On one possibility for application of new thermoelectric materials based on Ag_2Te

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***Abstract**: The thermoelectric characteristics of Ag_2Te and $Ag_{1,84}Cd_{0,08}Te$ (solid solution based on Ag_2Te) are investigated and analyzed. The main thermoelectric characteristics of the solid solution: α=118 μV/K; σ = 2230 S/cm and $\lambda = 2,45.10^{-2}$ W/(cm.K) ensure coefficient of thermoelectric efficiency $z = 1,27.10^{-3}$ K^{-1} (at 300 K), which increases this of the Ag_2Te. A composition for commutation material is developed, which connects the N- and the P-branches of a single thermo element (52 wt. % In + 48 wt. % Sn) with melting temperature of 390 K. The possibility for application of the $Ag_{1,84}Cd_{0,08}Te$ solid solution as N-branch of a thermo element in combination with the solid solution $Bi_{0,5}Sb_{1,5}Te_3$ (P-branch) is investigated. The thermo element guarantees values of z from $0,71.10^{-3}$ to $1,27.10^{-3}$ K^{-1} in the temperature interval 250 - 350 K. The maximum z value is registered at 300 K ($z = 1,27.10^{-3}$ K^{-1}).*

***Keywords:** Silver telluride, Solid solutions, Thermoelectric properties, Thermoelement.*

1.INTRODUCTION

The fast development of the contemporary technologies during the last 10-15 years continuously requires more effective and reliable materials with better characteristics. Due to this reason the new materials have become a key section, from which to a great degree depends the success of the engineering solutions in different areas of the human activities. This leads to more effective assimilation of the already known classical materials and to widening of their spectra of properties, on the one hand, and to a purposeful research of new materials with new preliminary given properties, on the other. This is valid mostly for the energetic technologies: elaboration and increase of the efficiency of the already used materials, as well as searching of innovative solutions in this area. The thermoelectric phenomena, which form the basis of the thermoelectric energy transformation, mark a significant progress during the last years due to the possibilities, which they offer for direct transformation of the heat energy into electricity, and also due to their wide application range in different thermoelectric devices: thermocouples, thermoelectric cooling devices and transformers for measurement of electrical constants, thermoelectric calorimeters, emission receivers, thermoelectric transformers, pumps and many others.

The main requirement towards the thermoelectric materials is that they have to possess high values of the thermoelectric efficiency coefficient (z), which have to be kept in a wide temperature interval ($z = \alpha^2\sigma/\lambda$; α – thermo-electromotive tension coefficient; σ – specific electroconductivity; λ – heat conductivity coefficient). The materials are qualified as thermoelectric, i.e. appropriate for a practical application, if their $z \geq 0{,}3.10^{-3}\ K^{-1}$ [1]). The most appropriate for thermoelectric application are the semiconductor materials, which to a great degree allow the managing of α, σ and λ with the aim the highest z values to be reached.

The increase of the z coefficient of the thermoelectric materials is a complicated task and a complex method is needed for its solution, since the change of certain thermoelectric parameters towards positive direction leads others to get worse. For example, the decrease of the charge carriers' concentration leads to increase of α, but in parallel with this σ decreases. Furthermore, if σ increases the λ significantly decreases, etc.

One of the most widely used methods for increase of the thermoelectric efficiency coefficient is this, by which isovalent substitution atoms are introduced in the one or in both sub-lattices of the semiconductor compound. By this way isomorphous solid solutions (partially or fully substituted) are formed, as depending on the substitution character and the valence of the participation atoms, a limiting influence on λ or on σ is reached [2].

The interest towards the Ag_2Te is not new and is owed to several reasons: it belongs to the self-compensating compounds [3], on the one hand. On the other it is part of the group of the narrow-gap semiconductors ($\Delta E \leq 0{,}3$ eV), on which basis a row of devices are constructed: thermoelectric transformers [4], optical quantum generators [5], photoelectric receivers, working in the near and far IR-region [6], heat switchers [7], etc.

It is known that the appearance of self-conductivity in Ag_2Te is masked by the conductivity of the "defect" zone and by its junction with the conductivity band, due to which the experimentally determined value of the thermal band gap (ΔE_o) varies in wide range: from 0,025 to 0,5 eV. The value of 0,18 eV is accepted as the most trustworthy [3,8].

The electrical conductivity (σ) of $Ag_{2-x}Te$ at room temperature varies in the range 250-1100 S/cm [9-11]. According to A.S.Okhotin et al. [12], the heat conductivity coefficient (λ) decreases from 2.10^{-2} at 300 K to $1{,}75.10^{-2}$

at 475 K, after which is increases again to 7,8.10^{-2} W/(cm.K) at 673 K. The thermo-electromotive tension coefficient (α) of $Ag_{2-x}Te$ changes its sign both with the temperature increase and the deviation from the stoichiometry [13]. α also decreases when the sample is not with stoichiometric composition [14]. The over-stoichiometric Ag-atoms cause negative values of α, while their insufficiency – to positive.

The stoichiometry deviation, the doping with appropriate admixtures and the development of solid solutions based on $Ag_{2-x}B^{VI}$ open possibilities for increase of z [15]. Data is reported in the literature about z of a doped Ag_2Te of about (0,3-1,0).10^{-3} K^{-1} [1]. The silver telluride $Ag_{2-x}Te$ is characterized by structural disorder and strong intrinsic defectness, by complicated energetic structure and high concentration of the charge carriers, i.e. it covers the requirements of the highly effective thermoelectric materials [2,15].

The phase diagram of the Ag_2Te-CdTe system is investigated [16]. Existence of boundary solid solutions in the concentration interval $0 \le x \le 8$ mol % CdTe is observed. There is very small quantity of data in the literature about the properties and the application possibilities of solid solutions based on Ag_2Te. In our previous work, the main characteristics of the solid solutions $Ag_{2-2x}Cd_xTe$ ($0 \le x \le 8$ mol %) are investigated and it is established that the solid solution with composition $Ag_{1,84}Cd_{0,08}Te$ has the maximum thermoelectric efficiency coefficient [17].

The aim of the present report is to examine the possibility for application of the solid solution $Ag_{2-2x}Cd_{0,08}Te$, as an N-branch of a semiconductor thermo element, working in the interval 250-350 K.

2.RESULTS AND DISCUSSIONS

The initial components Ag_2Te and CdTe, as well as the $Ag_{1,84}Cd_{0,08}Te$ solid solution are obtained by direct monotemperature synthesis [18] from the elements with purity: Ag – 3N; Cd – 2N3 and Te – 3N.

For the α, σ and λ measurements of the polycrystalline samples Ag_2Te and $Ag_{1,84}Cd_{0,08}Te$, equipment for complex materials investigations in the temperature interval of 100÷500 K is used (developed and constructed in the Department of Non-Ferrous Metals Metallurgy and Semiconductor Technologies), which is protected by author certificate [19]. The construction of the equipment allows simultaneous measurement of all three temperature-dependent characteristics of the materials: α(T), σ(T) and λ(T) in the mentioned temperature interval.

The measurements were led at temperatures of 250, 300 and 350 K at residual pressure in the cryostat of 1,33.10^{2} Pa. Liquid nitrogen is used for reaching of the working temperature of 250 K. The methods used for the measurements were: direct method for the α measurements, two-point probe for σ and absolute stationary method for λ. These characteristics of the thermoelectric materials were measured with accuracy of: ± 1 % for α, ± 3 % for σ and ± 5 % for λ.

The samples were welded to the forehead planes of a special holder with In-Sn solder (52 % In + 48 % Sn; T_m = 390 K).

The thermoelectric characteristics of Ag_2Te and the $Ag_{1,84}Cd_{0,08}Te$ solid solution are summarized in Table 1. The obtained values are in good conformity with the reported in the literature [17,20].

Tab. 1: Main characteristics of Ag_2Te and the $Ag_{1,84}Cd_{0,08}Te$ solid solution.

T	Ag_2Te				$Ag_{1,84}Cd_{0,08}Te$			
	α, 10^{-6}	σ	λ, 10^{-2}	z, 10^{-3}	α, 10^{-6}	σ	λ, 10^{-2}	z, 10^{-3}
K	V/K	S/cm	W/(cm.K)	K^{-1}	V/K	S/cm	W/(cm.K)	K^{-1}
250	103	850	2,30	0,392	80	2600	2,35	0,708
300	114	815	2,42	0,438	118	2230	2,45	1,267
350	95	780	2,57	0,274	102	2115	2,62	0,840
Characteristics of P-$Bi_{0,5}Sb_{1,5}Te_3$ at 300 K					160	850	1,60	1,360

The analysis of the results from Tab. 1 shows that the solid solution $Ag_{1,84}Cd_{0,08}Te$ possesses better thermoelectric properties and it is appropriate for practical application in the temperature range 250-350 K.

The investigated samples are of N- type conductivity.

The investigations of the thermoelectric properties of various solid solutions based on Ag_2Te or doped with different admixtures Ag_2Te are preliminary, but even this investigation shows that the thermoelectric efficiency coefficient of the solid solutions can increase significantly compared to the basis compound, in this case the Ag_2Te. On the other hand, the fact that the introduction of CdTe to Ag_2Te leads to significant increase of σ/λ is direct evidence [17], that the initial Ag_2Te ahs hidden reserves towards the zT factor, which gives optimism for the research of new Ag_2Te based solid solutions and improvement of the properties of the already obtained ($Ag_{1,84}Cd_{0,08}Te$) towards structure, purity of the initial components, additional thermal treatments, substitution in the tellurium sub-lattice, etc.

One of the possibilities for application of this semiconductor material ($Ag_{1,84}Cd_{0,08}Te$) is its usage as N-branch of a thermo element. For P-branch of this thermo element, a solid solution based on Sb_2Te_3 ($Bi_{0,5}Sb_{1,5}Te_3$) with basis characteristics at 300 K shown in Table 1, has been chosen. The thermo element is consisted by two semiconductor blocks – the one with N-type conductivity and the other – with P-type, which are connected in one of their ends with massive Cu-plate. The other two free ends of the blocks are also connected by soldering of two electrodes (copper plates). The mutual copper plate is put at temperature $T_2 = T_{hot}$ and the other two are at temperature $T_1 = T_{cold}$ (T_1 is near to the room temperature).

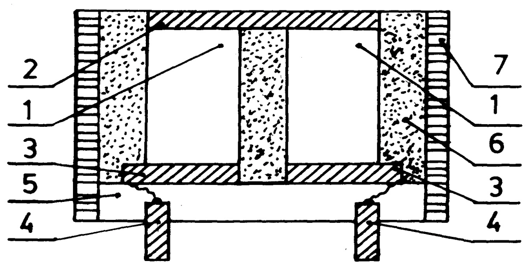

Fig. 1: Semiconductor thermo element: 1 – semiconductor blocks with N- and P-type conductivity; 2 – connecting Cu-plate; 3 – Cu-plates; 4 - leads; 5 – insulating plate (Teflon); 6 – polymer (epoxy raisin); 7 – plastic body.

The N- and P-branches of the thermo element as a rule are immovably connected in the circuit (by alloying) or movably (by pressing) using special rims. The used contact materials have to have low electrical resistivity, high heat conductivity and stability of these characteristics during the exploitation of the device.

The finding of appropriate commutation material is one of the hardest tasks during the development of thermoelectric devices, since a row of heavy requirements are claimed for them: to wet well the surface of the thermoelectric material, to have low electrical resistivity, which changes slightly during the temperature increase, to have linear expansion coefficient values near to these of the semiconductor thermoelectric material, to have high mechanical strength, not to have solid state transitions, etc.

Three compositions for commutation material (Tab. 2) were developed for the used system $Ag_{1,84}Cd_{0,08}Te/Bi_{0,5}Sb_{1,5}Te_3$. Commutation material III has been used for production of the thermo element.

Tab 2: Compositions of commutation alloys and their melting temperatures.

Composition, %	In	Cd	Zn	Sn	T_m, ºC
I	74,0	24,2	1,8	-	116
II	52,2	-	1,8	46	108
III	52,0	-	-	48	117

Thermo-electromotive tension appears in each branch of the thermo element, which is summed up for the whole thermo element. The maximum efficiency coefficient for this thermo element is [2]:

(1)
$$\eta_{max} = \frac{T_2 - T_1}{T_2} \cdot \frac{\sqrt{1 + z.\overline{T}} - 1}{\sqrt{1 + z.\overline{T}} + \frac{T_1}{T_2}}; \quad z = \frac{(\alpha_1 + \alpha_2)^2}{\left(\sqrt{\frac{\lambda_1}{\sigma_1}} + \sqrt{\frac{\lambda_2}{\sigma_2}}\right)^2};$$

where: α_1, α_2; λ_1, λ_2 and σ_1, σ_2 are the coefficients of thermal electromotive tension, the coefficients of heat conductivity and the specific electroconduc tivities of the N- and P-branches of the thermo element, respectively.

The efficiency coefficient depends on the consumed power. The condition for maximum extracted power from the thermo element is equalization of the consumer's and the thermo element's (thermo generator's) resistivities:

(2)
$$\eta_{(W=max)} = \frac{1}{2} \cdot \frac{T_2 - T_1}{T_2 + \frac{2}{z} - \frac{1}{4}(T_2 - T_1)}.$$

Using the parameters of the investigated thermoelectric materials (Tab. 1) at T_1 = 300 K, T_2 = 350 K, $\overline{T}$=325 K, the efficiency coefficients have been determined by Eqs. (1) and (2): z = $1,32.10^{-3}$ K^{-1}; η_{max} = 1,36 %; $\eta_{(W=max)}$ = 1,35 %, i.e. the conditions, at which the investigations were led, correspond to work of the thermo element at full power regime. The obtained values of η seem low, but this is characteristic for all thermoelectric materials. The best thermo elements of the low-temperature materials group possess efficiency coefficient η = 2-3 % (values of 4-5 % have been reached in certain samples). These results give the reason to conclude that the solid solution $Ag_{1,84}Cd_{0,08}Te$ is appropriate for thermoelectric purposes: thermo-batteries, sensor for small gradients determination, thin film flow meters, structures for measurement of the thermo-electromotive tension coefficient of thin films, etc.

3.CONCLUSIONS

As a result of the performed investigations, the following conclusion can be made:

- the thermoelectric characteristics of Ag_2Te and the solid solution on its base ($Ag_{1,84}Cd_{0,08}Te$) have been investigated and analyzed;
- the main thermoelectric characteristics of the $Ag_{1,84}Cd_{0,08}Te$ solid solution α = 118 μV/K; σ = 2230 S/cm and λ = $2,45.10^{-2}$ W/(cm.K) ensure thermoelectric efficiency coefficient z = $1,27.10^{-3}$ K^{-1} (at 300 K), which surpasses this of the Ag_2Te;
- composition for commutation material, connecting the N- and P-branches of a single thermo element (52 wt. % In + 48 wt. % Sn) with T_m = 390 K, is developed;

-the possibility for application of the $Ag_{1,84}Cd_{0,08}Te$ solid solution as N-branch of a thermo element in combination with the solid solution $Bi_{0,5}Sb_{1,5}Te_3$ as a P-branch. The thermo element guarantees z values from $0,71.10^{-3}$ to $1,27.10^{-3}$ K^{-1} in the temperature range 250 -350 K. The maximum value of z is registered at 300 K ($z = 1,27.10^{-3}$ K^{-1}).

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