

TECHNOLOGY FOR PREPARATION OF THERMAL ELEMENTS OF SbBiTe ALLOYS FOR THERMOELECTRIC COOLERS

M.P.Dyntu, V.G. Kantser, D.F.Meglei, A.I.Rusu

*International Laboratory of Superconductivity and Solid State Electronics,
Academy of Sciences, Academiei str., 3/3, Chisinau - 2028 MD, Republic of Moldova*

An improved technology for treatment of thermal elements of SbBiTe alloys is given. Optimal technological regimes for their cutting, mechanical and chemical polishing are found. The electric spark method of cutting, double-sided mechanical polishing without preliminary grinding are found to improve the surface state, to increase output of valid thermal elements and to save material. Optimal conditions for chemical plating of nickel on butt-ends of thermal elements are found.

1. Introduction

Solid solutions of SbBiTe are the most efficient materials for preparation of thermoelectric cooling devices in the region of low temperatures [1,2]. Efficient work of thermocooling devices depends on both physical parameters of a semiconductor material they are made of and a technology for preparation of thermal elements themselves. The thermal element surface state influences greatly the quality of thermoelectric devices, however the process of cutting of thermal elements and their treatment is not well studied in literature.

Low hardness and layered crystal structure of these alloys determine formation of broken surface layers of a significant thickness in the process of cutting and abrasive mechanical treatment. Due to this, it is practically impossible to obtain a perfect surface of thermal elements of given parameters without a post-treatment.

Hence, this paper shows results of improvement of the technology for treatment of thermal elements based on SbBiTe alloys of p- and n-types of conductivity, with the purpose to achieve high values of thermal efficiency $Z=3\cdot 10^{-3} \text{ K}^{-1}$ and approximately equal values of parameters of the thermopower α , conductivity σ and thermal conductivity κ of the branches of both conductivity types in the temperature range 300-200 K.

2. Experimental results

We studied the technology for treatment of thermal elements having the sizes $1,1\times 1,1\times 1,8 \text{ mm}^3$ and $0,95\times 0,95\times 1,4 \text{ mm}^3$ cut out of SbBiTe alloys of p- and n-types of conductivity with the figure of merit Z no less than $3,1\cdot 10^{-3} \text{ 1/K}$ and $\sigma=(1100-1200) \text{ Ohm}^{-1}\text{cm}^{-1}$. Fragility and splitting along the cleavage plane restrict the methods of cutting and mechanical polishing of thermal elements.

The following methods were studied: cutting with metal saw, diamond disks and electric spark cutting. It was found that the first two methods are not suitable since the cutting process causes appearance of large splits along the cut planes due to fragility of this material, and is accompanied by a rivet formation. The electric spark cutting gives a positive result.

The cutting was carried out using the electric spark device of the type A207.23 allowing to decrease thermal and mechanical overloads and the sample deformation. As a washing liquid 25% spirit solution in distilled water was used.

The wire diameter determined the cutting regime. Thus, for example, for a nickel wire of the diameter 0,065 mm, the open-circuit voltage is $U=55$ V, the short-circuit current is equal to $I=0,1 \div 0,2$ A. For a brass wire of the diameter 0,09 mm, $U=70$ V, and $I=0,15 \div 0,2$ A.

A condensation battery in machine-tools of this type is built in the power supply of the RC generator. Due to this, the cutting regime may be controlled only by the supply voltage and short-circuit current. Higher values of the latter cause splitting of a larger number of thermal elements while cutting. Thus, for example, at $U=70$ V, $I=0,15$ A the output coefficient is 88%, and at $U=70$ V, $I=0,2$ A it decreases down to 73%. Optimal regimes for cutting of SbBiTe alloys were found when the coefficient of the thermal element output was $\sim 100\%$.

Mild regime of cutting, in spite of the low electric erosion stability of this material, allows to obtain rather high roughness of the thermal element surface - $\nabla 6\text{-}\nabla 8$, and the deformed layer is about 20-50 μm .

An attempt to polish the deformed layer obtained after the sample cutting with diamond pastes resulted in the broken layer increase and in a breaking of thermal elements along the cleavage plane. Therefore, in order to remove the broken layer of the butt-ends, double-sided mechanical polishing on felt with the chromium oxide powder was used, without the grinding process. As a result, a layer having the thickness of about 20-30 μm was removed. Microscopic investigations of the thermal element surfaces after polishing have shown that they were light, without cuts and breaks, and corresponded to the $\nabla 8\text{-}\nabla 9$ purity class. Let us also note that the double-sided polishing of the samples eliminated the necessity of rejection of spoilage of the thermal elements according to height.

After the chemical polishing the thermal elements were repeatedly washed in organic dissolvents (benzine, toluene, isotropil spirits, acetone) in order to remove contamination, then they were washed in distilled water and went to chemical treatment of the surface.

The analysis of the literature data has shown that for thermoelectric alloys of bismuth telluride two types of polishing etching - electrolytic and chemical are used with an etchant based on $\text{HNO}_3\text{-HCl}$ and $\text{CH}_3\text{COOH-Br}_2$ [3-5]. Use of electrolytic etching of thermal elements has not given a practical result due to the fact that on the sample surface there took place formation of films of yellow or black colour, i.e. films of oxides and products of the sample interaction with the etchant, which are not always dissolved. Besides, the etching kinetics is significantly influenced by the temperature, density of the current and concentration of the solution, that impedes obtaining of demanded sizes of the thermal elements.

One of the peculiarities of the etchants given in literature is that usually they are intended for one plane, in the majority of cases for the cleavage plane of perfect crystals, while thermal elements are cut usually not of perfect crystals, but of ingots with a special texture of the cleavage plane due to necessity to increase mechanical strength of branches of the thermal elements.

The chemical etching of the thermal elements was carried out in etchants of different composition for one and the same material, they were composed both as it is recommended in literature and on our own.

It is found that the chemical polishing of the thermal elements includes two stages of etching: the first is etching in a solution of mineral acids ($3\text{HNO}_3 + 1\text{HCl}$ during 5-10 sec.)

and the second is etching in a solution containing 20-25 g of $\text{CH}_3\text{COOH} + \text{I}_2\text{Br}_2$ during 30-60 sec.

After the mechanical polishing, the thermal elements underwent the chemical one. It was noted that the degree of the material removal while polishing depended on the surface state, composition of the material, temperature and freshness of etching solutions.

Optimal conditions for chemical polishing of the thermal elements were found, resulting in pure surfaces, without residuum of oxide film, with a metal glitter and with the surface roughness of $\nabla 10$ - $\nabla 11$ purity class. The etching regime ensuring the demanded sizes of the thermal elements was found as well.

Then a possibility of chemical plating of nickel film layer [3] on butt-ends of the thermal elements after the above mentioned preparation of the surface was studied. Main advantages of chemical nickel-plating in comparison with other metal coverings are the following: the possibility to plate nickel as a uniform layer upon parts of any configuration, absence of pores, the possibility to plate nickel simultaneously on a large number of thermal elements under similar conditions. Besides, nickel-plating of working butt-ends of thermal elements of SbBiTe alloys allows using solders which do not wet the thermoelectric material, that is solders of series ПОС and ПОСК with a flux consisting of a saturated solution of ammonium chloride in glycerine.

Chemically polished butt-ends of thermal elements after washing with hot and then cold distilled water were subjected to chemical activation, whereupon nickel-plating was performed in the following solution, g/l:

nickel chloride - 21;
sodium hypophosphite - 24;
sodium cytrate - 45;
ammonium chloride - 30;
distilled water up to 1 l,

during 30 minutes at the temperature 50-60°C, and the solution PH was corrected with the 30% aqueous solution of ammonia. However, coverings obtained of this solution are often fragile, this impeding their use for thermal elements.

It turned out that sodium hypophosphite significantly influences the quality of covering of thermal elements of SbBiTe based alloys. The best result is obtained when its content is 10-15 g/l. If its amount is less than 7 g/l the covering is porous and has weak adhesion. When hypophosphite content is increased higher than 20 g/l the covering is fragile and rough, and the solution stability decreases.

It should be noted that in order to obtain a uniform covering and the solution stability nickel-plating should be performed while the solution mixing. For increasing of adhesion and decreasing of the resistance of the contact after plating of nickel the thermal treatment was carried out in vacuum $5 \cdot 10^{-6}$ - $1 \cdot 10^{-5}$ mm Hg during 30-45 min at the temperature 250-300°C. In order to avoid large mechanical stresses the cooling velocity did not exceed 5 degree/min.

Investigation of the covering microstructure has shown that it is expedient to plate nickel layer of the thickness 8-12 μm , because the thin covering having the thickness 3-5 μm was dissolved by the solder in some places while soldering.

The plated nickel turned out light, dead, and the pitting phenomenon is not observed. At this treatment of the thermal element surface the covering adhesion was 46-68 kH/cm². This, in its turn, increases reliability of operation of thermoelectric coolers assembled of the branches with these nickel layers.

3. Conclusions

Optimal technological regimes for cutting and for treatment of thermal elements after cutting are selected. The spark method of cutting allows to increase the output of valid thermal elements, to improve their quality and to save the material. It is shown that the doubled-sided mechanical polishing, without the grinding process, improves the state of the thermal element surface and eliminates the necessity of rejection of spoilage of the elements according to height. For decrease of the contact resistance of thermal elements and for increase of their mechanical and thermal durability optimal conditions for chemical plating of nickel on butt-ends of thermal elements of alloys based on SbBiTe solid solution are found.

References

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