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Electrochemical Studies in the Subsolidus Area of Tl_2Te – CdTe Solid System

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Solid alloys Tl_2Te – CdTe have been investigated by concentration cell EMF measurements. Partial molar thermodynamic functions of thallium at 373 K and 473 K have been determined for the ternary phases in the system. An evidence has been obtained for a new compound formation that was not found earlier.

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

We studied formerly six quasibinary thallium(I) telluride – metal telluride systems, *i.e.* $Tl_2Te – M_xTe_y$, where M = Ag(I), Sb(III), Bi(III), Sn(II), Cu(I), Hg(II) [1–6], respectively, employing thermal analysis as a main experimental method. All of the systems were also studied by the concentration cell electromotive force (EMF) method [7–12] in order to verify the results obtained by the former one. The EMF measurement data were always consistent with respective phase diagrams established by thermal methods. The only exception occurred in case of the title system. The phase equilibria in the system thallium(I) telluride – cadmium telluride were studied twice. According to the first Guseinov's *et al.* data [13], the system is of simple eutectic type, the eutectic coordinates being *ca.* 9 mole % CdTe and *ca.* 650 K. From the data reported in [14] it follows that in the system one chemical compound is formed ($CdTl_{12}Te_7$) melting congruently at 704.3 K, as well as two eutectics (Fig. 1).

From the comparison of both the data [13] and [14] it follows that they differ considerably from one another. Consequently, the Tl_2Te – CdTe system demands further studies. This was the reason why we performed another study on the system employing quite a different method, namely concentration cell EMF measurement.

EXPERIMENTAL

The following reversible concentration cells were assembled:

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

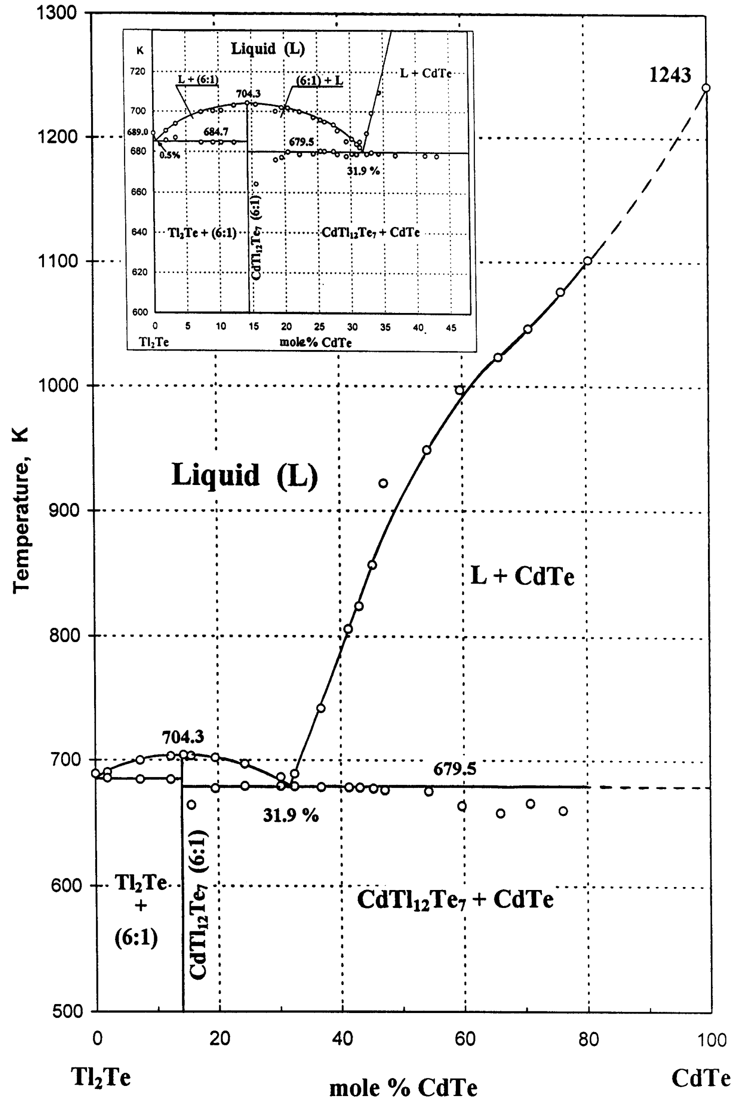

Figure 1. Phase diagram for the system Tl_2Te – CdTe according to [14].

Preparation of thallium(I) telluride and cadmium telluride was described earlier in [6] and [14], respectively. The Tl_2Te + CdTe alloys were made by fusing together appropriate amounts of the components in quartz tubes under pure argon atmosphere. Both the thallium reference electrode and the alloy ones were prepared by melting 1–2 g of the metal (alloy) in small test tubes (5 mm in diameter, 50 mm long) made of glass or quartz dependent on the melting point of the alloy and then letting it to solidify. The tubes had small holes of 15 mm above the bottom to make possible contact of an electrode with an electrolyte. The electrolyte was a solution of a small amount of TlCl (99.9% pure, BDH Chemicals Ltd.) and NaCl (p.a., POCh) in glycerine. The glycerine (p.a., POCh) was heated prior to use at 435 K for a few hours to remove traces of moisture. The electrolyte was placed in a quartz vessel filled with argon 5N pure (BOC Gazy, Poznań). The electrodes, connected to the voltmeter (F-541 Meratronik) with tungsten wires sealed in a quartz tubes, were immersed in the electrolyte.

The EMF measurements started not earlier than 7 days after the cell had been assembled and heated at 400 K or 450 K (according to the measurement temperature range). The temperature of the cells was measured with an accuracy of ± 1 K. The EMF readings were done every hour with an accuracy of ± 1 mV, and then the temperature was raised (or decreased) by *ca.* 10 K. Each series of measurements continued for 2–3 weeks.

RESULTS AND DISCUSSION

Thirteen Tl_2Te + CdTe alloys of different compositions, covering the whole concentration range, have been investigated by the concentration cell EMF method within 373–507 K. The EMFs showed linear dependence on temperature that might be expressed as E = a + bT (where E = EMF, T = temperature in K, a and b are constants, b being the temperature coefficient of EMF, *i.e.* b = dE/dT). On the graphs E *vs.*T for the cells containing alloy electrodes from 50 to 95 mole % CdTe a "break" appeared at 430–440 K (see Fig. 2). This was the reason why in this concentration region the EMF measurements were accomplished within 373–434 K and 431–507 K. The break was not observed in the case of alloys of composition from 5 to 13 mole % CdTe.

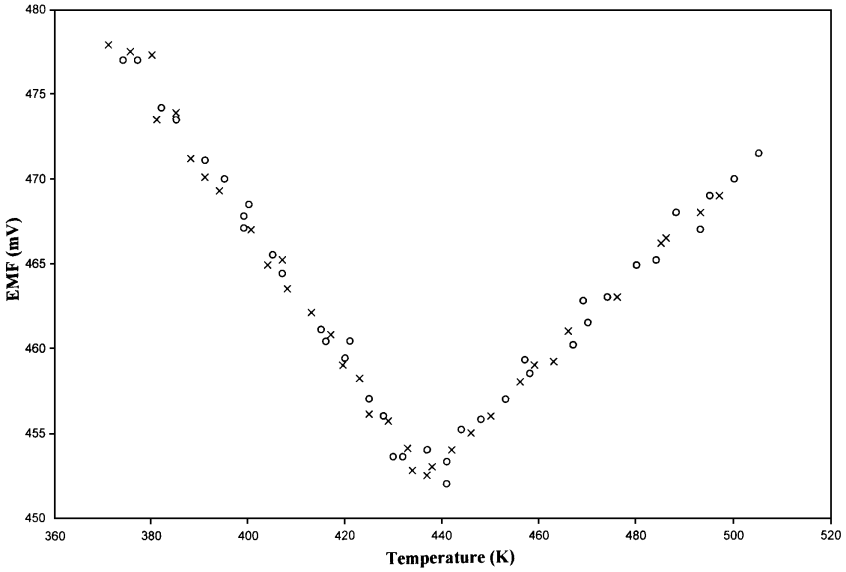

Figure 2. Example of EMF measurement series of concentration cells containing the Tl_2Te – CdTe alloy electrodes within the composition region 50–100 mole % CdTe (crosses – at increasing temperature, circles – at decreasing temperature).

Results of measurements and calculations have been listed in Table 1. The table comprises the compositions of alloys examined, their respective phase regions, equations E = a + bT and EMF values at 373 K (E_{373}) and at 473 K (E_{473}) for the respective temperature ranges. The constants a and b of the equations and separately E_{373} and E_{473} (including respective errors) have been calculated by the least squares method from experimental data of respective series of measurements.

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

Composition mole % CdTe	Phase region		Equation E = a + bT	E_T
			Temperature range: 373–507 K	
				E_{473} (mV)
5.0		Tl_2Te	(84.9 ± 2.8) + (0.4131 ± 0.0189) T	280.3 ± 3.0
10.0	I	+	(98.1 ± 3.2) + (0.4559 ± 0.0262) T	313.7 ± 3.6
13.0		$CdTl_{12}Te_7$	(83.7 ± 2.5) + (0.4247 ± 0.0145) T	284.6 ± 2.5
Arithmetic mean for the I phase region:			(88.9 ± 2.9) + (0.4312 ± 0.0199) T	292.9 ±3.0
			Temperature range: 373–434 K	
				E_{373} (mV)
50.0			(518.5 ± 4.9) – (0.2664 ± 0.1840) T	419.1 ± 6.3
60.0		$CdTl_{12}Te_7$	(454.2 ± 1.4) – (0.1142 ± 0.0653) T	411.6 ± 2.2
65.0	II	+	(447.2 ± 1.0) – (0.0900 ± 0.0468) T	413.6 ± 1.5
70.0		α-$Cd_3Tl_2Te_4$	(485.4 ± 1.2) – (0.1839 ± 0.0590) T	416.8 ± 1.6
73.0			(480.2 ± 1.4) – (0.1693 ± 0.0597) T	417.1 ± 1.9
Arithmetic mean for the II phase region:			(477.1 ± 2.0) – (0.1648 ± 0.0830) T	415.6 ± 2.7
77.0			(589.9 ± 1.1) – (0.3041 ± 0.0172) T	476.5 ± 1.6
79.0		α-$Cd_3Tl_2Te_4$	(537.9 ± 0.8) – (0.1936 ± 0.0137) T	465.7 ± 0.9
85.0	III	+	(544.4 ± 0.8) – (0.1966 ± 0.0109) T	471.0 ± 0.8
92.0		CdTe	(564.8 ± 1.3) – (0.2489 ± 0.0201) T	471.9 ± 1.4
95.0			(549.0 ± 1.0) – (0.1939 ± 0.0138) T	476.7 ± 1.0
Arithmetic mean for the III phase region:			(557.2 ± 1.0) – (0.2274 ± 0.0151) T	472.4 ± 1.1
			Temperature range: 431–507 K	
				E_{473} (mV)
50.0			(321.0 ± 2.1) + (0.2156 ± 0.0578) T	423.0 ± 2.2
60.0		$CdTl_{12}Te_7$	(360.2 ± 0.4) + (0.1018 ± 0.0068) T	408.3 ± 0.4
65.0	II	+	(341.2 ± 0.5) + (0.1490 ± 0.0083) T	412.0 ± 0.5
70.0		β-$Cd_3Tl_2Te_4$	(363.0 ± 0.6) + (0.1042 ± 0.0141) T	412.3 ± 0.6
73.0			(341.1 ± 1.0) + (0.1502 ± 0.0210) T	412.1 ± 1.8
Arithmetic mean for the II phase region:			(345.3 ± 0.9) + (0.1442 ± 0.0216) T	413.5 ± 1.1
77.0			(334.8 ± 2.4) + (0.2703 ± 0.1014) T	462.7 ± 1.0
79.0		β-$Cd_3Tl_2Te_4$	(305.1 ± 3.2) + (0.3309 ± 0.1007) T	461.6 ± 1.0
85.0	III	+	(314.0 ± 3.6) + (0.3310 ± 0.1519) T	470.5 ± 1.6
92.0		CdTe	(288.6 ± 4.1) + (0.3812 ± 0.1739) T	468.9 ± 1.5
95.0			(339.1 ± 1.8) + (0.2431 ± 0.1823) T	454.1 ± 2.6
Arithmetic mean for the III phase region:			(316.3 ± 3.0) + (0.3113 ± 0.1420) T	463.6 ± 1.5

From Table 1 it followed that the EMF values (E_{373} and E_{473}) and their temperature coefficients (b) were found to be approximately constant for the telluride alloys within the following concentration regions: I (0–13.0 mole % CdTe), II (50.0–73.0 mole % CdTe) and III (77.0–95.0 mole % CdTe). The constancy of an EMF value within a respective phase region is an evidence for that the region is a two-phase one. If the EMF values within the region varied continuously with composition, it should indicate that in the region continuous solutions occur [15]. On the other hand, the E_{473} values (and E_{373} as well) are quite different in the regions I, II and III (292.9, 413.5 and 463.6 mV, respectively), which in turn is an indication of different phase composition of each region alloys. The results provided a strong evidence for formation of both the $CdTl_{12}Te_7$ compound (found formerly [14]) and the another one of composition 75.0 mole % CdTe (*i.e.* of components molar ratio Tl_2Te:CdTe = 1:3), to which the formula $Cd_3Tl_2Te_4$ may be ascribed.

There was no need to examine the alloys from the region 14.3–50 mole % CdTe, which is only a part of that covering the compositions from 14.3 to 75 mole % CdTe. Accordingly, the EMF values of the cells are the same within the whole latter region.

Now a conclusion may be driven that there are in equilibrium in the I phase region (0–14.3 mole % CdTe): Tl_2Te and $CdTl_{12}Te_7$; in the II (14.3–75.0 mole % CdTe): $CdTl_{12}Te_7$ and β-$Cd_3Tl_2Te_4$ (or α-$Cd_3Tl_2Te_4$ at 373 K); in the III (75.0 –100 mole % CdTe): β- (or α) $Cd_3Tl_2Te_4$ and CdTe.

From Table 1 it appeared also that in the case of the cells containing alloy electrodes of the content from 50.0 to 95.0 mole % CdTe, *i.e.* on either side of the compound $Cd_3Tl_2Te_4$, the slope of the straight lines ($E = a + bT$) within the range 373–434 K was quite different than that within 431–507 K. The temperature coefficients of EMFs in the former range were negative, whereas in the latter – positive (Fig. 2). This provided an evidence for the polymorphic transition ($\alpha \leftrightarrow \beta$) of the compound $Cd_3Tl_2Te_4$. The temperature of the transition occurring in all examined samples (50.0 - 95.0 mole % CdTe) may be determined from the intersection of respective lines $E = a + bT$ for both of the temperature ranges. The mean value of the temperature is 439.6 ± 4.5 K.

The results obtained in this study enabled us to verify the phase diagram (Fig. 1) determined in [14]. The corrected phase diagram for the system is presented in Fig. 3.

The melting (or decomposition) temperature of the compound $Cd_3Tl_2Te_4$ was impossible to be determined by the EMF measurement method employed in the present work. From Fig. 3 we can hardly estimate that its value may lie somewhere between 1000 and 1070 K.

It must be noted here that in the system Tl_2Te – HgTe an analogous compound $Hg_3Tl_2Te_4$ was found melting incongruently and also undergoing polymorphic transformation α-$Hg_3Tl_2Te_4 \leftrightarrow \beta$-$Hg_3Tl_2Te_4$ at *ca.* 426 K [12].

An additional advantage resulting from the concentration cell EMF method is the possibility of determining thermodynamic characteristics of the studied alloys. From the E_{373}, E_{473} and dE/dT values, the following thermodynamic functions of thallium in solid Tl_2Te + CdTe alloys at 373 and 473 K have been calculated: partial molar free

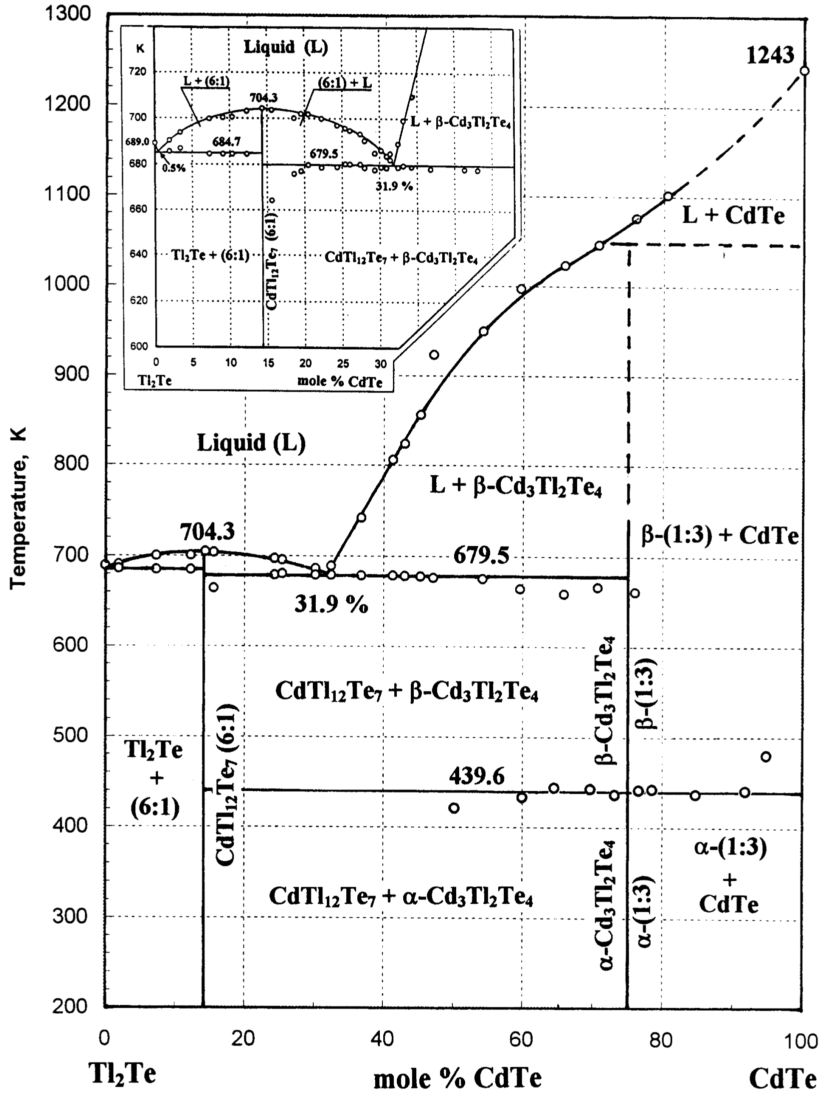

Figure 3. Corrected phase diagram for the system Tl_2Te – CdTe.

enthalpies (ΔG_{TI}), entropies (ΔS_{TI}), and enthalpies (ΔH_{TI}). All these values have been listed in Table 2. From the table it follows that the (ΔS_{TI}) values are different in various phase regions at a given temperature. The differences result from different structures of the compounds formed. The most important conclusion may be derived, however, from the comparison of the ΔS_{TI} values at 373 and at 473 K in the alloys from the II and III phase regions. The considerable differences in the ΔS_{TI} are indicative of significant change of crystal structure on polymorphic transition of the compound $Cd_3Tl_2Te_4$.

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

Composition (mole % CdTe)	Phase region		$-\Delta G_{Tl}$ (kJ·mole^{-1})	ΔS_{Tl} (J·mole^{-1}·K^{-1})	$-\Delta H_{Tl}$ (kJ·mole^{-1})
		at 373 K			
0–14.3	I	Tl_2Te + $CdTl_{12}Te_7$	24.1 ± 1	41.6 ± 2	8.6 ± 2
14.3–75.0	II	$CdTl_{12}Te_7$ + α-$Cd_3Tl_2Te_4$	40.1 ± 0.3	–15.9 ± 8	34.2 ± 3
75.0–100	III	α-$Cd_3Tl_2Te_4$ + CdTe	45.6 ± 0.1	–21.9 ± 2	53.8 ± 0.7
		at 473 K			
0–14.3	I	Tl_2Te + $CdTl_{12}Te_7$	28.3 ± 0.3	41.6 ± 2	8.6 ± 1
14.3–75.0	II	$CdTl_{12}Te_7$ + β-$Cd_3Tl_2Te_4$	39.9 ± 0.1	13.9 ± 2	33.3 ± 1
75.0–100	III	β-$Cd_3Tl_2Te_4$ + CdTe	44.7 ± 0.2	30.0 ± 14	30.5 ± 6

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