ELECTRICAL CONTACT RESISTANCE IN THERMOELECTRIC PELLETS BASED ON Bi-Sb CHALCOGENIDES

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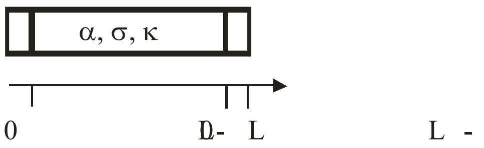
Introduction

It is well-known that electric contact resistance in thermoelectric pellets causes several per cent growth of the module electrical resistance and results in the drop of its efficiency in comparison with that of the thermoelectric material and the dependence of the efficiency on the pellet length. The contact resistance also causes a dependence of the module maximum temperature difference on the pellet length. In the paper the nature of the contact resistance is studied. The reasons of the above mentioned growth can be both the presence of the broken layer on the semiconductor border and the difference between the contact actual area and the geometrical one [1], the latter resulting in tightening lines of the electric current. The analysis of the relative contribution of these factors is done. The relation of the contact resistance with adhesion of the antidiffusion layer is considered.

Contact Resistance Nature

In papers [2,3] it is shown that when thermoelectric (TE) materials based on antimony-bismuth chalcogenides are cut, irrespective of the cutting way and the type of electric conductivity, there appears a broken layer in the direction perpendicular to the cleavage planes (001). In this broken layer the cleavage planes are located at various angles to the cutting plane, even parallel to it. The thickness of the broken layer depends on a mode and way in which the samples are cut and for the p-type sample cut by electroerosion it makes 5-10 microns. The biggest thickness of the broken layer up to 150 microns is formed when cutting by a diamond disk.

We study how the broken layer resulted from the angled cleavage planes influences the properties of a thermoelectric material. Assume that on both ends of a TE pellet of the length L a broken layer of the thickness δ is formed (Fig. 1). Let this TE material have the Seebeck coefficient α, electrical conductivity σ, thermal conductivity κ, the broken layer - the corresponding parameters $\alpha_\perp, \sigma_\perp, \kappa_\perp$.



If TE parameters do not depend on temperature, the Figure-of-Merit Z of a TE pellet with the broken layer at ideal electric and thermal contacts between basic material and the broken layer can be appr. written as

$$Z = \frac{\alpha^2\left(\frac{L-2\delta}{\kappa}+\frac{2\delta}{\kappa_\perp}\right)}{\left(\frac{L-2\delta}{\sigma}+\frac{2\delta}{\sigma_\perp}\right)} = \qquad (1)$$

$$= \frac{\alpha^2\sigma}{\kappa}\left(1+\frac{2\delta}{L-2\delta}\left(\frac{\kappa}{\kappa_\perp}-\frac{\sigma}{\sigma_\perp}\right)\right)$$

where the series connection of the layers and the base is taken, the Seebeck coefficient anisotropy is supposed to be absent, i.e. $\alpha_\perp = \alpha$ [4,5,6]. From Eq. (1) it follows that if the anisotropy factors of electrical conductivity and thermal conductivity coincide in the broken layer, the pellet efficiency remains the same, in spite of the fact that its resistance grows by the factor $1+\frac{2\delta\sigma}{(L-2\delta)\sigma_\perp}$ and the current corresponding to the maximal temperature difference proportionally decreases. If the ratios of anisotropy of the values σ and κ differ, for the small thickness of the broken layer $\delta \leq$ 0.01-0.02 mm the reduction of the efficiency Z will be within the limits of accuracy of definition Z. Allowing for the temperature dependences of TE parameters the heat conduction equation:

$$\nabla(\kappa\nabla T)+\left(\vec{j},\vec{j}\right)\rho-T\left(\vec{j},\nabla\alpha\right)=0 \qquad (2)$$

was solved in one-dimensional approach, where $\vec{j}$ is electric current density, T is temperature. The temperature boundary condition is the following: *T(0)=300 K*, and the heat flux density $\vec{Q}=-\kappa\nabla T+\vec{j}\alpha T$ meets the requirement $\vec{Q}(L)=0$. Besides, the temperature and heat fluxes on the border between the broken layer and the bulk material should be continuous, i.e. $T(\delta-0)=T(\delta+0)$, $T(L-\delta-0)=T(L-\delta+0)$, $\vec{Q}(\delta-0)=\vec{Q}(\delta+0)$, $\vec{Q}(L-\delta-0)=\vec{Q}(L-\delta+0)$. The electric and thermal contacts between the broken layer and the bulk material are assumed ideal, and the ratios of anisotropy are taken according to the data [4,5,6]. For the p-type sample the Seebeck coefficient anisotropy is considered absent, and $\frac{\kappa}{\kappa_\perp}=\frac{\sigma}{\sigma_\perp}=2$. Whereas for the n-type we take $\alpha_\perp=0.95\alpha$, $\frac{\kappa}{\kappa_\perp}=2$, and $\frac{\sigma}{\sigma_\perp}=4$. At L=1 mm and δ=0.1 mm the temperature distribution along the p-type pellet is given in Fig. 2. The temperature distribution for the case $\delta=0$ is given in the same picture.

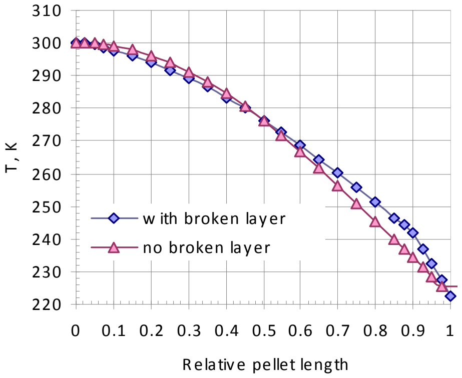


Fig. 2. The temperature distribution along the p-type pellet with and without the broken layer δ *=0.1 mm.*

In particular, the change of the temperature distribution is clearly visible at the border of the broken layers on the pellet ends, where the slope of the dependence *T(x)* is more abrupt (Fig. 3).

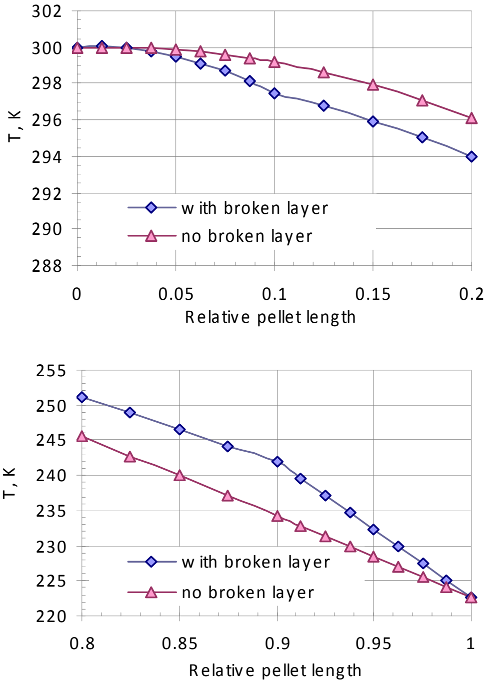


Fig. 3. The temperature distribution along the p-type pellet with and with no broken layer δ *=0.1 mm near the pellet ends.*

The dependences of the minimal temperature of the pellet cold end T_{cold} on the pellet length at the broken layer thickness 10 microns, which is characteristic of the electroerosion cutting, are given in Fig. 4.

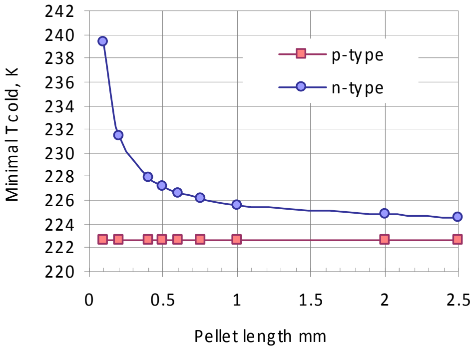


Fig. 4. The dependences of the minimal temperature of the pellet cold end T_{cold} *on the pellet length for the p- and n-type samples at the broken layer thickness* δ *=0.01 mm*

We see that for the p-type sample over a wide range of the pellet length T_{cold} does not depend on the pellet length, while for the n-type sample a strong dependence resulting in a sharp increase of T_{cold} with the pellet length reduction is observed. This dependence is explained by the relative growth of the broken layer resistance contribution. Thus, if the contact resistance results from the broken layer at ideal electric and thermal contact of the broken layer to the bulk material, the effects in the p-type and n-type pellets would be different. In the p-type the pellet resistance would increase but the dependence of T_{cold} on the pellet length would be absent, and in an n-type the resistance would also grow and the dependence T_{cold} on the pellet length will be much more vividly expressed. Therefore, the effect of dependence of the maximal temperature difference on the pellets length shall be mainly related to the n-type broken layer.

If the electric contact is executed in such a way that the contact resistance is absent, there is no dependence of the maximal temperature difference on the pellet length.

However the experimental data do not agree with the above-stated model of the ideal electric and thermal contact. Thus, in paper [7] the results of the measured contact resistance obtained from the dependence of the electric potential on the distance between the probing point and the contact at the alternating current are given. The test sensitivity was 10^{-7} Ohmcm^2. The electric contacts to the ternary materials (p-$Bi_{0,5}Sb_{1,5}Te_3$ и n- $Bi_2Te_{2,7}Se_{0,3}$) were made by the eutectic solder Sn-Bi in two ways: either on the preliminary solder $Bi_{0,96}Sb_{0,04}$, or on the successively cathode- sputtered layers Mo and Ni. In the first case the surface was prepared by the electrochemical etching, in the second one - by the ionic etching. The samples were cut out from zone-melted polycrystalline ingots by the electroerosion cutting and had a section from 0.8 mm^2 up to 3 mm^2. It was proved that for the n-type samples the contact resistance is always less than the measurement sensitivity. The p-type samples with the contacts of the first kind had the contact resistance of $3\cdot10^{-7}$ Ohm·cm^2, those with the contacts of the second kind at a good ionic cleaning the contact resistance was $2\text{-}3\cdot10^{-7}$ Ohmcm^2). In case of a bad ionic cleaning it was $1\text{-}1.5\cdot10^{-6}$ Ohmcm^2. From the resulted data it also follows that the area of the increased resistance in the p-type sample considerably exceeds the size of the broken layer at the electroerosion cutting. It equals 100-150 microns. To relate such sizes of this area to diffusion processes is rather embarrassing as the duration of the elevated temperature influence while soldering is very short.

However, if we consider the contact between the basic material and the contact layer not ideal (irrespective of the presence or absence of the broken layer) the tightening of the lines of the electric current to the contact points can result in the occurrence of the area of the increased resistance. Such contact resistance is quite common in electric contacts [1]. Its value of R_c in this case can be estimated [1]:

$$R_c \approx \rho d \pi \frac{s_g}{s_c} \tag{3}$$

where $\rho = 1/\sigma$, d is the contact points average diameter, s_g is the contact geometrical surface, s_c is the actual contact geometrical surface (the summed surface of all the contact points). From Eq. (3) we see that the diameter of the contact points plays the main role in the contact resistance definition. To obtain the contact resistance at the level $10^{-6}\text{-}10^{-7}$ Ohmcm^2 the contact points average diameter must equal $10^{-3}\text{-}10^{-4}$ cm. The small diameter of contact spots results in quite a significant length of the area of the electric current lines tightening to the contact spots. This effect is not related in any way to the defects in this area. For the reason that the area of the contact resistance is not located on the contact surface and can have a significant length, the pulse methods of the contact resistance measurement [8], based on the assumption that the areas of the Peltier heating/cooling and the Joule contact heating coincide, have not the necessary accuracy for the contact resistance measuring.

After the chemical etching of the contact surface (or after any other method of the contact preparation) the remains of the broken layer with a bad adhesion to the basic material can be a factor not allowing a contact on all the geometrical surface of the contact. It implies the relation of the contact resistance with the adhesion of the antidiffusion covering. As the durability of the broken layer in the detachment direction is determined by weak connections between the cleavage planes, an incomplete removal of the broken layer considerably weakens the adhesion [2] and simultaneously the contact resistance should increase. From the data [2] it follows that the adhesion in p-type usually appears worse than that in n-type. It correlates with the fact that the contact resistance in p-type is higher than in n-type [7]. However the available experimental data do not allow us to reply why in an n-type contact spots appear bigger than in p-type, which results in a greater size of contact resistance in p-type. It is also necessary to emphasize that a strong anisotropy of the crystal structure, even if there is no transitive layer at all, can result in the absence of the continuous contact on the contact surface.

Conclusion

The contact resistance nature is theoretically studied. The relative contribution of the broken layer on the semiconductor border and the difference between the contact actual area and the geometrical one are simulated and analyzed. It is shown that the latter should be a predominant reason for the contact resistance rather than the broken layer created by curved cleavage planes. However we admit that the contact area can be characterized by the properties just different from the bulk ones, not resulting from the cleavage planes turn. This is the subject of microscopic theory and testing.

The paper involves the measured data that is, unfortunately, quite aged. It should be emphasized that there is a “high vacuum” in such experiments. Therefore the work can be considered a foreground that welcomes experimental contact resistance testing on the up-to-date level. It is very appreciable for thermoelectric cooling technology and its adequate mathematical simulation.

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