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The ternary subsystem Sn_4As_3-Bi-SnAs

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The portion of the Sn-Bi-As ternary system bounded by the Sn_4As_3-SnAs, Sn_4As_3-Bi, and SnAs-Bi joins has been investigated by thermal analysis, metallographic and X-ray procedures. No ternary phases are formed. A binary liquidus trough runs uninterruptedly from the SnAs-Bi join to the Sn_4As_3-Bi join. All alloys completed their freezing process at 255° C. An SnAs-rich crystal is the primary phase of precipitation over practically all of the compositional area studied.

1. Introduction

This work was carried out as part of a group of investigations concerning the alloying behaviour of arsenic in binary and ternary systems which have not been reported before or which have been only roughly surveyed [1-14]. Because arsenic has very poor physical properties and high vapour pressure at relatively low temperatures (the vapour pressure of the solid reaches one atmosphere at 613° C) arsenic-rich alloys have not found industrial application. However, at intermediate and low-arsenic contents intermediate phases often form which stabilize the arsenic.

The Sn-As system has been investigated by Parravano and de Cesaris [15] in 1911, Mansuri [16] in 1923, and by Peretti and Paulsen [7] in 1969. The latter confirmed the existence of SnAs, but found the tin-rich intermediate phase to occur peritectically at the composition Sn_4As_3 instead of Sn_3As_2. The melting points were determined to be 594.8 ± 0.5° C and 587.8 ± 0.5° C for SnAs and Sn_4As_3, respectively, and the liquidus falls uninterruptedly from the melting point of SnAs to that of Sn_4As_3. SnAs has the sodium chloride crystal structure, with a lattice parameter of 5.7248Å as measured by Swanson *et al* [17]; Hägg and Hybinette [18] found the following parameters for rhombohedral Sn_4As_3: $a = 12.33$Å and $\alpha = 19.22°$.

The nature of the Sn_4As_3-Bi join was explored by Coyle, Vacha, and Peretti [14]; the pair does not form a true quasibinary diagram, but has a liquidus eutectic minimum at 266° C with 98.8 wt % Bi and 1.2 wt % Sn_4As_3. Freezing of all compositions on the join is completed at 136° C, a ternary eutectic lying in the Sn_4As_3-Bi-Sn compositional triangle.

No reports were found in the literature concerning the nature of the SnAs-Bi join, and this subject forms part of this paper. Bismuth has a melting point of 271.3° C and crystallizes in the hexagonal system; its lattice constants according to Swanson *et al* [19] are: $a = 4.546$ and $c = 11.860$Å at 25° C.

2. Experimental

2.1. Materials

The arsenic used in this study was supplied in lump form by the United Mineral and Chemical Corporation; it had a purity of 99.99 + %, and before alloying it was resublimed and stored under vacuum. Mallinckrodt's (St Louis, Missouri) analytical reagent grade tin was used; it had a batch analysis of 0.005% Fe, 0.005% Pb, 0.001 % Cu, 0.005 % Zn, and 0.001 % As. The bismuth was obtained in the form of shot from the American Smelting and Refining Company of South Plainfield, New Jersey and had the following spectrographic analysis in ppm: 5 Ag, 2 Cu, 1 Fe, 10 Pb, < 1 Si, and < 1 Mg.

2.2. Procedure

The intermediate phases, SnAs and Sn_4As_3, were first prepared from the elements in evacuated, sealed, borosilicate glass tubes which were first heated to 250° C to start the dissolution of arsenic and then brought to 610° C. Fifteen minutes at this temperature, with periodic vigorous shaking of the tubes ensured complete dissolution of the contents. Ternary alloys were prepared in a

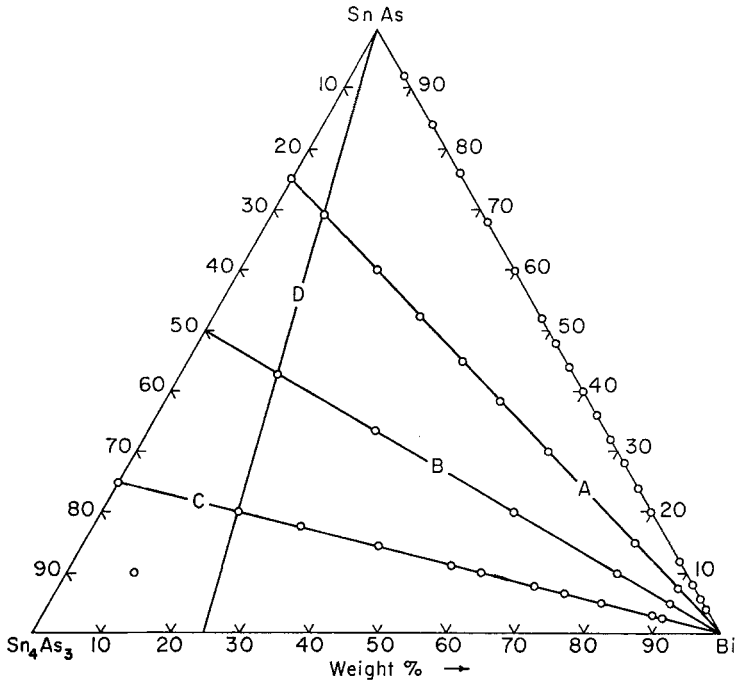

Figure 1 Location of alloys studied.

similar fashion by combining the SnAs, Sn_4As_3 and Bi in the desired proportions.

For thermal analysis 40 to 80g of alloy were contained in mullite crucibles under a protective atmosphere of argon. A chromel-alumel thermocouple, calibrated at the freezing points of tin (231.9°C), lead (327.4°C), zinc (419.5°C), and antimony (630.5°C); was protected by a thin-walled mullite tube and centred in the alloy to measure the temperature. The emf generated by the thermocouple was measured on a Honeywell extended range recorder. Critical points were checked with a Leeds and Northrup type K-4 potentiometer. The temperature was changed at a fairly constant rate of from one to three degrees per minute by a motorized, variable transformer in series with an electric resistance furnace. Vigorous mechanical stirring was carried out while each alloy was in the liquid or mushy stage.

Selected alloys were X-rayed with characteristic copper *K*-alpha radiation in a 57.3 mm Debye-Scherrer camera and in an X-ray diffractometer to help identify phases.

For microscopic examination samples were hand ground and polished in the rougher stages and final-polished on a vibratory polisher with 0.1 and 0.05 alumina suspensions. The most satisfactory etchant tried consisted of equal parts of aqueous $FeCl_3$ and $Fe(NO_3)_3$, followed by a rinse in Vilella's reagent.

3. Results

A series of compositions was systematically studied according to the plan shown in Fig. 1. Individual thermal points are listed in Table I, and Figs. 2 to 6 portray the established isopleths. From these graphs there has been drawn in Fig. 7 a polythermic projection of the liquidus surface at arbitrarily chosen temperatures.

As can be seen from Fig. 2 the SnAs-Bi isopleth does not form a true quasibinary section, but has a binary eutectic liquidus minimum at 98.5 wt % Bi and 268°C. The SnAs-rich constituent is the primary phase of precipitation over most of the compositional area of the system, and the microstructures are all very similar, differing only in the quantity of each constituent. Fig. 8 is a photomicrograph of a typical alloy in the area.

A binary eutectic valley crosses the diagram from the SnAs-Bi eutectic at 98.5% Bi to the Sn_4As_3 eutectic at 98.8% Bi. No ternary compound is formed in the system.

At this point in our investigations we have

TABLE I Thermal data for the Sn_4As_3-Bi-SnAs subsystem

Composition of alloy (wt%)			Temperatures (± 0.5 °C)		
Bi	SnAs	Sn_4As_3	1st arrest	2nd arrest	3rd arrest
8.00	92.00	0.00	583.6	253.5	259.3
8.00	69.00	23.00	583.1	547.1	251.5
14.50	42.75	42.75	573.6	545.1	252.7
16.00	84.00	0.00	572.1	253.1	—
20.00	60.00	20.00	567.1	488.1	256.2
20.00	20.00	60.00	564.1	543.1	251.5
24.00	76.00	0.00	561.4	254.5	—
30.00	52.50	17.50	550.6	259.6	254.0
30.00	17.50	52.50	551.1	516.1	252.7
32.00	68.00	0.00	549.8	251.9	—
33.33	33.33	33.33	547.0	520.0	259.4
40.00	45.00	15.00	538.8	453.8	255.2
40.00	60.00	0.00	538.2	254.2	—
43.00	14.25	42.75	530.3	516.0	254.3
48.00	52.00	0.00	526.2	261.7	253.5
48.47	39.41	12.12	524.1	—	255.8
52.00	48.00	0.00	520.1	261.5	255.8
55.00	11.25	33.75	513.4	469.5	255.0
56.00	44.00	0.00	512.4	262.7	254.3
60.00	30.00	10.00	505.4	470.0	254.8
60.00	20.00	20.00	505.5	411.9	257.0
60.00	40.00	0.00	505.9	263.3	254.8
64.00	36.00	0.00	497.4	264.8	254.3
68.00	32.00	0.00	488.4	267.4	256.0
69.00	7.75	23.25	484.9	468.0	257.0
72.00	28.00	0.00	479.5	265.3	256.0
74.00	6.50	19.50	472.1	456.0	259.3
76.00	24.00	0.00	467.3	267.4	255.5
80.00	15.00	5.00	454.0	405.0	256.0
80.00	10.00	10.00	453.8	362.5	256.3
80.00	20.00	0.00	453.5	267.8	254.3
80.00	5.00	15.00	453.3	430.0	257.0
88.00	12.00	0.00	430.1	266.7	—
88.91	2.77	8.32	410.1	392.0	264.5
90.00	7.50	2.50	403.1	348.0	257.3
90.00	5.00	5.00	403.1	266.1	255.5
90.00	2.50	7.50	402.6	264.8	255.8
92.00	8.00	0.00	386.3	268.5	256.8
96.00	4.00	0.00	328.5	268.3	—
97.00	3.00	0.00	311.2	267.9	—
98.00	2.00	0.00	283.2	268.3	256.3
99.00	1.00	0.00	269.7	267.4	—

delineated the salient features of three ternary systems [1-14]: In-Sb-As, Sn-Te-As, and Sn-Bi-As. The melting points vary from 942°C for InAs to 136°C for a ternary eutectic in the Sn-Bi-As system. No ternary intermediate phases exist in either of the three systems. InAs and SnTe manifest their relatively good stability by persisting in all compositions in the respective ternary compositions under discussion. Combinations of SnTe with As_2Te_3, SnAs or Sn_4As_3 contain no free arsenic and exhibit low vapour pressures. On the other hand, all compositions on the SnTe-As join contain free arsenic and thus have a high arsenic vapour pressure. Similarly, in the In-Sb-As system no free arsenic exists in compositions encompassed by the sub-

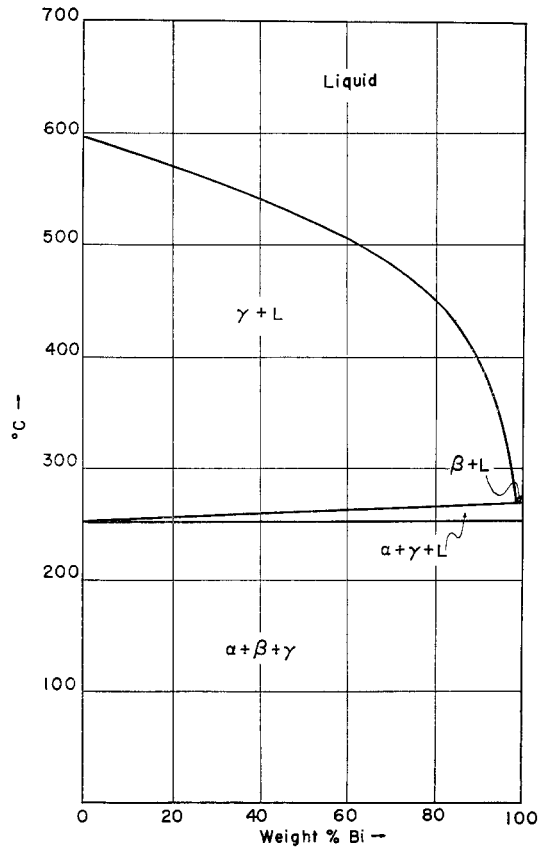

Figure 2 The SnAs-Bi join.

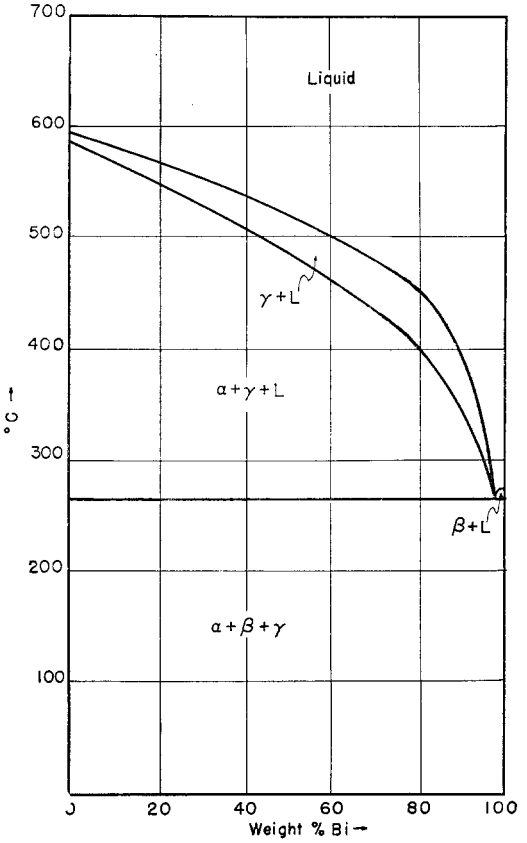

Figure 4 Isopleth B, SnAs:Sn_4As_3 = 1:1.

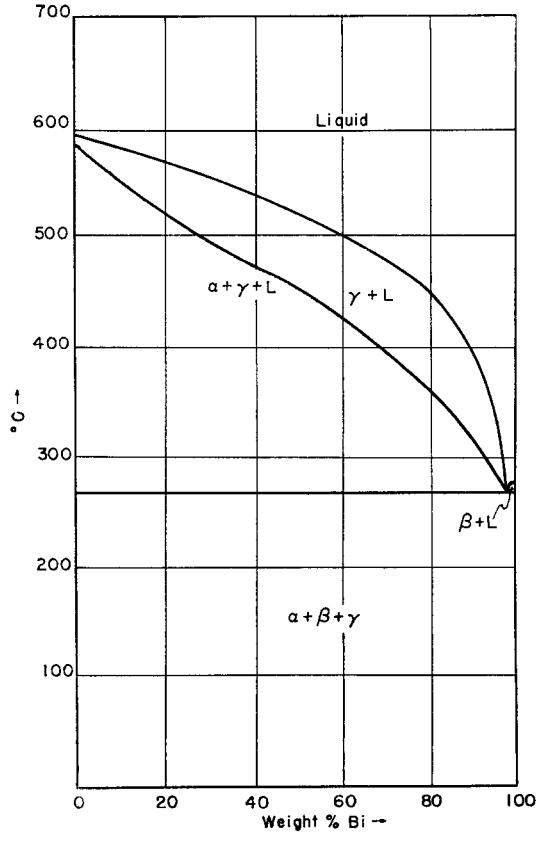

Figure 3 Isopleth A, SnAs:Sn_4As_3 = 3:1.

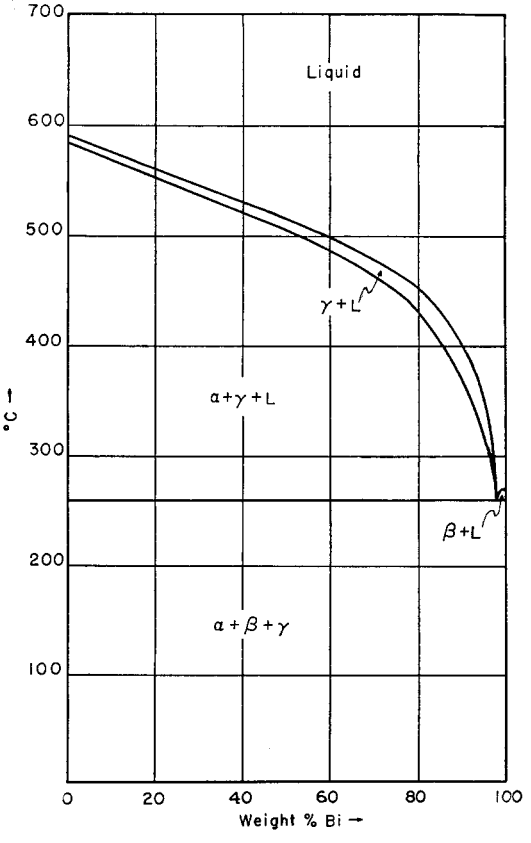

Figure 5 Isopleth C, SnAs:Sn_4As_3 = 1:3.

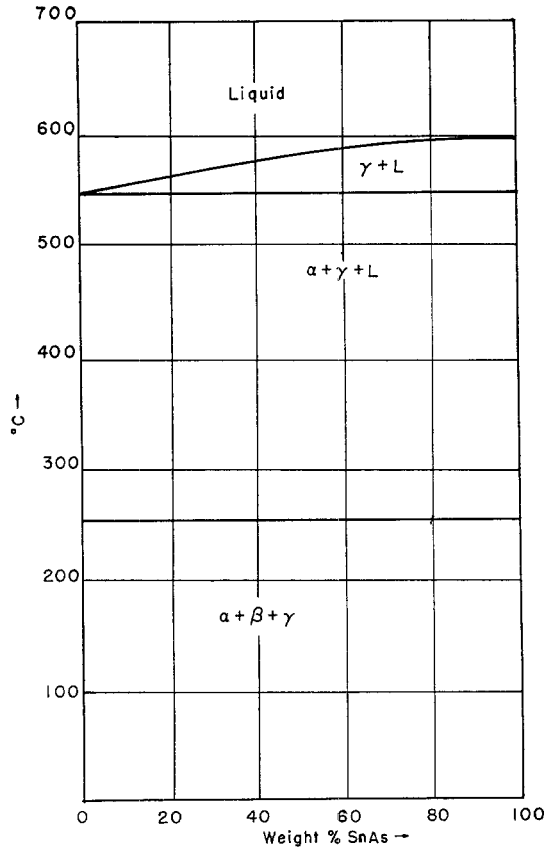

Figure 6 Isopleth D, Sn_4As_3:Bi = 3:1.

Figure 8 Microstructure of a furnace-cooled alloy with 14.5 wt% Bi, 42.75% SnAs, and 42.75% Sn_4As_3. Primary SnAs (white) secondary Sn_4As_3 (grey), and eutectic (black). Etchant – 1 aq. $FeCl_3$ plus 1 aq. $Fe(NO_3)_3$, followed by Vilella's reagent (× 30).

ternary area InAs-Sb-In; all contain InAs, and the arsenic vapour pressure is low. In the Sn-Bi-As system the compounds Sn_4As_3 and SnAs exist over limited compositional ranges; all alloys with more arsenic than that given by the SnAs-Bi join contain free arsenic and have a large arsenic vapour pressure.

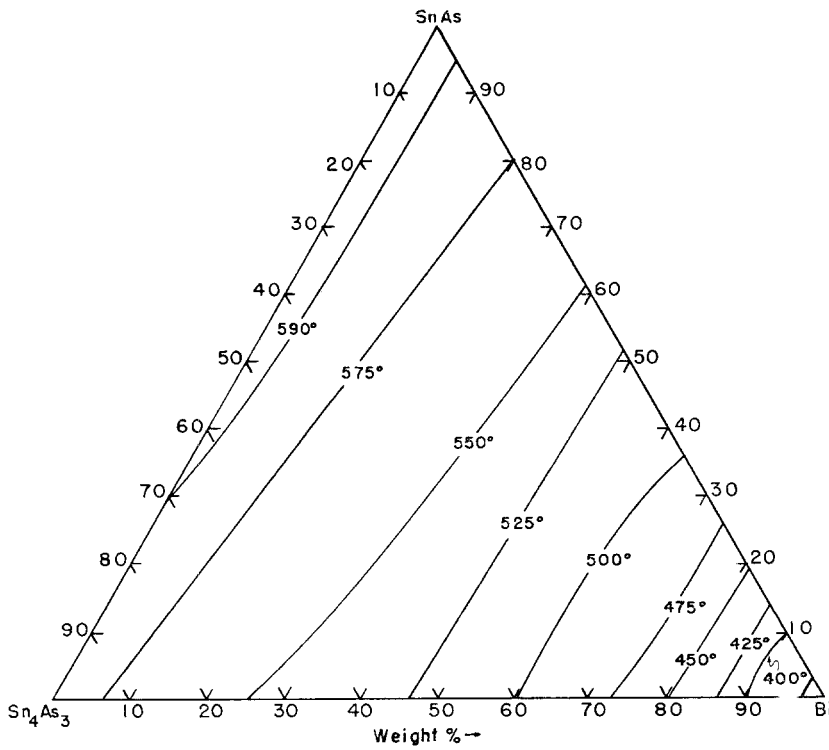

Figure 7 Polythermic projection of the liquidus surface of the Sn_4As_3-Bi-SnAs area.

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