INFLUENCE OF SURFACE DISTURBANCES OF Bi$_{0.5}$Sb$_{1.5}$Te$_3$ CRYSTAL ON THE TRANSPORT OF ELECTRONS IN ITS VOLUME, SURFACE AND IN THE INTERFACE WITH Bi-Sn ALLOY

N.M. AKHUNDOVA[1], T.D. ALIYEVA[2], G.J. ABDINOVA[3]

[1]*Azerbaijan State University of Economics (UNEC)*
AZ-1001, Azerbaijan Republic, Baku, Istiglaliyyat street, 6
[2]*Institute of Physics NAS of Azerbaycan*
AZ-1143, Azerbaijan Republic, Baku, H. Cavid avenue, 131
e-mail: tunzalaaliyeva@mail.ru
[3] *Azerbaijan State Pedagogic College*
AZ-1143, Azerbaijan Republic, Baku, İnshaacılar avenue, 14

Polarization investigations have shown that the influence of inhibitors containing inorganic oxidants and monoethanolamide reduce the corrosion rate of steel, which clearly testify about the slowdown of the cathodic process, the restoration of molecular oxygen and the anodic metal ionization reaction. Confirmation of this is the fact, that the developed mixtures are functioning as inhibitors of mixed type.

1. INTRODUCTION

In the manufacture of samples from ingots of crystals of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ solid solution, widely used in various thermocouples, by the methods of mechanical or electroerosive cutting on their cut surface a disturbed layer appears, which differs from the crystal in composition and structure [1]. Such disturbed layers will differ in electrical properties from the sample. Therefore, the electrical parameters of the samples, their interfaces with metal alloys and electronic converters based on them will be determined by the parameters of the surface layer. In order to identify the regularities and mechanism of the effect of the disturbed surface layer on the electrical properties of samples of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ solid solution and the interfaces between them, we studied the effect of surface treatment of samples cut from Bi$_{0.5}$Sb$_{1.5}$Te$_3$ crystal ingots on their surface conductivity, bulk electrical conductivity σ, thermo-e.m.f. α and Hall R$_H$ coefficients, as well as on the electrical and adhesive properties of the contacts of structures (Bi-Sn) - Bi$_{0.5}$Sb$_{1.5}$Te$_3$ in the temperature range of 77-300 K.

2. EXPERIMENTAL METHODS

The compositions were synthesized by direct fusion of the initial components of the Bi-000 brand bismuth, the Sb-000 brand antimony, the T-hP grade tellurium (99,999) (additionally purified from impurities by the zone melting method). Crystal ingots were grown from the synthesized composition by directional crystallization.

Samples for research in the form of rectangular parallelepipeds with dimensions of 12x6x3 mm^3 were cut out of crystalline ingots on an electroerosive cutting installation. The measurements of these parameters were carried out on samples immediately after they were cut from ingots and on the same samples after processing their side and end surfaces by electrochemical etching in a special installation in a solution of KOH + C$_4$H$_4$O$_6$ + H$_2$O (taken in a certain ratio) at ~ 25-30 ^{0}C for 40 seconds. The interfaces (mutual diffusion of components, thickness and composition of the

formed intermediate phases) of the solid solution crystals with the indicated contact alloys were studied by local X-ray spectral microanalysis using a Cameca-Ms-46 microanalyzer. Metam-RIM microscope was also used with a magnification of 500 times. The depth of the disturbed layer on the cut surface of the crystal samples was estimated from the dependence of the etching rate on time, and the nature of the structure of the damaged layer was studied by X-ray diffraction. The adhesive strength was determined by the avulsion method [2], the adhesion work of A$_a$ calculated from the measured surface tension σ_s (according to the method [3]) and the limiting wetting angle (according to the "lying drop" method [4]) according to the formula A$_a$= σ_s (1+cos θ).

The electrical parameters of the crystals and contacts of the samples were measured by the probe method [5], and the surface conductivity σ_s was measured by the wedge method [6].

The current-voltage characteristics of the structures indicated that contacts were ohmic in all cases.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The data obtained are presented in figures 1-3 and in the table.

It can be seen that the temperature dependence of the surface conductivity σ_s of untreated samples of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ crystals is quite complex and very different from those for the processed samples (Fig. 1). After surface treatment by electrochemical etching σ_s decreases several times over the entire temperature range and becomes almost independent of temperature. These data suggest that the specific temperature dependence of σ_s in untreated samples is due to the surface layer that occurs when cutting samples from ingots. It should be noted that the temperature dependence σ_s of the samples in all cases is reversible, i.e. the observed features of σ_s are due to electronic processes in the surface layer of the cut of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ sample.

Table

Dependence of surface tension σ_s (mJ/mm^2), limiting contact angle θ (deg), adhesion work A_a (mJ/m^2), contact resistance r_k (10^{-5} $\Omega \cdot$cm^2) of an alloy mass.%: 57 Bi + 43 Sn with a crystal ($Bi_{0.5}Sb_{1.5}Te_3$) as a result of changes in surface conductivity σ/σ_{s0}, bulk conductivity σ/σ_0, Hall R_H / R_{H0} and thermo-e.m.f. coefficients α/α_0 during electrochemical processing of the crystal surface.

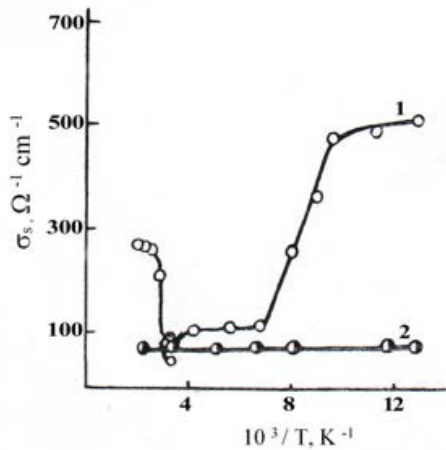| T,K	σ_s	θ	A_a	r_k, 300K	σ/σ_{s0}		σ/σ_0		R_H/R_{H0}		α/α_0	
					77K	300K	77K	300K	77K	300K	77K	300K
413	409	60	463									
433	409	12	809									
453	413	11	816	0,70	7,10	0,80	1,12	1,33	1,01	1,06	0,94	0,95
473	413	11	817									
493	414	11	820									
513	415	11	823									

Fig. 1. Temperature dependence of the surface conductivity of $Bi_{0.5}Sb_{1.5}Te_3$ samples before (1) and after (2) treatment.

It follows from Fig. 2 that the surface treatment of the samples does not change the character of the temperature dependences of σ, α, R_H for $Bi_{0.5}Sb_{1.5}Te_3$ crystals. However, the numerical values of these parameters after processing undergo certain changes. Due to the fact that the disturbed surface of the crystal has a higher surface conductivity than

σ_s than the treated surface, it can lead to shunting (shorting) of the ends of the sample, i.e. an increase in σ measured before treatment and a decrease in α and R_H.

The structure and depth of the disturbed layer arising on the surface of the $Bi_{0.5}Sb_{1.5}Te_3$ sample in the process of electroerosion cutting are investigated. The depth of the disturbed layer was estimated from the time dependence of the rate of electrochemical etching in a KOH + $C_4H_4O_6$ + H_2O solution. The nature of the structure of the disturbed layer was studied by X-ray diffraction when shooting a fixed sample for reflection to the RKSO camera, in the radiation of a tube with a copper anticathode; the depth of the semi-absorbing layer is ~ 15 µm.

The experiments showed that during electroerosive cutting of crystals of the $Bi_{0.5}Sb_{1.5}Te_3$ solid solution into samples a disturbed layer ~ 40 µm thick appears on the surface of the cut. This disturbed layer consists mainly of two sublayers with different compositions: a sublayer formed by melting and partial combustion of a semiconductor material during cutting and quenching of the liquid phase, which is heavily contaminated with the products of the electrode and the dielectric medium, and the sublayer which is formed due to deformation of the surface of the sample at cutting, leading to fragmentation of crystallites, bending of atomic planes and the formation of polycrystalline areas on the surface of the single crystal.
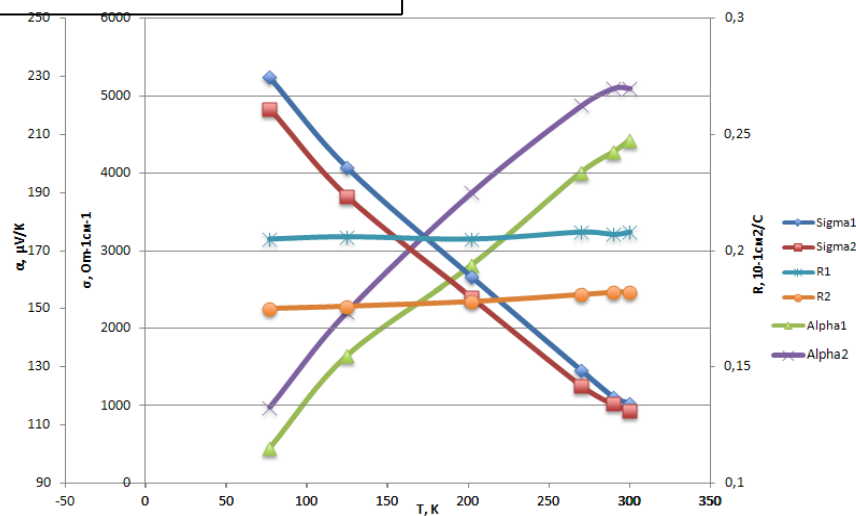

Fig. 2. Temperature dependence of the electrical conductivity σ α, thermo-e.m.f. α and Hall R_H coe_cients of $Bi0:5Sb1:5Te3$ samples before (1; 2; 3) and after (10; 20; 30) treatment of their surface.

The table presents data on the dependences of the surface tension coefficient σ_s, limiting contact angle θ, adhesion work A_a, and contact resistance r_k at the contact alloy-$Bi_{0.5}Sb_{1.5}Te_3$ interface on preliminary processing of the crystal surface and temperature.

It can be seen that the contact angle θ decreases rapidly with increasing temperature and at temperatures 20–40 degrees higher than the melting temperature of the contact material is almost independent of temperature. With increasing temperature the work of adhesion also increases.
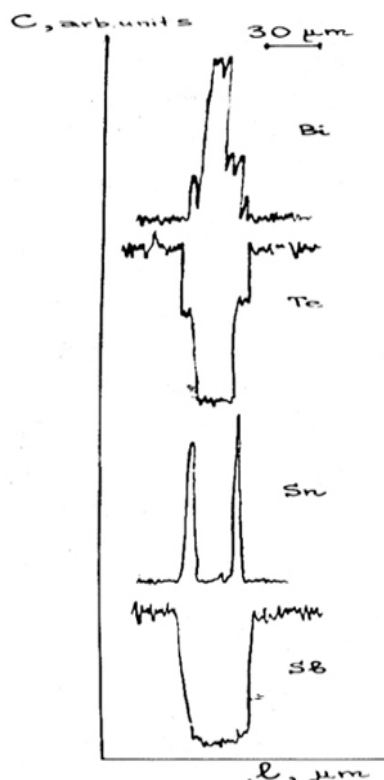

Fig. 3. Distribution curves of $Bi0.5Sb1.5Te3$ crystal components and the contact material in the crystal-contact material-crystal structure.

The measured adhesive strength of $Bi_{0.5}Sb_{1.5}Te_3$ contacts with the alloy at ~ 300 K was ~ 73 kg/cm^2.

When creating contacts to $Bi_{0.5}Sb_{1.5}Te_3$ crystal by the tinning method, contact alloy simultaneously dissolves the crystal in the contact material melt, diffusion the ingredients of the contact material melt into the near-contact region of the crystal, and reactions leading to the formation of new intermediate phases at the interface.

Figure 3 shows a characteristic diagram illustrating changes in the distribution of the constituent elements of the crystal matrix ($Bi_{0.5}Sb_{1.5}Te_3$) - Bi-Sb-Te and contact material (Bi-Sn) at the interface $Bi_{0.5}Sb_{1.5}Te_3$ - contact material - $Bi_{0.5}Sb_{1.5}Te_3$.

It is seen that the concentration of the elements that make up the crystal and the contact alloy at the interface changes quite sharply. At the interface SnTe interlayers of 5–7 μm thick are formed. In this case the tin atoms that make up the contact material are mainly localized in the end parts of the initial contact layer, i.e. at the crystal-contact material interface, and the bismuth atoms are localized closer to the central part of the contact layer.

Microscopic studies have shown that at the crystal-contact material junction boundary a band is observed that clearly stands out in color against the background of the bulk of the contact material. The intermediate phases formed have different electrical and adhesive parameters which determine the electrical and adhesive properties of the interface of $Bi_{0.5}Sb_{1.5}Te_3$ crystals with the considered contact alloy.

4. CONCLUSION

It was found that during electroerosive cutting of single crystals of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution single crystals into samples, a layer with disturbed composition and structure up to 40 μm thick appears on the surface of the cut. Disturbance of the surface substantially changes the electrical properties of the surface, volume, and interface between the crystal and the contact alloy. When the contact alloy crystals are applied to the ends of the samples, mutual diffusion and chemical interaction of the ingredients of the contact material and the crystal occurs, as a result of which an intermediate phase of the SnTe type is formed, which affects the electrical and adhesive properties of the interface. A correlation is observed between the parameters r_k and θ, A_a of the contacts.

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