

Short Communications

CONTRIBUTION TO THE STUDY OF THE Al–Zn PHASE DIAGRAM

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Calorimetric measurements in the Al–Zn system rule out the existence of an  $\alpha''$ -phase and of a second monotectoid reaction at 340<sup>o</sup>.

Two types of phase diagrams have been published for the Al–Zn system [1]; they differ in the presence or absence of the  $\alpha''$  phase and of two reactions, a monotectoid one at 340<sup>o</sup> and a peritectic one at 443<sup>o</sup> (Fig. 1). For the second monotectoid reaction, two different temperatures are proposed : 275<sup>o</sup> or 236<sup>o</sup> [2]. The  $\alpha$ -phase is face-centred cubic and the  $\beta$ -phase hexagonal compact; the phases  $\alpha'$  and  $\alpha''$  are also fcc and differ in their lattice parameters by as little as 0.001 Å [3]. It is believed that due to this very minor difference the transformation at 340<sup>o</sup> cannot be observed, but many authors still use the diagram presented by Fig. 1 [4].

### Experimental

DSC studies have been carried out on an Al–Zn alloy (60 weight %) prepared from high purity elements. Chemical analysis has given the following: Zn 60 ± 2 %; Fe < 0.005 %; Si < 0.005 %; Cu < 0.001 %. A Du Pont thermal analyser model 990, has been used. Experiments were carried out from room temperature to 400<sup>o</sup> at heating rates between 1 deg/min and 50 deg/min. For slower heating and cooling rates and for isothermal studies at 30<sup>o</sup>, a Tian-Calvet microcalorimeter has been used.

### Results and discussion

Figure 2 shows the heat release which accompanies the isothermal ageing of the alloy homogenised at 400<sup>o</sup>, quenched into iced water and introduced into the microcalorimeter isothermed at 30<sup>o</sup>. A very strong initial heat release characterises the spinodal decomposition of the supersaturated solid solution and is superseded by a second one which rises to a maximum before slowly decaying over several days; the latter

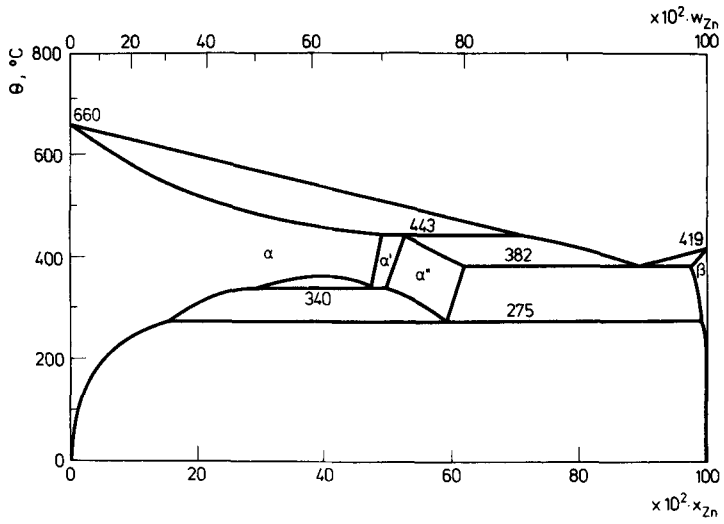


Figure 1 Phase diagram of the system Al-Zn according to [1]

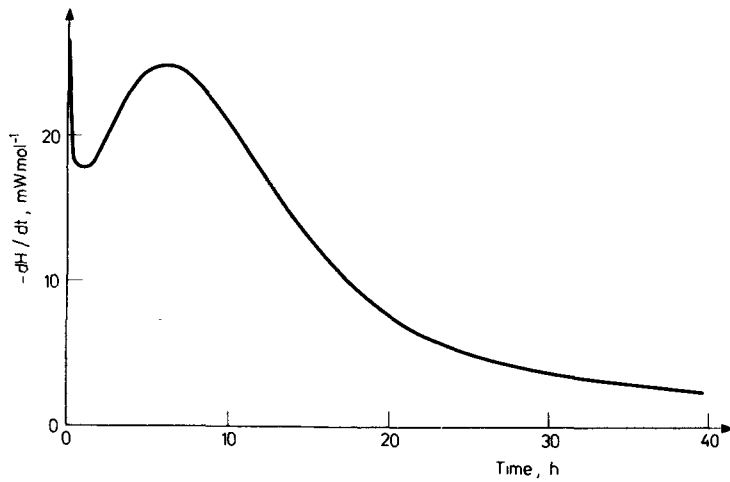
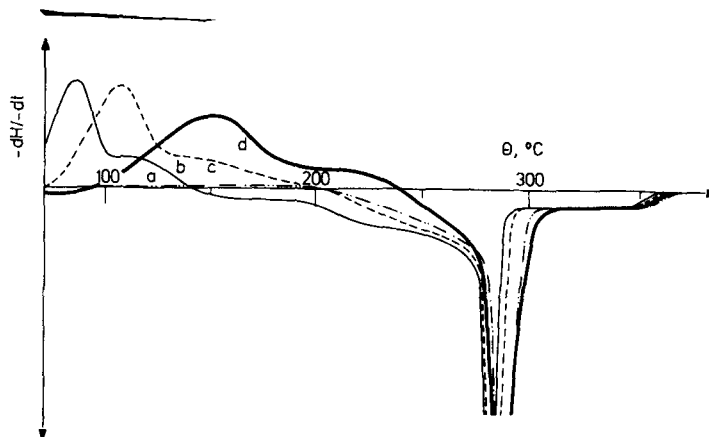


Figure 2 Heat release accompanying the ageing of an Al-60% Zn alloy at 30°C



**Figure 3** DSC curves of an Al-60 % Zn alloy. Cooled from 400<sup>o</sup> at 20 deg min<sup>-1</sup> and aged at room temperature for 1 day: curve (a) at a heating rate of 10 deg min<sup>-1</sup>. Water-quenched from 400<sup>o</sup>: curve (b) at a heating rate of 2 deg min<sup>-1</sup>; curve (c) at 5 deg min<sup>-1</sup>; curve (d) at 20 deg min<sup>-1</sup>

corresponds to the nucleation and growth of the  $\beta$ -phase starting from grain boundaries, according to the competing discontinuous reaction mechanism [5-7].

After rapid cooling from 400<sup>o</sup> and ageing at room temperature for 24 hours, an important amount of  $\beta$ -phase is present [6]. Upon heating the alloy in this precipitation state at a rate of 10 deg min<sup>-1</sup> in the DSC apparatus, curve (a) of Fig. 3 is obtained. The partial dissolution of the  $\beta$ -phase gives rise to the endothermic heat effect above 200<sup>o</sup> and is followed by a very strong one characterising the monotectoid reaction  $\alpha + \beta \rightarrow \alpha + \alpha'$ . The following portion of the thermal curve which corresponds to the crossing of the  $(\alpha + \alpha')$  region is horizontal, as the alloy composition under study divides the miscibility gap into two nearly symmetrical parts. The solid solution region is rejoined at 364-369<sup>o</sup>. No indication of a second monotectoid reaction around 340<sup>o</sup> can be seen.

If the Al-60 % Zn alloy is homogenised at 400<sup>o</sup>, quenched into water and again heated up to 400<sup>o</sup> at different heating rates within the DSC apparatus, the decomposition of the supercooled solid solution takes place during the experiment and this is seen as two exothermic reactions (Fig. 3, curve (b): 2 deg min<sup>-1</sup>; curve (c): 5 deg min<sup>-1</sup>; curve (d): 20 deg min<sup>-1</sup>). The two peaks reflect the formation of metastable  $\alpha$ -type phases which transform to the stable  $\beta$ -phase. The following endotherm is due to the partial dissolution of the  $\beta$ -phase, as in curve (a); this is followed by the very pronounced monotectoid reaction. The curves (b), (c) and (d) resemble closely those obtained by Ciach et al. [8] during isochronal heating of the same alloy using dilatometric measurements. X-ray studies showed that they correspond to the formation and decomposition of the  $\beta$ -phase.

Special attention is drawn to the important exotherm observed during the iso-

thermal decomposition of the supercooled  $\alpha'$ -phase and the equally strong endotherm accompanying the formation of the  $\alpha'$ -phase from the  $\alpha$ - and  $\beta$ -phases during heating. It is believed that the energy necessary to transform zinc from the hexagonal to the face-centred cubic structure (in  $\alpha'$ -phase) is responsible for this.

When using a heating rate of  $10 \text{ deg h}^{-1}$ , the monotectoid transformation starts at  $275^\circ$ , and at  $277^\circ$  at a rate of  $0.5 \text{ deg min}^{-1}$ . Previous DTA measurements of Simerksa et al.[9] have shown the monotectoid reaction at  $277.5 \pm 0.5^\circ$ .

Increasing heating rates shift the curves to higher temperatures, as one moves away from equilibrium conditions. Decreasing the rate of cooling in experiments over the range  $400^\circ$  to room temperature results in displacement of the monotectoid reaction to higher temperatures, as the  $\beta$ -phase grows to larger dimensions during the long cooling periods and thus becomes more stable. The general form of the present curves resembles to that published by Hirano [10] on the same alloy composition, but the interpretation is different.

The curves obtained during the cooling of the solid solution from  $400^\circ$  at very slow rates ( $< 10 \text{ deg h}^{-1}$ ) show two exotherms; they correspond to the precipitation of some metastable  $\alpha'$ -phase starting around  $330^\circ$  and the monotectoid transformation  $\alpha + \alpha' \rightarrow \alpha + \beta$  below  $260^\circ$ . DSC curves obtained at faster cooling rates ( $20\text{--}80 \text{ deg min}^{-1}$ ) have been published recently by Vijayalakshmi et al.[11]. According to Simerksa et al.[12], the formation of the metastable phase  $\alpha'_R$  begins at  $328.5 \pm 1.5^\circ$ , when cooling an Al–58.8 % Zn alloy at  $2 \text{ deg min}^{-1}$ . Neutron diffraction experiments of Schwahn and Schmatz [13] have assessed the coherent critical temperature for rapid decomposition of the supersaturated solid solution to be  $323 \pm 0.5^\circ$ ; this highest point of the spinodal appears at 61.9 % Zn.

In summary, the present calorimetric investigations rule out the existence of an  $\alpha''$ -phase and of a second monotectoid reaction at  $340^\circ$ . These findings are in accord with ternary phase diagrams involving the Al–Zn system [14]. The very strong heat effect which accompanies the transformation  $\alpha_{\text{fcc}} + \beta_{\text{hex}} \leftrightarrow \alpha'_{\text{fcc}}$  is probably due to the transformation energy of hexagonal zinc to a fcc structure, in which form it exists in the region above the miscibility gap.

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