

## **LOW TEMPERATURE DECOMPOSITION OF Al-Mg ALLOYS: GP ZONES AND L<sub>12</sub> ORDERED PRECIPITATES**

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### **Abstract**

Low temperature (< 100°C) ageing experiments were performed on ice-water quenched and on slowly cooled Al-Mg alloys with 11, 14 and 16 at%Mg. Differential scanning calorimetry (DSC) generally reveals two overlapping endothermic events in the range 50-150°C which are identified to be due to the dissolution of GP zones and the spherically shaped L<sub>12</sub> ordered β'' phase precipitates. Data on the stability limits of GP zones and β'' phase is obtained from isothermal calorimetry and DSC experiments. Our data on the solvi agrees well with literature values provided that resistometry data, which is inconsistent with all other data, is not considered. Possible reasons for the unreliability of the latter are discussed and new solvus lines for GP zones and β'' phase are presented.

### **1. Introduction**

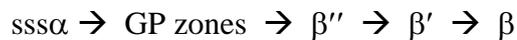
The early stages of precipitation at temperatures below 100°C in Al-Mg alloys have been studied by transmission electron microscopy (TEM) (Eikum and Thomas 1964, Boudili, Denanot and Dauger 1977, Sato, Kojima and Takahashi 1982, Gault, Dauger and Boch 1980, Bernole and Graf 1972, Bernole, Graf and Guyot 1973), high resolution electron microscopy (HREM) (Sato and Kamio 1991) resistivity measurements (Sato et al. 1982, Gault et al. 1980, Osamura, Ogura and Murakami 1982, Osamura and Ogura 1984), differential scanning calorimetry (DSC) (Nozato and Ishihara 1980, Nebti, Hamana and Cizeron 1995, Boucheur, Hamana and Laoui 1996, Van Rooyen, Sinte Maartensdijk and Mittemeijer 1988, Sato and Kamio 1991), small angle neutron scattering (Roth and Raynal 1974, Raynal and Roth 1975, Dauger, Boudili and Roth 1976, Dauger, Fumeron, Guillot and Roth 1979) and measurement of the elastic modulus (Gault, Dauger and Boch 1975). DSC and resistivity experiments generally show features which resemble those which have been taken as evidence for the formation of so-called Guinier-Preston (GP) zones in other alloy systems, i.e. the resistivity initially increases during room temperature ageing and room temperature aged alloys show a low temperature dissolution event during a DSC run. For this reason many researchers have interpreted the low temperature processes as due to the formation of so-called GP zones, a general indication for reactions which do not yield a phase with a well defined 3 dimensional structure but instead result in clusters of alloying atoms or 2 dimensional structures. The classic example of the latter is Al-Cu in which monoatomic Cu-rich layers on the {100} matrix planes form (Sato and Kamio 1991). TEM has shown that in Al-Mg alloys after ageing for a few days around room temperature spherical precipitates appear whilst selected area diffraction (SAD) reveals that these precipitates are an L<sub>12</sub> ordered phase (Sato et al. 1982). The formation of this

phase is related to a decrease in resistivity. As it would be inappropriate to term these particles with a well defined 3 dimensional structure a 'zone', we will here term them  $\beta''$ .

Whilst the evidence for the formation of  $L1_2$  ordered precipitates is quite clear and abundant, the evidence for the formation of a pre-precipitate, which may be termed a GP-zone, is less clear. The mentioned increase in resistivity during the first day of ageing at room temperature (Osamura and Ogura 1984) combined with the observation of a somewhat mottled structure with TEM (Sato et al. 1982) indicates that modulated structures or solute clusters do form during this very first stage of ageing.

When solid solutions with up to 18 at%Mg are aged at temperatures in excess of about 100°C, no  $L1_2$  ordered structures or zones form. In solid-quenched and liquid-quenched Al-Mg alloys aged between about 110°C and 250°C first a semi-coherent hexagonal intermediate phase termed  $\beta'$  (approximate composition  $Al_3Mg_2$ , with lattice parameters  $a = 1.002$  nm and  $c = 1.636$  nm (Bernole, Raynal and Graf 1969)) forms, and the equilibrium  $\beta$  phase (complex FCC structure with  $a = 2.824$  nm and approximate composition  $Al_3Mg_2$ ) only appears in the later stages of ageing when the Mg depletion of the matrix is nearly completed (Bernole 1974, Starink and Zahra 1996, Van Mourik, Maaswinkel, De Keijser and Mittemeijer 1989).

In summary, most work on the precipitation in Al-Mg (e.g. Refs. Osamura and Ogura 1984, Nozato and Ishihara 1980, Boucheur et al. 1996) indicates the following precipitation sequence (symbols as used by Osamura and Ogura 1984):



where  $sss\alpha$  is the supersaturated solid solution, GP zone (also indicated as  $\delta''$ ) is the modulated structure,  $\beta''$  (other indications:  $\delta'$ , ordered GP zone (Dauger et al. 1979) or GP zone<sup>\*</sup>) is an  $L1_2$  ordered phase (Sato et al. 1982),  $\beta'$  is the semi-coherent hexagonal intermediate phase (Bernole 1974), it is the main hardening precipitate (Nebti et al. 1995), and  $\beta$  is the equilibrium phase (approximate composition  $Al_3Mg_2$ ) which has a complex FCC structure.

Although precipitation in binary Al-Mg alloys has been studied by many researchers, several questions relating to the effect of vacancies on the nucleation of GP zones and the stability limits of  $\beta''$  and its precursor have remained unanswered. For this reason a range of isothermal and non-isothermal ageing experiments were performed on three Al-Mg alloys using isothermal calorimetry and DSC, whilst TEM was used for phase identification. The ageing experiments were devised to illuminate two main topics. Firstly, low temperature isothermal ageing was used to obtain the maximum temperatures at which  $\beta''$  and GP zones form. Secondly, DSC was performed on room temperature aged alloys with different compositions.

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\* Note that in the present work we will consistently use the presented indications for the phases/zones. When referring to work by other authors we will use this consistent identification independent of which indications were used in the original work, e.g. spherical  $L1_2$  ordered precipitates are always indicated as being  $\beta''$  and not as GP zones.

## 2. Experimental

### 2.1 Alloys

High purity alloys with nominal compositions Al-11Mg, Al-14Mg and Al-16Mg were produced by conventional casting and subsequent rolling at Centre de Recherches de Voreppe (Aluminium Pechiney). The chemical analysis of the alloys is presented in Table 1. Typical total impurity content is about 0.03 mass % (mainly Si). The grain size is large: about 0.2 mm.

Table 1 Composition of the alloys.

| Alloy   | Mg (at%) | Mg (mass%) | Al      |
|---------|----------|------------|---------|
| Al-11Mg | 11.1     | 10.1       | balance |
| Al-14Mg | 13.7     | 12.5       | balance |
| Al-16Mg | 15.8     | 14.5       | balance |

### 2.2 Calorimetry

The calorimeter used for the subsequent isothermal heat flow experiment possesses an excellent base line stability coupled with a high sensitivity (down to a microwatt). Generally 3 experiments per temperature were performed on a batch of 20 disk shaped samples of 1 mm thickness. The baseline of the microcalorimeter at each temperature was determined by performing experiments with pure Al. More details about the experimental procedures of the calorimetry experiments can be found elsewhere (Starink and Zahra 1996).

### 2.3 Differential Scanning Calorimetry

For DSC experiments disks of 6 mm diameter and height 1 mm (average mass about 70 mg) were machined from homogenised ingots. The alloys were solution treated (typically 2 hours at temperatures between 390 and 490°C) and subsequently quenched in ice-water (IWQ). Alloys were aged at 20°C for up to 3 years. Artificial ageing treatments were concluded by cooling in air. In addition, selected samples were cooled from 460°C at about 200°C/min within the DSC instrument.

DSC experiments were performed using a Perkin-Elmer 1020 series DSC7. For a description of the system and its performance see Zahra and Zahra 1996. The heat flow is calibrated by measuring the heat of fusion of In. The temperature is calibrated by taking the deviation  $\Delta T$  from the uncalibrated temperature equal to the following expression:

$$\Delta T = \Delta T_0 + p T + \tau \Phi$$

(T in °C) where  $\Phi$  is the heating rate, p is a (small) constant,  $\tau$  is a parameter depending on the time constant of the DSC apparatus in combination with the sample used (Zahra and Zahra 1996)

and  $\Delta T_0$  is  $\Delta T$  extrapolated to  $\Phi=0$ .  $\Delta T_0$  and  $p$  are determined by measuring the onset of melting of In and Zn at various heating rates and subsequently extrapolating to zero heating rate, whilst  $\tau$  is determined from the variation of the onset of (incipient) eutectic melting with heating rate in the Al-16Mg alloy. The value of  $\tau$  found (9.94 s) corresponds well with values determined earlier for samples of similar mass (Zahra and Zahra 1996). As in our Al-16Mg samples (incipient) eutectic melting occurs, this reaction can serve as a check for the calibration. For  $\Phi \leq 10$  °C/min the eutectic temperature was constant within  $\pm 0.1$  °C and averaged 449.7°C. This corresponds well with the values quoted in the literature of  $550 \pm 1$  °C (Chartrand and Pelton 1994, Murray 1982). For higher  $\Phi$  the measured eutectic temperature increased to 550.5°C, which is ascribed to small inaccuracies in the method of calibration at these high heating rates. Temperatures at these heating rates were further corrected by taking the eutectic melting point (449.7°C) as an internal reference and adding a (small) heating rate dependent  $\Delta T$  term to the above equation.

The procedures for baseline correction are described elsewhere (Starink and Zahra 1997a). DSC curves presented reflect the heat flow due to reactions. Generally three experiments per heating rate were performed, characteristic temperatures were reproducible within about  $\pm 0.7$ °C.

## 2.4 TEM

All specimens were ground to about 100  $\mu\text{m}$  and electropolished in a 3:1 mixture of methanol and  $\text{HNO}_3$  at -20°C. The foils were examined in a Philips EM 400 T microscope operated at 100kV, a JEOL JEM 2000 microscope operated at 200 kV and a JEOL JEM 2010 F microscope operated at 200 kV.

## 3 Results and discussion

### 3.1 Room temperature ageing

DSC curves of the samples aged at room temperature for 2 years are presented in Fig. 1. The identification of the DSC events for the Al-16Mg alloy has been discussed in an other publication (Starink and Zahra 1997b), in which DSC curves of the Al-16Mg alloy after several other heat treatments are also given. In the range 20-445°C a total of 6 heat events have been observed (see Table 2), but in the DSC curves presented in this work generally only events B (dissolution of GP zones and  $\beta''$ , see below), C (formation of  $\beta'$ ) and F (dissolution of  $\beta$ ) can be observed clearly. In the second half of event C some evidence of event E (transformation  $\beta' \rightarrow \beta$ ) can be observed for some curves. At the heating rate used in the present study event E appears as a weak shoulder of event C, whilst at lower heating rates the two effects become separated (Starink and Zahra 1997b). Further, it should be noted that for the alloys with lower Mg content the main exothermic event may be due mainly to formation of equilibrium  $\beta$  phase.

Fig. 1 shows that event B consists of two subevents: B1 and B2. For an Al-14Mg alloy naturally aged for 1 day, event B consists of one single event, whilst on continued ageing the event shifts to higher temperatures and the second subevent develops (see Fig. 2). Events B1 and B2 can be

identified on the basis on TEM experiments performed on our Al-16Mg alloy in combination with TEM experiments on an Al-10at%Mg reported by Sato et al. (1982). Our TEM experiments reveal that the microstructure of the Al-16Mg alloy aged for 2 years at room temperature contains spherical particles (Fig. 3), whilst selected area diffraction (SAD) shows superspots that are consistent with an  $L_{12}$  ordered phase (no streaks are observed). Thus, in agreement with work by other authors (Sato and Kamio 1991, Sato et al. 1982, Gault et al. 1980, Dauger et al. 1976, Bernole 1974), the particles are considered to be an  $L_{12}$  ordered phase, and are hence indicated as  $\beta''$  phase. In an Al-10at%Mg alloy the  $L_{12}$  ordered precipitates have been observed to develop gradually from a modulated structure during natural ageing (Sato et al. 1982). As discussed in the introduction, these modulated structures or clusters will be indicated as being GP-zones. After one day of natural ageing SAD on Al-10at%Mg does not reveal  $L_{12}$  superspots, but they gradually appeared after several weeks of ageing (Sato et al. 1982). Further, our Al-16Mg samples heated in the DSC at  $20^\circ\text{C}/\text{min}$  to  $150^\circ\text{C}$  did not reveal  $L_{12}$  superspots. In comparing the described TEM data with the DSC curves (Figs. 1 and 2), it is clear that there is only one consistent identification for the low temperature events: B1 is due to the dissolution of GP zones whilst B2 is due to the dissolution of  $\beta''$  phase particles (see also Sato and Kamio 1991). In view of the relatively high heating rate (at  $20^\circ\text{C}/\text{min}$  the temperature range for  $\beta''$  phase is being passed within a few minutes) and the relatively slow development of event B2 during room temperature ageing (several days of ageing), no transformation from GP zones to  $\beta''$  phase is expected to occur during a DSC run.

Also DSC curves of IWQ Al-16Mg alloys naturally aged for various times show two dissolution events in the temperature range to  $150^\circ\text{C}$  (Fig. 4). The presence of event B2 after quenching and 5 min room temperature ageing indicates that some  $\beta''$  phase has formed in this alloy. On (further) room temperature ageing first event B1 (GP zone dissolution) develops whilst the magnitude of B2 starts to increase after about a day ageing. This indicates that the  $\beta''$  phase present after 5 min ageing at room temperature was formed during the quench and not during the 5 min at room temperature. In terms of the sequence of appearance of the phases (first GP zones followed by  $\beta''$  phase), the room temperature ageing behaviour of the Al-16Mg alloy is similar to that of the Al-14Mg alloy.

Apart from quenched specimens also specimens cooled at  $200^\circ\text{C}/\text{min}$  after solutionising at  $460^\circ\text{C}$  were investigated. The results (Fig. 5) show that after this cooling rate smaller but similar heat events occur as compared to the quenched samples. The main exothermic and endothermic events above  $250^\circ\text{C}$  are of about equal size, indicating that this cooling rate is sufficient to prevent the formation of  $\beta'$  or  $\beta$  phase during cooling.

### 3.2 The GP zone and $\beta''$ phase solvus

The heat content of event B,  $\Delta Q_B$ , as a function of the Mg content of the IWQ samples aged for 2 and 3 years at room temperature is presented in Fig. 6. In agreement with results obtained by other researchers (Van Rooyen et al. 1988),  $\Delta Q_B$  is in good approximation a linear function of the Mg content. This straight line crosses the  $\Delta Q_B = 0$  axis at about 9.5at%Mg and the slope equals 11.4 kJ/mole Mg. As event B contains both the dissolution of GP zones and  $\beta''$  phase one may conclude that in the metastable phase diagram the point  $20^\circ\text{C}$  at 9.5at% Mg is between the solvi for GP zones

and  $\beta''$  phase. (As the dissolution event is a mix of two processes, the slope can not be taken as a measure of the enthalpy of formation of either process, but is instead a combination of the two.)

To further study metastable solvi isothermal calorimetry experiments between 60 and 100°C were performed on the Al-16Mg alloys air-cooled from 440°C. Exothermic events were observed for ageing at temperatures of 85°C and lower. Superspots observed by selected area diffraction on TEM foils prepared from the samples aged at 80 and 85°C indicated that the  $L1_2$  ordered phase had formed, whilst DSC experiments showed a dissolution event (see Fig. 7). At 90°C no exothermic event was detected during two weeks of isothermal ageing. These results are in agreement with an extrapolation of the heat content of the dissolution event B for IWQ alloys aged between 80 and 100°C (Fig. 7) which indicates a  $\beta''$  phase solvus temperature of about 90°C. (The very small endothermic events in Fig. 7 observed for samples aged at temperatures of 90°C and higher are attributed to dissolution of minor amounts of  $\beta''$  phase formed below 90°C during cooling after ageing.) The DSC experiments on IWQ Al-16Mg samples aged for 7 days between 70 and 100°C show that dissolution event B for samples aged at 70, 80 and 85°C occurs in two stages (see Fig. 7 for selected experiments). Hence these dissolution events are ascribed to GP zone and  $\beta''$  phase dissolution, and from this we conclude that for this alloy 70, 80 and 85°C are points below the GP zone solvus. Similarly we used DSC to check whether  $\beta''$  phase and/or GP zones had formed in the Al-11Mg during ageing at 40°C and in the Al-14Mg alloy during ageing at 50 and 65°C. The experiment at 50°C showed events B1 and B2 indicating presence of  $\beta''$  phase and GP zones, whilst the other experiments showed a single small dissolution event indicating the presence of only  $\beta''$  phase.

Table 2 Identification of the DSC events. Al-16Mg alloy at heating rate 20°C/min.

| Event | Endo/Exo    | approx. range<br>(°C) | identification             |
|-------|-------------|-----------------------|----------------------------|
| A     | exothermic  |                       | $\beta''$ formation        |
| B1    | endothermic | 40–100                | GP zone dissolution        |
| B2    | endothermic | 80–150                | $\beta''$ dissolution      |
| C     | exothermic  | 180–290               | $\beta'$ formation         |
| D     | endothermic | 200–300               | $\beta'$ dissolution       |
| E     | exothermic  | 280–330               | $\beta' \rightarrow \beta$ |
| F     | endothermic | 330–430               | $\beta$ dissolution        |

In Fig. 8 the values for the  $\beta''$  phase solvus as obtained in this work are compared with other data on the  $\beta''$  phase and the GP zone solvi. The data is subdivided in three groups: i) data on the GP zone solvus, ii) data on the  $\beta''$  phase solvus, and iii) data on points between the two solvi. We will review this data below.

*i) data on the GP zone solvus (open symbols in Fig. 8)*

In the works by Osamura and Ogura (1984) and Sato et al. (1982) resistometry on quenched alloys is used to obtain solvus data: an increase in resistivity has been taken by them to be evidence for GP

zone formation. In these works the solvus is obtained by varying the ageing temperature and extrapolating to the temperature at which no resistivity increase occurs. Gault et al. (1980) studied decomposition of an air-cooled Al-13.3at%Mg alloy using similar resistivity experiments. Using the same extrapolation method as employed in the publications by Osamura and Ogura (1984) and Sato et al. (1982), the GP zone solvus in the Al-13.3at%Mg alloy studied by Gault et al. (1980) can be estimated to be at 33°C. Van Rooyen et al. (1988) used an extrapolation method identical to the one in Fig. 6 to obtain solvus data. As their DSC experiments show only event B1, we will interpret their data as the solvus for GP zones.

*ii) data on the  $\beta''$  phase solvus (black symbols in Fig. 8)*

Gault et al. (1980) used ultrasonic measurements to deduce the solvus of  $\beta''$  phase for Al-13at%Mg and Al-16at%Mg. Nozato and Ishihara (1980) used DSC to study the heat due to dissolution of  $\beta''$  phase after isothermal ageing and from this data the solvus of  $\beta''$  phase can be deduced to be about  $70\pm 10^\circ\text{C}$  for an Al-12.5at%Mg alloy.

*iii) data on points between the two solvi (grey symbols in Fig. 8)*

Nozato and Ishihara (1980) observed a single dissolution event B2 and no B1 in an Al-12.5at%Mg alloy aged at 55°C. Hence this point is interpreted as being in between the two solvi. Raynal and Roth (Raynal and Roth 1975, Roth and Raynal 1974), using TEM and small-angle neutron scattering, failed to detect  $\beta''$  phase particles in an Al-7at%Mg alloy aged for 9 months at 0°C, whilst Nebti et al. (1995) detected DSC dissolution events in the range of 50-100°C for an Al-9at%Mg alloy aged for 6 years at room temperature, and interpreted them (without presenting any microstructural or diffraction data) as due to GP zone and  $\beta''$  phase dissolution. However, as in the latter work no chemical analysis of the alloy concerned is presented, this data is not useful in the present analysis and thus not considered.

The curves in Fig. 8 are obtained by assuming that the GP zone solvus and  $\beta''$  phase solvus correspond to a simple regular solution (see for instance Starink and Gregson 1995). The parameters (the two pre-exponential constants and the two heats of formation) are obtained by fitting to the data presented whilst neglecting the resistometry data (see below). It is noted that this model is an oversimplification and it is only used to give an approximate indication for the solvi. Fig. 8 shows that all data except the resistivity data can be rationalised by the two presented solvi. Data obtained by resistometry is internally inconsistent, as at temperatures between 20 and 33°C the data on the GP solvus obtained by resistometry vary between 5 and 13at%, and is inconsistent with the  $\beta''$  phase solvus data, because some resistometry data on the GP solvus seems to be situated at lower concentrations than the  $\beta''$  phase solvus. It is thought that these discrepancies are caused by the presence of vacancies, whose influence has been wrongly neglected in several publications in which resistometry was employed. We will discuss this point in detail in the next paragraph. At this point it is further noted that the temperature difference between the two solvi in Fig. 8 (about 10 to 15°C, depending on composition) corresponds closely with the temperature difference between the peaks of the dissolution events of GP zones and of  $\beta''$  phase in the three Al-Mg alloys studied (see Figs. 1,2,4,10). This is a further indication that the solvi in Fig. 8 are correct.

Fig. 9 shows that naturally aged Al-16Mg contains vacancy type defects (probably mostly vacancy loops). Hence water-quenched Al-Mg alloys contain vacancies which are mobile during ageing. These mobile vacancies can influence the experimental determination of the solvus of GP zones in a

number of ways. In resistometry experiments clustering of vacancies with Mg atoms will cause a decrease in electrical resistivity, whilst GP formation, which is thought to occur in about the same temperature range, will cause an increase in resistivity. Osamura and Ogura (1984) and Sato et al. (1982) have shown that for Al-Mg alloys with Mg contents between 5.1 and 14.8 at% there is a cross over temperature below which the resistivity initially increases on isothermal ageing and above which the resistivity initially decreases, and they assumed that this temperature is the solvus temperature of the alloy. However, in making this assumption one neglects the possibility that GP zone formation and clustering occur simultaneously and one also neglects the possible effects of the clustering of vacancies on the resistivity. As further no microstructural evidence has been presented in the literature that confirms the inconsistent room temperature solvus data of Sato et al. (1982), Gault et al. (1980) and Osamura and Ogura (1984), solvus determination by resistometry experiments is thought to be generally unreliable. On this point it is interesting to note that in both Al-Mg and Al-Li spherical L<sub>12</sub> ordered precipitates form, and that in both alloys precursors to the L<sub>12</sub> ordered phase have been reported. (Note that the presence of such a precursor in the Al-Li system is still a matter of debate in the literature, see Noble and Trowsdale (1995a, 1995b), and references therein.) Noble and Trowsdale (1995a, 1995b) deduced the presence of a precursor to the L<sub>12</sub> ordered phase from DSC experiments on as-quenched Al-14at%Li, which revealed an exothermic event preceding a second exothermic event due to the formation of L<sub>12</sub> ordered precipitates. They further showed that the quenching rate has an important influence on the formation of these precursors and it is likely that the same is the case for precursors in Al-Mg. This may well explain the large difference between the solvus data obtained from the work of Gault et al. (1980) on the one hand and the works of Sato et al. (1982) and Osamura and Ogura (1984) on the other hand, as these researchers employed very different quenching rates: Gault et al. used air cooling whilst the others quenched the samples in water. Further, closer scrutiny of Fig. 7 in Osamura and Ogura's (1984) work shows that even following their assumptions, the solvus for the Al-14at%Mg can not be determined more accurately than as being between 62 and 90°C. Hence their data is consistent with the GP zone solvus and even with the β'' phase solvus as presented in Fig. 8.

As a further note of caution concerning interpretation of the data it is noted that in samples aged for long times at low temperatures β' and β phase may be present. Evidence for this is shown in Fig. 10 in which DSC curves of the Al-11Mg alloy aged for 35 days and for 3 years are presented. Between 280 and 380 °C these curves show a small but nevertheless clearly identifiable endothermic event which is attributed to β' and/or β phase dissolution. Moreover, this event seems to increase and shift to higher temperatures with prolonged room temperature ageing, which indicates that β' transforms to β. The presence and growth of β' and/or β phase will reduce the amount of Mg available for GP zone or β'' phase formation, and thus influence solvi determinations. However, as Fig. 10 shows that in our room temperature aged Al-11Mg alloy very little β' and/or β phase is present, it is thought that for our experiments this event is negligible. As van Rooyen et al. (1988) investigated rapidly solidified Al-Mg alloys, with small grain sizes and hence a large amount of potential nucleation sites for β phase, some caution with respect to their data is appropriate.

## Conclusions

Ice-water quenched and slowly cooled Al-Mg alloys with 11, 14 and 16 at%Mg were investigated using differential scanning calorimetry (DSC), isothermal calorimetry and transmission electron microscopy (TEM). The results can be summarised as follows:

- TEM experiments on Al-16Mg samples aged for 2 years at room temperature confirmed the presence of spherical L1<sub>2</sub> ordered  $\beta''$  phase precipitates.
- Two overlapping endothermic DSC events in the range 50-150°C were identified to be due to the dissolution of GP zones and the  $\beta''$  phase precipitates.
- DSC and isothermal calorimetry experiments show that the stability limit of  $\beta''$  phase in Al-16Mg is 90°C. Points below the solvus of GP zones as well as points between the solvi of GP zones and the  $\beta''$  phase have been obtained for the three alloys.
- A good correspondence between our data on the solvi and literature data is obtained provided that resistometry data, which is inconsistent with all other data, is not considered. Possible reasons for the unreliability of the latter data are discussed and new solvus lines for GP zones and  $\beta''$  phase are presented.

## Acknowledgements

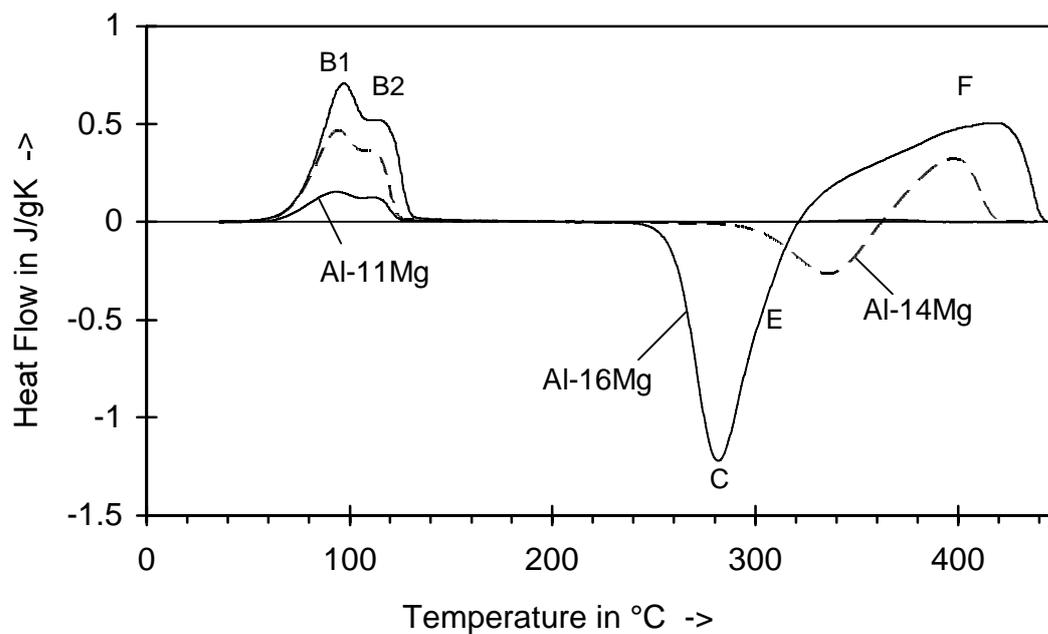
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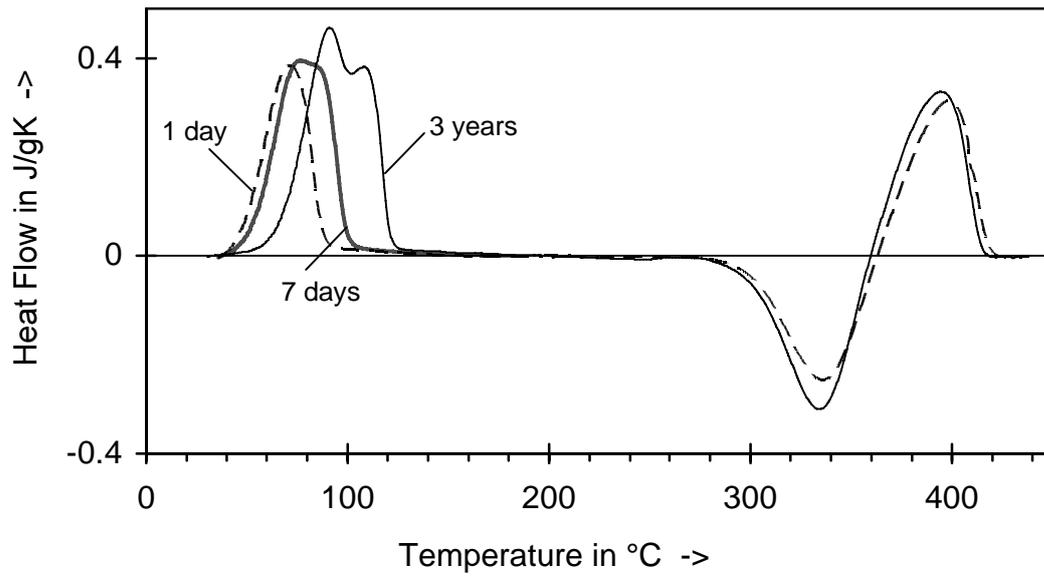
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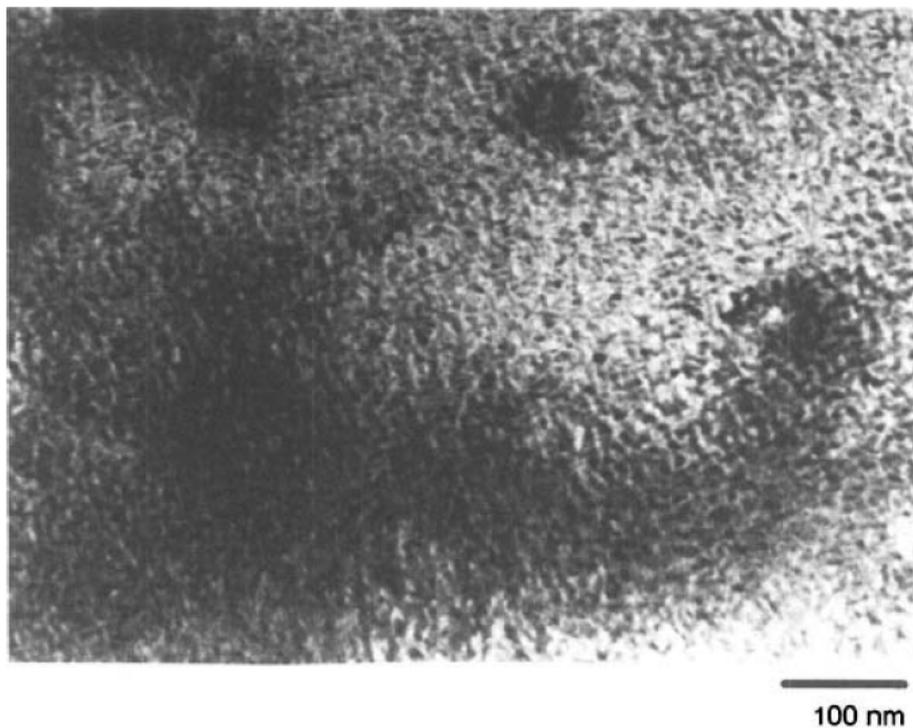
## Figures



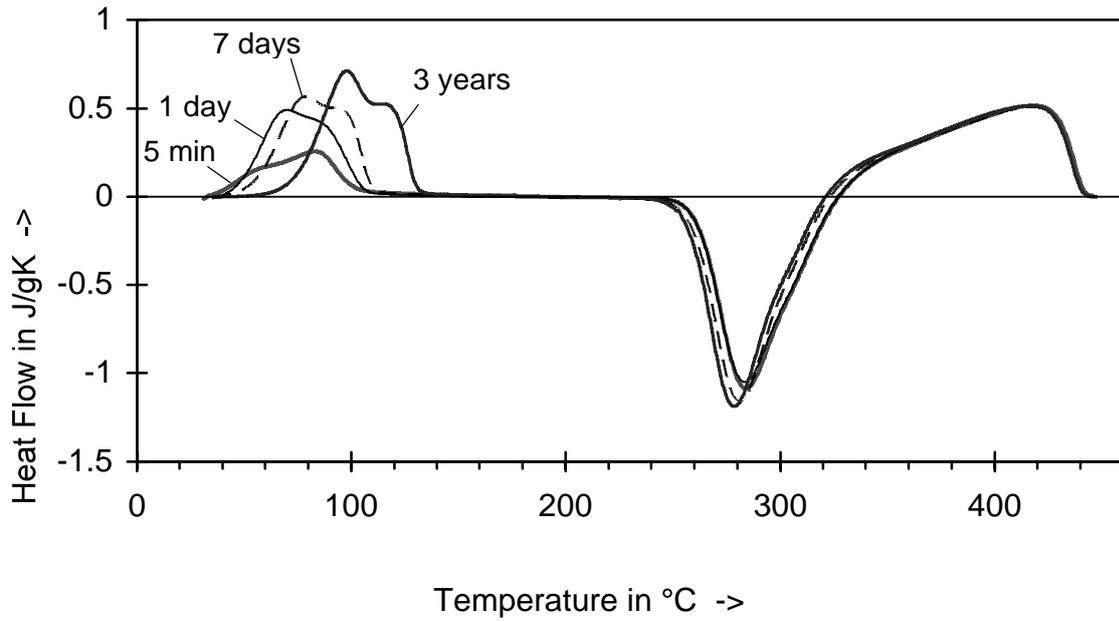
- 1 DSC curves of the Al-11Mg, the Al-14Mg and the Al-16Mg alloy aged at room temperature for 2 years. Heating rate is 20 °C/min.



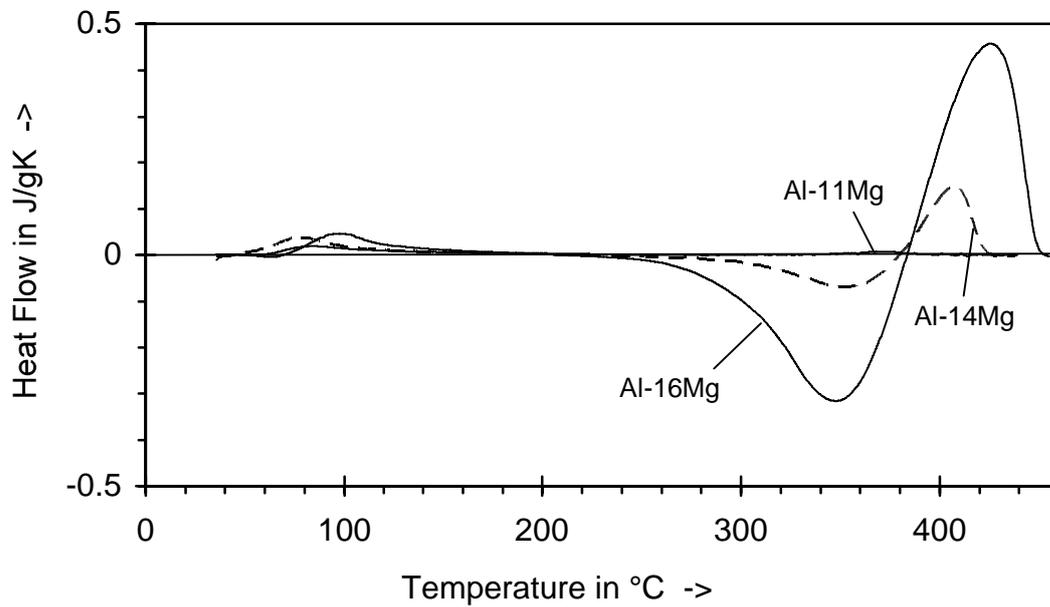
- 2 DSC curves of Al-14Mg samples naturally aged for 1 day and 3 years after solutionising at 440°C, and part of the curve of Al-14Mg aged for 7 days after solutionising at 420°C. Note the change in shape of the first endothermic event.

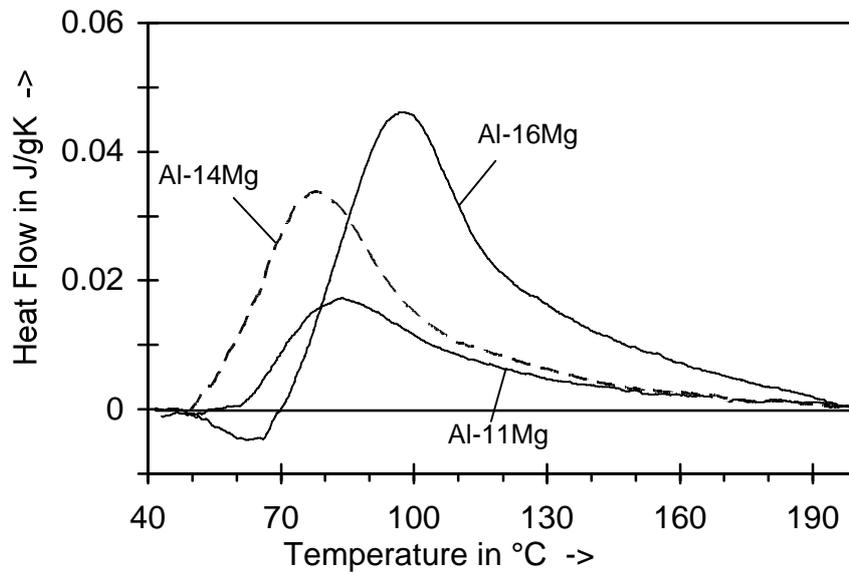


- 3 TEM micrograph of the Al-16Mg alloy naturally aged for 2 years after solution treatment at 440°C.

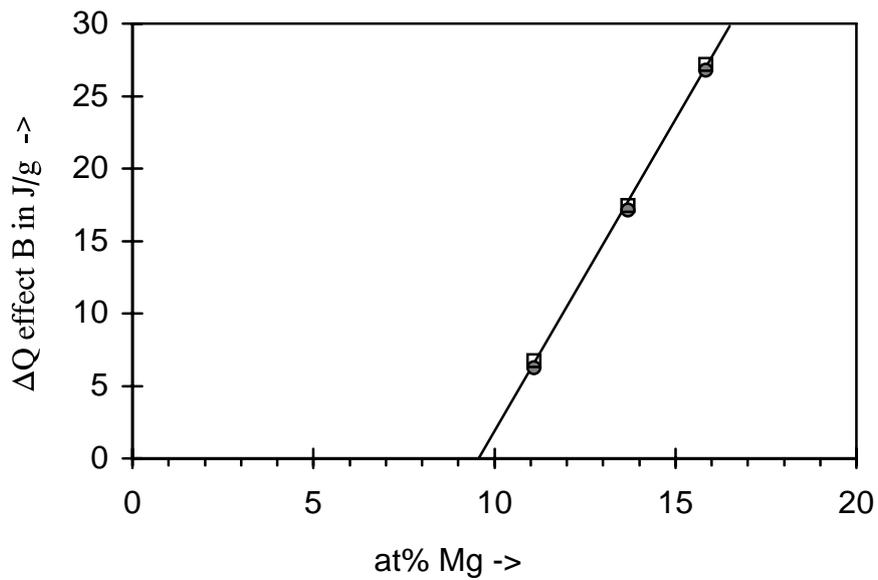


- 4 DSC curves of IWQ Al-16Mg samples aged for 5 min, 24 h, 7 days and 3 years at room temperature after solutionising at 440°C.

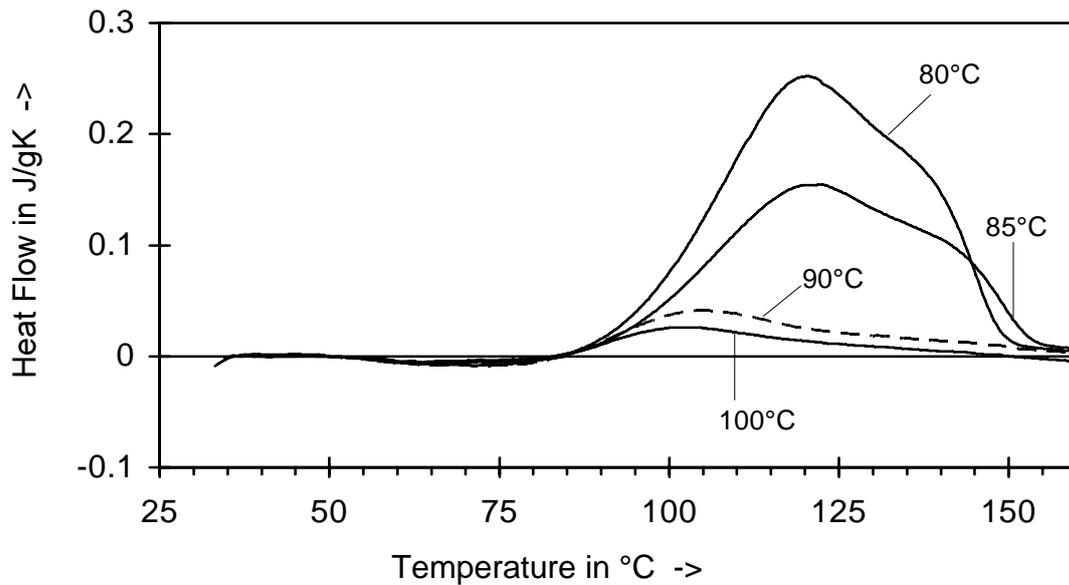




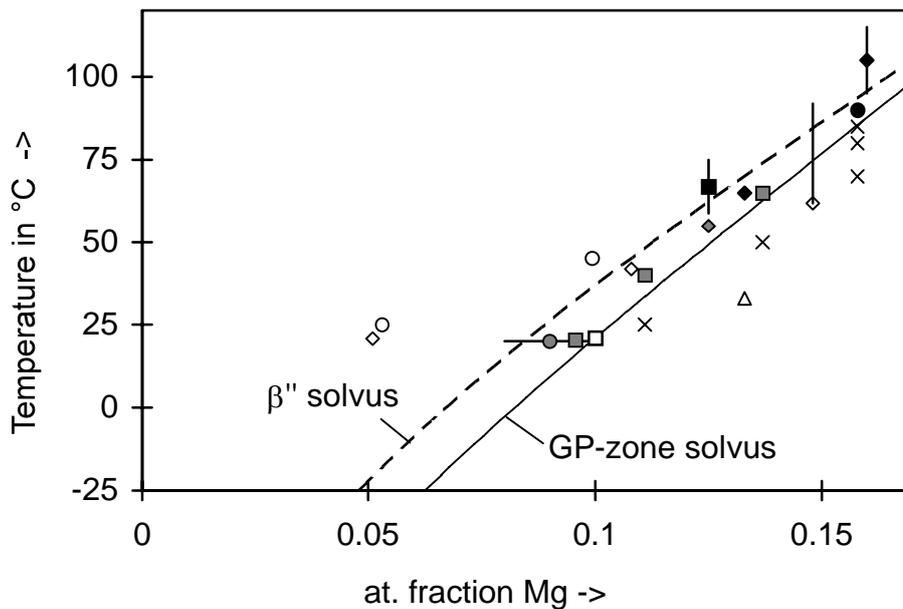
5a,b DSC curves of the Al-11Mg, the Al-14Mg and the Al-16at%Mg alloy cooled at  $-200^{\circ}\text{C}/\text{min}$  from  $460^{\circ}\text{C}$ . Heating rate is  $20^{\circ}\text{C}/\text{min}$ .



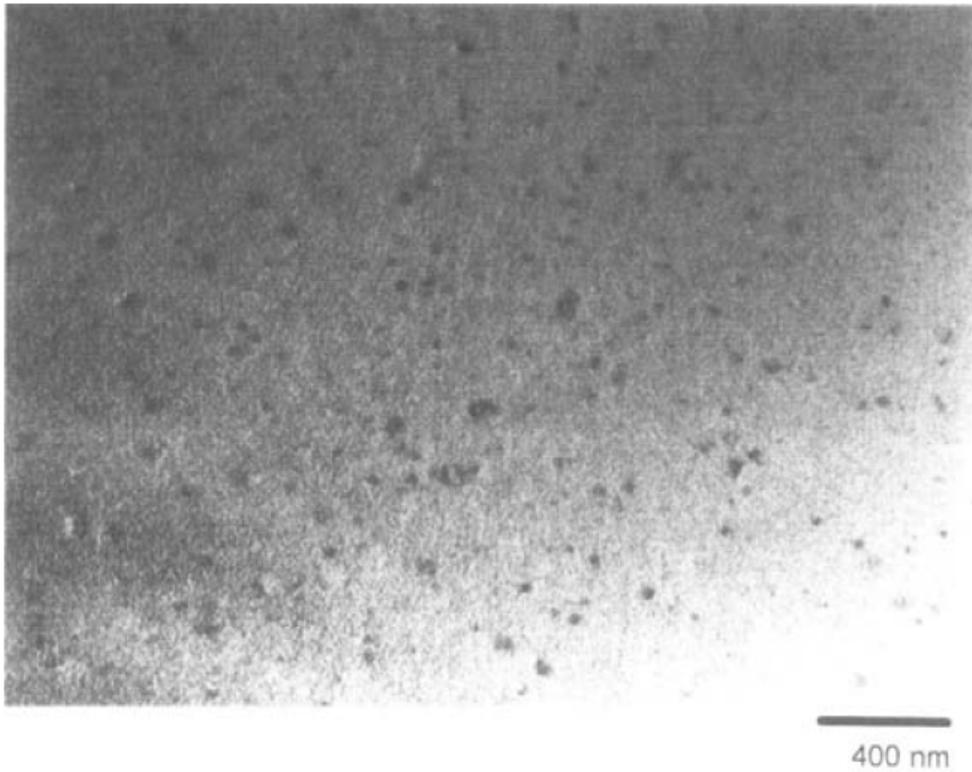
6 Heat content of effect B vs. Mg content for samples solution treated at  $440^{\circ}\text{C}$  and naturally aged for about 2 years (●) and about 3 years (□).



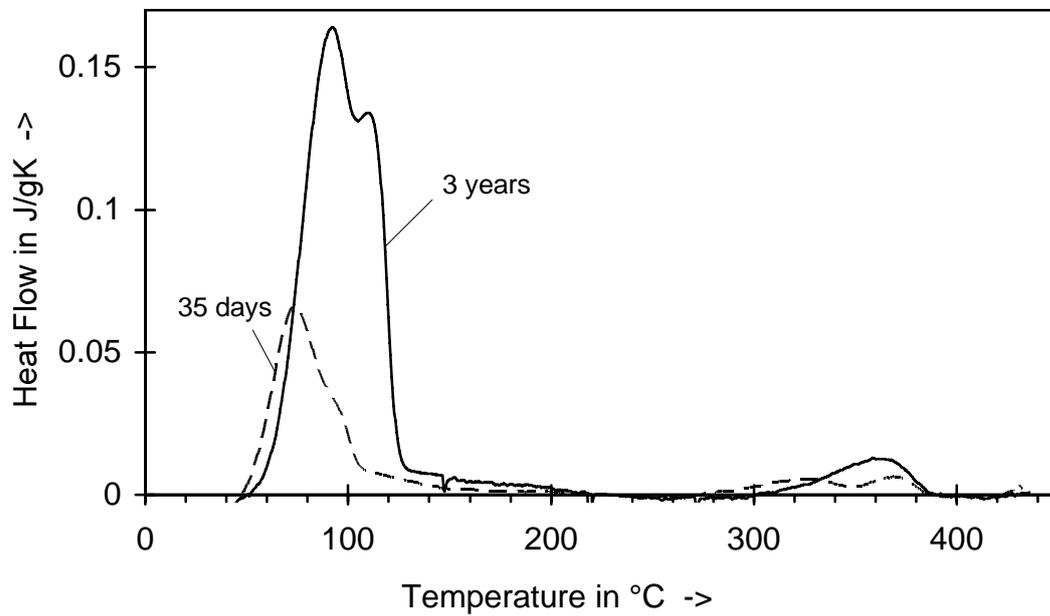
7 DSC curves of the IWQ Al-16at%Mg alloy aged for about a week at temperatures between 80 and 100°C. Heating rate is 20 °C/min.



8 The GP zone solvus according to Van Rooyen et al. 1988 (□), Gault et al. 1980 (△), Sato et al. 1982 (○), and Osamura and Ogura 1984 (◇); with data on the β'' phase solvus from this work (●), by Nozato and Ishihara 1980 (■) and by Gault et al. 1980 (◆); points between the two solvi by Raynal and Roth 1975 (●), Nozato and Ishihara 1980 (◇) and this work (■); and points below the two solvi from the present work (×). Resistometry data (△, ○ and ◇) is thought to be unreliable (see text).



- 9 TEM micrograph showing defect structures in the Al-16Mg alloy naturally aged for 2 years after solution treatment at 440°C.



- 10 DSC curves of Al-11Mg samples aged for 35 day and 3 years after solutionising at 440°C.