

DSC EXAMINATION OF ALLOYS

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ABSTRACT

The formation and thermal dissolution of dispersed particles was studied in aluminium alloys. It was found that only high heating rates ($80^{\circ}\text{C min}^{-1}$) could provide DSC curves characteristic of the phase structure of the samples. The kinetic evaluation of the DSC curves was carried out by least squares curve fitting. In this way reasonable kinetic parameters and reliable peak resolution could be obtained for the overlapping peaks.

INTRODUCTION

The formation of dispersed particles (second phases and GP zones) may be of great importance in hardening alloys. In several cases the usual measurement methods of the metallurgy cannot provide sufficient information on these particles. However, thermoanalytical investigations (DTA and DSC) may be useful in these cases, as well. The DTA and DSC have proved suitable for the determination of the precipitation sequence^{1–7} as well as for the study of the dissolution kinetics^{8–15}.

Based on the DSC study of a large number of differently heat-treated aluminium alloys, the following questions will be discussed in the present paper:

- (i) the choice of the heating rate and baseline in the DSC measurements;
- (ii) the least squares kinetic evaluation of the overlapping DSC peaks;
- (iii) the discussion of the resulted kinetic parameters.

The results having only metallurgical interest will be published elsewhere¹⁶.

MATERIALS

We have applied the presented method to a wide variety of Al alloys, including Al–Fe–Si, Al–Mg–Si, Al–Zn–Mg and Al–Zn–Mg–Cu alloys. The examples given in this paper belong to Al–Zn–Mg alloys containing Fe and Si impurities. To study

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the precipitation processes in the hardening, the examined samples were subjected to different heat treatment procedures. The heat treatment carried out on Al–Zn–Mg alloys consisted of the following steps:

- (i) homogenization at 470°C during 30 min and quenching in room temperature water;
- (ii) storage at room temperature for 7 days;
- (iii) preheating at 120°C during 3 h;
- (iv) 3 h of final heat treatment at a temperature chosen between 160 and 320°C.

The disc-shaped samples had a diameter of 6 mm and a thickness of 1.5 mm. The reference samples in the measurements were discs of the same size made of high purity (99.999%) aluminium.

DSC MEASUREMENTS

The measurements were carried out in a Perkin-Elmer DSC-2 device. The heating rate was chosen as high as possible to ensure that mainly the dissolution of the particles took place during the measurements. This method could provide DSC curves characteristic of the phase structure of the samples before the measurements. The effect of the heating rates was checked in the following two ways.

(i) A part of the samples was examined at several heating rates (4, 20, 40 and 80°C min⁻¹). At lower heating rates (at 4 and 20°C min⁻¹) exotherm peaks appeared on the curves, indicating the existence of undesired side reactions. At higher heating rates (at 40 and 80°C min⁻¹) these exotherm peaks disappeared.

(ii) After achieving 500°C the samples were quickly recooled in the DSC and the measurements were repeated. At higher heating rates no peaks were observed in the repeated measurements, indicating that the particles had fully dissolved during the first measurements without forming new phases. Regarding the Kopp–Neumann rule¹⁷ these second DSC curves were accepted as baselines.

Thus the highest heating rate we could apply, 80°C min⁻¹, was chosen. Regarding the thinness of the samples (1.5 mm), the small reaction heats and the good heat conductivity of the aluminium alloys, there was no danger of significant thermal lag or temperature gradient in the samples. We checked this factor experimentally by repeating a few measurements with samples of different thickness. The variation of the thickness between 1.5 and 0.45 mm has not significantly affected the shapes and positions of the DSC peaks.

For the numerical calculations the DSC curves were digitized in equidistant t_i points by a HP 9864A digitizer. The $t_i - t_{i-1}$ increments were 3 sec.

KINETIC EVALUATION

Let x_j be the molar conversion of the j th reaction (i.e. the dissolved fraction of reactant j) and let us suppose that x_j satisfies the following equation

$$dx_j/dt = A_j e^{-E_j/RT} f(x_j) \quad (1)$$

where A_j , E_j and $f(x_j)$ are the pre-exponential factor, the energy of activation and a function associated with the mechanism, respectively. For dissolution reactions $f(x_j)$ should be monoton decreasing, thus it can be approximated in the usual way

$$f(x_j) = (1 - x_j)^n \quad (2)$$

If eqns. (1) and (2) are valid, the value of n can be determined from the degree of asymmetry of the DSC peaks^{18, 19}. However, it is rather difficult to prove the validity of eqns. (1) and (2). But the validity of these equations can be accepted if least squares curve fitting is carried out, the theoretical curves are close to the experimental ones and the obtained parameters are reasonable.

Let $q(t)$ stand for the heat adsorbed by the dissolution reactions up to time t . Then dq/dt corresponds to the difference between the DSC curve and the baseline. dq/dt is a linear combination of the partial reaction rates

$$dq/dt = \sum c_j dx_j/dt \quad (3)$$

where the c_j coefficients are the initial amounts of the reactants multiplied by the reaction heats. (In other words, the c_j 's are the areas below the peaks of the dq/dt curve.) Using the least squares method we choose those A_j , E_j and c_j values which minimize the following sum

$$S = \sum_{i,j} \left[\frac{dq}{dt}(t_i) - c_j \frac{dx_j}{dt}(t_i) \right]^2 \quad (4)$$

Here t_i stands for the points of time in which digitized dq/dt values were taken and the dx_j/dt functions are calculated by solving differential equation (1). The details of the calculation can be found in ref. 20.

RESULTS

Depending on the composition and heat treatment of the samples, the DSC curves have shown peaks differing in size, number and position.

In each case when the peaks were sufficiently separated, the degree of asymmetry clearly indicated that $n \approx 1$. To obtain more evidence, some of the least squares calculations were carried out using different n values, as is shown in Figs. 1 and 2. These calculations have also proved that $n \approx 1$. Thus the $n = 1$ value was accepted in further calculations. In this way a good fit was obtained in each of our nearly 160 kinetic calculations. The deviation between the observed and calculated curves was less than the experimental errors. Typical peak resolution and curve fitting are shown in Figs. 3, 4 and 5.

To check the reliability of the calculations, a part of the calculations was repeated varying the position of the base line within the range of the experimental uncertainty. Other calculations were repeated limiting the permitted range of the E_j parameters arbitrarily to $E_j \geq 28 \text{ kcal mole}^{-1}$ ($28 \text{ kcal mole}^{-1}$ is an approximative value for the activation energy of the diffusion of alloying elements in alumi-

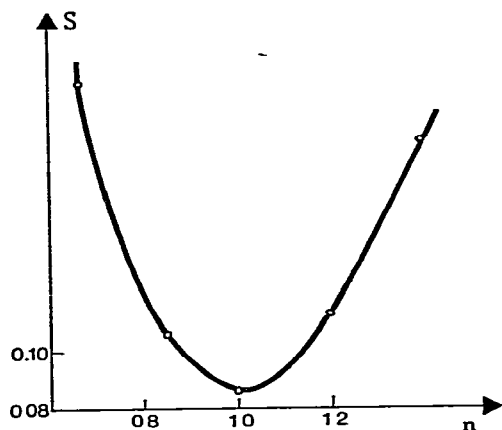


Fig. 1. Dependence of the value of the least squares sum, S , on the formal reaction order.

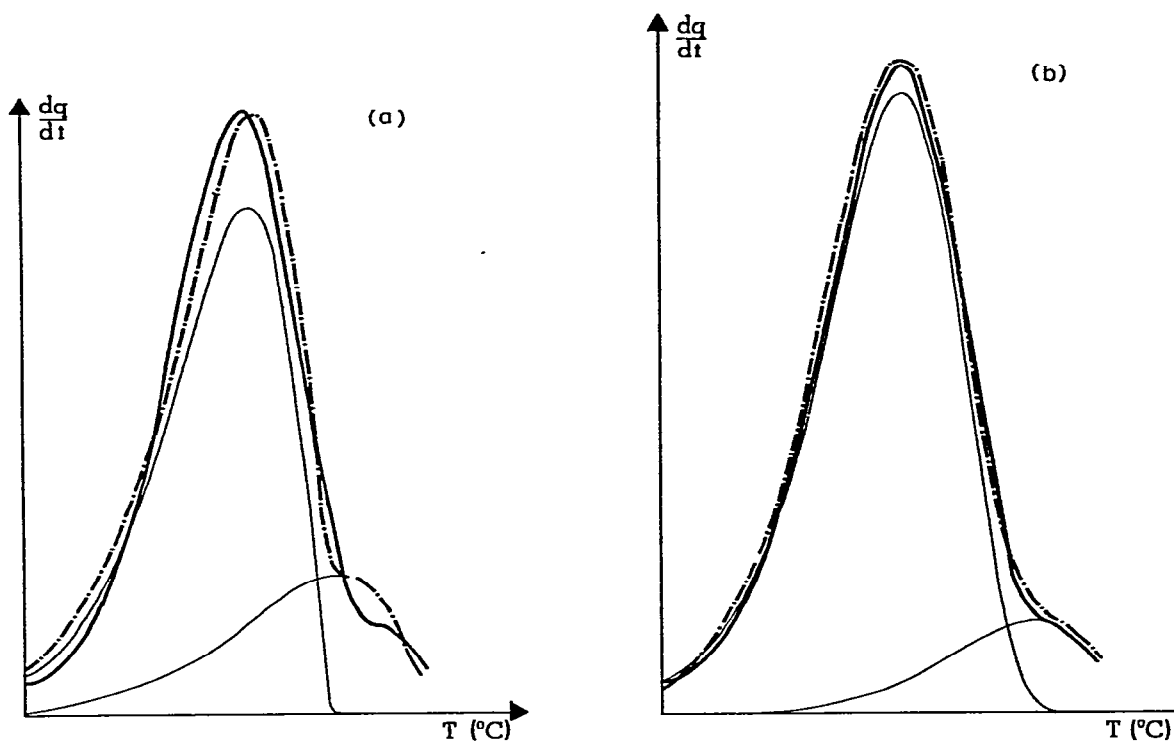


Fig. 2. Evaluation of moderately overlapping peaks at (a) $n = 2/3$ and (b) $n = 1$. — and —.— correspond to the observed and the calculated dq/dt curves, respectively; — represents the calculated partial curves ($c_j dx_j/dt$).

nium). These test calculations have shown that the highly overlapping peaks (e.g. the peaks in Fig. 6) can be approximated by theoretical curves in more than one way.

The c_j values belonging to a series of Al-Zn-Mg alloys are shown in Fig. 7. Here the abscissa shows the temperature of the final heat treatment. The corresponding E_j and A_j values as well as the temperature of the DSC peak maxima and the numerical values of the c_j parameters are given in Table 1. The data belonging to

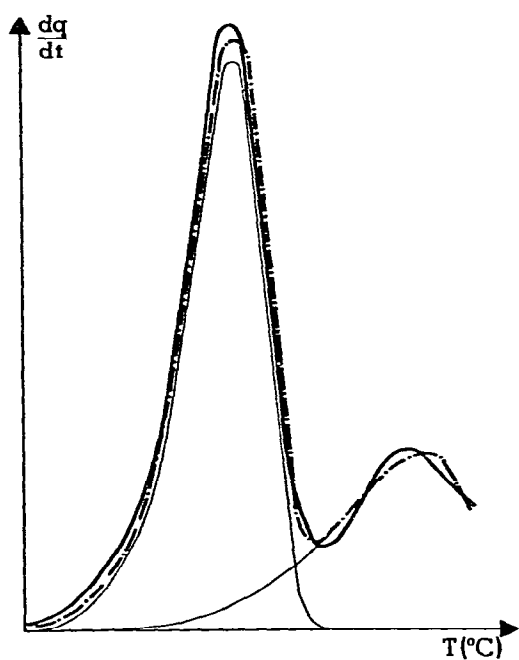


Fig. 3. Peak resolution and curve fitting in the case of two overlapping peaks.

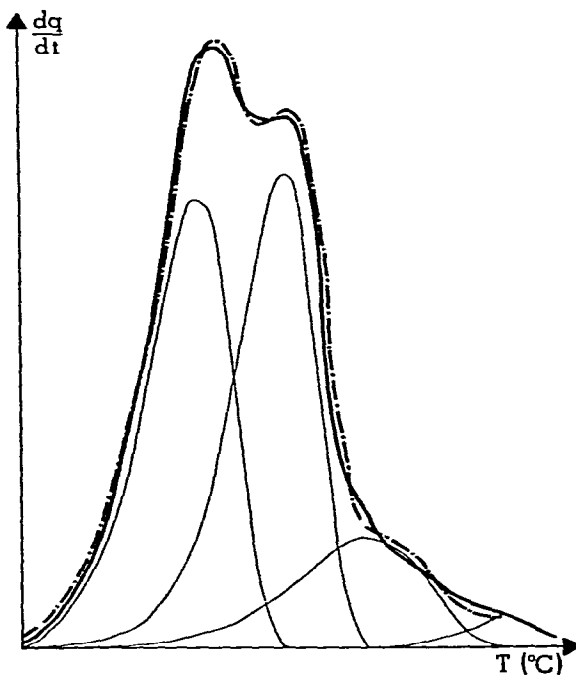


Fig. 4. Peak resolution and curve fitting in the case of four overlapping peaks.

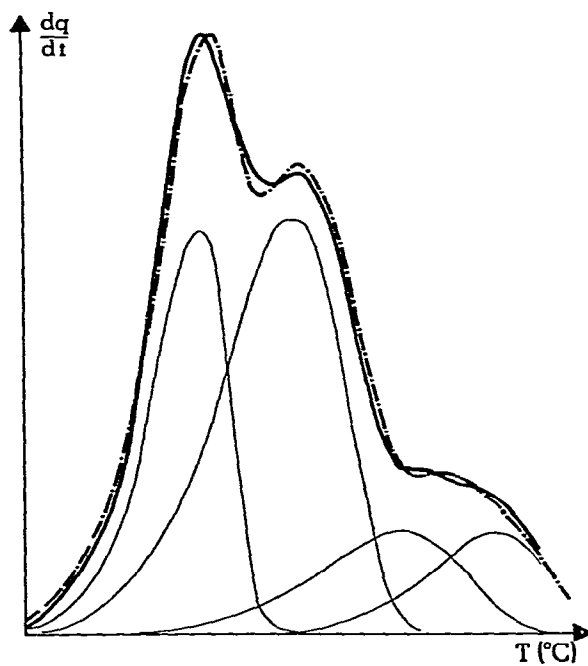


Fig. 5. Peak resolution and curve fitting in the case of four overlapping peaks.

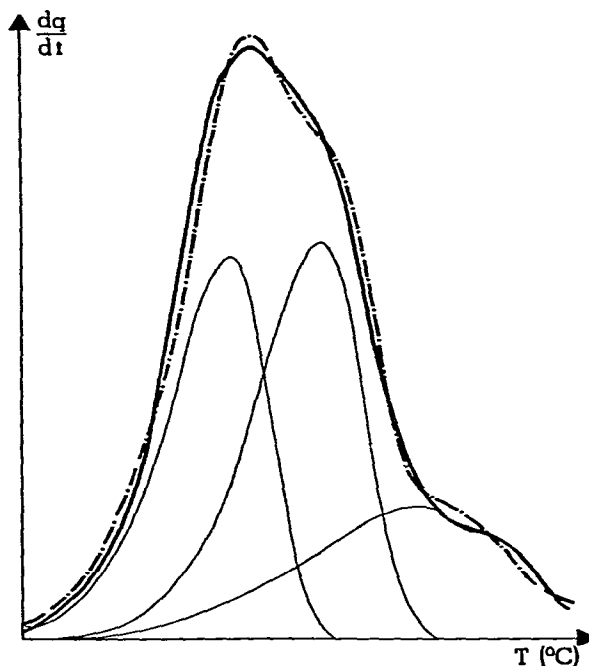


Fig. 6. Peak resolution and curve fitting in the case of highly overlapping peaks.

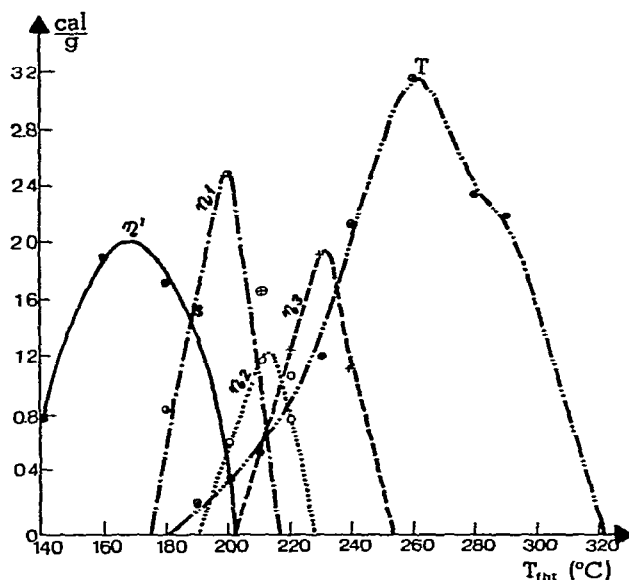


Fig. 7. Dependence of the obtained c_j parameters on the temperature of the final heat treatment, T_{fht} . Each c_j vs. T_{fht} curve is drawn with a different type of line. The symbols η' , η_1 , η_2 , η_3 and T denote the phases of the dissolving particles. At $T_{fht} = 210^\circ\text{C}$ the DSC peaks of phases η_1 and η_3 coincided. Their joint area is denoted by the symbol \oplus .

TABLE 1

CALCULATED PARAMETERS FOR Al-Zn-Mg ALLOYS

T_{fht} and T_{max} are the temperatures of the final heat treatment of the samples and the DSC peak maxima are given, respectively.

| Phase | T_{fht} ($^\circ\text{C}$) | T_{max} ($^\circ\text{C}$) | c_j (cal g^{-1}) | E_j (kcal mole^{-1}) | $\text{Log } A_j$ (sec^{-1}) |
|----------|-----------------------------------|-----------------------------------|----------------------------------|--------------------------------------|--|
| η' | 160 | 268 | 1.91 | 35 | 13.0 |
| | 180 | 264 | 1.75 | 32 | 11.8 |
| | 190 | 267 | 1.59 | 33 | 10.3 |
| η_1 | 180 | 300 | 0.82 | 29 | 9.8 |
| | 190 | 307 | 1.52 | 29 | 9.8 |
| | 200 | 307 | 2.49 | 24 | 7.6 |
| η_2 | 200 | 274 | 0.59 | 45 | 17.0 |
| | 210 | 284 | 1.19 | 34 | 12.0 |
| | 220 | 289 | 0.77 | 42 | 15.3 |
| η_3 | 220 | 309 | 1.24 | 35 | 11.8 |
| | 230 | 329 | 1.91 | 31 | 10.2 |
| | 240 | 318 | 1.11 | 38 | 12.8 |
| T | 240 | 353 | 2.12 | 31 | 9.5 |
| | 260 | 363 | 3.16 | 29 | 8.7 |
| | 280 | 369 | 2.33 | 33 | 10.1 |
| | 300 | 374 | 2.19 | 33 | 9.6 |

very small or highly overlapping peaks (i.e. the unreliable data) are not included in Table 1.

Among the calculated data the c_j parameters show the most definite dependence on the temperature of the final heat treatment. At the phases denoted by η' and T the E_j parameter does not vary significantly with the temperature of the final heat treatment. At the other three phases (at the phases denoted by η_1 , η_2 and η_3) the E_j values have considerable negative correlation with the corresponding c_j parameters. (The correlation coefficients are between -0.9 and -1 .)

The magnitude of the E_j parameters seems reasonable for dissolution processes in aluminium alloys. The A_j parameters scatter around the usual 10^{10} – 10^{13} range. (This scattering is not random, there is a strong correlation between $\log A_j$ and E_j in consequence of the well-known relation between T_{\max} , E_j and $\log A_j$.) The detailed interpretation of the obtained kinetic parameters, however, requires further investigations.

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