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Measurement of heats of solidification of eutectic alloys using differential thermal analysis

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Abstract

The technique of differential thermal analysis has been applied to the quantitative determination of heats of solidification of some eutectic alloys. A DTA modular unit of a Shimadzu DT-30 thermal analyser has been calibrated up to 1100 °C on the basis of the melting points of spectroscopically pure metals. Heats of solidification of Pb–Bi, Zn–Al and Pb–Te eutectic alloys have been determined using the calibration plots so established. The results are in good agreement with theoretically calculated heat values available in the literature. This shows the reliability of the DTA set-up.

INTRODUCTION

The theoretical and industrial importance of the latent heats of solidification of alloys cannot be over-emphasised. A knowledge of the latent heats of solidification of alloys is essential for the design of gating, risering, continuous casting and production of composite materials by solidification. Accordingly, many studies [1–3] have been made on this subject in order to predict the progress of solidification by solving the unsteady heat conduction equations by numerical techniques. It has been observed [4] that values calculated by numerical techniques are different from those determined experimentally. In the present paper, the latent heat of solidification of the eutectic alloy in the system Zn–Al (88.7 at.% Zn) has been calculated and compared with the experimentally determined value. The latent heat of solidification of the Pb–Te eutectic system could not be calculated theoretically because of a lack of thermodynamic data and hence the experimentally determined value has been reported as such.

The eutectic reaction in the Zn–Al system [5] occurring at 88.7 at.% Zn and 655 K, following the lever rule, may be represented as

$$L(X_{\mathrm{Zn}} = 0.887) \overset{655\,\mathrm{K}}{\rightleftarrows} 0.284\alpha(\mathrm{s}) + 0.716\beta(\mathrm{s}) \tag{1}$$

In this reaction, L is the liquid alloy, α(s) is the primary solid solution of zinc in aluminium and β(s) is the primary solid solution of aluminium in

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zinc. The latent heat of solidification of eutectic alloy has been calculated below by the method adopted by Tiwari et al. [6]

$$\begin{aligned}\Delta H^{\mathrm{f}}_{\mathrm{Zn-Al}} &= H^{1} - H^{\mathrm{s}}\\ &= \left(X_{\mathrm{Zn}} H^{\mathrm{l}}_{\mathrm{Zn}} + X_{\mathrm{Al}} H^{\mathrm{l}}_{\mathrm{Al}} + \Delta H^{1}\right)\\ &\quad - \left[0.284\left(X^{\alpha}_{\mathrm{Zn}} H^{\mathrm{s}}_{\mathrm{Zn}} + X^{\alpha}_{\mathrm{Al}} H^{\mathrm{s}}_{\mathrm{Al}} + \Delta H^{\alpha(\mathrm{s})}\right)\right.\\ &\quad \left. + 0.716\left(X^{\beta}_{\mathrm{Zn}} H^{\mathrm{s}}_{\mathrm{Zn}} + X^{\beta}_{\mathrm{Al}} H^{\mathrm{s}}_{\mathrm{Al}} + \Delta H^{\beta(\mathrm{s})}\right]\right. \qquad (2)\end{aligned}$$

where H^{1} is the heat content of the liquid eutectic alloy at eutectic temperature and H^{s} the heat content of the equilibrium mixture of solid phase, α and β, at eutectic temperature. X_{Zn} and X_{Al} are the atomic fraction of Zn and Al, respectively, in the liquid phase; H^{1}_{Zn} and H^{1}_{Al} are the heat contents of liquid Zn and Al, respectively, and ΔH^{1} is the heat of formation of the eutectic alloy. X^{α}_{Zn} and X^{α}_{Al} are the atomic fraction of Zn and Al in α phase, respectively. $H^{\mathrm{s}}_{\mathrm{Zn}}$ and $H^{\mathrm{s}}_{\mathrm{Al}}$ are the heat contents of solid Zn and Al, respectively, and $\Delta H^{\alpha(\mathrm{s})}$ and $\Delta H^{\beta(\mathrm{s})}$ are the heats of formation of α and β phases, respectively. By substituting in eqn. (2) $X_{\mathrm{Zn}} = 0.887$, $X_{\mathrm{Al}} = 0.113$, $X^{\alpha}_{\mathrm{Zn}} = 0.665$, $X^{\alpha}_{\mathrm{Al}} = 0.335$, $H^{1}_{\mathrm{Zn}} = 4030.0$ cal (g atom)$^{-1}$, $H^{1}_{\mathrm{Al}} =$ 4800 cal (g atom)$^{-1}$, $H^{\mathrm{s}}_{\mathrm{Zn}} = 2250$ cal (g atom)$^{-1}$, $H^{\mathrm{s}}_{\mathrm{Al}} = 2270$ cal (g atom)$^{-1}$ and $\Delta H^{1} = 325.75$ cal (g atom)$^{-1}$ from the data compiled by Hultgreen et al. [7] at 655 K, and values of $\Delta H^{\alpha(\mathrm{s})}_{655\,\mathrm{K}} = 750$ cal (g atom)$^{-1}$ and $\Delta H^{(\mathrm{s})}_{655\,\mathrm{K}} =$ 100 cal (g atom)$^{-1}$ obtained by extrapolation of the data from Hultgreen et al [7], the latent heat of solidification of the eutectic alloy has been calculated to be 7976 J (g atom)$^{-1}$. To verify the above theoretical prediction, the experimental determination of the latent heat of solidification of the eutectic alloy was made using a Shimadzu model DT-30 thermal analyser.

EXPERIMENTAL

Materials

Spectroscopically pure metals Cu, Ag, Al, Zn, Pb, Bi, Sn and Te, obtained from Bhaba Atomic Research Centre, Bombay, were used in the investigation.

Preparation of the alloys

About 5 g each of Pb–Bi (43 at.%Pb), Pb–Te (85.5 at.% Te) and Zn–Al (88.7 at.% Al) eutectic alloys were prepared by melting stoichiometric proportions of the constituent elements in evacuated pyrex glass capsules. After melting, individual systems were allowed to reach their corresponding eutectic temperatures and were kept at that temperature for two hours.

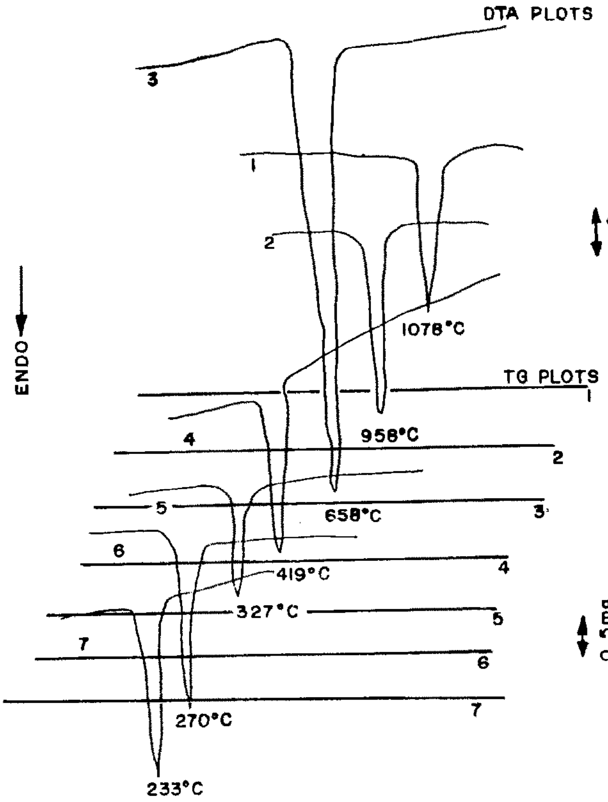

Fig. 1. DTA and TG plots for melting of metals: 1, Cu; 2, Ag; 3, Al; 4, Zn; 5, Pb; 6, Bi; 7, Sn.

Then the capsules were shaken and quenched in water at room temperature. The alloys were then analysed to determine their actual chemical composition. To check the formation of lead telluride, an X-ray diffraction study was carried out using a JEOL 8PX X-ray diffractometer.

Experimental procedure

The calibration procedure consisted of determining the area of the DTA peaks at the melting point of the metals. The details of the procedure have been given elsewhere [8].

The simultaneous plots of DTA and the corresponding TG for Cu, Ag, Al, Zn, Pb, Bi and Sn are shown in Fig. 1. Each of the endothermic dips (1, 2, 3, 4, 5 and 6) describes a melting process as indicated. For the DTA system, where sample holders are isolated by a low thermal conductivity medium (e.g. air, as in the present investigation), and both the thermocouples are located outside their respective holders, the peak area A is

TABLE 1

Determination of calibration constant for metallic systems

Sample	M.P. (K)	Heat of fusion (kJ (g atom)$^{-1}$)	Peak area [a]	Instrumental constants k (mg kJ^{-1})
Sn	506	7.07	12.7	7101.93
Bi	543	10.90	11.0	7038.13
Pb	600	4.81	4.8	6871.71
Zn	692	7.28	12.5	3736.27
Al	931	10.67	44.0	3707.57
Ag	1231	11.09	11.0	3564.45
Cu	1351	12.97	20.4	3320.00

[a] Expressed as weight of paper (mg).

represented by the equation [9]

$$A = \frac{M\,\Delta H}{2K_{\mathrm{m}}}$$

where K_{m} is the thermal conductivity of the separating medium of low thermal conductivity, M is the mass of the sample in g and ΔH is the enthalpy change of the reaction per g of the reactive substance. From this equation it is found that peak area is directly proportional to the heat of reaction; other properties of the sample are of no consequence. Thus $A \propto \Delta H$ or $A = k\ \Delta H$, where k is an instrumental parameter which can be obtained from the calibration. The DTA peak area and k values for different metals are shown in Table 1 along with their melting points. A plot of k versus temperature is shown in Fig. 2 which consists of two linear segments.

It was found that the value of k decreases slowly with increasing temperature up to 350 ° C, beyond which there is a sharp drop until 400 ° C. Beyond about 400 ° C, k again shows a linear relationship with T, slowly decreasing with increasing temperature. The sharp drop in the k versus temperature plot is due to emissivity of the samples which is particularily significant in the case of metals above 350 ° C. Metals such as Sn, Bi and Pb give high values for lower temperatures, whereas Zn, Al and Cu give low k values above 400 ° C. The sudden drop in the value of k may be ascribed to the onset of radiative heat losses.

RESULTS AND DISCUSSION

Figure 3 shows simultaneous DTA–TG plots of the Pb–Bi and Zn–Al eutectic systems. Table 2 summarises the data of Fig. 3. For the Pb–Bi system the experimental value was found to be 4091 J (g atom)$^{-1}$ which is

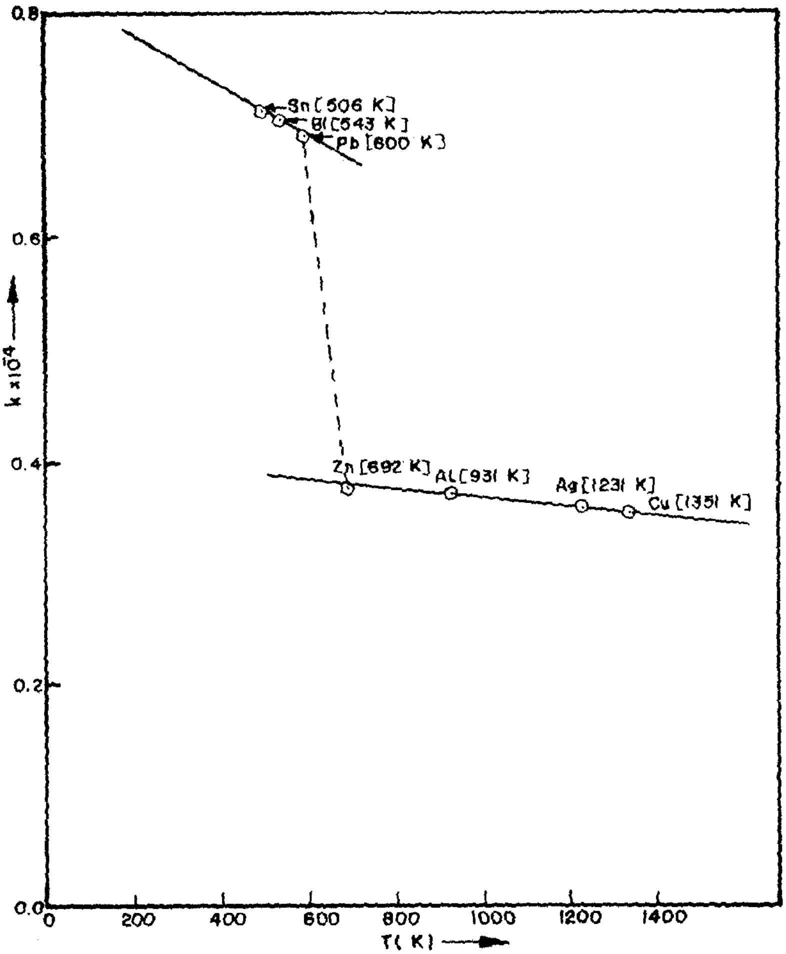

Fig. 2. Plot of *k* vs. *T* (K).

in close agreement with the calculated value of 4415 J (g atom)$^{-1}$ suggested by Tiwari et al. [6]. For the Zn–Al eutectic system, the experimental value was found to be 7766 J (g atom)$^{-1}$ which is close to the calculated value of 7976 J (g atom)$^{-1}$. Simultaneous DTA–TG plots for the Pb–Te eutectic system are shown in Fig. 4. The X-ray diffraction pattern for the Pb–Te alloy confirms the mutual solubility of the components. Table 3 summarises the data of Fig. 4. For Pb–Te eutectic compositions the heat of fusion is 1799 J (g atom)$^{-1}$.

CONCLUSION

The excellent agreement between the theoretical heat values for the Pb–Bi and Zn–Al eutectic systems and those obtained experimentally indicates that differential thermal analysis can be successfully used as a

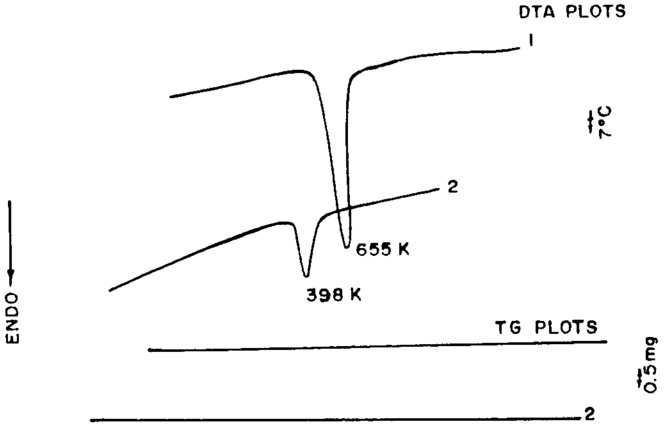

Fig. 3. Simultaneous DTA–TG plots for melting of: 1, Zn–Al eutectic; and 2, Pb–Bi eutectic systems.

TABLE 2

Heats of solidification of Pb–Bi and Zn–Al eutectic systems

Alloy system	M.P. (K)	DTA peak area (mg)	Calculated solidification value (J (g atom)$^{-1}$)	Experimental solidification value (J (g atom)$^{-1}$)
Pb–Bi (43.7 at.% Pb)	398	44	−4415	−4091 ± 4
Zn–Al (88.7 at.% Al)	655	10	−7976	−7766 ± 5

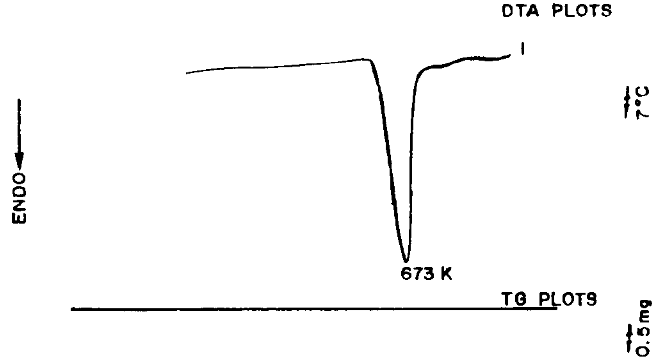

Fig. 4. Simultaneous DTA–TG plots for melting of Pb–Te eutectic system.

TABLE 3

Heat of solidification of Pb–Te eutectic systems

Alloy system	M.P. (K)	DTA peak area (mg)	Experimental solidification value (J (g atom)$^{-1}$)
Pb–Te (85.5 at.% Te)	673	14	-1799 ± 4

heat flux calorimeter for the measurement of heats of solidification of alloys. Conversion of DTA peak areas into heat values requires the use of an apparatus constant, which can be determined by relating peak areas to heats of fusion of known metals. An appropriate value of the instrumental constant may be derived for estimating heats of solidification of alloy systems, for which no thermodynamic data are available.

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