The Properties of Bi₂Te₃-Cu Joints Obtained by SPS/FAST Method

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One of the most important challenges connected with the production of thermoelectric modules and their parts is the development of an appropriate joining technology. The produced junctions must be characterised not only by high mechanical strength and good adhesion but also by high electrical conductivity, high heat conductivity and, due to working conditions, by a long-term chemical and temperature stability. This paper presents the results of the investigation of a Bi₂Te₃/copper junction obtained using lead-free solders. We analyse and discuss junction properties and quality. To produce this connection via resistance soldering under pressure, a spark plasma sintering (SPS/FAST) apparatus was used. The properties of the samples (electrical conductivity and Seebeck coefficient) have been characterized and presented. The microstructure investigations and analysis of the element distribution are also presented.

Key words: Electrical properties, energy harvesting, thermoelectric materials, junctions, spark plasma sintering

INTRODUCTION

Nowadays, constantly increasing energy consumption is forcing society to develop new power sources. One of these are thermoelectric modules (TEM) that allow us to direct energy conversion from heat energy into electrical energy.^{1,2} This feature may be used to recover waste heat energy from the exhaust gases of automotive engines and increase their efficiency, while also decreasing fuel consumption and environmental pollution.^{3,4} There is also a possibility to use a thermoelectric generator with a radioisotope source of heat to supply special space probes like the Voyagers and others.⁵ One of the most important challenges while building TEM is the production of junctions of proper quality, characterized by low electrical resistance, low thermal resistance⁶ and long-term chemical and

thermal stability. These properties are directly related to the quality of contacts between the thermoelectric material and the electrode. Very often, in order to avoid junction degradation, diffusion barriers are needed. Joints that do not fulfil the above requirements significantly reduce the TEM parameters such as power density and energy conversion efficiency.⁷ The produced joints must also fulfil mechanical requirements, such as good tensile strength and a thermal expansion coefficient close to those of the joined materials.⁸ Overall module efficiencies also have a significant impact on metal-ceramic junction properties⁹ and on the type of insulating ceramics used.¹⁰ Bismuth telluride-based alloys are the best thermoelectric materials for near-room-temperature applications because of their high figure of merit (ZT).¹¹ This is one of the most important reasons why Bi₂Te₃ thermoelectric materials (TE) are becoming increasingly vital in alternative applications for energy saving and conversion. At present, most thermoelectric generators (TEG) are constructed from

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commercially available modules made of doped bismuth telluride (Bi_2Te_3)¹² and antimony telluride (Sb_2Te_3).¹³ For the purpose of the work, an *n*-type $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ thermoelectric material was chosen,¹⁴ while Cu strips served as a connector. Another important aspect of the investigation is the type of conductivity of the produced junction, as the connection between the metal and the semiconductor (*m-s*) may have rectifying properties. If the *m-s* junction has linear, symmetrical current-voltage characteristics, it fulfils Ohm's Law. Constructing an Ohm's Law *m-s* junction is very difficult and may only be possible in the case of heavy doped materials, though it is possible in the case of some thermoelectric materials.¹⁵ Copper was chosen as a metallic connector because of the high electrical and thermal conductivity of Cu with a purity of 99.9% [$\sigma = 55.82 \text{ (MS m}^{-1}\text{)}$, $\lambda = 400.1 \text{ (Wm}^{-1} \text{ K}^{-1}\text{)}$]¹⁶. Based on research publications, Ti and Au were chosen for the first diffusion barrier.¹⁷ The second type of barrier, a Ni-P layer, was analysed.¹⁸ The RoHS directive issued by the European Union prohibits the use of lead. That is why this paper shows lead-free solders based on gold, tin, antimony and indium. The development of environmentally friendly, innovative technology is the main purpose of modern science. The presented results are the continuation of scientific work started in 2016,^{19,20} extended by the authors and presented in this work.

MATERIALS AND METHODS

Sample Preparation

The *n*-type $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ material was synthesized via the direct fusion technique. Weighed amounts of pure elements were prepared in the quantities corresponding to the stoichiometric composition of the $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ compound. As the initial materials, elemental Bi, Te and Se, with purities better than 99.99% (Alfa Aesar), were used. The material synthesis was performed in quartz ampoules closed in a vacuum ($P_{\text{vac}} = 1 \times 10^{-3} \text{ mbar}$). The reagents were heated up to 650°C in a rocking furnace, maintained for 1 h and subsequently slowly cooled. The prepared ingot was crushed in an agate mortar. The fine powders were prepared via mechanical milling in a planetary agate ball mill (2 h, rotational speed of 300 min^{-1}). The densification process was carried out under vacuum at the uniaxial compressive pressure of 50 MPa in an SPS apparatus.²¹ The powder was placed in a cylindrical graphite die with an inner diameter of 10 mm and pressed between two graphite punches. The compacted powder was heated up to 420°C with a heating rate of 50°C min^{-1} and held for 15 min, then cooled at a rate of 25°C min^{-1} . The relative density of the samples was determined by the Archimedes method and estimated to be c. 98–99% of the theoretical value.

Solder Preparation

In this study, five different solders were investigated. In order to obtain the solders (alloys: $\text{Au}_{80}\text{Sn}_{20}$, $\text{Au}_{10}\text{Sn}_{90}$, $\text{Sn}_{95}\text{Sb}_5$), stoichiometric amounts of the elements with high purities of 99.99% (Alfa Aesar) were weighed. The synthesis was carried out in a quartz tube closed under vacuum ($P_{\text{vac}} = 1 \times 10^{-3} \text{ mbar}$). The homogenisation of the solder was carried out in a resistance furnace at the temperature of 350°C for 2 h. The Sn and In ingots were melted from high purity elements (> 99.9%) at 350°C. The obtained solders were cold-rolled into films with a thickness of 0.15–0.2 mm, except $\text{Au}_{10}\text{Sn}_{90}$ and $\text{Au}_{80}\text{Sn}_{20}$, which were prepared in the form of powders.

Physical Vapor Deposition of the Diffusion Barrier

In order to reduce the degradation process of the thermoelectric segments, the formation of an appropriate diffusion barrier is required. The barrier must have good chemical stability and also good adhesion (ensuring good mechanical properties and very good electrical contact between the joined materials). For the purpose of the work, metallic layers were chosen, produced using the physical vapor deposition (PVD) method by magnetron sputtering. The diffusion barriers were deposited on a flat, matt surface of the Bi_2Te_3 samples in a vacuum apparatus equipped with a magnetron gun WMK-50 with replaceable cathodes made of the selected materials (Ti and Au). The deposition of the Ti and Au coatings on the $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ samples were performed according to the following procedure. The specimens were placed on a heating table and heated up to 200°C, under $7.0 \times 10^{-5} \text{ mbar}$ for 1 h. The magnetron with the Ti targets (2-inch (c. 5-cm) diameter) was power-supplied by a DORA POWER DC pulsed current source with the frequency of 160 kHz. The process of layer deposition was performed with a cathode current of 0.70 A at the power of about 500 W, with the pressure of Ar stabilised at the level of $4.5 \times 10^{-3} \text{ mbar}$. Under these conditions, the average rate of layer deposition was approximately 40 $\text{nm} \times \text{min}^{-1}$. The obtained titanium coatings were about 3 μm thick. The thickness of the gold layers did not exceed 0.5 μm . The first, Ti, layer was used in order to prevent the diffusion of the materials, and the second, Au, layer was applied in order to facilitate the soldering.

Chemical Deposition of Diffusion Barrier

The second part of the work was connected with junctions containing a chemically deposited Ni barrier.²² The nickel-deposited layer contained about 5% (by weight) of phosphorus. The basic advantages of these barriers are chemical stability

and high electrical conductivity. To prepare a substrate surface for the Ni-P layer deposition, it has to be activated by palladium deposition from palladium precursors coming from palladium(II) chloride. The deposition of a Ni-P layer took place in a bath at the temperature of 80°C and a pH equal to 4.6. The main substrates used in the bath were nickel salts and the reducing agent was sodium hypophosphite with a buffer solution stabilising the pH. The analysis of the obtained junctions showed that the layers deposited for 40 min were about 20 μm thick, and the approximated growth rate was equal to 0.5 $\mu\text{m} \times \text{min}^{-1}$.

Samples Characterization

For the x-ray diffraction (XRD) pattern, the X'Pert Philips apparatus with a CuK α_1 radiation source was used with the wavelength $\lambda = 1.5418 \text{ \AA}$. The measurements were performed on the powders or polished samples. For the microstructure examination, scanning electron microscopy (SEM) (JEOL JSM-840 and FEI NOVA NanoSEM) with an energy-dispersive (EDS) detector were used. Detailed analysis was also carried out to determine the chemical composition and characterisation of the developed junctions and the diffusion barriers. Thermoelectric materials prepared by various synthesis methods might have inhomogeneous electrical properties that strongly influence electrical conductivity. This fact may significantly reduce the ZT , so it is important to examine the electrical properties of the produced materials.

Figure 1a shows the idea of measurement of the electrical conductivity along the examined sample. The use of an alternating current makes it possible to separate the voltage drop caused by the Seebeck effect. The XY-movable probe makes it possible to determine the conductivity changes along the surface of the sample. The resistance and the character of the conductivity of the produced junction were measured using the technique shown in Fig. 1b. The use of the adjustable current source makes it possible to determine the resistance and rectifying properties. Finally, the Seebeck coefficient was

determined. Figure 1c represents the idea of the measurement of the Seebeck coefficient distribution at the sample surface. The heated probe scans the sample point by point in order to create the Seebeck coefficient maps, determining the practical usefulness of the produced TE legs.

Thermoelectric Material

Figure 2 shows the XRD pattern of the Bi₂Te_{2.9}Se_{0.1} sample used for the junction preparation. We can see that there is no impurity in the sample and that all the peaks match the crystallographic positions that were marked in the graph.

Prepared Solders

Table I presents the obtained solders with the compositions of all the solders used for low-temperature soldering. There are also photographs of the ingot with the temperatures of their preparation and the form in which they were later used for the junction preparation.

Fig. 2. XRD pattern for Bi₂Te_{2.9}Se_{0.1}.

Fig. 1. The idea of measurement of (a) electrical conductivity of a sample, (b) junction resistivity, (c) Seebeck coefficient with an XY-movable probe. 1 Cu electrode, 2 voltmeter, 3 junction, 4 thermoelectric material, 5a alternating current source, 5b adjustable current source, 5c heated voltage XY probe.

Diffusion Barrier

To avoid TE material degradation, two diffusion barriers were used. For the AuSn solders, a diffusion barrier was used containing the elements deposited by the PVD method. From the TE material side, there was a 3- μm Ti layer on which a 0.5- μm Au layer was deposited for better adhesion to the AuSn solder. For the rest of the solders, a chemically deposited NiP layer (Ni-7%P) was used as a diffusion barrier, with a few micrometres of thickness.

Junction Preparation

In Fig. 3a, a scheme of the spark plasma sintering (SPS/FAST) apparatus can be seen. The copper disc (1 mm thickness), the solder foil (0.15 mm thickness), and the sample with the diffusion barrier were placed in a graphite die. The heating program is presented in Fig. 3b, where the parameters of the soldering process are shown. For the AuSn solder, a powder was used instead of a film. The heating rate in the first step was about $50^\circ\text{C min}^{-1}$, and, below the melting temperature, the heating rate was

reduced to 5°C min^{-1} . When the shrinkage significantly increased, the heating was stopped, and the sample was cooled.

RESULTS

Microstructure

A detailed analysis was carried out in order to determine the chemical composition and characterisation of the developed junctions and diffusion barriers. For the In and Sn junctions, Ni-P diffusion barriers were used. We do not present the SEM image but there was very good adhesion between the joined materials, the solder and the diffusion barrier. There was no porosity or cracks, but the use of these materials is limited; for pure indium, due to the low melting temperature, 156°C , the material may only be used for Peltier modules working in low temperatures. The second soldering material (tin) is better due to higher electrical and heat conductivity, but it is not described in depth in this publication. This junction may not be used in thermoelectric generators due to the phase transition in pure tin at 13.2°C , connected with volume changes and junction destruction.

In Fig. 4, the cross section of $\text{Cu}/\text{Au}_{10}\text{Sn}_{90}/\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ junction is shown. There is no visible porosity in the thermoelectric and electrode materials. The adhesion of the solder to an electrode is good. A small number of cracks and some porosity are seen in the solder. Detailed studies have shown that layers deposited by PVD contain many cracks on the solder/thermoelectric material boundary, and it seems that the weakest part of the junction is the diffusion barrier. The production of a good quality junction with a PVD coating was a difficult task. The technique used was not sufficient to apply a layer that can meet the requirements for thermoelectric module preparation.

Figure 5 shows the SEM of the $\text{Sn}_{95}\text{Sb}_5$ junction with the Ni-P diffusion barrier. The SEM image

Table I. List of prepared solders

No.	Chemical Composition	Obtain ingots/temp	Form of solder	Soldering temperature
1	$\text{Au}_{80}\text{Sn}_{20}$		Milled	280°C
2	$\text{Au}_{10}\text{Sn}_{90}$		Milled	217°C
3	$\text{Sn}_{95}\text{Sb}_5$		Cold rolled	240°C
4	Sn		Cold rolled	232°C
5	In		Cold rolled	156°C

Fig. 3. (a) SPS/FAST apparatus: 1 graphite die, 2 graphite punches, 3 sample (Cu/solder/TE material), 4 electrical supply, 5 vacuum chamber, (b) shrinkage during soldering in the SPS of $\text{Sn}_{95}\text{Sb}_5$ solder.

Fig. 4. SEM image of the $\text{Au}_{10}\text{Sn}_{90}$ solder with the Au/Ti diffusion barrier. (a) Sample structure, (b) detailed magnification.

Fig. 5. SEM image of the $\text{Sn}_{95}\text{Sb}_5$ solder with the Ni-P barrier. (a) Sample structure, (b) detailed magnification.

Fig. 6. Position of EDS investigation points.

Fig. 7. EDS spectra of point p1.

confirmed very good adhesion between the joined materials, the solder and the diffusion barrier. There is no visible porosity in the thermoelectric

and electrode materials. The adhesion on all of the boundaries forming the metal electrode to the thermoelectric material is good. The visible traces

Fig. 8. Example characteristics of prepared junction with the $\text{Sn}_{95}\text{Sb}_5$ solder and Ni-P diffusion barrier.

Fig. 9. Example characteristics of prepared junction with the Sn solder and Ni-P diffusion barrier.

are grain boundaries disclosed by etching with a 5% hydrochloric acid solution. The continuous connection between the layers was also proved by electrical measurements. There are no cracks on any of the boundaries, including the solder/diffusion barrier/TE boundary. SEM maps proved that there were no solder elements inside the TE material.

Figure 6 presents the position of the EDS point measurement; the analysed points were about $5\text{ }\mu\text{m}$ away from the Ni-P layer.

Figure 7 shows the EDS spectra of point p1; bismuth, antimony and tellurium are the naturally expected elements. Small amounts of silicon and carbon are observed, but these elements come from the polishing process (Si-C) or are connected with some technological aspects of sample preparation for the SEM/EDS analysis. No presence of solder or diffusion barrier components was shown (theoretical positions of their spectrum are marked with $\times$ and labelled). The results of the EDS analysis are presented in Fig. 6.

Electrical Properties

Figure 8 shows the example characteristic of the junction with the $\text{Sn}_{95}\text{Sb}_5$ solder and NiP diffusion barrier, scanned by an electrode across the length of the sample with an applied electrical field or scanned with a hot electrode (red or green line). At the beginning of the sample, the increase of resistance (measured from the beginning of the sample) is very small because copper has very high conductivity and the signal is covered by the noise. Then, from the area of the junction, the resistance starts increasing. The increase in the resistance in the TE material is constant, so the material is homogenous and resistivity is constant. For the Seebeck coefficient, we can see small and constant values for the electrode material equal to $4\text{ }\mu\text{V K}^{-1}$. Then, through the junction, there is a significant drop of the Seebeck coefficient value. In the TE material, the Seebeck coefficient is constant and equal to about $204\text{ }\mu\text{V K}^{-1}$. The approximated thickness of the junction was estimated from the Seebeck coefficient changes from the electrode to the TE material, from which in turn the resistance of the junction was calculated. Electrical measurements confirmed the lack of solder-side components inside the thermoelectric material, and very good electrical properties of the produced junction, $\rho_j = 8\text{ }\mu\Omega\text{ cm}^2$, which compared to the values reported in²³ ($486\text{ }\mu\Omega\text{ cm}^2$ and $198\text{ }\mu\Omega\text{ cm}^2$) is a very good result in the case of similar Cu-Bi₂Te₃ junctions.

Figure 9 presents the electrical characteristics of junction fabricated using pure tin. This junction showed very good electrical parameters, but as it was mentioned before, the usage of this junction is limited. The junction fabricated using pure indium showed similar, very good electrical parameters, but the Sn reference junction is shown at its higher working temperature.

Electrical properties of other tested junctions ($\text{Au}_{10}\text{Sn}_{90}$, $\text{Au}_{80}\text{Sn}_{20}$) are not presented due to their very low electrical parameters and low mechanical properties caused by micro-cracks observed between the solder and the semiconductor material.

DISCUSSION

Issues related to the manufacture and characterization of junctions are a current and relevant topic, especially in the field of thermoelectric materials. Although junctions made of pure elements have good properties, the possibility of their usage for practical purposes is limited due to their low melting point, restricting the temperature range for the In and the phase transition for the Sn. For the Au/Ti layers deployed by PVD and the AuSn solder, the material contained many cracks on the solder/thermoelectric material boundary, and it seems that the weakest part of the junction was a diffusion barrier. The PVD techniques used were not sufficient to apply a layer that can meet the requirements of the TEM. Because of this, the next

part of the work focuses only on the SnSb solder and nickel-phosphorus layers deployed using the chemical method. The junction had good adhesion on the boundaries, confirmed by excellent electrical properties of the examined junction. The best properties were obtained for the Sn₉₅Sb₅ solder and the Ni-P diffusion barrier for which the contact resistance was equal to $\rho_j = 8 \mu\Omega \text{ cm}^2$.

CONCLUSIONS

- The presented work focuses on the *n*-type Bi₂Te_{2.9}Se_{0.1} and lead-free solders,
- five new types of solders and two types of diffusion barriers were tested, and the chemically deposited Ni-P layer shows much better properties than the Au/Ti PVD deposited barriers,
- The Au₈₀Sn₂₀ and Au₁₀Sn₉₀ have poor mechanical quality. The Sn, In and SnSb solders have good mechanical and electrical qualities, but the usage of the In and Sn solders is limited for TEG applications,
- Microstructure analysis confirmed good parameters of Sn₉₅Sb₅ solder with Ni-P barriers, allowing the application of the described solder in the metal–semiconductor junction in the TEM,
- Further work should focus on long-term tests of thermal and chemical stability.

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