ДОСЛІДЖЕННЯ РІДИННИХ МІКРОТЕРМОМЕТРІВ

DEVELOPMENT OF LIQUID-IN-TUBE MICROTHERMOMETERS

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Анотація. Існує низка проблем, які повинна вирішити мікро- й нанотермометрія, щоб забезпечити подальший прогрес та промислове освоєння виробництва й застосування мікрооб'єктів. Найпершою з них вважається визначення підстав застосування до цих об'єктів поняття "температура" подібно до того, як воно застосовується до макрооб'єктів. Наступною проблемою є оцінювання змін температури контрольованого об'єкта внаслідок акту термометрування, причому незалежно від застосування контактних чи безконтактних методів.

У роботі проведено дослідження на основі оптимізації основного рівняння стану термодинаміки в мікро- та нанообластях. Внаслідок його розв'язання встановлено термодинамічні фактори, що визначають метрологічну характеристику рідинного мікро- і нанотермометра, а також встановлено чинники впливу. З'ясовано, як і наскільки змінюються термометричні характеристики рідинних термометрів у міру зменшення їхніх лінійних розмірів із переходом у мікро- і надалі у нанообласть. Показано, що термометрична характеристика кардинально змінюється зі зменшенням лінійних розмірів, оскільки переважною термодинамічною силою, що визначає чутливість до температури, стає сила поверхневого натягу. Разом з тим, важливим стає фактор співрозмірності контрольованого об'єкта та термометра, проектованого й застосовуваного для вимірювань. Цей фактор визначає методичну похибку вимірювання температури розглянутим термометром. Остання стає доволі значною за умови термометрування об'єкта, співмірного за об'ємно-теплофізичними властивостями з термометром.

Для мікро- і нанотехнологій питання створення нанотермометрів набуває визначального значення, позаяк мінімізація методичної похибки до рівня, нижчого від 1 %, означає, що розміри разом з теплоємністю та питомою вагою термометра повинні бути на порядок меншими за відповідні параметри контрольованого об'єкта.

Ключові слова: рідинний мікротермометр, методична похибка, основне рівняння термодинамічного стану, термочутливий матеріал, метрологічні характеристики.

Abstract. Consideration of the liquid-in-tube thermometers envisages that the performance depends on their linear sizes and the row of thermophysical properties. Methodic error is defined by the ratio of the complex parameters that take into account the mentioned characteristics of the measured object and the thermometer. We consider the liquid-in-micro tube thermometers for measuring temperature. Permanent development consists first in minimization of their sizes due to the continuous diminishing of electronics production operation control of which is realized with help of nanosensors, nanoelements, and nanosystems.

Key words: Liquid-in-micro tube thermometer, Methodic error, Major equation of thermodynamic state, Thermosensitive substance, Metrological characteristics.

Introduction

In order to measure temperature, we should improve thermometers' sensitivity without losing the precision. In the world of nanotechnologies, unlike in the case of macro objects, where accuracy of research can be improved by extending the scope of the experiment, improving measurement conditions, and minimizing the influence of external factors, we face the problem of comparing expediency and significance of energy interference when using the measuring instrument, for the purpose of determining quantitative characteristics of an object, as well as the problem of the reproducibility of research results obtained with the help of different instruments of the same type.

On the other hand, nanotechnologies develop the methods of influence on materials, which are aimed at creating miniature and super-miniature devices, including those in which dimensional quantization plays the key role. These are methods of applying thin and superfine films during thermal evaporation, ion beam sputtering, and plasmochemical precipitation; ion implantation in semiconductors; plasmochemical etching of structures; various methods of annealing crystal lattice defects (laser annealing, electron beam annealing). Such technologies are being developed and are widely used when manufacturing integrated circuits for microelectronics, acousto-optic electronics, and micromechanics, as well as for the synthesis of new materials. In the recent decades, these technologies have been used to create devices based on nanoscaled objects (quantum wells, wires, dots). If a technological operation still requires high temperatures, the process is not performed in inertial tempering furnaces, where there are several dozens of substrates at the same time. It is instead performed in individual treatment reactors, where a single substrate is heated much (hundreds of times) faster due to the effect of powerful optical

radiation, while reactor walls remain practically cold. Typical characteristics: substrate heating rate reaches 30 – 100 K / s, heating time is 10 – 30 s (for comparison, in tempering furnaces, heating rate is only 0.1 ÷ 0.3 K / s, and heating process takes about 1 hour). Therefore, it is important to develop fast-response temperature sensors, which, however, may have a significant methodic component of measurement error due to the discrepancy between their size and the size of the monitored object.

Aim of work

The aim is the complex study of fast-response temperature microsensors with their metrological characteristics including the estimation of the methodic errors.

1. Liquid-in-tube thermometer, peculiarities of design and metrology

1.1. Microthermometers and their design.

Nanothermometers with carbon nanotubes are the most commonly used ones; they resemble a typical mercury thermometer which has been reduced in size by billions of times. A carbon nanotube is arranged in several concentric cylinders with capped ends with a length of about 10 microns and a diameter of about 75 nm – this is the sensitive element of a nanothermometer. Metallic gallium, which fills the internal space of a nanotube, is used as a thermosensitive substance (Fig. 1). When heated, the temperature of a stem of gallium rises, and an oxide layer is formed; due to its properties, the height of the metallic stem settles and can remain in this position for a long time, which is convenient when taking readouts [1]. However, nanothermometers are inherent in the drawbacks: repeatability of metrological characteristics and their uncertainty caused by the energy exchange between them and monitored object.

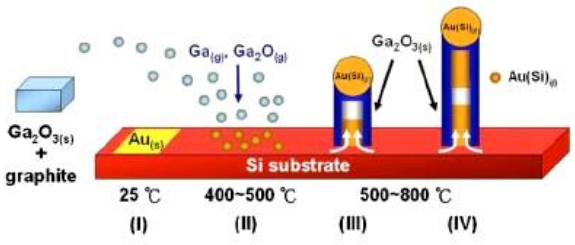

Fig. 1. Scheme of micro thermometer manufacturing [1]

An important aspect of further progress in nanotechnologies is the establishment and reproduction of the needed temperature mode of manufacturing with help of designed microthermometers. This issue has not been fully addressed yet, because it required both the development of nanotechnology (in particular, manufacture of micro- and nanothermometers), as well as the development of metrology – the emergence of nanothermometry. These outlined tasks contributed to the further advancement of nanotechnologies. Production of quantum-dot diodes as highly efficient light sources can serve as an example. For their manufacture, it is necessary to maintain the temperature regime ~ 1300 ^{o}C with the permissible error not exceeding ± 2 ^{o}C, otherwise the output of finished products is reduced by 5 times.

1.2. Influence of the dimensions of thermometers on their metrological characteristics. Liquid-in- (micro and nano) tube thermometers are among the first thermometers that were massively used, because they do not require additional devices and energy sources. Macrosized types of thermometers include mercury-filled thermometers, non-mercury-filled thermometers (alcohol, xylene, and toluene thermometers, which are used for measuring temperatures of minus 200 ^{o}C), and helium thermometers (when measuring temperatures of up to 120 °C), etc. Their production is rather trivial and consists in the superficial forces applying for the filling up the micro- and nanotubes with the thermosensitive substance. Nevertheless, metrological characteristics of the similar thermometers at their diminishing were not specially considered yet.

Let's analyze the sources caused by the effect of thermodynamic forces and flows on a temperature sensitive substance of a thermometer under the conditions of a reduction of its size into the micro- and nanodomain [2]. They lead to the formation of a calibration curve and to its change as a result of the effect of impact function. The latter forms an instrumental component of thermometer's error in case of a change in the thermodynamic state of a thermosensitive substance. In order to assess the influence of various factors on the readouts taken using thermotransducer during different transfer processes, the Gibbs and Gibbs–Duhem equations were used.

The effect of complex transfer processes in a thermodynamically isolated thermometric substance which fills a liquid-in-tube thermometer may be presented as follows. Volume transfer processes and surface transfer processes form the calibration characteristic of this thermometer; and the former or the latter processes prevail, depending on the thermometer size, or rather on the size of thermosensitive substance. In addition, other transfer processes can become responsible for the impact function formation.

In linear thermodynamics, when a thermodynamic system of this substance is near-by the equilibrium state,

the existing thermodynamic flows J and forces X are linked in accordance with the Onsager reciprocal relation:

$$J_i = \Sigma(\beta_{ij}X_j)j \ (i, j = 1\ldots l),$$
$$\text{where } \beta_{ij} = \beta_{ji},\ i, j = 1\ldots l)/$$

In the case of a liquid-in-tube thermometer, such forces may include forces of mechanical degree of freedom; superficial degree of freedom [3], and thermal degree of freedom. Then the system of transfer equations for the thermometric substance of thermometer looks as follows:

$$\begin{cases} I_V = -L_{11}\nabla V - L_{12}\nabla T - L_{13}\nabla M \\ I_h = -L_{21}\nabla V - L_{22}\nabla T - L_{23}\nabla M \\ I_T = -L_{31}\nabla V - L_{32}\nabla T - L_{33}\nabla M \end{cases}, \quad (1)$$

where I_v, I_h, I_T are flows of the transfer of thermosensitive liquid due to changes in volume; changes in surface tension, and temperature changes respectively; Lij are transfer coefficients. As a rule, thermometers measure temperature in areas where the spatial gradient of temperature is extremely small. Then (1) changes into:

$$\begin{cases} I_V = -L_{11}\nabla V - L_{13}\nabla M \\ I_h = -L_{21}\nabla V - L_{23}\nabla M \end{cases} \quad (2)$$

The 1st equation (2) describes mechanical flow as a flow of thermosensitive liquid movement under the influence of thermodynamic forces caused by the gradient of its volume and the gradient of its surface area. The 2nd equation (2) is to the flow of transfer of superficial degree of freedom – the flow of reduction (increase) in the size of the stem of liquid under the influence of thermodynamic forces described above. Using these equations, we can obtain an equation for the graduating characteristic of a thermometer with a liquid-in-micro tube sensitive element for the micro-world.

In macroworld the consideration for a liquid-in-tube thermometer under the condition of neglecting superficial force, when the diameter of thermometric tube is quite large and thermosensitive substance is practically uncontractible, could derive the equation describing the interrelation of the volume of the mentioned substance and its temperature:

$$V=Vo(1+\alpha_V\Delta T)$$
$$\text{or} \qquad \Delta V = V_o\,\alpha_V\Delta T \quad (3)$$

Here, V_o is the initial liquid volume; a_V is the thermo expanding factor. The latter indicates the extent of alteration in the initial liquid volume 1 m³ at the rising of temperature for 1 K. Considering that a spherical container for liquid of the diameter D in the spheroidal lower part of a thermometer practically does not change its dimensions with temperature raise, whereas the liquid itself is expanding in volume, the growth in volume is displacing into the thermometric tube of the diameter d. It gives the possibility to bind the changes of column sizes Δh of a thermometer and the increase in the temperature ΔT by the proportionality:

$$\Delta h = A\,\Delta T, \text{ mm} \quad (4)$$

Here, A is the constant. It is worth noting that the leading or diagonal member of the matrix corresponds to thermometer stem movement, whereas a member associated with the effect of surface tension – a non-diagonal member – causes problems with measuring temperature on the basis of its projection on the scale due to the distortion of the surface of its edge. Therefore, the meniscus can be either concave or convex, which depends on whether thermosensitive liquid is wetting tube walls. Meniscus curvature results in errors in liquid-in-tube thermometer readings in the macro-world.

In micro- and nanoworld. Under the condition of neglecting the influence of mechanical freedom degree and thus caused transposition processes, two interrelated factors, superficial tension and temperature that determine the shape of a graduating characteristic of a liquid-in-tube nanothermometer, could be found from the equation (2).

Our previous study [4], considered the Eötvös rule [5] and Rayleigh-Shield equation that determines the dependence of superficial tension of any clear liquid on the temperature: the coefficient of superficial tension is a linear function of temperature. The rule is proved correct for the majority of known equations. If one has constructed the graph of dependence of a superficial tension coefficient on the temperature, he could observe a quite straight line intersecting the X-axis at the critical temperature. For example, in the case of water, this temperature makes 547 K, the coefficient of superficial tension is equal to zero.

The temperature-dependence of superficial tension could be depicted for all liquids so that the data are placed along one common curve. In order to perform this, we should know molar mass, density or molar volume of the appropriate liquid. If V is the molar volume and T_c is the critical liquid temperature, then the coefficient of superficial tension γ is defined as:

$$s\,V^{2/3} = k\left(T_c - 6 - T\right) \quad (5)$$

Here, k is a constant for all liquids (Eötvös constant makes 2.1×10^{-7} J/K mole$^{-2/3}$). Having idea about the molar mass M and density ρ: $V = M/r$, the molar volume V could be determined. It is useful to transform the formula so that the units mole$^{-2/3}$ are absent. Avogadro number could be used for that purpose:

$$s = k'\left(\frac{M}{r\,N_A}\right)^{-2/3}\left(T_c - 6 - T\right) = k'\left(\frac{N_A}{V}\right)^{2/3}\left(T_c - 6 - T\right) \quad (6)$$

Thus, taking into account (5), (6), the equation of graduating characteristic of a micro thermometer with a liquid-in-tube sensitive element could be found (Fig. 2):

$$\Delta h = \frac{4k'}{g\,d}\left(\frac{N_A}{V}\right)^{2/3}(T_c - 6 - T) = C(T_c - 6 - T) = \\ = C(K - \Delta T). \quad (7)$$

Here, C is a constant, $K = T_c - T_0$; $\Delta T = T - T_0$.

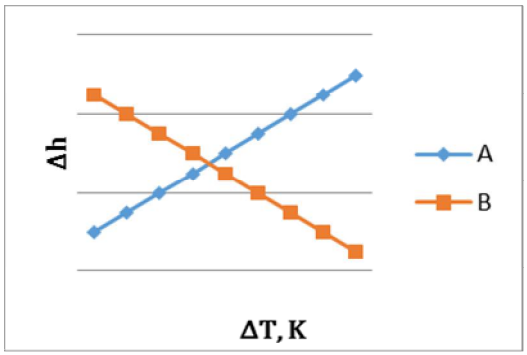

Fig. 2. Graduating characteristics $\Delta h = F(\Delta T)$ of macro (A) and micro (B) thermometers

Evidently, the constant C of graduating characteristic of a micro thermometer with a liquid-in-tube sensitive element decreases, when the tube inner diameter d grows. It is the main difference between the latter and the macro thermometer which sensitivity falls with diameter.

Considering the equation system (1), we can deduce that while liquid-in-tube micro thermometer application in the area of temperature gradient, the effect of thermo capillary flow arises. It lies in the appearance of superficial tension difference and thus, in the difference of capillary pressure in the liquid, which leads to the transposition of the liquid itself in the unevenly heated medium. This factor could become determinative in forming the additional source of a thermometer error in nanoworld. Anyway, it is already applied in nanotechnology while manufacturing nanoengines [6] whose motive force is the effect of a thermo capillary flow.

We'll underline that the 2nd equation (2) describes thermodynamic flow as a flow of thermosensitive liquid reducing / increasing under the influence of thermodynamic forces that are caused by gradients of volume and of surface area. The latter becomes predominant in the microworld and determinative in the nanoworld. Thus, in a liquid-in- micro tube thermometer, we deal with movement of liquid relatively to a certain mark due to changes in superficial force, caused by temperature changes. This movement serves as the basis for the graduating characteristic formation. The effect of a non-diagonal term (mechanical degree of freedom) leads to the formation of deviations from the graduating characteristic that is, to an error in temperature measurement made by a micro thermometer.

1.3. Methodic error of measurement. *In the macroworld*, it is assumed by default that linear dimensions of a sensor do not exceed 1/10 of the linear dimensions of a controlled object (the ratio of volumes is 1/1000). Then the relative procedural component of an error in temperature measurement taken by a sensor of the thermal converter does not exceed 1/1000 or 0.1 %. As a rule, this value is lost among a number of other components of measurement error. In particular, it is smaller than the instrumental component. Therefore, there are grounds not to consider and not to take into account methodic component of measurement error when measuring temperature in the macro-world. Moreover, in case of a contact method of measurement, information about the state of the monitored object is transferred to the sensor as a result of heat exchange between them. If there is thermodynamic equilibrium (if there is also long-term thermal contact), measurements are classified as equilibrium, and in the case of short-term contact they are considered as non-equilibrium.

In the microworld, when measuring temperature of objects, a sensor (for example, an ultra-thin wire or a laser beam which contains temperature information) violates thermodynamic equilibrium of an object to such an extent that there arises a significant methodic component of an error. Moreover, in case of a contact method of measurement, information about the state of the controlled object is transferred to the sensor as a result of heat exchange between them.

Let us assume that temperature of controlled object is a somewhat lower than of thermotransducer. If there is long-term thermal contact of the sensor and the object, the latter is heated or cooled as a result of heat exchange Q_H:

$$Q_H = c_{ob} m_{ob} (T_x - T_0), \quad (8)$$

where T_0 is the temperature of the controlled object before measurement; T_x is the temperature of the monitored object, which is established due to its thermal contact with the sensor; c_{ob}; m_{ob} are specific heat of an object and its mass, respectively. It should be noted that in this case the sensor will measure the resultant or weighted average temperature of the pair "monitored object – sensor", which exceeds the initial value of the temperature of the object by $\Delta T_{met} = T_x - T_0$. While measuring the cold object surface, the sensor cools down, transmitting heat Q_C to object:

$$c_{ob} m_{ob} (T_x - T_0) = c_{sen} m_{sen} (T_{sen} - T_x), \quad (9)$$

$$c_{ob} m_{ob} \Delta T_{met} = c_{sen} m_{sen} (T_{sen} - T_x). \quad (10)$$

If we express the mass in terms of the specific mass of material w and volume V and also assume that the object and the sensor have the same form of a flat disk, we obtain:

$$c_{ob} w_{ob} V_{ob} \Delta T_{met} = c_{sen} w_{sen} V_{sen} (T_{sen} - T_x), \quad (11)$$

$$c_{ob}w_{ob}D^2H\Delta T_{met}=c_{sen}w_{sen}d^2h(T_{sen}-T_x). \quad (12)$$

where D; d are the diameters of the disks of the monitored object and the sensor, respectively; H; h are the heights of the disks of the monitored object and the sensor, respectively. After dividing the left and the right part (11) by T_x, we obtain the thermal energy balance equation for the long-term contact of the sensor and the monitored object:

$$c_{ob}w_{ob}V_{ob}\delta T_{met}=c_{sen}w_{sen}V_{sen}\frac{T_{sen}-T_x}{T_x}=$$

$$=c_{sen}w_{sen}V_{sen}\left(\frac{T_{sen}}{T_x}-1\right) \quad (13)$$

Hence, we express the relative methodic error component in temperature measurement as the required value:

$$\delta T_{met}=\frac{c_{sen}w_{sen}V_{sen}}{c_{ob}w_{ob}V_{ob}}\left(\frac{T_{sen}}{T_x}-1\right)=$$

$$\frac{c_{sen}w_{sen}d^2h}{c_{ob}w_{ob}D^2H}\left(\frac{T_{sen}}{T_x}-1\right)=$$

$$\frac{c_{sen}w_{sen}sh}{c_{ob}w_{ob}SH}\left(\frac{T_{sen}}{T_x}-1\right) \quad (14)$$

where S; s are the areas of the end face of disks of the monitored object and the sensor, respectively. As we can see, if thermo-physical and mass-dimensional characteristics of a sensor and the monitored object are similar, methodic component of measurement error depends on the ratio of their volumes or linear dimensions. In Fig. 3, the value of relative methodic component of an error in the measurement of temperature of an object taken by a sensor is shown for the ratio of their volumes – 1:1, modified, taking into account thermo-physical and mass-dimensional characteristics.

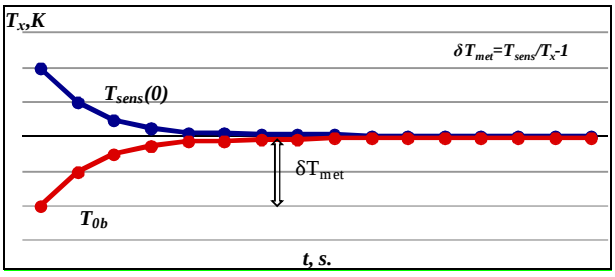

Fig. 3. Temporary - temperature changes in the event of contact of a "warm" sensor at initial temperature T_{sen} (0) with a "cold" object at initial temperature T_o :
$c_{ob}w_{ob}V_{ob} = c_{sen}w_{sen}V_{sen}$

Conclusions

1. The development of nanotechnologies is impossible without measuring the temperature of micro- and nanosized objects, which requires further development of liquid-in-tube thermometers, whose thermometric characteristics vary depending on linear dimensions.

2. The force of the surface tension is decisive in the formation of the graduating characteristic of the microthermometer. This characteristic is inversely proportional to the temperature, since the surface tension forces at a certain high temperature becomes zero. This determines the upper limit of the use of a liquid-in-tube microthermometer.

3. An important aspect is the ratio of thermo-physical and mass-dimensional characteristics of sensitive element of thermometer and of the monitored object; it determines the methodic error component of temperature measurements. For nanotechnology, the issue of the creation of nanothermometers becomes crucial, since minimizing the methodic error to a level below 1 % means that the each linear dimension of the thermometer should be 1 order smaller than the size of the monitored object.

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