JOURNAL OF MATERIALS SCIENCE 17 (1982) 1819–1825

A calorimetric study of aluminium alloy AA-7075

D. J. LLOYD
Alcan International Limited, Kingston Laboratories, P.O. Box 8400, Kingston, Ontario, Canada

M. C. CHATURVEDI
Department of Mechanical Engineering, Univeristy of Manitoba, Winnipeg, Manitoba, Canada

The differential scanning calorimetry (DSC) technique has been used to examine the precipitation process in the commercial Al–Zn–Mg–Cu alloy AA-7075. In general the results are in good agreement with previous DSC data on a similar alloy and can be related to the precipitation process observed by electron microscopy. However, an additonal precipitation process has been detected at low temperatures, which is usually masked by coarsening and dissolution of Guinier–Preston (G–P) zones formed during room-temperature ageing. This precipitate, which is referred to as the "precursor" to η' after Lyman *et al.,* does not redissolve on going to higher temperatures and is an important step in the ageing process in these alloys.

1. Introduction

The use of differential thermal analysis (DTA) for investigating precipitate reactions and phase transformations is common in published literature. Some of the earliest work on the more complex Al–Cu and Al–Zn–Mg alloys was reported by Thompson [1]. The only traces shown for 7000 alloys were for material pre-aged for different times at room temperature. These plots showed that the positions of the endothermic and exothermic reactions were influenced by room-temperature ageing and by composition, while the major exothermic peak (i.e. precipitation reaction) was in the 225 to 250° C temperature range.

More recently, the technique of differential scanning calorimetry (DSC) has been applied to the Al–Zn–Mg and Al–Zn–Mg–Cu alloys by Zahra and co-workers [2, 3], Lendvai *et al.* [4] and DeIasi and Alder [5, 6]. All the DSC graphs show an initial large endothermic peak, while the work of DeIasi and Alder show that this is followed by an exothermic doublet which is not apparent in the other papers. This thermal analysis work has been interpreted in terms of the precipitation sequence:

$$\text{solid solution} \rightarrow \text{G–P zones} \rightarrow \eta' \rightarrow \eta. \quad (1)$$

However, Ryum [7] and Lyman and Van der Sande [8] previously suggested that the precipitation reaction in 7000 series alloys is more complex than the above sequence.

The present work reports the results of a DSC investigation of a high purity version of 7075 alloy which was intended to check the previously published results and compare them with possible precipitation reactions.

2. Experimental procedure

High purity 7075 alloy with the composition shown in Table I was used in the investigation. Hot rolled 0.6 cm plate was cold rolled to 0.25 cm and then given one of the following treatments:

(1) T–4, material was solution heat treated at 480° C for 1 h, water quenched and aged 50 h at room temperature.

(2) T–6, T–4 material was aged for 24 h at 120° C.

(3) T–73, T–4 material was aged for 24 h at 163° C.

Discs of approximately 40 mg from each of the above conditions were examined in a DuPont 990 DSC using a standard heating rate of 10° C min^{-1}.

0022–2461/82/061819–06$03.22/0

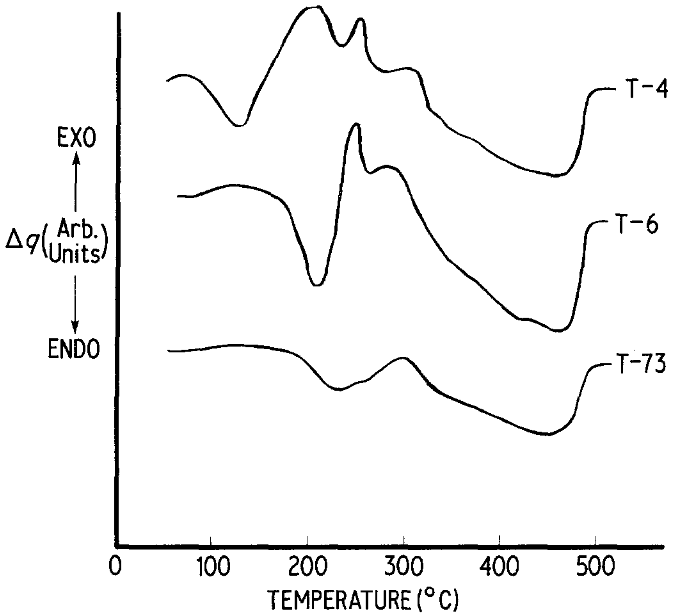

Figure 1 Differential scanning calorimeter graphs for AA-7075 alloy in different tempers.

3. Results and discussion

The DSC graphs for the different tempers are shown in Fig. 1. For T–4 the major features are an endothermic peak at 120° C, an exothermic doublet with peaks at 200 and 240° C and a broad endothermic reaction above 300° C. There is also some evidence for an additional small exothermic reaction around 60° C.

In the case of the T–6 temper, the first endothermic reaction is centered at 200° C and the double exothermic reaction is at 240 and 275° C. The exothermic peak at 275° C is very small and is followed by a broad endothermic peak above 290° C. There is also evidence of a small low-temperature exothermic peak extending over the temperature range 75 to 150° C.

Fig. 1 also shows the trace for the T–73 condition, which has an endothermic peak at 230° C and a further broad endothermic reaction above 300° C.

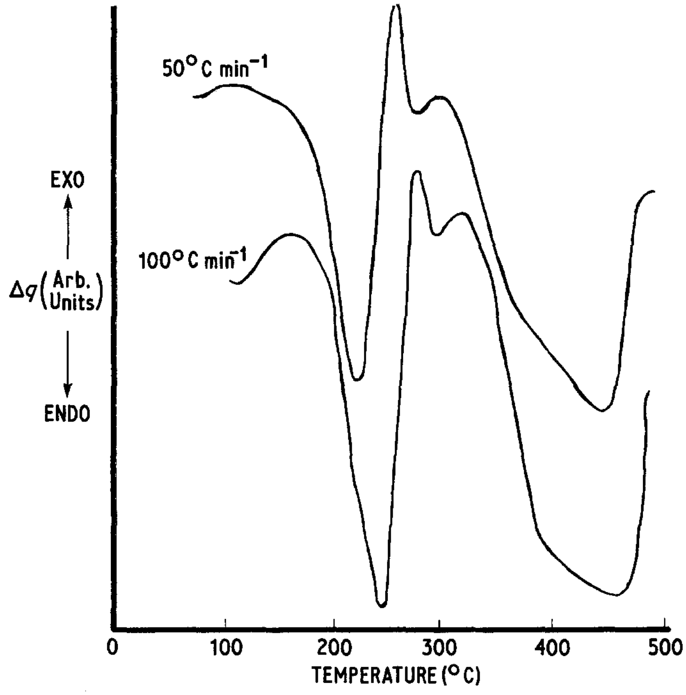

Figure 2 DSC graphs for AA-7075 alloy in the T–6 temper using different heat rates.

TABLE I Composition of 7075 alloy

Element	Mg	Zn	Cu	Cr	Fe	Si	Ti
Content (%)	2.75	5.79	1.64	0.18	0.03	0.03	0.005

Before comparing the present results with previous data and the precipitation reactions involved, it is necessary to assess the influence of heating rate. Fig. 2 compares the DSC traces for T–6 material using heating rates of 50 and 100° C min^{-1}. At the higher rates the peak temperatures are deflected to higher values. The shift in some of the peak temperatures with heating rate is shown in Fig. 3 and it should be noted that the heating rate used to develop the T–6 and T–73 tempers was 60 to 80° C min^{-1}.

The T–4 curve is in general agreement with the Thompson [1] traces for commercial 7075 alloy except that he only detected a single exothermic peak at 250° C. DeIasi and Adler [5] did observe an exothermic doublet in T–6 material at 230 and 250° C which is in good agreement with the present results. Their first endothermic reaction was at 190° C which also compares well with the present data. In general, the DeIasi and Adler results fall about 10° C below the present data. The results for the T–73 temper also compare very well and again there is about a 10° C difference in the temperatures for the first endothermic peak.

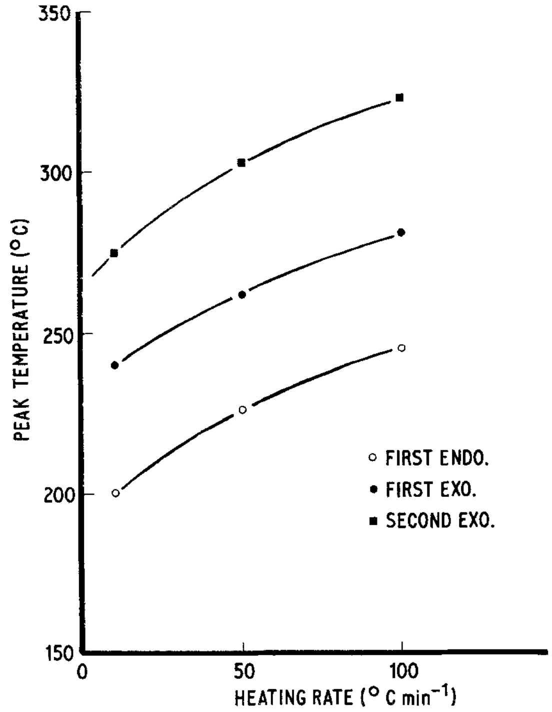

Figure 3 Variation in the peak–reaction temperatures with heating rate for AA-7075 alloy in the T–6 temper.

In Al–Zn–Mg alloys Lacom *et al.* [3] did not observe an exothermic doublet. Also, for material aged at 120° C for 24 h, which is comparable to our T–6 without the room-temperature ageing, Lacom *et al.* did not observe an endothermic peak until about 240° C and Lendvai *et al.* [4] observed the equivalent peak at about 275° C. The respective heating rates were 20° C min^{-1} and 80° C min^{-1}. Fig. 3 shows that the difference between these results and the present data cannot be explained on the basis of different heating rates. The differences must reflect the influence of composition and natural ageing.

The present results differ from the Delas and Adler [5, 6] data in that they indicate a small exothermic reaction prior to the first endothermic peak. However, before discussing this reaction we shall consider how the thermograms are related to the precipitation reaction occurring.

The microstructure after the T–4 treatment is shown in Fig. 4 and consists of angular particles, typically about 0.1 μm in size, in a precipitate-free matrix. Energy dispersive analysis in a scanning transmission electron microscope showed that these particles contained chromium, presumably $Al_{12}Mg_2Cr$. These particles were present in all conditions of heat treatment. From the increase in strength with natural ageing time, the matrix also

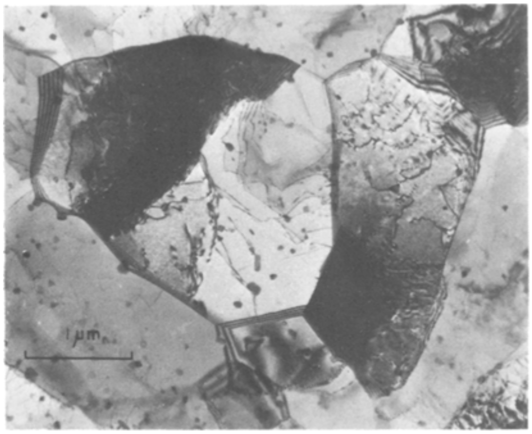

Figure 4 Microstructure of AA-7075 alloy in the T–4 temper.

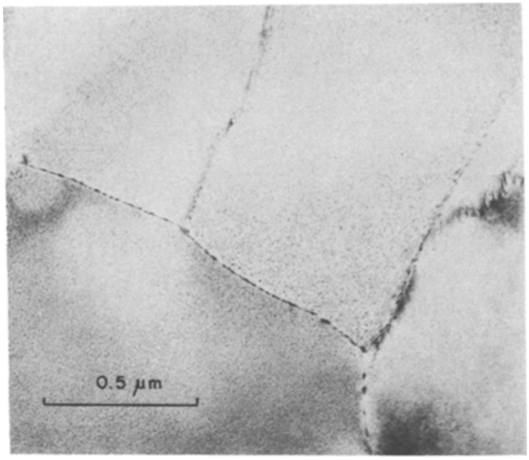

Figure 5 Microstructure of AA-7075 alloy in the T–6 temper.

contains G–P zones but these cannot be resolved at this early stage of development.

The T–6 microstructure is shown in Fig. 5 and consists predominantly of G–P zones in the matrix, which are now sufficiently large to be resolved in the microscope, and equilibrium η-phase along the boundaries.

The microstructure of T–73 temper is shown in Fig. 6. This is a much coarser structure than the T–6 temper and consists of η'- and η-precipitates.

As suggested by DeIasa and Adler [5], the DSC graphs can be explained in terms of the previously suggested precipitation path. For the T–4 and T–6 conditions, the first endotherm is associated with the dissolution of G–P zones, the exothermic doublet is associated with the formation of η' and η and the growth of η. The second endotherm reflects the dissolution of the equilibrium phase η. Transmission electron micrographs of material heated to the various peak temperatures prior to examination were consistent with the above explanation and, since they are very similar to those of DeIasi and Adler [5], will not be reproduced here. The fact that the peak temperatures are higher in the T–6 temper is consistant with the more advanced stage of precipitation in this temper. For the T–73 temper the lack of an exothermic reaction can be explained if the first endotherm is associated with dissolution of η' and this masks any exothermic effects due to formation and coarsening of η. It will be noted that for all tempers the second endotherm occurs above 295° C which is consistent with it being due to the dissolution of the equilibrium phase.

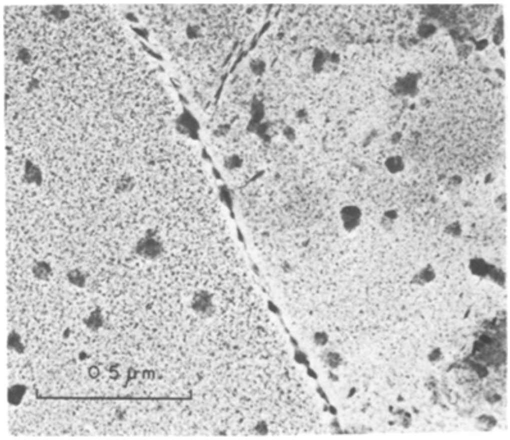

Figure 6 Microstructure of AA-7075 alloy in the T–73 temper.

On the basis of the precipitation path (SS) → G–P zones → η' → η, the small exothermic reaction prior to the G–P zone dissolution peak could be due to additional G–P zone formation and zone coarsening. Fig. 7 shows the microstructure of T–4 material which was heated to 95° C, which is just prior to the dissolution reaction, and then water quenched. Fig. 7 shows that zones can be resolved after this treatment, in agreement with the above hypothesis. However, in the traces obtained by Thompson an initial exothermic peak was only obtained in material examined immediately after water quenching, and was not observed after room-temperature ageing. To check this observation, specimens were water quenched from the solution treatment temperature and tested after different periods at room temperature.

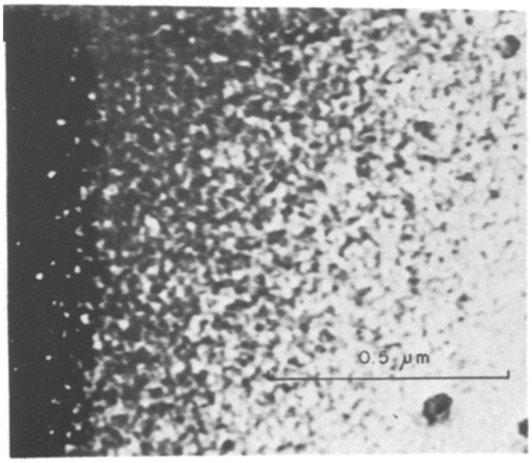

Figure 7 Microstructure of AA-7075 alloy in the T–4 temper after heating to 95° C at 10° C min^{-1} and water quenching.

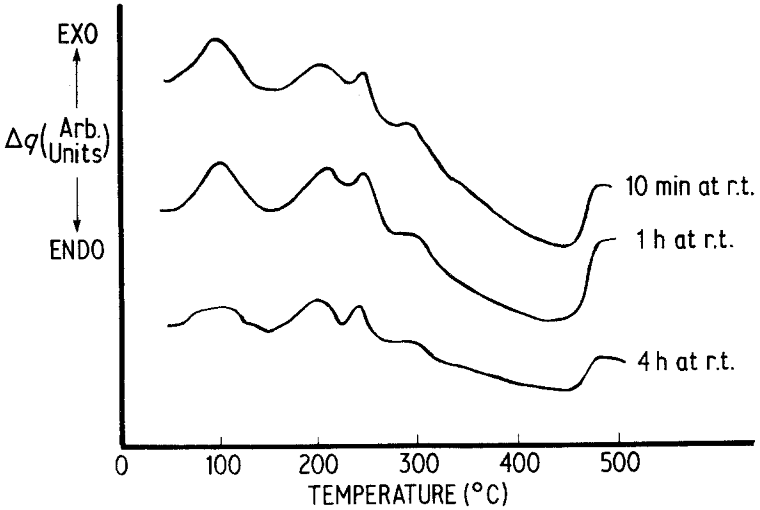

Figure 8 Differential scanning calorimeter graphs of AA-7075 alloy after solution treating at 480° C, water quenching and ageing for various times at room temperature.

Fig. 8 shows the DSC graphs obtained following this treatment. A low-temperature exothermic peak centered at 98° C is now clearly observed, the height of the peak decreasing with time at room temperature. There is also an absence of an endothermic peak at around 100° C, which is present in material aged for 50 h at room temperature (i.e. T–4 temper) in Fig. 1. The subsequent exothermic doublet is largely unaffected by the time at room temperature. The first peak occurs at 200° C, as was the case in the T–4 material and the second peak is at 250° C which is about 10° C higher than the T–4 specimen shown in Fig. 1.

The thermograms shown in Fig. 8 indicate that the precipitation process is not as straightforward as previously outlined. Comparison with the T–4 thermogram indicates that the zones formed during natural ageing at room temperature re-dissolve prior to the formation of η'. However, if "zones" are formed above room temperature, as was the case for the traces in Fig. 8, no re-dissolution occurs prior to the formation of η'. The fact that the exothermic peak associated with η' is unaffected by whether re-dissolution occurs or not suggests that the "zones" formed over the temperature range 60 to 125° C are important in the formation of η'.

Ryum [7], from the ageing response of an Al–Zn–Mg alloy quenched directly to the ageing temperature compared with material held at room temperature prior to heating to the ageing temperature, concluded that "nuclei" for the subsequent η' precipitate are formed very rapidly at room temperature in addition to G–P zones. Lyman and Van der Sande [8] also concluded from TEM results that a spherical precursor to the η' phase with an hexagonal crystal structure is formed in the 30 to 150° C temperature range. The present DSC graphs are consistent with this concept of an intermediate phase being formed. However, contrary to the suggestion of Ryum, they are formed above room temperature in this commercial alloy. The precipitation path appears to be

$$\begin{aligned} \frac{\text{SS} \rightarrow \text{GP zones}}{\text{RT}} &\rightarrow \frac{\begin{array}{c}\text{Dissolution of GP zones}\\ +\ \text{precipitation of}\\ \text{precursor}\end{array}}{30 \rightarrow 150^\circ\ \text{C}} \\ &\rightarrow \frac{\eta' \rightarrow \eta}{150 \rightarrow 300^\circ\ \text{C}} \\ &\rightarrow \frac{\text{Dissolution of } \eta}{300^\circ\ \text{C} \rightarrow} \qquad (2) \end{aligned}$$

On this basis the precipitates seen in Fig. 7 are a mixture of G–P zones and the "precursor" to the η'-phase.

4. Conclusions

The DSC technique can be used to follow the precipitation process in AA-7075 alloy and the results are in good agreement with those obtained by other workers over most of the temperature range. The present experiments have revealed an additional low-temperature exothermic reaction which is largely hidden in commerical tempers by the dissolution of G–P zones formed during room-temperature ageing. However, by examining material immediately after quenching from the solution treatment temperature, this reaction is clearly revealed and is referred to as the precipitation of "precursors" of η'. These precursors are not dissolved on subsequent heating and as a result a modified form of the classical precipitation path is suggested.

Acknowledgements

The authors are grateful to Alcan International Limited for permission to publish this work. One of us (MCC) would also like to thank the University of Manitoba for granting sabbatical leave.

References

1. D. S. THOMPSON, in "Thermal Analysis" Vol. 2, edited by R. F. Schwenker, Jr, and P. D. Garn (Academic Press, New York and London 1969) P. 1147.
2. A. ZAHRA, C. Y. ZAHRA, M. LAFFITTE, W. LACOM and H. P. DEGISCHER, *Z. Metalk.* 70 (1979) 172.
3. W. LACOM, H. P. DEGISCHER, A. M. ZAHRA and C. Y. ZAHRA, *Scripta Met.* **14** (1980) 253.
4. J. LENDVAI, Gy. HONYEK and I. KOVACS, *ibid.* **13** (1979) 593.
5. R. DEIASA and P. N. ADLER, *Metall Trans. A* 8A (1977) 1177.
6. P. N. ADLER and R. DEIASA, *ibid. A* 8A (1977) 1185.
7. N. RYUM, *Z. Metalk.* 66 (1975) 338.
8. C. E. LYMAN and J. B. VAN DER SANDE, *Metall. Trans A* 7A (1976) 1211.

Received 24 September and accepted 12 November 1981