PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the Tl₂Te-SnTe-Bi₂Te₃ System

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Abstract—phase equilibria in the $Tl_2Te-SnTe-Bi_2Te_3$ system were studied by differential thermal analysis (DTA), X-ray powder diffraction, and microhardness measurements. Some polythermal sections and iso-thermal (at 600 and 800 K) sections of the phase diagram and a projection of the liquidus surface were constructed. It was shown that the system is characterized by the formation of solid solutions with the Tl_5Te_3

structure (δ) and solid solutions based on SnTe (γ_1), Tl₂Te (α), Bi₂Te₃(β), and two TlBiTe₂(γ_2 and γ'_2) phases. Their homogeneity regions were determined. The liquidus surface consists of the primary crystallization fields of the β -, γ_1 -, γ'_2 -, and δ phases and the compounds SnBi₂Te₄ and SnBi₄Te₇. The liquidus of the α phase is degenerate. The primary crystallization fields of phases were determined, and the types and coordinates of in- and monovariant equilibria were found.

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Tellurides of heavy p elements, in particular, tin, bismuth, and thallium, are narrow-gap semiconductors and are considered to be promising matrix phases for producing new thermoelectric materials [1, 2]. A way to increase the efficiency of thermoelectric materials is to sophisticate their composition and structure [3]. For the directed search and development of scientific principles of production of new multicomponent telluride phases based on the above elements, it is reasonable to study phase equilibria in relevant systems.

The Tl-Sn-Bi-Te system is interesting because not only the binary compounds Bi₂Te₃, SnTe, and Tl_5Te_3 , but also the ternary compounds Tl_9BiTe_6 , TlBiTe₂, SnBi₂Te₄, and SnBi₄Te₇ in this system have good thermoelectric properties [1, 2, 4-6]. In this context, we studied phase equilibria in this guaternary system in some concentration planes: Tl₅Te₃- $Tl_4SnTe_3-Tl_9BiTe_6$ [7], $SnTe-TlBiTe_2-Te$ [8], and $Tl_2Te-SnTe-TlBiTe_2$ [9]. T-x-y diagrams were constructed for these systems. In the first of these systems, unlimited solid solutions with a tetragonal structure of the Tl₅Te₃ type (δ phase) were found to form [7]. In the second system, there are a ternary eutectic and wide regions of solid solutions based on SnTe (γ_1 phase) and TlBiTe₂ (γ_2 phase) [8]. In the Tl₂Te–SnTe–TlBiTe₂ system, wide fields of γ_1 -, γ_2 -, and δ solid solutions were found and their homogeneity regions were determined [9].

In this work, we presented the full pattern of phase equilibria in the $Tl_2Te-SnTe-Bi_2Te_3$ system (system A) in the *T*-*x*-*y* coordinates.

The binary compounds Tl_2Te , SnTe, and Bi_2Te_3 melt congruently at 698, 1080, and 858 K, respectively

[10–12], and have monoclinic [13], cubic, and rhomobohedral [10, 12] structures, respectively.

The boundary elements of system A were studied in a number of works. The Tl₂Te –SnTe system is characterized by the formation of the congruently melting (at 828 K) ternary compound Tl₄SnTe₃ with a wide homogeneity region (12–35 mol % SnTe) [14, 15]. This compound and its base solid solutions based (δ phase) crystallize in a tetragonal structure of the Tl₅Te₃ type (space group *I*4/*mcm*). The unit cell parameters of Tl₄SnTe₃ are *a* = 8.82 Å, *b* = 13.01 Å, and *Z* = 4 [16].

In the Tl₂Te–Bi₂Te₃ system, the congruently melting compounds Tl₉BiTe₆ (at 815 K) and TlBiTe₂ (at 830 K) form [17, 18]. Tl₉BiTe₆ has a tetragonal structure of the Tl₅Te₃ type (a = 8.855 Å, c = 13.048 Å, and Z = 2) [17, 19] and forms a continuous series of solid solutions with Tl₂Te [17]. TlBiTe₂ has two crystalline phases: the low-temperature orthorhombic phase at 780 K transforms to the high-temperature variable-composition disordered phase, which melts with an open maximum [20].

The results of numerous studies of the $SnTe-Bi_2Te_3$ system before 1991 were generalized [21]. However, data on the number and composition of species in system Are contradictory. A new detailed investigation of the $SnTe-Bi_2Te_3$ system was performed [4], and a phase diagram was compiled using all the available published data. According to this diagram, in the system there are three ternary compounds, $SnBi_2Te_4$, $SnBi_4Te_7$, and $SnBi_6Te_{10}$, which have tetradymite-like structures and melt with decomposition by peritectic reactions at 873, 863, and 855 K, respectively.



Fig. 1. Isothermal section of the T-x-y diagram of system A at 600 K.



Fig. 2. Polythermal section $1.5Tl_4SnTe_3$ -SnBi₄Te₇ of the phase diagram of system A.

 $\text{SnBi}_6\text{Te}_{10}$ forms a continuous series of solid solutions with Bi_2Te_3 .

EXPERIMENTAL

The initial binary and ternary compounds for studying system A were synthesized by alloying the corresponding elemental components of high purity in evacuated ($\sim 10^{-2}$ Pa) and sealed quartz ampoules at 750 K (Tl₂Te), 1150 K (SnTe), and 900 K (TlBiTe₂, Bi₂Te₃, Tl₄SnTe₃, and Tl₉BiTe₆), which somewhat exceeded their melting points, with subsequent slow cooling. The individuality of the synthesized compounds was checked by differential thermal analysis (DTA) and X-ray powder diffraction.

Alloys in system A were also prepared by alloying the initial tellurides in evacuated quartz ampoules. Alloys in the sections Tl_4SnTe_3 - $SnBi_4Te_7$, Tl_4SnTe_3 - Bi_2Te_3 , $SnBi_4Te_7$ - $TlBiTe_2$, and Tl_2Te - $SnBi_4Te_7$ and alloys outside these sections were prepared. To bring the alloys to a state that would be maximally close to the equilibrium state, samples were subjected to long thermal annealing. For this purpose, 1-g cast nonhomogenized alloy samples were ground to powder, carefully stirred, and compacted into pellets, after which they were annealed at 600 or 800 K for 1000 h. The



Fig. 3. Polythermal section $1/3Tl_4SnTe_3$ -Bi₂Te₃ of the phase diagram of system A.

alloys annealed at 600 K were cooled in a switched-off furnace, and the alloys annealed at 800 K were quenched in cold water.

The phase equilibria were investigated by DTA (HTP-72 pyrometer, Chromel/Alumel thermocouples), X-ray powder diffraction (DRON-2 diffracto-

Table 1. Invariant equilibria in the $Tl_2Te-SnTe-Bi_2Te_3$ system

Point in Fig. 6	Equilibrium	Composition, mol %		ТК
		Tl ₂ Te	Bi ₂ Te ₃	<i>1</i> , K
D_1	$L \Longrightarrow Tl_4SnTe_3$	66.67	—	828
D_2	$L \Longrightarrow Tl_9BiTe_6$	90	10	815
D_3^*	$L \Longrightarrow \gamma'_2$	50	50	825-830
e_1	$L \Longrightarrow \gamma_1 + \delta$	51	—	778
e_2	$L \Longrightarrow \gamma'_2 + \delta$	74	26	763
e_3	$L \Longrightarrow \gamma'_2 + \beta$	30	70	815
e_4	$L \Longrightarrow \gamma_1 + \gamma'_2$	42	42	815
E_1	$L \Longrightarrow \gamma_1 + \gamma'_2 + \delta$	65.5	23	755
E_2	$L \Longrightarrow \beta + \gamma_1 + \gamma'_2$	18	65	805
P_1	$L + \gamma_1 \Longrightarrow SnBi_2Te_4$	—	65	873
P_2	$L + SnBi_2Te \implies SnBi_4Te_7$	_	74	863
P_3	$L + SnBi_4Te_7 \Longrightarrow \beta$	—	78.5	853
P_4	$L + SnBi_2Te_4 \implies \gamma_1 + SnBi_4Te_7$	5	70	840
P_5	$L + SnBi_4Te_7 \Longrightarrow \gamma_1 + \beta$	11	69	820

Note: For explanation of the point D_3^* , see the text.



Fig. 4. Polythermal section $SnBi_4Te_7$ -TlBiTe₂ of the phase diagram of system A.

meter, CuK_{α} radiation), and microhardness measurements (PMT-3 microhardness meter, load 20 g).

RESULTS AND DISCUSSION

The experimental results and published data on the boundary systems and the $Tl_2Te-SnTe-TlBiTe_2$ system enabled us to determine the total self-consistent pattern of phase equilibria in system A (Figs. 1–7; Tables 1, 2).

Isothermal section of the phase diagram at 600 K (Fig. 1). A characteristic feature of this system is that

the γ_1 , γ_2 , and δ homogeneity regions significantly go beyond the SnTe–TlBiTe₂ and Tl₄SnTe₃–Tl₉BiTe₆ quasi-binary sections on both sides. The homogeneity region of the δ phase occupies a considerable (>90%) part of the Tl₂Te–Tl₄SnTe₃–Tl₉BiTe₆ elementary triangle. The unit cell parameters of the γ_1 - and δ phases vary almost linearly along the sections SnTe–TlBiTe₂ (a = 6.327-6.465 Å) and Tl₄SnTe₃–Tl₉BiTe₆ (a = 8.821-8.854 Å, c = 13.01-13.05 Å).

There are wide two-phase regions of the γ_1 phase both with γ_2 - and δ solid solutions, and with all the phases of the SnTe-Bi₂Te₃ boundary system. This gives rise to three phase regions in the system: $\gamma_1 + \gamma_2 + \delta$, $\beta + \gamma_1 + \gamma_2$, $\beta + \gamma_1 + \text{SnBi}_4\text{Te}_7$, and $\gamma_1 + \text{SnBi}_2\text{Te}_4 + \text{SnBi}_4\text{Te}_7$.

In Fig. 1 two regions near Tl₂Te, α and X, have been identified. Alloys in the α region consist of a monoclinic phase with the Tl₂Te structure [13]. An $\alpha + \delta$ two-phase region was not detected. Therefore, we assume that there is morphotropic phase transition $\alpha \leftrightarrow \delta$ in the system. Equilibrium alloys in the region X contain not only the α - and δ phases, but also a metallic phase based on thallium. This rare phenomenon, which was also observed in the Tl₂Te–SnTe boundary system, was explained previously [14, 15].

To revise the primary crystallization regions of phases and the coordinates of in- and monovariant equilibria, we constructed a number of polythermal sections of the T-x-y diagram of the system under investigation (Figs. 2–5). These sections are conveniently considered together with Figs. 1–7 and Tables 1 and 2.

Section Tl₄SnTe₃–SnBi₄Te₇ (Fig. 2) in the subsolidus intersects the $\gamma_1 + \delta$ and $\gamma_1 + \text{SnBi}_4\text{Te}_7$ two-phase regions, which are separated by the region of the γ_1 phase. The liquidus consists of three branches corresponding to the primary crystallization of δ - and γ_1 phases, and the compound SnBi₂Te₄. The horizontal line at 840 K characterizes the invariant peritectic

Table 2. Monovariant equilibria in the $Tl_2Te-SnTe-Bi_2Te_3$ system

Curve in Fig. 6	Equilibrium	Temperature range, K
e_1E_1	$L \rightleftharpoons \gamma_1 + \delta$	778–755
e_2E_1	$L \rightleftharpoons \gamma'_2 + \delta$	763–755
e_4E_1	$L \Longrightarrow \gamma_1 + \gamma'_2$	815-755
e_3E_2	$L \rightleftharpoons \gamma'_2 + \beta$	815-805
e_4E_2	$L \rightleftharpoons \gamma_1 + \gamma'_2$	815-805
P_1P_4	$L + \gamma_1 \Longrightarrow SnBi_2Te_4$	873-840
P_2P_4	$L + SnBi_2Te_4 \implies SnBi_4Te_7$	863-840
P_3K	$L + SnBi_4Te_7 \Longrightarrow \beta$	853-830
KP ₅	$L \Longrightarrow SnBi_4Te7 + \beta$	830-820
P_4P_5	$L \implies \gamma_1 + SnBi_4Te_7$	840-820
P_5E_2	$L \Longrightarrow \gamma_1 + \beta$	820-805



Fig. 5. Polythermal section $Tl_2Te-1/3SnBi_4Te_7$ of the phase diagram of system A.



Fig. 6. Liquidus surface projection for system A. The primary crystallization fields: (1) γ_1 , (2) δ , (3) γ'_2 , (4) β , (5) SnBi₄Te₇, and (6) SnBi₂Te₄. The dashed lines are substantially quasi-binary sections.

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Fig. 7. Isothermal section of the T-x-y diagram of system A at 800 K.

equilibrium P_4 (Table 1; Fig. 7). Comparison of Fig. 2 with Fig. 6 shows that, in this section, there are also monovariant equilibria along the e_1E_1 , e_4E_2 , and P_1P_4 curves (Table 2).

Section Tl₄SnTe₃-Bi₂Te₃ (Fig. 3) below the solidus intersects a number of two- and three phase regions: $\gamma_1 + \delta$, $\gamma_1 + \gamma_2 + \delta$, $\gamma_1 + \gamma_2$, $\beta + \gamma_1 + \gamma_2$, and $\beta + \gamma_2$. The thermal events at 750 K characterize the polymorphic transition $\gamma_2 \leftrightarrow \gamma'_2$. The liquidus comprises the primary crystallization curves of the δ -, γ_1 -, γ'_2 -, and β phases. In regions below the liquidus, there are monovariant equilibria e_1E_1 , e_4E_1 , e_4E_2 , and e_3E_2 (Table 2; Fig. 6) and four-phase eutectic equilibria E_2 and E_3 (Table 1).

Section SnBi₄Te₇-TIBiTe₂ (Fig. 4) presents the invariant peritectic (P_4 , P_5), eutectic E_2 (Table 1), and eutectoid ($\gamma'_2 \leftrightarrow \beta + \gamma_2$) equilibria and P_1P_4 , P_4P_5 , P_5E_2 ,

and e_3E_2 monovariant equilibria (Table 2). Below the solidus, this section intersects the phase regions of $\text{SnBi}_4\text{Te}_7 + \beta + \gamma_1, \beta + \gamma_1, \beta + \gamma_1 + \gamma_2, \beta + \gamma_2, \text{ and } \gamma_2$.

Section Tl₂Te–SnBi₄Te₇ (Fig. 5) is characterized by a complex pattern of phase equilibria and shows most of the in- and monovariant equilibria in system A. In the composition range >65 mol % Tl₂Te, the first phase to crystallize from melt is the δ phase, and in the range 4–65 mol % Tl₂Te, this is the γ_1 phase. The primary crystallization regions of the α phase and the compound SnBi₂Te₄ do not exceed 1 and 4 mol %, respectively. Numerous in- and monovariant equilibria in this section can be identified using Fig. 6 and Tables 1 and 2.

The liquidus surface of system A (Fig. 6) consists of six fields corresponding to the primary crystallization of γ_1 , δ , γ'_2 , β , SnBi₄Te₇, and SnBi₂Te₄. These fields are separated by 11 eutectic and peritectic curves and six invariant equilibrium points.

The coordinates of the invariant points and their corresponding equilibria are presented in Table 1, and the temperature ranges of monovariant equilibria are given in Table 2.

We confirmed the data [20] on a deviation of the dystectic maximum of the γ'_2 phase from the stoichiometric composition TlBiTe₂ toward BiTe. Therefore, the point D_3^* (Fig. 6) is actually somewhat (by 3–4 mol %) deviated from the true dystectic point, and the γ'_2 phase of this composition crystallizes within a narrow temperature range, rather than at a constant temperature (Table 1).

Isothermal section of the phase diagram of system A (Fig. 7) is constructed based on the results of studying the alloys quenched after annealing at 800 K with the consideration of the corresponding isotherm in Fig. 6.

The directions of the tie lines in the $L + \gamma_1$, $L + \gamma'_2$, and $L + \delta$ two-phase regions allow one to choose the compositions of alloys for growing single crystals of the corresponding solid solutions of given compositions by directional solidification.

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