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UNUSUAL PHASE CHARACTERISTICS IN BINARY THALLIUM TELLURIDE–METAL TELLURIDE SYSTEMS

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Abstract

The phase characteristics and some properties of alloys in the two most interesting of the binary thallium telluride systems (Tl_2Te–Ag_2Te and Tl_2Te–Bi_2Te_3) are discussed and the phase diagrams of the systems are reviewed.

Keywords: Tl_2Te–Ag_2Te, Tl_2Te–Bi_2Te_3

Introduction

For several years, considerable attention has been paid to ternary systems of elements of Groups III to V (and some transition elements) of the Periodic Table with chalcogens, and particularly tellurium. The greatest interest has been focused on the systems Tl–Te–M (M=any metal) because of the possibility of formation of ternary compounds with advantageous semiconductive properties. Such compounds are formed along the sections of the three-component systems, i.e. in the pseudobinary ones.

From among the phase diagrams of the binary telluride systems published to date (Tl_2Te–M_xTe_y, where M=Cu, Ag, Zn, Cd, Hg, In, Ge, Sn, Pb, As, Sb, Bi), only two (Tl_2Te–Ag_2Te and Tl_2Te–Bi_2Te_3) are distinguishable by their surprising shapes. A discussion of some unusual phase characteristics for these two systems involves not only the geometry of the phase diagrams, but also the history of their investigation and some properties of telluride alloys that influence even the measurement technique itself.

The system Tl_2Te–Ag_2Te

The pseudobinary system Tl_2Te–Ag_2Te has been studied three times to date. The phase diagram for the system was reported first by Kovaleva *et al.* [1] in 1975 (Fig. 1a) and then by Abishov *et al.* [2] in 1978 (Fig. 1b). At first sight,

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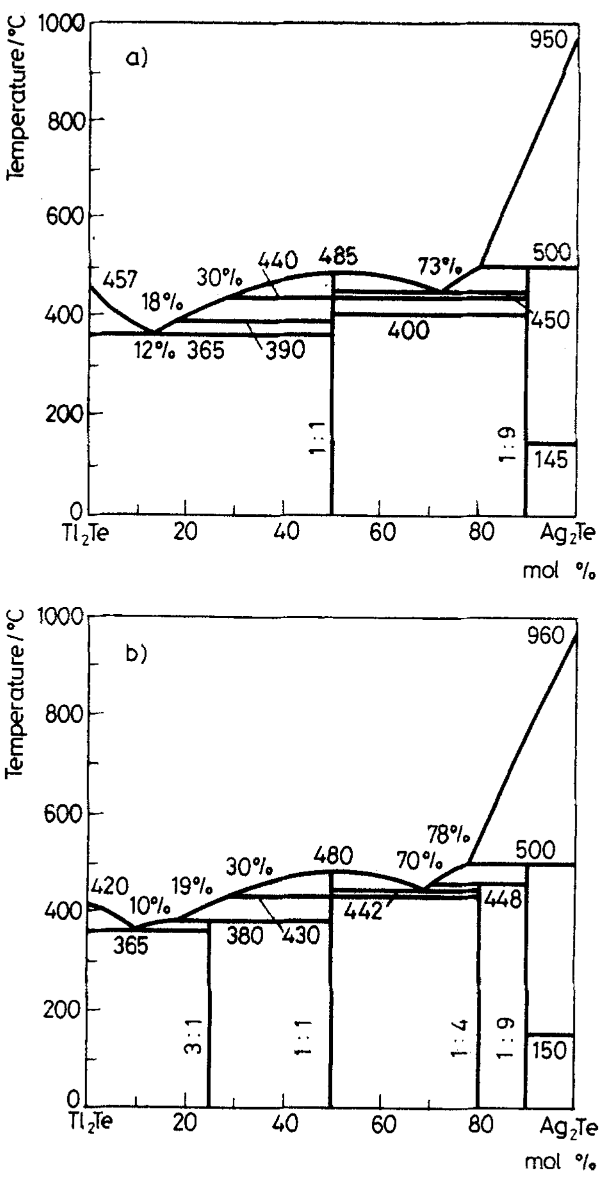

Fig. 1 Phase diagrams for the system Tl_2Te–Ag_2Te according to [1] (a) and [2] (b)

the two phase diagrams resemble one another, but this impression is a result of the almost identical shapes of the liquidus line. In other details, they differ considerably. According to [1], two compounds are formed in the system, with a component molar ratio of 1:1 (AgTlTe) or 1:9 (Ag_9TlTe_5), while according to [2] there are four compounds, the additional ones having ratios of 3:1

($AgTl_3Te_2$) and 1:4 ($Ag_8Tl_2Te_5$). The two publications reveal how different the results obtained by various authors with practically the same method (DTA, X-ray diffraction, microhardness, microstructural) can be. The reason for the discrepancies is undoubtedly the different interpretation of rough experimental data. One can imagine that the authors of [2], influenced by the results in [1], tried to explain some phase transitions (e.g. the lines at 390 or 400°C) reported by [1]. To be fair to the authors of [1], it must be stated that they reported the two transitions (although they could not interpret them), which was correct because the data proved to be valuable information for the authors of [3]. Since such unidentified transitions cannot occur in a binary system that obeys the phase rule, the authors of [1] and [2] considered the system to be non-quasibinary.

The system Ag_2Te–Tl_2Te appeared to be complicated because of certain phase characteristics demonstrated in [3] (Fig. 2) by a further investigation method: thermal analysis. The method permitted determination of the phase

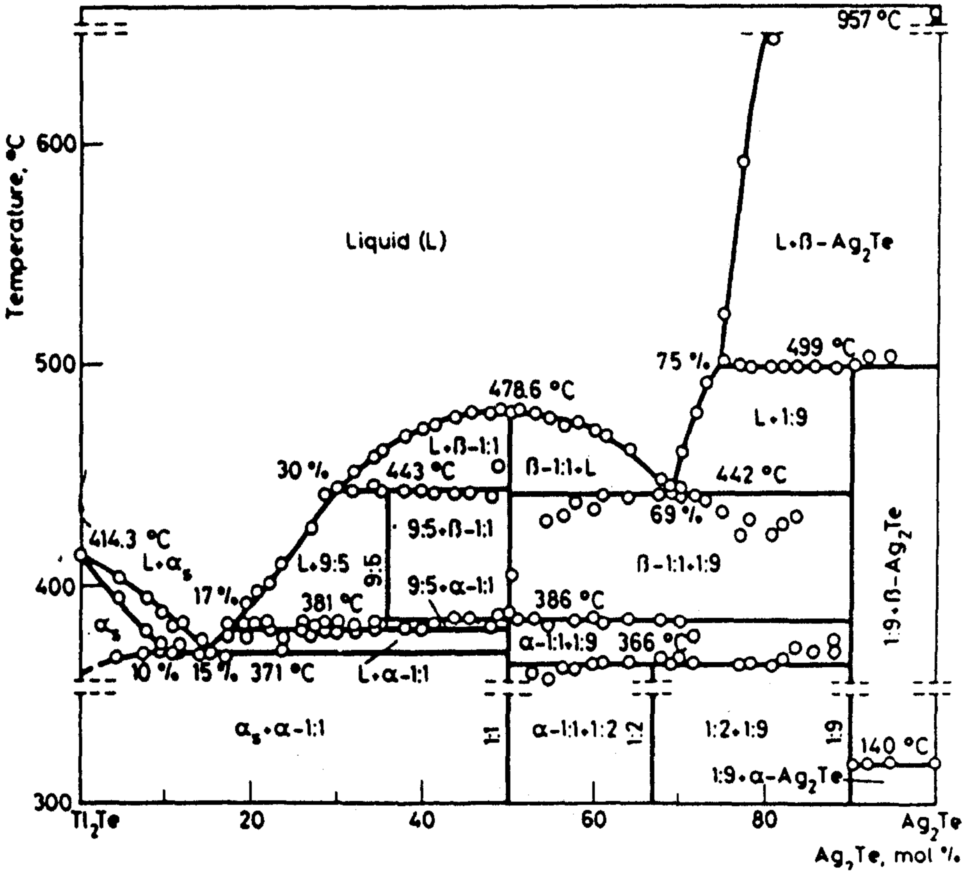

Fig. 2 Phase diagram for the system Tl_2Te–Ag_2Te according to [3]

transition temperatures quite precisely (with an accuracy of ±0.2 deg). It was shown that in this system an unusual compound was formed with a component molar ratio Tl_2Te:Ag_2Te=9:5. It was characterized as having two melting temperatures: when heated, it melted (with decomposition) at 443°C, and when cooled, it melted (with decomposition) at 381°C. Such 'double melting' is a result of coincidence and is not an extraordinary phenomenon in terms of the phase theory, but it occurs relatively rarely. Because of the features of the compound, determination of its composition proved difficult. It could not be established from the arrangement of the experimental points (they form a line exactly parallel to the composition axis, without any maximum), nor by Tammann's triangle method (the phase compositions of the melts on either side of the compound are quite different), nor by X-ray diffraction (the X-ray diffraction patterns of the neighbouring 9:5 and 1:1 compounds closely resemble one another). The compound composition 9:5 (i.e. 35.7 mol% Ag_2Te) was determined by observation of the motion of the stirrer in the apparatus used [4]. Throughout the measurements, the molten alloys were stirred by a quartz stirrer making vertical strokes. During the cooling of liquid mixtures Tl_2Te+Ag_2Te, the stirrer stopped at 443°C when the melt composition was 35.7 mol% Ag_2Te or more, whereas it stopped at much lower temperature (371 °C) when the melts were poorer in Ag_2Te.

An interesting detail is that the good adhesion of the melt to the quartz and the pressure in the solidifyig alloys resulted in crumbling of a stirrer of any shape (e.g. a coil, crescent, ball or cone) but one: an ordinary cylinder.

Another curiosity in the system Tl_2Te–Ag_2Te is that the upper decomposition temperature of the compound of ratio 9:5 and the melting point of the eutectic of composition 69 mol% Ag_2Te are almost equal (443 and 442°C, respectively). This is the reason why the two phase transitions were incorrectly considered to be one and the same transformation in [1] and [2]. Both groups of authors regarded them as a polymorphic transition of the compound AgTlTe (1:1).. Their distinction was greatly facilitated by one of the shortcomings of thermal analysis: supercooling. This frequently results in an arrangement of experimental points corresponding to eutectic crystallization, so that they form a curve convex upwards, the maximum of which lies at the melting temperature and composition of the eutectic, as was the case in [3]. Thus, the disadvantage of the method provided strong evidence that two different phase transformations occur at 442 and 443°C.

The system Tl_2Te–Bi_2Te_3

Another very interesting system among the pseudobinary thallium telluride systems is Tl_2Te–Bi_2Te_3. Figures 3a,b and c present the phase diagrams of the system reported by three groups of investigators [5–7].

The first (Fig. 3a) is a diagram of the system Tl_9BiTe_6–Bi_2Te_3, but as a matter of fact, it constitutes 90% of the system Tl_2Te–Bi_2Te_3 (the compositions on the abscissa are given for Tl_9BiTe_6+Bi_2Te_3 mixtures, and those on the diagram plane for the system Tl_2Te–Bi_2Te_3). The incompleteness does not impede the discussion since the central part of the system is the most controversial.

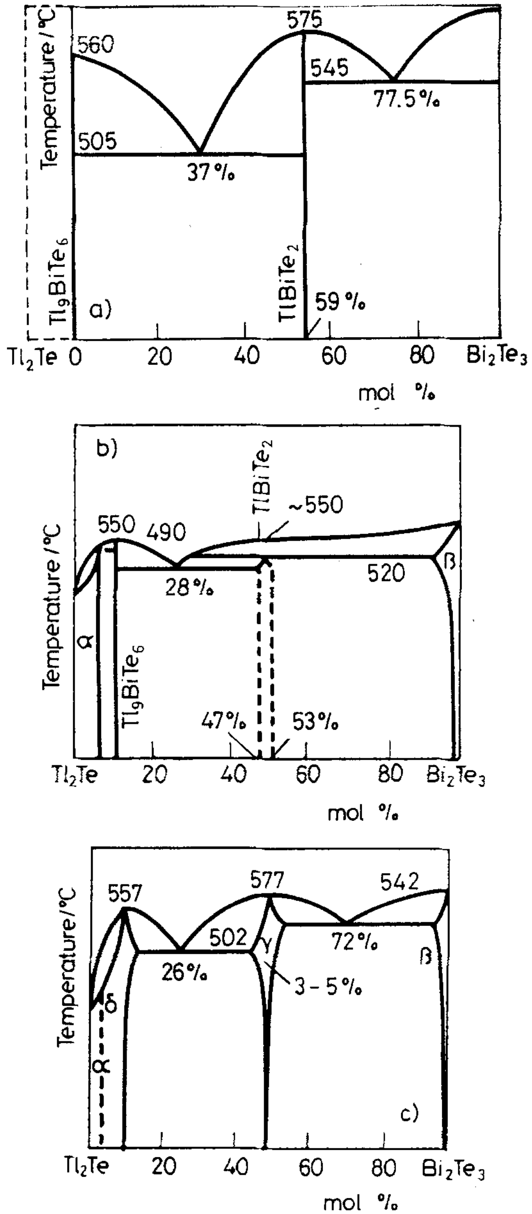

Fig. 3 Phase diagrams for the system Tl_2Te–Bi_2Te_3 according to [5] (a), [6] (b) and [7] (c)

The three phase diagrams may be seen to differ mostly in the middle part, and are even contradictory. Berg and Abdulmanov [5] (Fig. 3a; methods employed: DTA and microhardness) concluded that a chemical compound, $TlBiTe_2$, is formed, which melts congruently at 575°C. The formula of this compound demands that its composition should be 50 mol% of each component, whereas the authors found it to be 59 mol% Bi_2Te_3. They did not believe, however, that any compound other than $TlBiTe_2$ was involved and reported this formula.

The diagram of Popovich *et al.* [6] (Fig. 3b) was obtained by using the same main method (i.e. DTA) and additionally X-ray diffraction and microhardness. Nevertheless, their results were quite different from the previous ones. They also stated that the compound $TlBiTe_2$ was formed, but that it melted incongruently on decomposed at 520°C and was a phase of variable composition, its range of existence covering 6 mol%, i.e. from 47 to 53 mol% Bi_2Te_3.

Babanly *et al.* [7] examined the system by means of DTA, X-ray diffraction, microhardness and EMF measurements of concentration cells. Their results (Fig. 3c) differed from the former two. They found the compound $TlBiTe_2$ at almost exactly 50 mol% Bi_2Te_3, but stated that it melted congruently at 577°C, and within a certain temperature range was a phase with variable composition (3–5 mol%).

Pradel *et al.* [8] reported on the system TlTe–BiTe, in which the compound $TlBiTe_2$ was formed at 50 mol% of each component, the compound melting incongruently at 524°C.

Three different phase diagrams for the same system and four pieces of information on the same compound. What is the truth?

Let us consider the differences in melting (decomposition) temperatures of the compound $TlBiTe_2$: 575, 520, 577 and 524°C. These differences are too large (51–57 deg) to be explained by the low accuracy of measurements performed by the same method. Moreover, does the compound melt congruently or incongruently?

With the current high level of the experimental technique, such considerable discrepancies would appear to be impossible. The only explanation is unusual phase relations in the system Tl_2Te–Bi_2Te_3. The solution of this complex problem was given in [9]. Unexpectedly, it appeared that in fact there are not discrepancies between the results in [5–8]. How is this possible? Simply, the groups of authors examined two different compounds. It has been shown by thermal analysis (cooling and heating curves) that in the central part of the system Tl_2Te–Bi_2Te_3 two separate compounds are formed: $TlBiTe_2$ at 50 mol% Bi_2Te_3 (1:1) and a compound of component molar ratio Tl_2Te:Bi_2Te_3 = 11:14 (i.e. at 56 mol% Bi_2Te_3), to which the formula $Tl_{0.83}Bi_{1.06}Te_2$ can be ascribed. The compound with 1:1 composition of frequent occurrence melts incongruently at 520.0°C, while that with the rather strange formula appeared to be quite 'normal', melting without decomposition at 544.7°C.

Comparison of the four phase diagrams for the system $Tl_2Te–Bi_2Te_3$ demonstrates that the last diagram may be obtained approximately by superposition of the three previous ones. The compositions of the compounds $TlBiTe_2$ (50 mol%) and $Tl_{0.83}Bi_{1.06}Te_2$ (56 mol%) have been regarded ([6] and [7]) as two boundaries of the one-phase area (the supposed phase of variable composition within the range 5–6 mol%).

An additional unusual phase characteristic is the compound $TlBi_7Te_{11}$ (87.5 mol% Bi_2Te_3), which exists within the temperature range 310.5–501.0°C and decomposes into two solid phases on heating and on cooling.

The question arises of whether the most recent phase diagrams for the system $Tl_2Te–Ag_2Te$ [3] and $Tl_2Te–Bi_2Te_3$ [9] are the best and ultimate. Thermal analysis involving cooling and heating curves permits precise determination of the phase transition temperatures (unlike DTA; for a comparison of the results obtained by DTA and TA, see [9]). The most important evidence, however, is

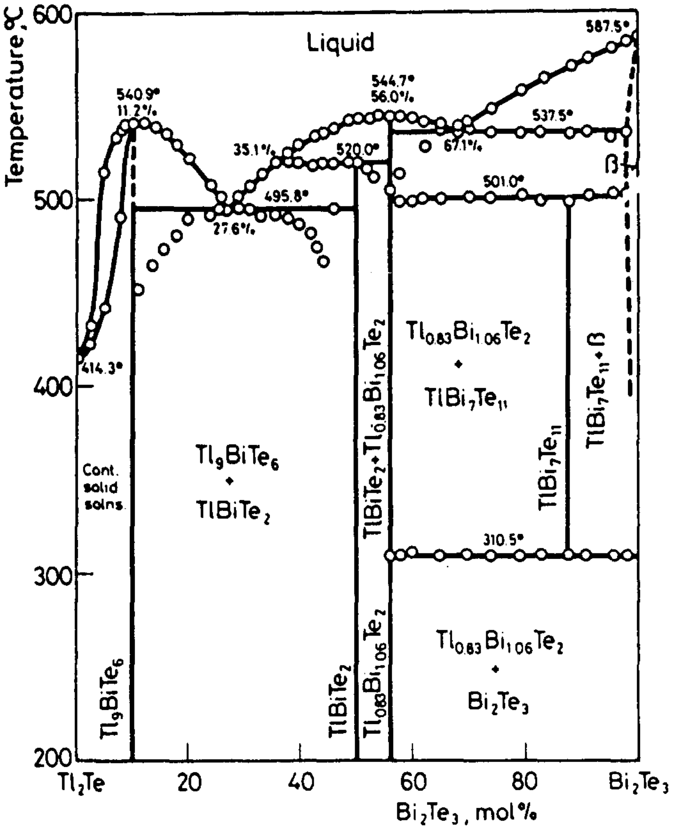

Fig. 4 Phase diagram for the system $Tl_2Te–Bi_2Te_3$ according to [9]

the fact that the results of the phase studies in [3] and [9], illustrated in Figs 2 and 4, explain the differences and contradictions between the earlier works.

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