

MEANS FOR MEASURING THE THERMAL QUANTITIES

CRITERIA OF MATERIALS METAL GLASSES SELECTION FOR THERMOMETRY

*Pylyp Skoropad, Dr.Sc., Prof.; Ihor Lihnovskyi, Ph.D., As.-Prof.; Pavlo Hamula, PhD, As.-Prof.,
Lviv Polytechnic National University, Ukraine; e-mail: pylyp.i.skoropad@lpnu.ua
Rostyslav Mastylo, Ph.D., Technical University, Ilmenau, Germany*

Abstract. In the current paper, there are considered the criteria for estimating the thermoelectric properties of metal glasses (MG) on suitability for thermometry. It is revealed that a principle of choice of thermoelectric materials based only on criteria is not quite efficient. It needs to examine also their mechanical durability, thermal, radiating, and anticorrosive properties, etc. More complete consideration proves that the use of MGs in thermometry is rather expedient.

Key words: Thermoelectric transducer, thermo-EMF, Thermal resistance, Electro resistance, Thermocouple, Criteria.

1. Introduction

At the transducer's creation, the tendency is developed to change the traditional thermo electrodes in the form of a wire or film to a new class of materials – MGs. The last are inherent in the better electro-physical and mechanical characteristics [1].

For example, The analysis of heat radiation in a stationary mode, for a perpendicular arrangement of thermal flows and the planes of transducers made from MG, have received expressions that allow estimating: sensitivity $K = U/P = SR_T$, sensitivity limit $P_0 = (4k\Delta f)^{1/2}R_\Omega^{1/2}/SR_T$ and constant of thermal inertia $\tau = CR_T$, where U is the output voltage; P is the power of a heat flow; S is an absolute thermo-EMF; R_T is the thermal resistance; R_Ω is the electro resistance; k is the Boltzmann constant; Δf is the passband of frequency; C is the heat capacity.

It was established that the optimal limit of sensitivity corresponds to the minimum content of the relation $R_\Omega^{1/2}/R_T$. Since thermoelectric converters are not intended for measurement in noise thermometry [2], it is advisable to use electrode materials with a high value of specific electrical resistance ρ and a small thickness inherent to MGs [3-5].

Also, it is necessary to operate with materials with high thermal resistance R_T . It contributes to enhancing sensitivity and lowering the heat capacity C finally decreasing the constant of thermal inertia.

For thermoelectric converters, a significant role is played by the ratio of heat transfer by radiation and thermal conductivity on thermocouples on the one hand and heat transfer and electrical insulation to the fixture on the other hand. Let's denote the radius of the spheres of the thermocouple's hot and cold junctions accordingly, as r_0 and R , and in dependences K , P_0 , τ instead of

R_T as well as let's consider the heat transfer by radiation G_B and thermal conductivity G_T :

$$R_T = 1/(G_B + G_T), \quad (1)$$

$$G_B = 8\varepsilon\sigma T_0^3\pi R^2, \quad (2)$$

$$G_T = \chi X_1^2 \pi d_\Sigma, \quad (3)$$

where ε is the emissivity factor of the object; σ is the Stefan-Boltzmann constant; T_0 is the hot junction temperature of the thermocouple for the monitoring system; χ is an average heat conductivity; d_Σ is the total thickness; X_1 is the first root of Bessel function of the zero order. Then:

$$C = C\pi R^2 d_\Sigma, \quad (4)$$

where $c = \Sigma C_i d_i / d_\Sigma$ and $\chi = \Sigma \chi_i d_i / d_\Sigma$. For a case $G_B \gg G_T$, at the given meaning r_0 and other equal conditions, $K = f(R)$ is considered only up to a certain value; then the significant contribution of radiation decreases, and the temperature almost does not differ from the temperature of the environment. At $G_B > G_T$ τ does not depend from R only at quite small thickness of insulating fixture. At $G_B < G_T$ τ is defined from dependence:

$$\tau = (C/\chi) (R^2/X_1^2). \quad (5)$$

As a result, the increase of thermocouple wire's diameter leads to powering the heat conductivity, and, hence, decreasing the constant of thermal inertia. For small diameters, this constant is defined by the heat conductivity of the insulating fixture.

2. Drawbacks

The selection of optimal thermoelectrode materials for thermoelectric transducers made from MG should be based on certain criteria. However, the widely used criterion of thermoelectric factor Z [6-7] is not quite suitable here; it is suitable for bulks where it can neglect the heat exchange with the environment.

3. Goal

The purpose of this work is the analysis of criteria for evaluating the thermoelectric and other properties of thermocouple materials and the implementation of specific criteria such as general suitability; applied suitability; expediency of application for the development of new types of thermo transducers that are considered the mechanical strength, thermal, radiation and corrosion resistance, and manufacturability of sensitive materials especially made from metal glasses.

4. Analysis of criteria of application of thermoelectrode from MG

For the thermoelectrode with MG, it is necessary to consider the electro-insulation impact of the fixture. It does not influence electrical, but essentially impacts on thermal parameters of thermotransducers. The expression for the definition of the thermoelectricity quality Z_{MG} for thermotransducers with electrodes from MG is the next:

$$Z_{MG} = S^2 / (\rho(\chi_{MG} + \chi_{EA}h_{EA}/h_{MG})), \quad (6)$$

where χ_{EA} is the specific heat conductivity insulating fixture; h_{EA}/h_{MG} is the ratio of thickness, accordingly, electro insulation of the fixture and thermoelectrode from MG. If $\chi_{EA}h_{EA} \gg \chi_{MG}h_{MG}$, then the choice MG for the thermoelectrode can be carried out with the use of the criterion:

$$q = S^2/r. \quad (7)$$

Since the thermoelectric transducers operate together with measuring devices, the correct choice of the thermoelectrodes essentially influences both the parameters of transducers and the method of measurement as well as the parameters of the device. While the output signal of the transducers is measured by a potentiometric method, we define the expressions for their factors of sensitivity K_E and resolution K_P :

$$K_E = (\Delta I_{min}/K_{IU}K_{TX}\Delta X)(R_{MI} + R_T)/R_{MI}, \quad (8)$$

$$K_P = (2K_0(kT_c\Delta f)^{1/2}/K_{TX}\Delta X)((R_{MI} + R_T)R_T/R_{MI})^{1/2}, \quad (9)$$

where ΔI_{min} is the step of the behavior of the measuring device indicator; K_{IU} is the factor of transformation ΔU on input resistance expressed in the readouts I of the measuring device; K_{TX} is the factor of transformation of measuring value X in temperature; R_{MI} is an electro resistance on an input of the measuring device; K_0 is the ratio "signal/noise".

While applying a potentiometer for measuring the thermo-EMF of the transducer from MG it is possible to determine the criterion of basic suitability of thermoelectric materials expressed by:

$$S_e/r_e \geq B, \quad (10)$$

where S_e , r_e is accordingly, thermo-EMF and electro resistance, and B is an angular factor asymptote of de-

pendence $K_P(R_\Omega)$. The criterion of suitability can be defined, proceeding from conditions $K_{UT} = nS_e \geq K_P$ at $R_\Omega \geq R_K$ or $K_{UT} \geq K_E$ at $R_\Omega \leq R_K$, where K_{UT} is the factor of transforming temperature in thermo-EMF; n is the number of thermoelements; R_K is the critical value of transducer's electro resistance:

$$R_K = (\Delta I_{min})^2 R_{MI} / (4K_0 K_{IU}^2 kT_c \Delta f R_{MI} - (\Delta I_{min})^2). \quad (11)$$

The expediency of using one or another MG can be determined based on the maximum content of relations K_{UT}/K_P at $R_\Omega \geq R_K$, or K_{UT}/K_E at $R_\Omega \leq R_K$. If in the thermoelectric transducer replace one electrode on «zero» and apply the potentiometric method of measurement of thermo-EMF, we receive:

- basic suitability:

$$S/\rho \geq 2K_0 L(kT_c \Delta f)^{1/2} / K_{TX} X A (R_{MI})^{1/2}, \quad (12)$$

- practical suitability:

$$S^2/\rho \geq 4K_0^2 L kT_c \Delta f / K_{TX}^2 (\Delta X)^2 A n, \text{ if } R_\Omega \geq R_K, \quad (13)$$

or

$$S - \Delta I_{min} L \rho / K_{IU} K_{TX} \Delta X R_{MI} A \geq \Delta I_{min} / K_{IU} K_{TX} \Delta X n, \text{ if } R_\Omega \leq R_K, \quad (14)$$

expediency

$$(R_{MI} A - n\rho)^{-1} (S^2/\rho) \rightarrow \max, \text{ if } R_\Omega \geq R_K, \quad (15)$$

or

$$(1 + Ln\rho/R_{MI} A) S \rightarrow \max, \text{ if } R_\Omega \leq R_K. \quad (16)$$

Here L , and A , are accordingly the length and area of a cross-section of thermo electrode made from MG.

5. Basic criteria of the thermoelectric properties of MG

As the area of application of analyzed MGs is the thermometry, we make the appropriate substitutions ($\Delta X = \Delta T$ and $K_{TX} = 1$) and receive criteria of an MG application in thermoelectric transducers. For heat radiation area of application of the thermoelectric transducer: $\Delta X = \Delta \Psi$, here Ψ is an intensity of radiation; $\Delta T = L\Delta \Psi/\chi$, $K_{TX} = L/\chi$. Hence, for a potentiometric method of thermo-EMF measuring with the help of the thermoelectric transducer made from MG, we receive expressions for the criteria:

- basic suitability

$$S/\rho\chi \geq 2K_0(kT_c\Delta f)^{1/2}/\Delta\Psi A(R_{MI})^{1/2}, \quad (17)$$

- practical suitability

$$(S/\chi) - \Delta I_{min}\rho/K_{IU}\Delta\Psi AR_{MI} \geq \Delta I_{min}/K_{IU}\Delta\Psi Ln, \text{ if } R_\Omega \leq R_K, \quad (18)$$

or

$$S^2/\rho\chi^2 \geq 4K_0^2 kT_c \Delta f / (\Delta\Psi)^2 L A n, \text{ if } R_\Omega \geq R_K, \quad (19)$$

expediency

$$(R_{MI} A + Ln\rho)(R_{MI} A)^{-1} (S/\chi) \rightarrow \max, \text{ if } R_\Omega \leq R_K, \quad (20)$$

or

$$(R_{MI} A - Ln\rho)^{-1} S^2/\rho\chi^2 \rightarrow \max, \text{ if } R_\Omega \geq R_K. \quad (21)$$

The mentioned criteria are given in Table for electrodes made from MGs.

Table. Values of criteria for the main thermoelectric properties of MG (* – own data).

Materials	χ , W/(cmK)	S/ρ , A/(CmK)	S^2/ρ , μ W/(CmK ²)	$S/\rho\chi$, 1/V	$S^2/\rho\chi$, 1/K	$S^2/\rho\chi^2$, Cm/W	S/χ , μ V Cm/W
*Fe ₉₀ B ₁₀	7,84E-02	-1,32E-02	2,44E-02	-1,69E-01	3,11E-07	3,96E-06	-2,35E+01
Fe ₈₇ B ₁₃	7,91E-02	-1,40E-02	2,71E-02	-1,76E-01	3,42E-07	4,33E-06	-2,45E+01
Fe ₈₆ B ₁₄	7,94E-02	-1,47E-02	2,99E-02	-1,85E-01	3,77E-07	4,75E-06	-2,57E+01
Fe ₈₅ B ₁₅	7,96E-02	-1,73E-02	4,14E-02	-2,17E-01	5,21E-07	6,54E-06	-3,02E+01
Fe ₈₄ B ₁₆	7,98E-02	-1,90E-02	5,01E-02	-2,38E-01	6,28E-07	7,87E-06	-3,31E+01
Fe ₈₃ B ₁₇	8,00E-02	-2,19E-02	6,69E-02	-2,74E-01	8,37E-07	1,05E-05	-3,81E+01
Fe ₈₂ B ₁₈	8,03E-02	-2,42E-02	8,17E-02	-3,02E-01	1,02E-06	1,27E-05	-4,20E+01
Fe ₈₀ B ₂₀	8,08E-02	-2,63E-02	9,58E-02	-3,25E-01	1,19E-06	1,47E-05	-4,52E+01
Fe ₇₈ B ₂₂	8,13E-02	-2,69E-02	1,01E-01	-3,31E-01	1,24E-06	1,52E-05	-4,60E+01
Fe ₇₅ B ₂₅	8,20E-02	-2,82E-02	1,11E-01	-3,44E-01	1,35E-06	1,64E-05	-4,78E+01
Fe ₈₀ Co ₃ B ₁₇	7,97E-02	-3,41E-02	1,57E-01	-4,28E-01	1,97E-06	2,47E-05	-5,77E+01
Fe ₇₄ Co ₁₀ B ₁₆	7,86E-02	-5,28E-02	3,48E-01	-6,71E-01	4,43E-06	5,63E-05	-8,39E+01
Fe ₈₀ Cu ₃ B ₁₇	8,98E-02	-3,33E-02	1,33E-01	-3,71E-01	1,48E-06	1,65E-05	-4,45E+01
Fe ₈₀ V ₃ B ₁₇	7,89E-02	-1,52E-02	2,97E-02	-1,93E-01	3,77E-07	4,77E-06	-2,47E+01
Fe ₈₀ Cr ₃ B ₁₇	7,98E-02	-1,38E-02	2,65E-02	-1,73E-01	3,32E-07	4,16E-06	-2,41E+01
Fe ₈₀ Ni ₃ B ₁₇	8,06E-02	-3,52E-02	1,58E-01	-4,36E-01	1,96E-06	2,44E-05	-5,58E+01
Fe ₈₀ Mn ₃ B ₁₇	7,83E-02	-1,69E-02	3,72E-02	-2,16E-01	4,75E-07	6,07E-06	-2,81E+01
Fe ₈₀ Ti ₃ B ₁₇	7,83E-02	-1,43E-02	2,86E-02	-1,82E-01	3,65E-07	4,66E-06	-2,55E+01
Fe ₄₀ Ni ₄₀ B ₂₀	8,72E-02	-5,17E-02	3,48E-01	-5,93E-01	3,99E-06	4,58E-05	-7,71E+01
Fe ₄₀ Ni ₄₀ P ₁₄ B ₆	7,20E-02	-1,51E-02	3,17E-02	-2,10E-01	4,41E-07	6,12E-06	-2,92E+01
Fe ₆₇ Co ₁₈ B ₁₄ Si ₁	7,74E-02	-7,26E-02	7,64E-01	-9,38E-01	9,88E-06	1,28E-04	-1,36E+02
Ti-Cu-Co-Si	1,45E-01	1,17E-02	2,19E-02	8,08E-02	1,51E-07	1,04E-06	1,29E+01
Ti-Cu-Ni-Si	1,52E-01	1,18E-02	2,21E-02	7,74E-02	1,46E-07	9,58E-07	1,24E+01
Ti-Cu-Co	1,58E-01	1,17E-02	2,19E-02	7,39E-02	1,39E-07	8,75E-07	1,18E+01
Zr ₇₅ Ni ₂₅	3,43E-02	7,48E-02	9,39E-01	2,18E+00	2,74E-05	7,98E-04	3,66E+02
Zr ₆₄ Ni ₃₆	4,27E-02	-5,22E-02	4,96E-01	-1,22E+00	1,16E-05	2,72E-04	-2,22E+02
Zr ₃₆ Ni ₆₄	6,43E-02	-1,18E-01	2,35E+00	-1,83E+00	3,66E-05	5,69E-04	-3,11E+02

6. Conclusions

1. According to the criterion S/ρ (where and in what), it is advisable to use metals, metalloids, and their alloys in thermoelectricity, for the metalloids and semiconductors are recommended criterion S^2/ρ ; MGs have the prospects for application in for heat radiation converters behind the criterion S/χ .

2. Since the principle of a choice of the materials for producing the thermoelectrodes of transducers/convertors based on only S , ρ , χ is not sufficient, is necessary to consider the operational parameters of thermoelectric materials, in particular, their mechanical durability, thermal, radiating and corrosive stability, technological peculiarities.

3. In addition, for thermo electrodes from MG, it is recommended to consider a temperature range of application, which lies between the temperature of the annealing relaxation T_r and the temperature of a beginning crystallization T_k . As a rule, the temperature of application T_U for MG makes $0.75T_k$, not exceeding the temperature T_B of plasticity loss.

4. While applying MGs in heat radiation converters [8], the maximal absorbed heat flow, should not exceed $Q_{max} \leq (0.65...0.75)(\chi cd)^{1/2} \epsilon^{-1} (\tau_1)^{1/2} T_U$ and the thickness of the thermo electrode should not be lesser $h_{uman} \geq (0.65...0.75)(\chi cd)^{1/2} (\tau_1)^{1/2} T_U$, where d is the specific density of a thermoelectric material; τ_1 is the duration of a radiation pulse.

7. Conflict of interests

The authors claim that there are no possible financial or other conflicts over the work.

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References

[1] S. Yatsyshyn, O. Hotra, P. Skoropad, T. Bubela, M. Mykyichuk, O. Kochan, O. Boyko, Investigating Ther-

- moelectric Batteries Based on Nanostructured Materials, *Energies* **2023**, 16, 3940. <https://doi.org/10.3390/en16093940>.
- [2] B. Stadnyk, S. Yatsyshyn, Thermometric noise and performance of thermoelectric thermometry, *Journal of Thermoelectricity*, 2015, No.2, P. 66-76. file:///C:/Users/Svyatoslav/Downloads/jtherel_2015_2_9.pdf
- [3] Tritt T.M., Subramanian M.A. Thermoelectric Materials, Phenomena and Applications: A Bird's Eye View, *MRS Bulletin*, March 2006, Vol.31, No.3, pp.188-198 DOI:10.1557/mrs2006.44.
- [4] D. Zh. Chen (2016) Atomic-Level Structure and Deformation in Metallic Glasses. Dissertation (Ph.D.), California Institute of Technology. doi:10.7907/Z95Q4T2B. <https://resolver.caltech.edu/CaltechTHESIS:05252016-155624343>.
- [5] S. Patel, B. Swain, A. Behera, S. Mohapatra, Metallic Glasses: A Revolution in Material Science, From the Edited Volume. *Metallic Glasses*, Edited by Dragica Minić and Milica Vasić, 2020, DOI: 10.5772/intechopen.90165 <https://www.intechopen.com/chapters/70175>
- [6] Y. F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang, High-entropy alloy: challenges and prospects, *Materials Today*, Volume 19, Issue 6, July–August 2016, pp.349-362. <https://www.sciencedirect.com/science/article/pii/S1369702115004010>
- [7] T. Jin, I. Park, T. Park, J. Park, J. H. Shim, Accelerated crystal structure prediction of multi-elements random alloy using expandable features, *Sc. Reports, Scientific Reports* | (2021) 11:5194, <https://www.nature.com/articles/s41598-021-84544-8.pdf?proof=t>
- [8] L. Heber, Ju. Schwab, T. Knobelspies, 3 kW Thermoelectric Generator for Natural Gas-Powered Heavy-Duty Vehicles—Holistic Development, Optimization and Validation, *Energies* **2022**, 15(1), 15; <https://doi.org/10.3390/en15010015>