

and

$$\frac{(kt)_{T_{f_2}}}{(kt)_{T_{f_1}}} = \frac{(k')_{T_{f_2}}}{(k')_{T_{f_1}}} = \left( \frac{3 + 5^{1/2}}{3 - 5^{1/2}} \right)^{1/3} \quad (8)$$

respectively, where  $\Delta T$  is the height of a point on the DTA curve (see Fig. 1 [1]).

Taking the logarithms of Equations 7 and 8 the proposed relations [1] can be derived:

$$\frac{E}{R} \left( \frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 1.59 \quad (9)$$

and

$$\frac{E}{R} \left( \frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 0.64 \quad (10)$$

where  $E$  is the activation energy for crystal growth and  $R$  is the gas constant.

It is evident that no terms, as suggested by Tang [2], were omitted. Finally, concerning the approximation of the  $m$ th temperature derivative of  $(kt)$ ,

$$\frac{d^m (kt)}{dT^m} \approx \left( \frac{E}{RT^2} \right)^m (kt) \quad (11)$$

it is assumed that in deriving Equations 4 and 5 from Equations 1 and 2, its validity is based, as properly remarked by Tang, on the assumption

that  $E/RT \gg 4$ . This assumption represents a limit to the general applicability of the method to solid state reactions, but Equation 11 can be considered adequate in glass devitrification owing to the high activation energy values.

## References

1. A. MAROTTA, S. SAIELLO, F. BRANDA and A. BURI, *J. Mater. Sci.* 17 (1982) 105.
2. T. B. TANG, *ibid.* 17 (1982) 3066.
3. A. MAROTTA and A. BURI, *Thermochim. Acta* 25 (1978) 81.
4. K. MATUSITA and S. SAKKA, *Phys. Chem. Glasses* 20 (1979) 81.
5. K. MATUSITA and S. SAKKA, *Bull. Inst. Chem. Res.* 58 (1981) 159.

Received 19 March

and accepted 23 April 1982

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## Comments on "The influence of Mg contents on the formation and reversion of Guinier–Preston zones in Al–4.5 at% Zn–xMg alloys

The aim of this communication is to present calorimetric studies which provide some comments on the recent publication of Honyek *et al.* [1].

We shall first report some measurements on binary Al–Zn alloys (total impurity content < 0.01%). Fig. 1 shows thermal curves obtained on heating alloys containing 5.8–11.9 wt% (2.5–5.3 at%) Zn at a rate of  $\frac{1}{3}^\circ\text{C min}^{-1}$ ; these alloys have been homogenized at  $400^\circ\text{C}$  over 6 h, quenched in iced water and aged for 1 day at room temperature. One or two endothermic peaks accompany the dissolution of the metastable GP-zones formed during ageing. In the case of the 10.1% (4.4 at%) Zn alloy, the dissolution is complete at around  $145^\circ\text{C}$ , whereas in equilibrium

studies, zones may not exist above  $110^\circ\text{C}$  [2] or  $120^\circ\text{C}$  [3]. This retardation of the dissolution process is quite normal under dynamic conditions; it increases with increasing scanning rate and attains a value of  $70\text{--}80^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ , as seen from Fig. 2. Moreover, the proportion of the peaks changes with heating rate. It is preferable to use small rates as far as possible, if conclusions on the equilibrium behaviour are to be drawn.

Fig. 2 is taken from [4] which describes the influence of homogenization temperature before water-quenching and ageing on the mean sizes of metastable phases in the Al–10.1% Zn alloy. Two endothermic peaks are observed with alloys quenched from  $400$  to  $525^\circ\text{C}$  and aged for 4 days at room temperature, three on alloys cooled from  $275^\circ\text{C}$  followed by ageing. Electron microscopic observations [5] have allowed these peaks to be attributed to the dissolution of spherical GP-zones, of ellipsoidal GP-zones and of the rhombohedral

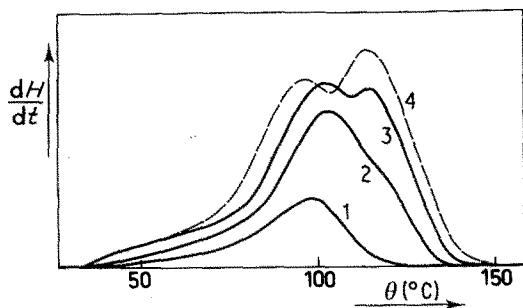


Figure 1 Calorimetric curves obtained on heating alloys quenched from 400 to 0°C and aged for 24 h at room temperature at a rate of  $\frac{1}{3}$  C min<sup>-1</sup>. 1, Al-5.8% Zn; 2, Al-8.2% Zn; 3, Al-10.1% Zn; 4, Al-11.9% Zn.

$\alpha'_R$ -phase (only present after quenching from 275°C). No clear distinction may be drawn between these coherent phases from an energetic point of view, the difference being mainly one of shape and dimension [6]. A bimodal size distribution is also present in step-quenched alloys and speculations as to its origin have been advanced [7]. The thermal curve obtained by Suzuki *et al.* on an aged Al-5 at % Zn alloy (Fig. 4a of [8]) shows faintly, but unadmittedly, the presence of a second (in fact, first) peak; two peaks are clearly discerned in the case of Al-Zn-Mg alloys and explained by the formation of two types of GP-zones.

DSC-measurements performed at a rate of 20°C min<sup>-1</sup> have been published [9] on an Al-5% (2.1 at %) Zn-1.1% (1.3 at %) Mg alloy. In Fig. 3, the influence of homogenization temperature is reproduced: it determines the amount of metastable and stable phases precipitated during the

ageing treatment (1 day at room temperature after water-quenching) and the DSC-scan. The dissolution of GP-zones gives rise to the first peak which is not very symmetrical. Smaller scanning rates increase all exothermal and endothermal peaks except the first endothermal one and let them appear at lower temperatures; the curves become increasingly complicated and take the shape represented by Fig. 4 ( $\frac{1}{3}$ ° C min<sup>-1</sup>). Above 130°C, the same curve appears independent of the heat-treatment employed (homogenization temperature, quenching rate, ageing  $\leq 40^\circ$  C followed or not by a short reversion treatment at 200 or 230°C) and resembles closely those published by Honyek *et al.* [1] on room temperature-aged Al-4.5 at % Zn-(1-3) at % Mg alloys examined at 40°C min<sup>-1</sup>. It is concluded that the lower the concentration of the alloy, the slower the heating rate has to be in order to show the main precipitation reactions. When the heating rate is too high to allow sufficient GP-zone production, the precipitation of Zn and Mg is governed by vacancy-rich clusters (VRC). This explains why, in Fig. 4, the absence of VRC after air cooling has no influence, whereas step-quenching suppresses any precipitation at 20°C min<sup>-1</sup> in Fig. 1 of [10].

Calorimetric measurements [9-11] have yielded indirect evidence for the presence of VRC in the ternary alloy quenched to low temperatures; direct evidence has been furnished recently by Dlubek *et al.* [12] using a positron annihilation technique. The cluster density depends on the quenching and ageing conditions (homogenization temperature, quenching rate, ageing time and temperature), in

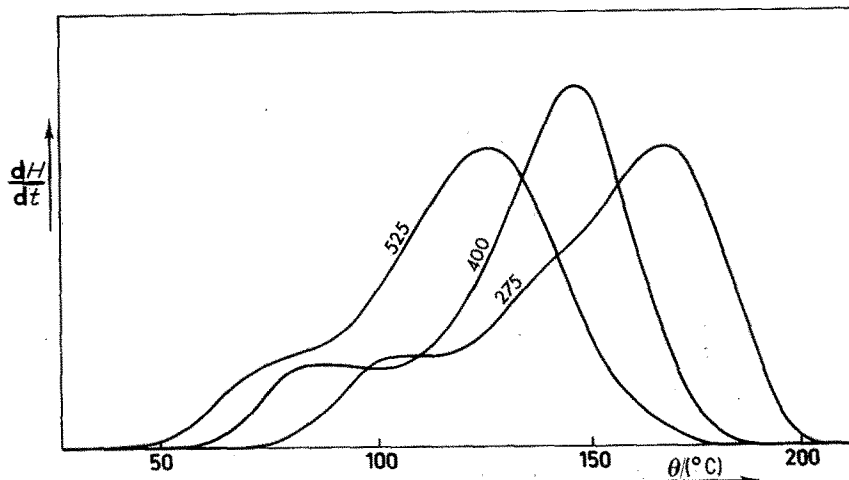


Figure 2 DSC-curves obtained at 20°C min<sup>-1</sup> on an Al-10.1% Zn alloy quenched from the homogenization temperatures indicated to 0°C and aged at room temperature for 4 days.

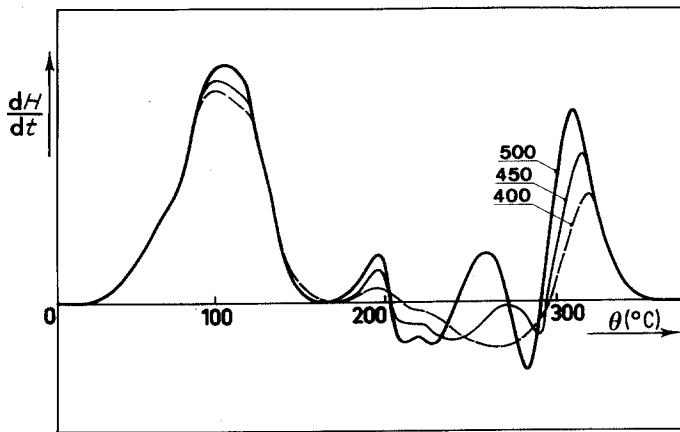


Figure 3 DSC-curve, at  $20^{\circ}\text{Cmin}^{-1}$ , on an Al-5%Zn-1.1%Mg alloy quenched from the temperatures indicated and aged at room temperature for 1 day.

agreement with [13]. Dlubek *et al.* have identified the VRC with the GP-zones. We do not share this point of view, as the kinetics of later GP-zone formation is independent of the quenching conditions (see [9], for example).

In a calorimetric study [14] of the influence of a reversion treatment on the new precipitation, it has been found that the formation of more stable phases sets in already during the GP-zone reversion, which is in accord with [1]. Furthermore, the VRC can be significantly reduced during the reversion, whereas at room temperature only a small loss of VRC is observed (see Fig. 4 in [9]).

With respect to phase identification by TEM-SAD shown in [1] we wish to point out that due

to the crystallographic orientation relations between the precipitates  $\eta'_2, \eta_{1,2,4}$  and the matrix described in [15], the diffraction patterns sketched in Fig. 5 should follow. It seems to be a very delicate operation to identify the phases by DFM, because of the close vicinity of various diffraction spots. This holds especially for the conclusion drawn by Honyek *et al.* [1] with respect to heterogeneously nucleated  $\eta'$ -precipitates; furthermore, we found enhanced  $\eta_4$ -nucleation around vacancy sinks (dislocations, etc.). Our TEM results reveal the simultaneous existence of rather similar precipitates which give rise to overlapping exo- and endothermal effects in a DSC-measurement.

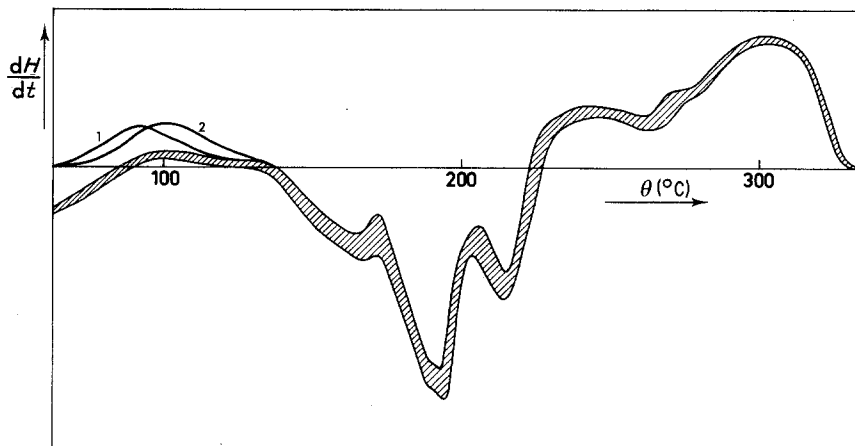


Figure 4 Calorimetric curves obtained at  $\frac{1}{3}^{\circ}\text{Cmin}^{-1}$  on an Al-5%Zn-1.1%Mg alloy subjected to the following heat-treatments:

- 2 h/400 or 500°C  $\rightarrow$  0°C
- 400°C  $\rightarrow$  air cooling to room temperature
- 400°C  $\rightarrow$  0°C  $\rightarrow$  3 min/200 or 230°C
- 1, 400°C  $\rightarrow$  0°C  $\rightarrow$  24 h/room temperature
- 2, 400°C  $\rightarrow$  0°C  $\rightarrow$  24 h/40°C.

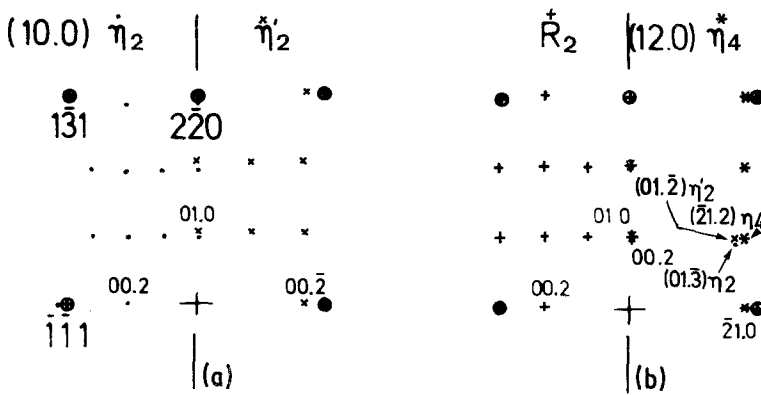
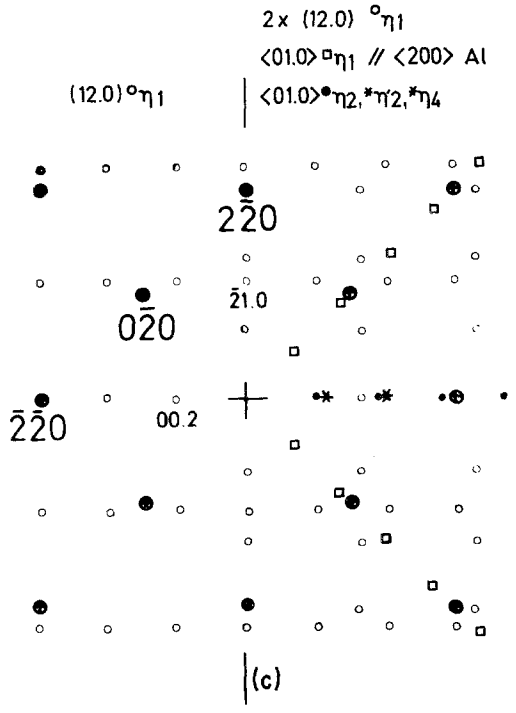


Figure 5 Constructed diffraction diagrams: (a)  $\eta_2$  and  $\eta'_2$ ; (b)  $R_2$  and  $\eta_4$  with inserted combinations around  $(01.2)\eta'_2$ , all for  $\langle 112 \rangle$  Al-beam direction (c)  $\eta_1$  patterns for  $\langle 001 \rangle$  Al-beam direction and corresponding additional  $\eta_1, \eta_2, \eta'_2, \eta_4$ -reflections.



7. A. ZAHRA and C. Y. ZAHRA, *Phys. Stat. Sol.* **A68** (1981) 141.
8. H. SUZUKI, M. KANNO and K. FUKUNAGA, *Keikinzoku* **22** (1972) 286.
9. A. ZAHRA, C.Y. ZAHRA, M. LAFFITTE, W. LACOM and H. P. DEGISCHER, *Z. Metallkde.* **70** (1979) 172.
10. W. LACOM, H. P. DEGISCHER, A. ZAHRA and C. Y. ZAHRA, *High Temp. High Press.* **12** (1980) 54-59.
11. A. ZAHRA, C. Y. ZAHRA, W. LACOM and H. P. DEGISCHER, *Mém. Sci. Rev. Mét.* **78** (1981) 17.
12. G. DLUBEK, O. BRÜMMER, P. HAUTOJÄRVI and J. YLI-KAUPPILA, *Phil. Mag.* **A44** (1981) 239.
13. H. LÖFFLER, E. KORNGIEBEL and R. GERLACH, *Cryst. Res. Technol.* **16** (1981) 475.
14. W. LACOM, H. P. DEGISCHER, A. ZAHRA and C. Y. ZAHRA, to be published.
15. H. P. DEGISCHER, W. LACOM, A. ZAHRA and C. Y. ZAHRA, *Z. Metallkde.* **71** (1980) 231.

**References**

1. G. HONYEK, I. KOVACS, J. LENDVAI, NG-HUY-SINH, T. UNGAR, H. LÖFFLER and R. GERLACH, *J. Mater. Sci.* **16** (1981) 2701.
2. T. SATO, Y. KOJIMA and T. TAKAHASHI, *Trans. Jap. Inst. Met.* **20** (1979) 475.
3. J. M. PELLETIER, J. MERLIN and R. BORRELLY, *Mater. Sci. Eng.* **33** (1978) 95.
4. A. ZAHRA, C. Y. ZAHRA and M. LAFFITTE, *Z. Metallkde.* **70** (1979) 669.
5. H. P. DEGISCHER, C. Y. ZAHRA and A. ZAHRA, *ibid.* (1982) in press.
6. A. ZAHRA, C. Y. ZAHRA and J. C. MATHIEU, *ibid.* **71** (1980) 54.

Received 17 February  
and accepted 4 March 1982

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