MEANS FOR MEASURING
THE THERMAL QUANTITIES

THERMOMETRY: FROM SENSITIVE MATERIAL
TO THERMOELECTRIC THERMOTRANSDUCER

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Abstract. The hard operation conditions of temperature thermotransducers which involve their thermal cycling require special attention to the study of processes occurring in structural elements, in particular in thermometric materials. Operation impacts cause the drift of thermometric characteristics due to the influence of the few factors main of which seem to be the thermo structural stresses.

Therefore, different kinds of sensitive elements were studied. Since traditional polycrystalline thermoelectrodes of thermocouples are inherent in the well-known drawback linked with recrystallization, there were investigated the liquid metals as the thermometric substances, melts, single-crystal materials, and metallic glasses. The need for metal glasses application in thermometry is substantiated, which allows eliminating thermally activated gradients of internal stresses in thermocouples ensuring high reproducibility and low drift of their thermo-EMF comparing to traditional materials.

The analysis of sources of the instability of thermocouples' drift is carried out. It demonstrates the density of heat and electric flows in stressed thermoelectrodes depends not only on temperature and electric potential gradient but also on the stresses' gradient. This causes the dependence of thermometric parameters of both poly- and single-crystal substance of thermoelectrodes on the value and nature of stresses occurring within the operation cycle.

Key words: Temperature, Thermo-EMP, Thermocouple, Amorphous metal alloy, Measurement error.

1. Introduction

The optimal choice of the material of the sensitive element of the thermocouple requires a comprehensive analysis of its physical, chemical, and mechanical properties in functional connection with the range of temperature measurement and other operating parameters [1-2]. The primary condition, however, is the stability and reproducibility of their electrophysical parameters, in particular, such electrokinetic properties as electrical resistance and thermo-EMF. In modern control and measuring devices, the energy of useful signals is only 5… 10 % of the consumed energy; the rest is converted into electromagnetic and thermal energies. In the vast majority, these devices operate under the influence of electromagnetic and thermal fields.

2. Shortcomings

Taking into account the wide variety of physical and chemical properties of materials of different elements of the mentioned devices, it can be predicted that in the process of measurement arises some local thermoelectric effects, which manifest themselves in the form of uninformative electrical voltages and currents.

In the contact zones of these materials that may be copper, silver, silicon, germanium, etc. on which the temperature difference of 20… 50 K is imposed, occurs the thermo-EMF up to 5… 10 mV [3-4]. Therefore, it is important to take into account the probable influence of additional thermoelectric effects on the stability of thermometric properties of thermocouple materials at the stage of their selection and thermotransducer design.

3. The Aim of the Work

The current work aims to research optimal materials for the manufacturing the high-reliable thermocouples for operating the thermotransducers with them in a wide range of temperatures, their cycling, and other hard conditions.

4. The Operation Impacts on the Thermoelectric Properties

Mainly the influence of the above factors on the thermo-EMF, and, accordingly, on the stability of the metrological characteristics of the thermocouples, is considered in [5-8]. Thermo-EMF and electrical resistance are the most sensitive kinetic parameters of thermometric materials to structural defects. Their calculation in the high-temperature range for precious metals, molybdenum, and tungsten, performed within the framework of Mott's ***s-d*** scattering model, has demonstrated that the temperature dependences of the mentioned properties largely depend on the type, function of the state density and the location of Fermi energy levels.

Investigation of the dependence of thermo-EMF on the deformation degree made it possible to establish that the thermo-EMF, caused by plastic and elastic deformations, is of different signs; and the change in thermo-EMF of the deformed metal is determined

mainly by changes in the electronic structure near the Fermi level. The hardened metal has a fairly long-time-interval (1… 10 hours) markedly increased, relative to the equilibrium, the concentration of vacancies. Its thermo-EMF regarding the annealed metal is proportional to the concentration of excess vacancies. Thus, when hardening silver, from lower temperatures to the melting temperature, the growth of thermo-EMF, measured at 823 K, is exponential, which corresponds to the content of excess vacancies and quenching temperature.

Influence of the impurities on thermo-EMF is additive [9] and determined by the slope of Nordheim – Gorter lines, and the change in electrical resistance is associated with the differential thermo-EMF depending on:

$$\Delta S = (S_i - S_0) \cdot \Delta\rho / (\rho_0 + \Delta\rho),\qquad(1)$$

where S_i is the thermo-EMF of impurity, S_0 is the thermo-EMF of the metal matrix at a certain temperature; ρ_0 is an electrical resistance of the matrix at a certain temperature; ΔS is a change of thermo-EMF, caused by the impurities impact; $\Delta\rho$ -is the change in electrical resistance caused by the impurities.

It is known that impurities cause the local deformations associated with the localization of electric charges around their immediate environment in a certain microvolume. Therefore, to interpret the effect of impurities of low concentrations on the kinetic properties of materials, we can use a model of configurational localization of valence electrons.

According to the mentioned model, the solute atoms change their electronic configuration in the direction of convergence with the electronic configuration of the solvent atoms by redistribution of valence electrons. However, atoms that have close to filling, or half-filled *sp-* or *d*-shells, complete them by the collectivized electrons of the solvent atoms to the nearest stable *sp³*-shell [10]. As a result, decreases the concentration of collectivized electrons, scattering of which on *d*-states determines the value of thermo-EMF, in particular, of transition metals and their alloys.

The considered changes in thermometric properties relate to the influence of impurities of low concentrations ($\leq 10^{-3}$ mass %), However, impurities often saturate materials to the solubility limit, forming segregations and the second phase, the effect of which on thermometric properties of thermoelectric materials is difficult to predict. According to [9], the change of thermo-EMF is determined by the change in electrical resistance. But, after heating in a gas environment at temperatures exceeding 1273 K, the electrical resistance and its temperature coefficient for platinum undergo the significant changes, while the thermo-EMF - almost unchanged. The same amount of impurities, being in the material in different states (solid solution or second phase), impacts non-similar on thermo-EMF. Thus, in metals with impurities whose levels are split by the crystal field, non-elastic scattering of conduction electrons on the impurities causes a sharp increase in thermo-EMF, relative to its standard value, proportional to temperature [26].

Thermo-EMF is extremely sensitive to various kinds of heterogeneities, creating a gradient of stresses along the thermoelectrodes, which in turn can cause the local inhomogeneities of thermo-EMF and alters the integrated value of thermo-EMF of thermocouples [12]. The latter can be supplemented by a recrystallization factor.

5. Materials with unique properties in electrothermometry

Electrical resistance and thermo-EMF are the most sensitive kinetic parameters of materials, which depend on a row of the factors, such as temperature, structure, impurities and their location, lattice defects, etc. They undergo some changes while temperature measuring. According to [13], such changes in thermo-EMF. in thermoelectrodes can be explained within the framework of the general theory of thermoelectric phenomena. It is usually assumed that the state of the material is permanent from point to point, which corresponds to the unchangeable specific Gibbs energy of the material or its chemical potential. Only two thermodynamic forces causing thermoelectric effects are considered. They are the temperature and the electric potential gradients. However, for the stressed thermoelectric material, due to the structure defects, the stress distribution becomes inhomogeneous. The Gibbs energy per volume unit of material increases. Its increment is estimated basing the dependence: $\sigma^2/2E_0$, where σ is the stress value; E_0 is the elasticity modulus. It can be argued that arises another thermodynamic component, determined by the change in the Gibbs energy of the material and estimated by the expression: $(\sigma/E_0) \cdot \nabla\sigma$. The contact potentials' difference also depends on the stresses' gradient. The considered causes the dependence of thermo-EMF on the value and nature of stresses occurring in the thermoelectrodes.

Single-crystal materials. The elimination of some causes of instability in the thermometric properties of thermocouples is possible for the thermometry of single-crystal materials. The latter are plastic, do not recrystallize at high temperatures, their structure is quite steady as well as electrophysical properties, and the diffusion factor of impurities is low. In particular, for molybdenum wire, this aspect of the problem was investigated in [14]. Besides, in polycrystals, the value of the gradient of mechanical stresses, in the order of

magnitude, is equal to the ratio of the stress to the average diameter of the grain, and in single crystals - to the average length of the crystal. Since the crystal length significantly exceeds the average grain diameter, the gradient of mechanical stresses in single crystals is significantly smaller than in polycrystals, and therefore the stability and reproducibility of thermometric properties of thermoelectrodes in the single crystal state are much higher. This aspect was studied for molybdenum wire.

Also, in polycrystal materials, the value of the gradient of mechanical stresses is equal to the ratio of the stress to the average grains' diameter, and in single crystals - to the average crystal's length. Since the latter significantly exceeds the grain diameter, the gradient of stresses in single crystals is sensibly smaller comparing with polycrystals. Therefore, the stability and reproducibility of thermo-EMF in the single crystal thermoelectrodes are much higher.

Liquid metals. Some components of the thermometer's drift are significantly reduced while using liquid metals as thermoelectrodes of thermocouples. Thus, there is no long-range order in the melt, which automatically excludes the main sources of the instability of the thermometric properties of solid-phase materials of sensitive elements [15]. However, the widespread use of liquid metal-based thermocouples is inhibited by two main factors: 1) the aggressiveness of the liquids concerning the transducer fittings; 2) the large contact area with the surface of the fitting causes the liquid-metal sensing elements become contaminated, and therefore the thermocouple readouts drift.

Metal glasses. The disadvantages of liquid metal sensitive elements can be largely eliminated by using a new class of materials - metal amorphous alloys, or, as they are called - metal glasses (MG), which are formed using high-speed tempering. Their electrophysical properties are close to the properties of the corresponding melts, and the mechanical ones exceed the similar properties of the best poly- and monocrystalline samples [16]. An important feature of MGs is that their structure is both micro- and macroscopically homogeneous, and therefore, in comparison with polycrystalline materials, they are practically insensitive to the details of the structural state. Amorphous MGs are characterized by high corrosion resistance and durability, which is typical for materials of the highly homogeneous structure. These properties arouse increased interest in MGs as to promising materials for sensitive elements of precision measuring transducers.

The application of MGs in thermometry allows minimizing thermally activated inner stresses in thermoelectrodes and to ensure high reproducibility of performance [17]. It should be noted that the phenomena of electric charge transfer in MGs and liquid metals are largely similar. The figure demonstrates the course of the typical temperature dependence of the resistivity of the MGs in the amorphous, crystalline, and liquid states.

Since MGs occupy an intermediate position between opposed structural states of matter - liquid and solid and combine their best properties, therefore there exists the reason to become promising materials for producing the measuring transducers of thermometry. The specific resistance of MGs which in the amorphous state is 10 - 20 % higher than the level predicted for melts by the modified Faber – Ziman theory, is a consequence of the manifestation of "imperfection" of the structure of metallic glasses concerning classical melts.
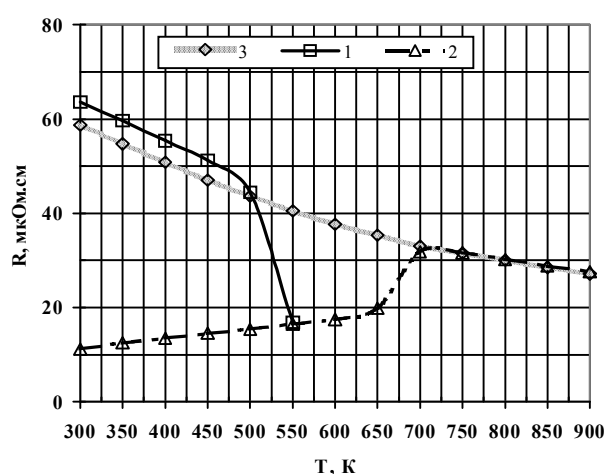

Figure. Temperature dependence of the electrical resistivity MG of the in the amorphous (1) and crystalline (2) states

6. The Way from Sensitive Material to Thermoelectric Thermometer. Determining Operational Parameter - Action of Cyclic Temperatures

In thermoelectric materials that are homogeneous and isotropic, thermal stresses during operation, as a rule, do not occur or are insignificant. However, polycrystalline materials of thermoelectrodes of thermoelectric thermometers are not considered to be homogeneous as well as monocrystalline materials are not isotropic. Their impact on performance must be characterized by parameters that can be taken into account and which must be observed during the operation of thermometers. First of all, this includes the impact of purity of the thermometric material, especially non-metallic inclusions, the precipitations of 2 phases for polycrystalline materials; anisotropy of coefficients of thermal expansion, electrical resistance, and thermo-EMF in single-crystal materials. Besides, polycrystalline materials are characterized by changes in thermo-EMF [18], due to recrystallization processes, annealing, and

increasing mechanical stresses caused by processes of various origins. In general, the simultaneous action of several types of thermal stresses in the presence of a corrosive environment activates much more powerful processes of combined destruction [19] compared to the total action of each factor. As a result, the direct cause of thermocouple of thermoelectric thermometer failures operating in particularly difficult conditions is the corrosion thermal fatigue [20].

If a rapid change in temperature causes a rather complex process of inducing the dynamic nature of changes in thermo-emf or calibration characteristics of thermometers, the regular thermal cycling of the latter fundamentally changes the nature of the action; it leads to metrological failure of the thermometer when its characteristic drifts beyond the permissible limits. Note that metrological failure always leads to mechanical failure, i.e. to the break of the electrical circuit of the thermometer, which mainly occurs in the hot-junction zone, where the highest intensity of all mechanic-structural and chemical processes is recorded.

Fatigue of thermoelectrodes, under the action of cyclic thermomechanical loads, is often associated with the concentration of mechanical stresses in the structural elements and, in particular, in the mentioned thermoelectrodes. We have studied the relationship between changes in the calibration characteristics of thermoelectric thermometers such as TTR 301-01 type; the level and distribution of mechanical stresses in thermoelectrodes caused by the multiple periodic measuring the melt iron temperature. A replaceable package of the thermometer with a C-type thermocouple was intended for 10-… 60-fold immersion lasting 5 s. each in the melt to a depth of 30 mm. The study of changes in characteristics was carried out concerning the standard B-type thermocouple pattern (2nd category).

As it turned out, the statistical distribution of calibration characteristics of the studied thermometers corresponds to the standard normal distribution with $\mu = 0$ and $\sigma^2 = 1$. The latter occurs when a given random variable (change in calibration characteristics) is the sum of a large number of independent random variables, each of which plays a minor role in the formation of the total amount. For thermometers before use, the calibration performed by immersion in the liquid tin at a temperature of 1473-1773 K, have demonstrated a permissible scatter of calibration characteristics within 0.7 K at the level of 3σ. After the 1st immersion in liquid metal, the average calibration characteristic shifted by +0.6 K with increasing standard deviation 3σ up to 1.5 K. 10 immersions of thermometers has led to a shift by +2.4 K with standard deviation 3σ − 2.3 K. The static distribution itself became asymmetric with the appearance of the tail in the direction of high deviations of the calibration characteristic. However, none of 1000

thermometers of one batch failed mechanically, i.e. did not break. However, a 60-fold immersion of the thermometers has led to the destruction of 17 of them. The average calibration characteristics have shifted by + 3.2 K with a further increase in the standard deviation of 3σ to 3.1 K.

Note that at high temperatures the main way to eliminate mechanical stresses that can lead to changes in characteristics is diffusion displacements of atoms and dislocations. However, under conditions of repeated temperature cycling, the diffusion displacements do not have time to occur. Then the processes associated with the formation of microcracks intensify, eventually leading to the emergence of the main microcrack that can break off thin thermoelectrodes. When nano- and then micro-cracks actively develop in the direction of their strengthening to the macrocrack, this is a plastic deformation that leads to destruction due to fatigue of the material. The rate of temperature changes during heating or cooling determines the value of temperature stresses, directly affecting changes in thermo-EMF of thermotransducer. Otherwise, the change in characteristics is more significant the higher is the rate of temperature change. The latter is described by the expression: $\lambda \tau_m / C\rho R^2$, where λ is the thermal conductivity of the material; ρ is the density; R is the characteristic minimal size; τ_m is the duration of heating or cooling; C is the specific heat. Since $\lambda / C\rho R^2 = 1 / \varepsilon$ (ε is an index of thermal inertia), the criteria for the rate of heating or cooling can be expressed as follows. If $\varepsilon / \tau_m \gg 1$, then the rate of change of the thermometer temperature is significant; if $\varepsilon / \tau_m \ll 1$, then the rate is insignificant.

7. Conclusions

The hard operation conditions of temperature thermotransducers which involve their thermal cycling require special attention to the study of processes occurring in structural elements, in particular in thermometric materials. Operation impacts cause the drift of thermometric characteristics due to the influence of the few factors main of which seem to be the thermo structural stresses.

The mentioned is proved by the performed studies. Excluding the traditional polycrystalline thermocouples inherent in the recrystallization impact, the modern materials such as liquid metals and melts get rid of this drawback. Single-crystal materials also are characterized by the low intensity of thermo structural stresses, so its thermometric characteristics are much more stable. The metal glasses are in a similar situation since thermally activated gradients of internal stresses that cause the thermocouple's drift are absent here. Therefore, their reproducibility of thermo-EMF is the best, and the drift of their thermo-EMF is the lowest compared to traditional materials.

The analysis of sources of the instability of thermocouples' drift is carried out. It demonstrates that the density of heat and electric flows in stressed thermoelectrodes depends not only on temperature and electric potential gradient but also on the stresses' gradient.

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Conflict of Interests

Conflict of interest while writing, preparing, and publishing the article as well as mutual claims by the co-authors is absent.

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