Current Status and Some Prospects of Thermoelectricity

L.I.Anatychuk

Institute of Thermoelectricity General Post Office, Box 86, Chernivtsi, 58002, Ukraine; E-mail: ite@inst.cv.ua; fax: (380-3722)-41917; phone: (380-3722)-44422.

Abstract

Analysis of trends in thermoelectricity development is provided. Progress and prospects for growth of the figure of merit of thermoelectric materials, including functionally graded ones are considered. Formulation and solving the problems of computer design of thermoelectric devices is analyzed. Approaches to constructing physical models of thermoelectric power converters are described. Possibilities of expanding practical applications of thermoelectricity are demonstrated. The paper is based on the investigations by Institute of Thermoelectricity of NAS Ukraine and proceedings of XII International Forum on Thermoelectricity.

Thermoelectric material research

It is generally known that the central task of thermoelectricity is to increase the figure of merit of thermoelectric materials. The major part of research in thermoelectricity is aimed at solving this task. The summary of achievements in this line is given in Fig.1.



Fig.1. Increase in the figure of merit of thermoelectric materials.

From the figure it follows that considerable figure of merit improvement achieved in the 50-70 of the last century and based on the use of classical methods for creation in materials of optimal current carrier concentration and phonon scattering increase has been largely exhausted. The rate of figure of merit increase has considerably decreased.

In recent decades a variety of novel materials with improved figure of merit values have been discovered. However, such materials require technological update for creating on their basis of industrial power converters. To improve the figure of merit of materials, the more and more sophisticated methods are being studied that are based on the use of composites, organic materials, various kinds of nanostructures with quantum effects, etc. There is a wide spectrum of opinions on the real prospects of using these exotic materials, from enthusiastic to pessimistic. It can be exemplified by the title of presentation made by P.Baransky at XII Forum on Thermoelectricity «On the way from myths to realities in mastering high performance thermoelectric converters based on the use of nanophysics». The greatest successes in mastering such structures refer to theoretical research where important peculiarities of thermoelectric effects in these materials have been established with rather limited experimental achievements due to technological and metrological problems.

Based on this situation, classic thermoelectric materials, proved by time and experience of industrial application, are still predominantly used in practice. Therefore, of particular interest are achievements in the improvement of efficiency of classic materials used in industry. Let us consider them by an example of the most widely used materials based on *Bi-Te*.

Fig.2 shows growth in thermoelectric figure of merit and, respectively, ΔT_{max} in cooling modules over the years. One can observe nearly linear increase and growth of $\Delta T_{\text{max}} = 78^{\circ}$ C by 2010 is predicted.



Fig.2. Increase in the figure of merit Z and ΔT_{max} in cooling modules.

However, it should be noted that modules with increased value of ΔT_{max} do not find a big market because of cost increase (Fig.3). (On evidence derived from presentation of E.Baukin at XII Forum on Thermoelectricity).



Thus, because of this situation, of particular appeal in thermoelectric material research become investigations aimed at improving the efficiency of thermoelectric power conversion, that are based not on *ZT* increase, but use alternative physical approaches.

Functionally graded materials (FGM)

These are materials with programmable inhomogeneity, with the optimal use of the bulk thermoelectric effects. To find the necessary inhomogeneity functions use is made of computer methods created on the basis of optimal control theory. An example of optimal functions for stage generator module is given in Fig..4. The expected efficiency is about 20%.



Fig.4. FGM for stage generator module.

Based on Bi-Te in company Altec (Ukraine) there has been created a series of generator modules (36 type sizes) providing under temperature difference 250 K the efficiency up to 7% (Table 1). The modules offer service life 10 years and cyclic on-off stability up to 20 thousand cycles. The cost of modules is 0.5 - 1.5 \$/W. The modules are encapsulated and placed into inert atmosphere. Due to the use of FGM, the efficiency of such modules is increased to 8%. Such modules can successfully solve the problems of using waste heat from industry and heat engines.

Typical Parameters of Bi-Te generator modules Altec

	5	0		
Туре	U	w	Q	η , %
	Homo	geneous m	ateria	-
Altec-1060	4.8	8	120	$\textbf{6.5} \pm \textbf{0.3}$
Altec-1074	3.8	16.5	250	$\textbf{6.5} \pm \textbf{0.3}$
Altec-1081	8.6	37	570	$\textbf{6.5} \pm \textbf{0.3}$
	FC	GM (2 sectio	ons)	•
Altec-1085	5	26	325	8 ± 0.3

The possibilities of using FGM for thermoelectric cooling have been considered as well.

At the present time the long known ideas of using segmented legs for cooling are being realized in modules. On two-segmented legs the increase in ΔT_{max} by $4 \div 4.5$ K has been achieved.



The most efficient for thermoelectric cooling is a combination of functionally graded material with optimally inhomogeneous magnetic field. As an example, Fig..5 shows the values of optimal inhomogeneity functions of Bi - Sb and Bi - Te material for a three-stage cooler in optimally inhomogeneous magnetic field. At temperature difference $\Delta T = 40$ K (Fig.6) coefficient of performance ε_F as compared to homogeneous ε_0 in the absence of a magnetic field is increased by a factor of 1.25, and at $\Delta T = 60$ K $\varepsilon_F / \varepsilon_0$ is increased to 2. Such results prove the efficient use of functionally graded materials for improving the efficiency of thermoelectric power conversion.



Fig.6. Increase in COP ε_F with the use of FGM in a magnetic field.

Computer design

Table 1.

It should be noted that even conservative efficiency values of thermoelectric generator and cooling modules are not used rationally enough in the products. For example, in thermoelectric air-conditioners due to inadequate quality of heat exchangers the coefficient of performance of the product is generally decreased by a factor of 1.5 - 2. Precise

design of both thermoelectric power converters and thermoelectric product as a whole, as a rule, allows considerable improvement of their performance.

For this purpose the method of object-oriented programming has been successfully developed of late. The concept of this method is shown in Fig.7.



Fig.7. Object-oriented design of thermoelectric products

The method of object-oriented programming has been used to create an hierarchy of computer modules of increasing complexity – from a unit cell of thermoelectric medium to multicomponent thermoelectric devices.

The library of elementary computer objects includes tens of components of thermoelectric devices – working media of thermocouple, anisotropic, thermomagnetic, eddy thermoelements; chemical and isotopic heat sources; heat spreaders of different materials; heat exchangers with flows of liquid and gas heat carriers, etc.

These computer objects serve as building blocks in the "assembly" of models of thermoelectric devices.

Computer model of a device makes it possible to obtain precise information on the distribution of interrelated physical fields in each device component under steady and unsteady conditions. These are the fields of electric currents **j** and potentials *U*, temperatures *T* and heat flows **q**, deformations u_{ik} and elastic mechanical stresses σ_{ik} , heat carrier flows and gas-fuel mixture v, fuel concentration *c*, etc. Technical parameters of the entire device, for instance, efficiency, are surface or linear integrals of physical field.

Such computer models have served the basis for creating programs of optimization of thermoelectric devices that reveal optimal device structure in the variety of permissible values of material parameters, shape and dimensions of device.



The number of patents dedicated to thermoelectricity is constantly increasing (Fig.8). A great number of such patents are devoted to thermoelectric products. However, very few of them have been brought to industrial production.

Object-oriented technologies of thermoelectric products design, beyond any doubt, should contribute to acceleration of practical applications of thermoelectricity.

Development of element basis of thermoelectricity

As a rule, configurations of thermoelements are created on the basis of conditions of reproduction of thermoelectric effects therein. As the effects considered in the media have the simplest shape (generally rectangular), hence, the legs of thermocouple elements, anisotropic and thermomagnetic thermoelements are also rectangularshaped. The latter also dictates the fabrication of thermocouple or other modules with all the technological problems involved (Fig.9).



Fig.9. Models of Thermoelectric Energy Converters A – from thermoelectric effects, B – from thermoelectric induction law.

A different approach is realized when creating thermoelements on the basis of the law of thermoelectric induction of currents. This approach is based on the use of eddy currents that determine configuration of thermoelements. This approach leads to creation of thermoelements in the form of spiral structures. The advantage of spiral structures lies in the absence of connections and in simple fabrication techniques.



Fig.10. Zone-inhomogeneous spiral thermobattery.

Consider a spiral zone-inhomogeneous thermoelement (Fig.10). The optimal configuration of thermoelement is determined by computer design methods. The fabrication technique of such spiral structures includes three main procedures: obtaining by extrusion method a zone-inhomogeneous tube, metallization of its surface, transverse cutting to obtain a spiral. Such spiral structures are quite competitive to thermocouple modules: being made of the same materials, they are not inferior in the efficiency (Fig.10). However, they are more reliable, and the absence of solder allows their use in a wide temperature range.

Besides, spiral anisotropic thermoelements have distinct advantages over conventional anisotropic rectangles in the developed voltages and fabricability. Spiral thermomagnetic elements offer similar advantages.



Fig.11. Double-layered thermoelement with a periodically profiled surface. 1 – p-type material, 2 – n-type material, 3 – fins in p-type material, 4 – slots in p-type material, 5,6 – electric contacts, 7,8 – lateral faces of thermoelement with heat sources

and sinks arranged thereupon.

The methods of object-oriented programming also allow devising basically new variants of artificially anisotropic thermoelements. A variant of such thermoelement is shown in Fig..11. It consists of a doublelayer bar, where one of the layers is cut at an angle. Computer optimization of geometry of thermoelement made of Bi-Te-based materials allows obtaining transverse EMF suitable for practical applications.



and FGM thermoelement.

New thermoelement types in many cases of practical applications make it possible to obtain better device performance than with the use of classic thermocouple modules, especially in measuring technique and when creating miniature thermogenerators working under extreme conditions, in gas automatic systems, etc.

It is also interesting to combine thermoelements with heat sources and heat sinks. Here refer permeable thermoelements based on transmission of heat carriers through porous or channel legs (Fig.12).

It is established that such thermoelements improve efficiency and coefficient of performance by 40-50%. Particularly attractive are permeable thermoelements with built-in catalytic heat sources (Fig.13). Computer design allows their optimization and experimental efficiency increase by a factor of 1,2.



1 - combustible mixture; 2 - thermoelectric material; 3 - channel with a catalyst.

Thermoelectric materials have been found that possess catalytic properties (Fig.14). Their application facilitates technology of creating permeable thermoelements with built-in heat sources.



Thermoelectric materials with catalytic properties

 $\begin{array}{l} La_{0.8}Ca_{0.2}CoO_3,\\ La_{0.5}Sr_{0.5}CoO_3,\\ La_{0.5}Ba_{0.5}CoO_3,\\ Mn_{0.4}Fe_{2.6}O_4,\\ \end{array}$

 $\begin{array}{l} Ni_{0.4}Fe_{2.6}O_4,\\ (Mn_{1/2}Ni_{1/2})_{0.4}\ Fe_{2.6}\ O_4. \end{array}$

Fig.14. Permeable thermoelement of materials with catalytic properties.

Sectional thermoelectric generators

The widest application was found in the past and is still found now by generators based on the use of organic fuels (Fig.15).

Attention is engaged by the fact that despite more than 10-fold improvement of module efficiency since 1950 up to now, the generator efficiency has increased only by a factor of 2 - 2.5 and is as low as 3.2 - 3.5 %. Analysis shows that the reasons for this are inevitable heat losses and inefficient thermodynamic use of thermal energy of fuel combustion products.



More efficient use of fuel thermal energy is achieved by using sectional generators the model of which is shown in Fig.16. In this figure n is the number of sections that represent modules 3 with heat exchangers 2, 4. Hot gases from heat source 1 pass along the heat exchangers of the sections, consecutively giving thermal energy to them. This model has been optimized by computer design. The rational number of sections has been found, as well as the optimal distribution of temperatures, thermal and electric powers in the sections.



Fig.16. Schematic of section thermogenerator operated by gas fuel.

Though the rational number of sections is 3, however, only 2 sections can be used without essential efficiency loss.. Fig.17 shows a structure of such generator and the parameters obtained. It can be seen that the efficiency has increased practically twice as compared to that of thermogenerators used today.



Fig.17. Schematic of two-section thermogenerator operated by gas fuel.

The above examples imply the possibility of considerable improvement of the efficiency of thermoelectric power conversion even with the currently achieved figure of merit of thermoelectric materials, which contributes to progress in practical applications of thermoelectricity.