

THERMODYNAMIC PROPERTIES, PHASE DIAGRAMS AND GLASS-FORMATION OF THALLIUM CHALCOGENIDES*

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The study of multi-component systems without exact knowledge of the binary phase diagrams and their thermodynamic properties leads to erroneous results of such systems. This work is devoted to a critical analysis of binary thallium-selenium, and thallium-tellurium systems, and presents a continuance of the thermodynamic analysis of the phase diagram of thallium-sulfur system^{*}). Thallium chalcogenides and their derived materials with other elements at the solid, liquid and glassy states have a wide range of properties for use in industry. The knowledge of thermodynamic properties and phase diagrams of binary, ternary and many component systems is necessary for solving material science problems and for designing new products and technologies fitted to actual needs.

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1. Introduction

The EMF method with a liquid electrolyte allows us to study both the thermodynamic properties and phase diagrams of semiconductor, metal and oxide systems. This method can also be applied to the glassy state of matter [1]. The use of different types of electrolytes from the molten salts to glycerol salt solutions make it possible to carry out electrochemical measurements from room temperature to the thermal stability of the material used as an electrochemical cell, namely for Pyrex to 800K and for quartz or alumina to 1300K. This wide temperature range allows us to study almost all of the phase diagrams of many systems, and independently from other methods obtains the information about this system. The EMF method and methodological problems are described in detail in the chapter "Electrochemical Cells with the Liquid Electrolyte in the Study of Semiconductor, Metallic, and Oxide Systems" [2]. Some aspects of using salt glycerin solution as an electrolyte are discussed within it.

In this communication the critical thermodynamic properties are reviewed for low-melting systems in comparison with the optimized data. We focus on the thallium chalcogenides, which have a wide range of semiconductor properties. In the solid state the thallium chalcogenides can be used as photoresistors and rectifiers. It can be used as detectors of infrared radiation, X-ray dosimeters and thermoelements. Some of them have superconducting properties. Liquid thallium chalcogenides possess considerable thermopower and they are used as heterophase generators [3-7]. Alloys based on thallium chalcogenides can also be used for the manufacture of high-speed optical disks [8], and they compose a part of the complex semiconductor materials [9-11]. The

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glass-forming ability is also calculated and the glass formation area is analyzed (predicted and experimentally obtained) in the thallium-chalcogen systems.

2. Brief analysis of published data Tl-Se and Tl-Te systems.

2.1. Phase diagrams of Tl-Se, Tl-Te.

The description of the phase diagrams, Tl-Se and Tl-Te system, is presented in monographies by Hansen and Anderko [12] and Abrikosov [13]. Both references are identical. During the period of 1964-1971, we obtained the experimental results, which have helped make significant adjustments in these systems. They were subsequently confirmed by other researchers and entered into the handbook Masalsky [14] with minor additions.

2.2. Thallium-selenium system.

According to the monography [12], Tl-Se phase diagram (Fig.1) has two phases, Tl_2Se and $TlSe$, with congruent melting points and peritectic phase composition, Tl_2Se_3 , which has a polymorphic transformation at 465K [15]. X-ray investigation of Tl-Se alloys is given in [16] and [17]. The results of both works are in full agreement. There are only two phases, Tl_2Se and $TlSe$. Other phases do not exist. In [16], results are presented as a line diagram of a powder pattern. Lattice parameters were found only for $TlSe$ [17]. The film of Tl_2Se was studied by electron diffraction analysis. It indicates the possibility of forming a phase of variable composition by the introduction of selenium atoms in the lattice, Tl_2Se [18].

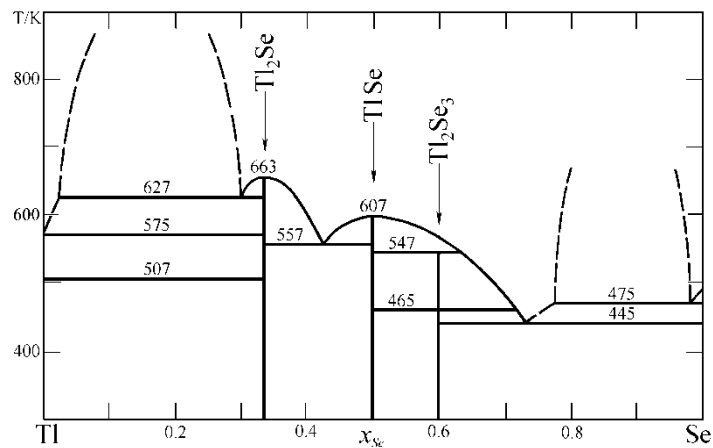


Fig.1. Phase diagram Tl-Se system [12]

2.3. Thallium-tellurium system

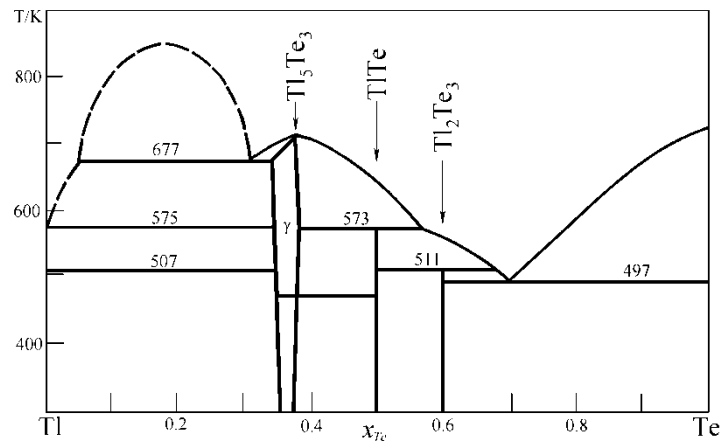


Fig.2. Thallium-tellurium phase diagram [19]

Hansen [12] proposes, for the Tl-Te system only, two phases TlTe and Tl_5Te_3 (62.5 at.% Tl) or Tl_3Te_2 (60 at.% Tl). Rabenau [19] specified the phase diagram of this system, using thermal, microstructural and X-ray analysis. This phase diagram is presented in Fig. 2. According to [19] this system has three intermediate phases, two of which, Tl_2Te_3 and TlTe, have the stoichiometric composition, and the third one is a phase of variable composition on the base of the Tl_5Te_3 compounds (γ -phase) that exist in the range of 62-64 at.% Tl, and it has a congruent melting point. The TlTe and Tl_2Te_3 phases form through peritectic reaction. At this time there are also the indications of the existence of the Tl_2Te phase [15, 20, 21], which is not detected in [19]. The character of the forming of this phase is not well-established. The melting point of the Tl_2Te phase is about 698K [21]. It should be noted that the alloys at a ratio of 2:1 thallium and tellurium manifest in the liquid state at the extreme points for properties such as viscosity, density, electrical conductivity, and heat of mixing [22-27]. These facts indicate the possibility of the existence of such a phase in the solid state.

The structure of the phase Tl_2Te had not been investigated until 2002. It was reported that X-rays of the Tl_2Te and Tl_2Se phase are similar [16]; however, in the position of the lines, there are some differences. An attempt to investigate the structure of the Tl_2Te phase by electron diffraction analysis [28] has not been successful since the deposition of the Tl_2Te composition on a substrate of collodion or rock salt forms the Tl_5Te_3 phase. The structure of the phase Tl_2Te was investigated for the first time in 2002 [29]. The congruent phase Tl_5Te_3 has two modifications [20, 28, 30]. The low-temperature tetragonal form is converted into a high-temperature cubic form at about 473K [28]. It is also known that another transformation of the Tl_5Te_3 phase at about 2 K, is obtained from the measurements of electrical conductivity; this phase becomes superconducting below 2 K [30].

2.4. Review of the thermodynamic properties of thallium chalcogenides.

a) The calorimetric method was used to study the enthalpy of the formation of solid chalcogenides of Tl_2Halk . Even in the 19th century, Fabre (1887-1888 years) determined the enthalpy of the formation of phases Tl_2Se [31] and Tl_2Te [32] by dissolving them in a mixture of bromine and bromine water. Maekawa [22, 23] investigated the enthalpy of the mixing of melted thallium-chalcogen at 753K by high-temperature calorimetry. He found minima in the curves of mixing for the compositions Tl_2Halk . The γ -phase in Tl-Te system has been studied using quantitative thermography in [33]. The γ -phase has been sustained for several hours at 10 K below the melting point before to determine the thermal effect of melting. Authors [33] explain the relatively small heat of fusion ($\Delta H_m = 966 \pm 5 \text{ J/mol-at}$) by disorder of the γ -phase near T_m . For the completely ordered and completely disordered γ -phase (Tl_5Te_3) the entropy of fusion (ΔS_m) is

equal to -17.7 and -10.7 J/(mol-at K), respectively. The last values were found by calculation. The experimental value $\Delta S_m = -10.75 \pm 0.6$ J/mol-at-K for Tl_5Te_3 shows that the phase Tl_5Te_3 is disordered near T_m [33].

The heat capacities of thallium chalcogenides are practically unknown. Low-temperature specific heat has been investigated only for $TlSe$ [34]. To measure the heat capacity, a vacuum calorimeter is used. The measurements were performed in the temperature range 13-304K. No phase transitions or anomalies within the specific heat were observed. The resulting dependence $C_p^o(T)$ for thallium monoselenide is not described by the known theoretical equations. The reported values at 298K for $TlSe$ are $C_p^o = 24.96$ J/(mol-at-K) and $S_{298}^o = 51.32 \pm 0.3$ J/(mol-at-K) [34]. The preliminary results on the measurement of the heat capacity of thallium alloys with tellurium compounds 59.0-63.5 at.% Tl in the temperature range 77-433K are reported in [35]. The results are presented in graphs $C_p^o(T)$. Authors [35] have not discussed or evaluated the entropy of alloys. It follows from the graph $C_p^o(T)$, that the heat capacity $C_{p,298}^o = 25.52$ J/(mol-at K) for Tl_5Te_3 (62.5 at.% Tl).

b) The EMF method was used to determine the thermodynamic functions of liquid and solid alloys of thallium with selenium and tellurium by Terpilovsky and co-workers [23, 36-38] and liquid thallium tellurides by Nakamura and Chimoio [27]. The study of liquid alloys of thallium with selenium and tellurium was carried out in [25, 37], using an electrochemical cell:



in the temperature range 660-740K for the thallium-selenium system and 670-970K for the thallium-tellurium system. Both systems have a minimum heat of mixing near the compositions of 66.7 at.% Tl, that correspond to the Tl_2Te or Tl_2Se phases in the solid state.

The results [25] were later confirmed by Nakamura and Chimoji [27]. These authors also used the EMF method with the same type of cells as Terpilowsky and co-workers [25]. The temperature interval of the study was 770-900K. The minimum heat of mixing, according to [27], accounts for 66.7 at. % Tl, which corresponds to the solid phase and Tl_2Te or Tl_2Se . Based on their own experiment, the authors [27] regard a liquid Tl-Te system as two Tl- Tl_2Te and Tl_2Te -Te pseudobinary systems. According to them the melt Tl_2Te has a high degree of short-range order.

The investigation of solid alloys of the Tl-Te and Tl-Se systems was carried out in the form of ingots in [36, 38]. Authors used an electrochemical cell:



where x is a mole fraction of thallium. The negative electrode of the cell is pure metallic thallium, and the positive electrode is its alloy with the chalcogen (Halk = Se, Te).

The EMF study of thallium-tellurium alloys were carried out in the temperature range 398-468K, and for the system thallium-selenium, such measurements were performed only for one temperature (433K). The main thermodynamic functions of formation (Gibbs energy, enthalpie and entropy) were obtained for Tl_2Te_3 , $TlTe$ and Tl_5Te_3 in [36], and only the Gibbs energy for selenides Tl_2Se_3 , $TlSe$, Tl_5Se_3 and Tl_2Se in [38]. It is necessary to emphasize that there is no consistency in the results between thallium-tellurium in the solid [36] and liquid [25] states (both works are from the same group of authors), Thus, the discrepancy between the chemical potential of thallium at the eutectic point ($x_{Tl} \sim 0.3$ and $T=497K$) attains to 6.7 kJ. Due to the fact that the results of liquid alloys [25] are in good agreement with data [27], and calorimetric measurements [22], the data [25] is reliable without a doubt. Consequently, data inconsistencies [25] and [36] should be attributed to the last work concerning the study of thallium-tellurium alloys in the solid state. Analyzing the way of preparing the alloys [36], we can assume that these alloys were in a nonequilibrium state.

A brief review of literature data on thermodynamic characteristics of thallium chalcogenides shows that only liquid alloys have been adequately studied. Solid alloys are practically unexplored, and available thermodynamic constants need to be revised. So the enthalpy of the formation of chalcogenides (Tl_2Halk) were investigated by calorimetry in the 19th century, and the Gibbs energies of formation of $TlSe$ have been investigated only at one temperature [38]; therefore, the thermodynamic data for thallium tellurides cannot be considered reliable. This conclusion follows a consideration of the entropy of thallium telluride [36]. The $A^{III}-B^{VI}$ compounds, including chalcogenides of thallium, have a typical additive value of the entropy [39], while according to [36], these values are underestimated at least two times.

3. Thermodynamic study of thallium- chalcogen system by EMF method in glycerol solutions

3.1. Electrochemical cell

Thermodynamic properties of thallium- chalcogen were studied by the EMF method in a glycerol solution as electrolyte in [40-45]. We measured the EMF with similar electrochemical cells (II):

We used the glycerol solution of sodium, potassium or calcium chloride with a small addition of thallium monochloride ($TlCl$) as the electrolyte. The relation between the chemical potential $\Delta \mu_{Tl}$ and the EMF is expressed by

$$\Delta \mu_{Tl}(T) = RT \ln a_{Tl} = -zFE \quad (1),$$

where $\Delta \mu_{Tl}$ is the chemical potential of thallium at the transition of one mole of thallium at a pure state into an infinite quantity of alloy (Tl_xHalk_{1-x}).

Earlier, the "glycerol electrolyte" was used in the thermodynamic study of liquid mercury-tin alloys in the temperature range 300-520K [46]. The solid phases in this electrolyte were not studied. Thallium chalcogenides have low melting points. A higher melting Tl_2S phase transforms it to a liquid state at 721K. As it is shown below, using a salt glycerin solution as an electrolyte is rather convenient when working with low-melting phases. The components of alloys vary greatly in their nature and electrochemical exchange reactions are excluded, and the interaction of thallium with glycerol is not observed [47]. In the absence of oxygen, thallium practically reacts neither with alcohols nor water. There is only an interaction of glycerol with thallium oxide Tl_2O . This is a positive fact for electrochemical measurements, because thallium oxide film dissolves in glycerin. The EFM measurements of electrochemical cells were carried out at sufficiently low temperatures (up to 470K) in an atmosphere of purified argon.

3.2. Preparation of alloys, electrodes and electrolyte, and procedure of experiment.

Thallium alloys with selenium or tellurium were prepared in an amount of 15-20 g by synthesis from the elements in evacuated quartz or Pyrex ampoules (0.1 Pa) at 25-50K higher of highest melting phase of the system. The purity of the elements was at least 99.99%. The initial components were weighed with precision to 0.2 mg for a total mass of alloys 15-20 g. The melt was stirred for a better homogenization by shaking the ampoule. Then the temperature was slowly lowered to 470K, and the solidified alloy ingots were subjected to homogenizing annealing at the same temperature for about 200 hours. This method of synthesis was used for the congruent phase. The preparation of the phase with the incongruent melting was different. In this case, the cooling of the melt led to the use of vibrational mixing (50 Hz), which contributed to a more efficient formation of peritectic phases. After rapid cooling below the solidus line at 30-40K, alloys were again heated to a temperature of 3-5K below the peritectic temperature and kept at this temperature for about two days. Then the samples were slowly (1.5-2 days) cooled to 370-470K, depending on the temperature of the peritectic phase formation. Further, the vibrator was switched off and at those temperatures, alloys annealed 200-250 hours.

The difference between the sum of the accurate weights and finished ingot alloys usually did not exceed 0.05 at. % and it was mainly due to the loss of crumbs at the opening of the alloy capsules. The compositions of alloys were accepted with precision to 0.1 at. %. All powdered alloys were stored in evacuated ampoules in order to protect them from oxidation by atmospheric oxygen. We recommend avoiding the use of alloy ingots. As a rule we used the pellets fabricated from powdered alloys. For this reason the dismountable mold is the best suited. The alloys containing the higher melting temperature phases were annealed in pellet form in 200-300 hours. The phase analysis of the composition of alloys was carried out by the X-ray diffraction method. All alloys leading up to the experiment and selectively after the experiments were subjected of this analyse. X-ray spectrums were obtained with the use of apparatus URS-50I (Cu K_{α} radiation). In addition, we have used a Guinier-type focusing camera for any alloys Tl-Se system.

The forming of an electrode-alloy is carried out from the powder obtained by grinding an ingot of alloy. The powder is pressed into a special mold on a tungsten wire 0.5 mm in diameter under pressure of 500 kg/cm². Dimensions of obtained tablets had a diameter of 6 mm and a thickness of 5 mm. Such tablets on the wire serve as an electrode-alloy in the electrochemical cell. Reference electrode is a metallic thallium, with dimension 10×5×5 mm, clipped from a large piece of thallium and mechanically fastened with tungsten current leads. This operation is performed under a layer of glycerin to protect the surface of thallium from oxidation.

To prepare the electrolyte, we used glycerin of "dynamite" grade, which is distilled under vacuum or dehydrated by calcinated CaCl₂ (analytical grade) for additional drying. Actually the electrolyte presents a saturated solution of sodium, potassium or calcium chlorides. The used salts were chemically pure grades or analytical grade. Monochloride thallium (grade "pure") was added in the ratio 0.1 g per 100 ml of glycerol. Glycerol solution, before filling the cell, was degassed by vacuum pump (1 Pa) at 350-360K.

The experiment was carried out in an electrochemical cell under argon. The placement of the cell in the device is shown in Fig.3. Measurements were taken every 2-3 hours with precision 0.01 mV. The cell was kept at a constant temperature. As many as 3-4 consecutive measurements did not differ more than ±0.2 mV. In each experiment, the equilibrium EMF values for each electrode were recorded during the heating and cooling of the cell. The temperature interval of the experiments depends on the object and did not exceed the range 300-470K. The duration of experiment is about one month. During this period, in the studied temperature range, we obtained 15-20 points of EMF values versus temperature.

The EMF method with glycerin electrolyte permits the definition of the main thermodynamic functions as Gibbs energy ($\Delta_f G^0$), enthalpy ($\Delta_f H^0$) and entropy ($\Delta_f S^0$) of formation. Because the study is conducted in the experimental temperature range 313-463K, we may extend the constancy of the enthalpy and entropy of formation to a standard temperature of 298K. The calculation of entropy of the intermediate phases was carried out using our experimental values $\Delta_f S^0$, and reference values of entropies of the components S_{298}^0 [39]. Taking into account all regions of the phase diagram, alloys of different concentrations for each system were prepared. The control of the phase composition of the samples was always accompanied by X-ray analysis. The presentation of experimental data and the discussion is separated for each system.

4. Thallium-selenium system

For studying the thallium-selenium alloys, we prepared 20 alloys with concentrations: 5.0, 32.5, 39.0, 40.6, 42.1, 44.8, 45.5, 48.5, 49.5, 51.0, 60.1, 61.0, 62.0, 61.5, 63.1, 63.5, 64.2, 65.5, 66.5, and 71.5 at. % Tl. The synthesis of thallium alloys with selenium was carried out in evacuated quartz ampoules at 670-530K. Melts were cooled slowly to 430-440K and annealed at this temperature for 3-4 weeks. Vibrational mixing (50Hz) was used for alloy compositions 39.0-49.5 at. % Tl. These alloys were kept at a temperature of 5-10K below the peritectic (547K) during 5-6 days, and then slowly cooled to 430-440K and annealed for about two weeks.

4.1. Powder diffraction alloys of thallium with selenium

The x-ray phase analysis of thallium-selenium alloys shows that there are only two intermediate phases TlSe and Tl₂Se (γ -phase) in the region 5.0-71.5 at. % Tl. The existence of the Tl₂Se₃ phase was supposed in [12] according to the thermal analysis [15]. Neither Ketelaar [17] nor we have detected the Tl₂Se₃ phase by x-ray analysis. Our powder diffraction spectrum of alloys shows that the specimens of alloys from 5.0 to 49.5 at. % Tl consist of two phases: TlSe and Se (hex.); selenium lines could be observed up to 45.5 at. % Tl. The number of the intermediate phases and parameters of their lattices in system are coordinated completely with the X-ray data [17, 18] (Table 2.7). A small distinction in parameter "a" for phase Tl₂Se is caused by its presence in the homogeneity area [18].

We have tried to establish the possibility of the formation of Tl₂Se₃ phase at temperatures above 465K, supposing that the thermal effect at 465K, attributed to polymorphic transformation of Tl₂Se₃ phase [12] (Fig.1), is actually caused by the disintegration of Tl₂Se₃ phase below this temperature. For this purpose we have used a Guinier-type focusing camera for an alloy 44.8 at. % Tl at 493K. The result has not given a definitive answer about the existence of Tl₂Se₃ above 465K. The spectrums of this alloy before and after heating (293K and 493K) differed only by change of intensity of some lines. The comparison of X-ray spectrums of the same specimen at room temperature and at 493K were similar, but the lines were discontinuous. This fact was indicated on a partial melting of the sample. Besides, we have noted the partial fusion of alloys 40.6-48.6 at. % Tl, after an additional annealing of them in the form of the pressed tablets at 453-463K. This phenomenon could not be observed if it is not guided by the diagram [12] with presence of heterogeneous area Tl₂Se₃-TlSe. This observation had permeated us to conclude that the eutectic line (445K) (the Fig.4 could be continued to composition 50 at. % Tl (TlSe phase).

Table 1. Lattice parameters of thallium selenides.

| Phase | Space group | Crystal structure | Lattice periods, nm | | Reference |
|---------------------------------|-------------|-------------------|---------------------|---------------|-----------|
| | | | <i>a</i> | <i>c</i> | |
| Tl ₂ Se | P4/n | tetragonal | 0.852 | 1.268 | [18] |
| | | | 0.862± 0.002 | 1.264± 0.005 | This work |
| Tl ₅ Se ₃ | P4/n | tetragonal | 0.8542± 0.001 | 1.2712± 0.001 | [48, 49] |
| TlSe | I4/mcm | tetragonal | 0.802± 0.001 | 0.700± 0.002 | [17] |
| | | | 0.803± 0.002 | 0.702± 0.005 | This work |

4.2. Discussion of results of Tl-Se system

The definition of the basic thermodynamic functions of the formation of the Tl-Se system was carried out by the EMF method with the use of electrochemical cells of type (II), with various concentrations of thallium from 5.0 to 71.5 at. %. The EMF was measured in the range 310-415 K for alloys 5.0-49.5 at. % Tl and 310-450 K for alloys 51.0-71.5 at. % Tl. The EMF values for alloys of the first series depended only on temperature, but not on composition of alloys, which were in agreement with the x-ray data. The EMF values depended only on temperature for concentration 51.0-62.5 at. % Tl.

While the EMF values of alloys 63.1-66.5 at. % Tl depended on two variables (T, x) which were the characteristic of homogeneous region of this part of phase diagram and the consideration of the Tl₂Se selenides as a phase of variable structure. An alloy 71.5 at. % Tl is already included free thallium, which could be observed visually. The EMF of such alloy is close to zero, in all investigated interval of temperatures. Isotherm E (x) (EMF versus mole fraction of Tl) is presented at 370K for the series of alloys 5.0-66.5 at. % Tl in Fig.3.

The treatment of experimental data $E(x)$ was made by the least squares method. The coefficients of linear equations $E(x)$ were calculated separately for each alloy of homogeneous region 63.1-66.5 at. % Tl.

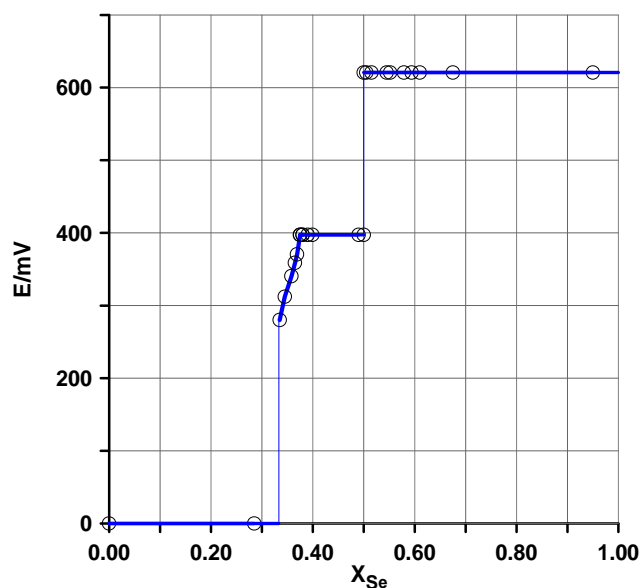


Fig.3. Isotherm $E(x)$ at 370K in Tl-Se system.

The experiment results of equations $E(x)$ and $\Delta\mu_{Tl}(T)$ for the corresponding forming potential reactions are shown in Tab. 2. The calculation of the standard integral values TlSe and Tl_2Se was cured out with use of the Gibbs-Duhem equation. The phase TlSe has been accepted as stoichiometric. The calculation of thermodynamic functions of thallium selenides (TlSe and γ -phases) are given in Table 3.

Table 2. Dependence EMF versus temperature and composition for Tl-Se system.

| Composition of alloys, x_{Tl} | Phase region | $E(T), V$ |
|---------------------------------|-----------------------|---|
| 0.050-0.495 | Se - TlSe | $(0.6319-0.30 \cdot 10^{-4}T) \pm 0.0055(1/80+(T-362.57)^2/111822)^{1/2}$ |
| 0.510-0.625 | TlSe- γ -phase | $(0.3481+1.33 \cdot 10^{-4}T) \pm 0.0055(1/133+(T-381.75)^2/111822.28)^{1/2}$ |
| 0.631 | γ - phase | $(0.2971+1.98 \cdot 10^{-4}T) \pm 0.0039(1/37+(T-391.76)^2/46854.81)^{1/2}$ |
| 0.635 | γ - phase | $(0.2843+2.01 \cdot 10^{-4}T) \pm 0.0034(1/28+(T-388.82)^2/39116.11)^{1/2}$ |
| 0.642 | γ - phase | $(0.2886+1.40 \cdot 10^{-4}T) \pm 0.0034(1/32+(T-384.50)^2/44542.0)^{1/2}$ |
| 0.655 | γ - phase | $(0.2651+1.27 \cdot 10^{-4}T) \pm 0.0027(1/60+(T-393.87)^2/64690.9)^{1/2}$ |
| 0.665 | γ - phase | $(0.2871-0.19 \cdot 10^{-4}T) \pm 0.0053(1/53+(T-402.20)^2/46478.7)^{1/2}$ |

Table 3. Values of the chemical potential of thallium versus temperature for different heterogeneous and homogeneous areas Tl-Se system.

| Phase area | Reaction | $\Delta\mu_{\text{Tl}} = f(T)$, kJ/reaction |
|---------------------------|---|---|
| Se-TlSe | $\text{Tl} + \text{Se} \rightarrow \text{TlSe}$ | $-(60.96 \pm 0.5) + (2.9 \pm 1.25) \cdot 10^{-3}T$ |
| TlSe- γ -фаза | $\text{Tl} + \text{TlSe} \rightarrow \gamma\text{-phase (62.5 at\%Tl)}$ | $-(33.6 \pm 0.63) - (12.9 \pm 1.67) \cdot 10^{-3}T$ |
| γ -фаза 63.1 at%Tl | $\text{Tl} \rightarrow \text{Tl}_{0.631}\text{Se}_{0.369}$ | $-(28.7 \pm 0.33) - (19.2 \pm 1.67) \cdot 10^{-3}T$ |
| γ -фаза 63.5 at%Tl | $\text{Tl} \rightarrow \text{Tl}_{0.635}\text{Se}_{0.365}$ | $(27.45 \pm 0.63) - (19.2 \pm 1.67) \cdot 10^{-3}T$ |
| γ -фаза 64.2 at%Tl | $\text{Tl} \rightarrow \text{Tl}_{0.642}\text{Se}_{0.358}$ | $(27.87 \pm 0.59) - (13.4 \pm 1.67) \cdot 10^{-3}T$ |
| γ -фаза 65.5 at%Tl | $\text{Tl} \rightarrow \text{Tl}_{0.655}\text{Se}_{0.345}$ | $(25.56 \pm 0.42) - (12.1 \pm 0.8) \cdot 10^{-3}T$ |
| γ -фаза 66.5 at%Tl | $\text{Tl} \rightarrow \text{Tl}_{0.665}\text{Se}_{0.335}$ | $(27.7 \pm 0.96) - (1.67 \pm 2.5) \cdot 10^{-3}T$ |

4.2.1. Comparison of our results with the literary data.

We can see from Table 4 that the entropy of the monoselenide of thallium, obtained in our work in 1967 [40], concur well with the entropy founded from the low temperature measurements of heat capacities [34] four years later. Discrepancy is less than 1 %. In regard to the enthalpy of formation of the Tl_2Se phase, this phase was formed with greater exothermic effect (on 5.9 kJ/mol-at) than the enthalpy of formation in [31].

It is necessary to focus on work [38] that was also carried out by the EMF method for the Tl-Se system. Terpilowsky [38] used the same type of a cell, as well as in the work [36], but measurements were made for only a temperature of 433K. The comparison of our results and [38] demonstrate the concordance for the regions 0-40 at. % Tl and 50-62 at. % Tl within experimental errors, whereas the results of area 41-49 at. % Tl are significantly different. Terpilowsky [38], on the basis of EMF difference between 10-39.0 and 41.0-49.0 at. %Tl areas, drew a conclusion on Tl_2Se_3 phase. We explain such divergence through the vaporization of selenium from the surface of the electrodes at 433K in [38]. Apparently, the rate of selenium evaporation from a surface prevails over the process of its diffusion from volume when the composition of heterogeneous alloy (TlSe+Se) make up the stoichiometric TlSe compound. So the equilibrium of selenium composition violates and it leads to the infringement of phase balance. We have also found the continuous reduction of EMF values if we worked above 410K. The obtention of reproduced EMF results in the area Se-TlSe is not possible between 410K and the eutectic line at 445K. Terpilowsky's [38] and our results also differ in the composition range 62-66 at. % Tl. Our values $E(T, x)$ change monotonically in this range, while the results [38] demonstrate absence of heterogeneous area Tl_5Se_3 - Tl_2Se . This difference of results is produced, probably through the preparation of alloys in rather long (20-30 mm) and narrow (3 mm) capsules, which provokes the formation of non-equilibrium alloys due to segregation in the specimens.

Table 4. Thermodynamic parameters of the formation of Tl-Se alloys.

| Phase | $-\Delta_f G^\circ_{298}$ (T/K) | $-\Delta_f H^\circ_{298}$ | $\Delta_f S^\circ_{298}$ | S°_{298} | Reference | Method |
|-----------------------------|---------------------------------|---------------------------|--------------------------|-----------------|------------|-------------|
| | kJ/mol-at | | J/(mol-at K) | | | |
| TlSe | 30.04±0.04 (298) | 30.46±0.25 | -1.46±0.25 | 51.71±0.92 | This work | EMF |
| | 29.87±0.04 (433) | - | - | - | [34] | calorimetry |
| | 28.45±0.4 (433) | - | - | - | [38] | EMF |
| γ -phase (62.5at%Tl) | 31.88±0.08 (298) | 31.25±0.33 | 2.13±0.92 | 58.03±1.13 | This work | EMF |
| | 32.17±0.08 (433) | - | - | - | [38] | EMF |
| | 30.96±0.4 (433) | - | - | - | [38] | EMF |
| γ -phase (66.7at%Tl) | 31.79±0.04 (298) | 30.84±0.37 | 3.18±1.00 | 60.04±1.21 | This work | calorimetry |
| | 32.22±0.08 (433) | - | - | - | [38] | EMF |
| | 31.38±0.4 (433) | - | - | - | [38] | EMF |
| | - | 25.1 | - | - | [31] | calorimetry |
| - | - | - | 57.5 | [50] | Estimation | |

These ingots, without violating their integrity, were used as electrode-alloys in [38]. In our opinion, the surface of these electrodes corresponds to some average composition of the homogeneous area and the EMF values evidenced this fact.

4.2.2. Phase diagram of Tl-Se system

On the base of our thermodynamic and XRD data we proposed a new variant of the Tl-Se system, slightly modified in comparison with [12] (Fig.2). According to our results, the area between 62.5 and 66.6 at. %Tl corresponds to the variable composition γ -phase. In addition, we have not found that the Tl_2Se_3 phase and the eutectic line at 445K should be extended to the TlSe phase. We made this conclusion on the base of XRD analysis and the visual monitoring of pressed tablets of alloys with the composition of 40.6-48.5 at. %Tl, which were heated up to 463K. In this case, the melting of tablets with composition 40.6-48.5 at. %Tl was observed. Since the alloys of these compositions were not investigated by means of EMF method above 465K, we admit the possibility of the existence of the Tl_2Se_3 phase at elevated temperatures between 465 and 547 K [43,44].

Additional study of the Tl-Se phase diagram using the differential scanning calorimetry (DSC) and the XRD analysis with the subsequent optimisation is given in Fig.6 [51]. In this paper we find a narrow heterogeneous region ($Tl_2Se + \gamma$) below 520K. The liquid phase is described by an associated model of solution. Phases TlSe and Tl_2Se have been taken as stoichiometric. The description of γ -phase is performed using the sublattice model. Our data of the chemical potential of the thallium for the solid phase heterogeneous area (Se + TlSe) differ from optimized values with error not exceeding 5 %. Agreement of the second heterogeneous area (TlSe + γ) is almost complete (Fig.7). The discrepancy of the chemical potential of thallium between our values and optimized can be explained by some of assumptions made in [51].

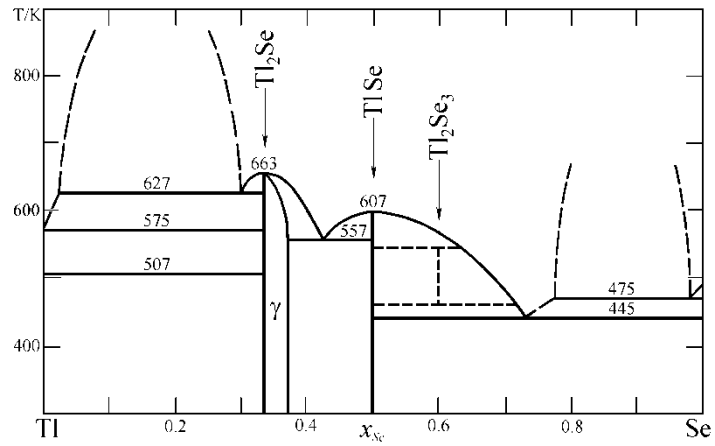


Fig.4. Phase diagram of Tl-Se system in [43].

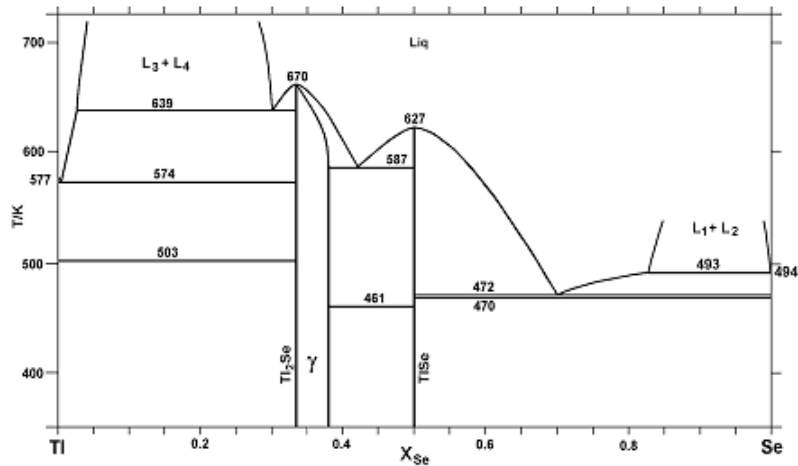


Fig.5. Phase diagram of Tl-Se system in [48, 49].

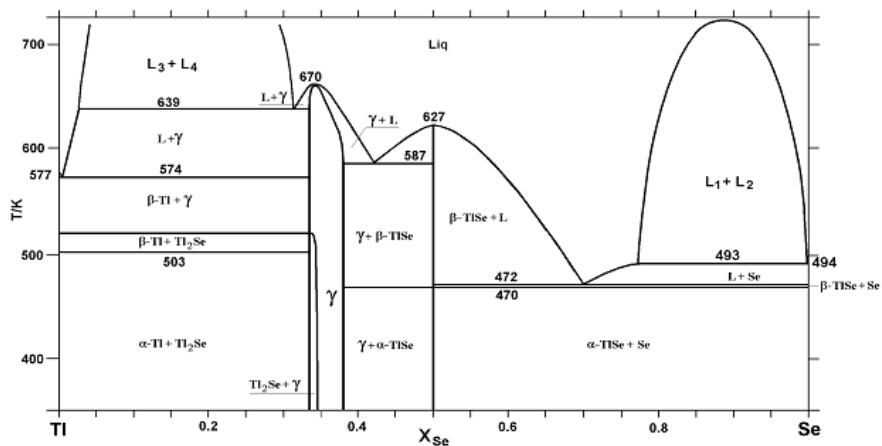


Fig.6. Phase diagram of Tl-Se system in [51].

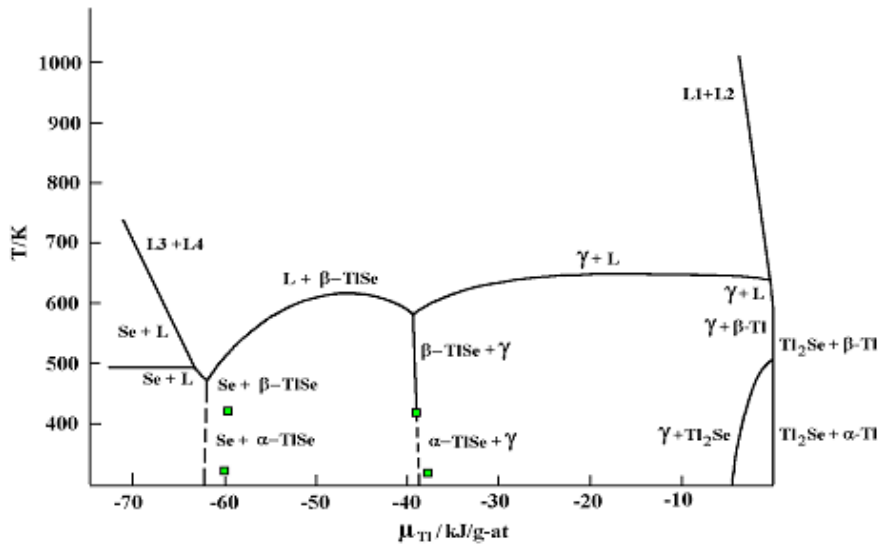


Fig.7. Chemical potential of thallium for two-phase areas in Tl-Se system vs. temperature [51].

■ – our values μ_{Tl} at minimal (310K) and maximal (415K) experimental temperatures.

5. Tl-Te system

Studies of the Tl-Te system were carried out for 21 alloys with thallium content: 4.5, 34.2* 36.0, 36.0*, 38.5*, 38.4, 41.0, 42.5, 45.0, 48.6, 51.5, 54.8, 61.0, 62.0, 62.5, 62.8, 63.8, 65.0, 66.5, 67.0, 68.0. Alloys with an asterisk were prepared from a mixture (40.0 at.% Tl) of stoichiometric composition and tellurium. The remaining samples were obtained by the melting of metals at 733-773 K in vacuum sealed ampoules (0.1 Pa). The cooling of the melts was carried out with a vibrational agitation (50 Hz). After rapid cooling below the solidus line, the alloys have been re-heated to 3-5 K below the peritectic line. In this condition the alloys have been sustaining for two days and have been slowly cooling to 573 K (over 1-1.5 days) and then have been annealing for 200-250 hours. The formation of the congruent γ -phase (Tl_5Te_3) requires less prolonged annealing.

5.1. XRD analysis of Tl-Te alloys

The results of the XRD analysis of the Tl-Te system showed that in this system, besides the three known phases Tl_2Te_3 , TlTe and Tl_5Te_3 , which structures had been investigated in [52], there is a telluride Tl_2Te . Table 5 shows the calculated lattice parameters of all thallium telluride in comparison with references. There is complete agreement of the lattice parameters. The Tl_2Te is not checked in [19] (Fig.2). It is not possible to determine the lattice parameters of Tl_2Te from a powder pattern. The quantitative result allows the admission that this phase has lower symmetry and is not a derivative of the Tl_2Se phase. Subsequently, this hypothesis was confirmed in [29] by studying a single-crystal Tl_2Te specimen. It is established that a unit cell of the Tl_2Te phase belongs to the monoclinic system. A single phase of this phase was grown by a modified Bridgman method in [53]. The Tl_2Te degraded easily in air and it has been transforming for a week into the Tl_5Te_3 phase with the formation of thallium oxide as the second phase. While the Tl_2Te phase has been stored indefinitely in a sealed ampoule, the thallium telluride was a very fragile light material that was gloss-prone, according to our observation to the vitrification. In the air it became dim and turned black. Alloys with a concentration of at least 62.5 at. % Tl were stable in air and were practically not oxidized.

Table 5. Lattice parameters of thallium tellurides.

| Phase | Space group | Crystal structure | Lattice periods, nm | | | Reference |
|---------------------------------|-------------|-------------------|---------------------|---------------|--------------------------|-----------|
| | | | <i>a</i> | <i>b</i> | <i>c</i> | |
| Tl ₂ Te | C2/c | monoclinic | 1.56622 | 0.89873 | 3.1196 β=100.762 | [29] |
| Tl ₅ Te ₃ | I4/mcm | tetragonal | 0.891± 0.001 | | 1.262± 0.001 | This work |
| | | | | | 1.263± 0.001 | [28] |
| TlTe | I4/mcm | tetragonal | 1.295± 0.001 | | 0.618± 0.001 | This work |
| | | | 1.295± 0.001 | | 0.6175± 0.001 | [20] |
| Tl ₂ Te ₃ | Cc | monoclinic | 1.741± 0.002 | 0.655± 0.002 | 0.791± 0.002 β=133 | This work |
| | | | 1.7413± 0.001 | 0.6552± 0.001 | 0.791± 0.001 β=133.16 | [52] |

5.2. Thermodynamic study of thallium-tellurium system

The basic thermodynamic functions of the formation of the Tl-Te system carried out by the EMF method in the temperature range 310-465K with the use of electrochemical cells of type (II) with various concentrations of thallium from 4.5 to 68.0 at. %. Isotherm E (x) (EMF versus mole fraction of Tl) is present at 370K for the series of alloys 4.5-68.0 at. % Tl in Fig. 8. This figure shows that the investigated area of compositions 4.5-68.0 at. % Tl consists of five heterogeneous fields. At the same temperature every field has the constant values of EMF, which are independent of the composition. According to the results of EMF, the six alloys with the concentration between 4.5 and 38.5 at. % Tl correspond to the (Te-Tl₂Te₃) phase area; four alloys between 41.0 and 46.8 at. % Tl conform to the (Te₂Te₃-TlTe) phase area, and three alloys 51.5, 54.8 and 61.0 at. % Tl belong to the (TlTe - γ- phase) area. The composition of alloys belongs to the heterogeneous field (γ-phase - Tl₂Te). We can conclude from the results of several experiments for the alloys 67.0 and 68.0 at. % Tl that there is a heterogeneous area Tl₂Te-Tl at the range of 310-340K since the EMF falls to zero at these temperature. At the higher temperature the EMF rises up to 30-40 mV. Perhaps, at the temperature above 340 K, there is a region of the primary solid solution on a base of thallium. We have not performed a detailed study in this part of the diagram. The results of the EMF measurements for alloys 62.5 and 61.8 at. Tl% indicate that these alloys belong to the homogeneous γ-phase. The composition 62.5 at. % Tl likely presents a limit of existence of the γ-phase of the tellurium side, because the EMF values of this alloy is close to the heterogeneous region (TlTe γ-phase). In our opinion, the alloy with concentration 62.8 % at. Tl is the limit of γ-phase of the thallium side. Note that the E (T) results for alloys 62.5 and 62.8 at. Tl are less accurate than those of heterogeneous areas. This is understandable since the FEM for the homogeneous region fell sharply between 62.5 and 62.8 at. Tl %. The experimental results for (γ-phase-Tl₂Te) field are also less accurate. This is probably related to a partial decomposition of the Tl₂Te phase during the experiment, because the Tl₂Te phase is very sensitive to oxidation even in the presence of oxygen traces. The treatment of measurement results E (T) is performed by the method of least squares to the correspondent phase areas. The results are presented in Table 6.

Equations $\Delta \mu_{Tl}$ (T) for reactions, forming the potential, are given in Table 6. The calculation of the standard integral values is achieved by a combination of reactions 1, 2, 3 and 6 of the Table 7, assuming that all thallium tellurides are stoichiometric phases. Taking into account, the deviations from the stoichiometric, phase Tl₅Te₃ (0.3%) gives an error, which does not exceed the limits of experimental error. The results of the calculation of the thermodynamic functions of formation for Tl₂Te₃, TlTe, Tl₅Te₃, and Tl₂Te phases are summarized in Table 8.

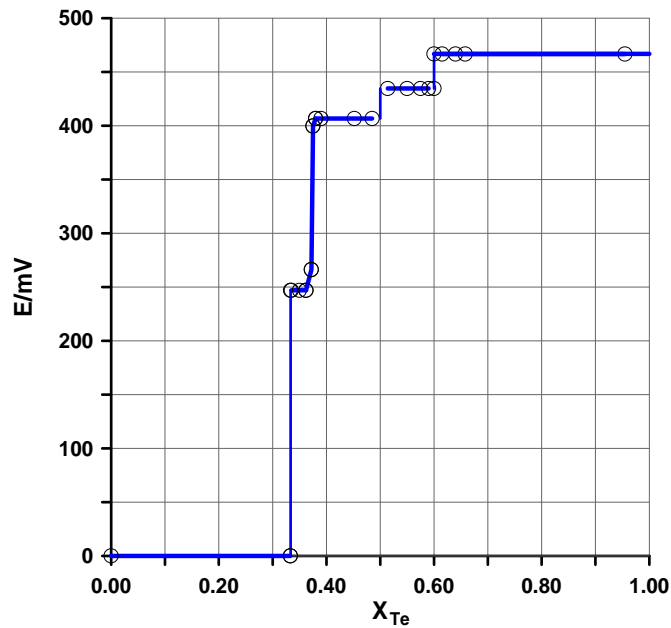


Fig.8. Isotherm $E(x)$ at 370K in Tl-Te system. Microheterogeneity is observed near 250 mV. This phenomena is confirmed in [54].

5.3. Discussion of results of Tl-Te system

a) Comparison with reference data.

The study of thermodynamic properties of thallium tellurides in the solid state have been held also in the references [32] and [36]. The results are presented in Table 6. Terpilowsky [36] used alloy electrodes in the form of ingots, whereas in our study they were used as tablets prepared from powder pressed into a mold. It is a fundamental difference as the preparation of the electrodes of the cell led to quite different results in respect to enthalpies and entropies of formation. The entropies of formation ($\Delta_f S^\circ_{298}$) obtained by Terpilowsky [36], differ more than in order of magnitude from our values. Very negative values $\Delta_f S^\circ_{298}$, for chalcogenides are not "a priori" possible because they belong to the layered structure, which is characterized by the additive values of entropy. In other words the values $\Delta_f S^\circ_{298}$ should be near zero. The comparison of our values of Gibbs energies of formation and those of [36] demonstrates that they are roughly equal at the temperature of 450 K, while the coefficients dE/dT are significantly different. Therefore, this difference is due to the determination of incorrect temperature coefficients for samples from ingots. We have made a control experiment, using the ingots as electrodes of cell for the domain (TlTe- γ \square -phase), and we obtained similar values as [36]. This experiment demonstrates that each researcher must make proper control of the measurement results before their publication.

The difference between the EMF results of the pressed and cast electrodes is associated with non-equilibrium state of ingots that can remain long in the experimental conditions at low temperatures. Comparisons of the enthalpy of formation for the Tl_2Te phase give the difference 7 kJ/g-at between our value and Fabre's one [32]. The error of measure [32] was not estimated, though the dissolution method could include a significant error. In addition, this work was done in the 19th century (1888).

Published data on the enthalpies of mixing [22, 23, 27, 36] and the electrical properties of liquid alloys of the system Tl-Te [24, 26] confirm the stability of the Tl_2Te phase in a liquid as well solid states. Based on the analysis of our data and those references, we made some corrections to the Tl-Te phase diagram [19]. It was presented as modified for a period before 1972 in Fig.9. All additions apply only to the rich thallium area 60-100 at. % Tl. The proposed liquidus curve of this area is indicated by dotted lines. It is based on thermographic data [15, 19, 54].

Table 6. Dependence of EMF versus temperature and composition of Tl-Te system.

| Number of region | Composition of alloys at. % Tl | Phase area | E(T), V |
|------------------|--------------------------------|---------------------------------------|---|
| 1 | 4.5-28.5 | Te-Tl ₂ Te ₃ | $(0.4662+1.5 \cdot 10^{-5}T) \pm 0.0044(1/106+T-377.03)^2/117954.9)^{1/2}$ |
| 2 | 41.0-48.6 | Tl ₂ Te ₃ -TlTe | $(0.4322+3.8 \cdot 10^{-5}T) \pm 0.0032(1/105+(T-393.19)^2/157804.2)^{1/2}$ |
| 3 | 51.5-62.0 | TlTe-Tl ₅ Te ₃ | $(0.4411-9.3 \cdot 10^{-5}T) \pm 0.0028(1/62+(T-387.79)^2/107172.2)^{1/2}$ |
| 4 | 62,5 | γ-фаза, тв. p-p | $(0.470-19 \cdot 10^{-5}T) \pm 0.0166(1/50+(T-4503.48)^2/65496.48)^{1/2}$ |
| 5 | 62.8 | γ-фаза, тв. p-p | $(0.218+13 \cdot 10^{-5}T) \pm 0.0066(1/27+(T-411.56)^2/27244.67)^{1/2}$ |
| 6 | 63.8-66.5 | γ-фаза, тв. p-p | $(0.248-03 \cdot 10^{-5}T) \pm 0.013(1/162+(T-403.62)^2/275022.0)^{1/2}$ |

Table 7. Values of the chemical potential of thallium versus temperature for different heterogeneous and homogeneous areas Tl-Te system.

| Number of region | Phase area | Forming potential reaction | $\Delta \mu_{Tl}(T)$, kJ/reaction |
|------------------|---|--|---|
| 1 | Te-T ₂ Te ₃ | Tl+ 3/2 → 1/2 Tl ₂ Te ₃ | $-(44.98 \pm 0.5)-(1.46 \pm 1.2) \cdot 10^{-3}T$ |
| 2 | Tl ₂ Te ₃ -TlTe | Tl+Tl ₂ Te ₃ → 3TlTe | $-(41.67 \pm 0.29)-(3.68 \pm 0.8) \cdot 10^{-3}T$ |
| 3 | TlTe-Tl ₅ Te ₃ (γ-фаза) | Tl+ 3/2 TlTe → Tl ₅ Te ₃ | $-(42.55 \pm 0.33)+(8.70 \pm 0.8) \cdot 10^{-3}T$ |
| 4 | γ-phase 62.5 ат.%Tl | Tl → Tl _{0.625} Te _{0.375} | $-(45.35 \pm 0.84)+(18.4 \pm 4.2) \cdot 10^{-3}T$ |
| 5 | γ- phase 62.8 ат.%Tl | Tl → Tl _{0.628} Te _{0.372} | $-(21.05 \pm 1.55)-(12.6 \pm 3.8) \cdot 10^{-3}T$ |
| 6 | Tl ₅ Te ₃ -Tl ₂ Te | Tl + Tl ₅ Te ₃ → 3Tl ₂ Te | $-(23.97 \pm 1.00)+(0.29 \pm 0.8) \cdot 10^{-3}T$ |

We have clarified the limits of the homogeneity of the γ-phase at room temperature according to our results. This phase has a width from 0.5 to 1.0 % instead of 1-2% [19]. The width of the γ-phase augments slightly with increasing temperature. This is illustrated in Figure 10, which shows that the EMF values for the alloys from 51.5 to 61.0 and 62.5 at. Tl% are closer to room temperature and these values diverge with the increase of temperatures. The same phenomenon has been observed for the alloys from 63.9 to 66.5 and 62.8 at. % Tl. We have also established the δ-area of the primary δ-solutions above 330K (δ-region). The dotted area was not studied (Fig.10).

Table 8. Thermodynamic parameters of the formation of Tl-Te alloys.

| Phase | $-\Delta_f G^\circ_{298}$ kJ/mol-at | $-\Delta_f H^\circ_{298}$ | $\Delta_f S^\circ_{298}$ J/(mol-at K) | S°_{298} | Reference | Method |
|---------------------------------|--|---------------------------|--|-----------------|-----------|-------------|
| Tl ₂ Te ₃ | 18.16±0.04 | 17.99±0.21 | 0.59±0.46 | 55.94±0.67 | This work | EMF |
| TlTe | 22.26±0.04 | 21.92±0.21 | 1.09±0.5 | 57.95±0.75 | | |
| Tl ₅ Te ₃ | 26.69±0.08 | 27.11±0.21 | -1.34±0.59 | 57.32±0.8 | | |
| Tl ₂ Te | 26.4±0.08 | 26.82±0.33 | -1.34±0.63 | 57.95±0.8 | | |
| Tl ₂ Te ₃ | 22.05 | 31.84 | -32.80 | 23.26 | [36] | EMF |
| TlTe | 26.53 | 37.03 | -35.31 | 21.76 | | |
| Tl ₅ Te ₃ | 31.8 | 44.35 | -42.26 | 16.32 | | |
| Tl ₂ Te | - | 19.67 | - | - | [38] | calorimetry |
| Tl ₂ Te | - | - | - | 61.9 | [50] | estimation |
| Tl ₂ Te | | 30.7 | | | [22, 23] | estimation |

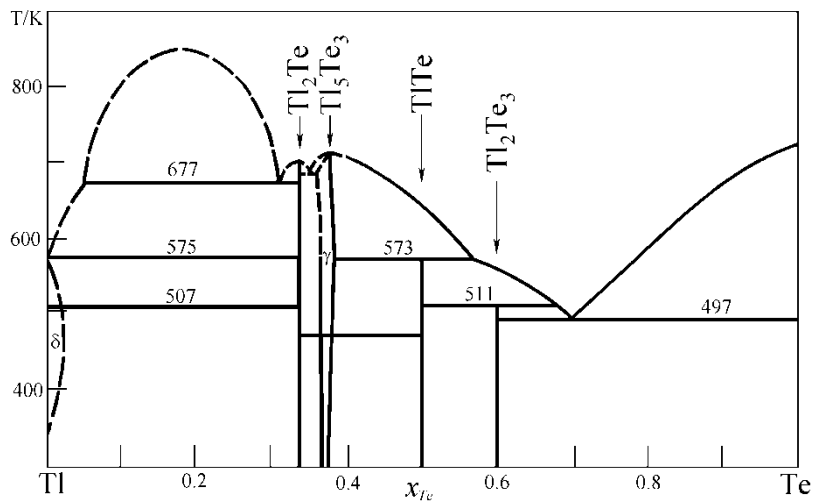


Fig.9. Tl-Te phase diagram [73] (our results).

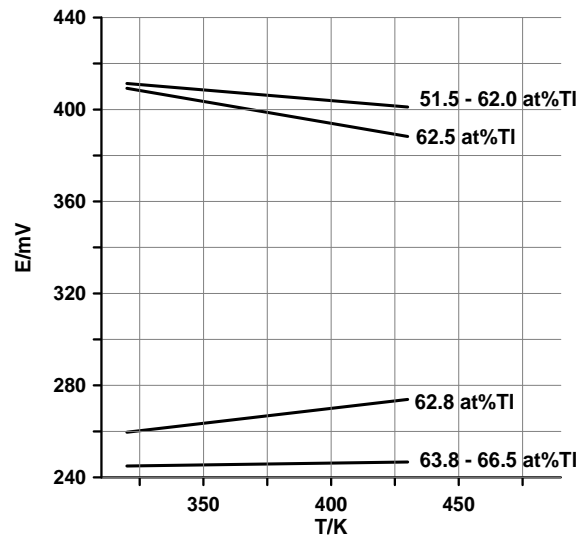


Fig.10. Tl-Te system. Dependence $E(T)$ of (γ)-homogeneous area (62.5 and 62.8 at.% T) and the adjacent heterogeneous areas (TlTe- γ -phase) and (γ -phaseTl₂Te) (our results).

The optimization of the system was carried out in 1997 with the participation of Professor Lucas [54] for all sets of experimental data on thermodynamic properties and phase diagram. The phase diagram of the Tl-Te system [54] (Fig.11 and 12) was not very different from the proposed version in 1972 [73] (Fig.9). The optimized values of the chemical potential of thallium $\mu_{\text{Tl}}(T)$ in the Tl-Te system [54] is compatible with our experimental results that do not exceed 5% uncertainty.

The values for $\mu_{\text{Tl}}(T)$ are presented for the minimum and maximum temperatures in Fig.13. In our opinion, a slight discrepancy between the experimental [41] and the calculated values of γ -phase was caused by an assumption of [54] the immutability of solid solution borders γ -phase (62.6 - 65 at.5% Tl) below 600 K. While according to our data, the width of γ -phase at room temperature does not exceed 0.5 % and it is between 62.8 and 63.8 at% Tl.

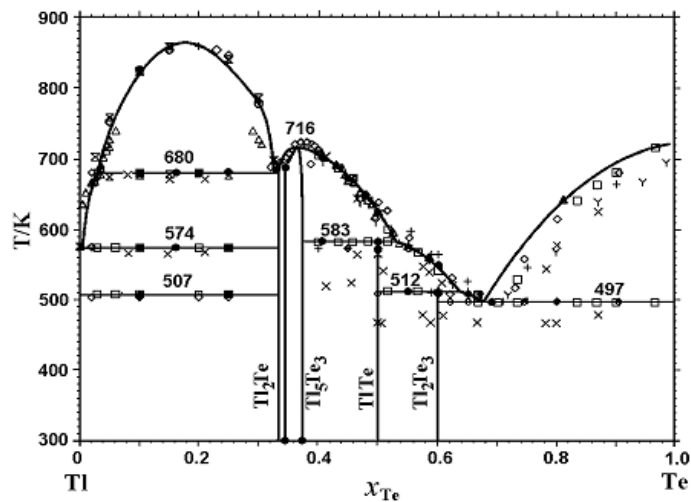


Fig.11. Optimized Tl-Te phase diagram [54]

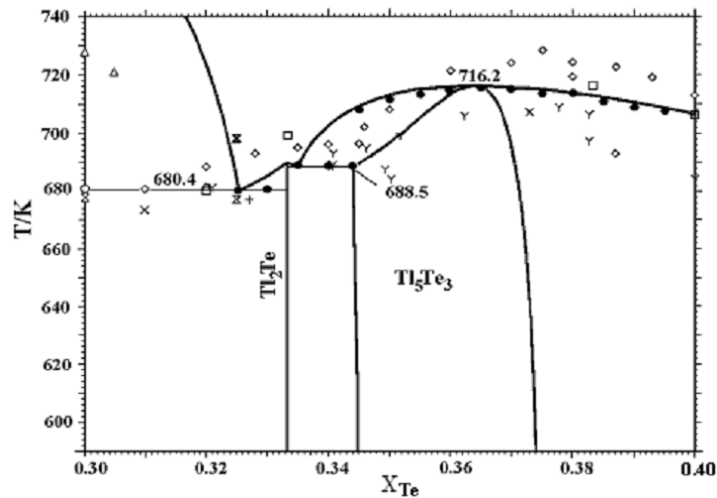


Fig.12. Fragment of optimized Tl-Te phase diagram [54]

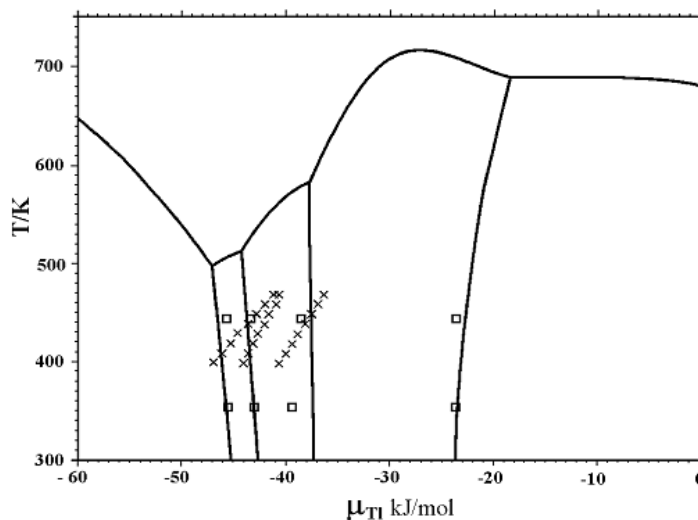


Fig.13. Optimized values of chemical potential $\mu_{Tl}(T)$ in Tl-Te system [54].

Experiment points: \square -[41] used, \times - [26] not used.

6. Glass-formation, polymorphism and nanoheteromorphism of thallium chalcogenides

Thallium chalcogenides, as mentioned above, find practical application being in the crystalline, liquid and glassy states [8]. Genetic relationship of these three states and correlation substance properties, contained in them, with the structure of phase diagrams, are described in detail within the concept of polymer-polymorphoid structure of glass and glass-forming liquid of individual chemicals substance (ICS), both elements and chemical compounds, and the more general (for multicomponent substances) concept of polymer nanoheteromorphous structure of glass and glass-forming liquid [55-58]. Nanoheteromorphism of liquid and glassy ICS represents a coexistence of structural fragments (polymorphoids) of various polymorphous modifications (PMs) at the nanolevel without translational symmetry (of long-range order), but possessing short- and intermediate-range orders (SRO and IRO) of these PMs. Multicomponent systems (in particular binary ones) along with polymorphoids, which are IRO carriers, also include the

structural units having only SRO of initial components and fragments with mixed SRO, formed by fragments with SRO of initial components [58-60].

According to [61], glass-forming phase TlS exists in three PMs, while [62] gives two PMs with the transition temperature of $T_{tr} = 318.6$ K (45.4 °C). TlSe manifests itself in two PMs with $T_{tr} = 470$ K [51]. We have not revealed any data on polymorphism of Tl_2S_3 , Tl_2S_5 and Tl_2Te_3 . From the standpoint of nanoheteromorphism, it can be clearly stated that glassy and liquid thallium monosulfide at the nanolevel consists of polymorphoids of high- and low-temperature PM (HTPM and LTPM). Other, more sulfur-rich glass-forming compositions of Tl – S system, contain the same polymorphoids, as well as polymorphoids Tl_2S_3 , Tl_2S_5 and sulfur (various PMs).

With regard to Tl-Se, its glass-formation is determined by the presence (copolymerization) of polymorphoids α - and β -TlSe and polymorphoids with different polymorphous modifications of Se with the predominant content of hexagonal and monoclinic PM, as evidenced by the phase diagram of the Tl - Se system (Fig. 4. [43] and Fig. 6 [51]) and the data given in [63].

The Tl-Te diagram, where glass-formation is observed only for the Tl_2Te_3 composition [64], we can confidently predict the existence of its second polymorphous modification, because among a variety of glass-forming ICS essentially all of them are produced by copolymerization of polymorphoids of two or more PMs [57]. It is possible that this PM in the crystalline form exists only at high pressures, but as shown in [65], its nanofragments may be formed by dispersing (size reduction) associates of the liquid when the temperature increases due to increase of their surface tension and rise of internal pressure.

The relationship between glass-formation and calculated glass-forming ability of the substance with its components position in the Periodic System is analyzed on the base of structural-energetic glass-formation concept proposed by Minaev [55, 57]. In line with this concept, the glass-forming ability (GFA) of the substance is the quotient of the chemical, usually covalent-ionic bonding of the mole of atoms (E_{cib}) of this substance associated with one averaged atom by its liquidus temperature (T_l) under normal pressure (quantitative criterion of San-Rawson-Minaev glass-formation - [55, 57, 66]):

$$GFA = E_{cib}/T_l = (E_{av}/2) \cdot K/T_l = \sum (E_i \cdot n_i) \cdot \sum k_j \cdot m_j / 2T_l \cdot \sum (n_i) \cdot \sum (m_j) \quad (2)$$

Where E_{cib} is energy of covalent-ionic bonding, kJ / mol;

E_{av} is energy of averaged chemical bond in the alloy, kJ / mol;

E_i is energy of such kind of bond, kJ / mol;

n_i is number of bonds of this type;

m_j, k_j are number of atoms and coordination number of this type of atom;

K is average number of covalent-ionic bonds per atom.

E_{cib} is calculated based on the values of energy, E , of chemical bonds and electro negativities (x), cited by Pauling [67] or calculated using his formula:

$$E_{A-B} = 1/2(E_{A-A} + E_{B-B}) + 100(x_A - x_B)^2 - 6,5(x_A - x_B)^4, \text{ kJ/mol} \quad (3)$$

Thallium chalcogenides form glass within the following ranges: Tl-S system from TlS to $TlS_{2,5}$ composition [68], Tl-Se system from pure selenium to TlSe₂ composition (in liquid state) [69], while in Tl-Te system there is only Tl_2Te_3 glass-forming composition [64] (Fig.14). Discoverers of glassy chalcogenide semiconductors Goryunova and Kolomiets [70] have established the congruity between the decreasing of glass formation area for binary systems and the increasing of atomic number of element in a given subgroup of the Periodic System. Minaev [55, 58] has clarified this rule. He has detected a few inversions in this congruity. One of them is imaginary or false inversion.

Calculation of GFA according to the above formulas (3, 4) [55, 57, 66, 67] for sulfide, selenide, and telluride alloys with thallium in the area of their glass-formation and, specifically, for compositions with the minimum liquidus temperature: $Tl_{31}S_{69}$, $Tl_{27}Se_{73}$, $Tl_{29}Te_{71}$ —0.522; 0.342 and 0.263 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$, respectively, confirms such appropriateness. But, as seen from the Fig. 14 [64, 68], the experiment shows a disturbance of this congruity – an inversion during transition

from the sulfide system to the selenide one. The glass-formation area in the latter (Tl-Se) is significantly larger than that in the former (Tl-S).

Smaller sizes of a glass-formation area in the Tl-S system as compared to the Tl - Se system can be explained by the fact that glass forming alloys with sulfur possess very low glass-transition temperature: for TlS_2 it lies just 6 °C above zero [68], and for numerous alloys it lies in the range of negative temperatures, since the glass-transition temperature of elemental sulfur equals 27 °C below zero [71]. Above glass-transition temperature alloys are usually found in the viscous-fluid state and show a significant tendency to crystallize, which prevents the glassy state display of numerous alloys with sulfur at room temperature. At the same time, the glassy state is identified at lower temperatures. Thus, TlS_2 becomes elastic or fluid-like at room temperature, and hard, brittle, and glassy at 0°C [68].

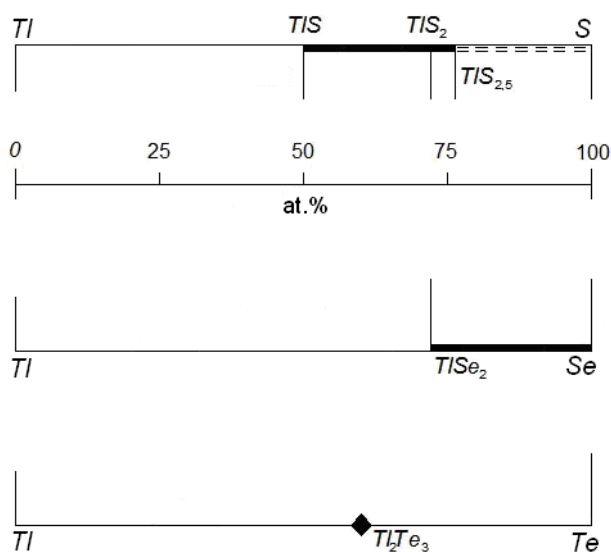


Fig.14. Glass-formation areas in Tl - S, Tl - Se, and Tl - Te systems [64, 68]; - and ♦ - glass-forming compositions; = = = - predicted compositions.

Our experiments with glass synthesis in the Tl-S system showed that alloys obtained by quenching in cold water in the amount of 10 g represented soft, elastic, stretching of the filament materials (two compositions were synthesized: $Tl_{25}S_{75}$ and $Tl_{29}S_{71}$). An x-ray phase analysis showed the presence of a crystalline phase in them. Subsequently, the materials obtained lost their glassy luster, elasticity and became completely crystallized. If the cooling conditions and identification of the glassy state of alloys with sulfur are matched with the nature of this element, which is hardened and studied at temperatures below the glass-transition temperature, t_g , it is possible to predict obtaining a much greater area of glass-formation in the alloys with sulfur containing from 50 to 100 % at. S, which in this case will exceed the glass-forming area with selenium. Thus, inversion in the tendency to decrease glass-formation during transition from sulfur to selenium resulting from the comparison of areas of glass-formation intervals will prove to be false or imaginary.

7. Conclusion

A detailed critique analysis of the thermodynamic properties of thallium chalcogenides and phase diagrams was made. Our thermodynamic functions of formation of thallium chalcogenides and refined phase diagrams were fully confirmed in the optimization of these systems. Our results were included in the handbook [72].

The proposal method of EMF with the "glycerin electrolyte" as applied to thallium chalcogenides received a successful continuation of the thermodynamic study of ternary systems based on thallium chalcogenides with other elements [73] and glassy semiconductors [1].

Within certain intervals of composition, thallium chalcogenides can exist in the form of glass and glass-forming liquid, structured from copolymerized to a more (glass) or less (liquid) degree nanofragments of the structure of various crystal polymorphous modifications (polymorphoids) of appropriate chalcogenides. Polymorphoids do not possess translational symmetry (of long-range order), i.e. do not represent crystallites, but have short- and intermediate-range order, characteristic of the relevant polymorphous modifications.

The calculated glass-forming ability of thallium chalcogenides [57] regularly decreases with increase of atomic number of chalcogen according to the rule proposed by Goryunova and Kolomiets [70], but change of glass-formation areas shows disturbance (inversion) of this appropriateness: thallium selenides have a larger area of glass-formation than that of sulfides. This inversion is imaginary or false, because the glass is produced under conditions (at temperatures $> 0^{\circ}\text{C}$), which do not agree with the nature of thallium sulfide glass-transition, essential part of which has glass-transition temperature, which lies below zero degrees Celsius.

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