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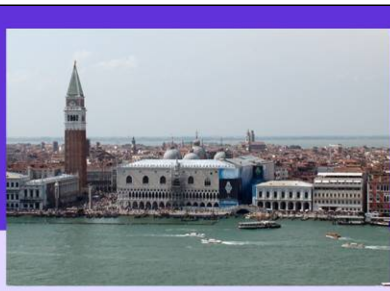

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Accuracy and Metrological Reliability Enhancing of Thermoelectric Transducers

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Abstract: This article is devoted to development and use of thermoelectric thermotransducers with an enhanced accuracy and metrological reliability. The actuality of a problem is stipulated. Investigating changes at typical external environments, the mechanisms of transformation function instability are considered; possibilities of thermodynamic presentation use are analyzed concerning a thermometric substance. The algorithm of thermotransducer instrumental errors' minimization is developed. *Copyright © 2010 IFSA.*

Keywords: Temperature, Measurement error, Thermotransducer, Thermometric substance, Statistic thermodynamics of irreversible processes.

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1. Introduction

Thermometric materials (ThM) of electrothermometry means are considered and thermotransducer (ThT) instrumental error caused by them is estimated on the basis of characteristic divergence, metrological verification practice and transformation function (TF) change evaluation. Majority of thermometry problems are associated with the irreversibility of measurement processes in both metrological and thermodynamic aspects consequently of controlled environment affect on ThT, including ThM. The industrial multifactor action is revealed in the intensification of TF instability.

2. Task Definition

The aim of proposed work is determination of the metrological characteristics for thermoelectric temperature transducer.

3. Methodology

Thermodynamic ThM singling out from the ThT in general lies in work methodology; in such case ThM state and characteristics could be explored with the application of the mentioned thermodynamics [1]. Electric genesis fluctuations, which appear as a result of ThM thermometric state alter, including the processes of diffusion and deformation, cause TF drift. Therefore the creation of ThT error minimization principles must be based on the study of fluctuation-dissipation phenomenon influence on TF.

Thermodynamic fluxes *J* and powers *X* are connected by Onsager reciprocity proportion (1) in linear thermodynamics valid for the system that is not too remote from its equilibrium. The reason to consider transmission processes in linear approximation under the condition $J_I(0) \to 0$:

$$J_I\left(X_1,...,X_6\right) = J_I\left(0\right) + \sum_J \left.\frac{\partial J_I}{\partial X_J}\right|_{(0)} \left(X_J - 0\right) = \sum_J \beta_{IJ} X_J \tag{1}$$

is ThM research results [2], where $grad\,T = 10^4\ K/mm$ is determined experimentally and above this value the connection of thermodynamic fluxes and powers becomes nonlinear. Mainly such a considerable gradient is not achievable.

4. Theoretical and Experimental Research

4.1. Transformation Function

The Transformation Function of $F\left(T,p,...\right)$ caused by the correlation of at least two thermodynamic fluxes (electric and heat) and the summary influence function $F_I\left(T,p,...\right)$ of ThT are given through the normalized TF value $F\left(T,0,0,...\right)$:

$$\begin{aligned} &F\left(T,p,...\right) = F\left(T,0,0,0,...\right) + F_I\left(T,p,...\right), \\ &where\ \ F_I\left(T,p,...\right) = \sum_{I=3...6} F_I\left(X_I\right) \qquad , \\ &F\left(T,p,...\right) = F\left(T,0,0,...\right)\left[1 + \frac{F_I\left(T,p,...\right)}{F\left(T,0,0,...\right)}\right] = F\left(T,0,0,...\right)\left[1 + K_\Sigma\left(T,p,...\right)\right] \end{aligned} \tag{2}$$

were $K_\Sigma\left(T,p,...\right) = K_X + K_M + ...$ is the summary relative influence function, caused by the total effect of other processes: K_{Ch} is the mass transmission, K_M is the deformation, etc.

Nowadays statistical thermodynamics considers ~ 6 thermodynamics fluxes; to determine them, we should solve 6-equation system with 6 unknowns. To simplify it to 3 equations with 3 unknowns, the determined below criteria ***Cr₁***; ***Cr₂***; ***Cr₃***. ***Cr₁*** are involved. The comparison of electron energy obtained in the magnetic field H with its heat energy: $Cr_1 = \frac{\zeta\zeta_0 H^2}{2kT}$ serves as criterion $\boldsymbol{Cr_1}$ is the negligence of the magnetic field action. Here $\zeta_0;\zeta$ are absolute and relative magnetic ThM penetration values, respectively. At $\boldsymbol{Cr_1} >> 1$ (considerable magnetic fields and low temperature values) we should take into account the influence of a magnetic field on the TF formation; otherwise – it is neglected.

Negligible or satisfactory surface influence is inherent in real ThM, except foams and thread-shaped crystals. According to the results of porous ThM conducted scrutiny, the criterion $Cr_2 = \frac{\rho_0 - \rho}{\rho}$ is proposed. At $\boldsymbol{Cr_2} > 2$ % the substantiality of surface factors in the influence function formation is evident. For instance, according to the results of experimental research of molybdenum wires, the influence function makes near 0.2 % at $\boldsymbol{Cr_2} = 1$ %. It could be neglected and we can proceed to the evaluation of other transmission processes' affect.

The criterion $Cr_3 = \Delta U_M / \Delta U_{Ch}$ suggested as the proportion of influence functions in the case of divided transmission processes caused by deformation/annealing, - ΔU_M - and by the temperature-activated diffusion - ΔU_{Ch}. At $\boldsymbol{Cr_3} >> 1$ - the processes of deformation or relaxation prevail, and at $\boldsymbol{Cr_3} << 1$ - the diffusion processes do. In the last case the system of transmission equations for ThM will be:

$$\begin{cases} I_e = -L_{11}\nabla\varphi - \frac{L_{12}}{T}\nabla T - L_{13}\nabla\left(\frac{\mu}{T}\right) \\ I_h = -L_{21}\nabla\varphi - \frac{L_{22}}{T}\nabla T - L_{23}\nabla\left(\frac{\mu}{T}\right) \\ I_m = -L_{31}\nabla\varphi - \frac{L_{32}}{T}\nabla T - L_{33}\nabla\left(\frac{\mu}{T}\right) \end{cases}, \tag{3}$$

were $I_e;I_h;I_m$ are the fluxes of electric-, heat- and mass-transmission respectively; m is the specific mass; μ is the chemical potential; φ is the electric potential. Coefficient $\boldsymbol{L_{23} = L_{32}}$ is describing thermal diffusion. Coefficients $\boldsymbol{L_{13} = L_{31}}$ concern with electric-diffusion, which is absent in conventional conditions, however, could be used for ThT error minimization.

The solution is an electric flux transmission equation ($k_1;k_2$ are the coefficients) in thermoelectricity under the condition that $I_e = 0$, since an electric circuit is broken:

$$I_e = k_1\left[e^2 E_l - eT\nabla\left(\frac{\mu}{T}\right)\right] - \frac{e}{T}k_2\nabla T = 0 \tag{4}$$

At the gained from (4) tension of an electric field $E_l = \frac{k_2 - k_1\mu}{ek_1T}\nabla T + \frac{1}{e}\nabla\mu = \alpha\nabla T + \frac{1}{e}\nabla\mu,$ the integral TEMF could be defined by the integrating along a thermocouple axis:

$$\mathrm{U} = \int_x \alpha\left[T(x)\right]\nabla_x T dx + \frac{1}{e}\int_x \nabla_x \mu\left[T(x)\right] dx \tag{5}$$

Here, the first component defines a TF with its TEMF coefficient α and the second – the chemical influence function. Since recently thermoelectrodes were treated as homogeneous, the latter was neglected. Something similar is not admissible for modern thermometry with its intention to minimize errors by the taking into consideration ThM micro inhomogeneity that defines not only the influence function but TF reproducibility as well.

Solving thermomass - transmission equations through the gained gradients of a chemical potential and concentration admixture distribution (*Fe* and *Ni* in monocrystal *Mo*), we can determine analytically the integral TEMF as a sum of TF normalized value U_0 and the chemical influence function ΔU_{Ch}:

$$U = U_0 + \Delta U_{Ch} = \int_T \alpha(T) dT + \frac{Q_{Fe}^{*} C_{Fe} + Q_{Ni}^{*} C_{Ni}}{e} \ln\frac{T_H}{T_C} \tag{6}$$

At the transmission heat $Q*_{Fe} \approx Q*_{Ni} \approx 0.34$ eV; C_{Fe}=3×10^{-3} %; C_{Ni}=2×10^{-3} %; T_H=1273 K; T_C=273 K the chemical influence function is evaluated as 21 μV that is a summary error methodical constituent. Therefore the experimentally determined function - 62 ± 12 μV – could be diminished to 41 ± 12 μV and its relative value $K_X = \Delta U_{Ch}/U_0$ - for 34 %.

The new thermometry class of ThT functional gradient sensitive elements with the decreased instrumental error [3] is proposed on the basis of mentioned above.

The indirect action of mass-transmission processes with substantially higher intensity for polycrystalline ThM in comparison with monocrystalline is evaluated concerning a grain border influence.

The recrystalization influence function K_R nonlinearly dependable in temperature and treated as a proportion of chemical functions for polycrystalline influence (K_{Ch}) and monocrystalline (K'_{Ch}) for ThM of equal chemical contents is introduced: $K_R\left[T;\nabla_x T;\nabla_r T;t;...\right] = \frac{K_{Ch}}{K'_{Ch}} = \lim_{t\to\infty}\frac{\Delta U_{Ch}(t)}{\Delta U'_{Ch}(t)} >> 1$.

It describes the experimentally determined regularity: the chemical influence function of polycrystalline ThM is more considerable in comparison with the monocrystalline ThM function.

The electric transmission complicating in deformed ThM (at low temperatures with absent mass-transmission) when ***Cr*₃** >> 1 allows defining the normalized value of TF U_0 and the mechanical influence function ΔU_M:

$$U = U_0 + \Delta U_M = \int_x \alpha\left[T(x)\right]\nabla_x T dx + \frac{1}{em}\int_x \frac{1}{E_U}\sigma\nabla_x\sigma\left[T(x)\right] dx \tag{7}$$

and its relative value is $K_M = \Delta U_M / U_0$. In the case of resilient deformation, the mechanical influence function $\Delta U_M = \int \alpha_\sigma dT$ where α_σ is the TEMF deformation coefficient is reversal:

$$\Delta U_M = \int_T \alpha_\sigma dT = -\frac{\varepsilon^2}{2em}\int_T \nabla_T E_U(T) dT \Delta U_M, \quad (8)$$

since it is the issue of the temporary intensification of non-equilibrium electric fluctuations for 2-3 degrees. The changes of TEMF deformation coefficient α_σ and the elastic module E_U correlate with the coefficient -0.598 at the resilient deformation of alloy Ni26UT3.

The mechanical influence function could be expressed per se through the thermodynamic parameters of volume ***V*** and pressure ***p*** in the temperature field:

$$\Delta U_M = \frac{p}{em}\int_{T_C}^{T_H}\int_{V_1}^{V_2} dV dT = \frac{p(V_2 - V_1)}{em}\left(\ln\frac{T_H}{T_C} - 1\right) \quad (9)$$

The achieved expression is proved by the experimental research results of ***PtRd/Pt*** ThT (Fig. 1): the influence function is multiplicative concerning thermodynamic parameters $T; p$.

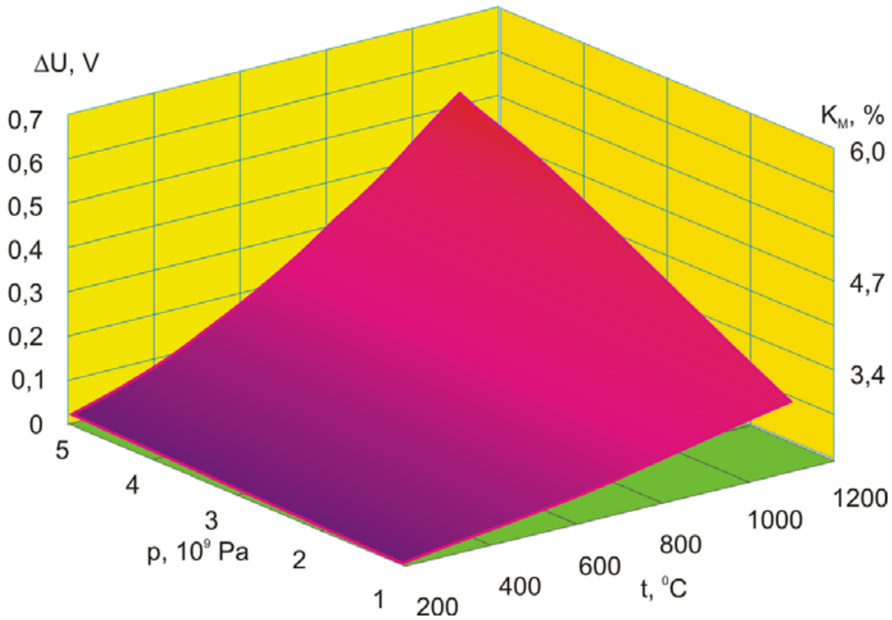

Fig. 1. Influence function of **PtRd/Pt** ThT.

In the case of ThM with high porosity, mechanical strain is applied directly to pores without causing any monolith changes. There is considerable relation between ThM specific mass ρ deviations and the influence function. Particularly, the elastic module is determined as $E_U(\rho) = E_{U0}\,\rho/\rho_0$, were $E_{U0}; \rho_0$ are the monolithic ThM characteristics. Then the mechanical influence function K_M attains a multiplication factor expressed by the porous influence function $K_П$: $K_П(\sigma,\varepsilon,T,t) = \frac{\Delta U'_M}{\Delta U_M} = \frac{\rho(\sigma,\varepsilon,T,t)}{\rho_0} \le 1$ at the expense of damping the proportion between mechanical strains and deformations.

Thermocycling swiftly firms the intensity of transmission processes in ThM. At the non-stationary thermodynamic state with increasing entropy producing (several consequent thermoblows with negligible time distance between) when relaxation is not in time, the summary influence function rises due to the temperature function K_T :

$$K_T = 1 + \frac{\tau_{in}}{\tau}\left(\frac{T_{\max}}{T_{\min}} - 1\right)N^i, \tag{10}$$

were $T_{\max};T_{\min}$ are maximum and minimum cycle temperatures respectively; τ_{in} is the inertia constant; τ is the stationary mode duration till the moment of measurement; N is the number of thermocycles; i is the power index (0 … 1), dependable on the convergence of temperature gradient and mechanical strain gradient directions.

4.2. The Results of ThM Fluctuation Concerning the Summary Influence Function

The results of ThM fluctuation concerning the summary influence function are estimated at the swift temperature alter and are expressed by the entropy influence function K_E that practically does not depend on temperature but rather a prehistory. With comparing the entropy influence functions of two different production technology ThMs that are exposed to thermoblow affect, the relative entropy influence function p is proposed: $K_{E\_rel.} = \frac{K'_E}{K''_E} = e^{-\Delta S/k} = e^{\zeta}$, were ζ is the factor describing mass-transmission process activation.

As a result, the summary influence function K_Σ at the influence of external thermodynamic fields is determined:

$$K_\Sigma = \left(K_X + K_M\right)K_T \tag{11}$$

Temperature, density, strain and etc. gradients created by the external effect in ThM are subordinated to the same statistical regularities as the gradients that appear consequently of fluctuations in ThM are (according to the sense of a fluctuation-dissipation thermodynamic theorem). At the availability of fluctuations, additional influence functions applicating multiplicatively on influence functions related by the fluctuation affect of external environment are formed:

$$K_\Sigma\left[F\left(T, p, V, ..., t\right)\right] = \left(K_X K_P + K_M K_\Pi\right)K_T K_E \tag{12}$$

This approach is quite precious since it enables us to consider a ThM thermodynamic system in terms of external environment and to penetrate into the essentiality of fluctuation processes, which take place in ThM.

The algorithmic principles of ThM error minimization realized for means of electro thermometry on the basis of the covered above are developed (Fig. 2). The consequent evaluation of influence functions caused by complicated transmission processes is foreseen. Preliminary algorithm settings comprise the values of: 1) ThM ThT; transformation function and its spread; 2) usage conditions: temperature range, environment, exploitation time and mode; 3) ThM manufacture and processing technologies.

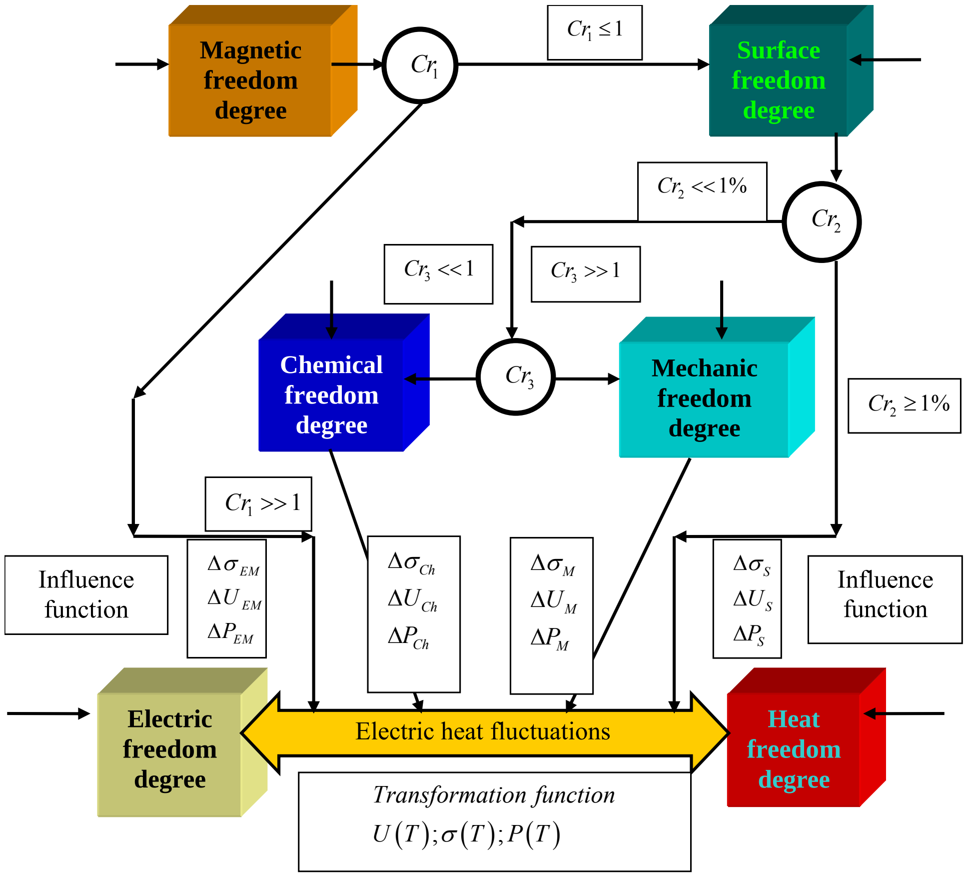

Fig. 2. Transformation and influence functions in thermotransducers: thermoelectric ΔU; thermoresistive Δσ ; thermonoise ΔP.

5. Conclusions

Thermotransducers with the foreseen and managed value of an instrumental error component are developed [4-5] on the basis of statistical thermodynamic approach.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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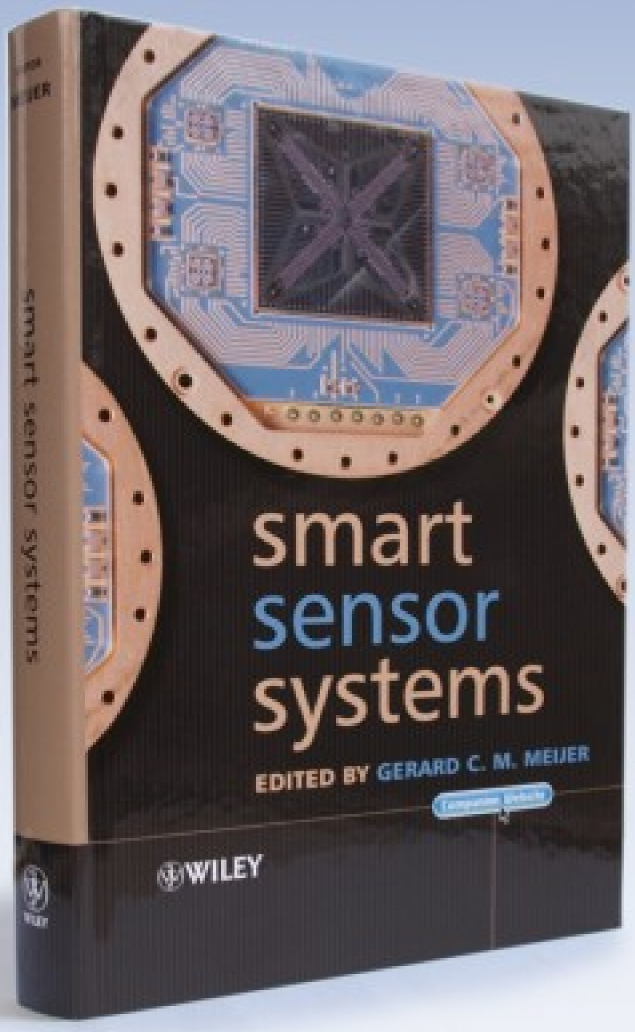
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