Technology for Manufacturing Working Substances for Thermoelements Branches and Determination of their Thermoelectric Characteristics

Mamadalieva Lola Kamiljanovna
Doctor of Technical Sciences, Docent, Fergana polytechnic institute,Uzbekistan

Tukhtasinov Azamat Gofurovich
Assistant, Fergana polytechnic institute, Uzbekistan

ABSTRACT

The article discusses the technology of producing thermoelectric materials under inert gas pressure, which makes it possible to provide reproducible results from melting to melting and to synthesize sufficiently large amounts of a working substance.

KEYWORDS: *Thermoelectric materials, solid solutions, thermo-EMF, semiconductor materials Bi2Te3, Bi2Se3, charge, tellurium, selenium, lead, crucible.*

Introduction. The quality of thermoelectric alloys depends not only on the composition of solid solutions, but also on the purity of the initial components. In practice, it is convenient to characterize the feedstock by the thermoelectric properties of the base (unalloyed material) alloyed from this feedstock. Quality control can also be carried out on the basis of rigorous analysis of the original alloy components. However, in the case of multicomponent connections, this method is not always the fastest, cheapest and most importantly, reliable. Therefore, the search for technological ways of optimizing thermoelectric material should be carried out in a single cycle of obtaining the base and its alloying.

Obtaining a working substance based on Bi_2Te_3 - Bi_2Se_3

For the preparation of alloys of the required composition, the initial components of the following purity were used: bismuth GOST 10928-64, grade VCh-00, tellurium GOST 9514-60, grade TA-1, selenium for rectifiers GOST 6738-53. The composition of the solid solution corresponding to 80 mol% was chosen as the n-type base. Bi_2Te_3 and 20 mol% Bi_2Se_3.

The charge was loaded in the following order: Selenium was loaded on the bottom of the crucible, then tellurium, and bismuth on top. Tellurium and selenium were used as super stoichiometric chalcogens introduced into the charge. [2]

The experiment was carried out with Bi_2Te_3 - Bi_2Se_3 mixtures in amounts of 20, 60, and 100 g by fusing the initial components in a quartz crucible with a quartz gate. The pressure of an inert gas (argon) during the fusion process was ~ 4 atm; fusion temperature $(750 \pm 10)^0$C. The alloy was held at this temperature for 30 min.

To obtain a thermoelectric base, over stoichiometric tellurium was introduced into the charge in amounts from 0.1 *wt*. % up to 0.6 *wt*. % of the weight of the initial charge. The amount of over stoichiometric selenium in the charge varied in the range of 0.05-0.30 *wt*.%. Experiments have shown that an excess of selenium in the charge has a more effective effect on the thermoelectric properties of the base than the same amount of excess tellurium. [3-5]

Figures 1 and 2 show the effect of an excess of tellurium and selenium, respectively, on changes in the thermoelectric properties of a base synthesized using the technology described above. As can be seen from these data, the optimal amount of superstoichiometric additive, providing the highest values of thermoelectric power α 2σ, for tellurium is 0.18-0.32 *wt*%, and for selenium is 0.08-0.20 *wt*%. In this case, the concentration of electrons in the base is $(0.9^{-1.1})$ $10^{19}sm^{-3}$.

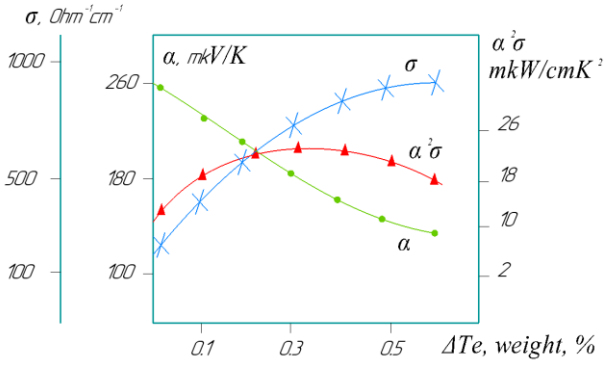

Fig.1. Dependence of thermoelectric properties of the Bi_2Te_3-Bi_2Se_3 base on the excess of tellurium in the charge

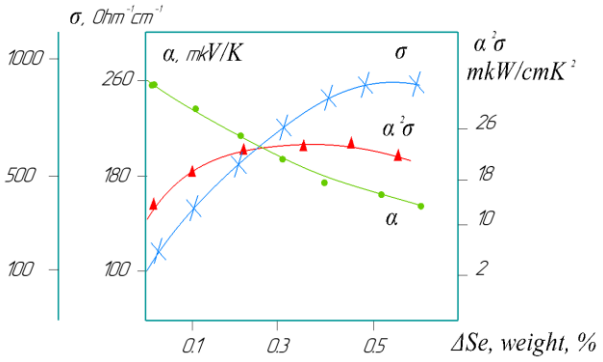

Fig.2. Dependence of the thermoelectric properties of the base in Bi_2Te_3-Bi_2Se_3 on the selenium excess in the charge.

In order to increase the operating temperature range of the synthesized material Bi_2Te_3 - Bi_2Se_3, the developed base was additionally doped. Ammonium iodide salt (NH_4I) was used as a dopant. As a dopant, ammonium iodide has a number of advantages. Firstly, it is almost not hygroscopic; secondly, it does not decompose when heated up to 551^0C; thirdly, it does not melt, it sublimates; fourthly, above 551^0C, ammonium iodide decomposes according to the scheme

$NH_4I = NH_3 + HI$,

and the released hydrogen iodide is a much more active chemical reagent than other iodides. In addition, the ammonia released in the reaction plays the role of a reducing agent, reacting with traces of oxides remaining in the charge and eliminating them.

All these advantages of ammonium iodide affect the improvement of the thermoelectric properties of alloys, ensure the reproducibility of the technology during melting.

To determine the effect of the concentration of the introduced dopant on the change in the thermoelectric properties of the base, ammonium iodide was introduced into the charge of the following composition: Bi - 54.1678 *wt*. %; Te - 39.6923 *wt*. %; Se - (6.1398 + 0.12) *wt*. %. The NH_4I concentration in the charge varied from 0.02 to 0.12 *wt*. %. Ammonium iodide was loaded into the charge first at the bottom of the crucible. The effect of alloying on the thermoelectric properties of the base is shown in Fig.3.

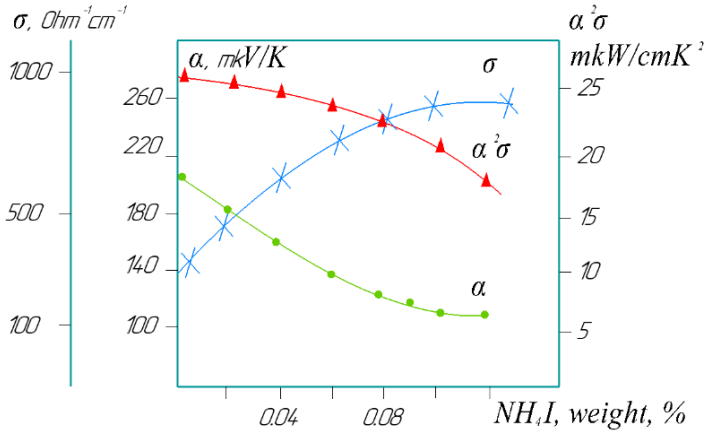

Fig.3. Dependence of thermoelectric properties of the Bi_2Te_3-Bi_2Se_3 base on the amount of dopant.

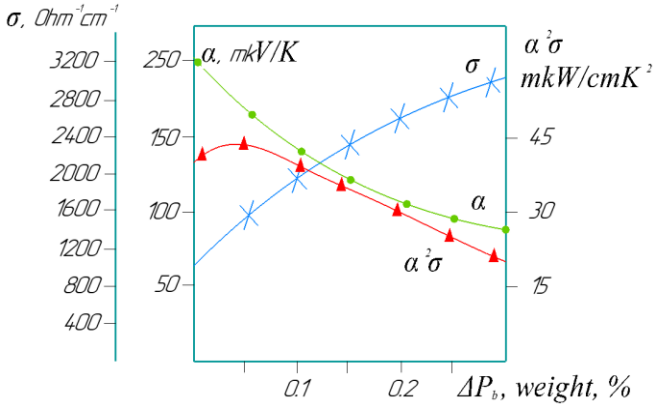

Fig.4. Dependence of thermoelectric properties of the $Bi_{2-x}Sb_xTe_3$ base on the amount of lead dopant.

According to these data, when the concentration of the alloying addition is changed to 0.08 *wt*. % thermo - emf coefficient and electrical conductivity have an almost linear relationship. Above this concentration, they almost do not depend on the amount of added NH4I, which is apparently due to the limited dissolution of iodide ammonium in Bi_2Te_3 – Bi_2Se_3.

Optimal thermoelectric properties of alloys for thermogenerator legs are obtained by introducing 0.04 *wt*. % NH_4I. The parameters of such a base are $\sigma \approx (950 \pm 30)$ *Ohm* $^{-1}cm^{-1}$, $\alpha \approx (150 \pm 5)$ *mkV / K*.

Obtaining a working substance based on Bi_2Te_3 - Sb_2Te_3

To prepare an alloy of the required composition, the initial components were of the following purity: bismuth GOST 10928 - 64 grade VCh-00, tellurium GOST 9514 - 60 grade TA-1, antimony GOST 1069 - 62 grade C-O and lead C - 00. As a basis for in the study, the composition of the solid solution corresponding to 74% Sb_2Te_3 and 26% Bi_2Te_3 was selected. The material of the crucible and the shutter was quartz. The charge was loaded as follows. Antimony, tellurium, and bismuth were sequentially loaded at the bottom of the crucible.

To obtain a doped material with hole conductivity in a quartz crucible, the following composition of the charge was taken: Bi - 16.179 *wt*. %. Te - 56, 993 *wt*. %, Sb - 26.828 *wt*. %.

As an alloying addition, lead was used in an amount of 0.05 *wt*. % up to 0.25 *wt*. %. Thermoelectric properties of materials are shown in Figure 2.4. Optimal thermoelectric properties of the alloy are obtained by introducing an alloying additive of 0.05 - 0.12 wt. %. In this case, the specific electrical

conductivity σ = (1500-2000) $Ohm^{-1} \cdot cm^{-1}$, the Seebeck coefficient is (145-175) *mkV / K*, the concentration of holes is (1.5 - 2) · 10^{19} cm^{-3}.

Table № 1.

ΔP_b, *weight %*	Before annealing			After annealing		
	σ, Ohm^{-1} ·cm^{-1}	*α, mkV/K*	*$\alpha^2\sigma$ mkW/cmK^2*	σ Ом-1 ·cm^{-1}	*σ, Ohm^{-1} ·cm^{-1}*	*α, mkV/K*
0,10	1800	160	45	1100	195	40
0,20	2250	150	50	1300	190	45
0,25	2600	130	45	1600	160	40
0,30	2800	125	45	1700	160	40
0,40	3000	105	35	2000	135	35

It was found that in the working substance $Bi_{2-X}Sb_XTe_3$<Pb>, the parameters are very sensitive to post-technological annealing. To study the effect of annealing, substrates with different lead contents were prepared. The results of measurements of the specific electrical conductivity and thermo-EMF coefficient of the base at T = 300 K before and after annealing are shown in Table 1 (annealing was carried out at temperatures of 350-400^{0}C for 10 hours).
According to the data in the table, an effective material for thermoelements can be selected using annealing of the fused substance (annealing leads to a decrease in the hole concentration).

Based on the real field of application of the available "AFN-thermo", we will analyze low-temperature materials (up to 500 ÷ 550^{0}C) for thermoelements. These include, first of all, Bi_2Te_3 and Bi_2Se_3 of stoichiometric composition. Depending on the type of doping, Bi_2Te_3 can have either electronic or hole conductivity. Bi_2Te_3 is characterized by electronic conductivity. The figure of merit of these materials is respectively equal: (for Bi_2Te_3) -Z = 2 · 10^{-3} deg^{-1} and higher, and (for Bi_2Te_3) -Z = 0.8 ·10^{-3} deg^{-1}.

Let's draw brief conclusions:

1. The most effective thermoelectric materials are semiconductors; whose current carriers are close to a degenerate state or even partially degenerate (with a low degree of degeneracy). In this regard, thermoelectric materials should be capable of deep doping (up to carrier concentrations of 10^{19}-10^{21} cm^{-3}).

Theoretical calculation and analysis of the studies carried out in the creation of "AFS-thermo" with volumetric and film thermopiles show that:

To create a thermoelement and a thermopile with the best values of the efficiency, it is necessary to select the optimal ratio of the transverse branches of the TE and the load. In this case, ηmax can be achieved in cases of using thermoelectric materials with the best Z.

Among the existing many materials, the most effective are thermoelectric materials based on the Bi Te Sb - Bi Te Se ternary alloy, obtained by the zone melting method.

It goes without saying that a thermoelectric material must also possess many other physical, mechanical and chemical properties that would ensure the normal operation of the material under conditions of variable temperatures, a given external environment in the presence of mechanical loads. Technological properties, questions of the synthesis of this material and its alloying are also important. One of the essential problems is reliable low-resistance electrical switching of thermoelements. This is one of the most difficult issues of modern practical implementation of the method of direct energy conversion using thermoelectric generators.

References:

1. Abdullaev E. T. et al. Optimization of parameters of n-branches of solar radiation thermoconverters //Applied Solar Energy. – 2008. – Т. 44. – №. 1. – С. 53.
2. Abduqaxxorovich O. S. et al. Development and research of heterostructures with an internal thin layer based on p-type silicon //European science review. – 2018. – №. 9-10-1.
3. Axmadaliyevich K. A. et al. Possibilities of getting electricity with the help of a small solar furnace //EPRA International Journal of Research & Development. – 2021. – Т. 6. – №. 6. – С. 147-151.
4. Kamildjonovna M. L. et al. Modern approaches to the management of energy resources of the industrial enterprises //Вестник науки и образования. – 2019. – №. 11-3 (65).
5. Kamiljanovna M. L. et al. Analysis of the Results of the Study of the Thermoelectric Part of the Source Sensor //Middle European Scientific Bulletin. – 2021. – Т. 19. – С. 191-196.
6. Kasimakhunova A. M. et al. Highly Efficient Conversion of Solar Energy by the Photoelectric Converter and a Thermoelectric Converter //Journal of Applied Mathematics and Physics. – 2018. – Т. 6. – №. 03. – С. 520.
7. Kasimakhunova A. M. et al. Photo Thermal Generator of Selective Radiation Structural and Energetic Features //Journal of Applied Mathematics and Physics. – 2019. – Т. 7. – №. 06. – С. 1263.
8. Kasimakhunova A. M. et al. Research of AHV-effect in films and crystals with the effect of the double luxurification //Computational nanotechnology. – 2018. – №. 3. – С. 44-48.
9. Kuchkarov A. A., Muminov S. A., Abdurakhmanov A. A. Combined Energy Supply for Sixty-Two Heliostats of the Big Solar Furnace //Journal of Siberian Federal University. Engineering & Technologies. – 2020. – Т. 13. – №. 4. – С. 449-454.
10. Mamadalieva L. K. Development of photothermoelectric converters and research of their design and operational features //Euroasian Journal of Semiconductors Science and Engineering. – 2019. – Т. 1. – №. 6. – С. 3.
11. Mamadalieva L. K. et al. Modern approaches to the management of energy resources of the industrial enterprises //Вестник науки и образования. – 2019. – №. 11-3. – С. 6-8.
12. Mamadalieva L. K., Minamatov Y. E. High Efficiency of a Photoelectric Converter in a Combined Design with a Thermoelectric Converter //Middle European Scientific Bulletin. – 2021. – Т. 19. – С. 178-186.
13. Mamadilieva L. K., Zokirov S. I. Automation problems of finding the optimal coordinates of a photocell in a selective radiation photothermogenerator. – 2019.
14. Muhammad-Sultanhan, Paizullahanov, Sobirov Muslimjon Mukhsinjonugli, Xolmatov Abdurashid Abdurakhimugli. "Materials processing in the solar furnace." ACADEMICIA: An International Multidisciplinary Research Journal. 10.10 (2020): 1233-1237.
15. Okhunov, M., & Minamatov, Y. (2021). Application of Innovative Projects in Information Systems. European Journal of Life Safety and Stability (2660-9630), 11, 167-168.
16. Paizullakhanov M. S. et al. Wear-Resistant Materials Synthesized in A Solar Furnace //Journal of Material Sciences & Manufacturing Research. SRC/JMSMR-111. – 2020. – Т. 80. – С. 3.

17. Payzullakhanov Mukhammad-Sultan Saidvalikhanovich, Xolmatov Abdurashid Abdurakhim ugli, Sobirov Muslim Muhsinjon ugli. Magnetic materials synthesized in the sun furnace // International Journal of Advanced Research in Science, Engineering and Technology. 2020. Vol. 7, Issue 4, pp.1499-13505.
18. Xolmatov A. A., Karimov J. X., Xayitov A. M. Effect of crystallizer catalyst on properties of glass-crystalline materials //EPRA International Journal of Research and Development (IJRD). – 2021. – С. 273-275.
19. А. М. Касимахунова, Р. Найманбаев, Л. К. Мамадалиева, Р. А. Нурдинова, Ш. А. Олимов, “Исследования некоторых явлений в АФН-структурах с изовалентными примесями для разработки приборов и устройств неразрушающего контроля и измерения”, Comp. nanotechnol., 2018, № 2, 72–75
20. Каримов Ж. Х., Фозилов И. Р. Управление многостадийными процессами путём оптимизации глобальных целей системы //Universum: технические науки. – 2020. – №. 3-1 (72). – С. 16-20.
21. Касимахунова А. М. и др. Исследования некоторых явлений в АФН-структурах с изовалентными примесями для разработки приборов и устройств неразрушающего контроля и измерения //Computational nanotechnology. – 2018. – №. 2.
22. Кучкаров А. А., Муминов Ш. А., Абдурахманов А. А. Комбинированное энергообеспечение 62 гелиостатов Большой Солнечной Печи //Журнал Сибирского федерального университета. Техника и технологии. – 2020. – Т. 13. – №. 4.
23. М.О. Узбеков, А.Г. Тухтасинов Тепловая эффективность солнечного воздухонагревательного коллектора с металлическим стружечным абсорбером//Journal of Siberian Federal University. Engineering & Technologies 2020 13(6): 712-720.
24. Мамадалиева Л. К. Анализ и выбор монохроматоров для фототермогенератора селективного излучения //Universum: технические науки. – 2020. – №. 6-1 (75). – С. 74-77.
25. Мамадалиева Л. К. и др. Роль «Мягкого» пуска в энергосбережении //Вестник науки и образования. – 2019. – №. 13-2 (67).
26. Мамадалиева Л. К. и др. Энергосберегающий частотноуправляемый асинхронный электропривод с вентиляторной нагрузкой //Вестник науки и образования. – 2019. – №. 13-2 (67).
27. Мамадалиева Л. К., Набиев М. Б., Усмонов Я. Легирование термоэлектрических материалов на основе Bi2Te3-Sb2Te3 для фототермопреобразователей солнечного излучения //Янги материаллар ва гелиотехнологиялар. – 2030. – С. 90.
28. Мамадалиева Л. К., Рахматшоев И. Н. Расчет кинетических коэффициентов при наличии разных типов носителей заряда полупроводниковых пленочных термоэлементах //Приоритетные направления научных исследований. – 2019. – С. 80-84.
29. Мамадалієва Л. Новий дизайн селективного фототермогенератору з фіксованою щілиною //ΛΌГОΣ. ОНЛАЙН. – 2020.
30. Узбеков М.О., Тухтасинов А.Г. Измерения температуры нагрева абсорбера солнечного воздухонагревательного коллектора // Universum: Технические науки : электрон. научн. журн. 2020. № 6(75).