The Search of New Ways of Thermoelements Production

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***Abstract*— This article presents the development trends and the areas of thermoelements usage. The basic commutation methods of thermoelements branches and the requirements to the materials for this thermoelements were showed. The main problem concerning producing of quality welded connection was analyzed. The new way of application of antidiffusion layer was proposed. As a part of investigation of diffusion processes, we determined the optimal thickness of antidiffusion layer that will allow to blockade the diffusion of atoms of conductor layer to the semiconductor.**

***Keywords*— thermoelement; commutation; antidiffusion layer; commutation plate; coefficient of diffusion**

I. Introduction

Annual world energy consumption is equivalently 13 TW. To the end of this century, the predicted quantity of population and economy growing will increase more than three times, that will result in the corresponding increase of the world energy consumption [1]. All of this and also the threat of global climate change put the new challenges that define the energy as priority foundation of present time: the search of new, environmentally clean and renewable perspective energy sources [2].

Energy safety is the development of unconventional, in particular, renewable energy sources. That is why the solution of the problem of the energy safety through the increase of the importance of the alternative energy is the key question of both the science and the economy. Furthermore, if in the beginning of 2000 year the main requirement was the increase of the electricity production, then in last 2-3 years the additional conditions bring to the fore: the energy must be produced in the environmentally friendly way; it must be renewable and unrelated to the carbon. Accordingly, the efforts of many scientists directed to the development of «green» energy in which particularly acute feel is needed in the Europe and in the USA [3].

A. Thermoelements Application

In the conditions of swift increase of world energy consumption that leads to the reduction of stocks of natural fuel, there is an unavoidable problem of alternative energy sources searching.

One of perspective variants is thermoelectric transducers that work on the basis of the interconversion of thermal and electric energy.

Mass implementation of thermoelectric transducers can solve the problem of transformation of idle heat that is emitting during the function of machines into electric energy. Thermoelectric transducers can be also of high demand in the production of effective coolers. Moreover, compact thermoelectric coolers can be integrated in the devices that require the local cooling of one or a few parts [4].

It is expected that in the near future, the efficiency of thermoelectric materials will be sufficient to displace the compressor refrigerating units by the thermoelectric. Another advantage of thermoelectrics is the ecological appeal because they do not contain harmful chemical substances [4].

It should be noted, that there are areas, where thermoelectricity is necessary and can not be replaced. Such transducers (Fig. 1) are already used as sources of electricity on space vehicles, in portable refrigeration aggregates, in electronic, medical and scientific equipment, in particular for cooling of infrared transceivers and optoelectronic equipment. However, for the new and economically sound industrial applications of thermoelectric energy transducers, it is necessary to increase substantially their efficiency [2].

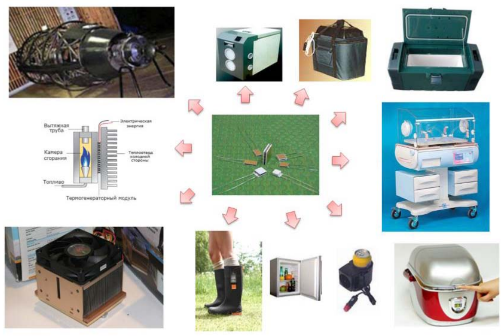

Fig. 1. The variety of thermoelements applications [5]

II. Background

Reliability and longevity are the important characteristics of any devices. At this stage of development of thermoelectric modules (TEM) their reliability and longevity is on a low level. That is why, nowadays, the investigations in the area of

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improvement of TEM construction are carried out with the aim to increase of its lifetime. The most perspective tendency for the increasing of the TEM lifetime is the problem of studying of the barrier coating properties and the method of its application [6].

The analysis of the available experimental data in the area of the development of thermoelectric materials demonstrates [7]:

- the major part of thermoelectric materials is the systems based on the Bi, Te, Se, Sb, Cd, which are used for establishing generative and refrigerative thermoelectric devices;
- the development of thermoelectric materials proceeds the way of the development of multicomponent systems with the introduction of a large number of alloying elements;
- the development of multicomponent systems proceeds the way of the experimental selection of components that are included in the thermoelectric materials;
- the research of the properties of thermoelectric materials is based on the experimental determination of characteristics of the developed composition, that leads to the undue number of small research works in the specified direction.

Currently the problem of the efficient choice of material properties is important for the thermoelectric energy conversion. Therefore it is necessary to analyze the actual thermoelectric properties of materials with one - and two-component composition and also to identify their patterns and interconnections.

From the point of view of the energy conversion efficiency and stability of thermoelectric properties of thermoelectric materials the following requirements should be meet [7]:

- high mechanical and electric strength;
- weak temperature dependence of the characteristics in the operating temperature range;
- high thermoeffectiveness;
- high manufacturability of materials;
- high chemical resistance;
- low cost of the thermoelectric semiconductor materials etc.

As the authors [8] mentioned, nowadays, one of the most effective traditional thermoelectric material that is used for the production of the working elements of thermoelectric devices and equipment is bismuth telluride Bi_2Te_3. The characteristic feature of Bi_2Te_3 single crystal is the presence of cleavage planes, along which it breaks easily. That is why it can be considered laminated with the sufficient approximation. In addition, the Bi_2Te_3 single crystal possesses the sufficiently well-marked anisotropy of the thermal and electrical conductivity. The thermal conductivity of such crystal along the cleavage planes is in 2 – 3 times greater than its thermal conductivity in the direction perpendicular to these planes. It is quite similar to the electrical conductivity of Bi_2Te_3 that is 2.7 times larger along the cleavage planes of p-type material and for the material n-type is 4 – 6 times larger than the conductivity in the direction perpendicular to the cleavage planes. Therefore, the thermoelectric modules are manufactured from the single crystal to maximize the thermoelectric figure of merit in such a way as to the electric current and temperature gradient were parallel to the cleavage planes.

The author [5] notes that among the most commonly used materials for the commutation plates of the thermocouples manufacturing are the Cu, Cr, Ni, Ti, Ag, Au and their alloys.

In spite of the fact that bismuth telluride Bi_2Te_3 is one of the most effective traditional thermoelectric materials, it possesses the sufficiently well-marked anisotropy of properties. Such anisotropy will result in the dependence of the diffusion coefficient and self-diffusion coefficient on the crystallographic directions. The diffusion coefficients for all admixtures are strongly anisotropic and they are also extremely large for Cu, Ag and Au. The high rate of diffusion of Cu, Ag and Au in the direction of the cleavage plane is due to the low bond and large spaces between layers $Te^{(1)}$ – $Te^{(1)}$. The diffusion of the admixtures perpendicular to the cleavage planes is complicated because of the presence of closely packed atoms of the matrix in this direction and more complicated links between them [5]. The authors of work [9] put forward another point of view. It is assumed that the copper (Cu) (or other material of the conductor layer) diffuses quickly along the dislocations, which possess the varied density in the different axis direction. The strong anisotropy of the growth rate of Bi_2Te_3 and its solid solutions leads to the fact that “directed” structure forms during the solidification with planar interface between the solid and the liquid phase. In such “directed” structure the cleavage plane of the grains is oriented parallel to the axis of the ingot (along the normal to the solidification front). The diffusion process of the atoms of the conductor layer into the semiconductor becomes possible due to the formation of such structure. The barrier layers are used to prevent the interdiffusion of the atoms of the conductor and to extend the lifetime of TEM. These layers separate the conductor and the semiconductor at the point of contact and are applied on the surface of the semiconductor in different ways. However, such technology does not always allow to achieve the necessary result, due to the influence of antidiffusion layer onto the structure of the semiconductor material and lifetime of TEM.

III. TEM Production Technologies

Nowadays, there are many methods of commutation of thermoelements (Fig. 2). Among them are the soldering [10], [11], [12], the combined heat pressing of thermoelectric branches and commutation material [13], the thermal spraying of commutation materials in a vacuum or inert gas [13], [14], the methods of the chemical and galvanic deposition of materials on semiconductors [15], the resistance welding [16] and the microwave welding through the powder layers [17], [18].

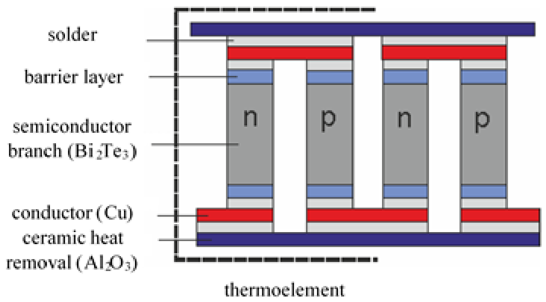

Fig. 2. The scheme of commutation of thermoelement branches [5]

However, all these methods have their disadvantages and may not fully satisfy the requirements as for the quality of welds of semiconductor material with a commutation plate. As for today, one of the most effective welding methods of heterogeneous materials that substantially differ in physical and chemical properties is the diffusive welding in vacuum [19].

Having made literature review a new approach to the producing of the antidiffusion layer with the aim to improve the TEM manufacturing techniques, was proposed. Such layer will be applied as a barrier layer on the surface of the commutation plate.

Cu, Ti, Cr, Ni, Sr, W and Mo are usually used as barrier layers [5]. That is why the optimal material choice of the layer and its thickness, which would prevent the diffusion of atoms of the conductor layer (Cu) into the semiconductor matreial (Bi_2Te_3) is important.

IV. The Investigation of Diffusion Processes

The authors [6] mention that, among the existing methods of applying of barrier layers the main are those that were used to obtain the antidiffusion layer directly on the surface of the semiconductor material. However, we assume that it is reasonable to perform the application of the barrier layer directly on the surface of the commutation plate by ionic implantation.

The investigation of diffusion processes of copper (Cu) into the barrier layer were carried out for the Cr, Ni and Ti antidiffusion layers under the condition that this layers will be applied by ion implantation. The diffusion coefficient D, which is one of the most important quantities that determines the rate of diffusion, was determined using the dependence of the diffusion coefficient on temperature (Arrhenius equation) [20]:

$$D = D_0 \times \exp(\frac{-Q}{RT}), \tag{1}$$

where Q is the activation energy of the diffusion process, which determines the correlation D(T), J/mole; D_0 is the preexponential factor, cm^2/sec; R is the gas constant, J/mole·K; T is the absolute temperature, K (the temperature of exploitation of TEM is $T_{exp} = 350$ºC).

The calculation of the diffusion coefficient was carried out using the mathematical package Mathcad.

The results of the calculation presented in the Fig. 3 demonstrate the highest diffusion coefficient appropriate to the pair of copper conductor (Cu) – nickel barrier layer (Ni). Such results can be explained by the fact that the Ni according to the phase diagrams of binary alloys dissolves in the Cu. As for pair of copper conductor (Cu) – chrome barrier layer (Cr) the results of the calculation demonstrate the lowest value of diffusion coefficient that may indicate the possibility to blockade the diffusion of atoms of the conductor layer (Cu) into the semiconductor material (Bi_2Te_3). It is achieved due to the limited solubility of Cr in Cu. That is why the chrome can be used as an effective barrier layer [21].

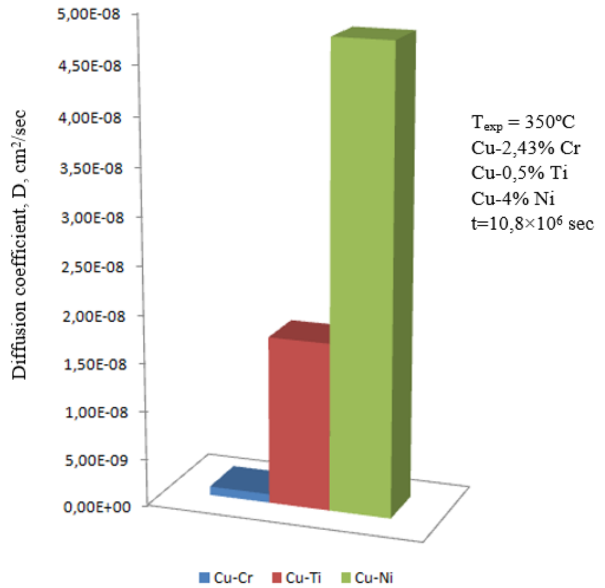

Fig. 3. The comparative histogram of diffusion coefficients of Cu for different variants of barrier layer at the Texp = 350ºC

The Fick's law was used to determine the required thickness of antidiffusion layer, which would certainly block the diffusion of atoms of the conductor layer (Cu) into the semiconductor material (Bi_2Te_3):

$$D = \frac{X^2}{2t}, \tag{2}$$

where X^2 is the average depth of the diffusion layer (the half depth of the diffusion layer was taken into account for the calculation), cm; t is the time of diffusion process, sec.

The time of the diffusion process for the calculation of the average depth of the diffusion layer was taken equal to $10{,}8 \cdot 10^6$ seconds. It is because the average lifetime of TEM is 3000 hours in cyclic mode.

Among the proposed barrier layers chrome (Cr) possessed the lowest coefficient of diffusion of copper (Cu). Therefore, this material was used for calculation of the required depth of the diffusion layer. According to the calculations, the thickness of the barrier layer should be $X_{(Cu\text{-}2.43\%Cr)}$ = 30 – 50 micron. It will ensure the blocking of diffusion of the atoms of the conductor layer (Cu) into the semiconductor material (Bi_2Te_3).

V. Conclusions

1. Taking into consideration of the widespread application of thermoelectric transducers in many industries the necessity of formation of high quality welded connections concerning production of thermoelements is important.
2. The most effective traditional thermoelectric material used for the production of the working elements of thermoelectric devices and equipment is bismuth telluride Bi_2Te_3.
3. The most commonly used materials for the commutation plates of the thermocouples manufacturing are the Cu, Cr, Ni, Ti, Ag, Au and their alloys
4. The diffusion barrier layers of Cu, Ti, Cr, Ni, Sr, W and Mo, which are applied to the surface of the semiconductor material, are used to prevent the interdiffusion of the atoms of the conductor and to extend the lifetime of TEM used.
5. However, such technology due to the influence on the surface layer of the semiconductor requires the improvement.
6. A new approach to the manufacture of thermoelements by creating the antidiffusion layer on the surface of commutation plate using ionic implantation method was proposed as the results of research of diffusion processes in copper barrier layer.
7. It was established that the optimum material for the barrier layer production on the surface of the copper commutation plate (Cu) is chrome (Cr).
8. It was also established that the thickness of the chrome (Cr) barrier layer must be $X_{(Cu\text{-}2.43\%Cr)}$ = 30 – 50 micron, which will ensure the blocking of diffusion of the atoms of the conductor layer (Cu) into the semiconductor material (Bi_2Te_3).

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