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The Ternary Subsystem Sn-Sn_4As_3-SnTe

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Thermal analysis, metallographic, and X-ray procedures were used to investigate the Sn-Sn_4As_3-SnTe subsystem of the ternary system tin-arsenic-tellurium. The subsystem is of the simple eutectic type with no ternary compound formation. A binary eutectic valley runs across the diagram from the Sn_4As_3-SnTe binary eutectic at 576.5°C to a ternary eutectic which is indistinguishable from the Sn_4As_3-Sn binary eutectic at 231.3°C with 0.5 wt % Sn_4As_3 and 99.5% Sn. More than 90% of the compositional area is dominated by the primary freezing of an SnTe-rich phase, and an Sn_4As_3-rich phase is the first to crystallise from the melt over most of the remaining area. Terminal solid solutions are very restricted.

1. Introduction

The Sn-SnTe system has been the subject of several reports which have been summarised by Hansen [1] and Shunk [2]. The crystal structure of SnTe is the sodium chloride type, and the melting point is 806°C. Sn and SnTe form a simple eutectiferous phase diagram with a eutectic at 0.23 wt % SnTe, which freezes at 232.0 ± 0.1°C.

The tin-rich end of the Sn-As diagram was studied in 1911 by Parravano and deCesaris and by Mansuri [1]. More recently Peretti and Paulsen [3] reinvestigated compositions between Sn and SnAs. They established the existence of the intermediate phase, Sn_4As_3, which melts at 587.7 ± 0.5°C; it was found by Hägg and Hybinette [4] to be rhombohedral with $a = 12.33$ Å and $\alpha = 19.22°$. Like SnTe, Sn_4As_3 forms a eutectic with Sn at a composition of 0.5 wt % Sn_4As_3 and 99.5% Sn; the eutectic melting point is 231.3°C.

The stable form of tin above room temperature has a melting point of 231.9°C and crystallises in the body-centred tetragonal system.

The nature of the SnTe-Sn_4As_3 isopleth of the Sn-Te-As system was reported by Arkoosh and Peretti [5]. This diagram also exhibits a eutectic which melts at 576.5°C and contains 12.5 wt % SnTe, 87.5 wt % Sn_4As_3. The mutual solid solubilities are less than 1 wt % at 550°C.

The results of a study of the subsystem SnAs-Sn_4As_3-SnTe have been reported by Kao and Peretti [6]. This report presents the findings of an investigation of the subternary Sn-Sn_4As_3-SnTe by thermal analysis, X-ray methods, and metallographic examination.

2. Experimental

2.1. Materials

The tellurium was obtained from the American Smelting and Refining Company of South Plainfield, New Jersey and had the following spectrographic analysis: 0.0001% Mg, 0.0001% Si, 0.0002% Fe, 0.0001% Cu, 0.0002% Ag, and 99.99+% Te (by difference). The United Mineral and Chemical Corporation of New York supplied the arsenic in lump form; it had a purity of 99.99+%, and we resublimed it and stored it under vacuum until ready for use. Mallinckrodt's (St. Louis, Missouri) analytical reagent grade tin was used; it had a lot analysis of 0.001% As, 0.005% Zn, 0.001% Cu, 0.005% Pb, and 0.005% Fe.

2.2. Procedure

All ternary alloys were prepared by melting together the desired quantities of the two binary compounds and tin. Sn_4As_3 was compounded from the pure elements in evacuated, sealed, borosilicate glass tubes at 600°C, but because of its melting point (806°C) the SnTe was prepared by melting the tin and tellurium in evacuated, sealed, quartz tubes at 880°C. Vigorous shaking of the contents of the tubes ensured excellent melts. Ternary compositions were also made in quartz tubes at a temperature which was at least

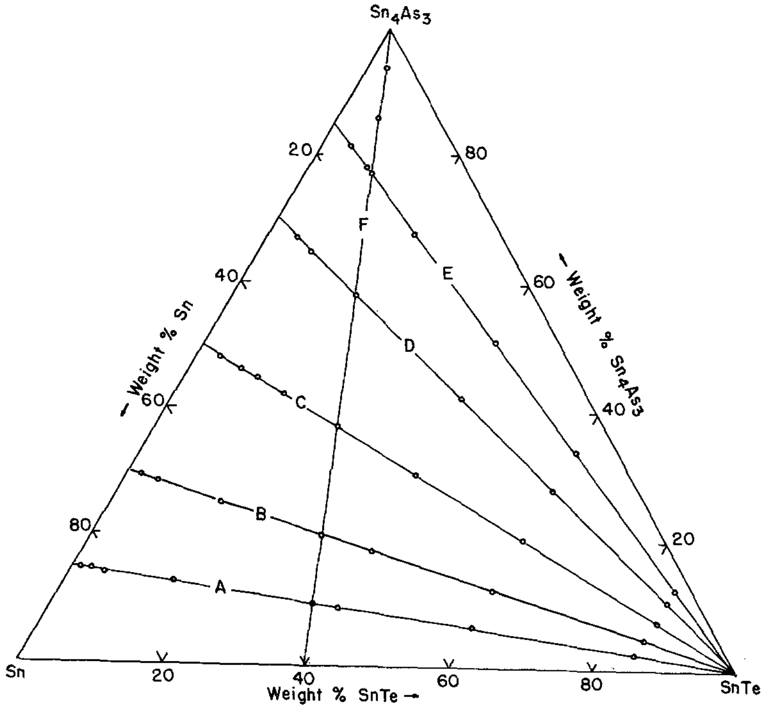

Figure 1 Location of alloys studied.

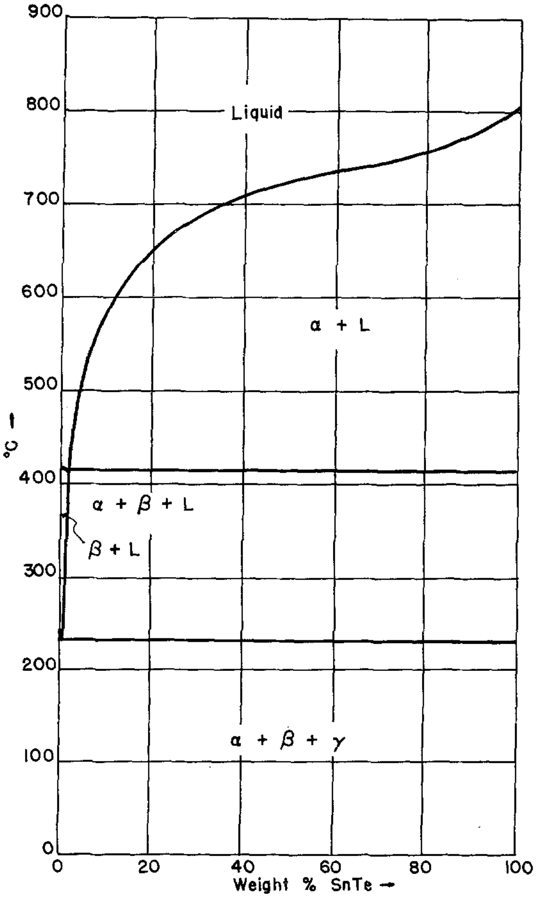

Figure 2 Isopleth A. Sn:Sn$_4$As$_3$ = 85:15.

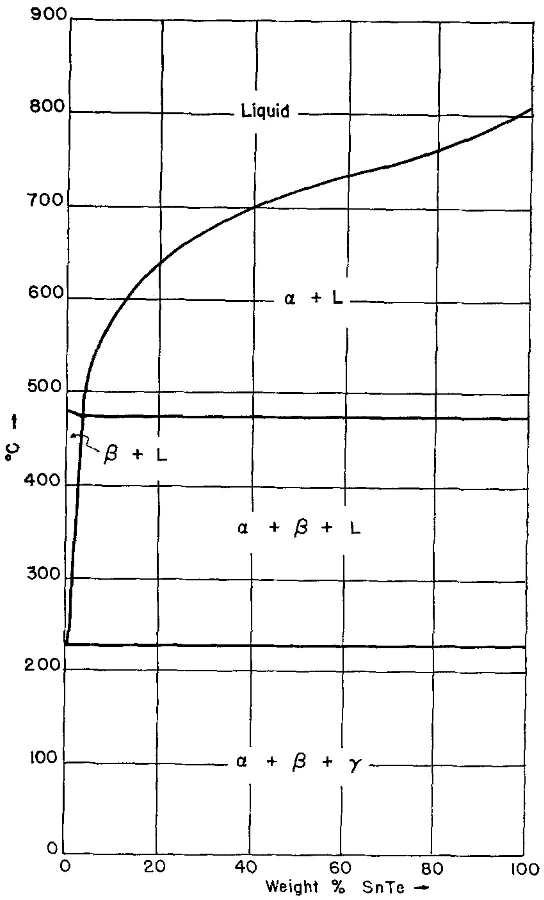

Figure 3 Isopleth B. Sn:Sn$_4$As$_3$ = 70:30.

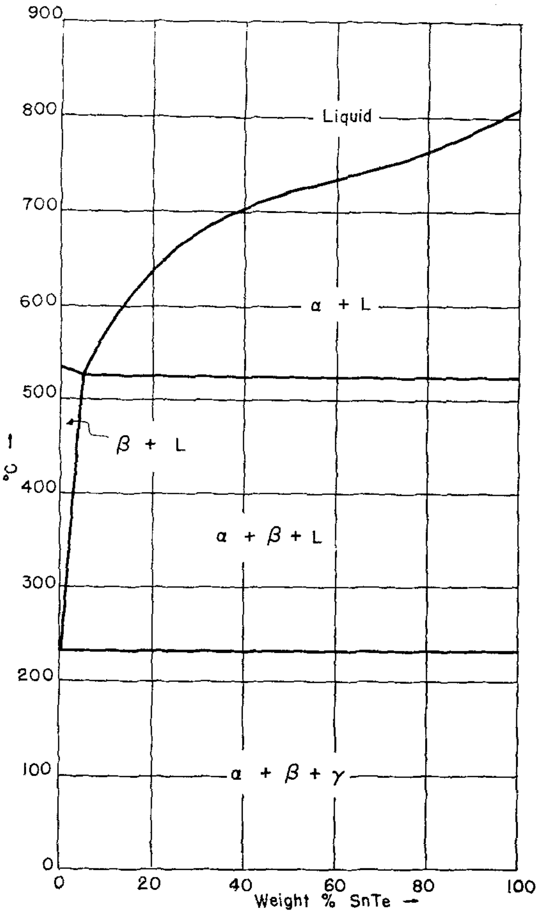

Figure 4 Isopleth C. Sn:Sn_4As_3 = 50:50.

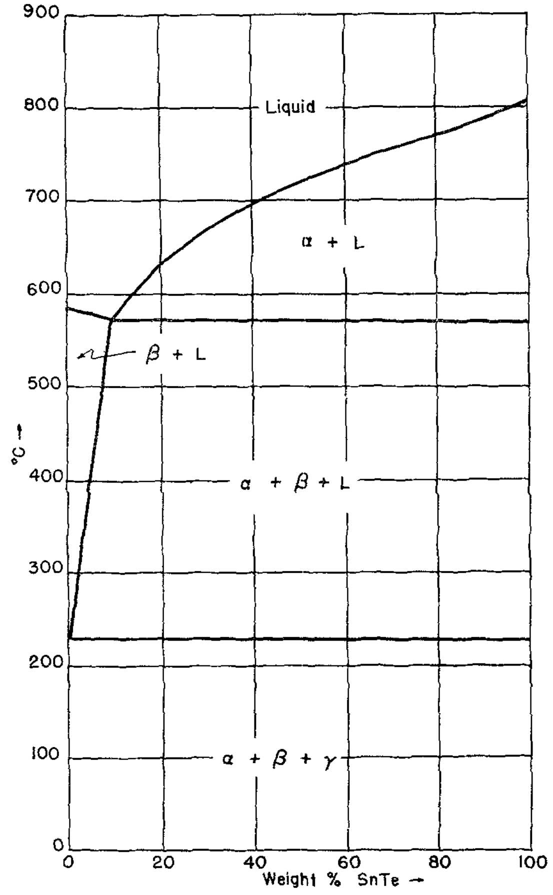

Figure 5 Isopleth D. Sn:Sn_4As_3 = 30:70.

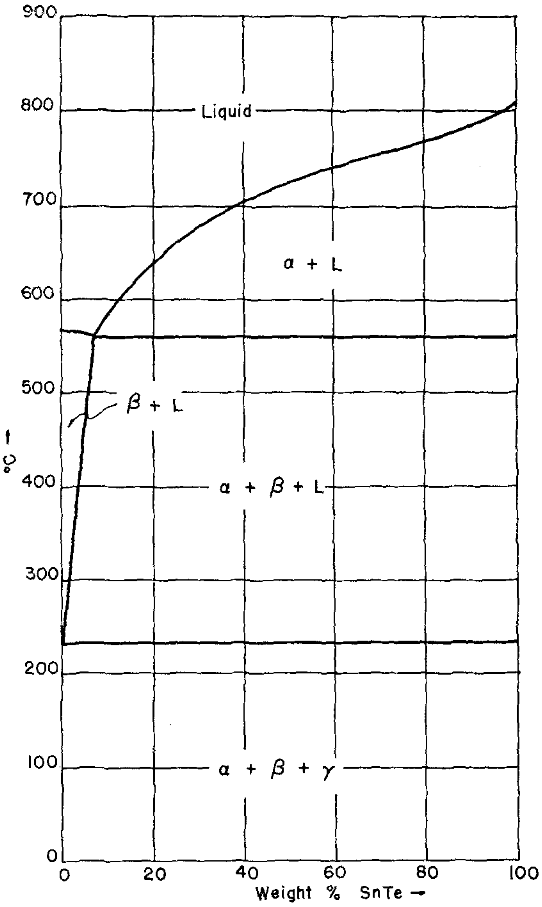

Figure 6 Isopleth E. Sn:Sn_4As_3 = 15:85.

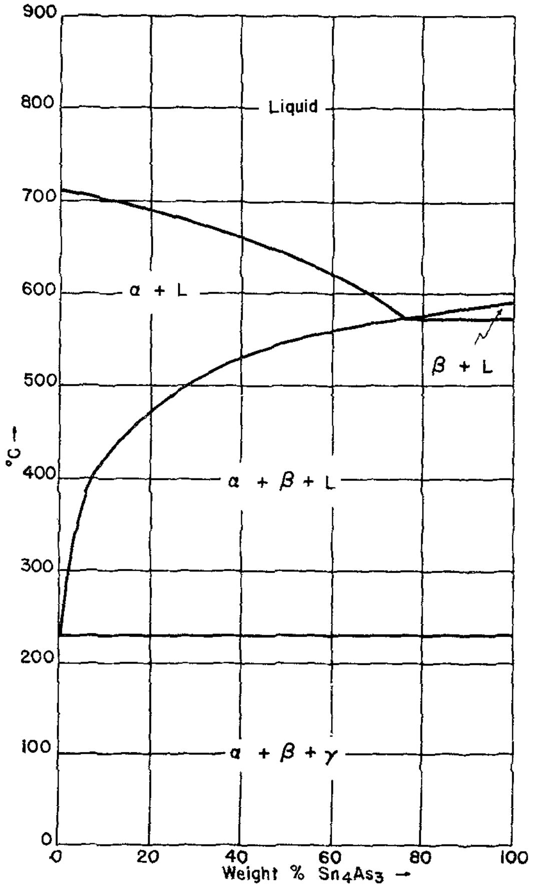

Figure 7 Isopleth F. Sn:SnTe = 60:40.

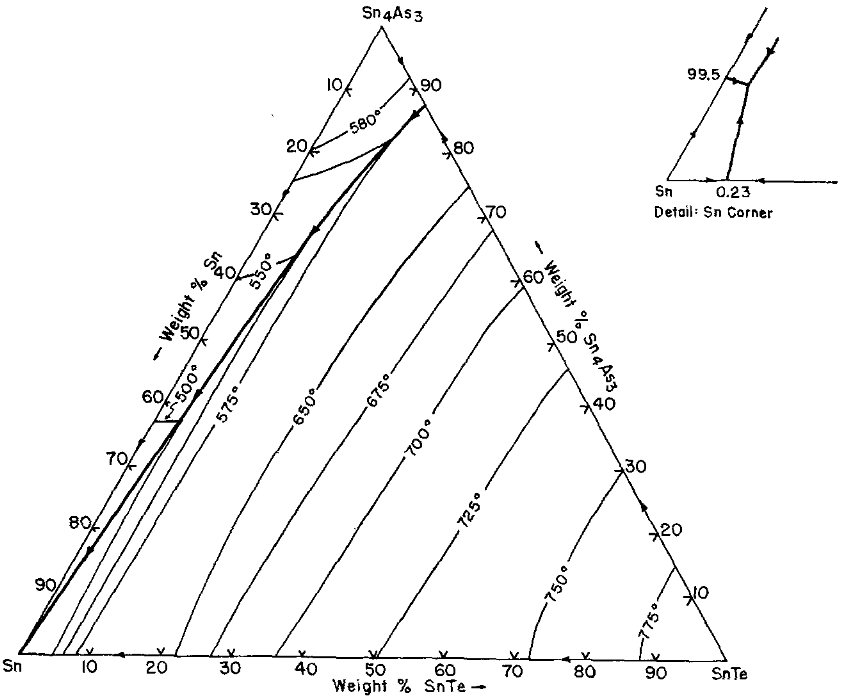

Figure 8 Liquidus polytherm of the system Sn-Sn_4As_3-SnTe.

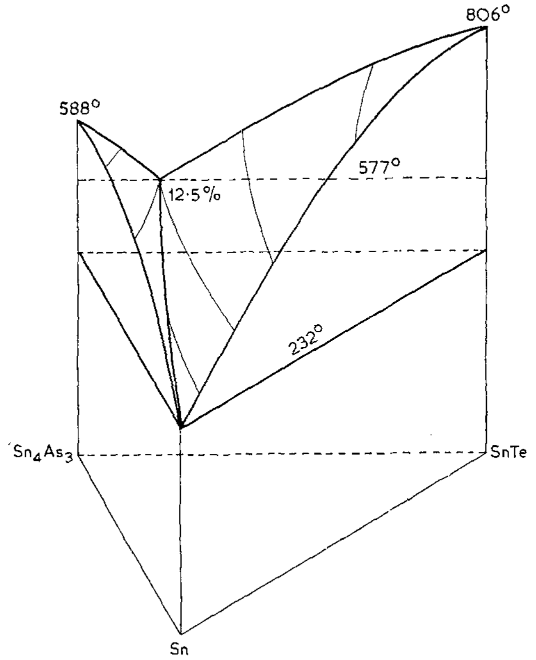

Figure 9 Space model of the Sn-Sn_4As_3-SnTe subsystem (not to scale).

50°C above the estimated melting point and held for 20 to 30 min at that temperature, with vigorous shaking. Melts used for thermal analysis weighed from 40 to 80 grams.

Mullite (aluminium silicate) crucibles served as alloy containers, with a protective atmosphere of argon, for thermal analysis. A calibrated kanthal thermocouple, protected by a thin-walled mullite tube, was centred in each alloy to measure the temperature. The emf generated by the thermocouple was graphed on a Honeywell extended range recorder in conjunction with a precision potentiometer. Critical points were checked with a Leeds and Northrup type K-4 potentiometer. Vigorous mechanical stirring was carried out above the freezing point of each composition while the temperature was changed at a fairly constant rate of from one to three degrees per minute by a motorised, variable transformer in series with the furnace.

Samples were prepared for microscopic examination by hand-polishing in the rougher stages and finishing on a Buehler vibratory polisher. Satisfactory etching was accomplished with the following reagents: alcoholic ferric chloride; aqueous ferric chloride or nitrate; mixtures of dichromate, 5% chromic acid, and hydrochloric or nitric acid and water.

X-ray patterns of selected alloys were made with characteristic copper K-alpha radiation in

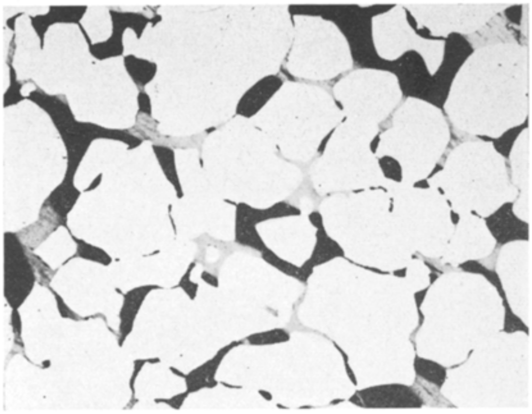

Figure 10 Microstructure of a slowly cooled alloy with 85 wt% SnTe, 7.5% Sn_4As_3, 7.5% Sn. Primary crystals of SnTe-rich alpha (white), beta (grey), and eutectic (black). Etchant: Dichromate-chromic acid (× 60).

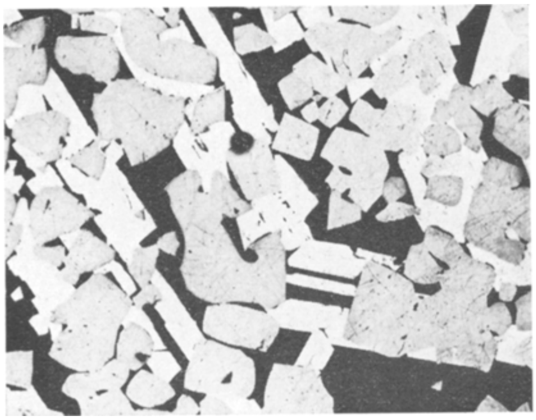

Figure 11 Microstructure of a slowly cooled specimen containing 40 wt% SnTe, 30% Sn_4As_3, 30% Sn. Primary crystals of alpha (grey), beta (white), and eutectic (black). Etchant: alcoholic ferric chloride (× 60).

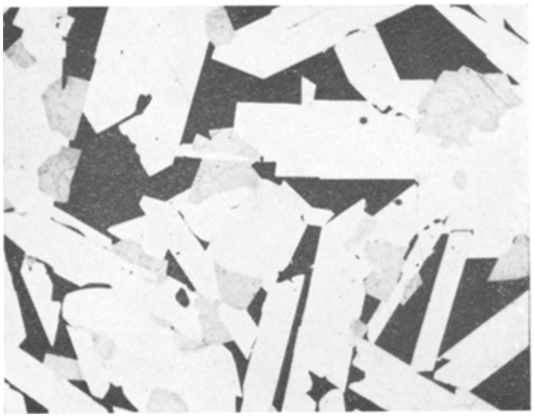

Figure 12 Microstructure of a slowly cooled alloy with 15 wt% SnTe, 59.5% Sn_4As_3, 26.5% Sn. Primary crystals of alpha (grey), beta (white), and eutectic (black). Etchant: alcoholic ferric chloride (× 60).

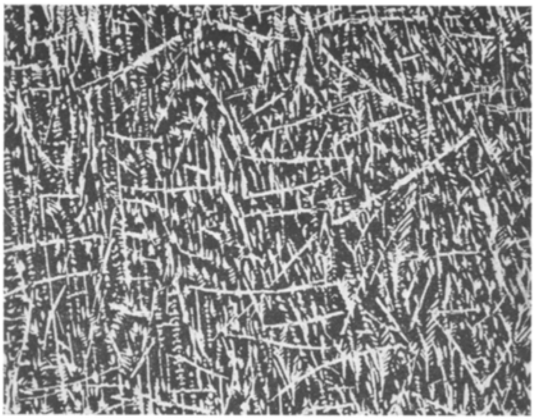

Figure 13 Microstructure of a water-quenched alloy with 40 wt% SnTe, 9% Sn_4As_3, 51% Sn. Primary dendrites of alpha, beta, and eutectic. Etchant: dichromate-chromate (× 60).

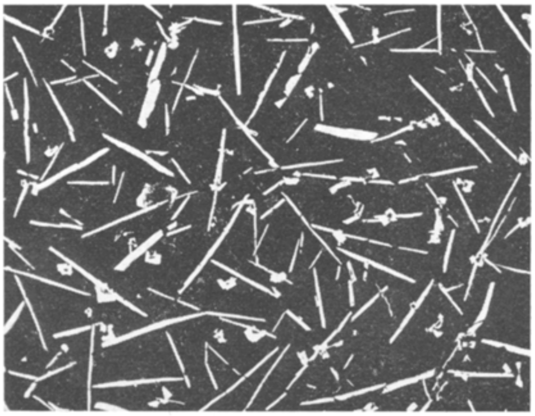

Figure 14 Microstructure of a water-quenched alloy containing 5 wt% SnTe, 14.25% Sn_4As_3, 80.75% Sn. Needle-like beta, irregular alpha, and eutectic (black). Etchant: Chromate-dichromate (× 60).

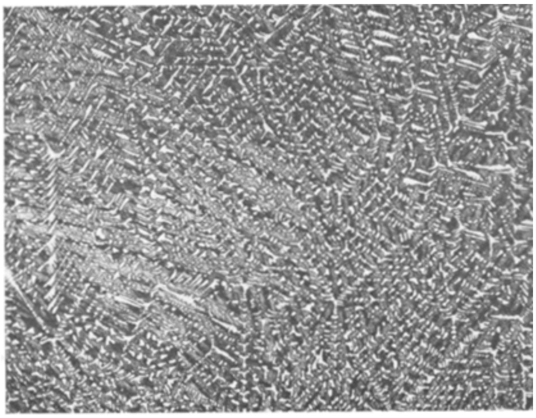

Figure 15 Microstructure of a water-quenched alloy with 40 wt% SnTe, 51% Sn_4As_3, 9% Sn. Primary dendrites of alpha, beta, and eutectic. Etchant: dichromate-chromate (× 60).

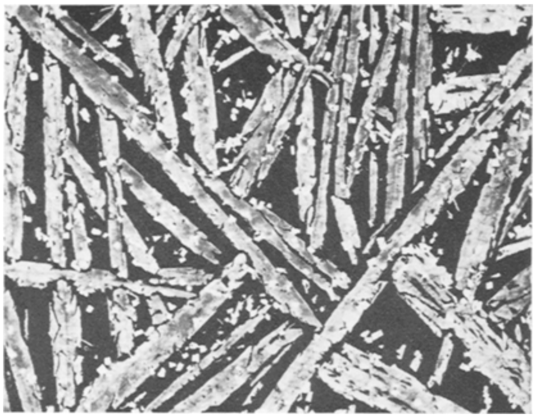

Figure 16 Microstructure of a water-quenched alloy containing 10 wt % SnTe, 45% Sn_4As_3, 45% Sn. Primary alpha (white), greyish beta and black eutectic. Etchant: chromate-dichromate (× 60).

a 57.3 mm Debye-Scherrer camera and an X-ray spectrometer to check some of the conclusions arrived at on the basis of thermal and microscopic studies.

3. Results

The system was studied according to the isopleths shown in fig. 1. Individual thermal points obtained are listed in table I, and figs. 2 to 7 portray the established isopleths. From these graphs have been delineated the liquidus and solidus surfaces of the system (figs. 8 and 9).

Figs. 10 to 16 illustrate typical microstructures of slowly cooled and water-quenched alloys, with varying proportions of the three ingredients.

The SnTe-rich constituent (alpha) is the primary phase of crystallisation over more than 90% of the compositional area of the system. A binary eutectic valley crosses the diagram from the SnTe-Sn_4As_3 eutectic (12.5 wt % SnTe, 87.5% Sn_4As_3) at 576.5°C to a ternary eutectic composition at 231.3°C which is indistinguishable from the Sn_4As_3-Sn binary eutectic with 0.5 wt % Sn_4As_3, 99.5% Sn. On the Sn_4As_3-Sn side of the binary valley the phase of primary precipitation is the Sn_4As_3-rich beta. No ternary compound is formed in the system, and the terminal solid solution regions are quite restricted.

Acknowledgements

Wei-hsiung Kao wishes to express his gratitude for an O'Brien Fellowship award by the University of Notre Dame, which made this work possible.

TABLE I Thermal data for the Sn-Sn_4As_3-SnTe system

Composition of alloy (wt %)			Temperature (± 0.5°C)		
Sn	Sn_4As_3	SnTe	1st arrest	2nd arrest	3rd arrest
Isopleth A					
12.75	2.25	85.00	763.8	403.3	232.0
34.00	6.00	60.00	734.5	405.5	231.8
51.00	9.00	40.00	704.0	412.5	231.8
54.40	9.60	36.00	698.0	415.0	231.8
76.50	13.50	10.00	592.5	415.0	231.7
80.75	14.25	5.00	529.5	417.0	232.0
82.45	14.55	3.00	416.6	293.5	231.3
84.15	14.85	1.00	415.8	250.3	231.5
Isopleth B					
10.50	4.50	85.00	762.8	455.5	231.5
28.00	12.00	60.00	733.5	468.3	231.2
42.00	18.00	40.00	701.3	475.0	231.5
47.60	20.40	32.00	685.0	475.0	231.5
63.00	27.00	10.00	581.8	476.8	231.4
66.50	28.50	5.00	520.5	477.8	231.4
68.60	29.40	2.00	478.5	298.0	231.3
Isopleth C					
7.5	7.5	85.00	768.3	517.8	—
20.0	20.0	60.00	737.5	525.3	231.3
30.0	30.0	40.00	704.8	524.8	231.8
37.5	37.5	25.00	663.0	528.0	231.8
42.5	42.5	15.00	591.5	528.0	231.1
45.0	45.0	10.00	573.0	527.3	231.3
46.5	46.5	7.00	541.0	528.8	231.8
48.5	48.5	3.00	532.5	413.0	231.6
Isopleth D					
4.50	10.5	85.00	770.0	552.0	231.8
12.00	28.0	60.00	740.8	555.8	231.6
18.00	42.0	40.00	706.0	558.5	232.0
26.50	59.5	15.00	612.8	560.0	231.6
27.90	65.1	7.00	562.0	—	231.3
28.80	67.2	4.00	563.6	425.0	231.3
Isopleth E					
2.25	12.75	85.00	769.0	569.0	230.5
6.00	34.00	60.00	739.3	572.5	231.8
9.00	51.00	40.00	701.8	572.3	231.5
12.00	68.00	20.00	633.3	573.0	231.9
13.80	78.20	8.00	575.8	—	231.3
14.40	81.60	4.00	579.2	—	231.8
Isopleth F					
54.60	9.00	36.40	700.0	415.1	231.3
47.70	20.50	31.80	685.0	475.0	231.5
37.50	37.50	25.00	661.5	527.3	231.5
25.20	58.00	16.80	625.2	560.0	231.2
13.80	77.00	9.20	573.1	—	231.6
8.40	86.00	5.60	580.0	573.0	232.0
3.60	94.00	2.40	585.0	573.0	231.6

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