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Electrochemical Studies on the Thallium(I) Telluride – Mercury(II) Telluride Solid System

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The concentration cell-EMF measurement method was employed in verifying two phase diagrams published earlier for the system Tl_2Te – HgTe. The thermodynamic characteristics of the system in solid state has been determined at 373 and 453 K.

Key words: concentration cell EMF, binary telluride system, phase diagram

The metal telluride quasibinary systems of the type $M_nTe_m – M'_uTe_z$ (where M and M′ are different metals) belong to the most promising field for new semiconductive materials. Especially ternary compounds are formed along the polythermal sections of ternary systems M – M′ – X, X being an element of the 4–6 group of the periodic system. The title system is a part of a „family" of Tl_2Te – M_xTe_y systems, studied by the present authors [1,2].

According to [1], in the system only one chemical compound is formed of composition $Hg_3Tl_2Te_4$ (at 75.0 mole % HgTe), melting incongruently at *ca.* 731 K. It undergoes a polymorphic transition at *ca.* 653 K. There exist in this system also two limited solid solutions: one that on the Tl_2Te side (α) covers a broad concentration range from pure Tl_2Te to 22 mole % HgTe and another on the HgTe side (β) – from *ca.* 92 mole % HgTe to pure HgTe. Coordinates of the only eutectic are: 46 mole % HgTe and *ca.* 623 K. These data were obtained mainly by differential thermal analysis (DTA).

According to our results [2], in the system under consideration three chemical compounds are formed: $HgTl_{10}Te_6$ (at 16.7 mole % HgTe) congruently melting at 696 K, $Hg_3Tl_2Te_4$ (75.0 mole % HgTe) melting incongruently at 653 K and $Hg_9Tl_2Te_{10}$ (90.0 mole % HgTe) melting incongruently at 713 K; the peritectic points being at 51 and 68 mole % HgTe, respectively. The data were obtained by DTA employing both the derivatograph Q 1500 D (MOM, Budapest) and the DSC 25 apparatus (Mettler Toledo).

The phase diagram delineated from our data is presented in Figure.

The discrepancies between the two phase diagrams [1] and [2] demand explanation by another experimental method. We decided to use the electrochemical analysis, *i.e.* electromotive force (EMF) measurements of concentration cells method, as it appeared to be the most suitable for the verification of the phase diagrams, especially those quite complicated as it was with the Tl_2Te – Ag_2Te [3,4] and Tl_2Te –

Bi_2Te_3 [5,6] systems. Additionally, it permitted to determine the thermodynamic characteristics of the phases formed.

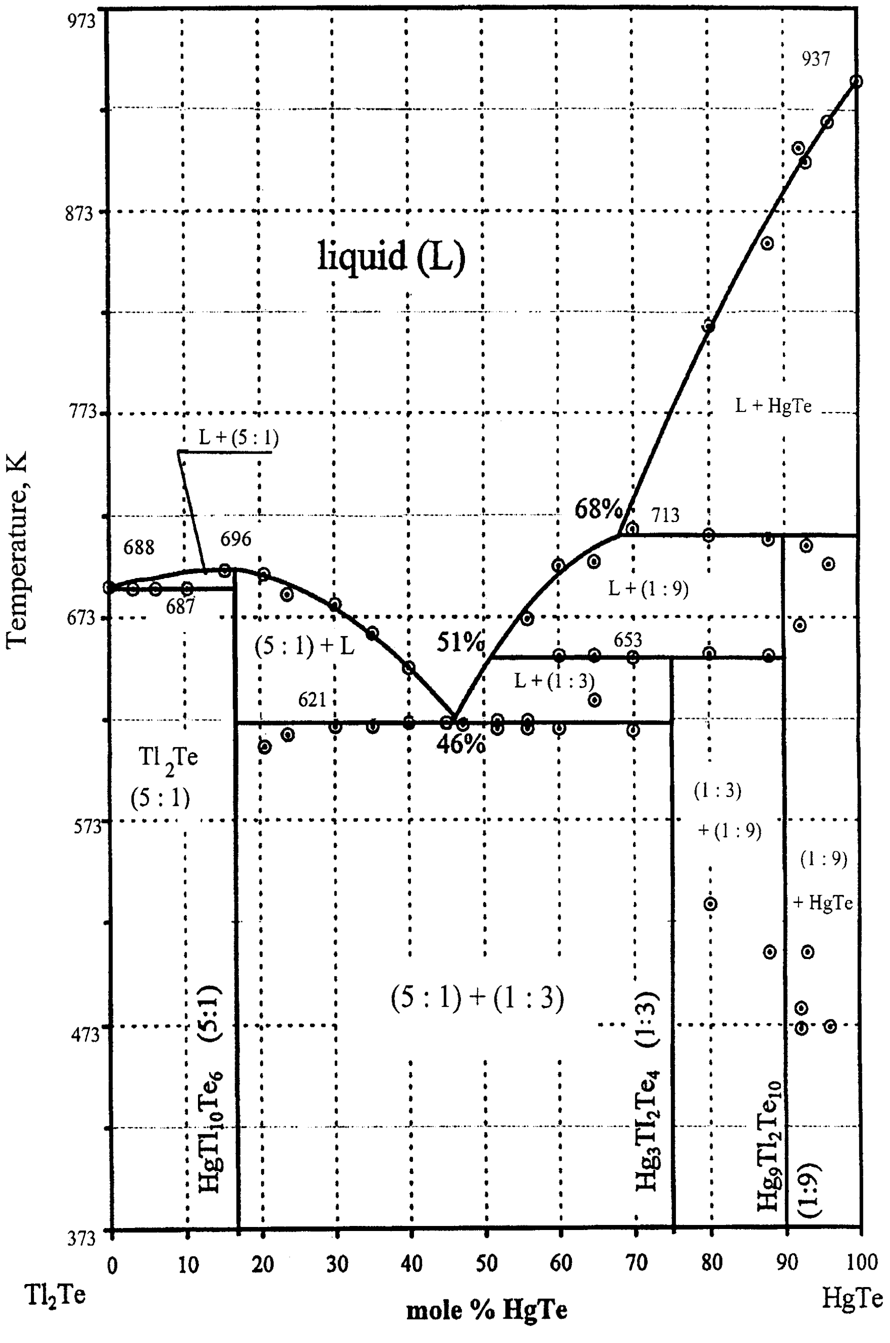

Figure. Phase diagram for the system Tl_2Te – HgTe according to [2].

EXPERIMENTAL

The following reversible concentration cells were used:

(–)		(+)
Tl	TlCl + NaCl solution in glycerine	$Tl_2Te_{(X)} - HgTe_{(1-X)}$
solid	electrolyte	solid alloy electrode
reference electrode		

The thallium(I) telluride and mercury(II) telluride were prepared as described in [2]. The Tl_2Te + HgTe alloys were made by fusion of weighed amounts of the components under vacuum in sealed quartz tubes.

Analytically pure glycerine (POCh) was used as the electrolyte in the cells. It was heated for a few hours up to 353 K in order to remove the moisture. Then small amounts of NaCl (p.a., POCh) and TlCl (99.9% pure, BDH Chemical Ltd.) were dissolved in dry glycerine.

The electrodes were prepared in the form of sticks, 5 mm in diameter, by sucking in a liquid metal (alloy) to glass tubes and then letting them solidify. They were immersed in the electrolyte under purified argon atmosphere and connected to the voltmeter F-541 Meratronik with tungsten wires, sealed in glass tubes to protect them from the electrolyte. The EMF measurements (with an accuracy of ± 0.1 mV) started 48 hours after the cell had been assembled. The EMF readings were done (at a fixed temperature controlled within ± 3 deg.) 1 hour after the temperature of the cell had been risen or decreased by *ca.* 10 deg. Each series of measurements lasted usually 4 weeks. The construction of the electrolytic cell was described earlier [7].

RESULTS AND DISCUSSION

The investigations by the concentration cell EMF measurements covered the solid alloys Tl_2Te + HgTe of HgTe molar fraction (X_{HgTe}) from 0.04 to 0.987. The dependence of EMFs on temperature was found to be linear for all the electrolytic cells. From the data obtained, the linear equations $E = a + bT$ (where E = EMF, T = temperature in K) have been established by the least squares method. Some of the relations showed „breaks” at *ca.* 426 K, which might be an indication of a phase transformation. Consequently, the EMF measurements have been performed within two temperature ranges: 340–426 K and 426–497 K.

Table 1 lists the compositions of the alloys examined, their respective phase regions, equations $E = a + bT$, E (EMF) values at 373 and 453 K (for respective temperature ranges) as well as the errors. As it is known, the electromotive forces at a fixed temperature and their temperature coefficients of cells, containing two-phase alloy electrodes, are constant and independent of the composition within the two-phase region. They change, however, considerably from one phase region to another.

From Table 1 it follows that EMFs (E_{373} or E_{453}) and their temperature coefficients ($dE/dT = b$) of cells were found to be constant for the telluride alloys within the following concentration regions (X_{HgTe}): I: 0.040–0.140, II: 0.200–0.700, III: 0.800–0.875, IV: 0.920–0.987. While the E_{373} values are approximately the same in both III and IV phase regions, the dE/dT are quite different both in sign and the magnitude.

Table 1. Results of electrochemical studies of the Tl_2Te – HgTe solid alloys.

X_{HgTe}	Phase region	Equation E = a + bT (mV)	E_T
		Temperature range: 340–426 K	E_{373} (mV)
0.040	(I) Tl_2Te + $HgTl_{10}Te_6$	(175.2 ± 1) + (0.1795 ± 0.026) T	242.2 ± 4
0.050			
0.090			
0.140			
0.200	(II) $HgTl_{10}Te_6$ + $Hg_3Tl_2Te_4$	(513.3 ± 3) – (0.2595 ± 0.096) T	416.5 ± 10
0.250			
0.400			
0.500			
0.550			
0.650			
0.700			
0.800	(III) $Hg_3Tl_2Te_4$ + $Hg_9Tl_2Te_{10}$	(448.1 ± 1) + (0.0594 ± 0.004) T	470.3 ± 2
0.875			
0.920	(IV) $Hg_9Tl_2Te_{10}$ + HgTe	(537.2 ± 1) – (0.1724 ± 0.017) T	472.9 ± 5
0.975			
0.987			
		Temperature range: 426–497 K	E_{453} (mV)
0.040	(I) Tl_2Te + $Hg_9Tl_{10}Te_6$	(168.4 ± 1) + (0.1623 ± 0.003) T	241.9 ± 1
0.090			
0.140			
0.200	(II) $HgTl_{10}Te_6$ + $Hg_3Tl_2Te_4$	(667.6 ± 4) – (0.6240 ± 0.076) T	385.9 ± 7
0.400			
0.550			
0.700			
0.760	(III) $Hg_3Tl_2Te_4$ + $Hg_9Tl_2Te_{10}$	(306.3 ± 3) + (0.3913 ± 0.115) T	483.6 ± 4
0.800			
0.880			
0.950	(IV) $Hg_9Tl_2Te_{10}$ + HgTe	(577.5 ± 1) – (0.1946 ± 0.040) T	489.3 ± 3
0.975			

Resulting values permitted us to conclude that the solid alloys Tl_2Te–HgTe of each of the concentration ranges constitute two-phase systems. Accordingly, it may be stated that there are in equilibrium in the I phase region ($0 < X_{HgTe} < 0.167$): Tl_2Te and $HgTl_{10}Te_6$, in the II ($0.167 < X_{HgTe} < 0.750$): $HgTl_{10}Te_6$ and $Hg_3Tl_2Te_4$, in the III ($0.750 < X_{HgTe} < 0.900$): $Hg_3Tl_2Te_4$ and $Hg_9Tl_2Te_{10}$, in the IV ($0.900 < X_{HgTe} < 1.000$): $Hg_9Tl_2Te_{10}$ and HgTe. The results provide a strong evidence for the existence of the three compounds at X_{HgTe}: 0.167, 0.750 and 0.900. Simultaneously no evidence has been obtained for solid solutions in this system. Probability of formation of the solid solutions seemed to be considerable on the Tl_2Te side, since they appeared in the systems made up from Tl_2Te and SnTe [8], PbTe [9], Sb_2Te_3 [10] or Bi_2Te_3 [5]. In these systems the continuous solid solutions covered the concentration range from pure Tl_2Te to the next compound. Besides, the authors of [1] found limited solid solutions within the range $0 < X_{HgTe} < 0.22$. According to our results, the E_{373} (and E_{453} as well) and dE/dT values were constant within the range $0 < X_{HgTe} < 0.167$, which indicated that the alloys from this range represent two-phase not one-phase ones.

Results of EMF measurements of the cells with alloy electrodes of HgTe molar fractions from 0.760 to 0.880 showed that within 426– 497 K the slope of the straight lines ($E = a + bT$) was quite different than that within 340–426 K (the temperature coefficient dE/dT for the former range was 6.5 times that for the latter). This is an indication of a phase transition. The probable temperature of the transition is *ca*. 426 K. The change (much smaller: *ca*. 2.5 times) of the coefficient dE/dT may be also observed within the concentration region from X_{HgTe} 0.200 to 0.700, when passing from one temperature range to another. From these data it may be supposed that the transition is a polymorphic transformation of the compound $Hg_3Tl_2Te_4$, the composition of which is 75.0 mole % HgTe. The heat effect of the transformation is certainly small, as it was not found by DTA [2].

The EMF measurements of concentration cells allow the determination of the thermodynamic characteristics. The E_{373}, E_{453} and dE/dT values obtained in this work permitted the partial molar free enthalpies (ΔG_{Tl}), entropies (ΔS_{Tl}) and enthalpies (ΔH_{Tl}) of thallium at 373 and 453 K, to be calculated. The values of the thermodynamic functions have been listed in Table 2. It is worthwhile to consider the ΔS_{Tl} values, which are different in various phase regions. This may be explained by different structures of the compounds formed.

Table 2. Partial molar thermodynamic functions of thallium in the Tl_2Te–HgTe solid system.

X_{HgTe}	Phase region	$-\Delta G_{Tl}$ (kJ mole^{-1})	ΔS_{Tl} (J mole^{-1} K^{-1})	$-\Delta H_{Tl}$ (kJ mole^{-1})
		at 373 K		
0.000–0.167	Tl_2Te + $HgTl_{10}Te_6$	23.4 ± 0.5	17.3 ± 3	16.9 ± 2
0.167–0.750	$HgTl_{10}Te_6$ + $Hg_3Tl_2Te_4$	40.2 ± 1	–25.0 ± 1	49.5 ± 1
0.750–0.900	$Hg_3Tl_2Te_4$ + $Hg_9Tl_2Te_{10}$	45.4 ± 0.2	5.7 ± 0.4	43.3 ± 0.3

Table 2 (continuation)

0.900–1.000	$Hg_9Tl_2Te_{10}$ + HgTe	45.6 ± 0.5	–16.6 ± 2	51.8 ± 1
		at 453 K		
0.000–0.167	Tl_2Te + $HgTl_{10}Te_6$	23.3 ± 0.1	15.7 ± 0.3	16.2 ± 0.2
0.167–0.750	$HgTl_{10}Te_6$ + $Hg_3Tl_2Te_4$	37.2 ± 0.1	–60.2 ± 7	64.5 ± 4
0.750–0.900	$Hg_3Tl_2Te_4$ + $Hg_9Tl_2Te_{10}$	46.7 ± 0.4	37.8 ± 11	29.6 ± 5
0.900–1.000	$Hg_9Tl_2Te_{10}$ + HgTe	47.2 ± 0.3	–18.8 ± 4	55.7 ± 2

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