Determination of the phase diagrams of the Cd–Sn(0.2)–Zn ternary system at high pressure

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Abstract

In order to verify the calculated result of the high-pressure phase diagram of the ternary alloy system, several vertical sections of the phase diagram of Cd–Sn–Zn system with a constant mole fraction $X_{Sn} = 0.2$ were determined by differential thermal analysis at high pressures. The working pressures were 0, 0.5, 1.0, 1.5, 2.0 GPa. The liquidus determined at ordinary pressure tallies well with that reported by Bray. The eutectic temperature of the system increases by about 50 K on going from atmospheric pressure to high pressure 2.0 GPa. The composition of the phase boundary $L/L + S_1 + S_2$ changes by about 0.1 mole fraction to the zinc-rich side.

1. Introduction

High-pressure phase diagrams are very important reference materials for the study of high-pressure physics, high-pressure chemistry and geology. The high-pressure phase diagram of an alloy is indispensable first-hand information for research into the relationship between the structures and properties of alloy materials at high pressure. The cadmium–tin–zinc ternary alloy can be used as one of the best examples for the study of a high-pressure phase diagram because of its low melting temperature and simple eutectic type. The phase-transition data obtained from studying this system theoretically and experimentally can be used to explore the phase-transition regularity of other alloy systems under given pressure conditions. In 1913 this ternary system was first investigated by Lorenz and Plumbridge [1] who determined the ternary eutectic temperature as 437 K, and its eutectic composition as: cadmium 25.42, tin 70.83, zinc 3.70 at.%. In 1957 the system was studied again by Bray [2] who obtained a value for the eutectic temperature of 429 K, and calculated the eutectic composition as cadmium

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26.71, tin 69.60, zinc 3.70 at.%. The liquidus of the whole system was depicted graphically. No phases were found other than those already observed in the three binary systems. In 1988 the high-pressure phase diagrams of this system at $X_{Sn} = 0.2$ were calculated theoretically by Xiao *et al.* [3] according to the boundary theory of phase diagrams [4].

The calculated pressures were 0, 1.0 and 2.0 GPa, but these calculated phase diagrams were not compared with experimental data since no determined phase-transition data of this system at high pressure were then available. Toop [5], Hillert [6] and others had put forward different methods of calculation for phase diagrams, but these methods cannot fit all systems because the methods were derived from different system models which were based on different types of systems. Calculated phase diagrams for which no experimental data are available are always estimated from personal experience, which means that errors cannot be discovered and corrected. In this paper, vertical sections of the phase diagram of the cadmium–tin–zinc ternary system at $X_{Sn} = 0.2$ and at different pressures were determined by high-pressure differential thermal analysis (HPDTA). The experimental data were used to verify probable deviations existing in the calculated high-pressure phase diagrams. The reason for the errors and methods of improving the calculations will be discussed in another paper.

2. Experimental methods

2.1. Preparation of alloys

The metals used in this work were the purest obtainable at 99.999%; they were weighed with a semi-microbalance, sealed in a hard-glass tube with the vacuum of 10^{-3} Pa, shaken while melting, solidified in liquid nitrogen and well-annealed at about 400 K for 150 h. A careful analysis of some random samples was carried out, and this showed that specimens could be prepared without deviation from the calculated composition by this method.

2.2. Differential thermal analysis at atmospheric pressure

About 15 mg of the alloy specimen was used to obtain the differential thermal analysis (DTA) data on a DTA instrument (Shanghai Instrument Factory of China) with model number CDR-1. The specimen was protected from oxidation by high purity nitrogen. The maximum determination error of the experiment was estimated to within ± 2 K.

2.3. Differential thermal analysis at high pressure

A sensitive high-pressure DTA measuring method was used to obtain the HPDTA curves on a piston–cylinder apparatus with 20 mm inner diameter. This apparatus was capable of applying up to 3.0 GPa. The sample capsule was made of the same material used for one pole of the thermocouple [7]. About 60 mg of the alloy specimen was pressed into a button shape in order

to hold more substance in the small capsule, and to maintain the sensitivity and the resolving power of the experiment. Owing to leakage of the liquid alloy under high pressure, the failure rate of the experiments was very high and even more than two-thirds when the pressure rose to 2.0 GPa. Therefore, the higher the experimental pressure, the fewer the data obtained.

The symmetrical and unsymmetrical frictions in the pyrophyllite medium around the specimen [8] and deviation in the measurement temperature produced an estimated maximum determination error within ± 4 K.

3. Experimental results

In the present work the vertical sections of the phase diagram of the system at $X_{Sn} = 0.2$ were determined. The DTA data at atmospheric pressure are listed in Table 1. The phase diagram obtained is depicted in Fig. 1. Figure 2 compares our results with those of Bray and Xiao. It is shown that the liquidus found by us tallies well with the literature values at atmospheric pressure, but there is a slight difference in the eutectoid compositions. Our eutectic temperature is 437 K, which is 8 K higher than Bray's result of 429 K, but agrees with Lorenz's measurement. It is also very close to Xiao's result of 436 K, indicating that this result is probably reliable.

For the same section with $X_{Sn} = 0.2$, the HPDTA data were obtained at pressures of 0.5, 1.0, 1.5 and 2.0 GPa. The data are listed in Tables 2 and 3. The high-pressure phase diagrams are illustrated in Figs. 3–6. The variation

TABLE 1

DTA data of Cd–Sn(0.2)–Zn system at atmospheric pressure

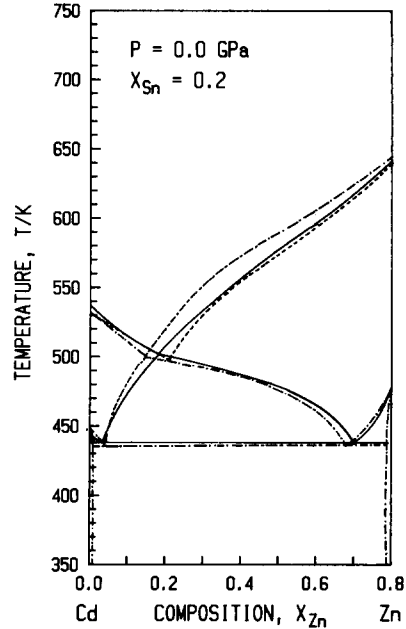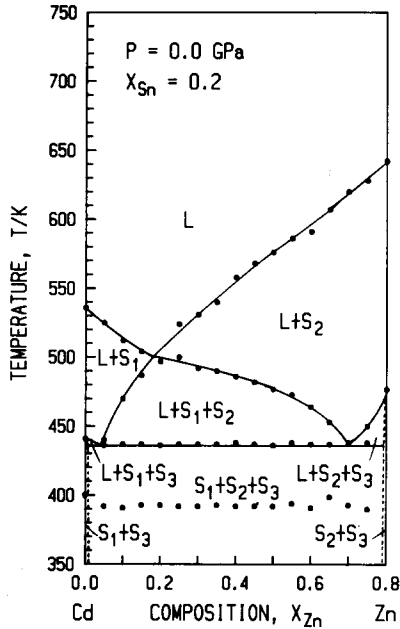| X(Zn)	T(K)			
0.00	536	441	400	
0.05	525	440	436	392
0.10	512	470	437	391
0.15	504	487	437	393
0.20	497	436	393	
0.25	524	500	437	392
0.30	531	492	437	392
0.35	540	490	437	393
0.40	558	486	438	392
0.45	568	482	437	392
0.50	576	477	436	392
0.55	586	473	438	394
0.60	591	464	437	391
0.65	607	453	437	399
0.70	620	438	393	
0.75	628	450	438	390
0.80	642	477		

Fig. 1. The determined vertical section of the phase diagram of the Cd–Sn–Zn system at $X_{Sn} = 0.2$ and atmospheric pressure.

Fig. 2. A comparison of results from this work with others' (Bray $\cdots$, Xiao $- \cdot - \cdot - \cdot -$).

TABLE 2

The high pressure DTA data of the Cd–Sn(0.2)–Zn ternary alloy system (T(K))

X(Zn)	0.5 GPa				1.0 GPa			
0.00	553	456	393		587	473	400	
0.05	544	440	388		575	454	394	
0.10	536	479	440	383	563	495	454	388
0.15	523	495	442	390	554	510	451	
0.20	525	505	440		551	533	464	
0.25	525	512	442	388	536	458	395	
0.30	540	501	439	385	553	528	456	395
0.35	555	498	440	385	572	527	458	395
0.40	571	496	441		580	521	455	
0.45	583	489	439		597	508	452	
0.50	592	486	440		604	511	456	
0.55	603	477	440		621	499	455	
0.60	611	466	439		631	493	455	
0.65	625	460	442	390	642	485	457	400
0.70	635	441	415		662	455	432	
0.75	646	450	439	381	670	463	455	389
0.80	660	478			685	494		

TABLE 3

The high pressure DTA data of the Cd–Sn(0.2)–Zn ternary alloy system (T(K))

X(Zn)	1.5 GPa				2.0 GPa			
0.00	616	487	405		648	504	411	
0.05	602	468	402		642	487	405	
0.10	594	506	470	397	621	519	482	402
0.15	582	532	473		602	540	481	
0.20	575	550	479		603	565	493	
0.25	561	556	474	400	587	574	490	407
0.30	567	554	472	402	579	486	407	
0.35	583	548	474	407	598	574	488	412
0.40	596	542	471		613	564	488	
0.45	611	530	467		626	554	482	
0.50	622	533	472		638	551	482	
0.55	638	526	473		651	549	488	
0.60	649	517	470		663	548	483	
0.65	661	508	471	405	674	522	485	407
0.70	674	487	476		696	512	487	
0.75	689	476	469	405	700	492	487	405
0.80	703	506			725	526		
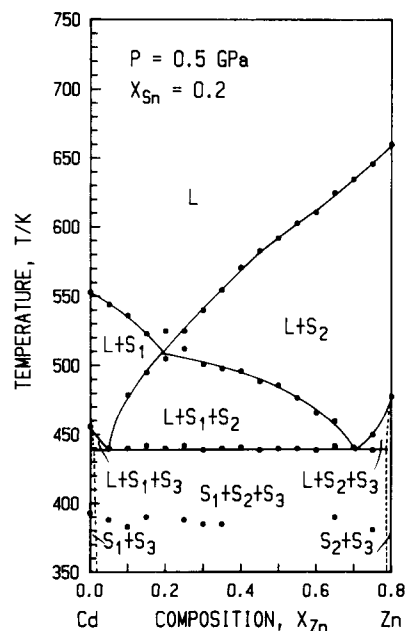
Fig. 3. The determined vertical section of the high-pressure phase diagram of the Cd–Sn–Zn system at $X_{Sn} = 0.2$ and $P = 0.5$ GPa.
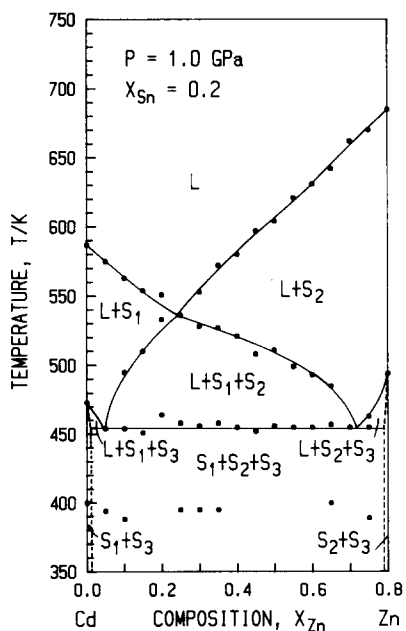
Fig. 4. The determined vertical section of the high-pressure phase diagram of the Cd–Sn–Zn system at $X_{Sn} = 0.2$ and $P = 1.0$ GPa.
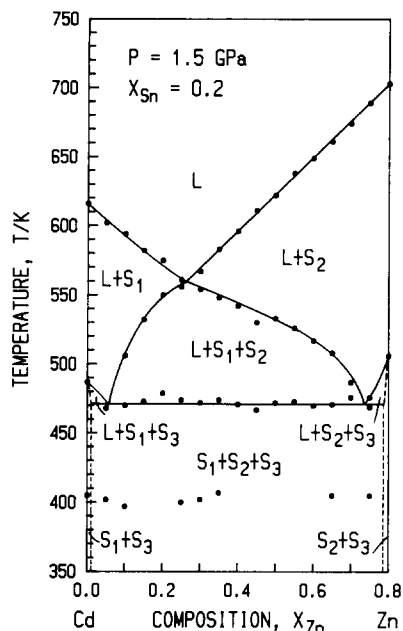
Fig. 5. The determined vertical section of the high-pressure phase diagram of the Cd–Sn–Zn system at $X_{Sn} = 0.2$ and $P = 1.5$ GPa.
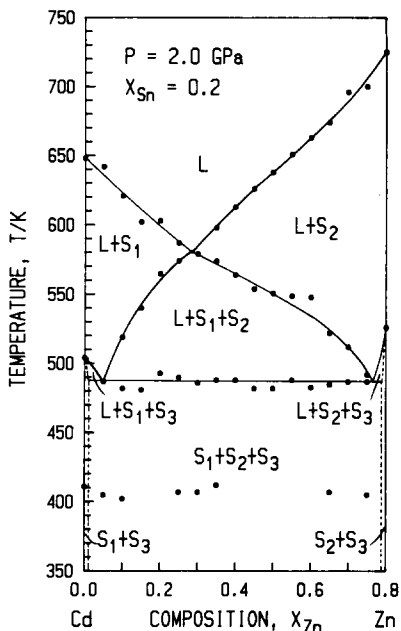
Fig. 6. The determined vertical section of the high-pressure phase diagram of the Cd–Sn–Zn system at $X_{Sn} = 0.2$ and $P = 2.0$ GPa.

in the eutectic temperature and liquidus with high pressure is shown in Fig. 7. Figures 3–6 show that the shapes of the diagrams do not change with pressure change. This shows that no new phase is formed in the system within the range of the pressure change, although the boundaries of the phase regions are shifted by the effect of high pressure.

From the comparison diagram (Fig. 7) it is clear that the shift of phase boundary with pressure change is a regular one. The eutectic temperature increases by about 50 K within the range of the pressure change, and the composition of the phase boundary L/L + S_1 + S_2 shifts about 0.10 mole fraction to the zinc-rich side at the same time. The intervals of the pressure change during the experiments are the same, but intervals of the phase boundaries such as the eutectic temperature intervals measured are not the same as those shown in Fig. 7. This deviation may be due to the fact that the solid pyrophyllite medium used in the pressure cell caused obvious symmetrical and unsymmetrical relative frictional losses according to the pressure of the system: the lower the pressure, the greater the relative frictional loss. If the solid medium of the system were replaced by a liquid medium, the observed deviation would obviously be reduced.
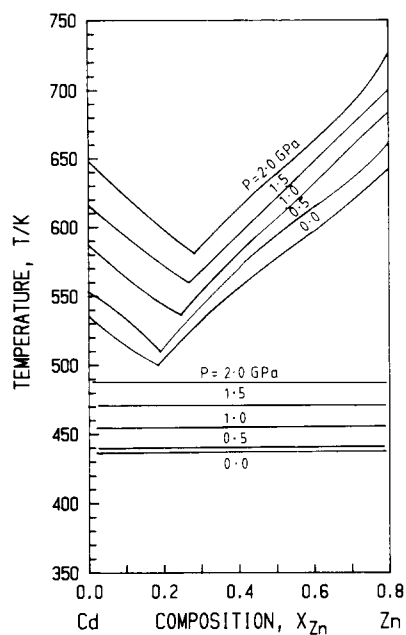
Fig. 7. The compared diagram of liquidus and eutectic temperatures of the Cd–Sn–Zn system at the section of $X_{Sn} = 0.2$ and at different experimental pressures.

Acknowledgment

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