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Junctions and Diffusion Barriers for High Temperature Thermoelectric Modules

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Abstract

Thermoelectric modules based on doped bismuth telluride (Bi_2Te_3) are commonly used for the construction of thermoelectric generators (TEGs) and heat pumps. However, due to low operating temperature (< 200ºC), TEGs based on this material reveal low efficiency. In order to obtain high effectiveness in energy conversion, one needs to design high temperature modules made of new thermoelectric materials.

The goal of the present work has been to develop the method of preparation of ohmic junctions between semiconducting $CoSb_3$ element and metallic Cu electrode, for temperatures up to 600ºC. In order to protect thermoelectric material from interaction with a solder and the electrode material, the appropriate diffusion barriers were applied.

The junctions were formed by the resistance soldering technique in the protective atmosphere of Ar + H_2. Lead-free alloys based on Ag and Cu were used as the solder. Diffusion layers of Ni were prepared via the magnetron sputtering technique. The chemical and microstructural properties of the junction area were analyzed by scanning electron microscope (SEM) equipped with EDX analyzer. Resistivity measurements and current–voltage characteristics were used to determine the contact resistance and ohmic contact quality between the metal and the semiconductor. Other physico-thermal properties, such as thermal expansion, were also characterized.

Keywords: Thermoelectric power, $CoSb_3$, Interfacial reaction, Resistance soldering

ZŁĄCZA I BARIERY DYFUZYJNE DO WYSOKOTEMPERATUROWYCH MODUŁÓW TERMOELEKTRYCZNYCH

Moduły termoelektryczne oparte na tellurku bizmutu (Bi_2Te_3) używane są powszechnie przy konstruowaniu generatorów termoelektrycznych (TEGs) i pomp ciepła. Jednakże, z powodu niskiej temperatury pracy (< 200ºC), generatory termoelektryczne wykorzystujące ten materiał wykazują małą sprawność. Aby uzyskać wyższą wydajność konwersji energii potrzebne jest opracowanie wysokotemperaturowych modułów wykonanych z nowych materiałów termoelektrycznych.

Celem prezentowanej pracy było opracowanie metody wytwarzania omowego złącza pomiędzy półprzewodzącym elementem $CoSb_3$ i elektrodą metalową Cu przeznaczonego do pracy w temperaturach aż do 600ºC. Odpowiednia bariera dyfuzyjna została zastosowana, aby chronić materiał termoelektryczny przed wzajemnym oddziaływaniem z lutem i materiałem elektrody.

Złącza wykonano za pomocą techniki lutowania oporowego w ochronnej atmosferze Ar + H_2. Jako lut wykorzystano stopy bezołowiowe oparte na Ag i Cu. Warstwy dyfuzyjne Ni naniesiono techniką rozpylania magnetronowego. Właściwości chemiczne i mikrostrukturalne analizowano za pomocą elektronowego mikroskopu skaningowego (SEM) wyposażonego w analizator EDX. Pomiary rezystywności i charakterystykę prądowo-napięciową wykorzystano, aby określić oporność kontaktową i omową jakość kontaktu pomiędzy metalem i półprzewodnikiem. Scharakteryzowano także inne właściwości fizyko-chemiczne, takie jak rozszerzalność cieplna.

Słowa kluczowe: energia termoelektryczna, $CoSb_3$, reakcja międzyfazowa, lutowanie oporowe

1. Introduction

Thermoelectric (TE) materials are commonly used as semiconductors applied in the production of thermoelectric elements, for instance of Peltier modules, which are used, among others, in thermoelectric refrigerators as well as in the active elements in thermoelectric generators (Fig. 1a). The latter application has enjoyed particular interest recently due to the potential use of thermoelectric devices in converting of renewable energy. Thermoelectric generators can be applied for example in direct conversion of geothermal or solar energy into electric one. They can also play a major role in recollecting waste heat produced in car internal combustion engines or industrial installations [1, 2]. Efficiency of TE device is highly dependent on the non-dimensional figure of merit *ZT* of the TE material, temperature difference inside the device and the contact properties of the TE material and electrode.

The scheme of thermoelectric module is shown in Fig 1. *n*-type and *p*-type thermoelectric elements are sandwiched between two high thermal conductivity ceramic support. With alternating top and bottom interconnects, the *n*-type and *p*-type elements are connected sequentially in series. The heat flow goes from the top ceramic support to the bottom one, what makes all thermoelectric elements thermal in parallel. In a cooling mode, an externally applied current forces the heat to flow from the top to the bottom. In power generation mode, heat flowing from the top to the bottom drives a current through an external load.

The power and efficiency of the thermoelectric device is directly related to the average value of ZT product over the operating temperature range, where T is the absolute temperature and Z is a dimensional thermoelectric figure of merit, which is given by

$$ZT = \frac{\alpha_*^2 \cdot \sigma}{\lambda} \cdot T_{aver}, \tag{1}$$

where α_* is the Seebeck coefficient, λ is the thermal conductivity, and σ is the electrical resistivity. The value of ZT for various TE materials typically varies significantly as a function of temperature, and each TE material has a temperature range over which ZT is near the maximum. To receive a maximum conversion efficiency of heat energy by TEGs it could be best by constructing each thermocouple leg with TE material segments so that each TE material segment in each leg functions within a temperature range at which its ZT is near-optimum (Figs. 1b and 1c).

We chose $CoSb_3$-based skutterudite as a top part of segmented TE module because it is one of the most promising material working at the intermediate temperature region [3-6]. However, an appropriate junction $CoSb_3$/electrode has not been developed with the right mechanical, electric and chemical properties, although a lot of projects are being undertaken in this area [7-9].

2. Experimental

2.1. Sample preparation

Highly pure metal powders of Co (99.9 %, Sigma Aldrich) and Sb (99.99 %, Alfa Aesar) were used as starting materials, and a one-step solid-stade reaction was used to prepare single-phase polycrystalline $CoSb_3$ compound. The reaction was carried out at a quartz ampoule in vacuum first at 1000ºC for 20 minutes. Then the ampoules were cooled down to 750ºC and maintained at this temperature for 7 days. Stoichiometric ingots were ground in an agate mortar to obtain the powders. Then the powder was placed in a graphite die and densified by hot-pressing method in Ar atmosphere under 30 MPa and 800ºC for 30 min. Thus received samples were annealed in order to remove internal stresses. For this purpose samples of $CoSb_3$ were closed in the quartz ampoule, partially filled with argon (~0.5 atm.) and annealed for 12 h at 500ºC. Afterwards, they were cooled down at the rate of 1ºC/min. The density of the samples was measured by a pycnometric method (99,3 % of theoretical density) by using water as a liquid medium. The constituent phases and microstructure were determined by powder X-ray diffractometry (Philips X'Pert Pro) and a scanning electron microscope (SEM) equipped with EDX analyzer (FEI Nova NanoSEM 200).

A layer of Ni was put onto the polished samples via magnetron sputtering technique. The purpose was to create diffusion barrier which would prevent penetrating the solder components into $CoSb_3$. In order to make a high-temperature junction, two types of lead-free solders were used: Ag-Cu-Zn of T_m = 600ºC, and Ag-Cu of T_m = 780ºC, prepared in a form of a foil (~100 μm thick). Copper rollers were used (0.8 mm thickness) (Fig. 2-I) as the electrodes.

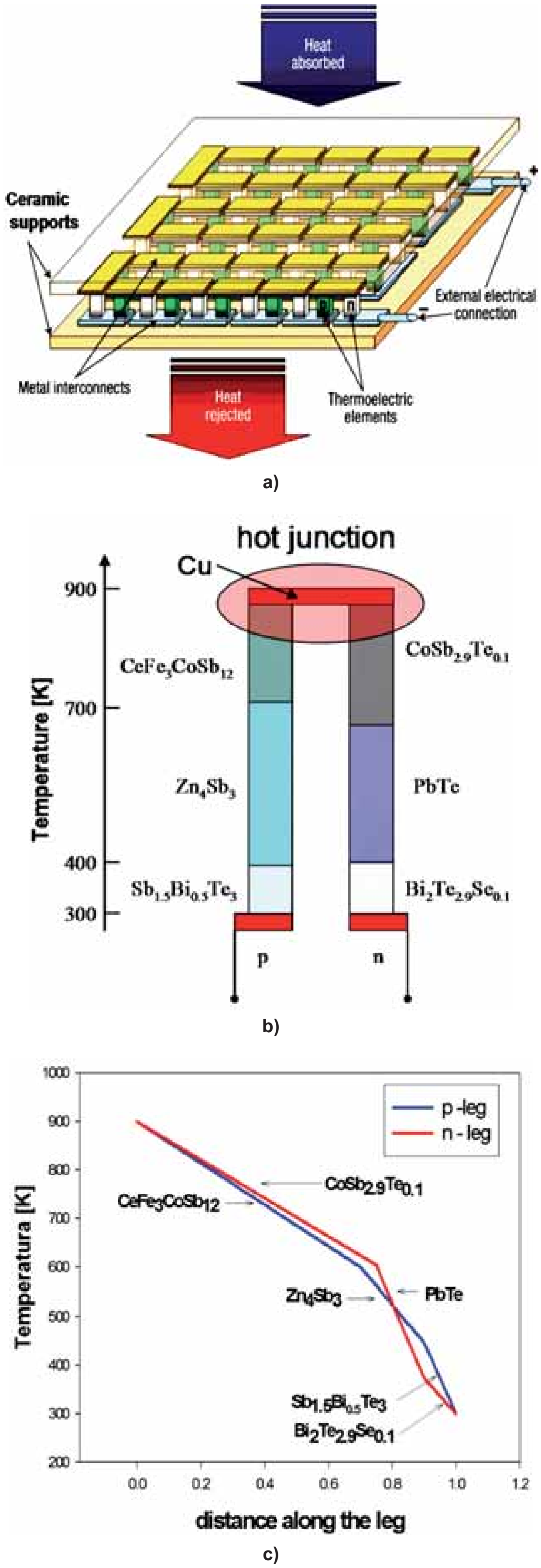

Fig. 1. a) scheme of a typical thermoelectric device, b) modular structure of the segmented thermoelectric couple, where the hot junctions and the temperature range are seen, c) calculated temperature distribution for segmented unicouple (b) along the leg.

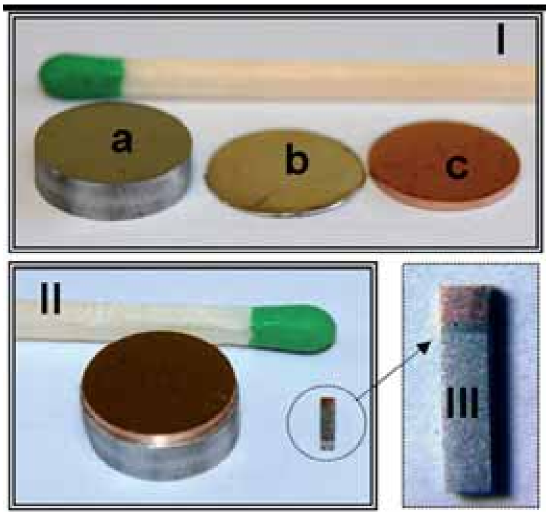

Fig. 2. Examples of studied samples. Picture I: a) $CoSb_3$ with 2 μm Ni film prepared via magnetron sputtering technique, b) Ag-Cu 100 μm solder, c) Cu electrode. Picture II shows a sample after soldering. Picture III shows a sample prepared for electric measurements.

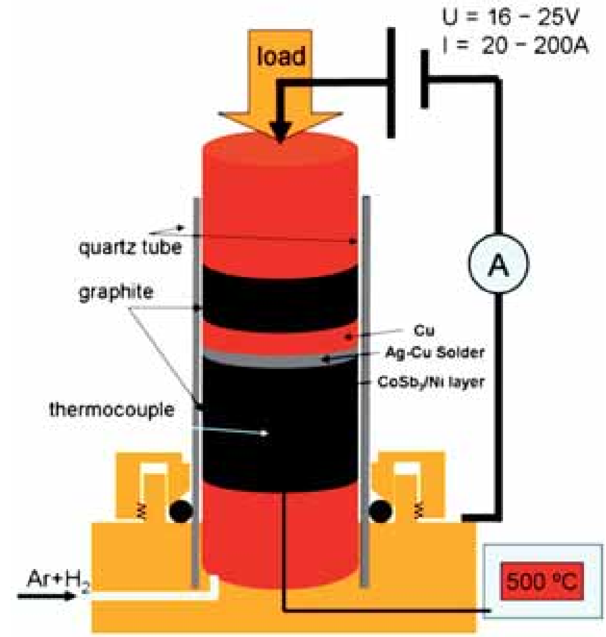

Fig. 3. Scheme of the resistance soldering apparatus.

2.2. Soldering

The resistance soldering method was selected for joining of materials because this method is much faster than traditional soldering and heat evolving is confined to the solder connection. Therefore the time for reaction of a liquid solder with TE material can be greatly shortened in comparison to classical soldering. It would allow us to create a solder joint both with satisfactory mechanical and electrical properties

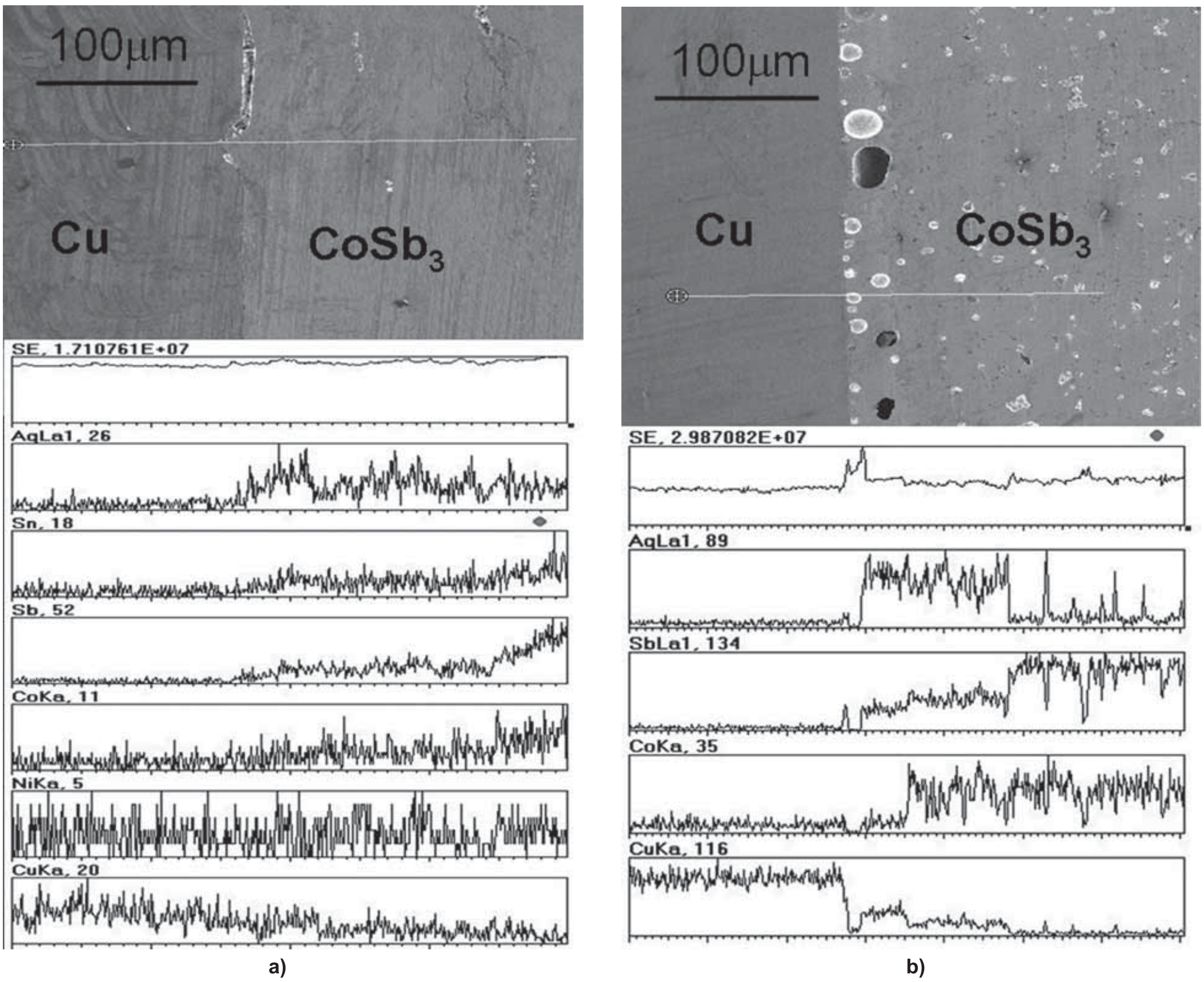

Fig. 4. SEM/EDX analysis of the junctions: a) Ag-Cu-Zn solder of T_m = 600ºC, b) Ag -Cu solder of T_m = 780ºC.

and to preserve chemical composition and thermoelectric properties of joined materials.

The junctions were formed in the protective atmosphere of Ar + H_2. Lead-free alloys based on Ag and Cu were used as the solder. The $CoSb_3$/solder/Cu samples were placed (Fig. 3) in a quartz tube between graphite punches. Then a gaseous mixture of Ar (90 %) + H_2 (10 %) was blown through the quartz tube and a mechanical load was applied. Through thus prepared pile, direct current was passed (I = 20 A) which made the pile heat up to 400ºC. After that, the current was increased to I = 200 A until the melting temperature of solder T_m was reached. The time needed to complete such a process was about 30 s. The temperature of soldering process was controlled with a thermocouple fixed just beneath the thermoelectric material.

The joints were cut into a long bar 1×1×4 mm in size (Figs. 2-II and 2-III) and then polished for resistivity measurements. The electrical contact resistance of TE junctions was measured by the three-probe method.

3. Results and discussion

3.1. Interfacial microstructures

Fig. 4a shows the SEM micrographs of $CoSb_3$/Cu electrode joint using Ag-Cu-Zn (T_m = 600°C) solder foil. No crack is observed and the joint is well bonded. Despite that the electron probe micro-analysis (EDX) proves the presence of various phases, Ni diffusion barrier is not visible.

Fig. 4b shows the SEM micrographs of $CoSb_3$/Cu electrode interface of joint using Ag-Cu (780°C) solder foil. Some small cracks appeare but the joint was still well bonded. We did not observe here, as in the previous case, the presence of the diffusion barrier. We suppose that the Ni layer has been completely dissolved during soldering, because possible solubility of this metal in the solder [10]. Therefore, we consider increasing of the thickness of the diffusion layer or applying another material having lower solubility in the Ag-Cu alloy (*e.g.*, Cr, or Mo).

The electron probe micro-analysis (EDX) shows that thickness of the solder zone is about 180 µm (mixture of Cu-Ag-Co-Sb) which is twice larger than we expected. This can be an effect of interdiffusion and/or dissolving of joined materials during soldering. Additionally, the small pores observed in Fig. 4b are the result of thermal decomposition of $CoSb_3$, caused by a too high temperature for this material.

3.2. Mechanical and electrical properties of TE junctions

Copper has the second highest electrical (σ_{Cu} = 9.6·10^6 S·m^{-1}) and thermal conductivity (λ_{Cu} = 401 W·m^{-1}·K^{-1}), after silver. This high electrical and thermal conductivity predisposed Cu to be used as an electrode material. One of the reasons to choose Ni as the diffusion barrier was the thermal expansion coefficient (α_{Ni} = 13.4·10^{-6}/ºC) which is just between $CoSb_3$ (α_{CoSb_3} = 10.2·10^{-6}/ºC) and Cu (α_{Cu} = 16.5 × 10^{-6}/ºC). Such a solution should reduce the mechanical stress in the $CoSb_3$/Cu junction.

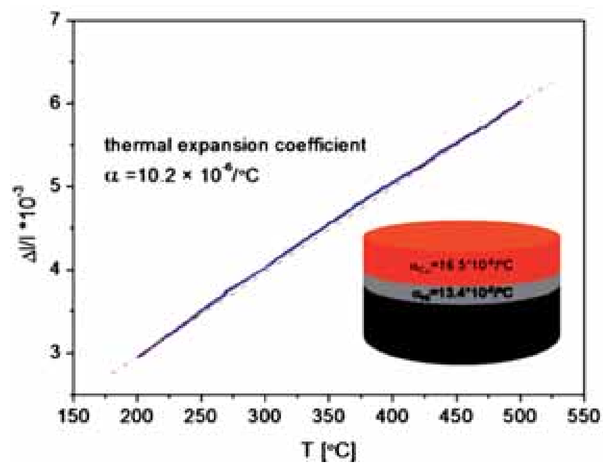

Fig. 5. Measurement of $CoSb_3$ thermal expansion coefficient.

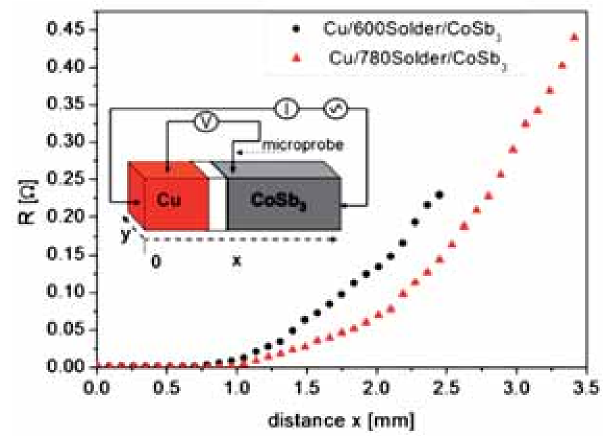

Fig. 6. Electrical resistance along joined elements.

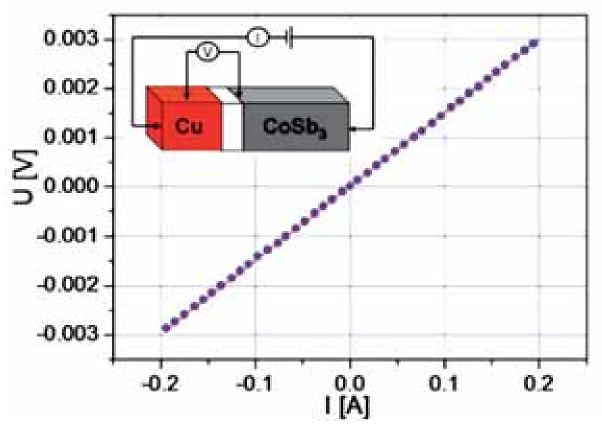

Fig. 7. Current–voltage characteristics of $CoSb_3$/Cu junction

The thermal expansion coefficient of $CoSb_3$ (Fig. 5) was measured using a conventional dilatometer and was found to be α_{CoSb_3} = 10.2·10^{-6}/ºC (200-500°C, Ar atmosphere).

The schematic diagram of experimental setup and results of electrical contact test are shown in Fig. 6. For measurements we applied AC current (I) (50 Hz, ~0.3 A) and measured the voltage drop (V) across the probes. In the case of the junction Cu/780solder/$CoSb_3$, we noticed a change in resistance which may prove a partial in-diffuse of the solder ingredients into the thermoelectric material. This process leads to deterioration of its properties.

The current–voltage characteristic for $CoSb_3$/Cu junction was also measured (Fig. 7). We applied a DC current (I) via probes Cu/solder/$CoSb_3$ and measured the voltage drop (V) at the junctions. The line shows a good quality of ohmic contact between the metal and the semiconductor.

4. Conclusions

The metallic Cu electrode has been successfully joined to $CoSb_3$ thermoelectric material by the resistance soldering method. Thin diffusion layers of Ni deposited by the magnetron sputtering technique are not sufficient and Ni should be replaced by another material. Moreover, soldering in a too high temperature (as it was in the case of $CoSb_3$/Cu junction with the use of the solder Ag-Cu of T_m = 780ºC) is not recommended because thermal decomposition of the thermoelectric material may occur. However, the results of investigations suggest that applying the resistive soldering technique and the solder with lower melting temperature (T_m = 600°C) allows us to obtain the $CoSb_3$/electrode junction with the desired mechanical and electrical properties.

Acknowledgements

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References

[1] Bandhari C.M., Rowe D.M.: CRC Handbook of thermoelectrics, CRC Press, Boca Raton, (1995).
[2] Rowe D.M.: „Renew", Energy, 16, (1999), 1251–1255.
[3] Wojciechowski K.T., Tobola J., Leszczyński J.: „Thermoelectric properties and electronic structure of $CoSb_3$ doped with Se and Te", J. Alloy. Compd., 361, (2003), 19–27
[4] Sales B.C., Mandrus D., Willams R.K.: „Filled skutterudite antimonides: a new class of thermoelectric materials", Science, 272, (1996), 1325–1328.
[5] Nolas G.S., Cohn J.L., Slack G.A.: „Effect of partial void filling on the lattice thermal conductivity of skutterudites", Phys Rev B, 58, (1998), 164–167.
[6] Mondt J., Johnson K., Fleurial J-P., El-Genk MS., Frye P., Determan B.W.: „Segmented thermoelectric multicouple converter technology development" In: El-Genk MS, editor. Proc space technology and applications international forum (STAIF-2005), AIP conference proceedings no. 746. Melville, NY: American Institute of Physics,(2005), 495–502.
[7] Fan J.F., Chen L.D., Bai S.Q., Shi X.: „Joining of Mo to $CoSb_3$ by spark plasma sintering by inserting a Ti interlayer", Mater. Lett., 58, (2004), 3876-3878.
[8] Zhao D.G., Li X.Y., Jiang W., Chen L.D.: „High temperature reliability evaluation of $CoSb_3$/electrode thermoelectric joints", Intermetallics, 17, (2009), 136–141.
[9] Zhao D.G., Li X.Y., Jiang W., Chen L.D.: „Interfacial evolution behaviour and reliability evaluation of $CoSb_3$/Ti/Mo–Cu thermoelectric joints during accelerated thermal aging", J. Alloy. Compd., 477, (2009), 425–431.
[10] Luo H-T., Chen S-W.: „Phase equilibria of the ternary Ag-Cu-Ni system and the interfacial reactions in the Ag-Cu/Ni couples", J. Mater. Sci., 31, (1996), 5059-5067.

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