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The Phase Diagram of the System Tellurium/Arsenic

J. R. EIFERT, E. A. PERETTI
Department of Metallurgical Engineering and Materials Science, University of Notre Dame, Indiana, USA

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Thermal analysis, metallographic and X-ray procedures have been used to investigate the system tellurium/arsenic. As_2Te_3 is the only binary compound present. It melts at 381° C and forms a eutectic with tellurium at 18.5 wt % As/81.5 wt % Te and at a temperature of 363° C. The As_2Te_3 and As also produce a eutectic at 31.5 wt % As/68.5 wt % Te, with a melting point of 380°C. The solid solubilities at the As and Te ends of the phase diagram are too small to detect by the methods used, and the compositional range of the As_2Te_3 is very restricted.

1. Previous Work

A search of the literature reveals that the only work reported on the As/Te diagram is that of Pelabon [1] whose exploratory work suggested the existence of a eutectic at 329° C, and 16.4% Te, the formation of As_2Te_3 with a melting point of 362° C, and a possible eutectic at 32.5 wt % As with a melting point of 358° C. Tsugane [2] and co-workers studied the system by X-ray analysis, and concluded that there are only three solid phases present in the system: Te, As_2Te_3, and As. They also found that slow cooling results in polycrystalline states for all Te/As compositions, but that the vitreous or part-vitreous/part-crystalline state could be formed by quenching specimens in the compositional range of 20 to 80 wt % As.

In 1955 Singer and Spencer [3] reported the As_2Te_3 structure to be monoclinic with $a = 14.4$, $b = 4.05$, $c = 9.92$ Å, and $\beta = 97°$. They calculated the specific gravity to be 6.1 at 25° C. More recently (1963) Carron [4] measured the lattice parameters and obtained $a = 14.339 \pm 0.001$, $b = 4.006 \pm 0.005$, $c = 9.873 \pm 0.005$ Å, and $\beta = 95.0°$. Arsenic and tellurium both crystallise in the hexagonal system, and at 25° C the lattice parameters are $a = 3.760$ and $c = 10.548$ for As [5] and $a = 4.4570$, $c = 5.59290$ for Te [6].

At one atmosphere pressure As sublimes at a temperature of 613° C [7], but melts at 811 ± 0.25° C, according to Geach and Jeffrey [8], if the As pressure is allowed to build up to 36 atm.

2. Experimental

2.1. Materials

The tellurium was obtained from the American Smelting and Refining Co,* and had the following spectrographic analysis: Mg, Si, Cu, Ag each 1 ppm; Fe 2 ppm; Sb, Te, Bi, Sn, Mn, Pb, Cr, Al, Ca, In, Cd, Zn and As were undetectable spectroscopically. The arsenic was Kawecki Chemical Co's 99.99+ grade, and was resublimed in an argon atmosphere and stored in sealed glass tubes under argon until used for alloying.

2.2. Procedure

Alloys containing up to 50 wt % As were made by melting the proper proportions of the elements in sealed, borosilicate glass tubes in an argon atmosphere. The arsenic-rich mixtures had to be prepared in quartz tubes because of the temperature and pressures involved. During the initial alloy-making operation each tube was held at temperature for ½ h, was intermittenly shaken vigorously, and then allowed to air cool in the tube, where it was stored until ready for use. The ingots made varied in size from 20 to 50 g.

Thermal curves were first taken with the

*Address: South Plainfield, New Jersey, USA alloys in closed tubes of glass or quartz, depending upon arsenic content, which were provided with a tubulation for a thermocouple. However, no vigorous stirring could be provided for this arrangement, and results obtained were erratic. As a consequence, for Te-rich alloys with more than 60 wt % Te the liquidus and solidus were determined by thermal analysis in open mullite crucibles under a protective atmosphere of argon, with constant mechanical agitation of the crucible contents with a mullite stirring rod driven by a motor at 1550 rev/min. For the As-rich solutions the vapour pressure is too high for open tube work, and the liquidus was measured in closed quartz tubes with no stirring.

Temperatures were measured with calibrated platinel or kanthal thermocouples, and time/temperature curves were automatically recorded by a Honeywell extended range recorder, checked with a Leeds and Northrup semiprecision potentiometer.

Eutectic compositions were established by plotting the liquidus curves and eutectic times, and by observing the disappearance of primary crystals in the microstructure of alloys on both sides of the eutectic point as determined by the liquidus plots.

Conventional hand-polishing techniques produced satisfactory samples for microscopic examination. Among the etching reagents which gave good results were: aqueous $FeCl_3$; 1 part conc HNO_3, 1 part dichromate solution, 4 parts water; 1 part KI/I_2 solution, 1 part 5% CrO_3; 1 part Eden's etchant, 1 part 5% CrO_3; 2 parts HF, 1 part HAc, 1 part conc HNO_3, 1 part 5% CrO_3; and 1 part 20% CrO_3, 1 part $FeCl_3$.

X-ray photographs were made of selected alloys in a Degye-Scherrer camera of 114.6 mm diameter with Cu or Cr K_α radiation to confirm the results obtained by thermal analysis and by the microscopic studies.

3. Results

Table I gives the results of thermal analysis, and fig. 1 shows the phase diagram. Tellurium and As_2Te_3 form a eutectic at 18.5 wt % As/81.5 wt % Te, which freezes at 363° C. The As_2Te_3 was found to have a melting point of 381° C; it enters into a eutectic reaction with As at a temperature of 380° C. This As-rich eutectic has 31.5 wt % As/68.5 wt % Te. The liquidus of the system then rises from 380 to 811° C, the melting point of As in a confined container.

This is the first time that details of the Te/As

TABLE I Thermal data for the Te/As phase diagram.

Alloy composition		Temperature (° C ± 0.5°)	
wt % As	at. % As	1st arrest	2nd arrest
2.00	3.36	437.8	360.0
4.00	6.63	428.8	362.5
8.00	12.90	410.1	363.0
10.00	15.91	402.0	363.2
12.00	18.85	393.1	363.1
14.00	21.71	381.3	363.5
16.00	24.49	371.9	363.0
18.00	27.21	363.0	—
19.00	28.55	365.0	—
20.00	29.86	369.5	363.3
22.00	32.45	374.4	363.0
23.00	33.72	376.2	363.2
24.00	34.97	378.0	363.1
25.00	36.21	379.2	363.0
26.00	37.44	380.0	362.1
27.00	38.65	380.8	360.0
28.13	40.00	381.0	—
29.00	41.03	380.9	380.7
30.00	42.19	380.6	—
31.00	43.35	379.9	—
32.00	44.49	384.2	380.7
33.95	46.68	410.3	380.6
34.00	46.73	407.8	379.0
36.00	48.93	432.8	380.0
38.00	51.07	465.8	380.4
40.00	53.17	495.8	380.2
42.00	55.22	514.3	380.6
48.00	61.12	558.0	380.3
55.00	67.55	615.0	380.0
80.00	87.20	746.8	380.5

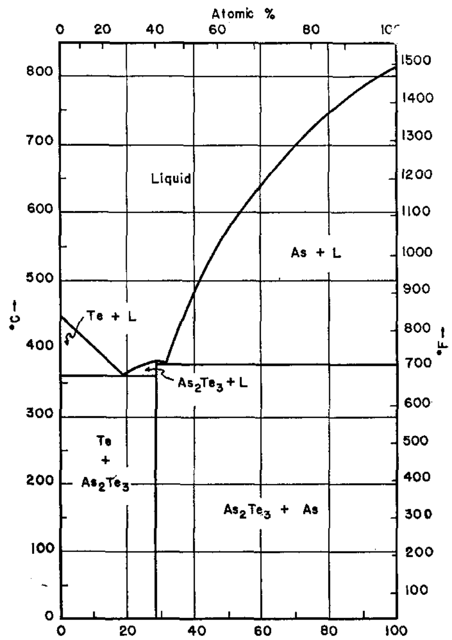

Figure 1 The tellurium/arsenic phase diagram.

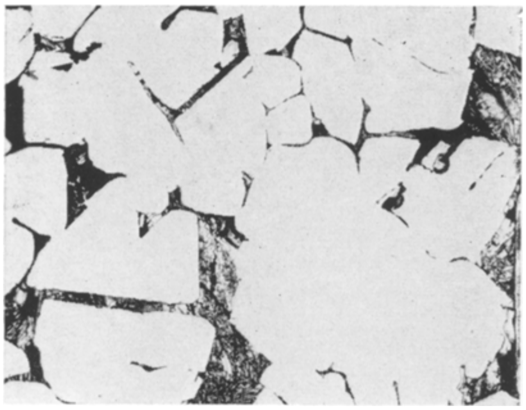

Figure 2 Microstructure of high-Te hypoeutectic alloy containing 4 wt % As/96 wt % Te. Primary Te plus eutectic. $FeCl_3$ etchant (×90).

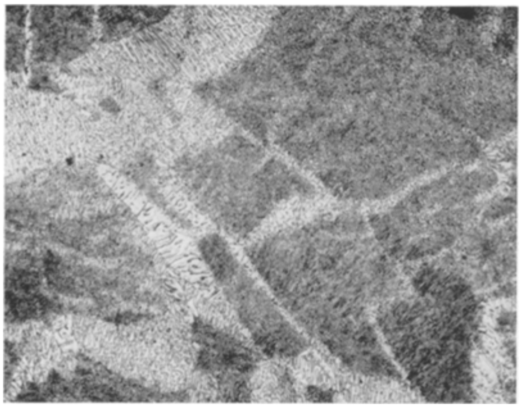

Figure 3 Microstructure of eutectic at 18.5 wt % As/81.5 wt % Te. Te plus As_2Te_3. Etchant: CrO_3/Eden (×90).

Figure 4 Microstructure of high-Te hypereutectic alloy with 21 wt % As/79 wt % Te. Primary As_2Te_3 plus eutectic of As_2Te_3. Etchant: CrO_3/Eden (×90).

system have been reported in the literature. The general outline is that suggested by Pelabon [1] but the temperatures are quite different, probably owing to a difference in purity of materials. Tsugane's [2] conclusions regarding the phases present in the system have been substantiated.

Fig. 2 is a photomicrograph of an alloy containing 96 wt % Te/4 wt % As, and shows a typical hypoeutectic structure. The appearance of the Te-rich eutectic is shown in fig. 3, and fig. 4 is typical of hypereutectic alloys with less than 28 wt % As. Figs. 5 and 6 are of the same area

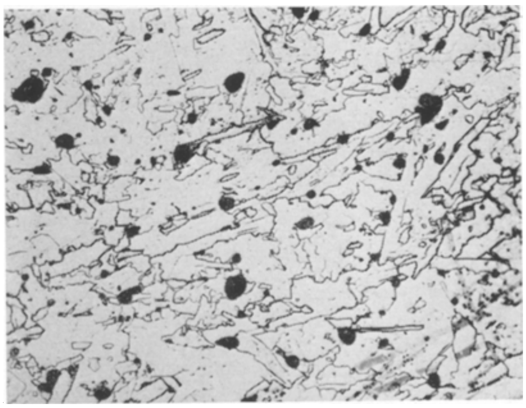

Figure 5 Microstructure of As_2Te_3. Etchant: CrO_3/Eden (×90).

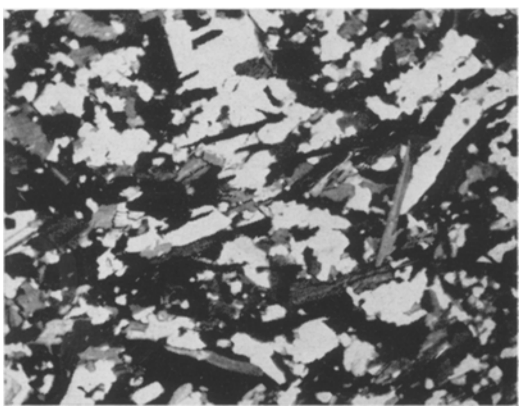

Figure 6 Microstructure of As_2Te_3. Same field as fig. 5 under polarised light (×90).

of As_2Te_3 taken under ordinary lighting and under polarised light, respectively.

The As-rich eutectic; which has a tendency to divorcement and glass formation, is shown in fig. 7. Fig. 8 is a photomicrograph of a typical high-As hypereutectic alloy.

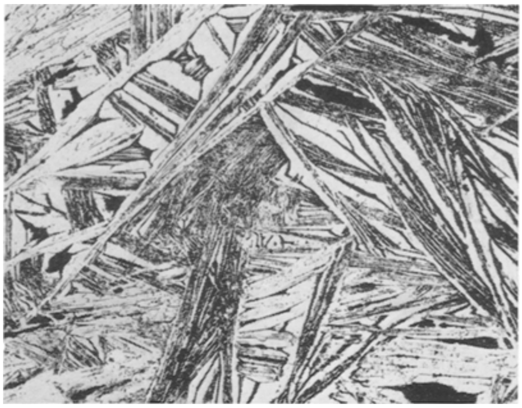

Figure 7 Microstructure of As_2Te_3/As eutectic at 31 wt% As/69 wt% Te. Etchant: $CrO_3/FeCl_3$ (×90).

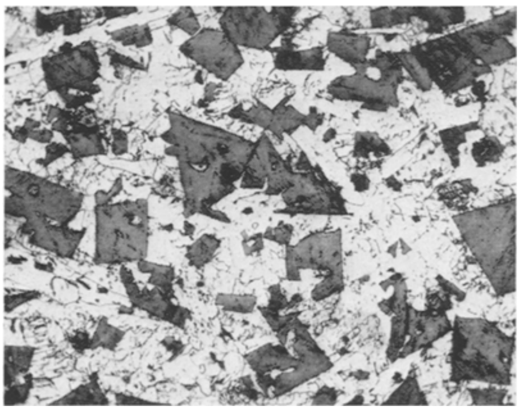

Figure 8 Microstructure of high-As hypereutectic alloy with 46 wt% As/54 wt% Te. Primary As plus eutectic. Etchant: CrO_3/Eden (×90).

Acknowledgement

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