

## Note

### THE TECHNICAL PROBLEMS OF SAMPLE PAN AND BASE LINE IN DSC: AN EXAMPLE WITH Al–Mn RAPIDLY SOLIDIFIED ALLOYS

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(Received 24 October 1989)

In DSC the sample pan is used to encapsulate the sample and, thus, to avoid any contamination of the DSC detecting head. The choice of the nature of the sample pan in DSC is subject to some basic requirements, including (i) the absence of any chemical reaction with the sample and (ii) the achievement of a high heat transfer between the sample and the DSC thermosensors. For these reasons metals, such as aluminium, copper, gold or platinum, are generally used for the sample pan. Among these metals, aluminium is the most usual, but it melts at 660 °C and its use is not recommended above 500 °C. Above this temperature, graphite pans may be used with the advantage that graphite does not alloy with the more common metals. The major drawback of graphite sample-pans is that they cannot encapsulate the sample within the pan, the graphite cover over the sample remaining unattached. Thus, some sample motion on heating is unavoidable. Such motion frequently results from stress relief of pre-strained materials and always occurs when rapidly solidified alloys are heated. It is generally detected as a spurious heat effect or base-line drift on the corresponding DSC curves.

Thus, copper appears to be an attractive material, because of its high melting point (1063 °C), its high thermal conductivity and its high malleability which allows the sample to be kept in a secure position inside the encapsulating sample pan. Unfortunately, copper is highly reactive with some metals, even in the solid state. Several examples of the drawbacks of using copper for the sample pan in the investigation of rapidly solidified Al–Mn alloys are reported below. The procedure used to successfully eliminate these drawbacks is also described. This was achieved simply and reliably by inserting thin alumina (or graphite) discs above and below the sample in order to avoid any physical contact between the sample and the inner surfaces of the copper pan.

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The advantages of such a procedure are demonstrated below using rapidly solidified Al–Mn alloys containing 2.5, 6 and 14 at.% Mn. Rapid solidification of these alloys results in the formation of metastable phases: a supersaturated  $\alpha$ -Al(Mn) solid solution in the Al–2.5 at.%Mn rapidly solidified alloy and a mixture of  $\alpha$ -Al(Mn) with a quasi-crystalline icosahedral phase [1] in the rapidly solidified alloys containing 6 and 14 at.% Mn. These metastable phases decompose on heating into the equilibrium phases (Al + orthorhombic-Al<sub>6</sub>Mn) [2–4], and thus, whatever the Mn content, aluminium is always formed during decomposition of these alloys and can react with the copper pan; the lower the Mn content, the higher the volume fraction of Al.

A supplementary difficulty for the DSC investigation of rapidly solidified Al–Mn alloys is the small intensity of the heat effects evolved and the large temperature range over which they take place: from  $\approx 200$ – $300^\circ\text{C}$  up to the eutectic melting temperature at  $658^\circ\text{C}$  [5]. In these conditions, the drift of the instrumental base-line may be of the same order of magnitude as the heat effects due to the phase transitions.

The base-line drift typical of each type of sample-pan configuration was eliminated by following the procedure described below. It should be noted that this procedure is only valid for irreversible phase transitions. For each specimen, three successive runs were carried out between  $50^\circ\text{C}$  and the upper temperature limit of the experiment (here  $630^\circ\text{C}$ ) without any change in the experimental DSC conditions. Thus, the heat effect due to the phase transition on heating is detected during the first run (here referred to as “curve A”) superimposed on the drift of the instrumental base-line typical of the experiment. The last two runs (here referred to as “curve B” and “curve C”) are used to determine the instrumental base-line drift. Because all the experimental conditions are kept identical, curves B and C must be perfectly reproducible and must coincide. The differential energy ( $S - R$ ) is recorded for each run and the reference is kept the same for all runs ( $R_A = R_B = R_C$ ), therefore

$$(S_B - R_B) - (S_C - R_C) = (S_B - S_C) \quad (1)$$

where  $S$  is the sample energy and  $R$  is the reference energy. The phase transition evolved during run A is irreversible ( $S_B = S_C$ ) and, thus

$$(S_B - S_C) = 0 \quad (2)$$

A horizontal straight line is thus obtained as a reference line by subtracting curve C from curve B. Thus the heat effects occurring during run A can be obtained, in a similar way, by subtracting curve C from curve A

$$(S_A - R_A) - (S_C - R_C) = S_A - S_C \quad (3)$$

In this way, the contribution of the reference side of the DSC is completely eliminated. The final record ( $S_A - S_C$ ) is the differential energy between the

sample in the as-prepared state (run A) and in the crystallised state (run C) for the sample side of the DSC detecting head. This procedure was previously used to successfully determine the enthalpy relaxation in amorphous alloys [6] but no details were published.

A Perkin-Elmer differential scanning calorimeter (DSC-2C) connected to a 3600 Thermal Analysis Data Station was used for the experiments. The sample weight was  $\approx 10$  mg. The copper pans were previously annealed at  $700^\circ\text{C}$  for 2 min in the DSC detecting head in flowing purified argon. The alumina or graphite discs were 5 mm in diameter and  $< 150\ \mu\text{m}$  thick. A copper cover was put over the upper alumina (or graphite) disc and was then firmly pressed with the manual Perkin-Elmer press. The final thickness of the sample pan ready for the DSC experiment was  $\approx 1$  mm. Care was taken to obtain a flat bottom and, thus, good thermal contact with the DSC

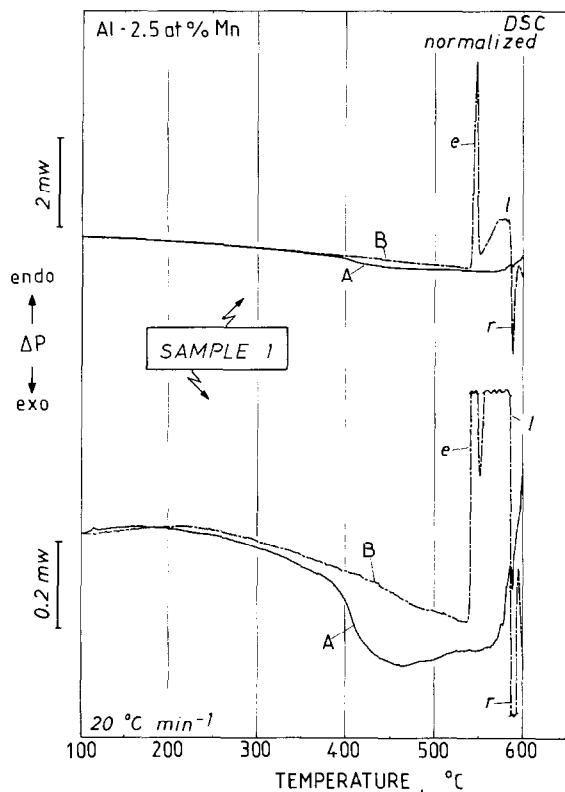


Fig. 1. Sample 1, rapidly solidified Al-2.5at.%Mn alloy. DSC curves obtained on heating the sample in direct contact with the copper pan; heating rate,  $20^\circ\text{C min}^{-1}$ ; upper temperature limit,  $600^\circ\text{C}$ . Curve A, first run; curve B, second run. The upper and lower curves are both representative of the same experiment but the sensitivity along the Y-axis for the lower curve is ten times greater than for the upper curve in order to enhance the exothermic effect below  $500^\circ\text{C}$ . The reactions referred to as *e*, *l* and *r* are interfering effects due to a reaction between the sample and the copper pan.

thermosensors. An identical configuration (without sample) was used as a reference.

An example of the interfering reactions observed when samples are heated up to 600°C without alumina or graphite protection discs is given in Fig. 1. Curve A is the direct curve obtained from the first run and curve B is the second run obtained after cooling at 320°C min<sup>-1</sup> from 600°C to room temperature and heating again. The small area starting from ≈ 350°C between curves A and B corresponds to the exothermic effect due to the decomposition of the supersaturated α-Al(Mn) solid solution—the phenom-

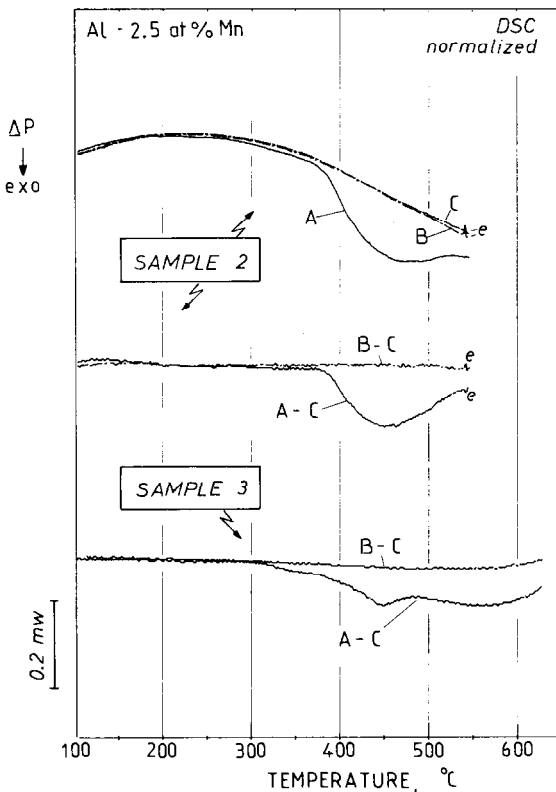


Fig. 2. Sample 2, rapidly solidified Al-2.5at.%Mn alloy. DSC curves obtained in the same conditions as sample 1, but with the upper temperature limit at 550°C. Curve A, first run; curve B, second run; and curve C, third run, with the same sample. The upper and lower curves obtained with sample 2 are both representative of the same experiment: curves A, B and C are the direct curves delivered by the data station; A-C and B-C are the curves obtained by subtraction of curve C from curves A and B respectively, in order to eliminate the instrumental base-line drift. Sample 3, rapidly solidified Al-2.5at.%Mn alloy. DSC curves obtained on heating the sample between protective graphite discs inserted inside the copper pan: heating rate, 5°C min<sup>-1</sup>; upper temperature limit, 630°C. A-C and B-C are the curves obtained by subtraction of curve C from curves A and B respectively, in order to eliminate the instrumental base-line drift.

enon of interest. In order to enhance this exothermic effect, the sensitivity along the  $Y$ -axis for the lower curve is ten times greater than for the upper curve.

Several intense, sharp endo- and exothermic effects, referred to as  $e$ ,  $l$  and  $r$ , appear on curve B. These phenomena are those which can be expected from the equilibrium Al–Cu system [7]. They result from the solid-state reaction which readily occurs between Al and Cu during the first heating and which is revealed by several discontinuities on curve A above  $550^\circ\text{C}$ . The eutectic melting at  $548^\circ\text{C}$  is clearly detected on curve B by the endothermic peak ( $e$ ), followed by the monovariant melting at  $\approx 580^\circ\text{C}$  ( $l$ ). Above this temperature the sharp exothermic peak ( $r$ ) indicates a strong, rapid reaction between the liquid phase which is formed and the copper pan. The phenomenon  $e$  is almost completely suppressed when the experiment is stopped at  $550^\circ\text{C}$ , as shown in Fig. 2 (sample 2).

When alumina or graphite protection discs are used, the Al–Mn alloys, even the Al-rich ones, can be heated up to near their melting point without any reaction with the copper crucible.

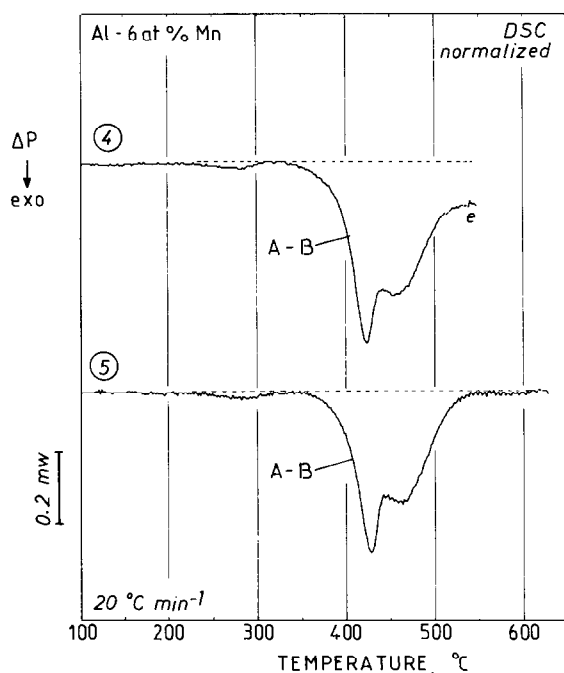


Fig. 3. Sample 4, rapidly solidified Al–6at.%Mn alloy. DSC curves obtained on heating the sample in direct contact with the copper pan: heating rate,  $20^\circ\text{C min}^{-1}$ ; upper temperature limit,  $550^\circ\text{C}$ . A–B is the curve obtained by subtraction of curve B from curve A in order to eliminate the instrumental base-line drift. Sample 5, rapidly solidified Al–6 at.%Mn alloy. DSC curves obtained on heating the sample between protective graphite discs inserted inside the copper pan: heating rate,  $20^\circ\text{C min}^{-1}$ ; upper temperature limit,  $630^\circ\text{C}$ .

A first example is given in Fig. 2 (sample 3) where the sample was heated up to 630°C at the rate of 5°C min<sup>-1</sup>. Note that the mechanism of precipitation on annealing rapidly solidified Al-2.5 at.%Mn is complex, as mentioned by Shechtman et al. [2]: as well as the formation of Al<sub>6</sub>Mn, the G-phase (Al<sub>12</sub>Mn) and the T-phase may also be formed. This might be an explanation for the rather complicated shape of the DSC curve obtained with sample 2.

A comparison of the DSC curves obtained on heating Al-6at.%Mn in copper crucibles with and without protective discs is given in Fig. 3. When no protective discs are used (sample 4), an exothermic effect on the high-temperature side is observed and remains uncompleted at 550°C. The use of protective discs (sample 5) reveals that this phenomenon is not specific to the sample but is due to a progressive exothermic reaction between the

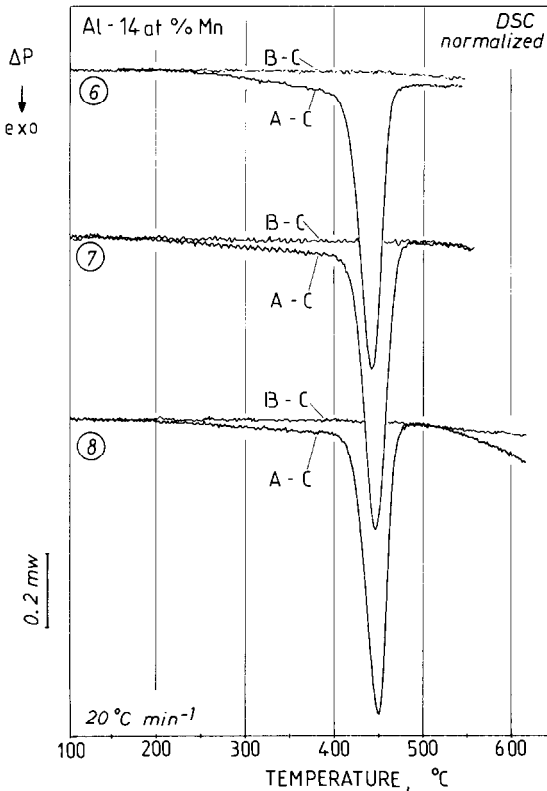


Fig. 4. Sample 6, rapidly solidified Al-14at.%Mn alloy. DSC curves obtained on heating the sample in direct contact with the copper pan: heating rate, 20°C min<sup>-1</sup>; upper temperature limit, 550°C. Sample 7, rapidly solidified Al-14at.%Mn alloy. DSC curves obtained on heating the sample between protective alumina discs inserted inside the copper pan: heating rate, 20°C min<sup>-1</sup>; upper temperature limit, 560°C. Sample 8, rapidly solidified Al-14at.%Mn alloy. DSC curves obtained on heating the sample between protective alumina discs inserted inside the copper pan: heating rate, 20°C min<sup>-1</sup>; upper temperature limit, 630°C.

sample and the pan, probably resulting from the formation of an Al–Cu solid solution.

A similar exothermic phenomenon was observed above  $\approx 470^\circ\text{C}$  with Al–14at.%Mn and no protective disc (sample 6), but with a smaller intensity than for Al–6at.%Mn. This difference in intensity is readily explained by the much smaller volume fraction of  $\alpha\text{-Al(Mn)}$  in Al–14at.%Mn. This exothermic peak disappears from the DSC curve obtained with sample 7, heated with protective discs up to  $560^\circ\text{C}$ : there is a perfect coincidence between the A – C and B – C curves. When the sample is heated up to  $630^\circ\text{C}$  with protective discs (sample 8), a third exothermic phenomenon appears above  $550^\circ\text{C}$  but its origin is different from that of the third peak obtained without protective discs. This effect is probably due to crystal growth of  $\text{Al}_6\text{Mn}$  obtained after the main exothermic peak. Note that the same DSC curve as that obtained with sample 6 was reported by Chen and Chen [8] but no experimental details were given.

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