Phase equilibria in the Sb_2Te_3–Ag_2Te system

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The Sb_2Te_3–Ag_2Te system has been reinvestigated and the phase relations identified by various independent techniques. An intermediate phase with $Ag_{19}Sb_{29}Te_{52}$ composition, through incongruently melting can be obtained as a single crystal from melts enriched in Ag_2Te. It behaves as a solid solution of narrow homogeneity range (from 42 to 44 % Ag_2Te).

1. Introduction

Ternary compounds of the $AgSbTe_2$ type are of considerable interest due to their potential use as thermoelectric devices [1–5]. In spite of numerous related information, the right conditions to synthesize and characterize this material are not yet well defined. Most of the results have been obtained on, at least, a two-phase material, a Widmanstätten precipitate of Sb_2Te_3 being formed epitaxially parallel to the planes of the $AgSbTe_2$ lattice [2–6]. Therefore, the measured electrical properties have to be considered cautiously and depend mostly on the metallurgical solution adopted to get a single-phased and well crystallized compound. Offergeld *et al.* [7], MacHugh *et al.* [8], Armstrong *et al.* [6], Burmeister and Stevenson [3] have studied the pseudo-binary Sb_2Te_3–Ag_2Te phase diagram. An intermediate compound is observed in each case, but its stoichiometry differs as well as its thermal behaviour. So, we set out investigating new ways of preparation from the data obtained through studying the pseudo-binary Sb_2Te_3–Ag_2Te phase diagram, once more.

2. Cross-section of the Sb_2Te_3–Ag_2Te diagram

2.1. Experimental data

Sb_2Te_3 and Ag_2Te congruently melt and the Sb_2Te_3–Ag_2Te should be a binary-like diagram. The system was re-examined over the full concentration range and the phase diagram constructed according to the data of differential thermal analysis and considering the results of X-ray diffraction and microstructural methods of analysis (Fig. 1). Twenty alloys were prepared. Sb_2Te_3 and Ag_2Te were prepared first by heating stoichiometric amounts of the components above the melting points (620 and 955° C, respectively) in quartz ampoules with slow cooling. The starting materials were Ventron products of very high purity (grade 6N). The alloys (except those near the Ag_2Te composition) were made by the single temperature method at 700° C, for 24 h, water quenched and brought into equilibrium by annealing at temperatures slightly below the invariant for 7 (or) 56 days.

For the medium range of the diagram, we have noticed that the results are significantly different for the two periods of annealing.

2.2. Discussion

As Fig. 1 shows, the general nature of the chemical interaction in this system is described by an equilibrium diagram with one incongruently melting compound called β and a solid solution α based on the initial compound Sb_2Te_3. The intermediate compound β is formed by the peritectic reaction, liquid $+ \alpha \rightarrow \beta$, at 574° C. The peritectic point corresponds to the composition $Ag_{19}Sb_{29}Te_{52}$ (41 mol% Ag_2Te). The homogeneity region of the α solid solution at 574° C extends up to 8 mol% Ag_2Te. The eutectic of the system is at Ag_2Te 70 mol%, 544° C.
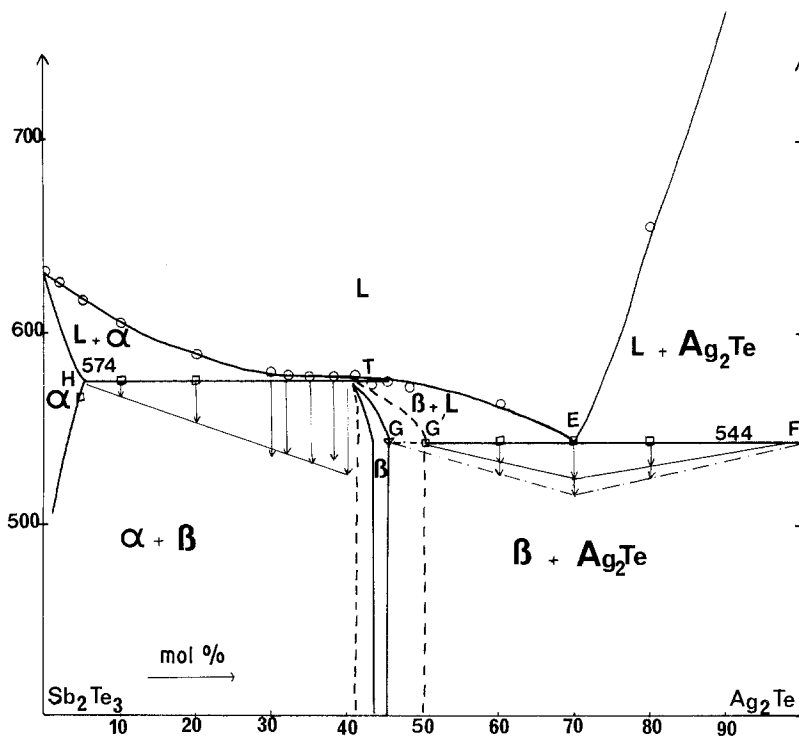
The β phase is a solid solution the boundaries of which depend on the thermal treatment of the sample: from 41 to 50 mol% Ag_2Te for a 7 day anneal but from 42 to 45 mol% Ag_2Te after a longer (56 days) homogenizing anneal. The different boundaries have been refined from Tamman results calculated for both series of measurements.

The stability of the intermediate phase mainly depends on the thermal history of the sample. The phase diagram (Fig. 1) was constructed keeping this in mind; the equilibrium state of the system is reached only after a long time.

3. Results from ingots directionally solidified

On the basis of the previous results and with the aim of extending them, several solidification runs were undertaken with alloys of different compositions. The samples were grown using a directional crystallization method (Vertical Bridgman method). The Vycor capsule is slowly lowered in a thermal gradient so that the liquid–solid interface shifts progressively up to the top. Large crystals are obtained with a single phase component.

Since the β phase melted incongruently; the $Ag_{19}Sb_{29}Te_{52}$ composition could not be obtained from a sample of the same stoichiometry. Nevertheless, since the Sb_2Te_3–Ag_2Te system is quasi-binary, crystallization must be carried out on alloys enriched with Ag_2Te. To prepare a large crystal of $Ag_{19}Sb_{29}Te_{52}$, it is important to start with a sufficient quantity of alloy. Two successive runs were carried out on each alloy to get good quality ingots.

Three different alloys were parpared by this technique.

Alloy A : 41 mol% Ag_2Te, 59 mol% Sb_2Te_3
Alloy B : 50 mol% Ag_2Te, 50 mol% Sb_2Te_3
Alloy C : 70 mol% Ag_2Te, 30 mol% Sb_2Te_3

3.1. Alloy A (41% Ag_2Te)

The conditions of solidification are: (a) regulation temperature: $569 \pm 1°C$; (b) run rate in the gradient: $0.4\,mm\,h^{-1}$; (c) gradient of temperature near the regulation point: $1°\,C\,cm^{-1}$; (d) annealing period of 15 days at $545°C$.

The ingot was cut in slices, the surfaces of which were mechanically polished, optically examined and chemically analysed. Fig. 2 shows a polished polycrystalline surface. We easily distinguish an acicular regularly distributed structure, whose intensity can be enhanced by convenient etching. Polyhedrons bounded by planes with shapes varying from thin sheets to small tetrahedrons stand out against the specimen
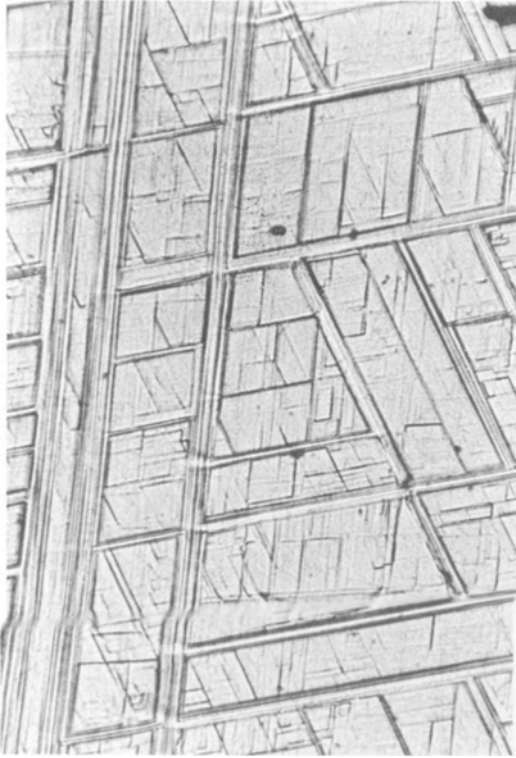
Figure 2 Optical micrographs of alloy A (41% Ag_2Te).

surfaces. The waviness and intersections exhibited by the striations are characteristics of a precipitation. These observations are consistent with similar observations of Amstrong *et al.* [6]. The most probable explanation is the occurrence of a Widmanstätten precipitate of Sb_2Te_3 plates formed epitaxially parallel to the (1 1 1) planes of the f c c lattice of "$AgSbTe_2$". This is conformed by microprobe analysis. Fig. 3 shows the composition profiles of the three elements (silver, antimony and tellurium) registered along a line between two points of the surface. The tellurium composition remains quite constant with the intensities of silver and antimony signals varying, while their extremes are complementary. The composition values of the background (A_1 and A_2) and of the extremes are given in Table I. The matrix material corresponds to an overall composition of $Ag_{19}Sb_{29}Te_{52}$; within the striation lamellae the observed values confirm the presence of Sb_2Te_3 (taking into account the averaging effect of the conditions of measurement). The composition of $Ag_{19}Sb_{29}Te_{52}$ is consistent with the conclusions of Armstrong *et al.* [6].

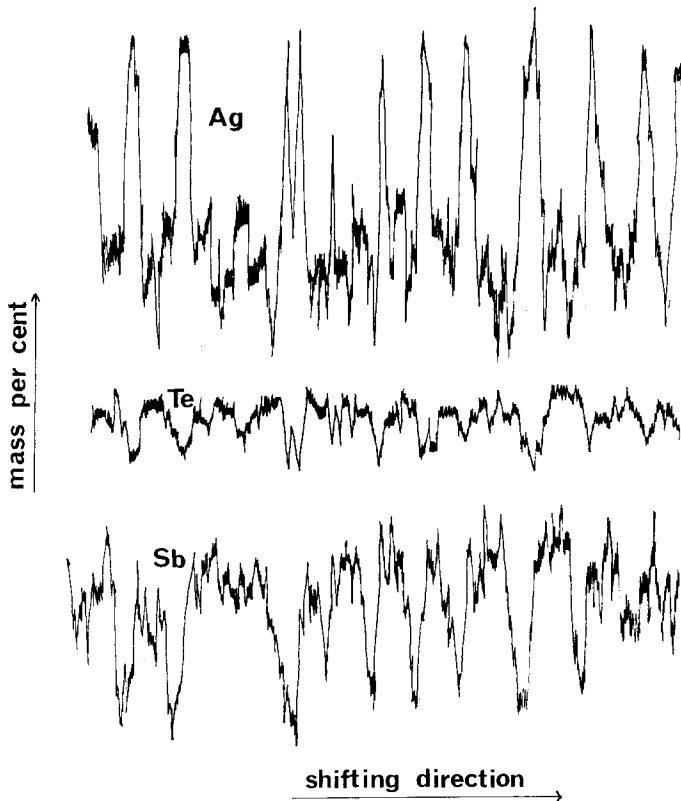From the phase diagram results it is quite obvious that the formation of a two phase

Figure 3 Alloy A; composition profile by microprobe analysis.

Atomic percent	Single crystal part		Precipitate	Theoretical percentage for Ag$_{19}$Sb$_{29}$Te$_{52}$	Theoretical percentage for Sb$_2$Te$_3$
	A_1	A_2			
Silver	18.8 ± 0.2	19.0 ± 0.02	6.1 ± 0.2	19	0
Antimony	28.8 ± 0.6	28.2 ± 0.2	33.9 ± 0.6	29	40
Tellurium	52.4 ± 0.7	52.8 ± 0.2	60.0 ± 0.7	52	60

component is due to the long residence time of the first crystallized alloy Ag$_{19}$Sb$_{29}$Te$_{52}$ between temperatures of 540 and 574° C. The consequent precipitate formation of Sb$_2$Te$_3$ is predicted by the aspect of the solubility limit. To prevent that extra formation we found it better to be starting with a composition enriched in Ag$_2$Te, so that the solidified alloy was a single phase over the whole range of temperature, say that of alloy B.

3.2. Alloy B (50% Ag$_2$Te)
The experimental procedure was as described above. From the microprobe analysis results, the lower part of the ingot is a single crystal whereas the remainder of the bar has the morphology and the composition of an eutectic alloy (Figs. 4
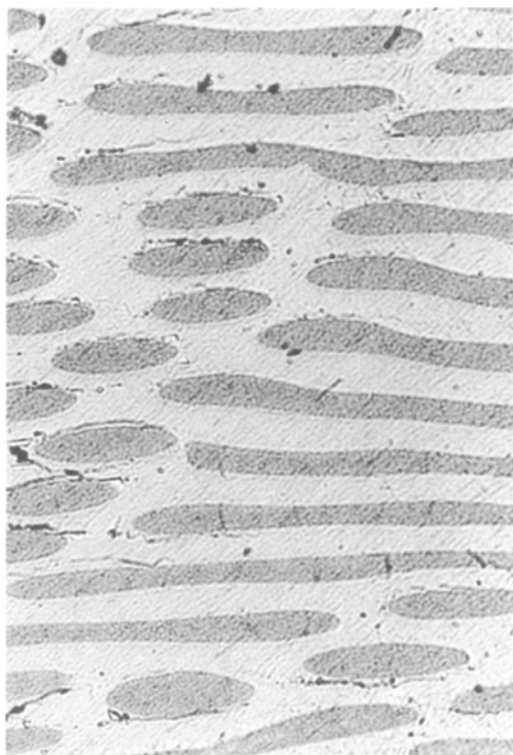
and 5) which corresponds to β + Ag$_2$Te. Microprobe analysis results are as follows:

(a) the composition profiles registered on the crystal show a regular atomic distribution of the elements (Fig. 6) corresponding to the optical photomicrograph without any array formation.

(b) the composition values do not vary very much from point to point and stay around the average, Ag$_{19}$Sb$_{29}$Te$_{52}$ (Table II).

3.3. Alloy C (70% Ag$_2$Te)
The solidification of an alloy of this composition (near the eutectic point) was aimed at determining the point G coordinates in the phase diagram. The composition values obtained by microprobe analysis are summarized in Table III. The eutectic

Figure 4 Optical micrograph of the eutectic part of the ingot (alloy B).

Figure 5 Optical micrograph of the single phase d zone of the ingot (Alloy B).

TABLE II Microprobe analysis in alloy B (% Ag_2Te = 50)

| Atomic percent | Single crystal part | | Eutectic white lamellae | Analysis grey lamellae | Theoretical percentage of $Ag_{19}Sb_{29}Te_{52}$ | Theoretical percentage of Ag_2Te |
	A_1	A_2				
Silver	19 ± 1	18.4 ± 0.7	20.2 ± 0.2	65.3 ± 0.6	19	66
Antimony	29 ± 0.2	28.8 ± 0.3	28.3 ± 0.7	0.3 ± 0.1	29	
Tellurium	52.5 ± 0.8	52.9 ± 0.9	51.5 ± 0.5	34.4 ± 0.8	52	33

TABLE III Microprobe analysis in alloy C (% Ag_2Te = 70)

Atomic percent	Grey lamellae	White lamellae
Silver	53.7	21.4 ± 0.2
Antimony	0.0	27.3 ± 0.7
Tellurium	40.4	51.3 ± 0.5

alloy is composed of Ag_2Te and β phase with the formula $Ag_{21}Sb_{27}Te_{51}$ which corresponds to a 44% Ag_2Te composition. The result confirms the boundaries of the homogeneity region of the solid solution β between 42% and 44% after a long anneal.

4. Conclusions

The Sb_2Te_3–Ag_2Te system has been reinvestigated and the phase relations identified by various independent techniques. The results are not consistant concerning certain details, with similar studies previously performed. The differences relate not only to the position and homogeneity range of the solid solution, but also to the occur-

rance of an eutectoid transformation at 360° C [7] not being detected in our results and probably due to a ternary eutectic residue, even though a complete analysis of the phase equilibria is complicated by the slow kinetics involved.

Like Armstrong et al. [6] we soon determined that the intermediate compound could not be congruently melting and that a new phase appeared upon prolonged annealing with an initial composition of $(Sb_2Te_3)_{0.59}$–$(Ag_2Te)_{0.41}$ [3]. A single phased and well crystallized compound of $Ag_{19}Sb_{29}Te_{52}$ composition can reliably be prepared, starting from Ag_2Te enriched melt, and using a directional crystallisation method. The atomic composition results reveal a narrow homogeneity region for the homogenous compound (from 42% to 44% Ag_2Te).

References

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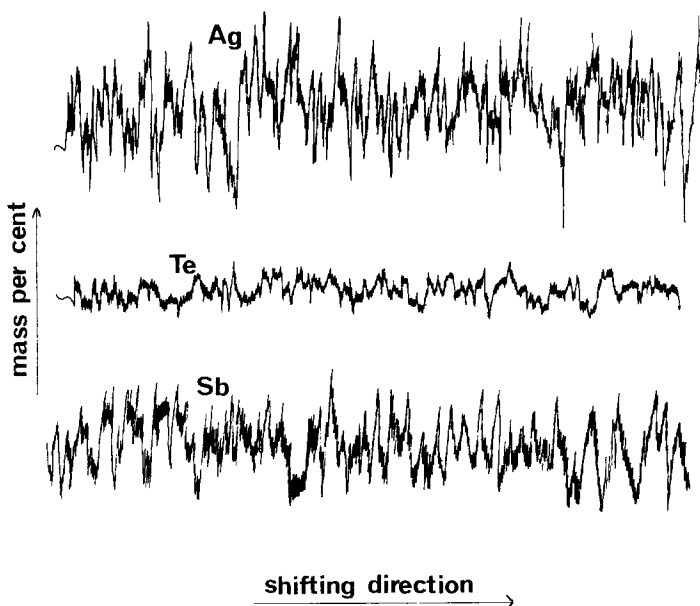
Figure 6 Alloy B; composition profile by microprobe analysis.

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