in [30], any of the macroscopic processes is the result of many more or less coherent microscopic processes. Microscopic degrees of freedom manifest themselves as fluctuations that can be described by introducing additional components in the equation for macroscopic quantities. This is exactly the path we took while studying the drift of thermoelectric transducers and to avoid the correlation effects of various impact factors. That is important for ensuring accuracy in thermometry. A thermodynamic approach was applied, in which the known thermodynamic quantities form an experimentally justified system of unrelated influencing factors.

3.1. Research Methods

During the current research, a computerised complex was developed for the study of electrophysical properties of thermoelectrode materials (MGs). The complex included temperature measuring devices covering the range of 4.2 . . . 1000 K, an oven with a PID temperature controller for heating samples, steam and zero thermostats, a cryostat (used to study the temperature dependencies of the electrical resistance and thermo-EMF of the samples in the range of 4.2 . . . 300 K), and a measuring cell (for studying the dependencies of electrical resistance and thermo-EMF at temperatures from 273 K to 1000 K).

The electrical resistance was measured using a four-wire circuit to minimise measurement error due to the small values of the electrical resistance. An integral method was used to measure thermo-EMF. Here, a thermocouple was made, one of the thermoelectrodes of which was the test sample and the other was a certain standard thermoelectrode. The latter could be a platinum sample or, in the study of deformation impacts, the same sample that, unlike the studied sample, was not subjected to deformation. Deformation of the sample was carried out by attaching a load to the investigated thermoelectrode in the room temperature zone. In this way, the thermo-EMF drift in particular was studied (Section 4). In the conditions of elastic deformation, there was a proportionality between the applied pressure and changes in thermo-EMF (Figure 1). A decrease in the sample temperature in the elastic region of deformation was recorded. While passing to the plastic deformation, temperature changes in local volumes of the deformed substance tended to change sign; and changes in thermo-EMF became complex and expectative [31].

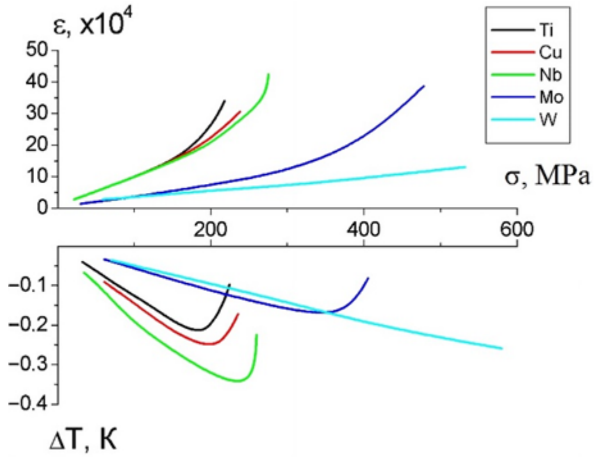

Figure 1. Dependence of deformations ε and temperature changes ΔT of samples on mechanical stresses σ [31] (the temperature is measured by additional thermocouple touched to the sample).

The possible deformation impact of complex nonmetallic samples while the temperature changes is shown below for different types of deformation. For example, the impact of shock loads on thermo-EMF of T-type thermocouples [32] is quite interesting. Under the pressure of 30 GPa, their thermo-EMF reached 250 mV at 200 °C and was characterised by reversibility; this indicates precisely the elastic kind of deformation applied to the thermocouple. However, according to [33], thermo-EMF should reach ~1100 mV at the specified temperature; that is, the changes in thermo-EMF are due to plastic deformation of nearly −850 mV, reducing the output signal of the thermocouple by almost 80%. It may be that, at the moment of the impact load, the connectivity effect accrues. This facilitates an understanding of the mechanisms of creation and action of eddy currents on thermo-EMF: at moments of significant deviations from the equilibrium, the interaction of independent components of the basic equation of thermodynamics occurs.

According to classical theory of heat conduction, the only cause of heat flow in the massive specimen is considered to be the nonzero temperature gradient. However, during thermal deformation of the specimen with the coefficient ε, in the case of a significant speed of the heat flow, there arises an effect that consists of the interaction of the deformation and the temperature fields. Its impact was evaluated on glass and steel samples, whose coefficients of thermal conductivity χ were approximately the same. Here, glass, and other similar plastics and ceramics, are characterised by high values of the connectivity effect parameter: $\varepsilon/\chi T$ << 400, while for steel this parameter is substantially less than << 20. That is, for ceramics a slight temperature drop leads to significant deformation changes, unlike steel, for which the same drop causes deformation changes 20 times smaller.

3.2. Drift of Thermo-EMF of Nanostructured Materials

Progress in technology is associated with the development of nanothermodynamics [34]. The most recent, compared to classical thermodynamics, implements two additional degrees of freedom inherent to nanomaterials into the main equation of thermodynamics. These are the degree of freedom associated with the presence of nanophases of a significant surface and surface tension, and the degree of freedom due to the presence of second phases precipitations with significant local mechanical stresses. Nanostructured materials include MGs; within their two-phase model, there are inclusions in the matrix, for example, pseudo phases, which are micro volumes dissimilar to matrix density; therefore, the properties of the nanostructured material depend on its manufacturing technology.

Thermo-electrodes are characterised by a significant stress drop in transverse direction in the absence of stress gradient along them. In the presence of significant local eddy currents, the thermo-EMF is set at a certain level that corresponds to the optimal characteristic; here the formed stress microrelief successfully stabilises the specified characteristic. Minor changes in thermoelectric properties confirm the determining role of the gradient of mechanical stresses in the drift occurrence. Due to the absence of grain boundaries, there are no grounds for the emergence of the specified gradient and the associated thermodynamic force in the studied materials. The latter is characterised by exceptional stability of the thermo-EMF of the thermoelectrode made from MG $Fe_{0.4}Ni_{0.4}B_{0.2}$. Its drift is less than <11 nV for 100-h of operation at 800 K due to the existence of local mechanical stress fields (Figure 2) [16]. For our studies, we manufactured the thermocouple from two identical thermoelectrodes, one of which was stretched, and registered the thermo-EMF while changing the temperature.

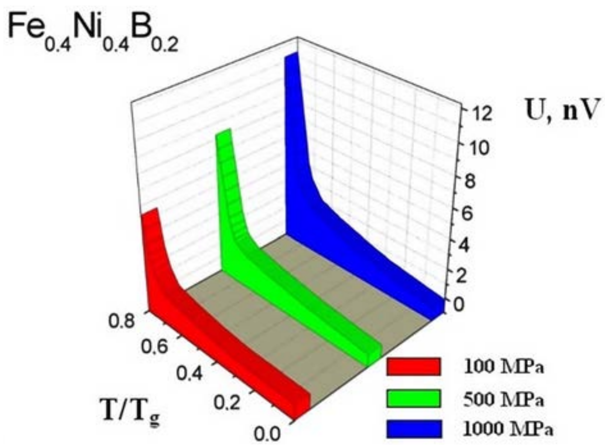

Figure 2. Temperature dependencies of the thermo-EMF drift U of metallic glasses on tensile forces 100, 500, and 1000 MPa (here T_g is the glass transition temperature) [16].

Local mechanical stress fields arise in the thermoelectrodes of a thermoelectric battery during the TEG operation, due to different temperature coefficients of linear expansion of thermocouple materials causing damage of the hot junction area. Thus, we have chosen thermocouples of similar thermoelectrode composition, where the content of metals in the thermoelectrodes was the same, i.e., 80%. Then, their temperature coefficients of linear expansion were close in value and the long-term durability was expected to be at its maximum. One of its thermoelectrodes was made from MG $Fe_{0.4}Ni_{0.4}B_{0.2}$ (another–from $Fe_{0.8}B_{0.2}$).

3.3. Specificity of Nanostructured Materials

Specificity is caused by exclusive properties of thermoelectric material due to its manufacturing technology, within which precipitations of liquid with its close order are frozen in the solid-state matrix. Such a state is described based on the nano-thermodynamical approach and considers 2 additional degrees of freedom compared to traditional thermodynamics. As a result, it is effective for the explanation of the thermoelectricity phenomenon (the model of eddy currents). The same is required in thermoelectric energetics, where progress in increasing the thermoelectric factor is associated with advances in nanotechnology [35]. On the one hand, nanothermodynamics should be developed, and on the other, the aforementioned phenomenon at the micro- and nanolevels (local eddy current approach [36]) should be studied. For example, based on nonequilibrium thermodynamics, the model of eddy currents during the laser melting of two different metals was developed in [37].

Since in nanostructured materials of thermocouples the direction of the temperature gradient is longitudinal and cannot coincide with the direction of the gradient of the mechanical properties, oriented radially, problems arise due to the different nature of eddy currents (for example, the problem of increasing the coefficient of thermoelectric power factor by directed mechanical–thermal modification of nanostructured materials [38]). The role of gradients in the formation of sensor signals is emphasised in [8,39], where a thermoelectric method of detecting various types of material defects based on gradients of physical quantities is developed.

4. Nanostructured Materials, Thermocouples and Batteries for TEGs

4.1. Studying of Nanostructured Materials

Nanostructured material samples of Fe-Ni-P-B (Table 1) were manufactured by pouring liquid onto the surface of a rotating cylinder. Here, the melt temperature T_m (column 2) and the rotation speed of the cylinder (column 4) were dissimilar. As a result, the regime defined the thickness of the obtained samples (column 5). Thus, the received samples were divided in five groups.

Table 1. Thermal and technological parameters of manufactured samples of metallic glasses.

Sample Group Number	Melt Temperature T_m, K	Crystallisation Temperature T_{Cr}, K	Rotation Speed of Cylinder n, 1/min	Thickness of Obtained Sample δ, μm
1	1373	653	1000	100
2	1373	653	3000	30
3	1273	653	3000	30
4	1523	653	3000	30
5	1100	653	2000	60

Electrical resistivity $R(T)$ of the samples mentioned was studied at reference points of He, H_2, and N_2 and in a water–ice mixture. The results of the studies of $R(T)$ were processed using the software "CurveExpert Professional 2.7.3" [40], which made it possible to characterise them with high accuracy and reliability. The obtained dependencies of R(T) were approximated (error of 10^{-3}% with a correlation factor of 0.99999998) by polynomials of the 3rd degree for each group of samples (Table 2).

Table 2. Factors of polynomials of the 3rd degree describing the obtained dependencies of $R(T)$.

Sample Group Number	Factor			
	A	B	C	D
1	1.9426	−0.0002635	4.62×10^{-6}	-9.59×10^{-9}
2	1.7518	−0.0002268	3.98×10^{-6}	-8.26×10^{-9}
3	1.3109	−0.0001200	1.84×10^{-6}	-3.07×10^{-9}
4	0.958	−0.0001200	2.22×10^{-6}	-4.35×10^{-9}
5	0.995	−0.0000642	0.844×10^{-6}	-1.11×10^{-9}

4.2. Study of Thermocouples and Batteries

At first, we studied the characteristic function of the produced thermocouple $Fe_{40}Ni_{40}P_{14}B_6/Fe_{80}Cu_3B_{17}$. Its sensitivity nonlinearly depends on temperature. Figure 3 demonstrates an important characteristic of the thermocouple usage, namely, the independence of readouts from the temperature of the cold zone (junction) since the thermocouple sensitivity for such a characteristic does not depend on environment temperature in the range of 240–380 K, and linear dependence on fuel combustion temperature in the range of higher temperatures. That is the most important characteristic of TEG exploitation, since it provides the possibility of stable temperature control and electricity production.

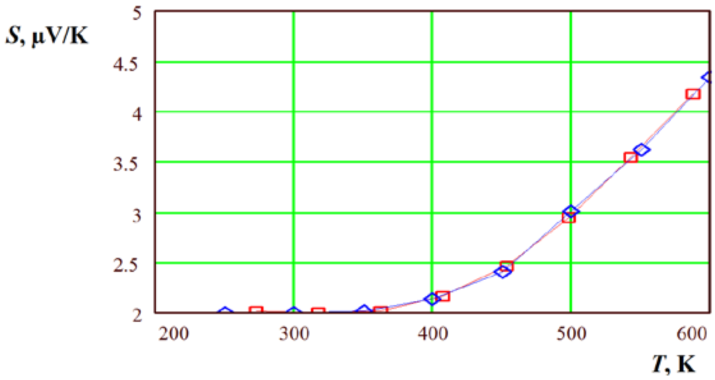

Figure 3. Temperature dependence of the sensitivity of the thermocouple $Fe_{40}Ni_{40}P_{14}B_6/Fe_{80}Cu_3B_{17}$ (blue points for experimental data, red points for estimated data).

Two thermoelectric batteries were assembled from a series of connected thermocouples made from MGs, namely $Fe_{40}Ni_{40}P_{14}B_6/Fe_{80}Cu_3B_{17}$ (Table 3). Hot and reference junctions were performed by spot welding. A glass disk (diameter 32 mm and thickness 0.1 mm) was used as a basis for the batteries' design. The free side of the thermoelectric battery was subjected to polishing to achieve a minimum emissivity factor and was covered with two layers of SiO, ensuring high protection, on top of which the layers of $Fe_{40}Ni_{40}P_{14}B_6$, as well as those of $Fe_{80}Cu_3B_{17}$, were settled down.

Table 3. The characteristics of thermoelectric batteries assembled from MG thermocouples.

Number of thermocouples	56	28
The resistivity of the thermocouple, 10^3 Ω	15.0	7.5
Inertia, s	1.0	0.7
Sensitivity, mV/W	100.0	60.0
Linear dimensions of electrode, mm^3	1 × 0.1 × 0.1	1 × 0.1 × 0.1
The total mass of electrodes, g, at a specific density of 6.9 g/mm^3 (except for insulator mass)	8.0	4.8
Sensitivity, reduced to a unit of mass, mV/W·g = V/W·kg	12.5	7.5

Since it was proposed [27,43] to access the materials' compatibility factor for segmented generators we studied and selected the thermoelectrodes of thermocouples for TEGs considering the compatibility of their linear coefficients of thermal expansion.

An interesting situation arose when relating the specified coefficient (e.g., the figure of merit) to a unit of mass, evaluating materials based on the characteristics of the produced signal (Table 3). This approach is vindicated because it determines the overall effectiveness of thermoelectric materials for society. It has to access the costs of extraction, enrichment of raw materials for the manufacture of the thermoelectric materials needed, the potential harmfulness of such metals as bismuth, antimony, tellurium, lead, etc.

Let us find out the reason for the description of these temperature dependencies by a four-term polynomial. While considering the two-phase MG model, assume that there are microvolumes of other phases in the matrix of dissimilar density. Then, when the specific electrical resistance of the matrix is described, following Matthiessen's rule [41], by the equation $\rho_1 = a + bT$ and of the second phase by $\rho_2 = c + dT = \rho_1 + \Delta\rho$, we obtain the abovementioned expression for the specific electrical resistance of the two-phase material. Since factors a and b do not depend on the manufacturing, the basis of MG is a homogeneous material. Factors c and d, characterising the nanostructure, depend on the material's quenching and heat treatment. The increment in MG volume grows with the melt temperature, which reaches several percent and significantly affects transfer processes. It becomes possible to evaluate the structural state of the samples as a nonhomogeneous two-phase material and to ascertain the appearance of nanostructured precipitations in the homogeneous matrix as a result of rapid quenching during manufacture [9,42].

5. Conclusions

The rather weak results of the expectations of last-decade's studies testify that the principle of selecting sensitive materials for TEGs, which relies on criteria based on S, ρ, and χ, cannot be considered comprehensive or sufficient. The development of thermoelectric batteries for TEGs is generally based on the development of materials science. Further progress consists of studying some different properties of materials, considering not only the major ones, such as figure of merit, but also specific strength, mechanical performance at high and low temperatures, ductility, and fracture toughness at low temperatures, facilitating exploration of thermoelectric generators in cold climates. Thermoelectric batteries made of approximately 100 thermocouples produced from metallic glass as materials of close chemical composition and thermal coefficient of linear expansion can provide long-term durability. Due to the nanostructuring of the materials mentioned (3-, 4- component alloys of Fe-Ni-P-B-system), the thermoelectric generators are inherent to improved performance related to a mass unit. MGs are suitable for effective use as materials of TEGs that absorb IR radiation in the wavelength range higher than 800 nm, where the photovoltaic effects of electricity generation become insufficiently effective. In addition, these materials are distinguished by the absence of toxic components harmful to the environment during manufacturing and operation.

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References

1. Heber, L.; Schwab, J.; Knobelspies, T. 3 kW Thermoelectric Generator for Natural Gas-Powered Heavy-Duty Vehicles—Holistic Development, Optimization, and Validation. *Energies* **2022**, *15*, 15. [CrossRef]
2. Hotra, O.; Boyko, O. Compensation bridge circuit with temperature-dependent voltage divider. *Przegląd Elektrotechniczny* **2012**, *88*, 169–171.
3. Champier, D.; Favarel, C.; Bedecarrats, J.P.; Kousksou, T.; Rozis, J.F. Prototype combined heater/thermoelectric power generator for remote applications. *J. Electron. Mater.* **2013**, *42*, 1888–1899. [CrossRef]
4. Jaziri, N.; Boughamoura, A.; Müller, J.; Mezghani, B.; Tounsi, F.; Ismail, M. A comprehensive Review of Thermoelectric Generators: Technologies and Common Applications. *Energy Rep.* **2020**, *6*, 264–287. [CrossRef]
5. Rowe, D.M. *Thermoelectrics Handbook: Macro to Nano*; CRC Press: Boca Raton, FL, USA, 2018.
6. Jeffrey, C. Ammonia-Based Battery System to Convert Low-Grade Waste Heat into Electricity. Available online: https://newatlas.com/ammonia-battery-waste-heat-electricity/35089/ (accessed on 7 March 2023).
7. Hotra, O. Microprocessor temperature meter for dentistry investigation. *Przegląd Elektrotechniczny* **2010**, *86*, 63–65.
8. Chen, J.; Su, J.; Kochan, O.; Levkiv, M. Metrological software test for simulating the method of determining the thermocouple error in situ during operation. *Meas. Sci. Rev.* **2018**, *18*, 52–58. [CrossRef]

9. Yatsyshyn, S.; Skoropad, P.; Karpiński, M. Electrical properties of Ti-Cu-Co-Si High-entropy alloy. *Meas. Equip. Metrol.* **2022**, *83*, 17–20. [CrossRef]
10. Harman, T.; Walsh, M.; Laforge, B.; Turner, G. Nanostructured thermoelectric materials. *J. Electron. Mater.* **2005**, *34*, L19–L22. Available online: https://link.springer.com/article/10.1007/s11664-005-0083-8 (accessed on 7 March 2023). [CrossRef]
11. Ye, Y.F.; Wang, Q.; Lu, J.; Liu, C.T.; Yang, Y. High-entropy alloy: Challenges and prospects. *Mater. Today* **2016**, *19*, 349–362. Available online: https://www.sciencedirect.com/science/article/pii/S1369702115004010 (accessed on 7 March 2023). [CrossRef]
12. Jin, T.; Park, I.; Park, T.; Park, J.; Shim, J.H. Accelerated Crystal Structure Prediction of Multi-Elements Random Alloy Using Expandable Features. *Sci. Rep.* **2021**, *11*, 5194. Available online: https://www.nature.com/articles/s41598-021-84544-8.pdf?proof=t (accessed on 7 March 2023). [CrossRef]
13. Stadnyk, B.; Skoropad, P.; Yatsyshyn, S. Electrokinetic characteristics of structurally disordered binary alloys Ni1-xPx. *Meas. Equip. Metrol.* **2022**, *83*, 5–9. [CrossRef]
14. Anatychuk, L. On physical models of thermoelements. *Thermoelectricity* **2003**, *1*, 5–17.
15. Davison, S.G.; Sulston, K.W. *Green-Function Theory of Chemisorption*; Springer Science & Business Media: Berlin, Germany, 2006; pp. 91–116. Available online: https://link.springer.com/chapter/10.1007/1-4020-4405-4_6 (accessed on 7 March 2023).
16. Skoropad, P. Thermotransducers from the Metallic Glasses—Conception, Normalization of Thermo Structural Properties, Implementation, Dr. Sc. Dis., Lviv Polytechnic National University, 2003. (In Ukrainian). Available online: https://dissertation.com.ua/node/684401 (accessed on 7 March 2023).
17. Wang, H.; Pei, Y.; LaLonde, A.D.; Jeffery Snyder, G. Material design considerations based on thermoelectric quality factor. In *Thermoelectric Nanomaterials: Materials Design and Applications*; Springer: Dordrecht, The Netherlands, 2013; Volume 182, pp. 3–32.
18. Patel, S.K.; Swain, B.K.; Behera, A.; Mohapatra, S.S. Metallic Glasses: A Revolution in Material Science. *Met. Glasses* **2020**. Available online: https://www.intechopen.com/books/metallic-glasses/metallic-glasses-a-revolution-in-material-science (accessed on 7 March 2023).
19. Ding, Y.; Qiu, Y.; Cai, K.; Yao, Q.; Chen, S.; Chen, L.; He, J. High performance n-type Ag2Se film on nylon membrane for flexible thermoelectric power generator. *Nat. Commun.* **2019**, *10*, 841. [CrossRef] [PubMed]
20. Hou, W.; Nie, X.; Zhao, W.; Zhou, H.; Mu, X.; Zhu, W.; Zhang, Q. Fabrication and excellent performances of Bi0.5Sb1.5Te3/epoxy flexible thermoelectric cooling devices. *Nano Energy* **2018**, *50*, 766–776. [CrossRef]
21. Adroja, M.N.; Mehta, S.B.; Shah, M.P. Review of Thermoelectricity to Improve Energy Quality. *Int. J. Emerg. Technol. Innov. Res.* **2015**, *2*, 847–850. Available online: http://www.jetir.org/papers/JETIR1503089.pdf (accessed on 7 March 2023).
22. Harrison, P.; Valavanis, A. *Quantum Wells, Wires and Dots: Theoretical and Computational Physics of Semiconductor Nanostructures*, 4th ed.; Wiley: Hoboken, NJ, USA, 2016.
23. Hori, T.; Shiomi, J. Tuning phonon transport spectrum for better thermoelectric materials. *Sci. Technol. Adv. Mater.* **2019**, *20*, 10–25. [CrossRef]
24. Chen, D.Z. Atomic-Level Structure and Deformation in Metallic Glasses. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, USA, 2016.
25. Anatychuk, L. Thermoelectric power converters. In *Thermoelectricity*; Publishing House of Institute of Thermoelectricity: Chernivtsi, Ukraine; Kyiv, Ukraine, 2005; Volume 2.
26. Jacyszyn, S.; Stadnyk, B.; Skoropad, P. Analiza efektywności stosowania w termometrii funkcjonalnie-gradientowych czujników termoelektrycznych. *Pomiary Autom. Kontrola* **2006**, *52*, 41–44.
27. Goldsmid, H.J. *Introduction to Thermoelectricity*, 2nd ed.; Springer: Berlin, Heidelberg, 2016.
28. Zhao, L.D.; Lo, S.H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Kanatzidis, M.G. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* **2014**, *508*, 373–377. [CrossRef]
29. Liu, Y.; Cadavid, D.; Ibáñez, M.; Ortega, S.; Martí-Sánchez, S.; Dobrozhan, O.; Kovalenko, M.V.; Arbiol, J.; Cabot, A. Thermoelectric properties of semiconductor-metal composites produced by particle blending. *APL Mater.* **2016**, *4*, 104813. [CrossRef]
30. Kjelstrup, S.; Bedeaux, D. Non-Equilibrium Thermodynamics of Heterogeneous Systems. In *Series on Advances in Statistical Mechanics*; World Scientific Publishing Co.: Singapore, 2008; Volume 16.
31. Bash, V. *Study of Stresses and Strains by Thermoelectric Method*; Naukova Dumka: Kyiv, Ukraine, 1984. (In Ukrainian)
32. Hanneman, R.E.; Strong, H.M. Pressure dependence of the EMF of thermocouples to 1300 C and 50 kbar. *J. Appl. Phys.* **1965**, *36*, 523–528. [CrossRef]
33. Stadnyk, B.; Yatsyshyn, S.; Lutsik, Y.; Bubela, T.; Frölich, T. Thermoelectric materials science and nanotechnology. *Pract. Theory* **2019**, *80*, 30–40.
34. Bedeaux, D.; Kjelstrup, S.; Schnell, S. *Nanothermodynamics: General Theory*; PoreLab: Trondheim, Norway, 2020.
35. Chen, Z.G.; Han, G.; Yang, L.; Cheng, L.; Zou, J. Nanostructured thermoelectric materials: Current research and future challenge. *Prog. Nat. Sci. Mater. Int.* **2012**, *22*, 535–549. [CrossRef]
36. Luste, O.J.; Kuz, R.V. Computer control of Eddy thermoelectric currents. *J. Thermoelectr.* **2004**, *2*, 11–19.
37. Paulini, J.; Simon, G.; Decker, I. Beam deflection in electron beam welding by thermoelectric eddy currents. *J. Phys. D Appl. Phys.* **1990**, *23*, 486. [CrossRef]
38. Jood, P.; Mehta, R.J.; Zhang, Y.; Peleckis, G.; Wang, X.; Siegel, R.W.; Borca-Tasciuc, T.; Dou, S.X.; Ramanath, G. Al-Doped Zinc Oxide Nanocomposites with Enhanced Thermoelectric Properties. *Nano Lett.* **2011**, *11*, 4337–4342. [CrossRef] [PubMed]

39. Carreon, H.; Lakshminarayan, B.; Faidi, W.I.; Nayfeh, A.H.; Nagy, P.B. On the role of material property gradients in noncontacting thermoelectric NDE. *NDT E Int.* **2003**, *36*, 339–348. [CrossRef]
40. CurveExpert Professional for Windows. Available online: https://softdeluxe.com/CurveExpert-Professional-1955046/download/ (accessed on 7 March 2023).
41. Komatsu, S.; Tatematsu, K.; Murakami, Y.; Kajiyama, T.; Matsuo, M.; Muramatsu, T. Application of Matthiessen's rule to resistivity measurement and behaviors of Fe and Si in A1050 rolled sheets. *J. Jpn. Inst. Light Met.* **1985**, *35*, 526–533. [CrossRef]
42. Klym, H.; Hadzaman, I.; Kostiv, Y.; Stadnyk, B.; Yatsyshyn, S. Free-volume defects/nanopores conversion of temperature-sensitive $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics caused by addition phase and monolithization process. *Appl. Nanosci.* **2022**, *12*, 1347–1354. [CrossRef]
43. Walker, K. How Can Thermo-Electrical Generators Help the Environment? *AZO Clean Tech.* **2013**. Available online: https://www.azocleantech.com/article.aspx?ArticleID=361 (accessed on 7 March 2023).