

Double glass drag spinning method of fabrication of thermoelectric coaxial cables and microthermocouples

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A double softening glass drag spinning method (DSGDSM) with thermal furnace heating was developed for fabrication of long glass coated coaxial microwires on the basis of semiconductor and semimetal. The technological path of fabrication of coaxial thermoelectric microwires base on bismuth telluride semiconductors is described. Several mechanical and physical parameters of coaxial wires, which underline their advantages, are presented. The method of manufacture of microthermocouples on the basis of coaxial microwire DSGDSM technology of fabrication is reported. Due to small diameters and thicknesses of thermoconductors as well as glass coating the obtained long coaxial microthermocouples are sufficiently flexible, have high sensitivity and can be used for different thermal management application.

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1. Introduction

In modern systems for temperature measurements and monitoring most often there are used thermal detectors based on transformation of measured value into electric signal, such as resistance thermometers and thermocouples. For temperature measurement by contact of different solid, liquid, gaseous or biological objects there are successfully used thermocouples of different materials, such as chromel-copel, chromel-alumel, copper-constant, platinum-platinorodium, etc. and their electric sensitivity is of the order of 2.54-6.5 $\mu\text{V/K}$.

Due to the miniaturization of devices and the needs of local thermal management, the problem of fabrication of detectors with both sensitivity and high reduced dimensions are of special importance. One of the routs in solving some aspects of this problem is offered by softening glass drag spinning method (SGDSM) of thermoelectric microwires in glass isolation [1-3].

In order to increase the precision of electric signal measurement, in fabrication of thermocouples it is necessary to use semiconductor materials, in particular based on the best thermoelectrics - bismuth telluride [1-3]. The obtained microwires based on this material using the SGDSM method have the following parameters: thermopower of samples with electric conductivity of type p is $\alpha_p=150-300 \mu\text{V/K}$, and of type n $\alpha_n=-100-140 \mu\text{V/K}$. These parameters are higher by about two orders than those of metal used wires and microthermocouples with high performance have been designed and fabricated. Such microthermocouples are manufactured by the procedure of contacting two microwires of different conductivities.

However, in the context of microthermocouple and others device applications are challenging to develop the methods of fabrication of coaxial microwires and cable. For metal based coaxial microwires a lot of methods are

used such as: method of obtaining of coaxial microwires of metals by their deposition in the form of cover on the glass surface of microwire by method of chemical deposition of copper, deposition of platinum in vacuum and method of deposition and annealing of liquid gold on glass cover of copper microwire [4].

Disadvantages of the known methods are the following:

a) at chemical deposition of copper on the glass surface a nonuniform coating is obtained and it is difficult to obtain wires of long lengths ([1], p.158);

b) using method of vacuum evaporation (for example of platinum) it is not possible to obtain long wires and after the evaporation process the wires worsen their elastic properties ([4], p.159);

c) the most qualitative covers are obtained by deposition of liquid gold film on the glass cover surface of the microwire ([4], p.159). However, this method is quite complicated, because it is necessary to introduce the microwire into microbaths of the microcapillary form, through which the microwire is stretched. By this method it is quite difficult to obtain covers of semiconductor materials containing volatile components;

d) the cover deposited on glass is not isolated from the surroundings.

Thus in the present paper we present the first technological results dealing with:

- fabrication of coaxial microwires of metal, semimetal and semiconductor materials in the process of microwire drawing [5],

- manufacture of coaxial glass coated microthermocouples based on bismuth telluride semiconductor materials.

The proposed technology path gives a possibility to simplify the technological process and to improve quality of coaxial microwires. The possibility of fabrication of both p- and n-types microwires in a coaxial structure

configuration open the way of efficient and non-expensive manufacture of microthermocouples with high sensitivity.

2. Double glass drag spinning method for coaxial microwire fabrication

The most important stages of the developed SGDSM method of coaxial microwire fabrication involve the following steps. At the first stage, one should take a glass tube with one end being soldered having the inner diameter 5÷6 mm, wherein several grams of metal, semimetal or semiconductor material in the form of small granules is introduced. After vacuuming up to the pressure of 10^{-5} torr it is soldered and introduced into another tube with one end being soldered of greater diameter, wherein several grams of metal, semimetal or semiconductor granulated material is also introduced. After vacuuming up to the pressure of 10^{-5} torr and soldering double ampule is obtained shown in Fig. 1.

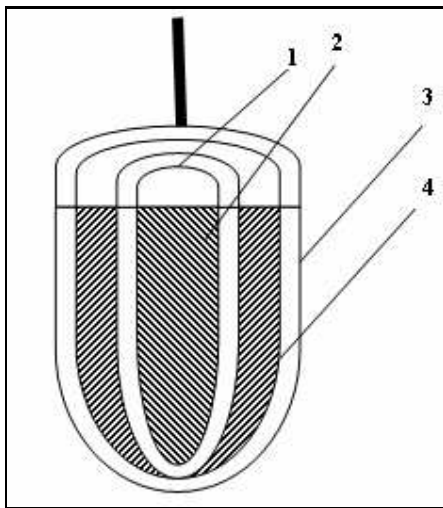


Fig. 1. Double ampule coaxially configured. 1 - the inner glass ampule, 2 - metal, semimetal or semiconductor material, 3 - the external glass ampule, 4 - metal, semimetal or semiconductor material.

As the next step, the double ampoule is introduced into a furnace with resistive heating. The method of obtaining of coaxial microwires is similar to the SGDSM Ulitovsky method, with the exception that in the place of high frequency inductor a resistance furnace is assembled being fed with stabilized electric current. As a function of the furnace temperature, the materials in both ampoules melt, and glass of the ampoules softens.

Then, with the help of a glass stick reaching the ampule bottom a part of the cover is stretched in the form of a coaxial capillary filled with the material on a special receiving device in the form of continuous coaxial conductor with glass cover. In dependence on the furnace temperature, velocity of the ampule falling in the furnace and on the velocity of the microwire drawing on the receiving device it is possible to obtain coaxial microwires of different diameters.

Fig. 2 shows as an example a segment of coaxial microwire obtained of metal, semimetal or semiconductor material.

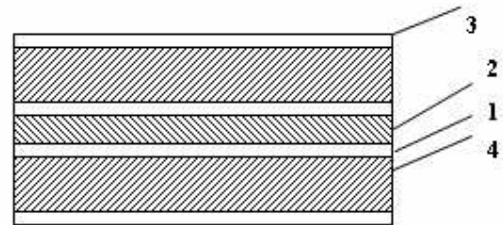


Fig. 2. Sketch of the glass coated coaxial microwire. 1 - isolating layer of glass, 2 - the coaxial microwire core, 3 - the external glass cover, 4 - the cylindrical electrode of metal, semimetal or semiconductor material.

As an example, we present some detailed underlines of coaxial microwire fabrication of thermoelectric semiconductor material of bismuth telluride. In the inner ampule 1 with the diameter 6-7 mm 4-5 g of bismuth telluride with n-type conductivity is introduced, and in ampule 3 (Fig. 1) with the diameter 10-12 mm 4-5 g of bismuth telluride with p-type conductivity is introduced. After vacuuming from the double ampule (Fig. 1), coaxial microwires with the external diameters 20-60 μm are obtained, and the diameter of the core 1 (Fig. 2) with the diameters 10-30 μm , consecutively. In dependence on the material quality, length of microwires can be varied from 10 m up to 100-200 m.

3. Glass coated coaxial microthermocouples

In different applications there are used microwire in glass isolation thermocouple. Usually a layer of metal is deposited on the glass isolation, which contacts by one end with the material of the microwire and which presents a second electrode that gives a possibility to microminiaturize the thermocouple [6]. This method is quite complicated concerning the process of metal layer deposition on the surface of the microwire in glass isolation and formation of contact with the microwire core. This method does not offer the possibility to obtain microthermocouples with lengths long enough and to use them in chemical aggressive media. Our goal was to obtain a coaxial microthermocouple of coaxial microwires by reducing the stages of technological processes in the manufacture of coaxial microthermocouple, which could uses for temperature management in chemical aggressive media [7].

For this purpose there is used a coaxial microwire made of metal and semiconductor materials with different electrical conductivity (of n- and p-types) [1]. When the coaxial microwire is obtained, it is cut in pieces of necessary lengths L as it is shown in Fig. 3, where 1 is the core of the coaxial microwire of metal and semiconductor,

2 is the glass isolation in the cylindrical form, 3 is coaxial cylindrical conductor of another metal and semiconductor with electric conductivity of opposite type, 4 is the glass external cylindrical cover. The end of the coaxial microwire is connected with one pole of the continuous current source, and the second one is introduced into a recipient with chemical solution, which consists of 16 g $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} + 4,5$ g $\text{Na}_2\text{SO}_4 + 27$ g $\text{MgSO}_4 + 0,7$ g $\text{NaCl} + 2,3$ g H_3BO_3 per 100 ml H_2O and which is connected to the other pole of the current source. Solution H_3BO_3 is prepared preliminarily separately, it is dissolved by boiling, and after cooling is added to the basic solution until $\text{pH} = 5.5$ is obtained. For the nickel contact deposition the recipient is connected to the pole plus, and the coaxial microwire - to the pole minus. In dependence on time of deposition and coaxial wire diameter it is possible to obtain contacts of different diameters. For example, for formation of nickel contact on a coaxial microwire with the diameter 40-60 μm at room temperature it is necessary to maintain the electric current density of 5 A/dm² during 30 minutes.

For illustration of the result in Fig. 3 it is shown coaxial microthermocouple obtained of coaxial microwires formed of one microwire 1 of bismuth telluride thermoelectric material of n-type in cylindrical glass isolation 2, the other cylindrical coaxial microwire 3 of bismuth telluride of p-type, covered with cylindrical glass isolation 4, connected by hot contact of nickel 5 with hot terminals 1 and 3 [7].



Fig. 3. Sketch of coaxial microthermocouple. 1 - n-type bismuth telluride thermoelectric material in cylindrical glass isolation 2, 3 - other cylindrical coaxial microwire of bismuth telluride of p-type, covered with cylindrical glass isolation 4, connected by hot contact of nickel 5 with hot terminals 1 and 3.

Due to small diameters and thicknesses of thermoconductors and glass covers the obtained coaxial thermocouple is sufficiently flexible. For example, flexibility rigidity of the microwire with the diameter of 15 μm is 0.4 mm, and for 30 μm it is 2.1 mm.

4. Conclusions

Double glass drag spinning method have been developed for obtaining glass coated coaxial microwire cable on the basis of semiconductor or semimetal materials. The technology paths of the method have been adapted to obtain thermoelectric coaxial microwires on the basis of the bismuth telluride compounds – the best room temperature thermoelectrics. The wires have small diameters of the central core (10-30 μm) and thin thickness of the second coaxial conductors. They have long length and are protected by glass isolation. A new technological route of coaxial microwire fabrication allows to fabricate both thermocouple elements of p- and n-types in one cycle. On this basis new type of coaxial lead telluride microthermocouples with high sensitivity and good mechanical properties have been manufactured.

It was established that in durability and flexibility characteristics the basic role belongs to the glass intermediate layer and coating, because the microwire core of bismuth telluride is very fragile and practically does not make contribution to the microwire breaking durability.

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