Differential Scanning Calorimetry Study on AA6016 Alloy

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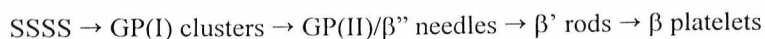A. Stocletlaan 87, B-2570 Duffel
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ABSTRACT

Alloys based on the Al-Mg-Si system are widely used in Europe for car body outer panels, the most prominent alloy of this system being AA6016. A systematic DSC investigation was carried out on the precipitation and dissolution behaviour of AA6016 during thermo-mechanical processing in the plant and the applied paint bake cycles at the car manufacturer. The presence of a high excess of Si in solution significantly contributes to the precipitation sequence. The Si excess induces an exothermic peak in the range 300-375 °C, caused by precipitation of Si particles, and an endothermic peak in the range 500-520 °C, due to dissolution of the Si phase. A precipitation peak occurring simultaneously with the precipitation peak of β" phase becomes distant after simulated paint bake cycles and indicates that the hardening response of AA6016-T4 can not be attributed only to the precipitation of coherent β" needles.

Keywords: *Aluminium, AA6016, DSC study, Mg-Si phases, Si phases*

1. INTRODUCTION

Alloys based on the Al-Mg-Si system are widely used in Europe for aluminium car body outer panels, the most prominent alloy of this system being AA6016. This alloy provides attractive properties, with good stamping performance and increased strength in the stamped and painted components. The main strengthening phases of AA6016 are Mg-Si precipitates, with additional precipitates of Si. Since the Mg-Si precipitates bind only a small portion of the total Si, an excess amount of Si remains in solid solution, which has proven to be beneficial to formability [1] and paint bake response [2].

The precipitation behaviour of Al-Mg-Si type alloys has been extensively studied [eg. 3-16], but at present there is no consensus on the precise sequence. In general, precipitation of Mg-Si related phases is found to occur as follows:-

$$SSSS \rightarrow GP(I) \text{ clusters} \rightarrow GP(II)/\beta" \text{ needles} \rightarrow \beta' \text{ rods} \rightarrow \beta \text{ platelets}$$

In this sequence, SSSS is the supersaturated solid solution stage, achieved after solution heat treatment and quenching. Immediately after solution heat treatment, independent clusters of Si and Mg appear to form, which after substantial ageing at room temperature transform into GP zones [6,9,11,12]. The GP zones have been divided into GP(I) zones, which are spherical clusters with no internal order, and GP(II) zones, which show an internal order and are needle-shaped. However, in the literature, there is disagreement concerning the nature of the needle-shaped

precipitates, also referred to as β". Some investigators regard β" as being GP zones [4,7,15], whereas others have identified β" as a separate phase having a monoclinic crystal structure [8,11,12]. Prolonged artificial ageing subsequently transforms the coherent β" needles into semicoherent β' rods, which have a hexagonal periodicity [3,4,10]. At higher temperatures, the β' rods are transformed into the equilibrium Mg_2Si β platelets, which display a cubic crystal structure and are fully incoherent with the surrounding matrix.

The presence of excess Si in Al-Mg-Si alloys contributes to the precipitation sequence with two types of precipitates [9-13]. The first is observed to occur simultaneously with the precipitation of β" needles, although no clear structure could be identified [11,12]. It was suggested that this phase is Si-rich, as precipitation of this type is more distinct in the higher Si containing alloys [11]. The second Si phase is observed to precipitate simultaneously with β' rods [9, 10-13]. This phase is lath-shaped [11,13] and has a hexagonal crystal structure [10,13]. The precipitation of Si phases modifies the overall precipitation behaviour of Al-Mg-Si type alloys into:-

$$SSS \rightarrow GP(I) \text{ clusters} \rightarrow [Si \text{ rich phase}] + GP(II)/\beta" \text{ needles} \rightarrow \beta' \text{ rods} + [Si \text{ laths}] \rightarrow \beta \text{ platelets}$$
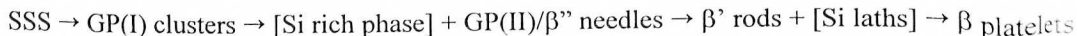
Figure 1 shows a typical DSC thermogram of AA6016-T4, which contains about 0.3 wt% Mg and 1.2 wt% Si. Starting from the lower temperature side, all peaks and troughs have been marked A through N. In this sequence, peak A is generally attributed to the formation of GP(I) zones. In DSC thermograms obta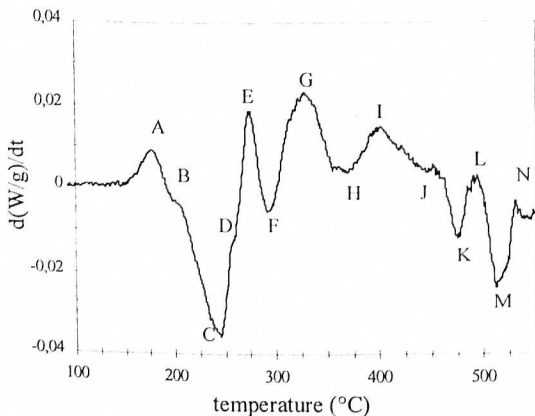ined immediately after solution heat treatment and quenching generally two peaks are observed [9,11,14], of which the one at a lower temperature disappears or merges into the other after substantial natural ageing [9,11]. After the first exothermic peak, a two stage dissolution trough is observed marked B and C. Whereas trough C is attributed to the dissolution of GP(I) zones formed at A [5,9], the small trough B may be related to the exothermic peak which is only observed immediately after solution heat treatment. Peak D has been identified as a precipitation peak [11,12] and is attributed to the formation of the Si rich phase [11]. Peak E corresponds to the precipitation of the β" needles, irrespective of being interpreted as GP(II) zones or as the intermediate precursors of the β' phase. The next exothermic peak, G, is generally attributed to the formation of β' rods, but it is now evident that a major part of the recorded exothermic energy is due to precipitation of Si laths [9,11,12]. Finally peak I corresponds to the formation of the equilibrium Mg_2Si β phase. Although a distinct dissolution stage between the β' and β precipitation peaks appears in $Al-Mg_2Si$ balanced alloys [5,14], it is not observed in AA6016-T4. This stage may be masked by the precipitation of excess Si. Generally the dissolution troughs K and M are not discussed in the literature, but they are of significant importance during thermo-mechanical processing.

Fig 1. Typical DSC thermogram of AA6016-T4.

Addition of Cu may also contribute to the precipitation sequence of AA6000 series alloys above a level of 0.25 wt% [13,16]. However, in AA6016 Cu is generally kept at low levels (<0.1 wt%) to maximise the corrosion resistance, and is therefore neglected in this study.

This paper presents the results of a systematic DSC investigation into the dissolution and precipitation behaviour of Mg-Si and Si related phases that occurs during thermo-mechanical processing of AA6016. It also identifies the phases responsible for the hardening response achieved during paint baking of car body sheet.

2. EXPERIMENTAL

A systematic DSC study was carried out during thermo-mechanical processing of a commercial ingot comprising 1.2 wt% Si, 0.33 wt% Mg, 0.2 wt% Fe, 0.07 wt% Mn and 0.07 wt% Cu. To investigate the onset temperatures of precipitation after homogenisation of the ingot, small specimens of the as-cast material were first completely solution heat treated at 570 °C and subsequently cooled down and held at temperatures of 540 °C, 510 °C, 480 °C and 450 °C for five hours to achieve equilibrium of phases, then quenched into cold water and naturally aged for two weeks.

The ingot was preheated in the plant, and hot rolling commenced at a temperature below 550 °C. Hot rolling was done on a breakdown mill to ~25 mm and then by a 3-stand tandem mill where the sheet was coiled. After cold rolling to final gauge, specimens were solution heat treated in a salt bath at 570 °C for 60 seconds and then quenched into cold water and naturally aged for two weeks. Subsequently, the material was aged for 20 minutes at temperatures of 160 °C, 175 °C, 185 °C and 205 °C to simulate paint baking cycles.

After each step, material was taken out to study the precipitation sequence. With the exception of the material at tandem gauge, which was taken after cooling of the coil, all thermo-mechanical processed materials were quenched into water and naturally aged for two weeks. The precipitation sequence was investigated at a heating rate of 20 °C/min, using a DSC 10 from Dupont.

3. RESULTS

Figure 2 shows DSC thermograms (W/g) of samples of the as-cast ingot, which were homogenised at 570 °C, and subsequently cooled down and kept at 540 °C, 510 °C, 480 °C and 450 °C for 5 hours. In the as-cast structure, two low melting peaks (LMP's) are observed. After homogenisation at 570°C and lowering to 540 °C, both LMP's have disappeared, indicating that the corresponding phases have dissolved completely.
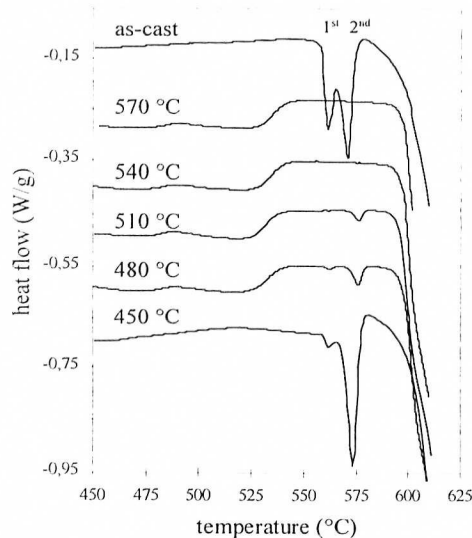

Fig. 2 DSC thermograms (W/g) showing the return of low melting peaks after homogenization at 570 °C.
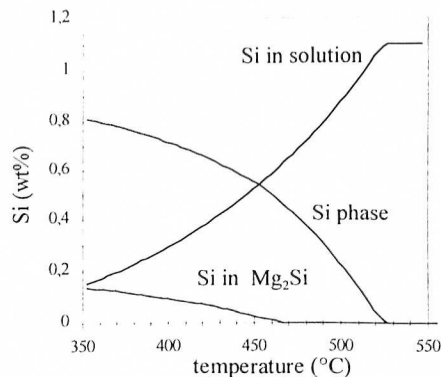
Fig. 3 Calculation of equilibrium of phases for a ternary Al-0.33wt%Mg-1.1wt%Si alloy [17].

After reducing the temperature to 510 °C, the second LMP has reappeared. Further lowering the temperature to 480 °C, the first LMP also reappears again. In general, a decrease in temperature leads to an increase in magnitude of both LMP's. Figure 3 shows the results of calculations on the equilibrium of phases for a ternary Al-0.33wt%Mg-1.1wt%Si alloy [17]. Although the results for the ternary alloy system cannot be compared directly with the actual equilibrium of phases in commercial AA6016, due to the presence of additional elements which may affect the solubility of Si and Mg, the figure gives quite a good indication of the temperatures at which precipitation of the Si and Mg_2Si phases commences.

Figure 4 shows DSC thermograms of samples obtained after each processing step of the commercial ingot. As it was not possible to obtain test material of the commercial ingot between homogenisation and hot rolling, a DSC thermogram of a specimen homogenised at 570 °C was used to obtain the figure. (a) In the as-cast condition, the presence of both Si and Mg_2Si phases in the material considerably influences the precipitation sequence. Only a small GP(I) precipitation peak is observed, followed by a two stage dissolution through. Subsequently, only two precipitation peaks are noticed. Whereas the second one, appearing in the temperature range 375-450°C, corresponds to β phase, the first peak has a maximum at 300 °C and can not be related directly to a single phase. At temperatures above 450 °C, a shallow but continuous two-stage dissolution trough is observed.
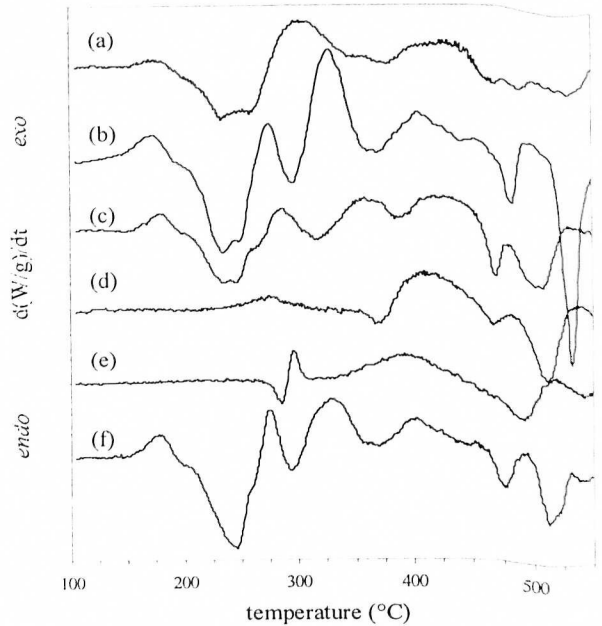(b) After homogenisation at 570 °C,

Fig. 4 DSC thermograms of (a) as cast, (b) homogenized at 570 °C, (c) at breakdown gauge, (d) after coil cooling at tandem gauge, (e) after cold rolling to final gauge, and (f) solution heat treated. For (b), (c) and (f), the samples are quenched and naturally aged for two weeks.

all Mg_2Si and Si related phases have dissolved, resulting in a typical precipitation sequence of AA6016-T4. (c) After breakdown rolling, a similar sequence is observed. However, most peaks and troughs are smaller. Moreover, the precipitation peaks E, G and I show a clear shift towards higher temperature, whereas the dissolution troughs K and M have shifted to lower temperatures. (d) After tandem rolling and subsequent cooling of the coil to room temperature, almost no response is observed below 375 °C, except for a small precipitation peak at 280 °C and a dissolution stage at 370 °C. Above 375 °C, a normal sequence is obtained, with precipitation of phase in the range 375-450 °C, followed by the dissolution troughs K and M. (e) Subsequent cold rolling to final gauge induces a small and sharp dissolution peak immediately followed by a sharp precipitation peak in the temperature range 275-300 °C. Then, a broad precipitation peak in the phase range is observed, followed by only one dissolution trough. (f) Solution heat treatment at 570 °C for 60 seconds results in the final precipitation sequence. The sequence shows quite similar behaviour as observed after homogenisation. The main differences are the lower magnitudes of peak G and trough M, and the slight shift of the troughs K and M to lower temperatures.

Figure 5 shows the influence of simulated paint bake treatments on the precipitation behaviour of AA6016-T4, indicating the phases associated with the hardening response. With increasing ageing temperature, the GP(I) formation and dissolution stages show a decrease in magnitude. The peaks D and E, which are attributed to the precipitation of a Si rich phase and β" phase respectively,
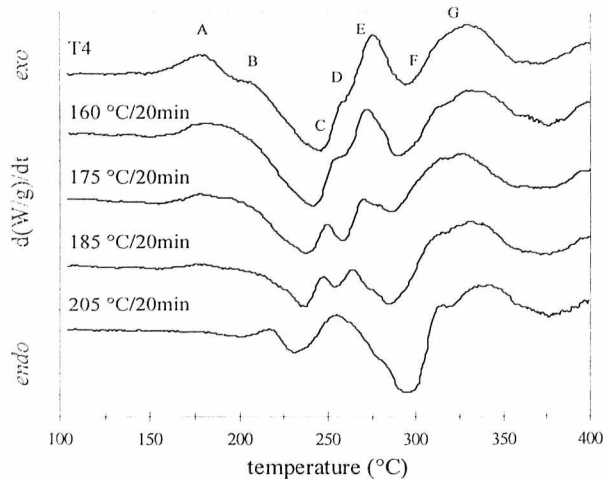

Fig. 5 DSC thermograms of specimens in T4 condition and artificially aged for 20 minutes at various temperatures.
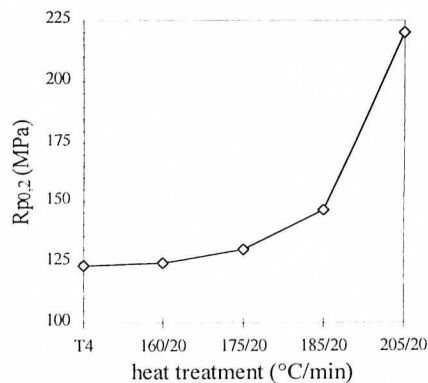
Fig. 6 Hardening response of AA6016 after the heat treatments.

show a remarkable change. With increasing ageing temperature, both peaks become distant and shift to lower temperatures. The separation results in a decrease of peak E, whereas peak D shows an increase in magnitude. At 205 °C, only one peak is observed.

After the ageing treatments two maxima also appear at peak G, which is attributed to the simultaneous precipitation of β' rods and Si laths [10-12]. Figure 6 shows the hardening response of the samples after the ageing treatments.

3. DISCUSSION

The precipitation sequences measured during thermo-mechanical processing are significantly altered after processing step. The magnitudes of the peaks and throughs as well as their shifts can be explained by the type and amount of phases precipitated. This will not be subject of discussion in this paper. The results show that after solution heat treatment of sheet material at final gauge, the precipitation sequence is comparable with the sequence obtained after homogenisation of the ingot. This suggests that the thermo-mechanical history hardly affects the Mg-Si distribution in the resulting AA6016 sheet material.

In the precipitation sequence, two distinct troughs are identified in the higher temperature range, corresponding to the dissolution of two separate phases. After homogenisation at 570 °C (fig. 4), the DSC thermogram shows the first phase to dissolve in the range 460-480 °C, whereas the second phase dissolves in the range 510-540 °C. This implies that starting at 570 °C and subsequently decreasing the temperature, the corresponding phases commence to precipitate at nearly the same temperatures, as is shown by the reappearance of the low LMP's in figure 2. Comparison with the calculated equilibrium of phases for an ideal ternary Al-0.33wt%Mg-1.15wt%Si alloy (fig.3) indicates that trough M at 510-540 °C corresponds to the dissolution of Si particles. Furthermore, comparison of (b) homogenised and (f) solution heat treated material (fig.5) shows that a close relationship exists between trough M and peak G, which is attributed to the formation of Si laths [9,11-13]. The results also indicate that trough K at 460-480 °C may be

related to the dissolution of Mg_2Si β phase. The difference between the calculated (fig. 3) and the measured (fig. 2) temperatures of precipitation may be attributed to the presence of additional elements in the commercial alloy.

The other precipitation peak that has been related to Si is peak D [11], which occurs with the precipitation peak of β" needles in AA6016-T4. After ageing for 20 minutes at modest temperatures, peak D separates from peak E, and shows an increase in magnitude (fig. 5). At 205 °C, at which the highest hardening response is obtained, only one peak is observed. The existence of two peaks suggests that the hardening response obtained during paint baking is not attributable only to the precipitation of coherent β" needles at peak E, as is generally stated in literature. There is not much known about the nature of the precipitates formed at peak D. A more detailed investigation of the phases responsible for the paint bake response of AA6016 is needed.

4. CONCLUSIONS

A systematic DSC investigation was carried out on the precipitation and dissolution behaviour of AA6016 which occurs during thermo-mechanical processing in the plant and during subsequent paint bake heat treatments at the car manufacturer. The presence of a high excess of Si is seen to contribute significantly to the precipitation sequence. The Si excess induces an exothermic peak in the temperature range 300-375 °C, caused by the formation of lath-shaped Si particles, and an endothermic peak in the range 500-520 C, due to the dissolution of the Si phase. A precipitation peak occurring with the precipitation of β" phase separates after simulated paint bake cycles and indicates that the hardening response of AA6016-T4 cannot be attributed solely to the precipitation of coherent β" needles.

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