Clustering in Age-Hardenable Aluminum Alloys

Phillip Dumitraschkewitz, Stephan S. A. Gerstl, Leigh T. Stephenson, Peter J. Uggowitzer, and Stefan Pogatscher*

This review gives an overview of the effects of clusters in various aluminum alloys. Characterization methods are discussed in general and results for the important AlMgSi alloys are presented in detail. Indirect characterization methods, such as hardness, tensile testing, electrical resistivity, differential scanning calorimetry, and positron annihilation spectroscopy are discussed, as well as atom probe tomography for the direct measurement of clusters. A particular focus is set on atom probe tomography, where possible artifacts influencing the cluster measurements as well as different cluster finding methods are summed up. A comprehensive summary of investigated alloys and cluster algorithm parameters is given. Moreover, the findings in AlMgSi alloys regarding clusters and changes upon different heat treatments are discussed, starting from early to the latest works. Drawn conclusions are discussed and compared to give a résumé.

1. Introduction

Low density, a broad strength spectrum ranging from 70 to 800 MPa, non-toxicity, high thermal conductivity, high electrical conductivity, and a wide range of forming and working processes are just a few reasons why aluminum alloys are currently used.\[6\]

Minimizing energy consumption is the driving force for the application of lightweight materials. Hence one of the main application areas for aluminum alloys is transport.\[29\]

Aluminum alloys typically have a low Hall-Petch coefficient, and therefore their strength cannot be increased extensively for technical applications via grain refinement. In addition, no allotropic phase transitions are known for aluminum at ambient pressure, which restricts hardening strategies in comparison with steels. Solid solution strengthening is indeed used as a strengthening mechanism in low to medium strength alloys. However, aluminum generally shows a tendency toward low miscibility with many other metals in thermal equilibrium. Often intermetallic phases with alloying metals form even at low alloying content. Together with the formation of metastable phases, which can be efficient barriers to dislocation movement, this is the basis for high strength aluminum alloys with age hardening as their dominant strengthening mechanism. Among these alloys the AlCuMg (2000) and AlZnMg(Cu) (7000) alloy series offer the highest strength. They are mainly used in aeronautical applications. The AlMgSi(Cu) (6000) alloy series shows somewhat lower strength, but exhibits a favorable properties profile (including good formability, weldability, and corrosion behavior) which makes it commercially most important of the three classical groups of age hardenable aluminum alloys. All these alloys have been reported to show clustering of super-saturated solute atoms in the very early stages of aging. The phenomenon has huge technological impact and has been intensively addressed in academia and industry over the last decades. However, the term “cluster” is not always well defined in literature and sometimes depends on the characterization method. Note that here we define clusters to be a homogeneous decomposition (local aggregation) of alloying atoms, without a detectable structure or ordering.\[1,3\] In this review, we focus primarily on two alloy classes where, particularly from the technological point of view, clustering plays the most important role: AlMgSi(Cu) and AlCuMg.\[1,3,5\]

The equilibrium phase common in the AlMgSi(Cu) series is Mg2Si (β); with additional small amounts of alloyed Cu the Q phase is also prominent.\[1\]

Figure 1\[6\] shows several 6000 series alloys and their Si and Mg concentration ranges. A representative Si-rich alloy is AA 6016, with typical 1.2 at% Si and 0.5 at% Mg, in contrast to a typical Mg-rich alloy AA 6061 (0.9 at% Mg and 0.6 at% Si). A low
content alloy AA 6060 is also shown. We define a balanced alloy as having an Mg/Si ratio of approximate unity and stronger deviating values whether Mg- or Si-rich.

The alloy properties are determined by the overall alloying element content, the Mg/Si-ratio, and possible Cu additions which alter the properties even at low content. AA 6016 is deployed in car body sheets, and 6061 can be used in bicycle parts and even in aerospace applications. These two alloys are typical examples where clusters have a strong negative effect on artificial aging performance: their presence slows down precipitation kinetics and reduces the achievable strength. However, there are also other alloys in the 6000 series (with low Mg and Si content, such as AA 6060) where clusters can have a positive effect on artificial aging.[7–9]

For the AlCuMg alloys — depending on the Cu/Mg ratio — the phases Al2CuMg (S), Al2Cu (θ), or a mixture of these is formed at equilibrium. Typical alloy compositions of the AlCuMg series where clusters do play an important role are in the range of approximately 1.1–1.6 at% Cu[1] and Mg 0.5 at%.[10] A typical AlCuMg-based alloy is AA 2024. Interestingly it also is an AlCuMg alloy in which Wils first discovered age hardening.[5,11]

Applications of AA 2024 are in airframe construction, for example, in fuselage/pressure cabin skins or lower wing covers.[12] Generally, the 2000 series of alloys is deployed in aerospace due to a high strength to weight ratio.

Clustering in AlCuMg alloys is important, because it is the reason for the “rapid hardening” observed during early artificial aging in these alloys.[5,13]

In the following, we address the main aging treatments and the complex role which clusters can play there. The effects of natural aging, pre-aging, and artificial aging, and their interdependent influences, are discussed in detail. We also address the techniques which have been used to indirectly and directly characterize clustering during the very early stages of aging in aluminum alloys. We start with indirect characterization techniques such as resistivity measurements, calorimetry, hardness and tensile tests, and positron annihilation. Although long in use, these techniques nevertheless require assumptions and models to link the presences of clusters to studied properties. The only technique which enables direct imaged observations of clusters is often atom probe tomography. This technique, its capability, the issues, and the most important results gained are a major part of this review.

2. Aging Phenomena

Aluminum alloys frequently undergo a homogenization treatment subsequent to casting, followed by a thermomechanical treatment. If we assume, as an example, that our final product is...
2.3. Conventional Precipitation Sequences

of clustering on transition. Often the earliest stage is clustering, which can have a hardening. This occurs in various distinct stages of phase solid solution, which can be used as a potential for precipitation condition to room temperature in order to form a supersaturated in the aluminum matrix (solid solution) and to increase the solution heat treatment is used to dissolve the alloying elements AA temperatures. For 7000 series alloys no significant impact on the AA response, clustering is important for 2000 series 6000 series clustering due to prior NA often has a deleterious effect on the 2000 series alloys, the natural aged state is in some cases used directly for application. In the 7000 series, clustering during NA is of minor importance because it is not an applied materials state and has no strong implications for final properties. 

2.2. Artificial Aging

Aging at elevated temperatures is called “artificial aging” (AA). The influence of clustering on hardness development during AA varies widely among the different alloy families. While in the 6000 series clustering prior to NA often has a deleterious effect on the AA response, clustering is important for 2000 series alloys because of the occurrence of the rapid hardening effect at AA temperatures. For 7000 series alloys no significant influence of clustering on final AA properties is known.

2.3. Conventional Precipitation Sequences

Typically the phase transitions which occur during aging are simplified by using sequences of different precipitates with increasing thermodynamic stability or decreasing formation kinetics. Recent investigations summarize the precipitation sequence in AlMgSi alloys, as follows in (1)[23,28]:

SSSS → atomic clusters → GP zones (pre β') → β' → β, Si(stable) (1)

This precipitation sequence should be interpreted as the chronological occurrence of the dominant metastable phases at isothermal aging at different temperatures for a certain amount of time, increasing from low (NA) temperatures for atomic clusters, over β' at the AA temperature to the equilibrium phases of β and Si at high temperatures or very long aging times. However, this is also observed in linear heating experiments (e.g., using differential scanning calorimetry).

A recent detailed tabulated overview of the different phases which occur is given in reference.[23] U1, U2, Si (diam.), and B' are present in Si-rich alloys in a typical aged state.[23] β' is present at peak hardness and aged states in Mg or Si rich alloys; it forms from β' or on dislocations.[19,23,24]

For AlMgSi alloys with Cu, L, “S,” C, Q’, and Q phases also occur, where L, “S,” C, and Q are predecessors of Q'. which is present at overaged and artificially aged states where Q is the overaged (equilibrium) phase.[23] It has been shown that at peak hardness a Cu-containing alloy (0.3% Cu), β' and pre-β' only account for 30% of precipitates; the rest is Cu-containing GP and the precursor of the Q'[25,26] phase.[27] A suggested precipitation sequence is given below (2): QP is possibly related to L, “S” is possibly related to QC (“S” should not be confused to the S phase in AlCuMg alloys)[22].

SSSS → atomic clusters → GP zones → β”, L, QP, QC → β’, Q’ → Q (2)

For AlCuMg alloys the precipitation sequence was constructed, as follows[23,28]:

SSSS → atomic clusters → S” → S’ → S (3)

There are different opinions on the exact precipitation sequence and the intermediate phases[5,23,29,30] and also on their impact on the rapid hardening effect. Earlier works declare GPB (Guinier–Preston–Bagaryatsky) zones to be the cause of the rapid hardening effect[28], later Cu–Mg clusters are explained as the source,[5] although in some publications the two are used synonymously.[29] For longer AA times overlapping S (or S’) phase formation is reported[25], their relative volume fraction is low in the plateau region, but becomes dominant in the peak-aged state. The designations S'[31] and S’ phase as precursor phases of the S phase is controversial, especially for the S’ phase due to its strong similarity to the structure of S.[32] For completeness it should further be mentioned that in Mg-rich AlCuMg alloys the T phase[32] can also occur, although it is “rarely found in commercial applications.”[23]

For a long time, a common general concept was sought regarding the formation of hardness-relevant phases in the different alloying classes, due to the recurrence of similar crystallographic features.[13] An interesting approach to this issue is briefly described as follows.

Recent analyses of metastable precipitates in the AlMgSi and AlCuMg systems have shown that the columns along the <100> Al extension follow “the same, simple arrangement principles; columns of large Mg atoms obtain a fivefold surrounding, while the smaller (Si, Cu) show a threefold surrounding.” A possible model explaining this behavior is shown in Figure 2. This principle uses a line defect, by which a segment of <100> Al column is moved half of the conventional unit cell size in the appropriate <100> direction. Therefore, atoms are moved to the

2.1. Natural Aging

The as-quenched material has a volatile nature, and exhibits diffusion induced changes even at room temperature (RT). When the material is stored at RT its hardness increases over time. This process has been dubbed “natural aging” (NA), and is caused by clustering of the solute atoms. Clustering at RT occurs in all age-hardenable Al alloys (2000, 6000, and 7000), but is technologically most important in the 6000 alloys. This is discussed in detail in Section 2.4. “Phenomenological description of the effect of clusters.” Alloys of types 7000 and 2000 also show NA, where hardness increases during storage at RT. In the 2000 series alloys, the natural aged state is in some cases used directly for application. In the 7000 series, clustering during NA is of minor importance because it is not an applied materials state and has no strong implications for final properties.
octahedral interstitial position. The fcc crystal is now partitioned in columns of 15 and 9 nearest neighbors (NN), instead of 12. The sites with 9 NN would fit smaller atoms like Si or Cu, and the sites with 15 NN would fit larger atoms like Mg. Such a defect needs only one vacancy, and ordering of such defects can explain, for example, the structure of GPB and \( \beta_0 \) phase. DFT calculations suggest ordering of Si or Cu, followed by Mg, prior to the defect. If the defect is produced, the direction of the precipitate is fixed. [34] Interestingly, this accords with previous statements which outline the importance of free excess vacancies in the formation of \( \beta_0 \) [35] and the latter’s interference with natural aging via the available concentration of free excess vacancies determined via the vacancy-prison mechanism. [9]

2.4. Phenomenological Description of the Effect of Clusters

While AlCuMg alloys show no essential influence of NA on subsequent AA, AlMgSi alloys exhibit a clear effect. This was already noticed by Brenner and Kostron. [36] They observe that for a 0.89 at\% Mg, 0.77 at\% Si alloy the yield strength (\( \sigma_{0.2} \)) increases about 50% within three days (Figure 3 [36]). After NA for 7 days they obtain a much slower hardening reaction and a lower maximum of yield and ultimate tensile strength upon subsequent AA compared to direct AA without NA [36] (Figure 4). Natural aging is also seen to increase the activation energies of subsequent AA precipitation kinetics. [9] This undesirable effect on the mechanical properties of NA is later called the “negative effect” in literature, and has its origin in the clustering which occurs during NA. [37] Note that some lean AlMgSi alloys with low strength can also show a positive hardening effect of RT storage on subsequent AA. [8, 38]

Brenner and Kostron investigated the effect of a pre-aging (PA) treatment directly after quenching. They observed that PA slows down hardening at RT and accelerates the aging response at elevated temperatures (Figure 5). It is proven that with PA the negative effect can be significantly reduced; nowadays this is the basis for industrial pre-aging treatments in the production of 6000 series alloys used for automotive body panels. [7, 39] Brenner and Kostron [36] also stated that even small amounts of Cu may lessen the negative effect, without changing the NA hardness evolution.

It was further demonstrated that interrupted quenching to AA temperatures for short periods of up to 10 min can also stabilize...
the material (similar to PA\[^{40,41}\]) and generate a beneficial aging response compared to a quenched and RT-stored material.\[^{35}\]

An interesting approach was applied in\[^{42}\] with a long-term PA (100°C/\(\text{Cu}^{25}\)/25 days) of a Si 0.72 at%, Mg 0.78 at%, low Cu alloy. The material exhibits a yield strength similar to the T6 condition, but higher tensile strength and significantly higher total and higher uniform elongation.\[^{42}\]

A different strategy to hinder the negative effect of NA, microalloying for AlMgSi alloys with Sn or In, was recently introduced by Pogatscher et. al.\[^{43–45}\] The study in ref. [43] demonstrates a significant delay of NA for AA 6061 due to microalloying of Sn (see Figure 6\[^{43}\]). The Sn-enhanced material with NA and subsequent AA also reaches the T6 hardness of the non-Sn-enhanced reference, which was artificially aged directly; see Figure 7.

For an AA 6061 with traces of Sn an unusually high and fast hardness increase for high AA temperatures (250°C) was obtained, although not reaching full T6 hardness at this temperature. The effect of Sn alloying was phenomenologically similar to the known effect of PA on high AA temperatures.\[^{46}\] The temperature influence (5–45°C) for NA was also studied for AA 6061 with and without Sn, Sn + In additions. Higher temperatures lead to faster increase in hardness; Sn + In delayed the hardness increase the most. Sn and Sn + In were seen to increase the effective activation energy.\[^{44}\] When Si is substituted by Ge the NA kinetics is notably retarded.\[^{47}\] This is also attributed to vacancy solute interaction energies and could be interpreted as an effect similar to Sn.

A design strategy for microalloying in AlMgSi alloys was also proposed by Werinos et. al.\[^{48}\] They outline the importance of solution heat treatment temperature, to ensure the dissolving of the micro-alloyed elements. A strong detrimental effect of Si on the delaying nature of microalloying NA was observed. A smaller influence of Mg was seen; less Mg led to a delayed increase in hardness. Cu marginally retained NA with higher content. A designed alloy was shown to exceed 180 days RT stable hardness values with increased AA response at higher AA temperatures.\[^{48}\]

Various microalloying elements for Al–Cu were investigated in refs. [49,50]. In this alloying system, too, adding trace amounts of Sn, In, and Cd reduces clustering upon NA due to their large binding energy to vacancies and the limited orbit motion of vacancies around these solutes.\[^{43}\] However, compared with 6000 series alloys the influence of NA on AA is different for 2000

![Figure 5](image-url) Yield strength of an AlMgSi alloy for different heat treatments. Artificial aging and pre-aging at 150°C, given is the total aging time. a) Direct artificial aging. b) 7 days natural aging, subsequent artificial aging. c) 1 h pre-aged, 7 days natural aging and artificial aging. d) 1 h pre-aged, 7 days natural aging, 4% straining and subsequent artificial aging. Redrawn with permission from ref. [36]. © 2018 Carl Hanser Verlag GmbH & Co.KG München.

![Figure 6](image-url) Evolution of hardness during RT storage after quenching for the AA 6061 alloy, with and without Sn addition. The increase in hardness is retarded with increasing amount of Sn. Sn additions above the solubility limit (approx. 100 at ppm) are marked with an asterisk. Adapted with permission from ref. [43]. © 2018 by the American Physical Society.

![Figure 7](image-url) Evolution of hardness during artificial aging at 170°C with and without Sn for different prior natural aging times. Minute additions of Sn hinder the negative effect. Sn additions above the solubility limit (approx. 100 at ppm) are marked with an asterisk. Adapted with permission from ref. [43]. © 2018 by the American Physical Society.
series alloys, since small precipitates are formed serving as nuclei during AA. Moreover, no negative interdependence of NA and AA has so far been reported. Nevertheless, cluster formation is present during NA in 2000 series alloys, which is a material state of application, and AA incorporates an important hardening phenomenon which is linked to clustering. The aging process at elevated temperatures has a two-step nature in 2000 series alloys. Figure 8 shows a typical AA response. The first stage of hardening occurs very rapidly (within about 60 s), and generates about 60% of the absolute hardness increase. This technologically important hardening phenomenon has been linked to very fast cluster formation and is called “rapid hardening.” Interestingly, this behavior actually needs a minimum of about 0.5 at% Mg to be present (Figure 8). The hardness increases with further increasing alloying content of Mg for the rapid hardening response and the later aging peak. Cu–Cu or Mg–Mg clusters were not found to correlate to the rapid hardening effect, but Cu–Mg clusters. An approximate ratio of Mg/Cu of 2 and small cluster sizes with high number density are seen as most potent strengthening agents.

3. Indirect Characterization of Clusters

The presence of clusters is deduced from various different measurement methods. Often indirect methods are utilized to follow the temporal property changes. “Indirect” means that only the effect of clusters is measured, and not the distribution or size of clusters themselves. In this section, we discuss important results regarding electrical resistivity, differential scanning calorimetry, hardness and tensile test findings, and finally positron annihilation studies. Characterization methods are discussed in general and major results for the important AlMgSi alloys are presented in detail. Although we try to sketch the overall picture in the literature, we do not claim completeness.

3.1. Resistivity

A very precise way to measure early stages of decomposition in metals is via specific electrical resistivity measurements. Due to the high conductivity of metals, high precision measurement setups are required. An advantage is that in situ data can be obtained quite easily by measuring over time at a fixed temperature or heating rate. The resistivity signal is sensitive to structural evolution such as vacancy annihilation, solute depletion, cluster formation, ordering of phases, and precipitation.

The classical view is that resistivity is dependent on the mean free electron path. This mean free path is disturbed by several sources, that is, crystal defects (vacancies, grain boundaries, dislocations), solute atoms in the matrix, phase boundaries, ordering in precipitates/phases, and temperature, due to electron-phonon interactions. To reveal changes due to clustering and precipitation effects the resistivity change is usually measured at a fixed temperature. As to precipitation, one would expect decreasing resistivity changes due to decreased matrix solute content, which typically increases the electron mean free path in the matrix; this is indeed obtained for precipitation at AA temperatures. Although counter-intuitive, clusters generate an anomalous resistivity maximum due to increased electron scattering, with a maximum cluster size at the scale of approximately 1 nm.

In situ resistivity measurements at several temperatures were performed on Mg-rich AlMgSi alloys decades ago. Large differences in the evolution of resistivity change over time were revealed for different temperatures, as shown in Figure 9 and confirmed by other authors. Most significant is the resistivity increase over aging time in the temperature range (10–50 °C) the material behavior changes for temperatures >50 °C. An early fast increase of resistivity is obtained followed by a log(t) resistivity change. Based on considerations of Hirosawa et al., Zurob et al. concluded that the logarithmic time dependence of the resistivity change is due to cluster growth, which is dominated by vacancy escape. But in later works cluster growth could not be obtained for natural aging, only an increase in number density of clusters was observed with APT (Figure 10).

Figure 8. Artificial aging at 150 °C. Three different alloys are studied Al–1.1Cu–xMg for x = 0, 0.5, and 1.7. Above a critical Mg concentration a rapid hardening effect is seen. Redrawn with permission from ref. [10].

Figure 9. Resistivity change over natural aging time for different temperatures. Material (0.60 at% Mg, 0.30 at% Si, and 0.02 at% Cu) is quenched to –78 °C. Redrawn with permission from ref. [57].
Cao et al.\cite{61} reports about changes in the slopes of the resistivity over log(t). Several “stages” were obtained, with temperature dependent changes between stages.

The relationship of resistivity changes to alterations in mechanical behavior is complex and is alloy dependent as can be seen for hardness change over resistivity change (Figure 11). For the low Si containing alloy in the work of Kim et al.\cite{6} an increase in electrical resistivity is connected to an increase in hardness, but with high Si content a region (“region 2”) is built up where relative large changes in resistivity do not result in increased hardness. Generally higher Si of the alloy leads to lower measured hardness increase for the same electrical resistivity change.

A linear relationship was found between the number density of aggregates and the maximum of the electrical resistivity anomaly for pre-aging and artificial aging temperatures. It is concluded that the larger spacing in between clusters results in smaller resistivity anomaly.\cite{62}

Generally, the drawback of the resistivity method is the weak connection between signal, cluster development, and mechanical properties. On the opposite, the in situ measurements can be conducted with a high sensitivity and time-resolution, and it has the potential to investigate early vacancy related processes.

### 3.2. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) has been widely used to study phase transitions in metallic systems and has been also used to measure clustering in aluminum alloys.\cite{54,63} It enables access to thermodynamics and kinetics of phase changes and reveals the heat related to a phase transition in dependence on temperature and/or time.\cite{54,63}

Note that compared to steels, Al alloys usually lack in measureable thermal expansion changes induced by phase transitions, which is why DSC is used much more than dilatometry.\cite{64,65} However, recently it became possible to observe precipitation reactions in AlMgSi alloys via dilatometry. This was achieved by high stability laser dilatometry measurements, which may also become an interesting method for measuring clustering stages.\cite{66}

Generally, DSC experiments measure the difference in the heat flow required to heat a sample mass. The exact measuring procedure depends on the type of DSC used. The sample is measured in a crucible in reference to an empty crucible or a crucible with a reference mass. In case of the very small heat-release associated with clustering in aluminum alloys, the excess quantities are usually measured, that is, the thermograms of the samples are measured against an equi-mass reference of pure Al. For a detailed description of execution and analysis we refer readers to ref. \cite{67}.

In the following, typical results of DSC measurements of AlMgSi alloys are discussed. The Mg-rich alloy AA 6061 was first investigated by DSC by Dutta and Allen.\cite{68} The thermograms show typical cluster formation peaks at \(\approx 50–100^\circ\text{C}\) and endothermic traces at \(\approx 210^\circ\text{C}\) due to cluster dissolution. Further clusters formed during NA generate a change in the following precipitation; a right shift of the \(\beta^0\) peak to higher temperatures due to NA is observed. In the as-quenched condition the \(\beta^0\) peak is an overlapping double peak (see Figure 12) and no endothermic traces are found.

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**Figure 10.** Effect of natural aging time on the volume fraction of solute aggregates (Mg, Si, and Cu) and on the electrical conductivity in a) T4 and b) T61 condition. Aggregate sizes are binned into 4–9, 10–22, 23–75, and >75 solutes (not corrected for detection efficiency). Adapted with permission from ref. [60], © 2018 Elsevier.

**Figure 11.** Micro-hardness over electrical resistivity change due to Cluster (I) formation at RT for different Si concentrations. Changes are grouped into three regions. Redrawn with permission from ref. [6]. © 2012 The Japan Institute of Metals and Materials.

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The exact shape of the thermogram is dependent on the heating rate used, suggesting that the processes are kinetically controlled. Note that the DSC curves are different for Mg-rich and Si-rich alloys; in Si-rich alloys Si-precipitates are formed at higher temperatures and the Mg$_2$Si phase precipitation is suppressed. The thermogram of an Si-rich alloy for different heating rates is shown in Figure 13; compare with Figure 12.

Several different heat treatments or thermo-mechanical treatments (such as NA, PA, pre-straining, and AA or combinations of these) change the appearance of the DSC signal. Important findings which focus on the formation of clusters and their influence on the precipitation sequence are summarized in the following.

1) Natural aging. Usually a double cluster peak is present for the solution heat treated material, and for NA only one of the two peaks is apparent. The double peak nature is attributed to the existence of two kinds of clusters, Cluster 1 (C1) and Cluster 2 (C2). The exothermic cluster peak was even fitted into three overlaying peaks in. The peak temperatures (C1, C2) and peak areas also depend on the Si and Mg content and ratios. Cluster formation generally increases with increasing Mg and Si alloying content and is most pronounced for the Mg/Si ratio of approximately 1.0 (Figure 14). The C1 reaction was seen to be completed within 60–100 min of NA; C2 exists up to one week of NA but is later low in signal. Two important changes with increasing NA time are relevant: a shift of the exothermic $\beta_{00}$ peak to higher temperatures and an increase in the $\beta_{00}$ peak. After roughly one week the DSC traces stabilize. Also in the Cu containing alloy AA 6111, naturally aging shifts the $\beta_{00}$ peak to higher temperatures and the exothermic cluster peaks disappear. The Q' peak was found not to be influenced significantly by NA. Although the exothermic cluster peak seems to vanish, the endothermic cluster dissolution peak is present.

2) Pre-aging. The $\beta''$ peak is shifted to lower temperatures with increasing PA time at 60°C, as well as decreasing...
endothermic traces of cluster dissolution, which indicates their increasing stability against NA with PA (Figure 15). For short PA times, the exothermic cluster peak (C1, C2) vanishes. With increasing NA after PA the endothermic traces re-appear.\(^{[75]}\)

3) Pre-straining\(^{[74]}\) results in a left shift of the \(\beta''\) peak and in a disappearance of endothermic cluster reactions.

4) When the temperature regime of the exothermic cluster reaction is rapidly overcome at a high heating rate the \(\beta''\) peak activation energy, measured via a Kissinger-like method,\(^{[63,76]}\) is significantly lowered. The lower activation energy for the \(\beta''\) peak demonstrates the essential changes for the following precipitation sequence due to low temperature cluster formation, and shows another DSC experimental verification of the delaying nature of the clustering on further precipitation reactions.\(^{[77]}\)

The double peak C1, C2 attribution to NA and PA clusters is possibly not as straight forward, since both, NA and PA, consume the exothermic peaks if applied, but increasing endothermic cluster peaks with NA after PA hints in the direction that at NA clusters are formed at RT which are resolved at AA temperature.

A direct connection from DSC to mechanical properties can be drawn for the occurrence of the endothermic cluster peak of NA material, where at temperatures around 225–250 °C a decrease of hardness is obtained i.e. reversion of NA clusters can be obtained (see Section 3.3). Also the delay for short artificial aging times for naturally aged material can be related by the shift of the \(\beta''\) peak, which for NA material moves to higher temperatures away from usual bake hardening temperatures of approximately 180 °C.

### 3.3. Hardness Evolution and Tensile Test Findings

Phase transitions often result in changes in mechanical properties, which is also the reason for using such transitions to optimize engineering materials. An old, but still frequently used method is to follow the change of hardness over time or temperature for a certain heat treatment. Unfortunately interpretation is relatively difficult because the processes monitored can be complex. Adequate models for hardness are also unavailable, and direct linking of hardness to atomic processes is not possible. Nevertheless, a set of clever experiments in composition-time-temperature space can still help us to understand the underlying processes\(^{[54]}\).

Tensile testing is also an established way to measure the decomposition of solid solutions.\(^{[78]}\) However, it requires more time and effort than hardness measurements. Note that linear conversion of hardness to yield strength is often performed in literature studies (e.g., ref. [79]). In certain cases this can be done, but experimental justification is almost always needed.\(^{[54]}\) For clustering one needs to be aware that models have been discussed for yield strength, but these are still subject to debate.\(^{[80–82]}\)

The complex kinetic situation of NA followed by AA in 6000 series alloys is demonstrated by hardness measurements in Figure 16,\(^{[23]}\) for an almost balanced alloy (Mg/Si ≈ 0.87). The AA response for longer holding times (120–480 min) at elevated temperatures exhibits a minimum in hardness in the range of prior storage of 30–6000 min at RT. The AA response shows a re-increase for longer prior NA times, although the negative effect is not fully restored. Especially the detrimental effect of natural aging for shorter artificial aging times is apparent and therefore most important for bake-hardening treatments.

Sometimes the hardness evolution during RT storage is also separated into different stages: see Figure 17. Hardness evolution is often seen to be proportional to \(\log(t)\) over RT in the stages, beginning with a stage with practical no hardness increase, followed by an accelerated stage and again a deceleration. Activation energies can be calculated from transitions between different stages.\(^{[144]}\)

For naturally aged material a decrease in hardness for short AA tempering times can often be obtained, as shown in

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**Figure 15.** DSC thermograms, excess heat flow, of an AA 6016 alloy (Si-rich) for different pre-aging times at 60 °C. a) naturally aged, b) 2 min, c) 10 min, and d) 30 min of pre-aging. Redrawn with permission from ref. [7], © 2018 Elsevier.

**Figure 16.** Artificial aging response as a function of prior natural aging time in an Al-0.67%Mg–0.77%Si alloy. Natural aging is presented as 0 min AA.\(^{[23,75]}\) Adapted with permission from ref. [23], © 2018 ASM International.
The decrease is interpreted from solving NA co-clusters (some authors refer to this as retrogression or reversion). The cluster dissolution kinetics was studied (AA 6061) via hardness curves, based on a simple model from,[83] which states:

\[ \Delta H \approx \sqrt{f}, \]  

where \( \Delta H \) is the hardness change and \( f \) is the relative volume fraction of clusters. This generates a \( Q_{\text{diss}} = 0.79 \text{ eV} \) in general agreement with values measured via isothermal calorimetry for AA 6111.[83] However, note that the model used has not been justified via experimental insight in the microstructure.[9] Further, short time reversion treatments at 225 \(^\circ\)C for several minutes lowered the yield strength and were shown to almost restore the BH response.[84]

In addition to simply following the evolution of strength or hardness upon the formation or dissolution of clusters, an interesting indirect effect of clusters can be seen for tensile test curves. As-quenched (or short NA) AlMgSi alloys exhibit the PLC (Portevin-Le-Chatelier) effect.[85] The PLC effect is eliminated with longer NA or PA times, as can be seen for NA in Figure 19[85] for an excess Si alloy. It is also found that the strain rate sensitivity (SRS) is higher for NA samples than for PA + NA samples. The PLC effect was more readily observed for the excess Mg alloy and cannot be eliminated with too short NA or PA in some cases.[83]

The effects of clusters on the mechanical properties can be followed by tensile tests and hardness measurements, although no direct conclusions to the cluster form or chemistry can be made. Also no general accepted model for the strength/cluster correlation exists, but kinetics are often interpreted by means of a monotonous function, that is, increased strength corresponds to more clusters (e.g., the mentioned \( \Delta H \approx \sqrt{f} \) relation based on shearable obstacles, or \( \Delta \tau \approx f \)) based on short range ordering contributions).

### 3.4. Positron Annihilation Spectroscopy

Positron annihilation lifetime spectroscopy (PALS) and Doppler broadening (DB) can be used to study clustering phenomena. Positron lifetime is sensitive to electron densities around annihilation sites in the material; earlier, PALS has been used for measuring vacancy concentrations in metals. In principle, DB can be used to study the chemical environment of trapping sites. For positrons different annihilation sites exist in the material, but mixtures of different lifetime signals can be difficult to separate in PALS.[10,37]

Clustering during NA phenomena in AlMgSi alloys has been studied via PALS.[86] A schematic signal for the positron lifetime (\( \tau \)) is shown in Figure 20.[37] The NA process has been subdivided into five stages by Banhart et al.[37] according to the curve found (where stage 0 is not observable). The first stage is characterized...
by a constant lifetime for Si-excess, followed by a decrease to a minimum at about 60–80 min, followed by a re-increase (stage 3). After reaching a local maximum at approximately 800 min the lifetime decreased slowly until >10^4 min (stage 4). For a balanced alloy stage 1 is different.\[37\]

Stage 2 was investigated in detail for a balanced low content alloy; the measured signal was seen to be influenced by the sort of quenching (Figure 21).\[87\] The measuring signal was seen to be dependent on the temperature during the measurement, which generally caused parallel shifts of the curves to lower lifetimes for lower temperatures.\[87\] The quench sensitivity was also studied by Strobel et. al.\[88\]. They investigated a balanced low content alloy (AA 6060) and found the above mentioned type of curve in their measurements of a water-quenched (WQ) sample. However, the overall picture changes for slower cooling rates, as shown in Figure 22.\[89\] Increasing lifetimes are seen until the end of stage 2 of the oil-quenched sample in.\[89\] Similar behavior was seen for NA at elevated RT (37°C) in,\[86\] but with lower absolute increase. The effect of additional elements has also been investigated. For example, adding Cu causes a concentration dependent time-shift to longer times of the local minimum (end stage 2) and seems to reduce the time from local minimum to local maximum.\[47\] This corresponds to a delay in hardness increase for Cu alloyed samples early in time and the outpace later in time of the non-Cu added alloy.\[47\]

Such behavior has not been seen in pure Al 99.99% during RT storage after quenching.\[89\] The authors show that the lifetime decreases monotonously (Figure 23) and that the lifetime for WQ material is reasonable higher after 10^4 min than for Al nearly free from quenched vacancies.

The lifetime signal for a pure Al is interpreted that vacancies (as positron traps) concentration decreases over RT time. For AlMgSi alloys early vacancy concentrations decrease (decreasing
signal) and superposition the signal from forming clusters. They also act as positron traps and finally dominate the signal contribution (increasing lifetime). The again falling lifetime for long NA times is somehow surprising, but could be interpreted by a change in chemistry/ordering of clusters.

3.5. Other Techniques

Other techniques are sometimes used to characterize cluster evolution in aluminum alloys. Note that for the 200097,98 and 7000 series,99 in situ small angle X-ray scattering (SAXS), and in ref. 29 SAXS with nuclear magnetic resonance (NMR), was used to characterize clusters. However, these techniques cannot be deployed in a satisfying manner for the important 6000 alloys.100 Small angle neutron scattering (SANS) has been applied for AlMgSi, but generated insufficient results.100 Time-dependent magnetization101 and muon measurements have also been used recently.99,102

4. Direct Characterization of Clusters — Atom Probe Tomography

In contrast to most microscopic imaging techniques, for example, scanning electron microscopy (SEM) or TEM, atom probe tomography measures direct particle properties of ions of the target material, compared to secondary signals resulting from impinging waves in other methods. This makes it a destructive technique. Nowadays it is a frequently used tool, especially in materials sciences due to its strength in content analysis at the nanometer scale of precipitates, grain boundaries, nano-particles, clusters, and the matrix compositions in three dimensions.95–97

The technique is unique for visualizing and measuring of fine-scaled microstructural (nanostructural) features with near atomic resolution and gaining precise information of compositions in 3D. Especially, where transmission electron microscopy does not produce distinct contrast (e.g., for low alloying element content and elements of similar atomic number, which is the case for AlMgSi alloys103–105), APT is the sole technique for gaining direct insight into the early decomposition of metallic systems.94

4.1. Functionality

A short overview is given over the principal functionality of an atom probe in the following text. A needle-shaped sample is fabricated, with a tip radius in the range of 50 nm. The most common techniques to achieve this is either by two-step electropolishing99 or sample preparation via a focused ion beam.97 In an ultra-high vacuum chamber a high positive voltage (DC or standing voltage) is applied to the specimen, creating a high field environment at its apex; an additional impulse signal, provided by a voltage or laser pulse is applied at a high repetition rate (typically between 100 and 500 kHz). Nowadays, atom probes with a local electrode setup are usually used. The local electrode is cone shaped with an aperture at its center; it is positioned in front of the specimen apex along the needle axis. In voltage mode, the pulsed voltage is applied on the local electrode (with a negative bias), thereby causing a momentary increase in electric field. This setup enables a much larger field of view than earlier setups, and additionally has instrumental advantages.97

The combined DC and pulsed high voltage yields to high electrical fields at the specimens’ apex and, when a critical field is reached, a surface atom of the specimen is ionized in a process called field evaporation. Tabulated evaporation fields values exist for each element (usually calculated via a simplified model97), however, the exact physical and electronic processes are still under debate in the community. There are various relationships between analysis parameters and it should be noted that the field evaporation process is temperature dependent such that at higher temperatures generally lower fields are required for field evaporation. The resulting ion is ejected from the sample and accelerated through the aperture in the local electrode by the local electric field, towards a two-dimensional position sensitive detector. To measure the field-evaporated ions in a controlled manner the pulsed signal is used as a start clock to a time-of-flight (ToF) mass spectrometer. The arrival time and two spatial coordinates are then recorded by the detector. The resulting ToF is used to calculate the mass-to-charge state ratio (typically measured in Da), which is then assigned to the species. This information, combined with the sequence of the arriving ions,100 is used to build a three dimensional reconstruction — the so-called atom map, ultimately representing relative positions of the atoms originating from the specimen apex.96,101

Multiple parameters define the “parameter space” for collecting a successful atom probe tomography experiment; the most important ones include: voltage pulse fraction or laser pulse energy, specimen temperature, detection rate, and pulse frequency.97

4.2. Artefacts, Trajectories, and Calibration

Besides its strengths, atom probe tomography also has its drawbacks, as with any characterization method. In general, the resulting analyzed volumes of material compared to other techniques are small (maximal spatial extensions up to hundreds of nanometers). A further aspect is that not all atoms are detected. The two-dimensional detectors have usually a detection efficiency of 37 to 57%, though most recent developments have improved detectors (as in the Cameca LEAP 5000) up to 80%.102 Therefore, only a fraction of the atoms of the original sample are pictured in the reconstruction. This is especially crucial for small sized features such as clusters. With high enough detection efficiency cluster size distributions can be estimated to real clusters size distributions.103 Another limitation is the loss of crystallographic information, strongly dependent on the alloy, and — experimental parameters; in some regions of the reconstruction can lattice planes of certain directions be resolved (pole regions – poles). Although, in special cases, APT can be used to clarify occupancy of elements on sub-lattices104,105 or it has been shown that crystallographic arrangement of atoms may be regained altogether.106,107
Pole regions are visible due to crystallographic faceting of the sample during the experiment; the field-evaporated ions near to a pole are deflected away locally from the flat regions, which leads to lower density of pole regions in the reconstruction. This is a so-called trajectory aberration since the trajectory of the ion is influenced by its local neighborhood on the specimen surface. A similar artefact exists for precipitates which have a different evaporation field (high-field, low-field) compared to the matrix of the sample; this leads to precipitates appearing less dense, respectively, denser in the final reconstruction. These are known as local magnification (demagnification) artifacts.  

Crystallographic pole regions are often present when Al alloys are investigated with APT. With the use of spatial distribution maps (SDM) or other techniques where the inter-planar lattice spacings can be measured, the reconstruction can be calibrated. Often the protocol based on a modified stereographic projection is used for the reconstruction, here the two parameters (namely the image compression factor and the field factor times the evaporation field) can be used to tune the reconstruction, so that the inter-planar distances in the atom map fit to the real inter-planar distances. It should be noted that there are large and ongoing efforts being made to increase the accuracy of the reconstruction algorithm, recently also revisiting a different projection model or building the reconstruction in a reverse manner and calculating the ion trajectories. Distorted or bad reconstructions would affect cluster analysis in shape or absolute size analysis, and worsen comparability in between different measurements.

In general, different elements have different evaporation fields. In alloys, the evaporation field of an element can be different from the evaporation field of the pure metal since the evaporation field depends on the chemical (local bonding) environment, this is especially true if the species is bound in an intermetallic phase. However, if the evaporation field of solute elements differ largely from the matrix evaporation field, preferential retention (for solutes with a higher evaporation field) can occur. To hinder this an adequate choice of measurement parameter space is important, chiefly among them being specimen temperature and pulse fraction.

Preferential retention of one species can lead to surface migration during the APT experiment. Surface migration is possible to occur for interstitial and substitutional elements. A prominent example in Al alloys is Si, which is known to migrate to the (111)-pole. The migration of solutes during the experiment results in false reconstructed location, and thus errors introduced in elemental distributions. To minimize this artefact optimized parameter spaces are to be applied, and if still present in the reconstruction, usually the distinct regions affected by this known artifact can be removed – though one should keep in mind that this potentially could affect the analysis, since the starting positions of the migrated atoms are unknown.

A similar effect, but for precipitates, is seen for example in Al–Ag alloys, where the Ag atoms in the precipitates tend to be shifted to the nearest low-index pole. It is concluded that subtle changes of the evaporation field of the matrix atoms in the precipitates cause this aberration, by changing the local field distribution. This is known to occur in various systems. Due to the aberrations specific to certain atomic species this is called chromatic aberration.

In general, it is not straightforward to characterize clusters even with APT, due to the above mentioned challenges. In recent literature, these issues are gaining consideration more and related topics are continuously being discussed in the community. However, this has not always been the case and full evaluations of these influences on the analysis of clusters is usually not given. Although one needs to be aware of these artifacts APT is still the most powerful technique to gain insight into clustering.

4.3. Analysis of Solute Distribution

There are many approaches to analyze the solute distributions that can occur within APT datasets and many can consider fine-grained and possibly subtle variation in composition. Two of interest to the analysis of fine solute clustering are cluster-finding algorithms and pair correlation algorithms.

4.3.1. Clusterfinding and Algorithms

The most frequently used cluster-finding algorithm for APT analysis of aluminum alloys was named “maximum separation,” but in other fields it has been known as “single linkage” and “friends-of-friends.” For APT data, maximum separation connects data points from a particular solute range, and two solute atoms are connected if they are closer than a certain distance $d_{\text{max}}$ this parameter chosen by the user. Choosing a $d_{\text{max}}$ value filters the solute data based upon its first nearest neighbor (1 NN) distance distribution.

Better discrimination between physical clusters and the adjacent matrix, though with a lower sensitivity to smaller clusters, can be achieved through applying this filtering upon the $k$th nearest neighbor distance distribution. In other words, a population of core atoms are identified by testing the expression $d_{k\text{NN}} < d_{\text{max}}$ for each solute atom. To find clusters, these core atoms are then linked with any solute atoms (both core and filtered) that are closer than $d_{\text{max}}$. This is the basis of the DBSCAN algorithm.

Further filtering can be applied by removing found groups smaller than $N_{\text{min}}$ detected solute atoms, and for a chemical analysis, enveloping, and erosion steps were then used to include non-solute atoms. The “maximum separation” technique has long been implemented in the commercial IVAS™ software by Cameca Instruments Ltd. as “envelope.” The DBSCAN algorithm (of which the maximum separation algorithm is a special case where $k = 1$) is separately implemented in IVAS™ under the option “Create Cluster Analysis.”

Results can be sensitive to the choice of algorithm and parameter values. Results are also dependent upon the studied material and the capabilities of a particular atom probe instrument. In other words, these methods cannot be taken from a particular study and applied to another without considerable thought.

This review study confines itself on the use of the maximum separation and DBSCAN algorithms for their ubiquitous use. However, we must acknowledge that these algorithms may not...
be optimal for all purposes. There are many other algorithms that have been developed and considered for APT data analysis, some similar to maximum separation and DBSCAN, some employing mixture models, and others dependent upon computational or networking geometry. This should not be regarded as an exhaustive list and there are many more algorithms besides which have not yet been applied to APT data analysis.

Justifying “good” parameter selection is often an annoyingly difficult task and, in many respects, it must be remembered that it is merely ancillary to the materials science problem. Rigorous approaches to using the maximum separation algorithm have been developed; exploring the sensitivity of maximum separation, examining a manifold of results with the variation of parameters, and using simulations to determine optimal parameters. It can be hoped that unsupervised machine learning approaches can be developed and trained in combination with APT data simulations.

Heuristic rules have also been used to establish consistent cluster-finding analyses (but not necessarily providing optimal or correct results) and many of these have been considered in Table 2. Selecting parameters based upon establishing the least conservative parameter values that resulted in no “random” clusters being found in a random labelled version of the original APT data. Other more elaborate approaches using randomized datasets to generate various heuristic metrics have been developed but could be considered as less than physical so caution must be employed to at least apply these consistently.

4.3.2. Interpretation Via Pair Correlation Functions/Partial RDF

Pair correlation and partial radial distribution functions provide the means to directly investigate solute-solute interactions on short- to long-range orders in aluminum alloys. Pair correlation functions were developed for such analyses without recourse to the complexities behind cluster-finding algorithms. The similar application of radial distribution functions was investigated for bulk metallic glasses. APT data can provide the means to directly query short range order; for multicomponent alloys, this has been recently formalized.

4.4. Findings on Clustering in Aluminum Alloys

Over time different atom probe instruments applying varying APT measurement parameters and sample preparation methods have been used. Moreover there are differences in the solution heat treatment and quenching which is the basis for the studied SSSS. This information on measurements needs to be considered and is comprised in Table 1 for all referred studies. Since often also different parameters for the clustering algorithm are used, this information is summarized in Table 2. Additionally, the investigated aluminum alloys are summarized in view of content in Table 3. In terms of detailed results on clusters we focus here on the important class of AlMgSi alloys.

4.4.1. Important Early Findings

An early and famous reference investigation of clustering and precipitation sequence of the AlMgSi system via an atom probe like technique (atom probe field ion microscopy APFIM) was done by Edwards et al. The studied alloy was AA 6061 and the results are interpreted in terms of concentration profiles along cylinders of approximately 1.6 nm in diameter. For a heating of an as-quenched alloy with 5 K min$^{-1}$ to 100 °C Mg, Si, and Mg–Si co-clusters were detected. Longer times (8 and 60 h) of aging at 70 °C showed existing Mg–Si co-clusters, for 0.5 h of aging the data was not conclusive and did not show Mg–Si co-clusters via contingency table testing. Here, the data is grouped into blocks and the number of blocks containing different amounts of specified atoms are counted and can be compared and tested against randomized data. The Mg/Si ratio for most of the clusters found for 8 h aging was 0.7 and strongly deviating in both directions. For 60 h of aging at 70 °C the ratio of most of the clusters was close to unity, which is close to the Mg/Si ratio in the $\beta'$ precipitates. Interestingly these finding already fit well into the recent picture of early clustering, which was developed during the subsequent 20 years (see Section 4.5). Cu has not been found enriched in the clusters. It was concluded that independent Si and Mg clusters do form first followed by the formation of Mg–Si co-clusters. It was speculated that either or both Mg and Si clusters formed directly after quenching. It is already outlined that measuring the as-quenched state of the alloy is difficult due to preparation time needed at RT after quenching. Finally the following initial cluster sequence based upon previous thermal analysis and atom probe analysis was suggested:

$$SSSS \rightarrow \text{clusters of Si and clusters of Mg} \rightarrow \text{dissolution of Mg clusters} \rightarrow \text{Mg/Si co-clusters}$$

Note that, although this was a reference for numerous studies over last two decades, the dissolution of Mg cluster in the sequence has not been confirmed and seems to be questionable.

Another important early APT work by Murayama et. al. investigated the interaction for a balanced and a Mg excess AlMgSi alloy without Cu. The balanced material was studied in detail as described in the following text if not otherwise mentioned. Only a uniform fringe contrast for long-term NA could be obtained in high resolution transmission electron microscope (HRTEM), in comparison to PA (here 16 h at 70 °C) where approx. 2 nm sized clusters (arbitrarily termed as GP zones) are observable. Contingency tables from APT data indicate positive correlation for Mg and Si for long-term NA, although no visual appearance can be found. Integral profiles of Si and Mg show the presence of Mg, Si, and Mg–Si clusters, and the Mg–Si cluster have a Mg/Si-ratio close to unity. Strong correlation in between Mg and Si is found for PA where enriched regions can also be observed by eye. Mg–Si co-clusters show a Mg/Si-ratio of approximately unity. Also the interaction of different types of clusters created via PA and NA on the formation of $\beta''$ precipitates was studied. It was concluded that NA clusters do not act as nucleation sites for $\beta''$, while PA clusters act as nuclei. Moreover, the authors summarize that in the
as-quenched condition separate Si and Mg clusters exist and Mg and Si clusters aggregate during NA. The different effect of co-clusters formed upon NA and PA was argued based on a critical radius for nucleation of \( \beta'' \) precipitates, so that small co-clusters (NA) revert at AA temperatures. It is also already stated that co-clusters, GP zones, and \( \beta'' \) precipitates follow the overall alloy composition.\(^{[3]}\)

### 4.4.2 Latest Findings

Since these early works, numerous studies have been carried out. As time progressed, the atom probes evolved and the data analysis methods got more powerful and extensive.\(^{[143,144]}\) Even the earlier used analysis tools such as the 1D concentration profiles could be misleading due to random statistical fluctuations which could be wrongly interpreted as clusters.\(^{[143,144]}\) Today much larger data sizes are usually gained in the experiment, but due to the small size of clusters, APT is still operating at its limits for this purpose. In later works, the effect of clusters on further different heat treatment procedures is investigated. The evolution of clusters during RT storage and PA, influence of combined heat treatments as NA and AA, or PA and AA is studied. Also the influence of alloy chemistry on the clustering behavior is analyzed. The findings have been grouped by the different applied heat treatment states and are discussed in the following.

#### 4.4.2.1 Natural Aging

Only recently, it was shown that the as-quenched condition for an excess Si alloy (\( \approx 1 \) min of RT storage) can be measured via APT.\(^{[145]}\) Natural aging times <60 min became available due to the use of a customized cryo-transfer system to the APT measurement chamber.\(^{[146,147]}\) No Si–Si, Mg–Mg, nor Mg–Si correlation, with a radial distribution function – like measure, is seen.\(^{[145]}\)

Based on a 5th nearest neighbor distribution it is shown that no clusters are expected for the Cu-containing alloy AA 6111 for 2 h of NA.\(^{[136]}\) In ref. \(^{[148]}\) it is stated that also for an Mg excess alloy for the quenched state (time at RT for APT sample preparation and transfer into the APT analysis chamber is not given in ref. \(^{[148]}\) but is technologically expected to be >1 h for the used setup), no clusters were found. However, these data\(^{[136,148]}\) contradict the results of other studies.
Contrary, in ref. [139] for the alloy 6016 and 60 min natural aging the material already shows positive autocorrelation for Mg–Mg and Si–Si, but not for Si–Mg. Therefore, it was concluded that two distinct populations of clusters form for short RT storage, as already stated in the sequences (9). A large proportion of Mg is involved in the clusters as compared to Si, where the proportion in solution is higher. For 1 week at RT only significant Si–Si correlation was found, which would actually support sequence (9) where early Mg-clusters again revert.

This finding is often contradicted by other studies where usually Mg–Si co-clusters are found, although radial distribution functions as a measure of clustering in literature is rare[106,139,145] and therefore direct comparison to other measures is difficult.

Cao et al. reported that after 1.1 h of NA, Mg, and Si show correlation in contingency table analysis for an excess Si alloy, whereas Mg–Cu and Si–Cu show no significant difference from a random solution. With NA time the significance is increased for any of the two combinations of Mg, Si, and Cu. Cu is therefore concluded to cluster after slightly higher NA times (>1 h). The number density of identified clusters stagnates after 24 h of NA[140].

For AA 6111, increasing number densities within up to two weeks of Mg–Si clusters are reported in.[136] In general, the found clusters have a size expressed in solute atom numbers ≤50 (here the number of solutes in the APT datasets are given, not the physical values, these values should be corrected for detection efficiency of the specific atom probe, Table 1). Mg–Si clusters dominate the cluster population, Mg–Si–Cu, Cu–Mg, and Mg–Mg clusters roughly follow this scheme of increasing number densities. About 10–20% of the solutes are reported to be bound in aggregates for NA samples. Also only small changes in cluster size is reported for NA. The volume fraction of atoms in aggregates is seen to increase over the first week of NA (which is correlating with yield strength). They also observe a decrease of the number densities of clusters after one week of NA, which is however not explained and seems to be physically unrealistic.[136]

For increasing NA time starting from 3 h to 325 days Aruga et al. obtained increasing number density in a balanced alloy in ref. [132]. The Mg/Si ratio of 0.8–1.0 had the highest number density in all NA states. The number density of Si-rich clusters is shown to stagnate already after short NA times. It is concluded that Si-rich clusters can form at the earlier stage of NA. Moreover, Aruga et al.[132] suggest that non-solvable Si-rich clusters may reduce supersaturation and lead to a retardation of the hardness increase during AA. No influence of the size of clusters on reversion was seen, contradicting the conclusions of Murayama et al.[5,132]

For Si-rich alloys the cluster number density is shown by Jia et al.[133] to be higher, in comparison to Mg-rich alloys, after 2 weeks of NA. The average composition of the clusters is reported to follow the alloy composition.[133] Recently, Zandbergen et al. show a substantial number of clusters to be formed within 100 min of NA which then only slightly increase in size for further NA, but the number density increases up to 1 week of NA.[130,131] The clusters contain mainly Mg and Si, 2% of them are only-Si-clusters, but no Mg-only clusters have been detected at any stage.[130,131] It is concluded
that limited diffusion capabilities drives the clusters at NA toward a “metastable state from which it is difficult to escape either energetically or kinetically.”

Zandbergen et al. report that only small differences are obtained for NA of AlMgSi alloys with the addition of Cu in cluster numbers and sizes. The most important difference is obtained in the composition, the majority of clusters do contain Cu (high-Cu content alloy). The Mg/Si ratio is increased for the high-Cu alloy, also the \((\text{Mg} + \text{Cu})/\text{Si})\) ratio is increased, here to about unity.

Jia et al. also show that for Cu added alloys the larger clusters found approached a Mg/Si ratio of 1.0. Furthermore, Cu is suggested to change the stability of Mg–Si co-clusters through its incorporation and enables them to transform more easily to hardening phases upon AA.

Trace elements have been reported to suppress clustering during NA via APT. For 2 weeks of NA of AA 6061 alloy with the addition of Sn, a 1st NN spatial distribution shows no discernable difference from a random distribution of Mg and Si atoms.

We conclude the following:
1) No clusters are found in the as-quenched state.
2) Mg, Si, and or Mg, Si co-clusters are detected after a very short time of NA (60–100 min) by several studies, but there are also contradictions.
3) Mg, Si co-clusters have been always found after long-term NA.
4) Mg, Si co-clusters increase small in size for short times, then stagnate in size.
5) Si-rich clusters number densities already stagnate after short NA times.
6) Increasing number densities of clusters up to one year of NA are confirmed by several studies, but there are also contradictions.
7) Cu aggregates at later stage of NA to the clusters.

| Alloy # | Mg/at% | Si/atom | Cu/atom | Mg | Mg + Si | Aging | Refs. |
|--------|--------|---------|---------|----|---------|-------|-------|
| 6061   | 0.89   | 0.76    | 0.08    | 0.54 | 1.65    | PA, AA | [9]   |
| N/A    | 0.70   | 0.33    | 0.00    | 0.68 | 1.33    | NA, PA | [9]   |
|        | 0.65   | 0.7     | 0.00    | 0.48 | 1.35    |       |       |
| 6016   | 0.44   | 0.96    | 0.00    | 0.32 | 1.41    | NA, PA, AA + AA | [130] |
| 6111   | 0.90   | 0.60    | 0.30    | 0.60 | 1.50    | PA, AA | [62]  |
| N/A    | 1.05   | 0.78    | 0.00    | 0.57 | 1.83    | NA, PA, BH, NA + BH, PA + NA, PA + NA + BH | [77]  |
| 6182A  | 0.97   | 0.83    | 0.01    | 0.54 | 1.80    | PA + NA, NA, | [138] |
| 6022-type | 0.54 | 1.03    | 0.12    | 0.34 | 1.57    | NA + AA, PA + NA + AA | [116] |
| 6111   | 0.90   | 0.60    | 0.30    | 0.60 | 1.50    | NA, PA, AA | [116] |
| N/A    | 1.01   | 0.78    | None/Cu/Ag | 0.57 | 1.78    | NA, PA | [148] |
| 6061   | 0.92   | 0.58    | 0.09    | 0.61 | 1.50    | AA T6, NA + AA T6 | [149] |
| N/A    | 0.86   | 0.43    | 0.00    | 0.67 | 1.29    | NA + PA, PA | [117] |
|        | 0.40   | 0.84    | 0.00    | 0.32 | 1.24    |       |       |
| N/A    | 0.53   | 1.03    | 0.12    | 0.34 | 1.56    | NA, NA + BH | [60]  |
| 6061 + Sn | 0.90 | 0.59    | 0.09    | 0.60 | 1.49    | NA, AA | [43]  |
| 6061   | 0.92   | 0.58    | 0.09    | 0.61 | 1.5     | NA, NA + AA, IQ to AA | [9] |
| N/A    | 0.51   | 0.94    | 0.01    | 0.35 | 1.45    | AA, NA, PA, PA + NA, NA + BH, | [130,131,134] |
|        | 0.51   | 0.94    | 0.01/0.06/0.34 | 0.35 | 1.45    | PA + NA + BH, spike + PA |       |
| N/A    | 0.69–1.31 | 0.35–1.1 | 0.03–0.21 | 0.38–0.7 | 1.77–1.88 | NA, NA + BH, NA + AA | [133] |
| N/A    | 0.69   | 0.89    | 0.00    | 0.44 | 1.58    | NA, NA + BH | [132] |
| N/A    | 0.69   | 0.89    | 0.00    | 0.44 | 1.58    | PA + NA | [135] |
| 6016   | 0.40   | 1.00    | 0.03    | 0.29 | 1.40    | NA     | [145] |
| N/A    | 0.69   | 0.89    | 0.00    | 0.44 | 1.58    | NA, PA | [102] |
| N/A    | 0.36   | 0.31    | 0.00    | 0.54 | 0.66    | NA, AA | [40]  |
| N/A    | 0.33   | 1.13    | 0.00    | 0.23 | 1.47    | NA, AA | [150] |
|        | 1.12   | 0.39    | 0.00    | 0.74 | 1.51    | NA + AA | [132] |
| N/A    | 0.69   | 0.89    | 0.00    | 0.44 | 1.58    | NA, NA + BH | [132] |
|        | 0.87   | 0.67    | 0.00    | 0.56 | 1.54    |       |       |
In the following, we discriminate in between NA and PA means NA followed by PA and for PA + NA the reverse sequence. Moreover, interrupted quenching treatments are considered as PA treatments here.

In ref. [139] it was reported for AA6016 that PA (90 °C for 8 h) plus NA lead to Si-Mg pair correlation values >1.

Esmaili et al. [62] also performed APT investigations for different PA temperatures ranging from 60 to 180 °C for the alloy AA 6111, while adjusting the time to be at a local electrical resistivity maximum. Generally, Mg-Si aggregates were obtained, where a majority also contains Cu. It was revealed that with increasing temperature the number density of small clusters was reduced and a second family of large clusters arise, also the average Mg/Si-ratio was seen to increase. [62]

A difference between NA and PA was revealed by Serizawa et al. [71] for an Mg-excess alloy. Clusters do not grow during NA and the majority of the clusters has \( N_{\text{clusters}} < 50 \) (not corrected for detection efficiency). Clusters formed upon PA at 100 °C increase in size (see Figure 24) for a time, recalculated from PA time to time at RT, equating diffusion distances and assuming an Ahrrenius type form of the diffusion constant with an activation energy of 130 kJ mol\(^{-1}\). They postulated that clusters formed during NA and PA are different types of clusters (C1 and C2 respectively). The clusters showed various Mg/Si-ratios, especially if the clusters are small. Larger clusters were found to have a narrow Mg/Si-ratio distribution (C2), approaching a Mg/Si ratio of 1.5–2.0 and are believed to be able to transform into \( \alpha \) precipitate upon AA. Serizawa et al. [71] also performed a comparison of PA and PA followed by NA (=28 days), which showed similar Mg/Si-ratio over \( N_{\text{Mg}} + N_{\text{Si}} \) (number of solutes in a cluster, \( N_{\text{Mg}} \) number of Mg atoms and \( N_{\text{Si}} \) number of Si atoms in a clusters) plots. The Clusters (2) are therefore considered not to grow or dissolve at RT. [71]

Torsæter et al. [135] reported in contrast that PA of Si-excess and Mg-excess alloys showed clusters of a Mg/Si ratio of approximately unity (broad peak of distribution around 1.0), which means that the composition of clusters formed upon PA does not depend on the alloy composition. This is in contrast to NA, where the average composition of NA clusters was concluded to follow more the overall composition of the alloy. If NA is examined prior to PA a large decrease in identified aggregates can be observed and a dual distribution of Mg/Si ratios is present. [137]

Prolonged NA after PA (examined via quenching into heated water at 90 °C) is investigated in ref. [135]. NA after this PA resulted in an increase in number density and a decrease in average Mg/Si ratio of clusters. The number density of low Mg/Si ratio is seen to increase and cause the shift in average Mg/Si ratio. Larger Clusters are seen to have a higher Si content after PA + NA compared to PA only. It is believed that Si aggregates to the clusters formed during PA rather than the independent formation of Si-based clusters. [135]

Cao et al. [138] investigated AA 6181A and an AA 6022-type alloy. Natural aging of 24 h resulted in a high number density of small clusters in AA 6181A. PA (20 s at 200 °C) plus NA 24 h yielded lower number density of small aggregates. Interestingly a strong correlation between the amount of large aggregates and yield strength was obtained, but the overall number density did correlate less with the yield strength. The alloy AA 6022 showed similar trends, but generally the fraction of solutes in the aggregates was lower and yielded lower mechanical properties. [138]

In ref. [40], it was shown that PA at 160 °C for 2 min (examined via interrupted quenching) can strongly suppress subsequent cluster formation during NA in a lean AlMgSi alloy. This was explained by a reduction of quenched-in vacancies rather than a formation of clusters upon this short term PA.

Zandbergen et al. also confirmed that for approximately equal time spans of NA and PA, PA resulted in larger-sized clusters of higher Mg/Si ratio and the Mg/Si ratio distribution is narrower with a peak at unity. These clusters continue to grow upon further PA. Also it is reported that smaller clusters are fewer in the PA than in NA condition. For 10 h of PA at 80 °C the number density stagnates for \( N_{\text{min}} = 5 \) in comparison to two hours PA at 80 °C, while for \( N_{\text{min}} = 10 \) the number density increases — which is interpreted as growth of clusters. Applying a spike (10 s at 180 °C) heat treatment after quenching prior to PA, the number density of

![Figure 24. Growth rate of clusters formed at room temperature (Cluster (1)) and at 100 °C (Cluster (2)). The values \( N_{\text{av}} \) (average solute number of clusters, \( N_{\text{av}} \approx \text{average cluster radius} \) are plotted against the square root of the normalized room temperature time, \( t_{\text{RT}} \). Data recalculated from [71]. © 2018 Springer Nature.](image-url)
larger clusters after PA is increased. Clusters formed upon PA are suggested to be similar in Mg/Si ratio like β0 precipitates and the average Mg/Si ratio is reported to be substantially lower for clusters formed during NA, which confirmed prior findings.\textsuperscript{130,131}

Latest research compares the findings on NA and PA between the newly available high detection efficiency atom probe (LEAP 5000 XS) and atom probe data generated by lower detection efficiency (LEAP 3000 HR) for an excess Si alloy (see Table 3).\textsuperscript{102} Generally, a shift to larger cluster sizes, in the plot number density over Guinier radius, is obtained for a high detection efficiency atom probe. Also the average Mg/(Mg + Si) ratio is found slightly increased with higher detection efficiency. The atomic density of clusters is further investigated in detail. For clusters with a Mg/(Mg + Si) \textless 0.4 almost constant, significantly lower than average density is found. Therefore a ratio Mg/(Mg + Si) \textless 0.4 is used to define Si-rich clusters. The volume fractions for short-time NA, long-term NA and PA for the so defined classes of clusters are analyzed. A significant lower volume fraction of Si-rich clusters for PA treated material is found in comparison to the NA treatments. Long term NA leads to higher volume fraction of Si-rich clusters, which are concluded to be the critical constituent for the occurrence of the negative effect.\textsuperscript{102}

We conclude:

1) Clusters formed during NA and clusters formed during PA are possibly two different kinds of clusters.
2) PA forms Mg, Si co-clusters which act as nucleation site or can transform into β0 during AA.
3) PA clusters often show a Mg/Si-ratio of unity, while NA clusters show various Mg/Si-ratios.
4) PA plus NA increases the number density of Si-rich clusters and decreases the average Mg/Si-ratio of the clusters.
5) NA leads to a significant amount of Si-rich clusters, whereas PA leads to larger volume fractions of Mg, Si co-clusters with a lower amount of Si-rich clusters.

In general, clusters formed upon PA are better understood than those formed by NA and can be clearly distinguished. The work of the last 20 years made clear that PA leads to clusters, which represent a pre-state of the precipitates formed upon AA. This is well resembled by the found composition spectrum.

4.4.2.3. Artificial Aging

In this section, APT results on short AA (called bake hardening (BH)) and AA to T6 illustrate the effect of clusters from NA and PA.

A sample NA and a sample PA + NA are additionally artificially aged at 185 °C for 2 h and investigated in.\textsuperscript{139} The PA sample showed higher number densities of aggregates and besides needle shaped β0 precipitates also spheroidal shaped ones in AA condition.\textsuperscript{139} It is proposed that Mg–Si co-clusters act as nucleation sites for hardening phases.\textsuperscript{139} Two hours of PA (80 °C) was seen to not fully restore the BH response in comparison to direct AA, but increases it compared to naturally aged material.\textsuperscript{130}

The difference in short AA (20 min 170 °C) with and without NA is quantitatively shown for the identified clusters/precipitates in Figure 25.\textsuperscript{721} A narrow Mg/Si-ratio distribution with lots of large precipitates is found for the direct BH in comparison to the NA + BH state, where a high number of small clusters is found with a large spread in Mg/Si-ratio and a second fraction of larger size but few in number. It is suggested that clusters from NA remains after BH.\textsuperscript{721}

This is confirmed in ref. [9] where a decreasing density of clusters remaining from NA was observed upon AA. Already after 10 min of NA, the inhibiting nature of NA on BH is reported in ref. [130]. The incompatibility of average Mg/Si ratio of NA clusters and precipitates is suggested as a mechanism of inhibition.\textsuperscript{130} The difference in the T6 state upon longer AA with and without NA is illustrated in Figure 26 for the alloy AA 6061.\textsuperscript{149} Artificial aging without NA resulted in spheroidal precipitates and short needle-like β0 precipitates with high number density. For NA + AA clusters, spheroidal precipitates and long needle-like β0 precipitates with low number density are found. No significant compositional difference in between precipitates for NA + AA in comparison to direct AA was found. However, a bimodal size distribution for β0 precipitates is obtained for the NA + AA heat treatment.\textsuperscript{149}

For NA + AA (170 °C 30 min), still a relatively high number of small solute aggregates is apparent, whereas the number of large aggregates decreases with increasing NA before AA (Figure 10b).\textsuperscript{660} The average size of clusters for NA + AA reaches a plateau after 3 h of NA. For NA only, average size increases slightly within the first few hours, but then remains constant (Figure 10a). Comparing NA and NA + AA, for longer NA times, average cluster sizes are the same, only the maximum cluster size is larger for NA + AA.\textsuperscript{660}

Aruga et al.\textsuperscript{152} also found that the impact of increased NA after 3 h of NA on the T6 state upon AA investigated via APT is low for an excess Si alloy, though with longer NA, a larger drop in hardness during short AA times is obtained.

Poznak et. al.\textsuperscript{150} conclude that the negative effect on AA is a function of bulk Mg/Si ratio as stated by.\textsuperscript{151} Further, they analyze cluster evolution during AA at 175 °C for Si- and Mg-rich alloys. They conclude that NA clusters of the Mg-excess alloy are thermally stable at this low aging temperature and an irrecoverable negative effect is introduced as compared to the Si-rich alloy.\textsuperscript{150} Similar findings are made by Aruga et al.,\textsuperscript{152} where also a better recoverable (but not full in comparison to direct aging) for a Si-rich alloy in comparison to Mg-rich alloy for longer AA times is seen. Though, here for long NA plus BH a small increase in Si-rich clusters and a decrease for Mg-richer clusters is seen.\textsuperscript{152}

With higher Cu content Zandbergen et al.\textsuperscript{134} reported that the direct BH response increases and a larger number density of short length precipitates is found. The (Mg + Cu)/Si ratio increases from the low- to high-Cu content alloy, while the Mg/Si ratio decreases. In increased Cu content alloys all precipitates contain Cu. It is concluded that Cu partly substitutes Mg in the precipitates. Cu additions showed greatly enhanced formation of elongated precipitates for NA (1 week) + BH. The hardening phases for the high-Cu alloy corresponds broadly to Q' precursors, the hardening precipitates of Cu-free alloy to β0. For short time AA (5 min 180 °C), Cu additions lead to increased number densities of clusters. The AA response after NA is concluded to be dominated by residual solutes in the matrix, for a
Figure 25. Relationship between size ($N_{Mg} + N_{Si}$ – number of solutes) and Mg/Si ratio of clusters and the $\beta''$ phase for specimens a) direct bake hardening treatment and b) naturally aging for 604.8 ks and bake hardening. Reproduced with permission from ref. [71], © 2018 Springer Nature.

Figure 26. Three-dimensional reconstructions of atom positions for Mg, Si, and Cu and isoconcentration surfaces of Mg embedded in the Al matrix with corresponding proximity histograms for Al, Mg, Si, and Cu based on short needles and long needles for a) direct artificial aging and b) artificial aging after long-term natural aging (all in T6 condition). Adapted with permission from ref. [149], © 2018 Elsevier.
Mg-rich alloy, without Cu additions, the lower Si residual is suggested to cause the lower AA response.\textsuperscript{[134]}

Recently, Jia \textit{et al}.\textsuperscript{[133]} reported for Cu added alloys a low influence of the Mg/Si ratio on the negative effect of NA on the AA response.\textsuperscript{[133]}

We conclude:

1) Direct BH results in a high density of precipitates with a narrow Mg/Si ratio. In the T6 state, a uniform distribution of needle like precipitates is observed.
2) Prior NA causes a high number of small clusters with large Mg/Si-ratio spread after BH. For T6 a bimodal size distribution of few large elongated needle precipitates and short needle like precipitates is found.
3) The impact of NA to further AA on APT results stagnates for NA $\geq$3h.
4) Cu incorporates into precipitates.
5) Cu reduces the influence of the Mg/Si ratio on the NA + AA.

5. Summary and Conclusion

The occurrence of clusters can have important technological influence on the material properties of aluminum alloys. Ranging from natural aging in general, the rapid hardening reaction at artificial aging for AlCuMg alloys, over an increase in artificial aging response with prior natural aging for low alloyed AlMgSi alloys, to strongly decreased artificial hardening kinetics of high alloyed AlMgSi due to prior natural aging.

In general, the evolution of clusters at RT is well characterized by indirect methods as resistivity measurements, differential scanning calorimetry, positron annihilation lifetime spectroscopy, hardness, and tensile testing.

Hardness measurements are seen to be an easy way to follow the strength evolution of the material due to clustering. The strength to cluster relationship is often interpreted by means of a monotonous function, that is, increasing strength contribution corresponds to more clusters. The increase of hardness is either proportional to the square root of the volume fraction of clusters (shearable obstacles), or direct proportional to the volume fraction of clusters (short range ordering contribution). Further, effects of clusters are seen from tensile testing, such as differences in the Portevin Le-Chatelier effect for as-quenched and naturally aged alloys.

Resistivity measurements can be used to study the evolution of clusters at the early stages due to high sensitivity and time-resolution. Resistivity is sensitive to cluster number density/inter-cluster distance. Although, the resistivity/hardness relationship for natural aging is seen to be alloy dependent. Hence, the drawback of the method is the weak connection between signal, cluster properties, and mechanical properties.

Positron annihilation spectroscopy is especially a sensitive tool in vacancy-related processes, which play an important role for clustering. The positron lifetime signal over natural aging time can be interpreted as an overlaying decrease due to vacancy annihilation and an increase due to cluster formation. The increase in lifetime signal can be correlated to the hardness increase and thus the impact of additional alloying elements or substituting alloying elements can be studied. The effect of clusters on the following precipitation sequence is best revealed via differential scanning calorimetry. The peak corresponding to $\beta''$ is shifted to higher temperatures and endothermic traces in this region arise and increase with natural aging time. Also storage periods of short time pre-aged material for longer times at RT arise and increase endothermic traces.

The most important technique for direct visualizing and measuring of clusters with near atomic resolution and gaining precise information of the compositions of clusters is atom probe tomography. Clustering in AlMgSi alloys is studied by numerous authors in detail. It is seen that effects caused by clusters, formed during RT, undergo a transient change during storage. Therefore, the evolution of clusters during RT is suggested to be grouped into distinct stages. A practical viewpoint is to treat the clusters formed at room temperature as their own “metastable state.” Strong evidence exists that natural aging clusters revert upon elevated artificial aging temperatures. Their effect on artificial aging in AlMgSi alloys is attributed to solutes depletion, a concurrent cluster solution, and precipitate forming reaction, and their interaction with vacancies. Most authors find that cluster formed during natural aging are difficult to transform to the major hardening phase upon artificial aging, while clusters formed during pre-aging at moderate temperature can transform to subsequent phases at artificial aging temperatures. From atom probe tomography results natural aging clusters are seen to stagnate in size early and increase further in number density in long-term RT storage. Pre-aging clusters are seen to grow significantly with increasing pre-aging time. Often a narrow distribution (approx. unity) in the Mg/Si ratio is observed for pre-aging clusters, whereas for natural aging clusters a large Mg/Si ratio spread over the population is obtained. This is suggested to be the origin of non-transformable clusters, since later precipitates in AlMgSi alloys are equally often a ratio around unity. Other authors blame specifically the Si-rich clusters. Moreover, it is stated that the matrix Mg/Si-ratio influences the stability of NA clusters at artificial aging temperatures. For early cluster forming upon natural aging, Si is often suggested to have a leading role. Separate Si (Si-rich) and Mg (or at least Mg-rich) clusters are suggested to form, followed by transforming into Mg, Si co-clusters. Solute additions can influence the clustering (e.g., Cu is suggested to aggregate to clusters and to change the cluster chemistry and their transformation upon artificial aging; Sn retards the formation of clusters due to vacancy trapping).

With advanced analysis algorithms and improved methods new in use today, that is, the latest developments in atom probe tomography detectors and cryo-atom-transfer probe equipment, further and more detailed insights into the nature of clusters will be possible in the near future.

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Conflict of Interest
The authors declare no conflict of interest.

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