

R.G.Cherkez

R.G.Cherkez

Institute of Thermoelectricity of the NAS and MES Ukraine, 1 Nauky str., Chernivtsi, 58029, Ukraine

PERMEABLE GENERATOR THERMOELEMENTS OF Co-Sb BASED MATERIALS

Results of computer investigations of permeable themoelements based on Co-Sb are presented. Optimal parameters and concentrations of doping impurities whereby maximum efficiency of thermal into electric energy conversion is accomplished are determined. Possibility of 1.1-1.3-fold efficiency increase of permeable thermoelements of Co-Sb based materials as compared to conventional ones is demonstrated.

Key words: permeable thermoelements, computer design, Co-Sb based materials.

Introduction

The use of thermal waste from industry and internal combustion engines is a promising line of solving the tasks of conservation of energy resources [1]. Attractive properties of thermoelectric method of direct thermal into electric energy conversion, namely the absence of movable parts and possibility of functioning under extreme conditions, make thermoelectric generators advantageous over the others. In so doing, it is customary to use thermoelectric modules of homogeneous materials whose maximum value of thermoelectric figure of merit is achieved in a rather narrow temperature range [2]. This is responsible for insufficient efficiency of thermoelectric power converters, hence restricts the possibilities of their practical use.

In recent decade, increasing researchers' attention has been drawn to promising thermoelectric materials based on *Co-Sb* [3]. They are ecologically safe and characterized by rather high values of the Seebeck coefficient and electric conductivity with maximum values of a dimensionless parameter of thermoelectric figure of merit *ZT* at a level of 1 - 1.1 in the temperature range of 700 - 750 K [4-5].

At the same time, growing interest has been observed recently in the study of permeable thermoelements, where heat input and removal occurs not only on the junctions, but also due to the use of a developed heat exchange surface in the bulk of legs material [6]. Such thermoelements are made permeable for pumping gas or liquid flows, which allows improving the efficiency of thermoelectric energy conversion. The use of permeable structures in thermoelectric modules with *Bi*-*Te* made it possible to improve the efficiency of energy conversion by 30 % [7].

However, the use of permeable thermoelements of promising materials based on *Co-Sb* has received no attention in the literature. Therefore, the purpose of this work is to determine characteristics of permeable generator thermoelements based on *Co-Sb*, to reveal their optimal thermophysical and design parameters whereby maximum efficiency of thermal into electric energy conversion is realized.

A physical model and its mathematical description

A physical model of a permeable thermoelement in electric energy generation mode is represented in Fig. 1. The thermoelement consists of n- and p-type legs whose physical properties are temperature-

dependent. Heat input is realized by passing heat carrier along the legs through the channels (pores). Each leg comprises N_n and N_p – segments, respectively, the contact resistance of compound is r_0 . The lateral surfaces of the legs are adiabatically isolated; heat carrier temperature at thermoelement inlet T_m is assigned. The temperature of cold junctions T_c is thermostated.



Fig. 1.A physical model of a permeable segmented thermoelement.
1, 8, 9 - connecting plates; 2, 10 -connecting layers;
3, 5, 6, 7 - segments (sections) of n-type leg; 4, 14 - heat carrier;
11, 12, 13 -segments (sections) of p-type leg.

A system of differential equations describing the distribution of temperatures and heat fluxes in a steady-state one-dimensional case, in the infinitely small part dx of each k-th segment of n- and p-type legs, in the dimensionless coordinates is given by relations [7]:

$$\frac{dT}{dx} = -\frac{\alpha_{k}j}{\kappa_{k}} T - \frac{j}{\kappa_{k}} q,$$

$$\frac{dq}{dx} = \frac{\alpha_{k}^{2}j}{\kappa_{k}} T + \frac{\alpha_{k}j}{\kappa_{k}} q + j\rho_{k} + \frac{\alpha_{T}\Pi_{K}^{1}N_{K}l_{K}^{2}}{(S - S_{K})j}(t - T),$$

$$\frac{dt}{dx} = \frac{\alpha_{T}\Pi_{K}^{1}N_{K}l_{k}}{Gc_{p}}(t - T),$$

$$(1)$$

where Π_{K}^{1} is channel perimeter; N_{K} is the number of channels, S_{K} is cross-sectional area of all the channels, S is section of a leg together with the channels, G is heat carrier expenditure in the channels, c_{p} is specific heat of heat carrier, t is heat carrier temperature at point x, T is leg temperature at point x, α_{T} is heat-transfer coefficient, α , κ , ρ are the Seebeck coefficient, thermal conductivity and resistivity of leg material.

Specific heat fluxes q and the reduced density of electric current j are determined through

$$q = \frac{Q}{I}, \qquad j = \frac{Il}{S},\tag{2}$$

where Q is power of heat flux passing through thermoelement leg, I is electric current, S is cross-sectional area of thermoelement legs.

The boundary conditions necessary for solving (1) with regard to the Joule-Lenz heat release due to contact resistance r_0 at points of connection of leg segments are formulated as:

$$T_{n,p}(0) = T_{\rm C}, \qquad t_{n,p}(1) = T_{m}, \qquad q_{n,p}(1) = 0,$$

$$T_{n,p}(x_{k}^{+}) = T_{n,p}(x_{k}^{-}), \qquad q_{n,p}(x_{k}^{+}) = q_{n,p}(x_{k}^{-}) + \frac{r_{0}}{S_{n,p}}I,$$
(3)

where indices "-" and "+" denote the value of functions immediately to the left and right of the interface of segments x_k ; k = 1, ..., N is the index which determines leg segment number.

In the case of search for optimal values of doping impurities which determine carrier concentrations in leg segments it is necessary to assign the dependences of material parameters α , κ , ρ on temperature and concentration of carriers (or impurities).

The main task in the design of a permeable segmented generator thermoelement is to determine such agreed parameters (reduced current density j in the legs, heat carrier expenditures in channels G, concentration of doping impurities in materials of each segment whereby the efficiency of thermoelement reaches a maximum.

The efficiency will be determined through the relation of electric power P generated by the thermoelement to a change in heat carrier enthalpy:

$$\eta = \frac{P}{\sum_{n,p} Gc_p \left(T_m - T_C \right)}$$
 (4)

The maximum efficiency can be conveniently reduced to achievement of functional minimum:

$$J = \ln\left[\sum_{n,p} \left\{ Gc_p \left(T_m - T_C \right) \right\} \right] - \ln\left[\sum_{n,p} \left\{ Gc_p \left(T_m - t(0) \right) + q(0) \frac{j(S - S_K)}{l} - I\left(\frac{r_0}{S_n} + \frac{r_0}{S_p} \right) \right\} \right].$$
(5)

This problem was solved through use of the Pontryagin maximum principle [8] on which basis the relations giving the necessary optimality conditions were obtained. Such procedure as applied to thermoelectric energy conversion was described in many works, for instance, [9, 10], and was used for creation of computer program and study of a permeable thermoelement made of *Co-Sb* based thermoelectric materials [11].

Results of computer investigation of the energy characteristics of a permeable segmented generator thermoelement based on *Co-Sb*

Experimental data on the dependences of parameters α , κ , σ of *Co-Sb* based materials on the temperature and doping [12, 13] were approximated as polynomial dependences (Fig. 2) and used in computer investigation program. Calculation of a permeable segmented thermoelement was done under conditions when heat exchange coefficient of heat carrier – gas in the channels was assumed to be equal to $\alpha_{\rm T} = 0.01$ W/cm²·K, which is achieved in the channels with diameter 0.02 - 0.2 cm at a laminar motion of heat carrier and is a typical value of heat exchange coefficient under such conditions [14, 15]. The cross-sectional area of a leg together with the channels was S = 1 cm², contact resistance at points of legs connection was $r_0 = 5 \cdot 10^{-6}$ Ohm·cm². The calculation was done under condition of thermostating the cold junctions at temperature $T_c = 300$ K for different values of heat carrier temperature at thermoelement inlet $T_m = 900$ K, 1100 K, 1500 K. In so doing, the temperature of thermoelement hot junctions was software controlled not to exceed the value of 800 K, namely the limiting value of temperature dependences of *Co-Sb* based materials (Fig. 2).

As a result of calculations, the optimal values of j, G and doping parameter x were found whereby maximum efficiency of thermal into electric energy conversion is achieved. The dependences of efficiency and power on the leg height, channel diameter and the number of channels were determined.

The dependences of maximum efficiency η and specific electric power W of a permeable

generator thermoelement with the optimal values of *j*, *G* and doping parameter *x* of legs on the leg height l_k for different hot junction temperatures are given in Fig. 3. The data is given for channel diameter $_k = 0.1$ cm and the number of channels $N_k = 25$ pcs per 1 cm².



a) b)
Fig.2. Temperature and concentration dependences of Co-Sb based material:
a) n-type material CoSb_{2.875-x}Ge_{0.125}Te_x for different values of x-components of Te impurity [12];
b) p-type material Yb_xLa_yFe_{2.7}Co_{1.3}Sb₁₂ for different x-components of Yb impurity (x+y = 1) [13];
(1-x = 0.050, 2-0.150, 3-0.250, 4-0.350, 5-0.450, 6-0.550).



Fig. 3. Efficiency and electric power of a permeable Co-Sb based thermoelement as a function of leg length l_k . 1 - heat carrier temperature at thermoelement inlet $T_m=900$ K; $2 - T_m=1100$ K; $3 - T_m=1500$ K.

It is seen that as the leg height increases, the efficiency grows and attains saturation achieving maximum value ($\eta = 6.7$ %) for heat carrier temperature $T_m = 1500$ K. The electric power has a maximum at the leg height $l_k = 1.4$ cm which corresponds to optimal height of leg whereby maximum electric power is generated by thermoelement. In so doing, the efficiency for heat carrier temperature 1100 K is about 1.2 times that of an impermeable thermoelement η_0 working under similar conditions.

The results of research of the effect of channel diameter d_k on the efficiency and electric power of a permeable generator thermoelement under optimal conditions for different heat carrier temperatures T_m with the leg height $l_k = 1$ cm and the number of channels $N_k = 25$ pcs per 1 cm¹ are given in Fig. 4.



Fig. 4.Dependences of the energy characteristics of a permeable single-segmented thermoelement on channel diameter d_k : 1 – heat carrier temperature $T_m = 900$ K; 2 - $T_m = 1100$ K; 3 - $T_m = 1500$ K.

As is evident from Fig. 4, the efficiency of a permeable thermoelement increases with increase in channel diameter and has maximum values at heat carrier temperature $T_m = 1500$ K, as in the previous case. From the above dependences it is also seen that the efficiency of a permeable thermoelement can exceed that of classical thermoelement by a factor of 1.15. The electric power has an extremum with increase in channel diameter for all considered hot junction temperatures, however, it has the greatest value for heat carrier temperature 1500 K P = 1.75 W. This value is achieved with channel diameter $d_k = 0.14$ cm, which is optimal for obtaining maximum electric power.

Dependences of the efficiency and electric power of a permeable thermoelement on the number of channels N_k under optimal conditions of *j*, *G*, *x* for channel diameter $d_k = 0.2$ cm, leg height $l_k = 1$ cm are given in Fig. 5.From the data is follows that the efficiency increases with increasing the number of channels and reaches maximum, as in the two previous cases, at heat carrier temperature $T_m = 1500$ K and makes $\eta = 6.8$ %. There can be 1.3-fold efficiency increase as compared to a conventional thermoelement. Electric power has a maximum at $N_k \sim 16$ pcs per 1 cm² and makes P = 1.57 W.

For different operating conditions of permeable generator thermoelements of *Co-Sb* based materials it is necessary to determine their own optimal design parameters (leg height, diameter and number of channels) whereby maximum electric power will be obtained. Under optimal operating conditions the efficiency is 1.1.-1.3 times that of a conventional thermoelement.

R.G. Cherkez Permeable generator thermoelements of Co-Sb based materials



Fig. 5. Dependences of the energy characteristics of a permeable segmented thermoelement on the number of channels N_k . 1 – heat carrier temperature $T_m = 900 \text{ K}$; 2 - $T_m = 1100 \text{ K}$; 3 - $T_m = 1500 \text{ K}$.

Conclusions

- 1. Procedure of calculation and design of permeable generator thermoelements of *Co-Sb* based materials is represented.
- 2. The effect of design parameters (leg height and the number of segments) under optimal efficiency operating conditions on the basic characteristics of energy conversion is determined. Optimal design parameters have been found, namely leg height $l_k = 1.4$ cm, channel diameter $d_k = 0.14$ cm, the number of channels $N_k \sim 16$ pcs per 1 cm² whereby maximum electric power is obtained.
- 3. It is shown that the efficiency of permeable generator thermoelements of *Co-Sb* based materials can be approximately 1.1 1.3 times that of conventional thermoelements working under similar conditions.

References

- 1. L.I.Anatychuk, R.V.Kuz, and Yu.Yu.Rozver, Efficiency of Thermoelectric Recuperators of the Exhaust Gas Energy of Internal Combustion Engines, *J.Thermoelectricity* **4**, 78-83 (2011).
- 2. E.P.Sabo, Technology of Chalcogenide Thermoelements. Physical Foundations. Chapter 1. Structure and Properties of Materials, *J.Thermoelectricity* **3**, 30 (2000).
- 3. C.Uher, Skutterudite-Based Thermoelectrics. Thermoelectrics Handbook. Macro to Nano. Edited by D.M.Rowe (CRC Press, 2006), P. 34-1-34-13.
- 4. Jae-Yong Jung, Kwan-Ho Park, and Il-Ho Kim, Thermoelectric and Transport Properties of *In*-filled and *Ni*-doped *CoSb*₃ Skutterudites, *J. of the Korean Physical Society* **57**(4), 773-777 (2010).
- G. A. Lamberton, S. Bhattacharya, R. T. Littleton, M. A. Kaeser, R. H. Tedstrom, T. M. Tritt, J. Yang, and G. S. Nolas, High Figure of Merit in *Eu*-Filled *CoSb*₃-Based Skutterudites, *Appl. Phys. Lett.* 80, 598 (2002).
- 6. L.I.Anatychuk, R.G.Cherkez, Permeable Thermoelement in Electric Energy Generation Mode, *J.Thermoelectricity* **2**, 35-46 (2003).

- 7. L.I.Anatychuk, R.G.Cherkez, Permeable Segmented Thermoelement in Electric Energy Generation Mode, *J.Thermoelectricity* **3**, 5-12 (2010).
- 8. A.J.Zhou, T.J.Zhu, X.B.Zhao, et al., Improved Thermoelectric Performance of Higher Manganese Silicides with Ge Additions, *J. of Electronic Materials* **39**(9), 2002 (2010).
- 9. L.I.Anatychuk, L.M.Vikhor, *Thermoelectricity. Volume IV. Functionally-Graded Thermoelectric Materials* (Chernivtsi: Bukrek, 2012), 180 p.
- 10.R.G.Cherkez, M.V.Maksimuk, and P.P.Fenyak, Design of Thermoelectric Permeable Structures Based on *Mg* and *Mn* Silicides, *J.Thermoelectricity* **6**, 62-70 (2013).
- 11.V.R.Bilinsky-Slotylo, L.M.Vikhor, V.Ya.Mikhailovsky, R.N.Mochernuyk, and A.F.Semizorov, Efficiency Improvement of Generator Modules Based on *CoSb* through Use of Segmented and Multi-Stage Structures, *J.Thermoelectricity* **3**, 71-76 (2013).
- 12.X.Su, H.Li, Q.Guo, X.Tang, Q.Zhang, and C.Uher, Structure and Thermoelectric Properties of *Te*and *Ge*-Doped Skutterudites $CoSb_{2.875-x}Ge_{0.125}Te_x$, *J. of Electronic Materials* **40**(5), 1286-1291 (2011).
- 13.Ch.Zhou, D.Morelli, X.Zhou, G.Wang, and C.Uher, Thermoelectric Properties of p-type *Yb*-filled Skutterudite *Yb*_x*Fe*_y*Co*_{4-y}*Sb*₁₂, *Intermetallics* **19**(10), 1390-1393 (2011).
- 14. Yu.N.Lobunets, *Methods of Calculation and Design of Thermoelectric Power Converters* (Kyiv: Naukova Dumka, 1989), 176 p.
- 15. G.K.Kotyrlo, G.M.Schegolev, *Heat Diagrams of Thermoelectric Devices* (Kyiv:Naukova Dumka, 1973), 215p.

Submitted 27.06.2014.