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THE As–Te SYSTEM: PHASE DIAGRAM AND GLASS SEPARATION

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ABSTRACT

The As_2Te_3 compound is usually described as showing non-congruent melting, or congruent melting at a temperature which cannot be differentiated from that of the next eutectic. The As–Te system is here presented using an isochoric diagram, and the specific volume variable is taken into account to explain this anomalous melting. From analyses by electron microprobe of quenched liquid and vapour phases, it may be assumed that the melting of As_2Te_3 is non-congruent.

Vitreous materials are obtained from quenching of the liquid in two zones adjacent to As_2Te_3, and from fast quenching of liquid As_2Te_3. When glassy products containing 55–80 mol% of As are annealed at temperatures lower than that of the liquidus, separation of a large vitreous phase occurs.

INTRODUCTION

Although many papers which deal with the As–Te phase diagram have been published, some problems have not yet been resolved. Two points need further study: the melting of As_2Te_3, and the miscibility gap in the As-rich part of the diagram related to glass formation phenomena.

MELTING OF THE As_2Te_3 COMPOUND

Pelabon [1], Dembovskii et al. [2], Eifert and Peretti [3], Cornet and Rossier [4] and Blachnik et al. [5] describe a phase diagram including a

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TABLE 1

Melting point of As_2Te_3, and temperatures and compositions of eutectics E_1 and E_2

	Temperature (°C)	Composition (mol% As)	Reference
Eutectic E_1	329	25	1
	355 [a]	20	2
	363	27.1	3
	362	27±1	4
	362	28	5
As_2Te_3	362	–	1
	393 [a]	–	2
	381	–	3
	378	–	4
	381	–	5
Eutectic E_2	355	–	1
	360 [a]	45	2
	380	44	3
	378	46±1	4
	380	47	5

[a] Temperatures not mentioned in the text; evaluated from the diagram.

congruent melting point for As_2Te_3. Values of the temperature and composition of the E_1 eutectic (richer in Te) are not discussed. However, many values for the temperature and composition of the E_2 eutectic (richer in As) have been published, as the values of Table 1 demonstrate.

In the studies of Pelabon [1] and Dembovskii et al. [2], the congruent melting of As_2Te_3 is marked by a sharp maximum of the liquidus curve, whereas the temperatures of the E_2 eutectic are not separated from the As_2Te_3 melting point in the three other descriptions. The question may be asked whether the As_2Te_3 melting point results in congruent melting or a peritectic decomposition.

It should be admitted that there is some error in the liquidus curve. Now, only Blachnik et al. [5] give experimental values for the liquidus curve. The Eifert diagram [3], which was used by Cornet [4], shows no liquidus experimental results. According to Blachnik et al. [5], the liquidus curve meets the eutectic line for 47 mol% of As, i.e. beyond the composition As_2Te_3, which means that the As_2Te_3 melting point is congruent.

Elsewhere, Kirkinskii and Yakushev [6] have studied the As_2Te_3 melting as a function of pressure up to 20 kbar. These authors state that the As_2Te_3 melting becomes incongruent for pressures above 8 kbar.

It must also be noted that Dembovskii considers that As_2Te_3 is unstable at melting [2]. This is deduced from a study of vapour pressure, since As_2Te_3 dissociates on vaporizing by the following reaction

$$As_2Te_3(\text{solid}) \rightleftharpoons 0.4\ As_2(g) + 0.3\ As_4(g) + 3\ Te(\text{solid}) \qquad (1)$$

Influence of vapour pressure on melting of As_2Te_3

The peculiar shape of the liquidus curve near the eutectic of the arsenic-rich part of the As–Te diagram led us to undertake a study of this diagram.

As the vaporization phenomena are important in the arsenic-rich part of this system, the action of vapour pressure must be taken into account. This is why we used for this study the same method, which allowed us to resolve several systems in which vapour pressure is not negligible [7–10].

This method consists in describing the binary system by a three dimensional pattern: temperature T, mole fraction x, and specific volume $v = V/m$, where V/m is the ratio of the internal volume of the ampoule (including the dead volume) to the total mass of the sample.

For setting this three dimensional diagram, the volume of the ampoule must be decreased for each molar fraction. For each V/m value so obtained, the sample is analysed by DTA. In the DTA furnace, the position of the ampoule is vertical and is chosen in such a way that the upper part of the vessel is in the warmest zone of the furnace. Vapour condensation at the top of the vessel can be avoided by this technique.

Sample preparation

The samples are contained in evacuated silica vessels. The specific volumes vary from 2–3 $mm^3\ mg^{-1}$. The samples are heated up to 600 °C for one week in a horizontal furnace, then up to 820 °C in a vertical furnace, in a position such that the top of the ampoule is in the hottest part of the furnace.

Isochoric diagram

The DTA results appear in Fig. 1. The two eutectic invariants lie near 380 and 360 °C (653 and 633 K). These values are in good agreement with those of Eifert [3], Cornet [4] and Blachnik [5]. No monotectic invariant can be observed, and the arsenic-rich part of eutectic E_2 is similar to that described by these authors at the temperature of the As_2Te_3 melting point and for a composition very close to this compound.

Specific volume influence and T–v–x description

Two parts of the diagram have been studied more closely: the zone of the miscibility gap described by Dembovskii and the eutectic zone between As_2Te_3 and As described by Blachnik and by Cornet. The corresponding V/m values are 0.8 $mm^3\ mg^{-1}$ upwards. The results for samples with smaller specific volumes are less accurate because of the small mass of product which must be used, since the DTA apparatus limits the size of the ampoule.

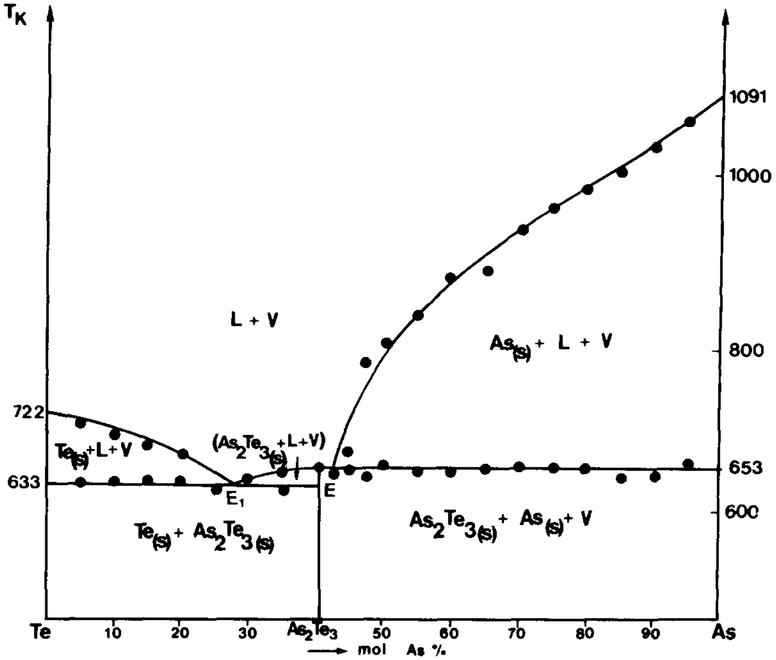

Fig. 1. As–Te diagram obtained from the DTA results for $2 < V/m < 3$ mm^3 mg^{-1}.

Liquid–liquid–vapour miscibility gap

In a sealed silica tube, the liquid–liquid miscibility gap cannot exist without a vapour phase occupying the dead volume. Thus the miscibility gap, as described in the T–V/m–x diagram, must be a three phase domain: liquid 1 + liquid 2 + vapour. In a previous paper [9] we showed how a monotectic invariant plane could be described and measured in the T–V/m–x diagram.

The experimental study was carried on with V/m values up to 10 mm^3 mg^{-1}. No change of the invariant peak was observed which could indicate a miscibility gap for mole fractions from 65–80 mol% of As.

Melting point of As_2Te_3

The eutectic which is drawn from our own results in Fig. 1 is close to the diagrams of Cornet and of Blachnik. However, the shape of the eutectic between As_2Te_3 and As seems to be unusual. We attempt to offer another interpretation of this kind of unusual eutectic and to answer the question concerning congruent or incongruent melting of As_2Te_3.

In terms of a classical isobaric T–x description of binary systems, it is not possible to explain the shape of the liquidus as due to incongruent melting. An incongruent melting would be possible only if the binary compound was richer in As (for example, in the case of a solubility range). As a matter of fact, the diagram of Fig. 1 is not isobaric: it is isochoric.

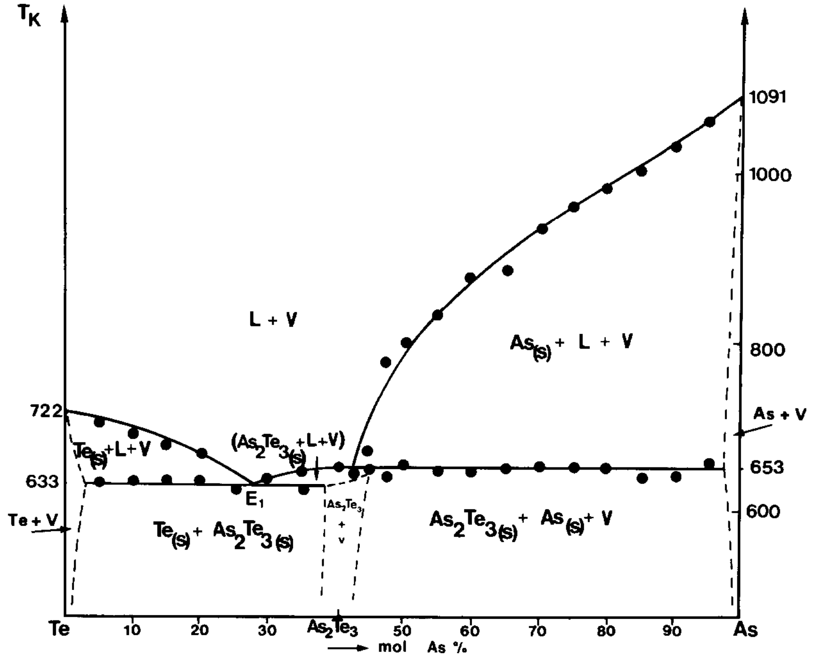

Fig. 2. Agreement of the experimental results with the hypothesis of a peritectic decomposition.

Therefore, this diagram is an isochoric section of the T–V/m–x diagram. In this diagram, the solid binary compound is conjugated with a vapour phase. So, if the peritectic equilibrium vapour phase composition is different to the solid phase composition, the solid + vapour domain can be crossed by an isochoric section for any different composition. It can be seen in Fig. 2 that the experimental data may corroborate this assumption. The top of the As_2Te_3 + vapour domain of the isochoric section of Fig. 2 has a composition which is richer in As than stoichiometric As_2Te_3.

There are few changes on the DTA curves when V/m varies. Only for the 45 mol% As composition can it be observed (Fig. 3) that the invariant peak area grows as a function of V/m, for $V/m < 3$ mm^3 mg^{-1}. The largest value for the area is obtained for $V/m = 2.3$ mm^3 mg^{-1}, and extrapolation to $S = 0$ leads to $V/m = 5$ mm^3 mg^{-1}.

Nevertheless, no invariant plane limit can be fixed with only these two values, and the invariant peak is still quite visible for V/m values from 6–7 mm^3 mg^{-1}. Furthermore, these results are in accordance with the two schemes of Fig. 4 (vertical line 2), on which the thermic effect isointensity curves are shown for an eutectic invariant as well as for a peritectic invariant. These DTA curves cannot afford any conclusion about the type of melting of As_2Te_3.

Meanwhile, on stoichiometric As_2Te_3 DTA curves, a weak liquidus-like endotherm can be observed for $V/m < 3.3$ mm^3 mg^{-1}. This DTA peak may

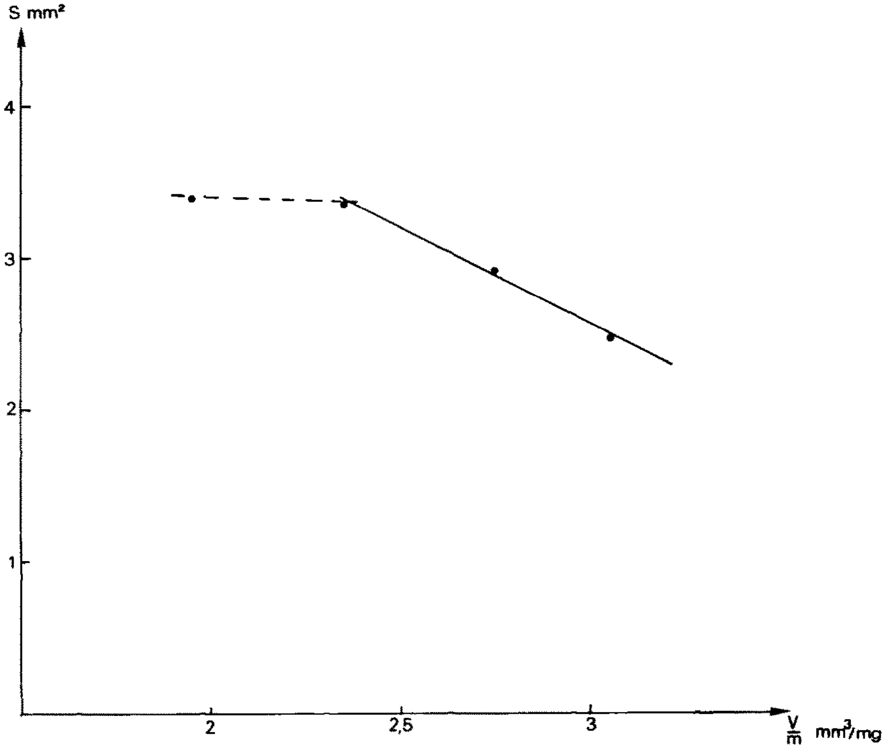

Fig. 3. Variation of the invariant peak area at 653 K for a composition of 45 mol% As.

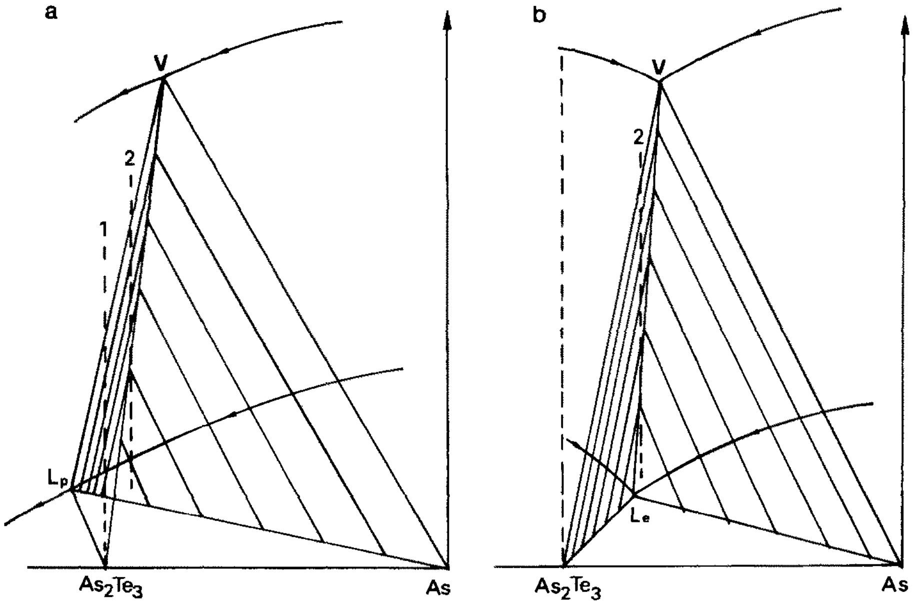

Fig. 4. Thermal effect at the invariant (lines of isointensity): (a) case of peritectic; (b) case of eutectic.

TABLE 2

Results of electron microprobe analyses

Sample No.	Composition (mol% As)	V/m (mm mg^{-1})	Quenching temperature (K)	Vapour phase (mol% As)	Liquid phase (mol% As)
1	85.0	1.48	1093	92.8–100	80
2	70.0	0.99	953	54–69	70
3	42.5	2.44	680	40–44	39–40

be compared with the peaks observed on the As-richer DTA curves, where the peak temperature grows as V/m decreases. This is consistent with a peritectic equilibrium.

This phenomenon is also observed at 45 mol% As: the liquidus marking peak is very close to the invariant peak when $V/m = 3.05$ mm^3 mg^{-1}, but it becomes quite well separated for lower V/m values. This may be in agreement with both invariant equilibria of Fig. 4 if, as is probable, the liquid phase is conjugated with an As-richer vapour phase.

Since these observations, although they corroborate the existence of an invariant equilibrium vapour phase, do not help to define the type of equilibrium, we carried out a series of electron microprobe analyses.

Electron microprobe analysis

The samples are quenched in such a way that at least a part of the vapour phase can be solidified on the vessel walls.

Three samples were analysed. The results are shown in Table 2. The first two samples were quenched from a temperature slightly higher than the liquidus temperature. The third one has the supposed eutectic composition, and was quenched from a temperature slightly higher than the invariant temperature. At the quenching temperature, for the three samples, the phases are liquid + vapour. The phase which solidifies on the ampoule walls is the initial vapour phase, and the solidified phase lying at the bottom of the ampoule is the initial liquid.

In the As-rich zone, a 100 mol% As vapour phase is conjugated with a liquid whose composition is close to that of the initial mixture (Sample 1). In Sample 2, the liquid phase has become richer in As than the vapour phase. With Sample 3, the vapour phase is again richer in As than the liquid phase. It should be noted that the change in As composition of sample 2 occurs while the liquidus curves of Figs. 1 and 2 show some irregularity (65 mol% As).

The compositions of the four phases at equilibrium can be arranged on the x axis, as follows

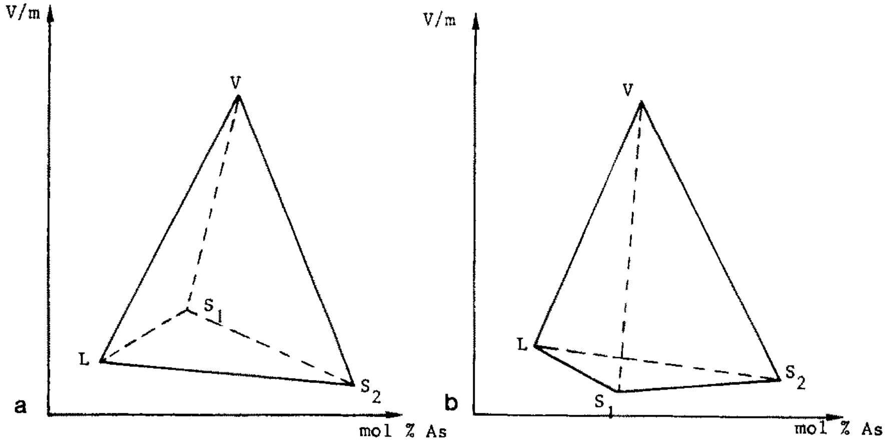

Fig. 5. Possible representations of the peritectic: (a) triangular representation; (b) quadrilateral representation.

liquid	As_2Te_3 (s)	vapour	As (s)
39–40	40	40–44	100 (mol % As)

If the equilibrium vapour phase specific volume is higher than the other three, there are two ways of describing the invariant plane $x-V/m$: triangular, and quadrilateral. These two cases are illustrated in Fig. 5.

Although the DTA results are not sufficient to set the limits of the invariant plane between As and As_2Te_3, nor to indicate the type of invariant, analysis of the phases of the equilibrium mixture indicates that the liquid phase is As-poorer than both the two solid phases and the vapour phase.

According to these results, it may be assumed that the invariant plane is a peritectic plane which can be described by one of the two examples of Fig. 5. A eutectic plane would imply the existence of a central liquid phase, which would necessarily be richer in As than the As_2Te_3 stoichiometric compound.

MISCIBILITY GAP IN THE As-RICH PART OF THE DIAGRAM AND GLASS FORMATION

Miscibility gap

A liquid miscibility gap was observed by Dembovskii et al. [2] between 55 and 50 mol% of As. The monotectic line stays at 390 °C. These authors specify that the diagram is like that of Pelabon [1] when thermal analysis is conducted with samples prepared near 650 °C. On the other hand, if these samples have been annealed at 300 °C for 2 weeks, the miscibility gap appears. Dembovskii et al. explain this phenomenon by an equilibrium being reached slowly. They conclude that the equilibrium phase diagram is the one with the liquid miscibility gap.

Since then, this miscibility gap has never been observed by any other author. Particularly, Cornet and Rossier [4] carried out a micrographic study of samples prepared at 640 °C and cooled in the furnace. During the cooling, it can be observed by micrography that 'primary arsenic' forms first as large crystallites with angular sides. Then, from the eutectic temperature, 'secondary arsenic' forms as small crystals with uncertain shape, dispersed in the material.

These results led us to study carefully the influence of cooling conditions, since it is known that glassy materials can easily be obtained by fast cooling, and since the presence of these materials, when annealed at low temperature, may have led to the observations of Dembovskii et al.

Glass formation

The formation of homogeneous glassy products by quenching of liquid is observed in a large range of compositions, viz. (mol% As): 40–66 by Tsugane et al. [11]; 20–70 by Cornet and Rossier [4]; 40–75 by Quinn et al. [12]; 43–70 by Tenhover et al. [13]; and 45–65 by Savage [14].

The effect of the cooling rate on the extent of the glassy region is important [4]. The largest extent, from 20 mol% As, can be observed only for a high cooling rate ($180° \text{ s}^{-1}$), whereas for slower cooling the vitreous region starts from the As_2Te_3 compound (40 mol% As) [4].

During thermal analysis, a very important supercooling phenomenon occurs during cooling for As_2Te_3, and stays nearly constant from 42 mol% As onwards, which means that As_2Te_3 and secondary arsenic are precipitated [4]. Simultaneously, the melting entropy is high for As_2Te_3, which indicates a change of configuration when liquid turns to solid.

This observation corroborates that of Han et al [15], who demonstrate that the cooling rate from a liquid state has a strong influence on the nature of products for the As_2Te_3 compound: thus, a glass is obtained by very fast cooling; metastable rhombohedral β-As_2Te_3 is obtained by fairly fast cooling; and monoclinic α-As_2Te_3 is stable over the whole range of temperatures in the solid state with slow cooling.

The influence of the cooling rate on the nature of the products must reflect the phenomena that were described in the previous paragraph.

Subliquidus phase separation in the glassy state

When samples in sealed ampoules are quenched from 700 °C, for compositions between 60 and 80 mol% As, only a vitreous material is obtained.

TABLE 3

Metallographic analysis of vitreous products obtained by quenching from 700 ° C (800 ° C for 0.80 mol% As) and annealed at various temperatures

Annealing temperature (° C)	Annealing time (days)	Composition (mol% As)				
		0.55	0.60	0.675	0.75	0.80
600	2	G	G	G	G	G + As
600	10	G	G	G, D	G, D	G + As, D
550	8	G	G	G, D	G, D	G, D
500	8	G	G	G, D	G, D	G, D
450	8	G	G	G, D	Cr	
400	8		Cr			

Key: G, glass observed by X ray diffraction; D, glass separation observed by metallography; As, solid As; Cr, crystallised sample

Sometimes some crystallised arsenic may form, probably because of a partial vaporization of arsenic followed by condensation during the quenching, even though the ampoule volume is reduced to the smallest possible value. When examined by metallography, this arsenic seems to be the primary arsenic earlier described by Cornet and Rossier [4].

When samples, after quenching from 700 ° C, are annealed at temperatures lower than those of the liquidus, separated glasses form from the previous vitreous state, as explained in Table 3.

The phase separation occurs only for As compositions between 65 and 80 mol% As, whatever the annealing temperature. When there are small amounts of crystallised arsenic in the glass, as has been indicated above, and when these heterogeneous glasses are annealed between 450 and 550 ° C, arsenic progressively disappears as the zone of phase separation increases.

This is evidence that the origin of the cyrstallised arsenic can be explained by an interfering phenomenon. This phenomenon is dependent on the time of annealing, since, at 600 ° C, no separation can be observed by metallography after 2 days. The glass separation does not occur after annealing for 10 days at 400 ° C (for 60 mol% As) or 450 ° C (for 75 mol% As).

Thermal analysis of the quenched glass and separated samples shows a large exothermic peak at ca. 240 ° C. This is attributed to the crystallisation of glass followed by a return to thermodynamic equilibrium. Thus, only the endothermic peak and the liquidus line crossing point can be observed at ca. 380 ° C.

Interpretation of the subliquidus glass separation

Two interpretations may be proposed. In the assays of Dembovskii et al. [2], the miscibility gap only occurs after a long annealing at 300 ° C because thermodynamic equilibrium is established very slowly. The large supercooling observed by Cornet and Rossier [4] which occurs during cooling seems to corroborate this hypothesis. In these conditions, the system with a miscibility gap should be an equilibrium system, while the system without a miscibility gap should be out of equilibrium.

From our own point of view, this miscibility gap is due to a completely subliquidus metastable two-liquid immiscibility [16]. The reasons are as follows.

(i) There is no miscibility gap when samples are quenched from the liquid state.

(ii) Vitreous products form by quenching the liquid; indeed, when a crystallised phase does not occur during cooling, for kinetic reasons, a subliquidus miscibility gap may occur apart from the crystallisation, but only from the vitreous state; therefore this consists in an extrapolation to the lower temperatures of a two-liquid miscibility gap which becomes metastable.

(iii) There is an inflexion point on the liquidus curves in the two known series of experimental results; although the phenomenon is weak and may be due to some experimental inadequacy, the fact that disconnected points occur for the same range of compositions (62 and 79 mol% As from Blachnik et al. [8] and 65 mol% As from our own results) seems to prove that they are real.

From this work, it may be concluded that the melting of As_2Te_3 is non-congruent (though this must be considered as a limiting case) if the vapour phase is taken into account in the description of the phase equilibria of the As–Te system.

On the other hand, the existence of a metastable liquid–liquid miscibility gap, as has been described by Dembovskii [2], could explain the phase separation observed in annealed glasses. However, the corresponding invariant has not been corroborated. Thus, new experiments are required to explain glass formation accompanied by phase separation.

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