

Low-Temperature Differential Scanning Calorimetry of an Al-Mg-Si Alloy

C.S.T. CHANG and J. BANHART

The clustering behavior at room temperature of a pure ternary Al-0.59 wt pct Mg-0.82 wt pct Si alloy was investigated by low-temperature differential scanning calorimetry (DSC). We find three clustering reactions that take place in two stages. The first two reactions are linked to each other and are completed after 1 hour. The third reaction starts around 1 hour after quenching and is completed after 2 weeks. Only the latter reaction exhibits a strong shift of the peak position of the thermal signal, indicating a change in the activation energy during aging at room temperature caused by changing solute supersaturation or increasing trapping of vacancies. The first two stages are closely linked to the known adverse effect of room-temperature preaging on the ensuing age-hardening step, since 60 to 80 pct of cluster formation is sufficient to establish the full negative effect.

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IMMEDIATELY after solutionizing and quenching, many aluminum alloys of the 6000 series (Al-Mg-Si) undergo structural changes even at room temperature that, already after a few minutes, give rise to notable changes, *e.g.*, in the electrical resistivity and hardness. Although these changes at room temperature are technologically not relevant since such alloys are usually artificially age hardened to maximum strength at around 433 to 453 K (160 to 180 °C), there is considerable interest in this natural aging (NA) since it influences the subsequent artificial aging (AA) step. In alloys containing typically 0.5 to 1 wt pct of both Mg and Si, this response is negative; *i.e.*, AA is much slower and leads to lower peak strengths after NA,^[1,2] expressed by the decrease of the number density and the increase in length of the strengthening phase β'' in the peak-aged condition.^[3,4]

Although a lot of research work based on different experimental methods was performed to identify the processes during NA and the reasons for negative strength response, the exact mechanisms are not yet known. Using differential scanning calorimetry (DSC), two clustering reactions were shown to take place at temperatures up to 373 K (100 °C).^[5] It was assumed that the first reaction, which at room temperature is completed after 1 hour, corresponds to Si-rich clusters, whereas the second stems from Mg slowly diffusing to these clusters for at least 1 week and eventually forms Mg-Si co-clusters.^[5] There is actually not much experimental proof that this is true. The claim of a direct observation of Si clustering by transmission electron microscopy (TEM)^[6]

could not be verified in later work,^[7,8] and it is mainly atom probe (AP) work that provides some evidence that initially Si and Mg clusters are formed, whereas after 70 days of NA, clusters containing both Mg and Si are found.^[7] A similar observation was made for an alloy lower in both Si and Mg.^[9] Another AP study on alloys high in Mg claimed to have shown the increase in relative Mg content during clustering,^[10] but the NA times applied were very long compared to the time in which the first reaction is completed (1 hour). Moreover, there is still some controversy about the reliability of cluster identification from 3-Dimensional(3-D)AP data using different kinds of algorithms.^[11]

It was postulated that the first clusters formed at lower temperatures, *e.g.*, during NA,^[12,13] are not suitable nucleation sites for the strengthening β'' phase during ensuing AA, which could be the reason for the negative effect of NA. These clusters can neither further grow during AA nor are dissolved; therefore, less solute is available. On the other hand, if aging is carried out at temperatures between 323 and 373 K (50 and 100 °C), it is postulated that formation of the first cluster is suppressed and the second cluster forms immediately, which in turn can continuously grow to β'' precipitates during AA. The idea that there are two competing clustering pathways at different temperatures is not generally shared; the viewpoint that the first clustering reaction isothermally evolves into the second one is also found.^[5] It has also been found that clustering can occur below room temperature and causes an increase in hardness^[14] and resistivity^[15] when aged at as low as 253 K (−20 °C). Recently, positron lifetime measurements with high time resolution have shown that NA is more complex than assumed previously. The lifetime curve as a function of NA time shows four different stages of clustering, namely, up to 7 to 10, ≈ 50 , and ≈ 750 minutes after quenching.^[16] This provides a strong motivation to study clustering within the first hour in further detail. The method chosen in this work is DSC,

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because it can resolve the precipitation sequence in Al-Mg-Si alloys.^[4,5,13] Usually, these experiments are started above room temperature, *e.g.*, 303 K (30 °C),^[5,17] and information on reactions occurring close to room temperature will be lost. Low-temperature DSC was applied to Al-Mg-Si,^[12,13] but a systematic study is lacking. In this article, low-temperature DSC was performed with an emphasis on separating the various clustering reactions occurring isothermally at room temperature especially within the first hour.

An alloy Al-0.59 wt pct Mg-0.82 wt pct Si (code “F”) was provided by Hydro Aluminum (Bonn). The alloy was based on ultra-pure elements, implying that the level of all impurities detected was <10 ppm. This alloy was chosen because NA is known to have a fast negative effect on AA response here.^[18] Samples were received as 1.2-mm extruded bar. Solution heat treatment at 813 K (540 °C) for 1 hour in an air circulation furnace was followed by ice water quenching. The samples were dried, after which they were immediately used or aged at room temperature (≈ 295 K (22 °C)) for between 5 minutes and 2 weeks. In the experiments without NA, the estimated delay time between quenching and starting the DSC run was about 1 minute. The samples were loaded into a differential scanning calorimeter precooled to 223 K (−50 °C) and were left there to equilibrate for 5 minutes before starting the measurement. The DSC used is a Perkin Elmer “Pyris 6” (Waltham, MA) located at the Department of Mechanical Engineering at The University of Hong Kong. All experiments were performed with a constant heating rate of 10 K/min unless otherwise stated. Reference curves of 99.9 pct Al measured with the same heating schedule were used as baseline and were subtracted from all alloy heat flow curves.

Figure 1 shows DSC curves of samples used directly after solutionizing and quenching that were measured with two heating rates. The full curve (10 K/min) is typical for a DSC curve of this type of alloy and shows individual exothermic reactions that are numbered. The precipitation sequence assigned to these reactions is as follows: Clusters → GP zones → β'' → β' → β .^[5,19–21]

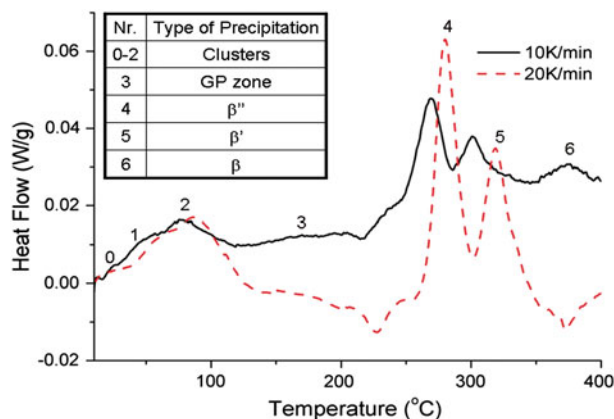


Fig. 1—Heat flow curves of the solutionized and quenched alloy showing the full precipitation sequence. Numbers identify stages of precipitation and are defined in the inset table. The full curve corresponds to a heating rate of 10 K/min, and the broken one to 20 K/min. Positive heat flows denote exothermic reactions.

Three overlapping cluster peaks could be observed in the temperature range from 283 to 403 K (10 to 130 °C). This has not been reported previously in the literature, most likely because, unlike there, we started DSC at 223 K (−50 °C). We number the reactions “Cluster 0 = C0,” “Cluster 1 = C1,” and “Cluster 2 = C2” to conform with the terms “Cluster 1” and “Cluster 2” in Reference 13. The heat release from C0 is very small compared to the other two cluster peaks, and the peak temperature is very low, around 298 K (25 °C). In order to confirm the existence of C0, one experiment was also performed at a heating rate of 20 K/min (broken curve). The three cluster peaks are even more clearly visible here, confirming that the “C0” stage actually exists. Despite the better resolution at 20 K/min, we stayed with 10 K/min in this article, since this rate is most frequently used in studies of Al-Mg-Si alloys^[4,5,12,13,17,19–21] and comparisons are facilitated. We will see later that C0 and C1 develop in parallel. The obvious question of whether C0 is just a transient stage of C1 cannot be answered without further input from methods other than DSC. At the higher heating rate, all the precipitation peaks are shifted to higher temperatures. This is similar to the results shown in Reference 5 and in accordance with the picture of a diffusion-controlled thermally activated clustering process.

Figure 2(a) shows additional heat flow curves of samples after different NA times. Clearly, the cluster peak areas decrease with NA time. For a better view of the clustering reactions, Figure 2(b) displays the cluster peaks only. From this figure, it is obvious that the peaks corresponding to C2 move to higher temperatures for longer NA times. In order to find a quantitative relationship between NA time and cluster formation, the cluster peaks are fitted, after which the peak areas are calculated. Figure 3(a) shows one of the fitting results. It is assumed that the exothermic reaction detected during the DSC run is due to cluster formation only, which means that dissolution reactions within the temperature range of cluster formation can be neglected.^[5] In Reference 8, it was suggested that C1 and C2 appear as separate peaks only because there is an endothermic Mg cluster dissolution peak in the same temperature range. In view of the DSC results obtained at different heating rates, however, this appears unlikely (also Reference 5). Moreover, if this were true, samples naturally aged for longer times should show a dissolution peak before C2.

The DSC baseline is set as the heat flow value of the starting point of cluster formation, *i.e.*, at 283 K (10 °C). The peaks are fitted by four Gaussian functions (12 variables in total),

$$q = q_0 + \sum_{i=1}^4 \frac{A_i}{w_i \sqrt{\pi/2}} e^{-\frac{2(T_i - T_{ci})^2}{w_i^2}} \quad [1]$$

where q_0 is the base line offset, A_i is the area below each individual cluster peak, T_{ci} is the peak center, and w_i is the full-width at half-maximum of the peak. In order to obtain a better fit of the observed three cluster peaks ($i = 1 \dots 3$), an additional Gaussian including both the low-temperature tail of the GP zone peak and the residual background signal was included ($i = 4$).

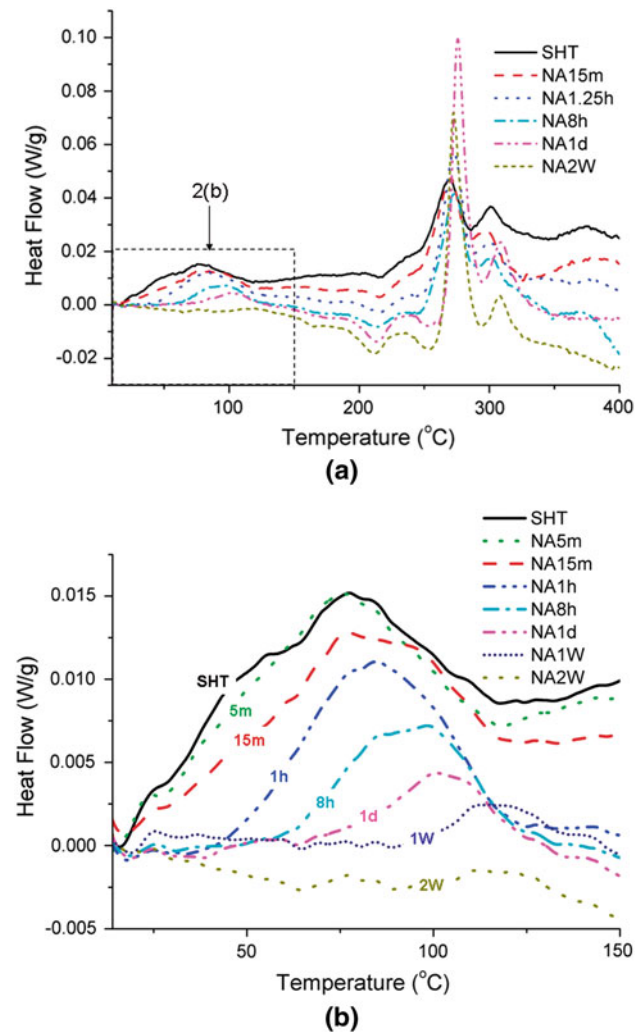


Fig. 2—(a) Heat flow curves of samples that were naturally aged before the DSC experiments and (b) close up of heat flow curves in (a) showing only the clustering stages.

The statistical errors of the values obtained for A_i are less than 0.02 J/g, but the actual systematic error should be much higher. Different fits based on three different pure Al reference curves, therefore, are used to obtain an average peak area plus an estimate for the error associated with the baseline subtraction. The area of the individual cluster peaks represents the specific heat released in the individual clustering processes. Figure 3(b) shows these various cluster peak areas against NA time. The starting value represents the sample just after quenching plus 1 minute delay at room temperature due to mounting of the sample into the DSC. The peak areas of C0 and C1 decrease simultaneously and completely disappear after 1 hour of NA, while the peak area of C2 shows no significant change within the error limits during the first hour of NA. After 1 hour, the peak area of C2 also starts to drop and has disappeared after 2 weeks of NA. The slight kink observed after about 1000 minutes of NA is very close to the confidence limit of the measurement. Figure 3(b) also displays data taken from the literature.^[5] The

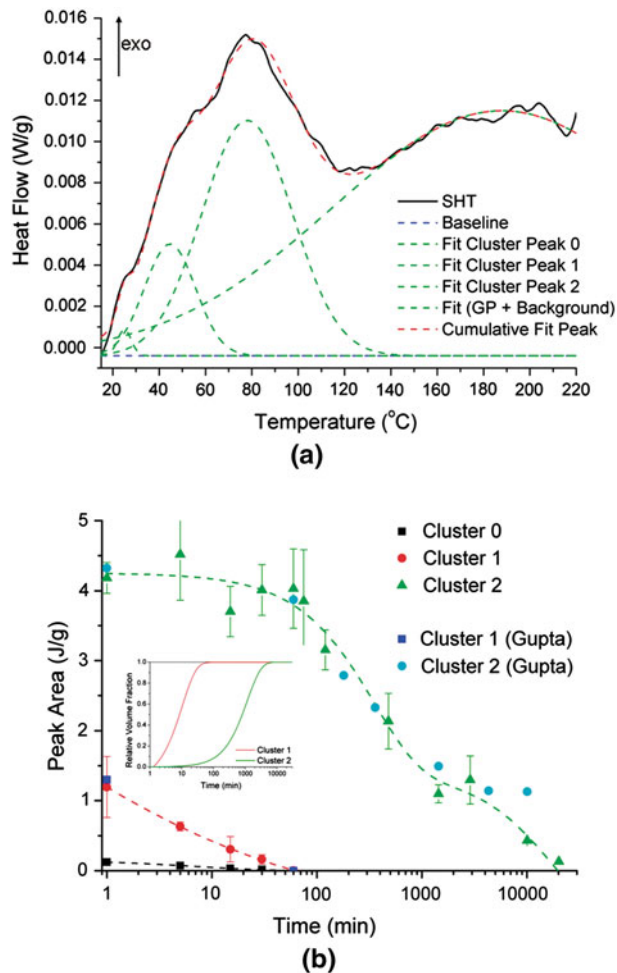


Fig. 3—(a) Enlarged heat flow curve of the solutionized and quenched sample showing how the peak area for clusters was obtained by fitting Gaussians to the peaks. (b) Change of peak area of the clusters with NA time. Variations caused by different baseline corrections are represented by error bars. The small graph represents the relative volume fractions of C1 and C2 as a function of NA time, as calculated from Eq. 2. Values taken from Ref. 5 are included.

agreement with the literature values is almost perfect even in terms of absolute values, except for the value after 1 week. This agreement is notable, especially because in the work cited, an alloy richer both in Mg and Si, namely, 0.8 wt pct Mg and 0.9 wt pct Si, was used and one could expect higher heat flows. This is not the case, which could indicate that clustering is saturated above a certain (unknown) level of solute.

It was verified that the measured DSC peak areas correspond to the volume fractions of the precipitates formed by comparing the peak areas of β'' and β' with the volume fractions found by TEM statistical analysis.^[22] We assume that this holds for clusters too and calculate the relative volume fraction of a cluster as

$$f_r = 1 - \frac{P}{P_{\text{SHT}}} \quad [2]$$

where P is the peak area of either C1 or C2 and P_{SHT} is the corresponding quantity for the solution-heat-treated sample. In References 5, 20, and 23, the relative volume

fraction of β'' and β' is obtained by isothermal DSC at temperatures from 423 to 523 K (150 to 250 °C). Isothermal DSC is preferable from the viewpoint of accuracy but is hardly applicable to the clustering process considered here due to the stability issues of DSC (Figure 3(b)). If we assume that no dissolution reaction occurs in the temperature range from 293 to 413 K (20 to 140 °C), the peak area in constant heating rate measurements should be a good measure too. The inset in Figure 3(b) shows the relative volume fraction against NA time and demonstrates that the formation of C1 is finished after 1 hour of NA. This actually corresponds very well to the resistivity measurements on the similar alloy Al-0.46 wt pct Mg-1.05 wt pct Si described in Reference 15, which show that a first stage of fast resistivity increase during NA turns into a slower increase after ≈ 1 hour. Something very similar was also found for the alloy investigated in this work.^[16] This suggests that the regime of the fast resistivity increase, as given by References 15 and 16, corresponds to the formation of C1. Around the same time, changes of the rate of hardening and the average positron lifetime occur.^[16]

The formation of C2 is almost finished after 2 weeks of NA and the rate is much slower, as represented by a smaller slope of curve C2 in Figure 3(b). C2 starts forming after 1 hour of NA, which suggests that C2 might form after C1 or that C1 even evolves into C2. Note that if one accepts the kink in Figure 3(b) at ≈ 1000 minutes as real effect, it could be related to a further change in slope of the hardening curve, the electrical resistivity, and the positron lifetime.^[16]

During quenching from 813 to 273 K (540 to 0 °C), most of the thermal vacancies come into contact with solute atoms as they sample the lattice positions on their random walk. At high temperatures, their binding energy with either Mg or Si (a few tens of meV, no accepted values exist^[24]) is in the range of the thermal energy, but eventually they could be trapped and form solute/vacancy complexes. Alternatively, they could annihilate in grain boundaries or condense into dislocation loops,^[25] but only if the vacancy/solute binding energies are smaller than the room-temperature thermal energy (25 meV). It seems very likely that shortly after quenching, no more free vacancies exist.

The formation of Clusters 0 and 1, which is detected during the DSC run, should start from this state, *i.e.*, with an initial state of vacancy-solute pairs. The formation of clusters with more than two solute atoms will be considered as the formation process of C0/C1. Si is thought to form clusters before Mg comes into play. As pointed out earlier, this idea is generally accepted but actually supported by only a few studies,^[10] some of which represent measurements at higher temperatures.^[8] The recently observed decrease of positron annihilation lifetime during the first hour of NA^[16] points in this direction, but altogether our knowledge is very scarce.

The composition and structure of C2 is not directly observable. From the preceding results, C2 might be a transformation state of C1, forming at a much lower rate than C1. Mg enrichment was proposed as the main feature in this clustering stage,^[5] and the increase of positron lifetime after about 50 minutes of NA that is observed in

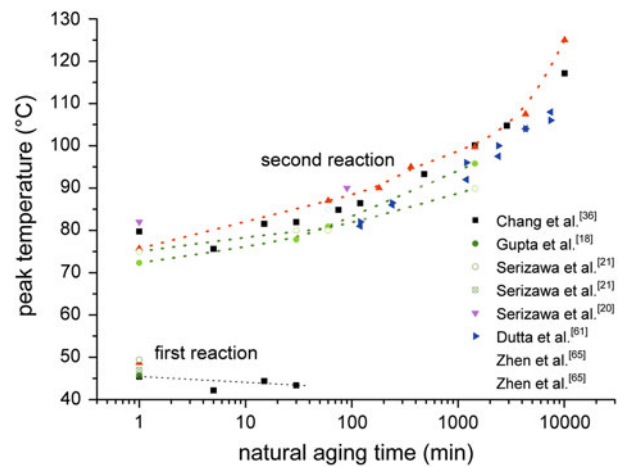


Fig. 4—Comparison of peak positions for C1 and C2. Squares: this work, other symbols: literature values.^[5,6,13,19,26]

Mg-containing but not in Mg-free alloys points in this direction.^[16] Moreover, AP analysis has shown Mg enrichment in samples naturally aged for a long time.^[7,13]

The peak position of C2 formation varies during NA, as shown in Figure 4. There is a very good agreement with other sources in the literature, although the compositions and impurity levels vary. The variation of peak position can be explained as follows: In the course of progressing NA, clusters of changing compositions are created. Due to the initial availability of a high concentration of solute/vacancy pairs and a high solute supersaturation, cluster formation is easily thermally activated. In the further course of clustering, vacancies are increasingly trapped in Si-rich clusters or Mg-Si clusters that become denser, and diffusion becomes more sluggish, especially because the driving force due to solute supersaturation also decreases. The clustering reaction is then more difficult to activate. The ensuing DSC analysis reflects this distribution of activation energies: after no or just a short NA, the easy to form clusters appear at low temperatures already; after long NA, the low-temperature part of the peak already formed during NA and just the clusters that require higher temperatures to be activated can be formed.

The C1 peak does not show this behavior. This can be explained if one assumes that the clusters formed are very open Si-rich agglomerates and the vacancies detach from these easily. This is necessary because the vacancy concentration is about 1/100 of the solute concentration only, so that each vacancy has to transport many solute atoms. (The concentration of the vacancies quenched from 813 K (540 °C) can be calculated by the equation $f_v \approx \exp\left(\frac{S_f}{R}\right) \exp\left(\frac{-E_f}{RT}\right) \approx 0.009$ pct, in which $E_f \approx 67$ KJ/mol is the formation energy of a vacancy in Al, R the gas constant, and T the quenching temperature and the entropy $S_f \approx 0.6R$.) Solute supersaturation is not the limiting factor in this stage. Therefore, the activation energy of cluster formation is constant, and in the ensuing DSC analysis, the peak remains at the same temperature.

Methods with a high sensitivity to individual solute and vacancy interactions such as positron Doppler broadening analysis would be required to obtain more definitive facts about the composition in the early stages of clustering.

Finally, the relationship between cluster formation during NA and the negative effect on AA shall be discussed. Serizawa and Sato concluded from their AP analysis that the size and composition of C1 does not change after prolonged NA, and they explain the negative effect by assuming that C1 cannot serve as a nucleus for precipitate growth during AA.^[13] However, the “C1” that they could observe is after 7 or more days of NA. From the DSC results shown previously, it is suspected that the cluster that Serizawa and Sato observed is our C2 and not C1, since C1 has already finished forming after 1 hour of NA (Figure 3(b)) and C1 might already have either transformed to C2 after 7 days of NA or, if C1 does not transform into C2, C2 is dominating the picture as its volume fraction is much higher. Obviously, the C2 clusters do also not serve as nuclei for precipitate growth during AA. As in Reference 13, 10 minutes of aging at 373 K (100 °C) is found to both create C2 and to remove the negative effect; one has to conclude that either the C2 formed at room temperature and 373 K (100 °C) has different structures or another aspect besides the presence of clusters has to be considered, e.g., the density or mobility of vacancies.

It should also be noted that the negative effect on AA is being settled within the first 10 to 18 minutes of NA,^[16] i.e., the age-hardening trend will be very similar after 10 to 18 minutes of NA and a further decrease in strength will not occur. This time period is within the formation process of C1. With increasing NA time, the strength response will not further decrease, meaning that the aging response will be similar even if the formation of C1 is complete or C2 is present. Therefore, from the inset in Figure 3(b), we estimate that roughly 60 to 80 pct of C1 formation is already sufficient to fully establish the negative effect.

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