

PHASE DIAGRAM FOR THE Tl_2Te - $SnTe$ SYSTEM

W. Gawel, E. Zaleska and E. Maskiewicz

DEPARTMENT OF INORGANIC CHEMISTRY, MEDICAL ACADEMY, UL. SZEWSKA 38,
50-139 WROCLAW, POLAND

(Received December 15, 1989)

The phase equilibrium diagram for the Tl_2Te - $SnTe$ system has been established by thermal analysis (cooling curve method) and differential thermal analysis. The results obtained are compared with the other data.

The present work is a part of the series of our studies on phase equilibria in the telluride systems of the type Tl_2Te - M_xTe_y , in which ternary compound formation may be expected with probable advantageous semiconductive properties. Up to now, systems have been investigated, the second component of which were the tellurides of following metals (M): Ag [1], Bi [2] and Sb [3].

The Tl_2Te - $SnTe$ system is one of the possible sections of the ternary Tl - Sn - Te one. The phase equilibria in the last system were studied earlier [4, 5]. In paper [4] the phase diagram for the Tl_2Te_3 - $SnTe$ system was given, while in [5] - the results of phase studies on eight different sections of the Tl - Sn - Te system, among them also the phase diagram for the Tl_2Te - $SnTe$ one were presented. However, for the phase diagram of the latter different interpretations have been offered, and, on the other hand, it appeared to be inconsistent with our electrochemical studies by EMF measurements of concentration cells containing solid alloy ($Tl_2Te + SnTe$) electrodes [6]. Accordingly, we have again undertaken the phase studies on the title system by thermal analysis (employing the cooling curve technique, TA) and differential thermal analysis (DTA).

Experimental

Materials

Initial materials for preparing $Tl_2Te + SnTe$ alloys were thallium 99.99 % pure (Fluka AG), tin 6N (POCh) and tellurium spec. pure (Johnson Matthey). Tin and thallium tellurides were prepared by fusing the components, weighed with an accuracy of $\pm 0.0001g$, in quartz tubes under purified argon atmosphere, and then mixing for about 15 min at temperatures at least 100° higher than the respective points of fusion.

Thermal analysis (DTA, TA), accuracy

Preliminary investigation of phase equilibria in the $Tl_2Te-SnTe$ system has been carried out by DTA method employing the Derivatograph Q-1500 D (MOM, Budapest). Alloy samples (2-3 g) were placed in evacuated and sealed quartz vessels furnished with a pocket for a thermocouple. The heating rate was 5 deg/min within the measurement range up to 1000° . It appeared that the values of temperatures determined by the derivatograph were in considerable error reaching even about 40° . Since the error was generally proportional to the measured temperature and always negative in relation to its true value, it might be supposed that it is a result of any structural defect of the measuring instrument (recorder). For that reason the measuring system of the derivatograph has been calibrated at the melting points of standards (indium, tin, cadmium, zinc, lead chloride, aluminium and silver). From the results of the calibration, the constants of the equation of thermometric characteristics of the derivatograph have been calculated employing the least squares method: $T_t = a + bT_d$, where T_t - true temperature value, T_d - the temperature determined by the derivatograph, a and b - constants. Due to the correction equation, the error has been decreased to about $\pm 6^\circ$ within most (up to 600°) of the temperature range of measurements used in this work. Above 600° it was $\pm 12^\circ$.

Results of measurements by DTA have been considered as initial, approximate ones because the accuracy is less than that of TA. The phase diagram for the system under investigation has been delineated by using experimental points obtained by TA only in the cryometric apparatus described in [7]. The phase transition temperatures were determined similarly as in the studies on the Tl_2Te-Ag_2Te system [1], i. e. by means of a thermopile Pt/Pt, Rh calibrated at the freezing points of standards: Pb, Zn, $PbCl_2$, Al, KCl and Ag. The accuracy of the measurements was $\pm 0.5^\circ$.

The compositions of the alloys examined were calculated from the masses of the components taken. There was no need to analyse the samples after each measurement series had been finished, as the mass loss due to evaporation of slightly volatile components was not more than 0.05 wt.%. The eutectic composition was given with an accuracy of only ± 0.5 mole %. This is the minimum error in the graphical determination of the composition from the scattered experimental points.

Results

The phase diagram for the thallium telluride - tin telluride ($\text{Tl}_2\text{Te}-\text{SnTe}$) system was established from the data obtained by thermal analysis (cooling curves) and differential thermal analysis (heating curves), (Figure).

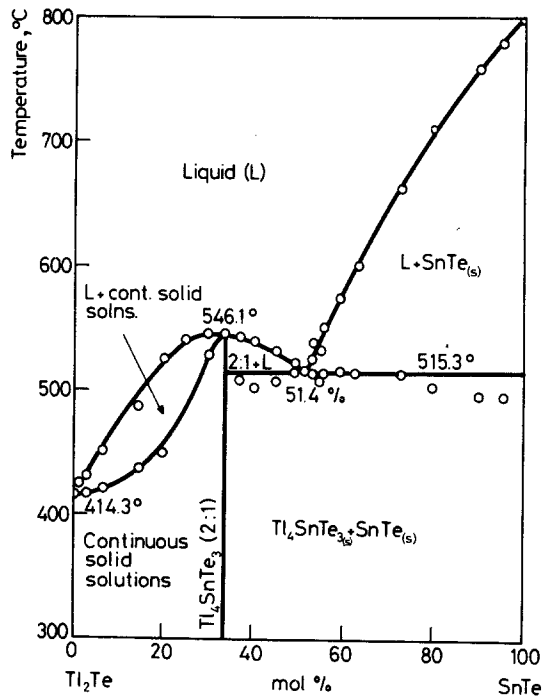


Fig. Phase diagram for the $\text{Tl}_2\text{Te}-\text{SnTe}$ system

In this system one chemical compound is formed of components with molar ratio of $\text{Tl}_2\text{Te} : \text{SnTe} = 2:1$ (i.e. 33.3 mole % SnTe) to which the formula Tl_4SnTe_3 may be ascribed. It melts congruently at $546.1 \pm 0.5^\circ$. The compound forms continuous solid solutions with thallium telluride, and with tin telluride it forms an eutectic containing 51.4 ± 0.5 mole % SnTe and having a melting point of $515.3 \pm 0.5^\circ$.

The fusion temperature of pure SnTe was determined to be $800.0 \pm 0.5^\circ$; the value is by about 10° higher than that reported in [4] and [5].

Discussion

The phase equilibrium diagram for the Tl_2Te -SnTe system established by us differs considerably from that published earlier [5], determined from the results of investigations by DTA, X-ray diffraction and microhardness. The liquidus line in both cases is similar excepting its first part near the pure Tl_2Te , where the authors of [5] found a minimum. From our results it follows, however, that the liquidus and solidus lines form a regular cigar-shaped pattern within the whole existence range of the continuous solid solutions (0 - 33.3 mole % SnTe). According to [5], within the above range of compositions the following areas occur: (1) 0-7 mole % SnTe: three-phase region (Tl_2Te , Tl and δ -phase, where δ is a continuous solid solution of Tl_4SnTe_3 and Tl_5Tl_3), (2) 7-12 mole % SnTe: two-phase region (δ and solid solution on thallium base). Within either of the two first regions a phase transition occurs in the solid state. (3) 12-40, and at higher temperatures up to even 50 mole % SnTe: as it appears from the phase diagram published in [5], there is a phase of variable composition with a maximum on the liquidus line at 555° , above 30 mole % SnTe. The authors of [5] do not consider, however, the formation of the intermediate phase, but instead, accept the existence of the Tl_4SnTe_3 compound without marking it in the diagram. They explain an internally inconsistent image of the phase equilibria in the concentration range as above, by assuming that the Tl_2Te -SnTe system is non-quasibinary in this part.

It seems that the reason of the above ambiguity is that only one method of determination of phase transition temperatures - DTA has been used. Results obtained by the method are unreliable especially when the phase transformations occur in succession at temperatures not too distant from one another [2]. In the preliminary examination of the Tl_2Te -SnTe system by differential thermal analysis, we observed within the range 0-55 mole % SnTe a considerable scatter of experimental points, that permitted their ar-

rangement to be interpreted in different ways. Further investigations by cooling curve method evidenced, however, that the system was quasibinary in the whole concentration range and the liquidus and solidus lines showed no anomalies. Neither of the two methods showed any phase transition in the solid state, and the numerical values obtained by them were in agreement, but differed from those published in [5], (e.g. according to [5], the melting points of the compound Tl_4SnTe_3 and the eutectic are 555 and 505°, respectively, eutectic composition < 50 mole % SnTe).

The phase diagram for the Tl_2Te -SnTe-system seems to be quite clear and, beside the electrochemical studies [6] started earlier, it demands no additional method investigation.

* * *

The present work was financed by the Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, from grant CPBP 01.12.

References

- 1 W. Gawel, E. Zaleska and J. Terpilowski, *J. Thermal Anal.*, 32 (1987) 227.
- 2 W. Gawel, E. Zaleska and J. Terpilowski, *J. Thermal Anal.*, 35 (1989) 59.
- 3 W. Gawel, B. Fuglewicz and E. Zaleska, *Polish J. Chem.*, 63 (1989) 93.
- 4 P. G. Rustamov, M. A. Alidjanov and Ya. M. Babayev, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 12 (1976) 843.
- 5 A. A. Gotuk, M. B. Babanly and A. A. Kuliyeu, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 15 (1979) 1356.
- 6 E. Zaleska and W. Gawel, *Polish J. Chem.*, to be published.
- 7 J. Terpilowski, W. Gawel and A. Bogacz, *Roczniki Chem.*, 46 (1972) 3.

Zusammenfassung — Mittels Thermoanalyse (Kühlkurvenverfahren) und DTA wurde für das System Tl_2Te - SnTe ein Phasengleichgewichtsdiagramm erstellt. Die erhaltenen Ergebnisse wurden mit anderen Angaben verglichen.