A.I. Anukhin, V.V. Razinkov

Institute of Thermoelectricity of the NAS and MES
of Ukraine, 1, Nauky str., Chernivtsi,
58029, Ukraine

A.I. Anukhin

V.V. Razinkov

CRYSTALLIZATIONS OF SOLID SOLUTIONS OF BISMUTH AND ANTIMONY TELLURIDES BY ZONE MELTING AND NORMAL CRYSTALLIZATION

This paper presents the results of mathematical simulation of normal crystallization and zone melting of solid solutions of bismuth and antimony tellurides. Components distribution along the ingot length for the cases of zone recrystallization and zone leveling is given.

Key words: thermoelectric materials, solid solutions of bismuth and antimony tellurides, zone melting, crystallization.

Introduction

The main *p*-type thermoelectric materials used for creation of thermoelectric cooling devices are based on the alloys of bismuth and antimony tellurides [1]. The highest thermoelectric figure of merit is attained by solid solutions as the most homogeneous materials among the alloys [2]. The solid solutions of bismuth and antimony tellurides are obtained from the melt by normal crystallization or zone melting that can also include zone leveling. Prediction of components distribution along the ingots and, hence, description of the distribution of their electrophysical properties seems to be a challenging task, since crystallization proceeds in multi-component systems with components distribution factors depending on chemical composition and the temperature of the melt. In the present paper, on the basis of mathematical model, iteration method is used to determine components distribution at crystallization of solid solutions of bismuth and antimony tellurides by zone melting and normal crystallization.

The basic concepts of the model

The solid solutions of bismuth and antimony tellurides possess a narrow homogeneity region near the stoichiometric composition, in which case the factor of antimony telluride distribution in bismuth telluride depends on the concentration of *Te – Sb* in the melt and the melt temperature [2]. Mathematical description of mass exchange process in the solid solutions is a complicated problem which has not been solved yet. Here, for the mathematical description of components distribution at crystallization in *Bi – Sb – Te* system the iteration method is used. As a first approximation, the equality to zero of tellurium distribution factor in *(Bi, Sb)$_2$Te$_3$* solid solutions is assumed [2], in which case the system is viewed as binary – *(Bi, Sb)$_2$Te$_3$ – Te*. As a second approximation, the dependence of antimony telluride distribution factor on the concentration of tellurium in the melt in *(Bi, Sb)$_2$Te$_3$ – Te* binary system is viewed as linear, since antimony telluride distribution factor depends on components concentration. As a third approximation, tellurium solubility in *(Bi, Sb)$_2$Te$_3$* solid solution is taken into account.

In the most general case of crystallization from the melt (irrespective of crystallization method) a differential equation for the description of concentration of superstoichiometric tellurium in Pfann's assumptions with an arbitrary ingot section is given below [4]:

$$\frac{dC}{dV} + \frac{C(\frac{dV_{liquid}}{dV} + k)}{V_{liquid}} = \frac{C_0(\frac{dV_{liquid}}{dV} + 1)k}{V_{liquid}} \quad, \tag{1}$$

where C is component concentration in solid phase, C_o is initial component concentration, k is component distribution factor, V_{liquid} is melt volume, V is crystallized part volume.

The boundary conditions for equation (1):

$$C(0) = kC_o,$$

$$V_{liquid}(0) = 0. \tag{2}$$

Let us consider mass exchange processes for both crystallizations individually. For normal crystallization $\frac{dV_{liquid}}{dV} = -1$. In the approximation of equality to zero of tellurium distribution factor for normal crystallization Eq. (1) is of the form:

$$\frac{dC}{dV} - \frac{C}{V_{liquid}} = 0 . \tag{3}$$

The concentration of superstoichiometric tellurium in the melt with regard to the boundary conditions (2) is given by equation:

$$C = \frac{C_0}{1-G} , \tag{4}$$

where G is specific part of solid phase in the ingot which is determined by coordinate X of crystallization front from the beginning of the ingot

$$C = \frac{C_0}{1-X} . \tag{5}$$

For the case of zone recrystallization $\frac{dV_{liquid}}{dV} = 0$ and Eq. (1) takes on the form:

$$\frac{dC}{dV} = \frac{C_0}{V_{liquid}} . \tag{6}$$

The distribution of superstoichiometric tellurium concentration in the zone melt is determined from Eq. (6):

$$C = C_0(1 + \frac{X}{V_{liquid}}). \tag{7}$$

The value of melt volume V_{liquid} for the case of constant ingot section is advisable to be replaced by the length of molten zone l. As a result, we get a change in the concentration of superstoichiometric tellurium along the length of zone recrystallized ingot which is determined by the width of molten zone. At zone leveling the concentration of superstoichiometric tellurium in the melt is not changed and remains constant during the entire back pass of the zone and is equal to:

$$C = C_0(1 + \frac{L}{l}), \qquad (8)$$

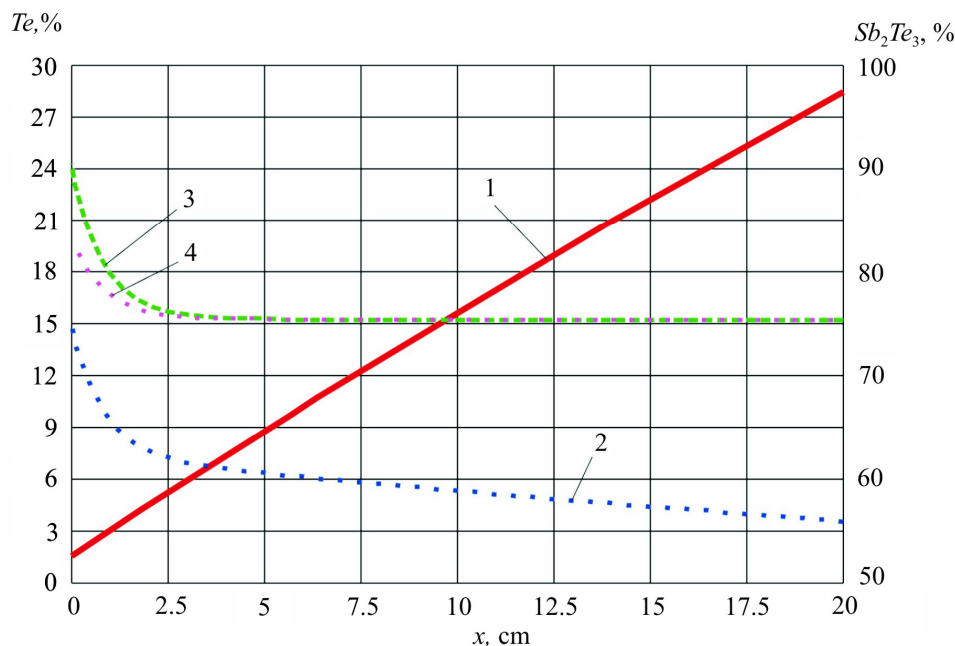where L is the length of zone forward pass along the ingot.

Fig. 1. Estimated change in components concentration along the ingot length:
1 – superstoichiometric tellurium $C_{Te\_liquid}(x)$, 2 – antimony telluride $C_{TeSb\_liquid}(x)$ in
the melt in the first pass of the zone, 3 – antimony telluride in the solid phase $C_{TeSb\_solid}(x)$
in the first pass of the zone, 4 – antimony telluride in the solid phase $C_{TeSb\_back\_solid}(x)$
in the back pass of the zone.

The result of integration of material balance equation is represented in Fig. 1.
For the case of zone recrystallization the dependences of distribution factors have been obtained under the following assumptions:

- antimony telluride distribution factor $k_{Sb_2Te_3}$ is linearly dependent on the concentration of

stoichiometric tellurium C_{Te} / $k_{Sb_2Te_3} = k_0 + \alpha * C_{Te}$, where $\alpha = 0.05$;

- superstoichiometric tellurium distribution factor is equal to 0.01;
- the concentration of antimony telluride is equal to 75 % (the most common compositions);
- antimony telluride distribution factor for stoichiometric compositions is equal to 1.02 [3];
- the ingot length is assumed to be equal to 20 cm;
- the initial concentration of superstoichiometric tellurium is assumed to be equal to 1.5 %.

It follows from the plots that concentrations of components and their change in the zone melt do not affect the distribution of antimony telluride at zone leveling. Therefore, the concentration of dissolved tellurium will be determined only by the achieved value of superstoichiometric concentration in the zone melt at the end of the ingot. With a single zone pass along the ingot, the concentration of tellurium will linearly increase in the zone melt.

Discussion of the results

As a first approximation, the result of solving the problem of components distribution in the first zone pass is a linear change in the concentration of superstoichiometric tellurium in the zone melt when moving along the ingot (Fig. 1, dependence 1). At the same time, at normal crystallization

the concentration of superstoichiometric tellurium in the zone melt changes inversely proportional to crystallization front coordinate from the beginning of the ingot. This result is important, since it enables one to determine of which composition (with respect to tellurium) the solid solution was crystallized at zone melting. The latter is a simple method of controlling the chemical composition of the zone melt. For instance, changing ingot length, one can easily change melt composition, since in the back pass of zone leveling the concentration of tellurium in the zone will be constant and depend only on three values, namely the initial concentration of tellurium C_{Te} in the charge, ingot length L and molten zone length l. The value $\dfrac{L}{l}$ can be assumed as a technological parameter of ingot growth process.

The linear dependence of the concentration of superstoichiometric tellurium on the zone coordinate enables one to get "property-chemical composition" diagrams for a specific crosscut of zone recrystallized ingot along its length. As it follows from the numerical solution of differential material balance equation, antimony telluride concentration in the solid phase remains equal to its concentration in the charge, except for the initial part of the ingot. Therefore, after zone recrystallization the ratio between the concentrations of bismuth and antimony tellurides remains unchanged. In the initial part of the ingot the concentration of antimony telluride is higher than in the charge, and it must be taken into account in the construction of diagrams.

Conclusions

1. At zone melting, the concentration of superstoichiometric tellurium in the zone melt is linearly increased in proportion to crystallization front coordinate from the beginning of the ingot.
2. At zone leveling, the concentration of superstoichiometric tellurium in the melt is constant and equal to concentration achieved at the end of the first zone pass.
3. With a normal crystallization, the concentration of superstoichiometric tellurium in the melt is changed inversely proportional to crystallization front coordinate from the beginning of the ingot.
4. In the solid phase the concentration of antimony telluride remains constant along the ingot length, except for its initial part, both at zone melting and at zone leveling.
5. Linear change in the concentration of superstoichiometric tellurium in the zone and constancy of antimony telluride concentration along the ingot length must be taken into account in the construction of "property-composition" diagrams for different crosscuts of solid solutions of bismuth and antimony tellurides.

References

1. L.I.Anatychuk, Current Status and Some Prospects of Thermoelectricity, *J.Thermoelectricity* 2, 7 – 20 (2007).
2. A.F.Ioffe, L.S.Stilbans, E.K.Iordanishvili, and G.S.Stavitskaya, *Thermoelectric Cooling* (Moscow-Leningrad: AN SSSR Publ., 1956), 110 p.
3. W.M.Yin and A. Amith, *Bi – Sb* Alloys for Magneto-Thermoelectric and Peltier Cooling, *Solid-State Electronics* 15, 1141 – 1165 (1972).
4. V.N.Vigdorovich, *Zone Recrystallization Improvement* (Moscow: Metallurgiya, 1974), 200 p.