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A Smith thermal analysis and DSC study of the In–Cd system [1]

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Abstract

The Smith thermal analysis technique has been used to study phase boundaries and invariant reactions in the In–Cd system. Results obtained from measurements at eleven compositions are in full agreement with the phase diagram proposed by Heumann and Predel. DSC measurements at low scan rates have been carried out over the temperature range including the eutectic and eutectoid reactions. Measurements of the total heat effect together with the lever rule have been used to obtain, (i) enthalpies of reaction for both the eutectic and eutectoid reactions, and (ii) compositions of the phases involved in these invariant reactions. The method used should have wide applicability to eutectic and eutectoid reactions in a range of systems.

INTRODUCTION

This experimental investigation of the In–Cd binary alloy system forms the first part of an assessment of the ternary Ag–Cd–In system, alloys of which are used as the control rod material in pressurised water reactors (PWR). In order to assess the ternary, the limiting binary systems must first be studied to ascertain the reliability of available data for use in computer calculations of the thermodynamics of the system.

Early work on the binary In–Cd phase diagram was carried out by Wilson and Wick [1] and by Valentiner [2]; the currently accepted diagram, shown in Fig. 1, is that developed by Heumann and Predel [3,4] who were the first to propose the existence of the β-Cd_3In phase which exists as a single phase over approximately 1 at% centred on 75 at% Cd. The limited

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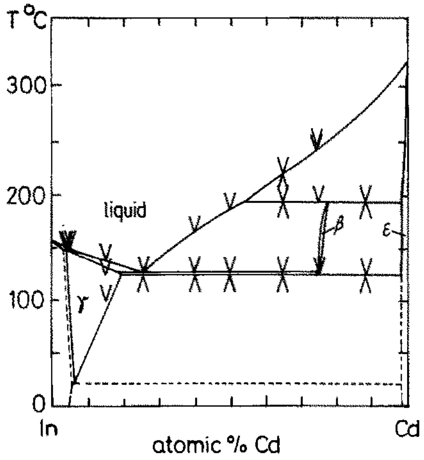

Fig. 1. The In–Cd phase diagram from Heumann and Predel [3,4] with present Smith thermal analysis results.

temperature stability range of this phase results in there being two invariant reactions which lie very close to each other at approximately 127°C, both involving the β-Cd_3In phase. In this paper we report the results of a study, by Smith thermal analysis, which confirms the general shape of the proposed phase diagram and which gives in particular, the temperatures of the eutectic and eutectoid reactions in the system. DSC measurements have been used to obtain enthalpies of reaction. The present results, together with thermochemical data for the liquid, and phase diagram points taken from the literature [5], form the basis of a new In–Cd assessment [6]. The present work was carried out to confirm the proposed phase diagram and to obtain thermochemical data for the invariant reactions.

EXPERIMENTAL

In determining accurate phase boundary temperatures, in cases where two or more phase boundaries lie very close together it is essential that the system is maintained close to equilibrium throughout the experiment. A method which fulfils this requirement and which provides very good resolution of temperatures of phase boundaries is Smith thermal analysis. First proposed by Smith [7] in 1940, and subsequently successfully used by Humpston and Davies [8], this technique maintains a constant difference in temperature between the specimen and the furnace. The furnace and specimen thermocouples are connected in opposition to form a differential couple, the signal from which is fed to the controller. A preset millivolt difference is maintained throughout which controls the power input such that when the sample undergoes an invariant reaction, the furnace ceases to heat/cool until the reaction is complete. In this way, a higher degree of resolution of neighbouring reactions can be obtained. The Smith technique was used for the accurate determination of boundary temperatures throughout this study in both heating and cooling runs. The Smith apparatus was calibrated using the pure metals zinc, tin, bismuth, lead and indium. Tests on pure metals after calibration revealed the apparatus to have a reproducibility within 0.2°C in the temperature range of interest here.

Heat effects from the invariant reactions were determined using a Perkin-Elmer DSCII differential scanning calorimeter with special precautions due to cadmium being a potentially dangerous material if it is not handled with care. It is carcinogenic and teratogenic and therefore steps need to be taken to prevent any leakages of cadmium vapour to the laboratory atmosphere. To that end, alloys were made from high purity metals (Johnson Matthey Specpure cadmium and Koch Light Labs. 99.9999% pure indium) in sealed pyrex tubes and were contained in sealed steel pans with screw on lids during the DSC work. All the DSC work was carried out at very slow heating/cooling rates on quenched and annealed alloy samples. By determining the total heat effects on heating equilibrated alloys through the invariant reaction range at different compositions, it is possible as shown below to obtain by means of the lever rule the enthalpies of reaction for both of the reactions

$$\text{Liquid} = \gamma(\text{fcc}) + \beta(\text{Cd}_3\text{In})$$

and

$$\beta(\text{Cd}_3\text{In}) = \gamma(\text{fcc}) + \varepsilon(\text{hcp})$$

RESULTS AND DISCUSSION

The results of the Smith thermal analysis work are presented in Table 1; they are superimposed on the phase diagram in Fig. 1.

The first four alloys studied, i.e. 3.7 at% Cd, 3.85 at% Cd, 4.7 at% Cd and 5 at% Cd were used to investigate the existence of the indium-rich peritectic reaction proposed by Heumann and Predel [3,4] since this has not previously been reported by any other authors. In general, very good agreement with the work of Heumann and Predel has been reached. They reported the peritectic temperature to be 148°C; the results of this study indicate that it is 148.7 ± 0.2°C.

The work undertaken here is in almost complete agreement with that of Heumann and Predel [3,4]. The presence of two reactions, clearly demonstrated in the present work, shows that the $\beta(\text{Cd}_3\text{In})$ phase proposed by Heumann and Predel [3,4] must exist. It is formed by a peritectic reaction

$$\text{L} + \varepsilon(\text{hcp}) = \beta(\text{Cd}_3\text{In})$$

TABLE 1

Smith thermal analysis results

Cadmium (at%)	Temperature (°C)					
	Invariant		Liquidus		Solidus	
	Heat	Cool	Heat	Cool	Heat	Cool
3.7	148.8	148.7				
	148.8	148.6				
3.85	148.8	148.8		150.8		
	148.7					
	148.6					
4.7	149.0	148.7	149.8	149.8	144.0	
	148.7	148.6	149.3	149.1	146.6	
		148.7		151.1	145.9	
				149.0		
5.0	148.6	148.9			145.9	
		148.7				
15.0				139.2		127.2
						102.5 [a]
25.7	127.5	127.6				
40.0	127.6	127.4		165.9		
	127.3	127.3				
		(127.4 + 126.3)				
50.0	127.3	(127.6 + 123.9)		187.8		
65.0	127.2	127.9	223.6	223.3		
	196.1	196.1				
75.0		127.7		240.6		
		128.0		242.6		
		196.8				
		196.6				
89.0	127.2	126.2				
	197.8	196.6				

[a] Result for the γ-fcc/(γ-fcc + ε-hcp) boundary.

at 196.7°C and exists over a very narrow range of composition. $\beta(Cd_3In)$ was found to decompose eutectoidally at 126.9 ± 0.2°C into γ(fcc) + ε(hcp); the eutectic temperature was found to be at 127.7 ± 0.2°C.

As an independent check and to completely characterise the eutectoid and eutectic reactions a series of differential scanning calorimetry experiments were carried out. A combined heating/cooling trace is shown in Fig. 2. It can clearly be seen that on heating there is a single peak whereas in fact, there are two reactions present. The weaker of the two is masked because, unlike the Smith technique, the furnace in DSC continues to heat irrespective of events occurring in the sample. On heating the eutectoid reaction is clearly incomplete before the eutectic reaction starts to occur.

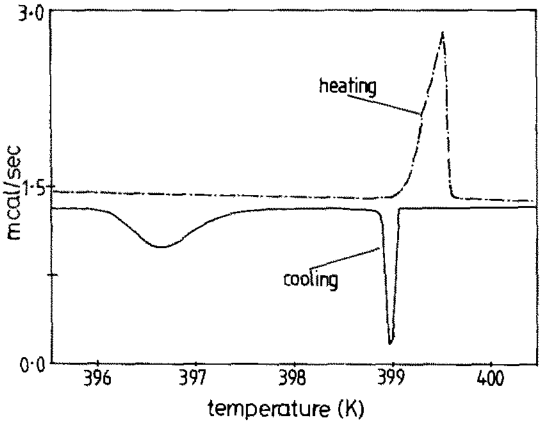

Fig. 2. Typical DSC trace on heating and cooling through eutectic/eutectoid region of In–Cd system. Sample mass, 53.10 mg; 65 at% Cd; scan rate, 0.1 deg min^{-1}.

On cooling, two distinct peaks are observed due to the separation of the two reactions. The eutectic is complete before the eutectoid begins, and so DSC is capable of resolving the reactions on cooling. For a fixed composition the combined heat effect from the reactions was found to be constant irrespective of whether the experiment was a heating or a cooling run.

The heat effects measured for a series of alloys are given in Table 2. These heats are derived using the Perkin-Elmer Thermal Analysis Data Station attached to the DSC and represent the area of the peak on the heating curve shown in Fig. 2. Included in Table 2 are the results of analyses carried out on the samples after DSC. These show that despite the

TABLE 2

Summary of DSC results

Cadmium (at%)	By analysis	Measured heats (J mol^{-1})
22.5	22.70	1845.6
		1998.6
25.0	24.94	3326.1
		3378.7
30.0	29.60	3341.7
40.0	38.00	2967.8
50.0	50.00	2509.9
		2530.1
65.0	64.88	1843.3
		1885.9
80.0	79.95	1124.2
90.0	88.61	603.6

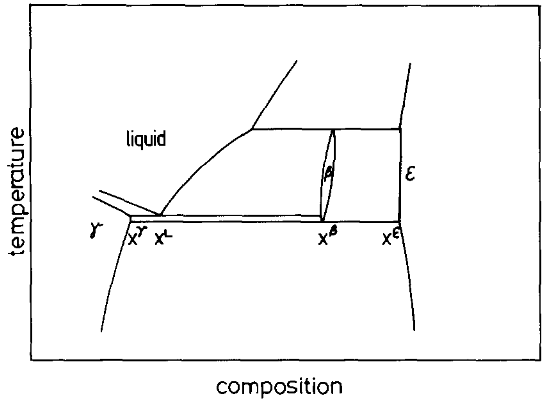

Fig. 3. Schematic diagram of In–Cd phase diagram showing symbols used in DSC/lever rule analysis.

tendency for cadmium to vaporise when it is melted, the alloy preparation technique employed proved very effective in actually obtaining the desired compositions. In order to calculate the enthalpy of reaction for both the eutectic and the eutectoid it is necessary to generate equations containing these quantities which can subsequently be solved to give the actual values. Figure 3 is a schematic diagram showing the part of the In–Cd phase diagram of interest. The four compositions involved in the invariant reactions are marked on the composition axis. Between x^{γ} and x^{ε} three distinct composition ranges exist over which the following combinations of reactions occur with increasing cadmium content:

(i) x^{γ} to x^{L}, both the eutectic and eutectoid reactions occur, each to an increasing extent with increasing x;

(ii) x^{L} to x^{β}, both the eutectic and the eutectoid reactions occur, the eutectic to a decreasing extent and the eutectoid to an increasing extent with increasing x;

(iii) x^{β} to x^{ε}, only the eutectoid reaction occurs to a decreasing extent with increasing x.

The total heat q_1 measured by careful DSC work over the temperature range from below the eutectoid to above the eutectic for compositions lying between x^{γ} and x^{L} is given by

$$q_1 = \frac{(x - x^{\gamma})}{(x^{\mathrm{L}} - x^{\gamma})}\Delta H^{\mathrm{L}} + \frac{(x - x^{\gamma})}{(x^{\beta} - x^{\gamma})}\Delta H^{\beta}$$

where ΔH^{L} and ΔH^{β} are the enthalpies of reaction for the eutectic and eutectoid reactions respectively. Similarly for the temperature range, the total heat q_2 measured between compositions x^{L} and x^{β} is given by

$$q_2 = \frac{(x^{\beta} - x)}{(x^{\beta} - x^{\mathrm{L}})}\Delta H^{\mathrm{L}} + \frac{(x - x^{\gamma})}{(x^{\beta} - x^{\gamma})}\Delta H^{\beta}$$

and the heat q_3 measured between compositions x^{β} and x^{ε} where only the eutectoid occurs is given by

$$q_3 = \frac{(x^{\varepsilon} - x)}{(x^{\varepsilon} - x^{\beta})} \Delta H^{\beta}$$

For each of the three composition ranges above the measured heat varies linearly with composition and writing the general equation for q as

$$q_i = A_i x + B_i$$

the various values of A_i and B_i can be written as

$$A_1 = \frac{\Delta H^{\mathrm{L}}}{(x^{\mathrm{L}} - x^{\gamma})} + \frac{\Delta H^{\beta}}{(x^{\beta} - x^{\gamma})}$$

$$A_2 = -\frac{\Delta H^{\mathrm{L}}}{(x^{\beta} - x^{\mathrm{L}})} + \frac{\Delta H^{\beta}}{(x^{\beta} - x^{\gamma})}$$

$$A_3 = -\frac{\Delta H^{\beta}}{(x^{\varepsilon} - x^{\beta})}$$

$$B_1 = -\frac{x^{\gamma}\,\Delta H^{\mathrm{L}}}{(x^{\mathrm{L}} - x^{\gamma})} - \frac{x^{\gamma}\,\Delta H^{\beta}}{(x^{\beta} - x^{\gamma})}$$

$$B_2 = \frac{x^{\beta}\,\Delta H^{\mathrm{L}}}{(x^{\beta} - x^{\mathrm{L}})} - \frac{x^{\gamma}\,\Delta H^{\beta}}{(x^{\beta} - x^{\gamma})}$$

$$B_3 = \frac{x^{\varepsilon}\,\Delta H^{\beta}}{(x^{\varepsilon} - x^{\beta})}$$

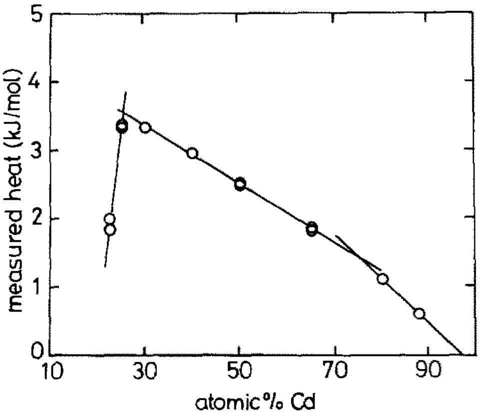

Fig. 4. Total heat effect obtained from DSC measurements versus composition. Three distinct linear portions are present in agreement with the current DSC/lever rule analysis.

There are six equations and six unknown quantities. Therefore, the equations can be solved to give solutions in terms of the coefficients of the linear best fit equations for the measured heats, i.e. A_i and B_i above

$$x^{\varepsilon} = -\frac{B_3}{A_3}$$

$$x^{\gamma} = -\frac{B_1}{A_1}$$

$$x^{\mathrm{L}} = \frac{(B_2 - B_1)}{(A_1 - A_2)}$$

$$x^{\beta} = \frac{(B_3 - B_2)}{(A_2 - A_3)}$$

$$\Delta H^{\beta} = B_3 + \frac{A_3(B_3 - B_2)}{(A_2 - A_3)}$$

$$\Delta H^{\mathrm{L}} = \frac{(A_1 B_2 - A_2 B_1)}{A_1(A_1 - A_2)}\left[A_1 - \frac{(A_1 A_2 B_3 - A_1 A_3 B_2)}{(A_1[B_3 - B_2] + B_1[A_2 - A_3])}\right]$$

The DSC results are given in Table 2. Figure 4 shows the results of DSC measurements of the total heat effect at several different compositions between x^{γ} and x^{ε} when alloy samples traverse the invariant reaction range. The linear variation of the heat effect with composition for each of the three composition ranges above shows that the extent to which each of the reactions occurs is in strict accordance with the above lever rule analysis.

Table 3 compares the results of the present work with those taken from the most recent phase diagram assessment [9].

TABLE 3

Comparison of assessed quantities with those found in this work

	Experimental (this work)	Assessed [9]	Diff. (%)
x^{ε} (at% Cd)	97.28	98.6	1.3
x^{γ} (at% Cd)	19.14	19.2	0.3
x^{L} (at% Cd)	25.37	25.7	1.3
x^{β} (at% Cd)	75.19	74.2	1.3
ΔH^{β} (J mol^{-1})	1437.4		
ΔH^{L} (J mol^{-1})	3405.2		

SUMMARY

The presence of four invariant reactions, two peritectic, one eutectic and one eutectoid, has been confirmed in the In–Cd system using Smith thermal analysis. DSC measurements have been used to obtain enthalpies of reaction and compositions of phases involved in the eutectic and eutectoid reactions. The method used in this work should have wide applicability in other binary and ternary alloys.

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