# DSC and HRTEM Study of Precipitation in Al-Mg-Si-Cu Alloys

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## Abstract

The precipitation sequences and kinetics of Al-Mg-Si alloys with the addition of Cu have been investigated by using DSC and HRTEM. Microstructure studies on each peak appearing in DSC curves were carried out on HRTEM to better understand which phases were contained along each peak. Also, the activation energy for each peak was calculated and the discussions were made about the reactions occurring during the annealings of this alloy.

## 1. Introduction

Aluminum alloys exhibit low density, high strength, high ductility and high corrosion resistance in the ambient environments. Consequently, they are considered promising candidates for vehicles industry. The resulting weight saving from using this light-weight alloys provides a great benefit of reducing the fuel consumption and exhaustion emission [1]. The Al-Mg-Si-(Cu) alloys are currently being used in automobile's body sheets. The age hardening response of these alloys is very significant and hence, the control of the precipitation during heat treatment is very important for attaining optimum alloy performance [2-6]. In this study, the non-isothermal DSC technique has been applied on Al -0.68 mass% Mg –0.37 mass% Si –0.5 mass% Cu alloy. Eight reaction peaks have been evolved. High resolution transmission electron microscopic (HRTEM) investigation was done also on these specimens heated during the corresponding DSC scans performed at a specific heating rate in order to characterize the precipitates formed these peaks.

## 2. Experimental

In order to follow the precipitation processes, which take place in a balanced Al-063%Mg-0.37%Si (wt%) alloy containing 0.5wt%Cu during continuous heating at constant heating rates, the differential scanning calorimetry (DSC) was used. Disc-shaped DSC samples of 4.5mm diameter and ~ 1.0 mm thick of average weight of ~ 43 mg were machined from the alloy ingot. The specimens were solution heat treated for 3.6 ks at 848 K in a standard convection furnace and then were quenched into chilled water. An annealed pure aluminum disc of similar shape and weight was used as a reference.

Non-isothermal scans for the as-quenched specimens with a DSC thermal analyzer (DSC 220 – S II, Seiko Instruments, Inc., Japan) at heating rates of 2.5, 5, 10, 20, 30, 45 and 60 K $\text{min}^{-1}$ were performed. DSC scans started at room temperature and completed at 800 K under a purified argon gas atmosphere with a flow rate of 80ml/min. The peak temperatures of the reaction processes were determined to an accuracy of ±0.1K by using the microprocessor of the thermal analyzer. Specimens for TEM observations were prepared by the conventional twin jet technique. Topcon EM-002B TEM was operated at 120 kV for HRTEM observations. The microstructure of the developed precipitates at the occurred reaction peaks has been investigated after the specimens having been heated at a rate of 10 K/min to the corresponding reaction peak.

## 3. Results and Concluding Remarks

Figure 1 shows selected non-isothermal DSC thermograms of the supersaturated Al-0.63 mass% Mg -0.37 mass% Si – 0.5 mass% Cu performed at constant heating rates of 5, 10 and 30 K/min. The DSC scans were carried out from room temperature to 800K. Eight main processes can be identified from the DSC thermograms indicated by (I) through (VIII). Five are exothermic labeled as I, III, IV, V and VII and three are endothermic labeled as II, VI and VIII. The exo- and endo-thermic reaction peaks labeled I, II, III, IV, V and VII are shifted towards higher temperatures as the heating rate increases. This information indicates that these reactions are thermally activated. In the present article, the activation energy associated with the individual reactions is calculated by Kissinger and Starink methods [7,8].

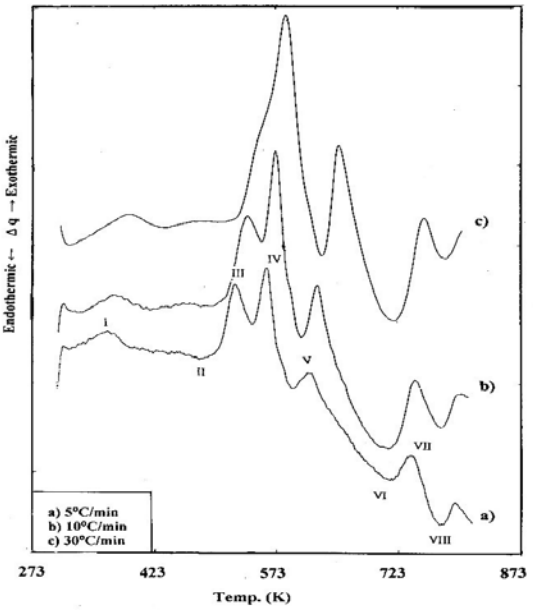

Figure 1: Typical non-isothermal DSC thermograms of the as-quenched Al-1%$Mg_2Si$-0.5%Cu (mass%) performed at constant heating rates of 5, 10 and 30 K/min, (thermograms a, b and c, respectively).

The reaction peaks can be explained as follows:

(i) Exothermic reaction I- This reaction can be ascribed to the early stage clustering of Si-Mg-Vacancy clusters. Its activation energy has been determined as 53.3 kJ/mol. This value is approximately equal to the migration energy of Si in Al (52.7 kJ/mol) which is calculated from the activation energy of diffusion of Si in Al (124 kJ/mol) [9] and the formation energy of vacancies in Al (71.3 kJ/mol) [10]. The activation energy is also too close to the activation energy of position change of Mg in Al [9]. Thus the kinetics of the clustering process can be controlled by migration of Si atoms and coalescence with Mg atoms. Due to the abundant concentration of excess quenched-in vacancies and high affinity to Mg, the Si-Mg-Vacancy clusters can be formed.

(ii) Endothermic trough II - The reaction can be attributed to the dissociation of vacancies and annealing out leaving behind the Si-Mg clusters.

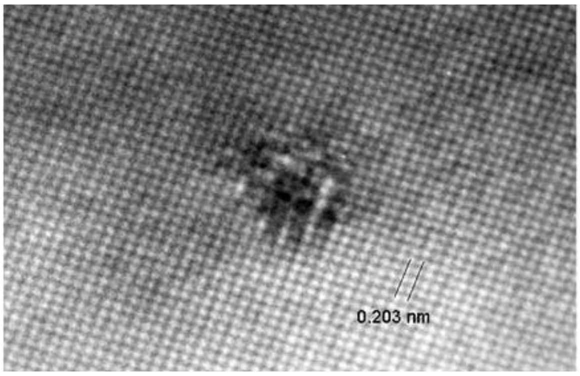

Figure 2: HRTEM image showing the random-type precipitate evolved as a result of heating the specimen at a heating rate of 10 K/min to 460.5 K and kept at this temperature for 5 min.

(iii) Exothermic reaction III - This reaction can be attributed to the growth of the preformed Si-Mg clusters to form random (disordered)-precipitates. This peak has a tendency to overlap with the next reaction peak as the heating rate increases which suggests that the formation of random precipitates possesses lower driving force in comparison with the subsequent process. Figure 2 shows a typical HRTEM image of a typical random precipitate. The activation energy associated with this random precipitates is 82.65 k/mol.

(iv) Exothermic reaction IV - This reaction is attributed to the precipitation of Q'-phase. The determined activation energy for this reaction is 130.5 k/mol. This energy is very close to the activation energy of Cu and Mg atoms in Al matrix, 135 and 131 kJ/mol, respectively [11] and comparable to the activation energy of Si diffusion in Al. Therefore, the kinetics of this reaction is controlled by diffusion Si, Mg and Cu atoms to form Q'-(Al-Mg-Si-Cu).

(v) Exothermic reaction V - This reaction is attributed to the formation of β′ and Q′- phases. The activation energy associated with these precipitates is 139.14 kJ/mol. This value is close to that calculated for the preceding process, which indicates that the mechanism of these precipitates can be explained by the same way.

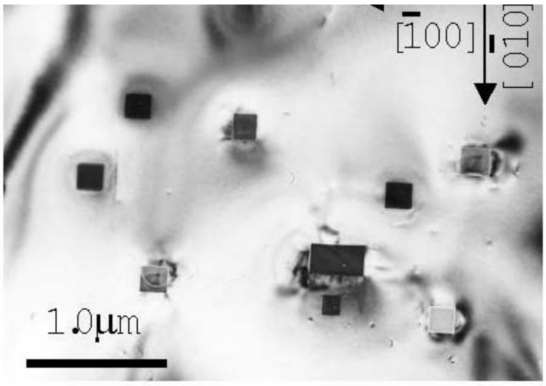

Figure 3: TEM micrographs for a specimen heated to the reaction peak VI developed at 745 K showing plates of equilibrium β-phase.

(vi) Endothermic reaction VI - this reaction can be explained by the dissolution of all preformed precipitates.

(vii) Exothermic reaction VII - This reaction could be due to the precipitation of large β-($Mg_2Si$) precipitates. A TEM microgragh showing β-phase is presented in Figure. 3.

(viii) Endothermic reaction VIII - This endothermic reaction can be interpreted by the dissolution of the large β-($Mg_2Si$) -phase in the matrix. This process is not thermally activated but rather, it is temperature dependent

Owing to the combined results of DSC and TEM, the following conclusions can be evolved:

(i) The precipitation sequence during continuous heating is: Mg-Si-Vacancy clustering, random precipitates, Q'-phase, Q'/β' precipitates and β-($Mg_2Si$) phase.

(ii) The optimum aging temperature to achieve the required strength of the alloy is 480.5 K when it is heated at a rate of 10 K/min.

## References

[1] I. J. Polmear, “Light Alloys: Metallurgy of the Light Metals” 3rd Ed., Arnold Publisher, London, UK (1995).
[2] K. Matsuda, S. Taniguchi, K. Kido, Y. Uetani, S. Ikeno, Materials Transactions, 43, 11 (2002) 2789-2795.
[3] K. Matsuda,Y. Sakaguchi,Y. Miyata, Y. Uetani, T. Sato, A. Kamio, S. Ikeno, J. Mater. Sci. 35 (2000) 179-189.
[4] W.F. Miao, D. E. Laughlin, Metall. and Mater. Transactions A, 31A (2000) 361-371.
[5] D. J. Chakrabarti, Y. Peng, D. E. Laughlin, Mater. Sci. Forum, vols. 396-402 (2002) 857–862.
[6] M. Murayama, K. Hono, W. F. Miao, D. E. Laughlin, Metall. And Mater, Trans. A, 32A (2001) 239-246.
[7] H. E. Kissinger, Analyt. Chem., 29 (1957) 1702-1706.
[8] M. J. Starink, A.M. Zahra, Phil. Mag., A77 (1998) 187-199.
[9] Kinzoku, data book, Japan Inst. Metals, Sendai, Japan (1994), P. 20.
[10] N. K. Gobran, F. M. Mansy, S. S. Hamza, Phys. Stat. Solidi A, 59 (1989) 69.
[11] W. D. Callister, Jr., “Materials Science and Engineering”, 2nd Ed., John Wiley & Sons, Inc., New York, 1990, P 105.