

Low-temperature differential scanning calorimetry of a Al-Mg-Si alloy

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The clustering behavior at room temperature of a pure ternary Al-0.59wt%Mg-0.82wt%Si alloy has been 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 h. The third reaction starts around 1 h 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 ageing 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 pre-ageing on the ensuing age hardening step, since 60-80% of cluster formation is sufficient to establish the full negative effect.

Immediately after solutionising 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 433K (160Celsius) to 453K (180Celsius), there is considerable interest in this natural ageing (NA) since it influences the subsequent artificial ageing (AA) step. In alloys containing typically 0.5 – 1 wt.% 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 has been performed to identify the processes during natural ageing (NA) and the reasons for negative strength response, the exact mechanisms are not yet known. Using Differential Scanning Calorimetry (DSC), two clustering reactions have been shown to take place at temperatures up to 373K (100Celsius) [5]. It has been assumed that the first reaction which at room temperature is completed after 1 h, 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 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 h). Moreover, there is still some controversy about the reliability of cluster identification from 3-DAP data using different kinds of algorithms [11].

It has been 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 and therefore less solute is available. On the other hand, if ageing is carried out at temperatures between 323K (50Celsius) and 373K (100Celsius), 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 253K (-20Celsius). 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 7-10, ≈ 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 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. 303K (30Celsius) [5,17] and information on reactions occurring close to room temperature will be lost. Low temperature DSC has been applied to Al-Mg-Si [12,13], but a systematic study is lacking. In this paper, 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-0.59wt%Mg-0.82wt%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 has been chosen because NA is known to have a fast negative effect on AA response here [18]. Samples were received as 1.2mm extruded bar. Solution heat treatment at 813K (540Celsius) for 1 h 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 (22Celsius)) for between 5 min and 2 weeks. In the experiments without NA, the estimated delay time between quenching and starting the DSC run was about 1 min. The samples were loaded into a differential scanning calorimeter pre-cooled to 223K (-50Celsius) and were left there to equilibrate for 5 min before starting the measurement. The DSC used is a Perkin Elmer 'Pyris 6' 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% 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 solutionising 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: Clusters \rightarrow GP zones \rightarrow β'' \rightarrow β' \rightarrow β [5,19,20,21].

Three overlapping cluster peaks could be observed in the temperature range from 283K (10Celsius) to 403K (130Celsius). This has not been reported previously

in the literature, most likely because unlike there we started DSC at 223K (−50Celsius). We number the reactions ‘Cluster 0 = C0’, ‘Cluster 1 = C1’, ‘Cluster2 = C2’ to conform with the terms ‘Cluster 1’ and 2 in Ref. 13. The heat release from C0 is very small compared to the other two cluster peaks and the peak temperature is very low, at around 298K (25Celsius). In order to confirm the existence of C0, one experiment was also performed at a heating rate of 20 K/min, see broken curve. The 3 clusters 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 paper since this rate is mostly frequently used in studies of Al-Mg-Si alloys [4,5,12,13,17,19,20,21] and comparisons are facilitated. We will see later that C0 and C1 develop in parallel. The obvious question 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 Ref. 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, **Fig. 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 Ref. 8 it has been suggested that C1 and C2 appear a 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, see also Ref. 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 283K (10Celsius). The peaks are fitted by four Gaussian functions (in total 12 variables),

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

where q_0 is the base line offset, A_i is the area below each individual cluster peak, T_{ci} is the peak centre 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 ($i=1..3$), an additional Gaussian including both the low temperature tail of the GP zone peak and the residual background signal was included ($i=4$). 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 are therefore 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 min delay at room temperature due to mounting of the sample into the DSC. The peak areas of C0 and C1 decrease simultaneously and have completely disappeared after 1h of NA, while the peak area of C2 shows no significant change within the error limits during the first hour of NA. After 1 h, the peak area of C2 also

starts to drop and has disappeared after 2 weeks of NA. The slight kink observed after about 1000 min of NA is very close to the confidence limit of the measurement. **Fig. 3(b)** also displays data taken from the literature [5]. The 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 0.8wt%Mg, 0.9wt%Si, was used and one could expect higher heat flows. That this is not the case which could indicate that clustering is saturated above a certain (unknown) level of solute.

It has been 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:

$$f_r = 1 - \frac{P}{P_{SHT}}, \quad (2)$$

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 Refs. [5,20,23], the relative volume fraction of β'' and β' is obtained by isothermal DSC at temperatures from 423K (150Celsius) to 523K (250Celsius). Isothermal DSC is preferable from the viewpoint of accuracy but hardly applicable to the clustering process considered here due to stability issues of DSC; see **Fig. 3(b)**. If we assume that no dissolution reaction occurs in the temperature range from 293K (20Celsius) to 413K (140Celsius), the peak area in constant heating rate measurements should be a good measure too. The inset in **Fig. 3(b)** shows the relative volume fraction against NA time and demonstrates that the formation of C1 is finished after 1 h of NA. This actually corresponds very well to the resistivity measurements on the similar alloy Al-0.46wt%Mg-1.05wt%Si described in Ref. 15, which show that a first stage of fast resistivity increase during NA turns into a slower increase after ≈ 1 h. Something very similar was also found for the alloy investigated in this work [16]. This suggests that the regime of fast resistivity increase as given by Refs. 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 **Fig. 3(b)**. C2 starts forming after 1 h 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 **Fig. 3(b)** at ≈ 1000 min as real effect, it could be related to a further change in slope both of the hardening curve, the electrical resistivity and the positron lifetime [16].

During quenching from 813K (540Celsius) to 273K (0Celsius), 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 in the introduction this idea is generally accepted but actually supported only by 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 results above, C2 might be a transformation state of C1, forming at a much lower rate than C1. Mg-enrichment has been proposed as the main feature in this clustering stage [5], and the increase of positron lifetime after about 50 min of NA that is observed in Mg-containing but not in Mg-free alloys points in this direction [16]. Moreover, atom probe 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 **Fig. 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 and/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 has 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 813K (540Celsius)

can be calculated by the equation $f_v \approx \exp\left(\frac{S_f}{R}\right) \exp\left(\frac{-E_f}{RT}\right) \approx 0.009\%$, 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 have concluded from their atom probe analysis that the size and composition of C1 does not change after pro-longed NA and they explain the negative effect by assuming that C1 cannot serve as 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 above, it is suspected that the cluster that Serizawa and Sato have observed is our C2 and not C1, since C1 has already finished forming after 1 h of NA, see **Fig 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 Ref. 13 ten minutes of ageing at 373K (100Celsius) are found to both create C2 and to remove the negative effect, one has to conclude that either the C2 formed at room temperature and 373K (100Celsius) have different structures, or another aspect beside 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 ageing response will be similar even if the formation of C1 is complete or C2 is present. Therefore, from the inset in **Fig. 3(b)**, we estimate that roughly 60% to 80% of C1 formation is already sufficient to fully establish the negative effect.

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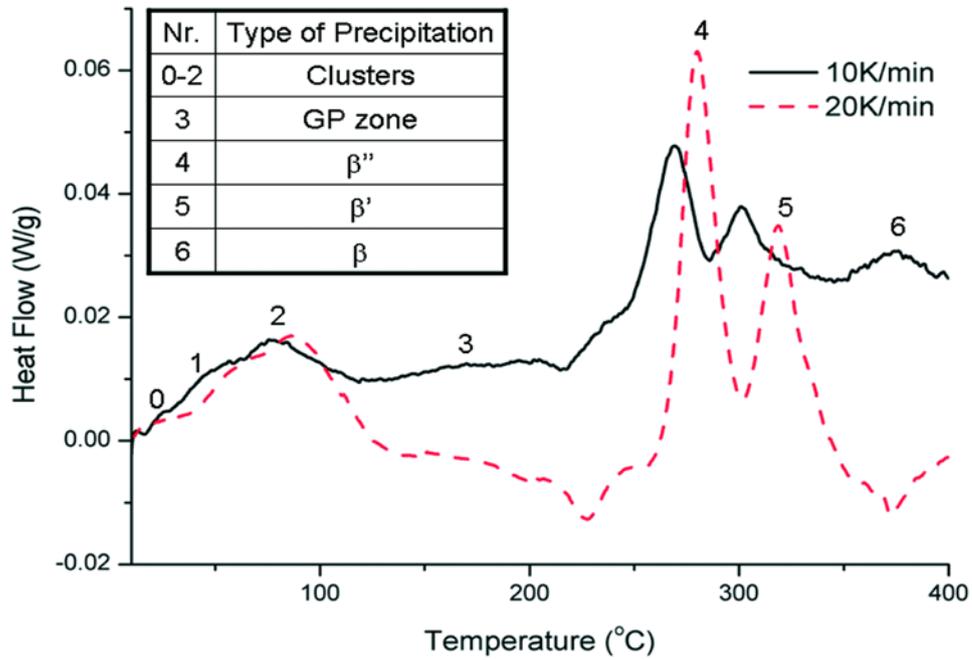


Fig. 1: Heat flow curves of the solutionised and quenched alloy showing the full precipitation sequence. Numbers identify stages of precipitation and are defined in the inset table. The full curve corresponds to a heating rate of 10 K/min, the broken one to 20 K/min. Positive heat flows denote exothermic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

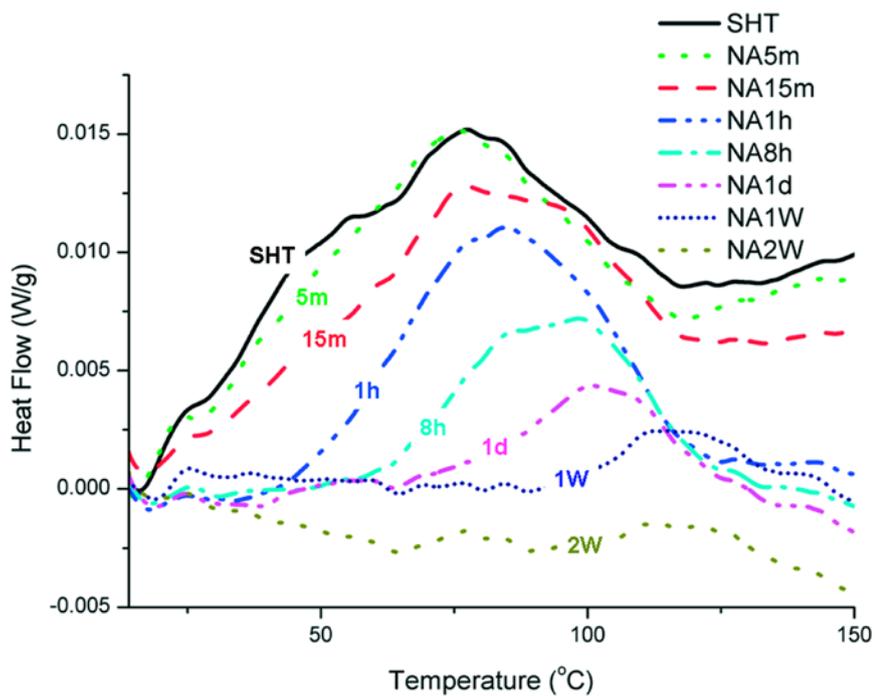
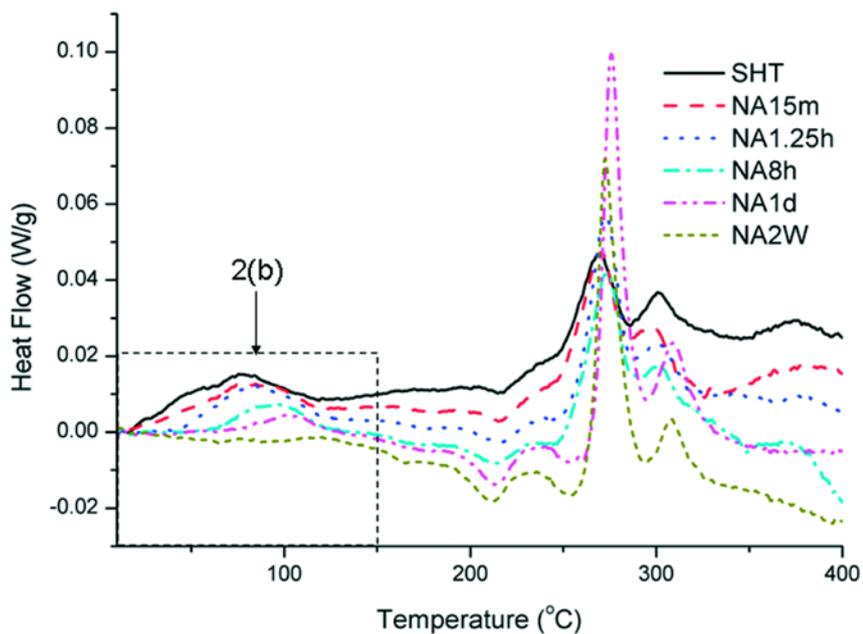


Fig. 2: (a) Heat flow curves of samples that were naturally aged before the DSC experiments and, (b) close-up of heat flow curves in (a) showing only the clustering stages.

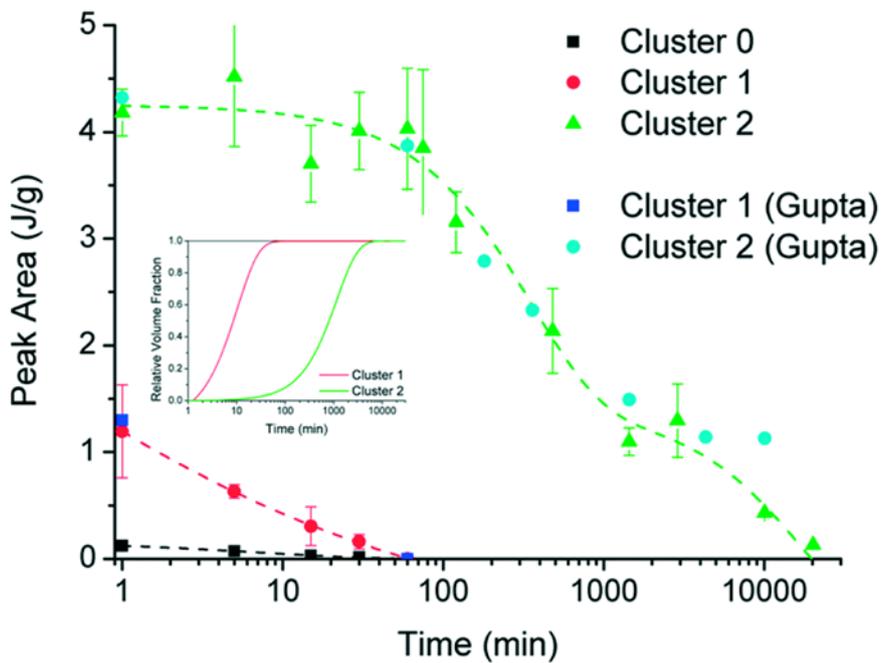
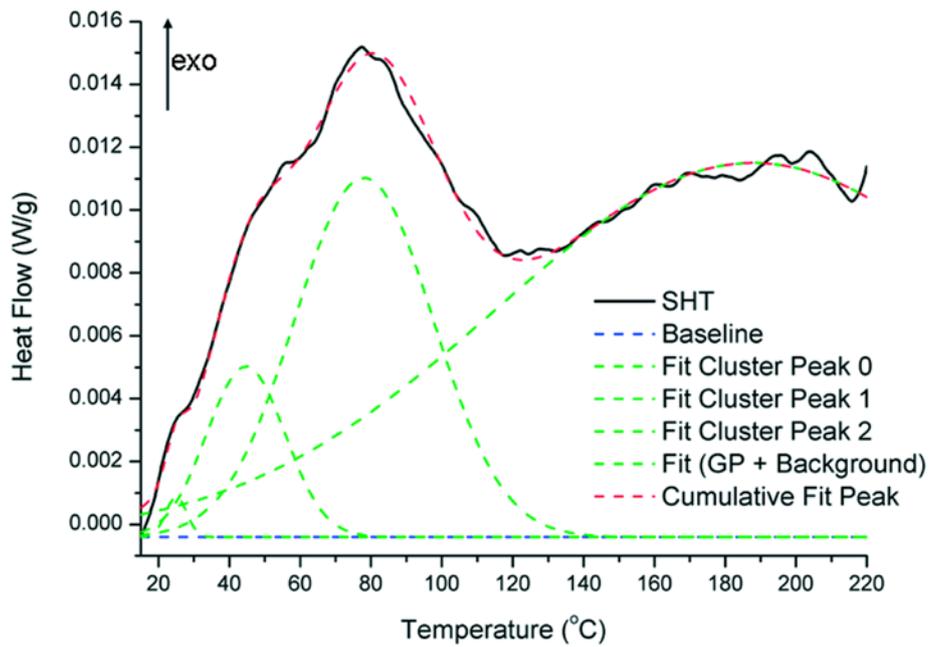


Fig. 3: (a) Enlarged heat flow curve of the solutionised and quenched sample showing how the peak area for clusters has been obtained by fitting Gaussians to the peaks and, (b) change of peak area of the clusters with NA time. Variations caused by different baseline corrections are represented by error 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.

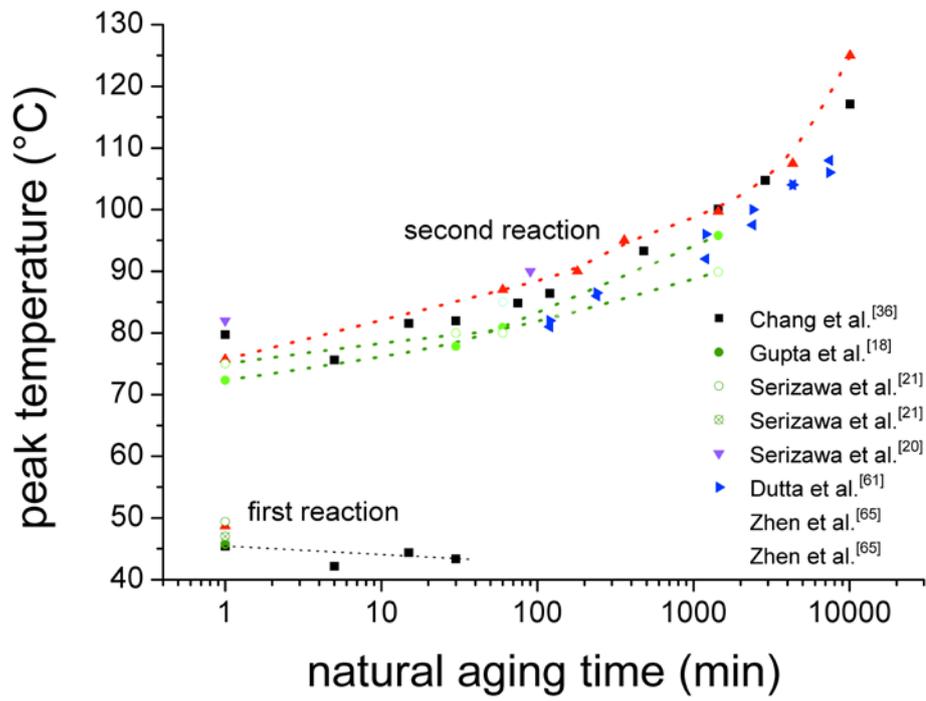


Fig. 4: Comparison of peak positions for C1 and C2. Squares: this work, other symbols: literature values [5,6,13,19,26].

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