Thermochimica Acta, 214 (1993) 33–40
Elsevier Science Publishers B.V., Amsterdam

Thermal Analysis Studies of the Precipitation and Dissolution Processes of Second Phases in the Al-Si and Al-Si-Mg Systems.

Lars Hälldahl

K-analys AB, Seminariegatan 33H, 752 28 Uppsala, Sweden.

Abstract

In the alloy systems Al-Si and Al-Si-Mg, where Si and Mg typically are in the range 0.5-1.5 w%, a number of second phase particles have been identified, with different composition and crystal structure. To control the conditions under which these particles precipitate and dissolve is very important for controlling the properties of the alloy, like fracture toughness and hardness.

In this paper, particularly the influence of the cooling rate in the DSC instrument, with which alloy samples are cooled from a homogeneous phase at high temperature to subambient temperature, has been investigated. Also the total number of heating-cooling cycles applied to a sample has been used as a parameter to explain the different reactions as identified by DSC.

The results show a close correlation between the cooling rate and the precipitation/dissolution processes. It was found that the characteristics after a certain cooling rate were different depending on how many cycles that material previously had been through. This can have some implication on estimating the properties of materials in applications were heat and load vary over time.

1. INTRODUCTION

Al-base alloys are used for their light weight and also high strength, compared to pure aluminium. Alloying elements are Cu, Zn, Mg, Si, Li, Mn and combinations of these. Properties depend on forming second phase particles through different treatments, like cold working and ageing at temperatures from RT to 150-180 C, for time periods of hours to months. Characteristics depend on the amount of particles formed, their distribution and sizes.

Phase transformations have been studied by thermal analysis DSC, and by microscopy, identifying particles structures and sizes. Normally, researchers are looking at DSC heating runs on quenched or aged samples.

In this work, heating and cooling runs have been studied, and also repeating experiments on the same sample.

This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992

2. MATERIALS USED

In this work, Al-base alloys with Si and Mg have been studied. In Table 1, the compositions are given.

Table 1
Samples composition

Sample	Base	w% Mg	w% Si	w% Mg2Si	w% Excess Si/Mg
A	Al	-	0.8	-	0.8 (Si)
B	Al	0.3	0.8	0.47	0.63 (Si)
C	Al	1.2	0.76	1.87	0.07 (Si)
D	Al	0.71	0.41	1.12	-

Sample A is a binary alloy with Al and Si. C and D are so called pseudo-binary alloys, where all contents of Si and Mg are supposed to form a compund Mg_2Si. B is a more complex alloy with both Mg_2Si and a considerable amount of Si.

All samples have been homogenized for 5 hours at 550 C and then quenched to RT.

Samples for the DSC measurements were cut from rods with a diameter of 5.2 mm and 2-2.5 mm height, giving masses between 60 and 70 mg. As reference, a pure Al-metal sample of the same shape and mass was used.

3. INSTRUMENTATION

A SEIKO Instruments DSC 220 C, equiped with an Auto Cooling System was used. The working range was from -150 C to 725 C. Control of the measurments were done by Disk Station 5200 H, and Standard Analytical Software was used for evaluation.

4. HEATING/COOLING CYCLES

All heating experiments were done from RT to 585 C, with a heating rate of 10 C/min. 50-60 ml/min of dry N_2-gas was always purging the DSC cell, preventing oxidation of the samples. The first heating was always a measurement on a quenched sample. At 585 C, the samples were soaked for 2 hours, then cooled with a controlled cooling rate to -50 C, taken up to RT again, and then the next heating was performed. The sequence of cooling rates differed between the samples. See table 2.

5. RESULTS AND DISCUSSION

The shape of the DSC-curves is in very good agreement with the results published in many papers. References 1-8. Based on this, the interpretation of the different reactions is the following. During quenching, and sometime also by storing at RT, spherical GP-zones form, and during heating in the DSC, the

Table 2
Runorder for different samples

Run No:	1	2	3	4	5	6	
Sample A:	q	50	30	20	10	3	C/min cooling rate
Sample B:	q	3	50	10	30	20	
Sample C:	q	3	10	20	30	50	"
Sample D:	q	3	50	10	30	20	"

first thing that happens is the dissolution of these particulates. At a somewhat higher temperature, non-spherical GP-zones form, and they are then transformed into rod-shaped β'-particles. These reactions overlap. The β'-phase dissolve, and another phase called β starts forming. With raising temperature, also this phase dissolves, and finally the material is a homogeneous single phase solution.

Figure 1 shows the DSC-results for sample A. In this material no indication of GP formation during quenching or cooling can be seen. The order here is from quenched to 3 C/min.

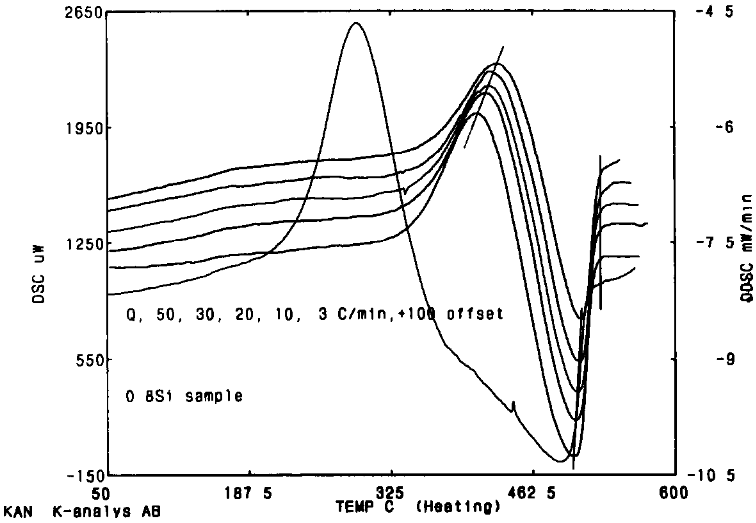

Figure 1.

The exothermal peak temperature, the endothermal peak temperature and the final temperature shift from lower to higher temperatures for each run.

The entalpies are also continuously decreasing, both with decreasing cooling rate and run-order.

The exothermal entalpy is equal to the endothermal entalpy in each experiment. The exothermal entalpy decreases from 5 mJ/mg for 50 C/min cooled, to 3.7 mJ/mg for 3 C/min cooled.

The exothermal and endothermal energies being equal, indicate that no precipitation occurres during cooling and that everything that forms during DSC-heating is also dissolved when the solvus line is reached.

The cooling thermographs from the same sample do not indicate any precipitation.

A part from cooling rates, the major difference is number of cycles that the sample experianced. For every cycle, there is a possibility of grain growth and increasing grain size would reduce the overall diffusion rate for Si atoms in the Al-matrix. This could explain why less and less precipitates are formed and therefore the peaks are smaller and smaller.

Figure 2 shows the DSC-curves for sample D, having a composition corresponding to a pseudobinary alloy with 1.12 w% Mg2Si.

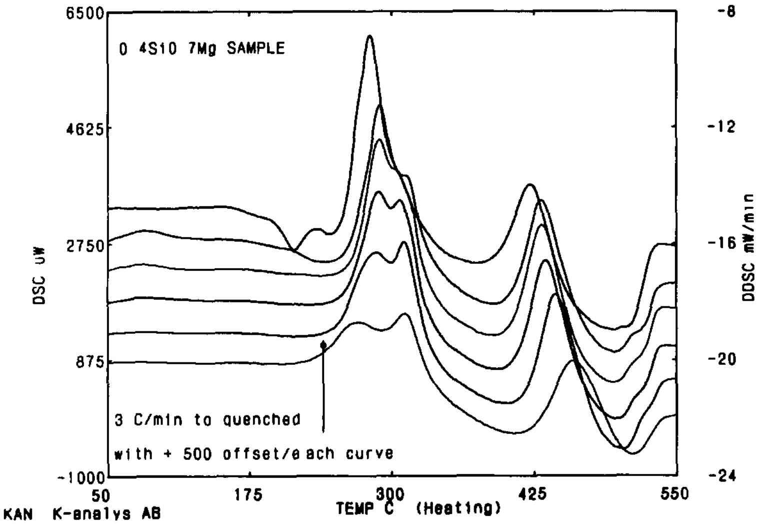

Figure 2.

The quenched sample and the 50 C/min cooled both show an initial endothermal peak indicating that in this system GP zones do form during quenching, cooling or at RT.

The splitting of the exothermal peak due to formation of noncircular GP-zones and β'-precipitates increses with decreasing cooling rate, and the second exotherm, the formation of β-phase, shifts to higher temperatures as a function of cooling rate. The difference is 32 C between quenched and 3 C/min cooled. The final temperature is much more stable, although it varies within 5 C.

The cooling graphs show some different features compared to the sample with only Si. The area under the graphs are larger, and the cooling graph for 50 C/min shows a larger exothermal portion in the lower regions (but not a distinct peak). This material also showed the first endothermal peak due to dissolution of spherical GP-zones during heating.

Comparing the DSC-runs after different cooling rates for the 1.87 w% Mg2Si sample, the peaks seem to look quite different. (Partial melting before the dissolution is finished for the 3 C/min cooled). Figure 3.

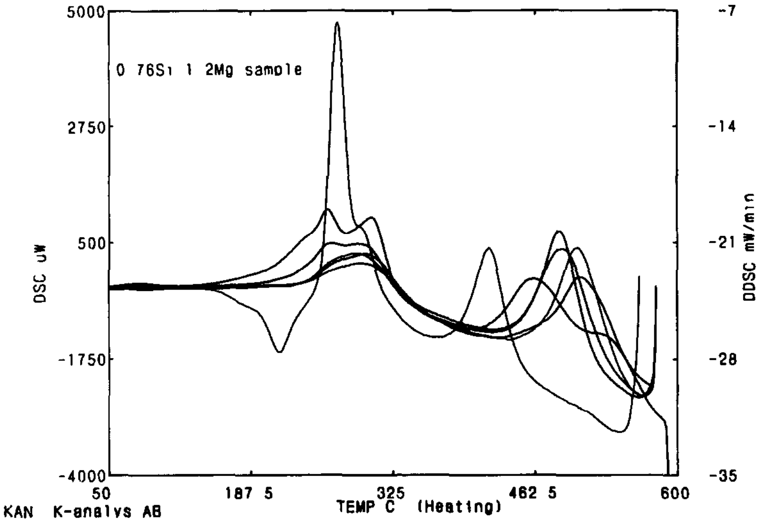

Figure 3.

In sample D the second exothermal peak temperature increased continuously with decreasing cooling rate, in sample C it is a random variation. That is not expected, comparing samples with the same composition, only different amounts. The only other difference is the run order.

DSC-runs on a sample C, after cooling with 10 C/min, are quite different as a second and a fourth run. See Figure 4.

After many runs, the results converge. Figure 5 compares the 4:th 7:th and 9:th cycle of sample D. The curves are very similar.

In the stoichiometric sample with high content, C, the cooling graphs now show very distinct peaks. See Figure 6. The temperature is too high for it to be the spherical GP-zones, and accordingly, no initial endotherms was shown in the heating experiments. It can be non-spherical GP-zones, or β'-phase.

In sample B, containing both Mg2Si and excess Si, the peak temperature for the first exotherm now increses with decresing cooling rate. Figure 7.

There is no tendency to splitting of the first exothermal (GP + β'), and the second exotherm, related to forming β-phase, is very suppressed. The final temperature when everything is redissolved is very well reproduced, all are within 1 C. The cooling curves do not show any distinct peaks.

Also for this sample there is an influence of run-order. In Figure 8, runs after 3 C/min as cycle 2 and 11 are compared.

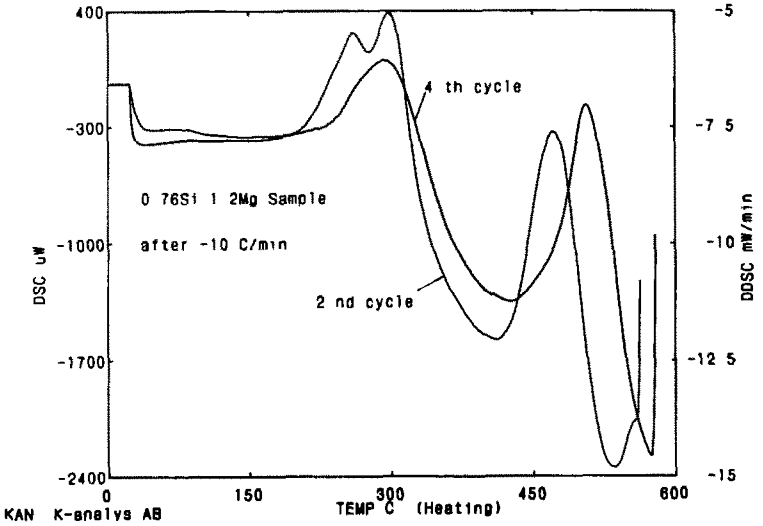

Figure 4.

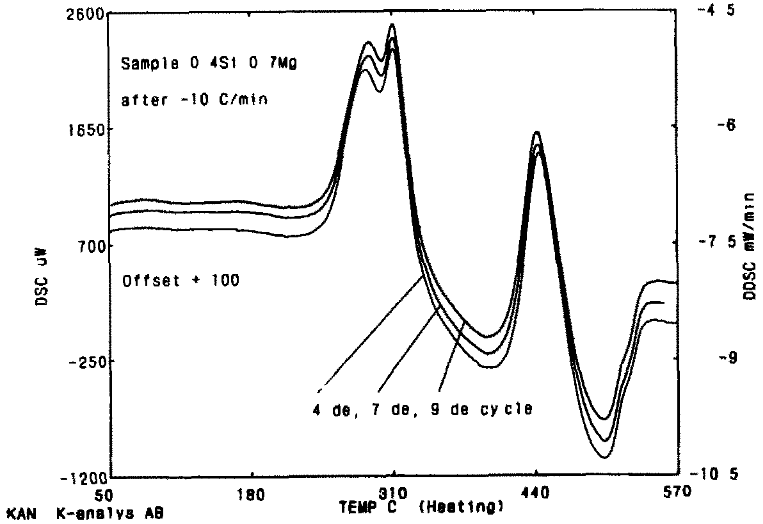

Figure 5.

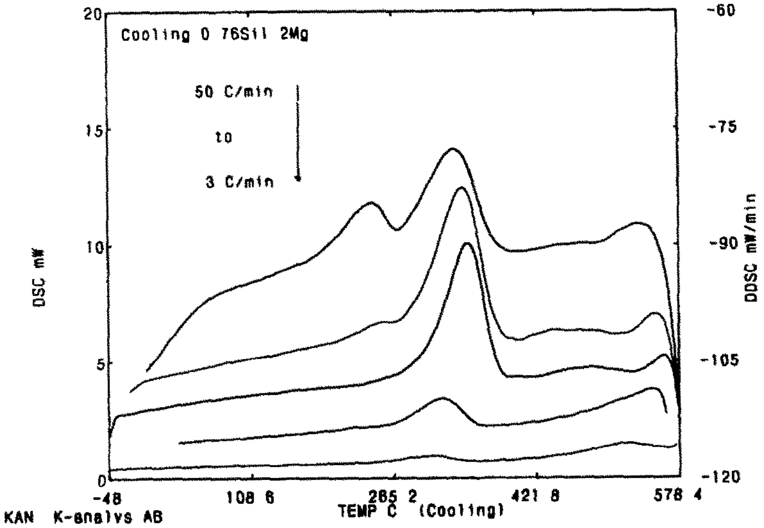

Figure 6.

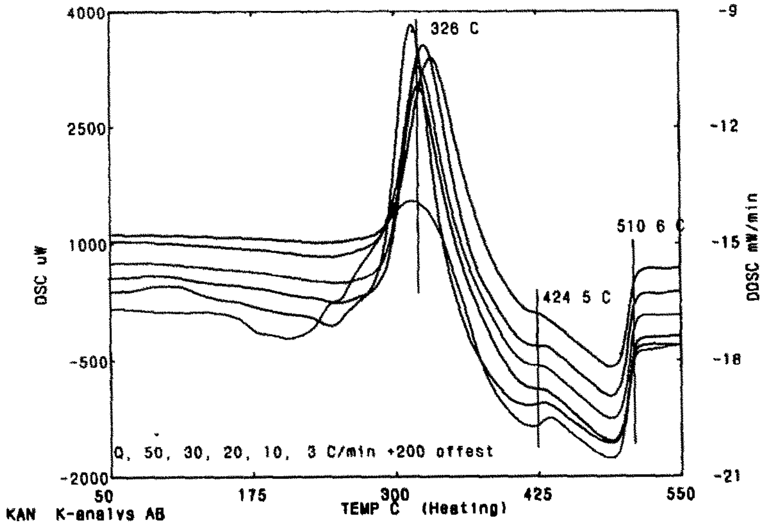

Figure 7.

The precipitation and dissolution of second phase particles in the Al-Si-Mg system is not entirely defined by the amount of alloying elements, quenching/cooling rates and ageing procedures. Also important are microstructural parameters like grain size and homogenity. These parameters influence the DSC runs until reaching a limiting value. The number of runs, or the cumulative soaking time at 585 C, to reach this value, was different for different samples in this investigation, probably de-

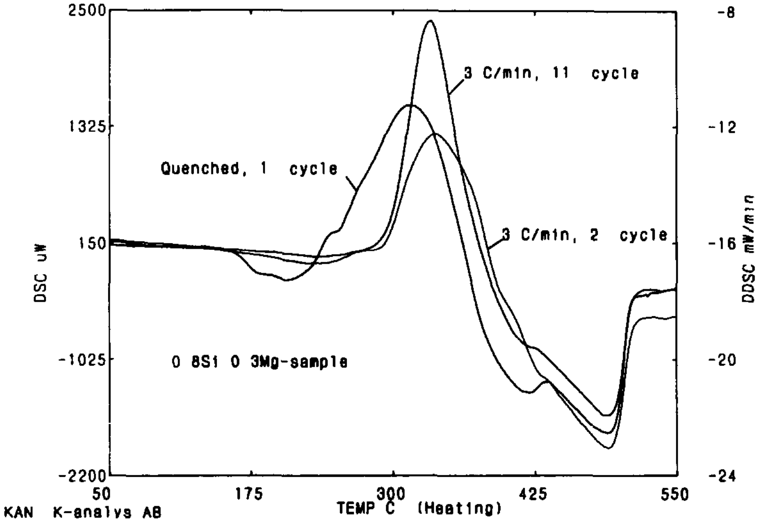

Figure 8.

pending on different treatment before the homogenization described here. The influence of these parameters on materials properties should also be considered for applications of Al-alloys exposed to varying temperature and load conditions.

6. ACKNOWLEDGEMENT

The autor would like to acknwoledge Professor Lars Arnberg and Dr. Anne-Lise Dons, NTH in Trondheim, Norway, for the sample material and for interesting discussions.

7. REFERENCES

1. A.K. Jena, A.K. Gupta, M.C. Chaturvedi, Acta metall. Vol.37 No.3, pp 885-895, 1989.
2. T. Miyauchi, S. Fujikawa, K. Hirano, Trans. JIM. Vol.21, No.9, 1971.
3. A. Zahra, C.Y. Zahra, M. Laffitte, W. Lacom, H.P. Degischer Z. Metallk. 70, p 172, 1979.
4. C. Garcia-Cordovilla, E. Louis, Metall. Trans. 15A, 389, 1984.
5. J.M.Papazian, Metall. Trans. 13A, p 761, 1982.
6. J.M.Papazian, Metall. Trans. 12A, p 269, 1981.
7. C. Garcia-Corodvilla, E. Louis, J.Mater. Sci. 19, p 279, 1984.
8. E. Donoso, Mater. Sci. Engng. 74, p 39, 1985.