Multi-Stage Ageing in an Al-Mg-Si Alloy

vorgelegt von

M. Sc.
Zi Yang

ORCID: 0000-0002-6548-7943

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Promotionsausschuss:
Vorsitzender: Prof. Dr. Dietmar Auhl
Gutachter: Prof. Dr. John Banhart
Gutachter: Prof. Dr. Stefan Pogatscher

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Erklärung

Ich erkläre hiermit, dass ich die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Berlin, Sep. 2019
Zi Yang
Abstract

Solute clustering and precipitation in Al-Mg-Si alloys have been extensively studied in the past decades owing to an increasing importance of these alloys in industrial applications. However, many details are still not well understood, especially during multi-stage ageing. In this study, several aspects of multi-stage ageing in a commercial AA6014 alloy were systematically investigated, namely 1) the role of various pre-ageing treatments in the multi-stage ageing process, 2) the influence of quench rate on multi-stage ageing, and 3) clustering and precipitation in a special type of multi-stage ageing — linear heating. Transmission electron microscopy (TEM), electrical resistivity measurement, differential scanning calorimetry (DSC), hardness testing, and positron annihilation lifetime spectroscopy (PALS) were applied either ex situ after various quenching or ageing stages or in situ during ageing to characterise the microstructure. It is found that, 1) the pre-ageing (PA) condition, in particular the PA temperature, plays a crucial role in controlling the natural secondary ageing (NSA) kinetics and paint bake (PB) hardening. High PA temperatures favour a higher PB potential but meanwhile lower NSA stability (resistance to clustering). If PA is conducted in two stages at two different temperatures, then the first stage has a greater influence. 2) Quench rate affects the supersaturations of both solutes and vacancies, and therefore also the subsequent ageing kinetics. Artificial ageing (AA) or PB hardening is observed to be more affected by slower quenching than natural ageing (NA), PA, and NSA. The influence of quench rate on PB hardening after NA or NSA is found also to depend on NA, and it is gradually diminished after longer NA/NSA. 3) Clustering and precipitation during linear heating are closely associated with the heating rate. A lower heating rate results in stronger cluster formation, which influences further the precipitation at higher temperatures. A discussion of the corresponding clustering and precipitation kinetics is developed concerning the evolution of vacancy site fraction, solute supersaturation, and the interactions between vacancies and solute clusters. The current study underlines the importance of solute clusters formed in the early stages of ageing by controlling the evolution of vacancies as well as influencing the further precipitate formation in the later stages.
Kurzzusammenfassung

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Three years of doctoral research was much faster, and much harder than I expected. I am very grateful that I got plenty of help from many people during this time. Therefore, I would like to use this opportunity to express my sincere appreciations to them. They should know that they have helped me more than what I mention here.

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My sincere appreciation also goes to Novelis Göttingen and Novelis Sierre, without whom this project will not exist. I had quite frequent discussions with Dr. Zeqin Liang and David Leyvraz, who have given me very useful suggestions and ideas, especially from the industrial side, which means a lot for me and for this project.

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I would also like to thank Mrs. Christiane Cicéron for her help in administrative stuffs.

Besides the help I received in work, I also got a lot of help in my life. I owe a lot to my girlfriend Fanxing and my parents. They have always supported me and my decisions. I am really lucky to have them in my life.
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AA</td>
<td>artificial ageing</td>
</tr>
<tr>
<td>AC</td>
<td>air cooling</td>
</tr>
<tr>
<td>AQ</td>
<td>as-quenched</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>IWQ</td>
<td>ice-water quenching</td>
</tr>
<tr>
<td>LH</td>
<td>linear heating</td>
</tr>
<tr>
<td>LT</td>
<td>lifetime</td>
</tr>
<tr>
<td>NA</td>
<td>natural ageing</td>
</tr>
<tr>
<td>NSA</td>
<td>natural secondary ageing</td>
</tr>
<tr>
<td>PA</td>
<td>pre-ageing</td>
</tr>
<tr>
<td>PALS</td>
<td>positron annihilation lifetime spectroscopy</td>
</tr>
<tr>
<td>PB</td>
<td>paint-baking</td>
</tr>
<tr>
<td>SHT</td>
<td>solution heat treatment</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>VC</td>
<td>ventilator cooling</td>
</tr>
</tbody>
</table>
Global warming and the associated climate change caused by a historically high and continuously rising atmospheric carbon dioxide concentration [1] have raised significant public attention and concerns. In the act of reducing carbon dioxide emissions caused by fuel consumption, replacing the conventional steel constructions by light-weight materials, especially Al alloys, is a practical solution for the automotive industry. This replacement has been very successful for some parts on the car. For example, the market penetration for aluminium alloys used in engine and transmission parts is higher than 80% [2]. However, the percentage for hang-on panels, such as hoods and doors, still has a great potential to grow [2].

As one of the major aluminium alloys for outer panel applications, 6xxx series (Al-Mg-Si based) aluminium alloys stand out for a combination of good formability, corrosion resistance, and medium to high strength after paint baking (PB) [3, 4]. The strength enhancement of the alloys mainly benefits from precipitation hardening, which is realised by a series of heat treatments, involving at least a solution heat treatment (SHT) at high temperature to dissolve solute atoms, a rapid quench to obtain a non-equilibrium supersaturated solid solution state, and an artificial ageing treatment (AA) to promote the decomposition of the supersaturated solid solution and eventually form densely distributed nm-sized precipitates in the matrix. In industry, AA as the last process step is accomplished during the PB treatment.

The development of Al-Mg-Si alloys can be traced back to about a century ago [5]. Although more and more has been known about this type of alloy during the past century there are still problems to be solved. One of them troubling both academic researchers and industrial users is the deleterious effect of natural ageing (NA), or the so-called “negative effect”, which refers to a delayed and compromised AA kinetics after the alloy being kept at room temperature for even just minutes after SHT [6]. As SHT is finished at aluminium producers and PB is performed at car manufacturers, this room temperature storage is practically inevitable. Industrial routine to suppress the “negative effect” is by performing a pre-ageing (PA) treatment at an intermediate temperature, e.g. 100 °C, after SHT but before NA. It has been demonstrated by a number of works that the subsequent ageing behaviour is dependent on PA conditions [7-12], but a systematic study showing how they are exactly related is still not available. Therefore, the first part of this thesis focuses on the pre-ageing conditions and their...
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influences on the subsequent natural secondary ageing (NSA) and PB hardening behaviour. It contains two sections. In the first, we systematically investigate the effect of single-step PA at various temperatures for various times, and the mechanisms determining the subsequent NSA and PB hardening. Associated results and discussions are presented in chapter 4.

Chap. 4. Effect of pre-ageing on natural secondary ageing and paint-bake hardening

In the second, PA treatment is divided into two consecutive steps at two different temperatures, and its effect on the ensuing age hardening is investigated and compared with that of single-step PA. Emphasis is put on how microstructure, namely clusters and vacancies, evolve when temperatures change from one to another. This study is shown in chapter 5.

Chap. 5. Two-step pre-ageing and its effect on multi-stage ageing

Quenching plays a crucial role as the first process after SHT. On the one hand, it ensures a high level of dissolved solutes and excess vacancies available later for precipitate formation. On the other hand, formation of clusters during NA, widely regarded responsible for the “negative effect”, is also related to such high solute and vacancy supersaturation [13]. How vacancies and solutes evolve during quenching and subsequently influence multi-stage age hardening remains elusive. Moreover, quenching in industrial production can be much slower than usually carried out in laboratory conditions due to much larger sample volumes and other limitations. Hence, investigating the quenching procedure and its influence on ageing kinetics is a task of both scientific and practical relevance. For that purpose, we developed a convenient laboratory-scale cooling device, providing quench rates similar to industrial conditions with a good reproducibility as shown in chapter 3. Microstructures after different quenches as well as the influence on single-, two, or three-stage ageing treatments are presented in chapter 6.

Chap. 6. Influence of quench rate on multi-stage ageing

The last part of the thesis focuses on ageing phenomenon during linear heating, which can be approximated as a special case of multi-stage ageing consisting of very short stages at linearly increasing temperatures. A good example of such heating is seen in differential scanning calorimetry (DSC) which has been widely applied to determine many physical properties and to characterise phase transitions in materials [14]. For Al-Mg-Si alloys, DSC has often been used to indirectly probe the clustering and precipitation processes during isothermal ageing [8-10, 12, 15-22]. However, for the processes occurring during linear heating, especially clustering,
our understanding is far from complete. Therefore, we applied other methods such as electrical resistivity measurements, positron annihilation lifetime spectroscopy (PALS), and hardness measurements, to reveal more details about clustering and precipitation during ageing by linear heating. In order to linearly heat samples for those measurements, we established a device to perform linear heating as introduced in chapter 3. The influence of different heating rates is also studied. The results and corresponding discussion are presented in chapter 7.

Chap. 7 Characterisation of clustering and precipitation during linear heating.
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2. Literature review

2.1. Age hardening and precipitation

2.1.1. General

In 1906, more than a century ago, Alfred Wilm accidentally discovered that the aluminium alloy containing 3.5% copper and 0.5% magnesium (all in wt.) can be considerably hardened after quenching from high temperature annealing and subsequent room temperature storage. Unlike the effect in steels, which Wilm was originally looking for, hardening (or strengthening*) in his alloy is not produced during the quenching, but instead continuously builds up during storage. These results were later published in 1911 [23]. Inspired by Wilm’s groundbreaking finding, researchers in the following years strived to develop other alloys which can be heat-treated in a similar way. By the year of 1935, the effect Wilm found was successfully realised in a great number of alloys [24], including not only aluminium alloys with other alloying elements such as Al-Mg-Si and Al-Zn-Mg, but also Mg alloys such as Mg-Al, Cu alloys such as Cu-Be and Cu-Ni-Sn, Ag alloys such as Ag-Cu-Cd, Au alloys such as Au-Cu, Ni alloys such as Ni-Cr-Fe, Fe alloys such as Fe-C-Ni and Fe-Cu, and many more alloys unlisted here but which can be found in Ref. [24]. This effect, named “age hardening”, had since then profoundly changed the way people treat and design alloys. Nowadays, after more than a century of application, it has become one of the most basic and important methods to enhance the mechanical properties of the material, and many more alloy systems were found with improved properties, e.g. [25, 26]. Some of the alloy systems designed at that time are still being used today, e.g. the Al-Cu-Mg alloys designed by Wilm. Of course, their properties have been much improved.

When Wilm found the age hardening in his alloys [23], the mechanism behind hardening was obscure. Wilm found that the primary cast-in structure disappeared after annealing at high temperature and quenching, but did not find any microscopic change during natural ageing, although mechanical properties markedly improved [23]. For several years it was considered a unique phenomenon applicable only to Duralumin (alloys patented by Wilm) and the

* Strengthening and hardening in this study are synonymous and interchangeable.
understanding of the phenomenon did not progress much [27] until two papers were published in 1919 by Merica et al. [28, 29] who took the phase diagram and solubility of the secondary phases at different temperatures into consideration and attributed the age hardening to the precipitation of the supersaturated solutes after rapid quench. The size of the precipitates formed, as they claimed, are too small to be directly observed in the optical microscope. It was until 1938 that Guinier [30] and Preston [31] finally proved the existence of these small precipitates, later termed as GP zones, in Al-Cu alloys by X-ray diffraction and claimed their structure as layers on \( \{100\} \) planes, but the success of Merica’s interpretation has been proved by the numerous new heat-treatable alloys found even before GP zones were observed [24].

By now it has become clear, much the same as proposed by Merica et al., that the mechanism of the precipitation process can be described as: 1) solution annealing at high temperature to dissolve solutes in the matrix; 2) rapid quench to retain solutes in the matrix; 3) ageing at an intermediate temperature to enable the decomposition of the supersaturated solid solution (SSSS) and form precipitates. The latter process can be quite complicated as multiple metastable phases might occur depending on temperature and time before the equilibrium phase is finally formed. For example, Al-Cu alloys undergoes a precipitation sequence of [32]:

\[
\text{SSSS} \rightarrow \text{GP(I) zone} \rightarrow \text{GP(II) zones (}\theta''\text{)} \rightarrow \theta' \rightarrow \theta \text{ (Al}_2\text{Cu).}
\]

The strengthening effect of precipitation comes from the interaction of dislocations and precipitates (or zones), which impede dislocation movement. Depending on the size, density, spacing of the precipitates, and the coherency of precipitates with the matrix, precipitates can be sheared or circumvented. Generally, strengthening can be expressed as \( \sigma \propto \sqrt{f} \cdot \sqrt{r} \), if precipitates are shearable; if not shearable, \( \sigma \propto \frac{\sqrt{f}}{r} \) [33], where \( \sigma \) is the strength increase by precipitation, \( f \) is the precipitate fraction, and \( r \) is the (effective) average radius of the precipitates. By introducing the obstacle strength at various stages, Esmaeili et al. [34] discriminated shearable precipitates as ‘weak’ and ‘strong’ obstacles, where for the former above equation remains the same and for the latter the expression is changed to \( \sigma \propto \sqrt{f} \). It was claimed that the ‘strong’ obstacle model fits well to AA at \( 160 \, ^\circ\text{C} \) – \( 220 \, ^\circ\text{C} \) for an 6111 alloy [34]. As dislocations always find the easiest way to pass the precipitates, the final strength should be the lowest one predicted by all mechanisms. For example, precipitates in the overaged stage are normally circumvented by dislocations instead of sheared due to a lower stress needed.
2.1.2. **Al-Mg-Si alloys**

The development of Al-Mg-Si alloys already took place in the early 1920s when people found that although small amounts of Si or Mg alone do not cause much age hardening in Al, considerable hardening can be obtained by addition of both [5]. The equilibrium precipitate phase is known to be Mg2Si, but metastable phases always occur before forming the equilibrium phase, and these metastable phases, in particular \( \beta'' \) precipitates, play a more important role in strengthening the material, especially in the industrial PB state or peak-aged state [35, 36]. A great number of studies contributed to understanding those metastable phases [35-47], and nowadays a generally accepted precipitation sequence can be given mainly based on DSC measurements [15, 39] as:

\[
\text{SSSS} \rightarrow \text{Mg-Si clusters} \rightarrow \text{GP zones (pre-}\beta''\text{)} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta (\text{Mg}_2\text{Si}),
\]

with some variations of the intermediate phases (see Fig. 1 in Ref. [6] for a more complete sequence). However, it has to be noted that the above mentioned precipitation sequence might not be standard for all ageing treatments. It has been recently reported that the sequence can be reversed in some naturally aged alloys [48, 49].

2.2. **Evolution of clusters during ageing in Al-Mg-Si alloys**

2.2.1. **Cluster formation**

Clusters are generally formed in early stages of AA or at low to intermediate temperatures (NA or PA clusters). It is thought that such clusters are too small, disordered, coherent with the Al matrix and contain neighbouring elements in the periodic table so that they are barely visible even under a high-resolution transmission electron microscopy (HRTEM). Only two studies have reported structures of clusters based on HRTEM. Fallah et al. [50] reported that clusters during early AA (5 – 20 min) undergo a transition from a spherical morphology to elongated clusters on different planes. Marioara et al. [47] reported that the structure of NA clusters consists of two types, spinodal decomposition induced Mg-rich clusters and Si-networks, and that the structure of PA clusters is the fractional \( \beta'' \) unit cell. Most direct information about clusters are obtained from atom probe tomography (APT), such as number density, size, and chemical composition of the clusters. A collection of this information is shown in Table 2.1.
Table 2.1. Collection of atom probe tomography data describing clusters. Real values can be higher due to the limited detection efficiency (DE) of an atom probe. (RT: room temperature)

<table>
<thead>
<tr>
<th>Alloy composition (%)</th>
<th>Ageing treatment</th>
<th>Average cluster size</th>
<th>Number density (10^{24} \text{m}^{-3})</th>
<th>Average Mg/Si ratio</th>
<th>Solute fraction contained in clusters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.78Mg-0.68Si (at.)</td>
<td>RT, 7 d</td>
<td>10 – 55 sol.</td>
<td>3</td>
<td>1.2</td>
<td>0.12</td>
<td>[51]</td>
</tr>
<tr>
<td>0.95Mg-0.81Si (wt.)</td>
<td>25 °C, 168 d</td>
<td>dia. 3.4 nm</td>
<td>1.6</td>
<td>-</td>
<td>0.06</td>
<td>[52]</td>
</tr>
<tr>
<td>0.51Mg-0.95Si (at.)</td>
<td>25 °C, 100 min 25 °C, 1000 min 25 °C, 1 w</td>
<td>12 sol. 13 sol. 14 sol.</td>
<td>0.2 (1.9) 0.7 (2) 1.2 (4.5)</td>
<td>0.7 0.6 0.7</td>
<td>-</td>
<td>[53]</td>
</tr>
<tr>
<td>0.51Mg-0.95Si (at.)</td>
<td>25 °C, 1 w 25 °C, 11 w 25 °C, 48 w</td>
<td>14 sol. 18 sol. 16 sol.</td>
<td>1.2 (4) 3.4 (4.9) 2.2 (4)</td>
<td>1 0.9 1.1</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td>0.62Mg-0.93Si (wt.)</td>
<td>RT, 3 h</td>
<td>dia. 2.6 nm</td>
<td>1.1</td>
<td>1.2</td>
<td>-</td>
<td>[55]</td>
</tr>
<tr>
<td>0.62Mg-0.93Si (wt.)</td>
<td>RT, 30 h</td>
<td>dia. 2.4 nm</td>
<td>1.5</td>
<td>1</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>0.78Mg-0.7Si (wt.)</td>
<td>RT, 2000 h</td>
<td>dia. 2.4 nm</td>
<td>1.7 b</td>
<td>1 b</td>
<td>-</td>
<td>[57]</td>
</tr>
<tr>
<td>0.62Mg-0.93Si (wt.)</td>
<td>RT, 100 h</td>
<td>dia. 2.9 nm</td>
<td>2.1 b</td>
<td>1 b</td>
<td>-</td>
<td>[58]</td>
</tr>
<tr>
<td>0.31Mg-0.99Si (at.)</td>
<td>RT, 28 d</td>
<td>9 sol. 8 sol.</td>
<td>2.1</td>
<td>0.5</td>
<td>0.06</td>
<td>[59]</td>
</tr>
<tr>
<td>0.78Mg-0.68Si (at.)</td>
<td>80 °C, 4 h</td>
<td>10 – 79 sol.</td>
<td>2.2</td>
<td>1.2</td>
<td>0.12</td>
<td>[51]</td>
</tr>
<tr>
<td>0.9Mg-0.6Si-0.3Cu (at.)</td>
<td>60 °C, 75 h</td>
<td>90 °C, 24 h 150 °C, 20 min 180 °C, 4 min</td>
<td>17 sol. 19 sol. 42 sol. 28 sol.</td>
<td>6.7 5.1 1.5 0.9</td>
<td>1.4 1.5 1.6 2.1</td>
<td>0.17 0.28 0.19 0.12</td>
</tr>
<tr>
<td>0.95Mg-0.81Si (wt.)</td>
<td>100 °C, 10 min</td>
<td>dia. 3.3 nm</td>
<td>1.9</td>
<td>-</td>
<td>0.08</td>
<td>[53]</td>
</tr>
<tr>
<td>0.41Mg-0.84Si (at.)</td>
<td>100 °C, 16 h</td>
<td>dia. 1.3 nm</td>
<td>2.6</td>
<td>1.1</td>
<td>0.08</td>
<td>[54]</td>
</tr>
<tr>
<td>0.86Mg-0.52Si (at.)</td>
<td>100 °C, 16 h</td>
<td>dia. 1.3 nm</td>
<td>2.7</td>
<td>1.4</td>
<td>0.07</td>
<td>[56]</td>
</tr>
<tr>
<td>0.51Mg-0.95Si (at.)</td>
<td>80 °C, 2 h</td>
<td>18 sol. 1 (1.9)</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>[57, 61, 62]</td>
</tr>
<tr>
<td>0.51Mg-0.95Si (at.)</td>
<td>80 °C, 2 h</td>
<td>18 sol. 1 (1.9)</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>[57, 61, 62]</td>
</tr>
<tr>
<td>0.62Mg-0.93Si (wt.)</td>
<td>90 °C, 5 h</td>
<td>dia. 2.6 nm</td>
<td>2.4 b</td>
<td>0.9 b</td>
<td>-</td>
<td>[57, 61, 62]</td>
</tr>
</tbody>
</table>

* Only the maximum size of all clusters was provided
b LEAP 3000 (DE: 50%)
c Number density outside parentheses (inside parentheses) is obtained using \(N_{\text{min}} = 10\) (\(N_{\text{min}} = 5\)) with \(N_{\text{min}}\) the minimum number of solutes in one cluster
d LAR-3DAP (DE: 35%)
\(\text{Si}\) LEAP 5000 XS (DE: 80%)

Direct comparison between values obtained in different studies can be challenging due to different alloys, heat treatments, atom probe models, and also cluster analysis parameters used.
in different studies. However, by comparing the results in the same study, following conclusions can be made:

1) Clusters formed at lower temperatures are smaller than those formed at higher temperatures but with a higher number density. This is not just valid for NA clusters compared with PA clusters [51, 53, 54], but also valid for PA clusters formed at different temperatures [59].

2) The Mg/Si ratio of an alloy has an impact on the Mg/Si ratio of solutes in clusters. Clusters have a higher Mg/Si ratio if the matrix Mg/Si ratio is higher [56, 58, 60]. However, the size and number density of clusters seem to be less influenced by the Mg/Si ratio.

3) During longer ageing, NA clusters do not change much in size but the number density increases [53-55, 57]. In contrast, PA clusters grow in size but their number density does not obviously change [54].

4) Apart from the above mentioned three observations, there is another one which cannot be seen from the table but has been concluded in several studies [52, 53, 57]: PA clusters have a narrower Mg/Si distribution than NA clusters.

APT provides valuable information about clusters such as size and chemistry. However, due to a limited time resolution, other methods such as hardness testing, electrical resistivity measurement, positron annihilation lifetime spectroscopy (PALS) are more suitable for analysing the kinetics of cluster formation, although these methods provide only indirect information about clustering. For example, the positron lifetime evolution divides NA clustering into 5 stages [63, 64]. The course of the positron lifetimes features in the initial stages a decrease of lifetime driven by the formation of Si-rich clusters and loss of vacancies, and later an increase of positron lifetime associated with an enrichment of Mg in the clusters, and eventually a re-decrease possibly caused by coarsening or internal ordering of clusters.

2.2.2. **Clustering during two-stage ageing**

Clustering during two-stage ageing depends on many variables, the most important two being the temperature at which clusters are formed in the first stage, and the temperature that the formed clusters are subjected to in the second stage. Besides, the alloy composition also plays
an important role, e.g. solute lean alloys behave differently as solute rich alloys. Next, we first introduce the behaviour of different clusters (NA and PA) in solute-rich alloys during various secondary ageing treatments, namely NA (20 °C), PA (~100 °C), AA (~180 °C), and RA (reversion ageing, ~250 °C). Solute lean alloys will be mentioned later.

**NA clusters + PA:**

Panseri and Federighi [65] measured the electrical resistivity change when temperature is instantaneously changed from 40 °C to 80 °C or from 20 °C to 120 °C. It was found that the maximum resistivity during the second stage increases with longer first stage but eventually tends to converge to the resistivity of single stage PA. It was interpreted by them that the clusters formed at low temperature will dissolve at higher temperature, but a longer NA stabilises the clusters thus resulting in a higher maximum resistivity. Marioara et al. [66] reported that NA clusters will dissolve at the beginning of ageing at 125 °C and 150 °C as indicated by a hardness decrease, and nucleation of the pre-$\beta''$ phase is delayed. Torsaeter et al. [60] investigated the effect of NA on PA clustering. It was observed that the Mg/Si ratio of the clusters after NA+PA shows a bimodal distribution, different as after PA where it is monomodal, indicating that another type of clusters has been formed during PA. It was also found that PA with preceding NA forms a lower number of clusters than PA without NA. Therefore, it can be summarised that NA delays the clustering process of PA and NA clusters seem to be reverted during PA.

**NA clusters + AA:**

The effect of NA on AA is more investigated due to its practical implications. Such studies can be found already in the 1920s. Gayler and Preston [67] reported that the peak hardness during AA hardening is lower when the alloy is stored at RT before. Later, Brenner and Kostron [68] also studied the effect and considered the effect of NA on AA resembles direct AA with a lowered concentration of solutes. With the help of TEM, Pashley et al. [13] found a coarser precipitate structure during AA after NA storage associated with a deterioration of mechanical properties. A model based on their observation claims that the coarse precipitates are caused by a preferential growth of stable clusters which have grown during NA to above a critical size and a dissolution of small clusters [69]. Based on the APT technique, more recent studies revealed new insights into the effect. Morley et al. [51] reported that the morphology of clusters does not change after AA and only a slight increase of size and number density of clusters was
Multi-stage ageing in an Al-Mg-Si alloy

observed. Serizawa et al. [52] suggested that clusters formed at ‘room’ temperature remain during AA at 170 °C. The factor determining whether clusters grow was argued not to be the size of the clusters but the Mg/Si ratio of the clusters. Pogatscher et al. [70] investigated the peak-AA structure after NA and demonstrated a bimodal size distribution of $\beta''$ precipitates. It is thought that the large precipitates have preferentially grown at dislocations or at several large NA clusters under the condition that a more homogeneous nucleation of $\beta''$ is suppressed by a shortage of excess vacancies. Zandbergen et al. [53] argued that during direct AA, elongated $\beta''$ precipitates are formed. During AA after short NA, clusters might further evolve into spheroidal precipitates or short elongated precipitates but have difficulties to further grow into larger $\beta''$ precipitates. After long NA, the clusters formed have to dissolve or change their structure to further develop into precipitates during AA.

Recently, Poznak et al. [58] reported the connection between the Mg/Si ratio of an alloy and the “negative effect” based on APT measurements. They claimed that the clusters in Mg-rich alloys are stable and are not inclined to dissolve during AA at 175 °C, thus causing an irrecoverable “negative effect”. In contrast, the clusters in Si-rich alloys are less stable and will dissolve, resulting in a recoverable peak age hardness. Another study based on TEM by Liu et al. [48] also pointed out the importance of the Mg/Si ratio of the alloy. It is claimed that the Mg-rich clusters formed in Mg-rich alloys will be nucleation sites for the $\beta'$ phase and thus will reverse the precipitation sequence, so that few $\beta''$ precipitates will be formed in naturally aged Mg-rich alloys during AA at 180 °C.

In summary, it is generally observed that clustering during NA causes a “negative effect” on AA kinetics. However, there still seems to be a dispute about whether NA clusters further grow or dissolve during AA, and which type of clusters grow or dissolve. Several studies pointed out that this might depend on the Mg/Si ratio of the alloy and the clusters.

**NA clusters + RA:**

NA clusters will be dissolved at the RA temperature. Madanat et al. [71] found that clusters are largely reverted in just few seconds at 250 °C. However, hardness is not reverted to the initial state even after longer time, indicating that probably a small fraction of NA clusters is not reverted or new clusters/precipitates are formed. During prolonged RA, a positive effect is observed compared with the alloy without prior NA [48, 72]. Liu et al. [48] claimed that this effect in the Mg-rich alloy is due to the formation of more homogeneous precipitates during
RA in the naturally aged condition instead of the $\beta'$ precipitates that are normally found in the non-naturally-aged alloy at such a temperature. The vacancy evolution during RA associated with NA clusters will be reviewed later in Sec. 2.3.3.

**PA clusters + NA:**

Aruga et al. [61] reported that PA clusters can grow after ~1.25 years of natural secondary ageing (NSA) after PA treatment, and more Si atoms are found to attach to PA clusters than Mg atoms. Panseri and Federighi [65] found that an abruptly decreasing temperature changes the course of electrical resistivity. It is thus speculated that clusters are formed independently at low temperature.

NSA hardening is delayed compared with NA. Such delay can be presented by a lower hardening during NSA [7-9, 12, 73] or by less loss of AA hardening potential after NSA (threepstage ageing) [7-10, 12, 13, 68, 73, 74]. NSA is found to be different for various PA conditions. However, how PA time and temperature influence NSA is still elusive.

**PA clusters + AA:**

Clusters formed at PA temperature are generally considered to grow when subjected to AA. Pashley et al. [69] argued that the reason for the growth is that the clusters formed during PA are mostly above the critical size so that they are stable at AA temperature. Similar explanations are given by Murayama and Hono [75] and Bryant [9]. However, another mechanism is argued to be that the Mg/Si ratio of the PA clusters is more similar to $\beta''$, which facilitates the transformation of the clusters into precipitates [52, 57, 76]. Therefore, the exact mechanism for cluster growth is still under debate.

**Solute lean alloys:**

Solute lean alloys (e.g. Al-0.4Mg-0.4Si, wt.%) behave quite differently than solute rich alloys. In these alloys, NA clusters exert a positive effect on the subsequent AA, e.g. at 180 °C. Chang et al. [77] showed that more precipitates are observed after AA for NA samples. Lai et al. [49] showed that there are not only more precipitates but also their phase structure is changed. It is argued that for direct AA, $\beta' (\beta'/\mathrm{U2})$ precipitates are directly formed, while $\beta''$ precipitates are formed during AA of naturally aged alloy. NA clusters are considered as nucleation sites for these precipitates.
2.3. Vacancy behaviour during ageing

2.3.1. Role of excess vacancies

Vacancies always exist in a material as an essential part of the thermodynamic equilibrium. The equilibrium vacancy site fraction at temperature $T$ can be calculated using:

$$c_{\text{vac}}^{\text{eq}} = \exp \left( \frac{S_v}{k} \right) \exp \left( - \frac{H_{f,\text{vac}}}{kT} \right),$$

with $S_v$ the vibration entropy, $k$ the Boltzmann constant, and $H_{f,\text{vac}}$ the vacancy formation enthalpy [33]. The equilibrium vacancy site fraction at the SHT temperature is generally several orders of magnitude higher than that at low temperature after quenching, therefore during quenching from SHT temperature to low temperature the vacancy site fraction in the matrix is reduced due to thermodynamic driving forces. If quenching is fast and the high vacancy site fraction does not have enough time to decrease to equilibrium, excess vacancies will be preserved in the matrix. Fischer et al. [78] modeled this behaviour and showed that the excess quenched-in vacancy site fraction is higher for higher quench rates.

Since substitutional Mg and Si atoms in Al diffuse under the assistance of vacancies, excess vacancies will enhance diffusion of these solute atoms. Excess vacancies are considered essential to explain the fast hardening at low-temperature ageing [13, 53, 79-81] in alloys. By annihilating out the excess vacancies, Pogatscher et al. [82] showed that NA in Al-Mg-Si can be suppressed. Similar suppression effect can be realised by adding trace elements such as Sn and In on the ppm level [83-86].

2.3.2. Mechanisms of vacancy site fraction reduction

Three mechanisms of vacancy site fraction reduction in the matrix are considered here, namely annihilation at sinks, formation of vacancy clusters, and trapping by solutes or clusters.

Vacancies can be generated at free surfaces, grain boundaries, dislocation jogs and so on. Vice versa, they can also annihilate at these sites. Here, two models of excess vacancy annihilation are presented. The first model was proposed by Schulze et al. [87, 88]. The rate of vacancy annihilation is given as $\frac{dc_{\text{vac}}(t)}{dt} \propto (c_{\text{vac}}(t) - c_{\text{vac}}^{\text{eq}})^q$, with $c_{\text{vac}}^{\text{eq}}$ the equilibrium vacancy site fraction and $q$ a reaction constant. When $q = 1$, the model can be understood as excess vacancies have equal opportunities to find sinks. The second model was proposed by Fischer
et al. [78]. This model takes the chemical potential of vacancies also into consideration. The rates of vacancy annihilation at different sinks are formulated differently and are quite complicated. However, under certain simplifications, e.g. if no hydrostatic stress is considered, it can be briefly given as \( \frac{dc_{\text{vac}}(t)}{dt} \propto c_{\text{vac}}(t) \times \ln \left( \frac{c_{\text{vac}}(t)}{c_{\text{eq}}(t)} \right) \).

Forming vacancy clusters, or their condensed structure—dislocation loops—is another mechanism to remove mobile vacancies from the matrix. Clustered vacancies (or dislocation loops) can still move but should be much less mobile. They are widely observed in quenched pure aluminium [89], its binary alloys [90, 91], and Al-Mg-Si alloys [38] in the as-quenched states. Therefore, these structures could be formed during quenching or during NA before TEM observation. Recently, it has also been reported that excess vacancies form loops during NA during the continuous generation of vacancies caused by cyclic loading [92].

Mobile vacancies can also be removed when locally trapped in clusters or by solute atoms. Such a mechanism will be presented in the next section. In the real process, those (or more) excess vacancy reduction mechanisms might co-exist and compete with each other, which complicates the scenario.

2.3.3. Vacancy trapping and release

Panseri and Federighi [65] proposed that a positive binding between vacancies and clusters exists, so that a transition of fast to slow reaction in resistivity change can be seen because vacancies are gradually trapped by forming clusters. By assuming that the vacancy-cluster binding energy is proportional to the size of a cluster, Zurob et al. [93] explained why the resistivity increase due to clustering is proportional to the logarithmic time. Pogatscher et al. [72] argued that the negative effect is due to lack of vacancies which are trapped by clusters. By dissolving those clusters at high temperature (e.g. RA at 250 °C), trapped vacancies can be released and contribute to the “positive effect”. However, Madadat et al. [71] argued that the trapped and released vacancies, if there are any, should not be very high in site fraction (i.e. <7×10^-8) since otherwise they would influence positron lifetimes. Solutes can also trap vacancies if the binding energy between the solute and the vacancy is positive (and high enough). Pogatscher et al. [83] demonstrated a thermodynamic model to evaluate the trapping effect quantitatively. Assuming a binding energy \( \Delta E_{SV} \) between a single vacancy and solute atom (positive value means attractive binding), the mobile (untrapped) vacancy site fraction in
the matrix under thermodynamic equilibrium, to a first approximation, can be conveniently expressed as

\[ c_{mob} = c_{tot} \frac{1}{1 + 12 c_s \exp\left(\frac{\Delta E_{SV}}{kT}\right)}, \]

with \( c_{tot} \) the total vacancy fraction, \( c_s \) the solute site fraction, \( k \) the Boltzmann constant and \( T \) the temperature. The vacancy trapping effect also influences the total vacancy site fraction when thermal equilibrium is reached. Apart from mobile vacancies which are in equilibrium, another fraction of vacancies are associated with solutes. Thus, the total amount can be expressed as

\[ c_{tot} = \exp\left(\frac{S_v}{k}\right) \exp\left(-\frac{H_{f,vac}}{kT}\right) \times \left(1 - 12 c_s + 12 c_s \exp\left(\frac{\Delta E_{SV}}{kT}\right)\right) \]

[94]. Binding energies between vacancies and solutes can be calculated via first principles calculations such as in Ref. [95, 96].
3. Experimental

3.1. Material

The commercial AA6014 alloy provided by Novelis Switzerland was used in this study. The material as-received was in form of cold-rolled sheets of 1 mm thickness. The composition of the alloy is listed in Table 3.1.

Samples were prepared into various geometries according to the characterisation method as summarised in Table 3.2. Sample preparation was generally done before any heat treatments, except for TEM foils, which were firstly heat treated and then polished.

**Table 3.1. Chemical composition of commercial AA6014 alloy**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.65</td>
<td>0.6</td>
<td>0.18</td>
<td>0.08</td>
<td>0.12</td>
<td>balance</td>
</tr>
</tbody>
</table>

**Table 3.2. Sample geometries for various characterisation methods**

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness measurement</td>
<td>10×10×1 mm³</td>
</tr>
<tr>
<td>Differential scanning calorimetry</td>
<td>Discs of 4.8 mm diameter and 1 mm thickness</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>Thin foils of 3 mm diameter</td>
</tr>
<tr>
<td>Electrical resistivity measurement</td>
<td>Coiled wires of 0.82 mm diameter and 300 – 600 mm length</td>
</tr>
<tr>
<td>Positron annihilation lifetime spectroscopy</td>
<td>Meander-shaped (Fig. 3.1) flat samples of 0.3 mm thickness</td>
</tr>
<tr>
<td></td>
<td>10×10×1 mm³</td>
</tr>
</tbody>
</table>
3.2. Heat treatment

3.2.1. Solution heat treatment

Solution heat treatment (SHT) was performed at 540 °C for 1 h for all samples. Two types of furnaces were used for conducting SHT. An air circulation furnace (Heraeus M104, temperature accuracy: ±2 °C) was used for samples for hardness measurements and DSC, while two vertical quenching furnaces (self-made, temperature accuracy: ±2 °C) operating under argon atmosphere were used for solutionising samples for electrical resistivity and positron lifetime measurements.

3.2.2. Quenching

Quenching after solutionising was performed in ice-water (IWQ) simply for all samples used in Chap. 4, 5, and 7. In Chap. 6, where the effect of quench rate was investigated, two other quenching conditions were also applied, namely in the air flow of a ventilator (VC) (Fig. 3.2), or in resting air (AC). Samples can be quenched completely to the ambient temperature via one of the above mentioned three routes (T1-type), or interrupted at an elevated target temperature during the process of VC or AC by applying a subsequent fast quench in ice-water (T2-type).
The samples treated by the T2-type quenching are labelled ‘VC_x’ or ‘AC_x’, where x stands for the target temperature in °C, which was controlled within ±15 °C for VC series and ±5 °C for AC series. Temperature evolution during cooling was measured by a thermocouple inserted into a hole drilled into the side of a dummy sample. Typical cooling curves are given in Fig 3.3. Average cooling rates from 533 °C to 250 °C are >980 K/s for IWQ, ~27 K/s for VC, and ~5 K/s for AC, respectively.

The VC condition produces a cooling close to industrial cooling conditions. During ventilator cooling, samples were placed in a meshed cage (Fig. 3.2) during SHT. To perform cooling the sample cage was mounted on the stand against the blowing air within ~1 s after being taken out of the air furnace. The height of the stand and the distance to the ventilator were fixed so that every time cooling was conducted the same position relative to the ventilator. Nine samples were quenched in every batch and there are three non-equivalent positions in the cage as illustrated in Fig. 3.2b. The average cooling rates (from 533 °C to 250 °C) measured at the three positions are 27.2 ± 1.3, 27.4 ± 1.7, and 27.8 ± 0.8 (all in K/s) for 1, 2 and 3 respectively, where the error margins are based on three different experiments. Thus, quenching in this device is well reproducible and the same applies to all 9 samples.
Fig. 3.2. (a) Cooling setup for ventilator cooling (VC) including the sample cage (in red box). (b) Schematic of the sample cage and the various non-equivalent sample positions: ‘1’ for centre (axis of ventilator), ‘2’ for edge, and ‘3’ for corner.

Fig. 3.3. Measured temperature evolution of samples exposed to T1-type cooling and two examples of T2-type. Cooling rates of the T1-type of quenching (in parentheses) are average rates between 533 °C and 250 °C.
3.2.3. Ageing

**Classification:**

Various ageing conditions were applied in this study. For a better understanding of the ageing condition, especially when complex treatments are encountered, several criteria were used in this study to classify the ageing treatments, as stated in the following:

- Depending on the extent of complexity, ageing can be classified into single-stage, two-stage, or multi-stage.
- Depending on whether the temperature is constant, ageing can be classified into isothermal or non-isothermal (linear heating in Chap. 7).
- Depending on the position in the ageing sequence, ageing can be classified into pre-ageing (PA) or secondary ageing (SA).
- Natural ageing (NA) refers to ageing at 20 °C, and artificial ageing (AA) is performed at 180 °C.

For instance, natural secondary ageing or NSA means NA after PA.

**Devices:**

Various devices were used for carrying out ageing treatments. The time interval between quenching and ageing was kept as short as possible (generally < 0.5 min). NA or NSA was conducted in a Peltier-cooled incubator (Memmert IPP55, temperature accuracy: ± 0.1°C) at 20 °C. PA was performed in an oil bath (Lauda ECO E4, temperature accuracy: ± 0.2°C) at various temperatures from 80 °C to 160 °C. AA was performed in an oil bath (Lauda C6 CP, temperature accuracy: ± 0.2°C) at 180 °C. Since various NA/NSA treatments and PA treatments were applied in this study, we use in the following text ‘NA_x’ or ‘NSA_x’ to abbreviate NA/NSA for x min and ‘PA y/z’ to abbreviate PA at y °C for z min. AA at 180 °C for 30 min was applied to simulate an industrial paint-bake (PB) process.

Linear heating (Chap. 7) was carried out on a self-made heating device (Fig. 3.4a). During heating, the sample was placed in the middle of two heating plates. The temperature was measured by a thermal couple in touch with the sample through a hole on the lower heating plate. More details about the device can be found in Ref. [97]. Fig. 3.4b demonstrates typical heating curves at heating rates of 3 K/min, 10 K/min, and 50 K/min. Only a very small
overshoot (<1 K) was sometimes found at the beginning and the end of heating. An excellent reproducibility of the heating curves was guaranteed by numerous tests.

Fig. 3.4. (a) Picture of the linear heating setup. (b) Measured heating curves at various heating rates.
3.3. Methods

3.3.1. Hardness test

Hardness is the most convenient method to characterise the precipitation hardening. Brinell hardness measurements were carried out on a Qness 60M hardness tester using 10 kg loading force, a 1 mm diameter tungsten carbide indenter and a holding time of 10 s. Eight indentations were performed on each sample, from which the average and standard deviation were calculated.

3.3.2. Differential scanning calorimetry (DSC)

DSC was used to indirectly study the clustering and precipitation during isothermal ageing or directly study linear heating by revealing the heat evolution. DSC measurements were performed in a heat-flux type Netzsch DSC 204 F1 Phoenix unit using a pure aluminium sample of similar mass as the reference sample. Heating was performed from 0 °C or -70 °C (Chap.7, 50 K/min) to 400 °C or to 450 °C at a constant heating rate accordingly, after which the samples were firstly held at 400 °C for 20 min or at 450 °C for 1 min and then cooled down to the initial starting temperature at -10 K/min. The signal obtained during the same reheating without changing the samples in the DSC chamber was used as the baseline and was subtracted from the signal during the first ramp. This method has been used also by others [22, 98-100]. This ‘double-ramping’ procedure outperforms the conventional correction method, in which two empty crucibles are used in an independent DSC run to obtain the baseline, as exemplified in Fig. 3.5 by measuring the DSC traces of an pre-aged sample (PA 120/60) using various baseline correction methods. It is seen that two ‘double-ramping’ experiments provide similar results, with much smaller baseline drift and offset than the conventional method, especially in the temperature range from 20 °C to ~320 °C.

3.3.3. Transmission electron microscopy (TEM)

TEM was used to directly characterise the microstructure in the material, especially the precipitates and intermetallic particles. TEM characterisation was carried out on a Philips CM30 unit operated at 300 kV and equipped with an energy dispersive X-ray (EDX) spectrometer. The electron beam was aligned along a 〈100〉 direction of the Al matrix. TEM
foils were prepared by mechanical thinning and then twin-jet electro-polished in an electrolyte mixture of 75% methanol and 25% nitric acid after corresponding heat treatments.

Fig. 3.5. DSC traces of a sample pre-aged at 120 °C for 1 h measured by various baseline correction methods: (a) individual signals during measurement and baseline runs; (b) final traces with baseline subtracted.
3.3.4. Electrical resistivity measurement

Clustering and precipitation cause also changes in electrical resistivity of the alloy. Electrical resistivity was measured using a four point probe. A constant current of 100 mA was provided by a power supply and the voltage measured by a Keithley multimeter. Polarity changes were applied to eliminate spurious thermoelectric effects. Resistivity can be calculated using Eq. (3.1), with $U$ the measured voltage, $A$ the cross section area, $I$ the current, and $L$ the effective length.

$$\rho = \frac{U \times A}{I \times L}$$  \hspace{1cm} (3.1)

For isothermal ageing treatments, coiled wires (Table 3.2) were used and resistivity measurements were performed in an oil bath (Lauda ECO RE 2025) at 20 °C or in liquid nitrogen at -196 °C. For the linear heating experiments in Chap. 7, the resistivity of the meander-shaped samples (Fig. 3.1) was measured in situ during the heating from room temperature (20 °C – 23 °C) to 400 °C while recording the temperature. To eliminate the phonon (temperature-dependent) contribution to the resistivity during heating and evaluate only the microstructural contribution, a ‘baseline correction’ has to be performed on the measured resistivity signal. Similar to the DSC baseline correction (Sec. 3.3.2), we measured the signal of the samples during a second heating run after being cooled down to room temperature, as exampled in Fig. 3.6. An excellent linearity is seen for the resistivity increase up to ~310 °C, i.e., electrical resistivity of the alloy follows Matthiessen’s rule. Above 310 °C, resistivity deviates from a linear increase, which can be ascribed to an increased concentration of thermal vacancies and dissolved solutes. Nevertheless, a linear resistivity increase for a phonon contribution up to ~310 °C is an excellent approximation and Eq. (3.2) was therefore adopted to correct the resistivity change during the first ramp. In this way, we evaluate the relative resistivity change only due to microstructural changes compared with the initial state before heating.

$$\rho_T = \rho_0 + \rho'(T - T_0)$$  \hspace{1cm} (3.2)

where $\rho'$ can be obtained by fitting the resistivity curve in the temperature range from 20 °C to 300 °C during the second ramp, and $T_0$, $\rho_0$ are the initial temperature and corresponding resistivity during the first ramp, respectively.
3.3.5. Positron annihilation lifetime spectroscopy (PALS)

Positrons are very sensitive to the local electron density in the material. Therefore, PALS can be used to monitor microstructural change, especially for the open volume defects, such as vacancies. Positron lifetimes were measured at room temperature using a ‘fast-fast’ coincidence method. Positrons were generated by a $^{22}\text{Na}$ source of an activity of 30 $\mu$Ci. During the measurements, two samples after identical heat treatments and the positron source were packed in a sandwich geometry. Software LT9 was used to analyse the obtained positron lifetime spectra. A positron lifetime of $\sim$160 ps in pure Al samples was used to determine the source corrections. The resolution of the spectrometer (FWHM) was $\sim$200 ps. More details about the instruments and experimental setups can be found in Ref. [101].
4. Effect of pre-ageing on natural secondary ageing and paint bake hardening

Motivation:
- To understand how PA time and temperature influences subsequent ageing kinetics.

4.1. Experimental results

4.1.1. Hardness measurements

4.1.1.1. NA and NA + PB

Fig. 4.1. Hardness of the alloy during NA after solutionising and quenching and after subsequent PB.

Hardness during NA and after subsequent PB is given in Fig. 4.1. The hardness increase during NA is pronounced within the first week and then marginal. PB enhances the hardness of the as-quenched sample (shortest NA time) significantly, with an increment of ~53 HBW. NA before PB is deleterious to the PB response (‘negative effect of NA’). After only 480 min of NA, the PB hardness decreases to ~70 HBW, and after 1 week of NA, there is no hardness benefit and even a slight reversion by subsequent PB.
4.1.1.2. PA and PA + PB

Fig. 4.2. (a) Hardening at different temperatures after direct quenching. Circle denotes simulated PB (=30 min at 180 °C). (b) Hardness after further PB of samples already pre-aged up to a certain hardness. Example: The red arrow in (a) shows the increase of hardness from the PA state (at 120 °C for 120 min, hardness ~65 HBW) to the state after PB (hardness ~102 HBW as indicated by a cross in both (a) and (b)). White areas in (b) are undefined due to missing data.

Isothermal hardening curves of the alloy aged at various PA temperatures and at the AA temperature are presented in Fig. 4.2a. Generally, hardness increases minutes after quenching, then enters a stage of almost linear increase on a logarithmic time scale, after which the
hardening levels off before reaching peak age. For ageing temperatures between 120 °C and 160 °C, similar peak age values are reached, with the fastest kinetics at 160 °C, whereas samples remain underaged at 80 °C and 100 °C.

Additional PB is applied on samples pre-aged up to ~82 HBW at different temperatures. The resulting end hardness is presented in Fig. 4.2b. Since the PA time at the lowest PA temperature is 2 orders of magnitude higher than at the highest PA temperature and because we wish to compare samples of equal PA hardness in this paper, PA hardness instead of PA time is used as a coordinate. Areas of same colour represent iso-hardness levels. Hardness after PB ranges from ~95 HBW to ~106 HBW depending on the PA treatment. For PA temperatures \( \leq 100 \) °C, PB hardness depends primarily on PA temperature and not so much on PA hardness (and therefore PA time). Furthermore, PB hardness of samples pre-aged at 80 °C is lower compared to hardness after direct PB (~98 HBW), thus revealing a slight “negative effect” of PA.

4.1.1.3. PA + NSA

During NSA after PA, the hardness of the sample first remains approximately constant for some time before it starts to increase. This time depends on PA treatment. Three examples of comparisons are presented in Fig. 4.3. Other data can be found in Appendix A1, Fig. SA1 – SA3. Fig. 4.3a compares NSA hardness after PA at 100 °C for various times. The initial hardness after PA for longer times is higher as already shown in Fig. 4.2a. The stable period during NSA is longer for longer PA and finally, for 960 min PA, the hardness changes only marginally during the NSA studied.

If PA temperature is varied while keeping the PA time constant (Fig. 4.3b), the initial hardness after PA is higher when PA is performed at higher temperature and the hardness increase during NSA starts later.

Fig. 4.3c presents the NSA hardness evolution after PA for three different temperature/time combinations that lead to a similar hardness of ~60 HBW. A clear PA temperature dependence is seen: For the highest PA temperature, hardness during NSA starts to increase earlier, and the hardness increment is higher in the same NSA time. Results of other iso-hardness levels show similar features (Appendix I), except for 50 HBW, where the difference between NSA hardness curves after PA at different temperatures is small.
A better overview of the effect of PA temperature on NSA is provided by the contour plot (Fig. 4.3d), where PA hardness is used as a coordinate. Without any NSA, the contour lines of the iso-hardness areas would be vertical lines with colours corresponding to the values on the PA hardness axis (as shown in Fig. SA2a in Appendix A1). The evolution of these stripes during 12 weeks of NSA then reflects the influence of PA conditions on subsequent NSA. Similar plots for other NSA times are shown in Fig. SA2. For instance, almost no PA temperature dependence of the colour can be seen for PA hardness ≤ 55 HBW and similarly also for PA hardness ≥ 77 HBW. The former is a result of almost saturated NSA after 12 weeks since the hardness indicated by the colour is far higher than its original value before NSA, whereas the latter is due to the not yet started (or very weak) NSA since the hardness is almost not changed during 12 weeks NSA. In the intermediate PA hardness regime, contour lines or colour stripes are curved towards lower temperature, indicating that the state after PA at lower temperature is more stable during NSA.
Effect of pre-ageing on natural secondary ageing and paint bake hardening

4. Effect of pre-ageing on natural secondary ageing and paint bake hardening

Fig. 4.3. Hardening during NSA after PA for (a) various times at the same temperature 100 °C, (c) the same time (10 min) at 100 °C and 160 °C, (c) different temperature/time combinations leading to a similar hardness level (~60 HBW), (d) various temperature/time combinations with fixed NSA time for $1.2 \times 10^5$ min (12 weeks). (e, f, g, h) analogous to (a, b, c, d) but after additional PB. White areas in (d) and (h) are undefined.

4.1.1.4. PA + NSA + PB

Samples after PA and NSA as presented in Figs. 4.3a – d are subsequently paint-baked, which leads to the hardneses given in Fig. 4.3e – h. Hardnesses after PB remain at a constant high value up to a certain NSA time before they start to decrease, i.e. the negative effect of natural ageing sets in. This period of uncompromised PB potential is longer for increased PA time at a given temperature (Fig. 4.3e), increased PA temperature when the PA time is the same (Fig. 4.3f), and decreased PA temperature when PA hardness is almost the same (Fig. 4.3g). With prolonged NSA time, the hardness after PB decreases but eventually reaches a stable value that is higher for an increased PA hardness (Figs. 4.3e,f), or similar for almost the same PA hardness (Fig. 4.3g).
In analogy to Fig. 4.3d, PB hardness can be displayed as a function of PA hardness and PA temperature with a given fixed NSA applied before PB. After 12 weeks of NSA and PB (Fig. 4.3h), the hardness in the high-PA hardness regime is still similar to the hardness after PB without prior NSA (Fig. 4.2b). Data for other NSA times are shown in Fig. SA3 in Appendix A1. In the lower-PA hardness regime, however, hardness is markedly reduced if 12 weeks of NSA take place before PB, and the dependence on PA temperature previously shown in Fig. 4.2b in this regime is eliminated. This also means that if samples are insufficiently pre-aged so that NSA compromises subsequent PB, then the negative effect is stronger for high PA temperatures.

4.1.2. Electrical resistivity

After quenching from SHT, the electrical resistivity at 20 °C is 3911 ± 21 nΩ cm. NA gives rise to a resistivity increase which is already observable within 10 min and exceeds 160 nΩ cm after 1 week (Fig. 4.4a). In comparison, the resistivity increase caused by PA at 100 °C (but measured at 20 °C) is much less (< 22 nΩ cm). During NSA after PA (Figs. 4.4b – 4.4d), resistivity starts to increase later compared with NA and the increment of resistivity within a given time is much smaller, in analogy to the behaviour of hardness (Figs. 4.3a – 4.3c & Fig. 4.1). The suppression of the resistivity increase is stronger if PA is performed longer at a given temperature (Fig. 4.4b), or at a higher temperature for the same time (Fig. 4.4c), or at a lower temperature to the same PA hardness (Fig. 4.4d) in analogy to hardness.
4. Effect of pre-ageing on natural secondary ageing and paint bake hardening

![Resistivity change of the alloy during (a) NA (lower axis) and PA at 100 °C (upper axis), (b) NSA after PA at 100 °C for different times, (c) NSA after PA for 10 min at 100 °C and 160 °C, (d) NSA after PA to a similar hardness (~60 HBW).](image)

4.1.3. DSC

For the as-quenched (AQ) sample, three main exothermic peaks are observed in the DSC trace, at ~80 °C (peak $a$), ~250 °C (peak $b$), and ~300 °C (peak $c$). After PA at 100 °C (Fig. 4.5a), peak $a$ is not seen in the DSC trace any more, while peak $b$ is shifted to lower temperature and now exhibits a double-peak structure. Peak $c$ grows and also moves slightly to lower temperature after PA (and also becomes unsymmetrical). Longer PA lowers the amplitude of $b$ but $c$ remains at the same height. DSC curves after PA for 10 min at 100 °C and 160 °C, Fig. 4.5b, show a similar shape, but the curve of PA 100/10 is slightly higher, especially for peak $b$. Fig. 4.5c gives DSC curves of samples PA to an iso-hardness of ~60 HBW and shows pronounced differences. The main difference lies in the shape of the double-peak structure of $b$. With PA temperature decreasing from 160 °C to 80 °C, subpeak $b_1$ shrinks but $b_2$ grows. Another feature is found at ~265 °C where a new peak $d$ is seen to emerge for a low PA temperature. This peak is significant for PA 80/480 but can also be weakly observed in Fig. 4.5a when PA is performed at 100 °C. It is hard to be discerned for PA at or above 120 °C.
After further NSA following PA, peak $a$ is observed to re-appear (Fig. 4.5d). Peak $b$ is delayed to higher temperature and a new dissolution trough $e$ is gradually formed at its original place. This trough is similar to the one observed after direct NA but less pronounced. Data analogous to Fig. 4.5d but for different PA conditions can be found in the Appendix A2 (Fig. SA4).

4.1.4. PALS

One-component positron lifetimes of an AQ sample and PA samples during NA/NSA are given in Fig. 4.6. For the AQ specimen, the initial positron lifetime $\tau_{1C}$ measured after 7 min of NA starts from ~233 ps and drops markedly to a minimum of ~222 ps within the first 120 min of NA. In the following, the lifetime rises up to a maximum ~225 ps and finally decreases to ~221 ps after 1 week of NA. After PA, $\tau_{1C}$ starts from much lower values, namely ~219, ~217,
4. Effect of pre-ageing on natural secondary ageing and paint bake hardening

and ~215 ps for PA 80/480, PA 120/60, and PA 160/10, respectively. During NSA, $\tau_{1C}$ for PA 80/480 barely increases for up to 7000 min of NA, while for PA 160/10 and PA 120/60 a slight increase of $\tau_{1C}$ to ~220 ns can be observed. The onset of the lifetime increase is estimated by the extrapolation of the constant stage and increasing stage. It appears to start slightly earlier for PA 160/10 than for PA 120/60.

Fig. 4.6. Single-component positron lifetimes in an AQ sample during NA or in PA samples (similar hardness ~60 HBW) during NSA. Dashed lines are guidelines.

4.2. Discussion

The material properties during NSA and/or after PB are closely related to PA temperature and time. Next, we will discuss 1) what happens during PA under various conditions and how this is related to PB response, 2) what happens during NSA and how it is influenced by various PA conditions, and, 3) the trade-off between PB response and NSA stability.

4.2.1. PA clustering and influence on PB

Previous studies have demonstrated that clusters formed at ‘room temperature’ deteriorate PB response while PA clusters do not [8, 102]. Compared with PB hardness after NA, which drops below 73 HBW for NA longer than 4 h (Fig. 4.1), the PB hardness after PA is truly enhanced, with values >95 HBW (Fig. 4.2b). A ‘negative effect’ on PB is only found when PA is
conducted below 100 °C (Fig. 4.2b), i.e., PB hardness is < 98 HBW. With increasing PA temperature, PB hardness after PA gradually increases and a ‘positive effect’ is created. This implies that differences exist between clusters formed at various PA treatments even though PA hardness is the same. Such difference can be seen also from DSC results (Fig. 4.5c). The exothermic peaks a, b, and c in the DSC traces are associated to the formation of Mg-Si clusters, \( \beta'' \), and \( \beta' \) phases, respectively [15, 39]. Sub-peaks b1 and b2 are thought to be linked to \( \beta'' \) precipitates grown from PA clusters and by independent formation in the matrix [12]. If the \( \beta'' \) phase during DSC is easier to form due to pre-existing PA clusters or by skipping low-temperature clustering stages during scanning [100], the peak shifts to lower temperature (or b1) [12, 100]. In our case, PA at 160 °C results in a strong signal of b1 and almost not observable signal of b2, indicating that the barrier for forming \( \beta'' \) phase is low. As PA temperature falls, this effect becomes less pronounced as b1 diminishes and b2 grows (or b shifts to higher temperature). All these results indicate that, 1) PB is not always a simple continuation of the PA process; 2) The clusters formed at different PA temperatures differ from each other.

Since PA at 80 °C does result in a slight ‘negative effect’ (PB hardness lower than after direct PB, Fig. 4.2b), we first discuss the effects of low PA temperature considering the same aspects as for the interpretation of the ‘negative effect’ of NA only (Fig. 4.1), namely, (i) cluster size [9, 69, 75], (ii) Mg/Si ratio in clusters [52, 53, 55, 56, 60], and (iii) mobile vacancy site fraction [72]. (i): Since resistivity is mainly determined by cluster number density as verified by APT [59], the fact that resistivity during PA at 100 °C (and also at 80 °C [65]) shows little change after a slight initial increase (Fig. 4.4a) indicates that after initial cluster formation primarily cluster size increases. APT applied to a comparable alloy recently confirmed this in finding that mainly size instead of number density grows after more than 2 h of PA at 80 °C [53]. However, such size increase (PA at 80 °C and 100 °C) does not result in an enhanced PB hardness (Fig. 4.2b), implying that cluster size is not the primary reason for the differences in PB response at different PA temperatures. (ii): The chemical composition of clusters and strengthening precipitates expressed by the Mg/Si ratio does possibly play an important role since higher temperatures favour formation of clusters with higher Mg/Si ratios [53] and perhaps also more order, which make them more similar to \( \beta'' \)-type strengthening precipitates and thus easier to transform to precipitates during PB. In addition, longer PA up to 1 week at 80 °C barely changes the Mg/Si ratio of clusters [54], which also explains why PB hardness response after longer PA is not increased (Fig. 4.2b). (iii): Pogatscher et al. [72] argued that the
imprisonment of quenched-in excess vacancies by NA clusters leads to a delay of the AA hardening kinetics after NA compared to direct AA at temperatures < 210 °C. As most of the excess quenched-in vacancies should have been annihilated or trapped during PA, we assume that the mobile vacancies present after PA are all thermal equilibrium vacancies. Upon heating to the PB temperature (180 °C), a new higher equilibrium vacancy site fraction is established. The time for this equilibration is estimated to be of the order of 1 min or less [71, 103] and therefore the PA temperature plays no role.

Thus, it is most likely that the Mg/Si ratio of the clusters created at higher PA temperature are more similar to strengthening precipitates formed during PB, which leads to an easier transformation, and hence also a higher PB hardness.

4.2.2. NSA clustering and dependence on PA

4.2.2.1. NSA clustering characteristics

During NSA, hardness and electrical resistivity increase, and PB hardness response decreases in a similar way as during NA, just slower. The microscopic state after PA is different from that in the as-quenched state as PA clusters exist and fewer excess vacancies are present due to annihilation during PA. Solute atoms have two possible destinations during diffusion, namely formation of new NA clusters or attachment to pre-existing PA clusters. As presented in the electrical resistivity data (Fig. 4.4a) and in accordance with the literature [59, 65, 102, 104], NA gives rise to a much larger resistivity increase than PA due to a higher density of clusters formed at lower temperatures. Therefore, the resistivity increase during NSA, e.g. after PA 100/10 (Fig. 4.4b), which surpasses the resistivity evolution during PA (Fig. 4.4a), must be associated with an increased number of clusters that are newly formed during NSA. Further evidence for the formation of new NA clusters come from DSC data (Fig. 4.5d) and PALS (Fig. 4.6): The DSC trace after long NSA shows a pronounced dissolution trough e, which is analogous to the curve after pure NA (Fig. 4.5d) pointing at the formation of new NA clusters, which cannot transform to precipitates and thus dissolve during DSC scanning. $\tau_{1c}$ in the PALS signal after PA drops to 215 – 220 ps, which is the typical lifetime of positrons in clusters. The lower value for PA at higher temperature might result from ordering effects or a small bulk contribution due to a lower cluster density. During NSA $\tau_{1c}$ is stable for some time and then increases in analogy to NSA after cluster reversion (RA) [71]. Such an increase of lifetime is either caused by the increase of a component with higher lifetime or by reduction of a low-
lifetime component [63, 64, 101]. The rise of a vacancy-related component is unlikely as well as a Mg enrichment of clusters because after PA at 80 °C the matrix should contain more Mg (and the clusters less) than after PA at 160 °C and therefore additional clustering is thought to increase the one-component (average) positron lifetime because the contribution of bulk annihilation (typical contribution \( \leq 160 \text{ ps} \)) is reduced.

Next we discuss whether solute atoms attach to pre-existing PA clusters. Aruga et al. [61] reported this after NSA for ~1.25 years. To discuss whether this happens also during short NSA, we estimate the amount of solute able to diffuse to PA clusters during NSA. For simplicity, we assume that solutes around the PA clusters are homogeneously distributed after PA and PA clusters are spheres with an average radius \( r_{PA} \) and number density \( N_{PA} \). Previously published atom probe data on PA cluster sizes and number densities are summarised in Table 2.1. Numbers are found varying with different treatments, alloy types, APT instruments, and APT filtration parameters. We choose \( r_{PA} = 1 \text{ nm} \) and \( N_{PA} = 2 \times 10^{24} \text{ m}^{-3} \) which are in the intermediate range of values provided. The average diffusion distance of solutes in a given time \( t \) can be calculated by

\[
d_{i,t} = \sqrt{6D_iT_t}, \quad (i = \text{Mg, Si})
\]

with \( D_i = D_{i,0} \exp\left(-\frac{Q_i}{kT}\right) \) without taking excess vacancies after PA into account (see remark below). Activation energies \( Q_i \) and pre-factors \( D_{i,0} \) for diffusion are taken from Ref. [105]. After NSA for time \( t \), \( i \)-type solutes from within a sphere of radius \( (r_{PA} + d_{i,t}) \) are able to move to PA clusters. The relative fraction of those solutes can be calculated as

\[
\gamma_{i,t} = \frac{N_{PA}(V_{i,t}-V_{PA})}{(1-N_{PA}V_{PA})} \gamma_{i,0} \approx N_{PA} \left(V_{i,t} - V_{PA}\right) \gamma_{i,0}, \quad \text{with } \gamma_{i,0}
\]

the relative \( i \)-type solute fraction within the matrix directly after PA, \( V_{i,t} = \frac{4}{3} \pi (r_{PA} + d_{i,t})^3 \), and \( V_{PA} = \frac{4}{3} \pi r_{PA}^3 \). Table 4.1 shows calculated quantities after NSA for various times for a typical PA treatment and characterised by \( \gamma_{i,0} = 0.85 \) (estimated from the fractions of solute atoms bound in clusters as listed in Table 2.1 and averaged to 0.15). The relative fraction of solutes attaching to PA clusters after 1 week of NSA is 1.5 % for Si and 0.18 % for Mg, which should be put into relationship to the total possible solute clustering during long term NA (<14 % of all solutes after 14000 h of NA [106]). Note that the quantities in Table 4.1 at the beginning of NSA might be underestimated due to the presence of excess vacancies after PA that would speed up diffusion.

Solute attachment to PA clusters can be indirectly evidenced from the hardness-resistivity relationship during NSA given in Fig. 4.7. Similar curves have been obtained by Madanat et
al. [71] during NSA after reversion ageing. It is argued [71, 107] that cluster growth contributes mainly to hardness increase, while number density increase has a larger impact on resistivity. The curve during NA shows the highest resistivity increase relative to hardness, indicating formation of a high number density of NA clusters. After PA, for the same hardness increase during NSA, the resistivity increment is generally lower, presumably due to attachment of some solutes to PA clusters which contributes to hardness but less to resistivity. PA at lower temperature creates a higher number density of PA clusters, thus facilitating solute attachment, which also fits to increase of the slope of the curves in Fig. 4.7 as PA temperature drops.

Table 4.1. Amount of solutes that grow on PA clusters during NSA (calculated).

<table>
<thead>
<tr>
<th>NSA time t (min)</th>
<th>(d_{\text{Sil}} \times 10^{-10} \text{ m})</th>
<th>(d_{\text{Mgt}} \times 10^{-10} \text{ m})</th>
<th>(\gamma_{\text{Sil}})</th>
<th>(\gamma_{\text{Mgt}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.44×10^3</td>
<td>1.8</td>
<td>0.3</td>
<td>0.45%</td>
<td>0.065%</td>
</tr>
<tr>
<td>1×10^4</td>
<td>4.7</td>
<td>0.8</td>
<td>1.5%</td>
<td>0.18%</td>
</tr>
<tr>
<td>1.2×10^5</td>
<td>16.2</td>
<td>2.7</td>
<td>12%</td>
<td>0.75%</td>
</tr>
</tbody>
</table>

\(\gamma_{\text{Sil}} = \gamma_{\text{Mgt}}\) is assumed.

\(D_{\text{Sil}}_{293K} = 6.05 \times 10^{-26} \text{m}^2 \text{s}^{-1}\) [105]

\(D_{\text{Mgt}}_{293K} = 1.70 \times 10^{-27} \text{m}^2 \text{s}^{-1}\) [105]

**Fig. 4.7.** Hardness change as a function of resistivity change during NA and NSA for the AQ and various pre-aged samples, respectively.
Thus, based on the experimental results we conclude that both modes of clustering, i.e. formation of new NA clusters and solute attachment to PA clusters, take place and compete with each other during NSA. How important each mechanism is depends on the PA conditions.

4.2.2.2. Dependence on PA time and temperature

NSA clustering after PA is retarded compared to NA, as demonstrated by various characterisation methods. This is primarily due to the reduction of solute supersaturation and the loss of excess vacancies during PA. If $\alpha(t)$ stands for the relative transformed NSA cluster volume, in the simplest case the transformation rate $\dot{\alpha} = \frac{d\alpha}{dt}$ is proportional to a function of the supersaturation (or transformed fraction) of the solutes $\phi(u - \alpha)$ with $u$ the initial supersaturation before NSA, and a function only dependent on NSA temperature $K(T)$ [14], with $\phi$ being a monotonically increasing function and $K(T)$ following an Arrhenius relationship. Furthermore, the transformation rate should also be proportional to the fraction of vacancies that mediate solute diffusion [108]. It is implicitly contained in $K(T)$ if vacancies are in thermal equilibrium, but in our case excess vacancies exist, the fraction $c_{\text{vac}}(t)$ of which monotonically decreases to $c_{\text{vac}}^{\text{eq}}(T)$ throughout NSA from a starting value given by PA temperature. Therefore,

$$\dot{\alpha} = \frac{d\alpha}{dt} = \phi(u - \alpha) \frac{K(T)}{c_{\text{eq}}^{\text{vac}}(T)} c_{\text{vac}}(t)$$

(4.1)

**Fig. 4.8.** Hardness as a function of integrated DSC heat flow from 50 °C to 315 °C using hardness data presented in Fig. 4.3a,c and DSC data in Fig. 4.4d and Fig. S3 (when both hardness and DSC are measured for the same NSA time). DSC integration is documented in Appendix A2.
As the transformed solute fraction $\alpha$ is not directly measured, one needs an extra model to correlate $\alpha$ and the experimentally obtained properties, i.e. hardness, resistivity, or PALS. We opt for hardness here because the hardness increase $\Delta H$ and relative volume of NA clusters $\alpha$ are roughly linearly related in the range of interest as proposed by [76, 109, 110] and found by our DSC measurements (Fig. 4.8 and later in Chap. 7, Fig. 7.10). Thus, if $\alpha = a\Delta H$, both quantities are interchangeable (Appendix A3 shows how electrical resistivity is used to characterise ageing kinetics).

It is common practice to extract kinetic parameters for precipitation by assuming the validity of a given model in Eq. (4.1), mostly the JMAK model, and to fit resistivity [111, 112] or hardness (linearly [113] or squared [72] accordingly). Our attempts to do this did not lead to consistent and physical values for the parameters involved such as the Avrami index (Appendix A5). We therefore chose the approach documented in Fig. 4.9 where the hardness increment during NSA is collapsed onto the hardening curve of NA (AQ) by normalising NSA time for all except for very late ageing stages [71]. We use a retardation factor $\Theta$ to express that $\Delta H_{AQ}(t) = \Delta H_i(\Theta t)$, where $i$ labels all the PA states, and $t$ should be generally within the fast hardening stage (regime 2 in Fig. 4.9(b)). Replacing $\Delta H$ by $\alpha$ and differentiating we obtain $\Theta = \frac{\dot{\alpha}_{AQ}(t)}{\dot{\alpha}(\Theta t)}$. Fig. 4.10 represents the retardation factors for all PA conditions we have measured and shows:

- $\Theta$ increases monotonically with PA hardness (i.e. NSA is slower) because PA decreases solute supersaturation $u$ and therefore also $\varphi(u - \alpha)$ in Eq. (4.1). PA also reduces $c_{\text{vac}}(t)$ before equilibrium vacancy site fraction is reached.
- No clear PA temperature dependence is seen for a PA hardness <55 HBW but for higher PA hardnesses the curves for the different $T$ are offset.
- At the same PA hardness level, a lower PA temperature retards NSA more than a higher one, see vertical dashed arrow. The ratio of the retardation factors at the lowest and the highest temperature is $R_\Theta = \left. \frac{\Theta_{80^\circ C}}{\Theta_{160^\circ C}} \right|_{>55\text{ HBW}} = (2.3 \text{ to } 3.6) \approx 3$. 

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Multi-stage ageing in an Al-Mg-Si alloy

Fig. 4.9. (a) Hardening increment during NA (AQ) and NSA after PA at 100 °C for various times as calculated from data of Fig. 4.3a. (b) Superposition of the curves in (a) by normalising the time scale by factor $\Theta^{-1}$ relative to the AQ case.

Fig. 4.10. Hardness retardation factor $\Theta$ as a function of PA hardness. Curves in different colours represent different PA temperatures. PA time is an implicit parameter as indicated by one of the arrows.

The latter observation requires further discussion. Ageing to the same PA hardness should consume a similar amount of solutes and therefore in Eq. (4.1) the only difference should be the fraction of excess vacancies after quenching from the PA temperature. Using

$$c_{\text{vac}}^{\text{eq}} = \exp\left(\frac{\Delta u}{k}\right)\exp\left(-\frac{H_f \text{vac}}{kT}\right),$$  

(4.2)
with the formation enthalpy of a vacancy $H_{f,vac} = 0.67 \text{ eV}$, the vibrational entropy $S_v = 1.1k$, and $k$ the Boltzmann constant [33, 114], we calculate $c_{vac}^{eq}$ for 160 °C and 80 °C and obtain using Eq. (4.1) a ratio of concentrations and rates:

$$\mathcal{R}_c = \frac{c_{vac,160\,^\circ\text{C}}^{eq}}{c_{vac,80\,^\circ\text{C}}^{eq}} = \left. \frac{\dot{u}_{160\,^\circ\text{C}}}{\dot{u}_{80\,^\circ\text{C}}} \right|_{t=0} = 58. \tag{4.3}$$

$\mathcal{R}_\Theta$ and $\mathcal{R}_c$ should be similar, but are not because the measured kinetics of NSA after PA at 80 °C and 160 °C are more similar than expected from the vacancy site fractions in Eq. (4.3). During NSA after PA, vacancies go to sinks and the mobile vacancy site fraction decreases to a ‘room temperature’ equilibrium value. The ratio given in Eq. (4.3) refers to the state before NSA commences and gradually goes to 1, whereas $\mathcal{R}_\Theta$ is derived from quantities measured after some NSA. However, we show that this does not explain the discrepancy between $\mathcal{R}_\Theta$ and $\mathcal{R}_c$ (Appendix A6). Therefore, either (i) the vacancy argument in Eq. (4.3), and/or (ii) the assumption that NSA after PA at different temperatures is given by a simple expression such as in Eq. (4.1) must be incorrect.

(i) Eq. (4.3) is valid if all the vacancies after PA at a given temperature are thermal vacancies and are available for assisting solute diffusion during NSA. However, the picture is modified by the association between solute clusters and vacancies that exists already at the PA temperature. Firstly, apart from thermal vacancies at equilibrium, there will be extra vacancies associated with solutes (or clusters) if the interaction between them is attractive [94, 115]. Secondly, upon rapid cooling from the PA to ‘room’ temperature, the association between the vacancies and solutes/clusters lowers the number of free excess vacancies. This was observed for alloy containing traces of Sn atoms that form closely bound solute vacancy complexes [83]. If clusters take the role of Sn atoms we replace the binding energy $E$ between a vacancy and a Sn atom by that with an average cluster, and the total site fraction of trapping sites $x_{ts}$ around a Sn atom by that around an average cluster. The vacancy site fractions of mobile $c_{mob,T}$ and all $c_{tot,T}$ vacancies then define:

$$\eta(T) = \frac{c_{mob,T}}{c_{tot,T}} = \frac{1}{1 + x_{ts} \exp \left( \frac{E}{kT} \right)} \tag{4.4}$$

As an example, Fig. 4.11 shows $\eta$ as a function of temperature using reasonable values for $E$ and $x_{ts}$. The mobile vacancy site fraction in thermal equilibrium at the PA temperature can be calculated by Eq. (4.2), and thus the total vacancy site fraction is $c_{tot,PA} = \frac{c_{mob,PA}}{\eta(\text{PA})}$. 

41
This total vacancy site fraction is preserved after cooling to the NSA temperature and equals
\[ c_{\text{tot}, T_{\text{NSA}}} = \frac{c_{\text{mob}, T_{\text{NSA}}}}{\eta(T_{\text{NSA}})} \]
now, but the new mobile vacancy site fraction is diminished due to the repartitioning of the vacancies and a small \( \eta \) value:
\[ c_{\text{mob}, T_{\text{NSA}}} = c_{\text{vac}, T_{\text{PA}}}^{\text{eq}} \times \frac{1 + x_{ts} \exp \left( \frac{E}{kT_{\text{PA}}} \right)}{1 + x_{ts} \exp \left( \frac{E}{kT_{\text{NSA}}} \right)}. \] (4.5)

The second term on the right hand side of the equation is larger if PA temperature is lower.
In the scenario given by Fig. 4.11, the ratio \( R_c \) in Eq. (4.3) would be reduced by a factor of 9, i.e. no longer be 58 but around 6.
Using this model (Eq. (4.5)), one can find that the mobile vacancy \( c_{\text{mob}, T_{\text{NSA}}} \) decreases with a higher \( E \). This might contribute to another explanation of a stronger delay of NSA kinetics caused by longer PA (increase of \( \Theta \) in Fig. 4.10 for the same PA temperature), assuming that larger clusters after longer PA give a higher trapping energy \( E \) to vacancies.

**Fig. 4.11.** Fraction of mobile vacancies \( \eta \) as a function of temperature calculated using Eq. (4.4) and an interaction energy of \( E = 0.4 \text{ eV} \) and trapping site fraction \( x_{ts} = 10^{-4} \). The former is estimated to be comparable to Sn-Vacancy binding, while the latter derives from a typical cluster site fraction. These numbers have been chosen to illustrate the trapping effect qualitatively and do not originate from precise calculations.
(ii) Although PA at 80 °C and 160 °C in Fig. 4.3c was designed to reach the same hardness increment, the final state after PA might differ. APT measurements have shown an about 4.5 times higher number density of smaller PA clusters after ageing at 60 °C compared to 150 °C. A similar ratio can be suspected for 80 °C and 160 °C. The rate $\dot{\alpha}$ at which diffusing solute atoms attach to pre-existing clusters and let these grow is given by the rate $\Gamma$ at which they carry out jumps to neighbouring lattice positions multiplied by the site fraction $x_{cl}$ of such clusters. As $\Gamma$ is proportional to the vacancy site fraction $c_{vac}$ we obtain $\dot{\alpha} \propto x_{cl}c_{vac}$. Thus, the fraction in Eq. (4.3) is modified to
\[
\frac{x_{cl,160°C}c_{vac,160°C}}{x_{cl,80°C}c_{vac,80°C}} = \frac{1}{4.5} \times 58,
\]
i.e. NSA for the higher PA temperature is now just about 13 instead of 58 times faster for the hardness increment induced by the growth of PA clusters. Additional nucleation of new clusters between the PA clusters during NSA, however, could modify the picture in that instead of the factor 4.5 a lower factor would be valid.

The two corrections derived in (i) and (ii) together can explain why NSA kinetics after PA at 80 °C and 160 °C are just a factor of three apart, i.e. why $R_\Theta \approx 3$ instead of 58 since $R_c$ in Eq. (4.3) is modified to
\[
\frac{1}{9 \times 4.5 \text{ (or smaller)}} \times 58.
\]

4.2.3. Trade-off between NSA stability and PB response – optimisation strategy

The PB hardness response of the alloy after PA depends largely on the PA temperature, i.e. higher PA temperature favours a higher PB hardness (Fig. 4.2b). On the other hand, stability (resistance against secondary clustering) during NSA depends on both PA temperature and time (PA hardness); lower temperature or longer PA time improves NSA stability (Fig. 4.3a – 4.3c). Theoretically, both desirable properties could be combined by performing PA at higher temperature for as long as one needs to reach the required NSA stability. However, in industrial practice, usually PA strength (hardness) has to be limited to ensure good formability. In this case, a compromise should be sought between maximum PB response (without any NSA) and NSA stability, and the desired property tuned by controlling PA temperature.

These considerations are complete only when PA is carried out in a way that subsequent NSA does not increase hardness before PB is performed. If some NSA hardening does occur, one would like to minimise the resulting hardness after PA+NSA and maximise PB response. In Fig. 4.3h, one cannot simply replace PA hardness by hardness after PA+NSA because different PA/NSA combination can lead to the same hardness but cause different PB responses.
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(Fig. 4.3a,e). We proceed by overlaying some of the iso-hardness lines in Fig. 4.3d onto Fig. 4.3h and obtain Fig. 4.12. If for example, NSA for 12 weeks is permitted after PA in an industrial workflow and the maximum hardness after NSA is limited to 75 HBW (e.g. to allow for sheet stamping), then the broken contour line in Fig. 4.12 shows all possible states. By searching for the highest PB hardness along this line one can identify the optimal PB treatment, in this case PA at ~140 °C up to a hardness of 74 HBW. For different acceptable NSA times, the same procedure has to be applied to Figs. SA2 and SA3 of Appendix A1 and enables the materials producers to design and manufacture the alloys in a more reasonable way according to the demand of low hardness before and high hardness after PB. In fact, it is observed that the optimum PA strategy is to seek for the highest PA temperature which keeps the alloy stable or only slightly hardened during the required NSA period.

**Fig. 4.12.** Data of Fig. 4.3h with some iso-hardness lines of Fig. 4.3d overlaid. Note that interpolation errors may lead to small artefacts such as hardness after PA+NSA appearing 1 HBW higher that after PA only.

4.2.4. **Sensitivity of various characterisation methods to detect natural ageing**

The sensitivity of a given characterisation method can be defined by when during NSA a significant change of the associated property can be observed. The shorter this time the higher sensitivity. For hardness measurements we determine the transition time at which a measured
hardness including experimental scatter is higher than any previous point during NSA or lower than any previous point after PB. For electrical resistivity, we determine the time after which resistivity has increased to above the noise level. For the PALS signal we proceed in a similar way. A decrease of peak $b_1$ is a sign for changes detected by DSC measurement.

Fig. 4.13 shows the transition times for samples measured by at least three methods. Note that due to the limited measurements during NSA or due to the scatter of the signal, the transition time is always presented as a range instead by a single point. In most cases, the change of electrical resistivity is the first signal indicating a transition. The hardness increase during NSA and the decrease of PB response show similar sensitivity with the former being slightly lower for more PA conditions. PALS or DSC experiments show sensitivities roughly in the intermediate range before the former two.

![Graph showing transition times for different methods](image)

**Fig. 4.13.** Comparison of the times at which various methods indicate the onset of NSA (following 7 different PA conditions). Hardness measured during NSA, resistivity and PALS signal are direct measures, the reduction of the DSC peak and reduction of PB response indirect ones.

### 4.3. Conclusions

The influence of PA on subsequent NSA and PB hardening has been investigated systematically by covering a wide range of PA temperatures and times. The following conclusions can be drawn.
- PB hardening and NSA stability (resistance to clustering) after PA are both related to PA time and temperature. PB hardness can be enhanced primarily by increasing PA temperature. Prolonging PA time has a minor effect, especially when PA temperature is low. NSA stability can be improved by increasing PA time (hardness) or lowering PA temperature.
- If PA hardness is constant, a trade-off can be made between PB hardening and NSA stability according to the demand, i.e., to use lower PA temperature to ensure a higher NSA stability or higher temperature for a greater PB potential.
- The data allow for searching for PA conditions that minimise hardness after a given NSA time while maximising PB response.
- The delay of NSA clustering due to PA can be evaluated by a retardation factor $\Theta$. We observed that after performing PA to the same hardness but at different temperatures, the measured kinetics of ensuing NSA are less different than expected from the equilibrium vacancy site fractions. This discrepancy can be explained by taking vacancy trapping effects and attachment of solutes to PA clusters into account.
- Different characterisation methods show different sensitivity to NSA clustering. Among all the methods applied, electrical resistivity is the most sensitive one, whereas hardness measurement is the least sensitive.
5. Two-step pre-ageing and its effect on multi-stage ageing

Motivation:

- PA at 80 °C and 160 °C have advantages and disadvantages. What about combining the two?

- To investigate how microstructure evolves during two-step PA.

5.1. Experimental results

5.1.1. Hardness measurements

5.1.1.1. PA and PA + PB

In the current work, various combinations of pre-ageing treatments at two different temperatures (80 °C and 160 °C) were designed to create similar final hardesses (~64 HBW), as shown in Fig. 5.1. Different labels were used to denote different PA conditions. ‘H’ and ‘L’ stand for single-step PA at high (160 °C) and low (80 °C) temperatures for comparisons. The other four (H1, H2, L1, L2) are two-step PA with different weights of ageing at high and low temperatures.

Further PB at 180 °C for 30 min gives rise to different hardness increases for different PA treatments. Generally, PA conditions starting with higher temperature (‘H’ series: ‘H’, ‘H1’, ‘H2’) show a higher PB hardness than those starting with lower temperature (‘L’ series: ‘L’, ‘L1’, ‘L2’). Replacing just a small fraction of PA at another temperature in the second step does not have a significant influence on PB hardness (‘H1’ vs. ‘H’, ‘L1’ vs. ‘L’), while a small fraction of PA at another temperature in the first step does show a pronounced effect (‘H2’ vs. ‘L’, ‘L2’ vs. ‘H’). Therefore, PA in the first step plays a more important role.
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Fig. 5.1. Hardness increase during pre-ageing and subsequent PB hardening. ‘H’ and ‘L’ are single-step pre-aged conditions for comparisons. ‘H1’, ‘H2’, ‘L1’, and ‘L2’ are two-step pre-aged conditions.

5.1.1.2. PA + NSA and PA + NSA + PB

Fig. 5.2 shows the hardness change during NSA for all PA conditions. In agreement with previous chapter, hardness increase is delayed compared with no PA (Fig. 4.1). Moreover, such delay of the NSA hardening kinetics can be evaluated by using a retardation factor (Fig. 4.9). Here, instead of using the NA hardening for AQ samples as reference, we present Θ as a relative retardation factor with respect to the NSA kinetics of ‘H’ (Fig. 5.2b). For the single-step PA treatments, samples pre-aged at lower temperature (‘L’) shows a slower hardness increase during NSA than those pre-aged at high temperature (‘H’), in line with Fig. 4.10, although the retardation factor is slightly larger than shown in Fig. 4.10 possibly due to a slightly lower PA hardness of ‘H’ condition. For two-step PA treatments, NSA hardness of ‘H1’ is quite similar to ‘H’, and ‘L1’ is similar to ‘L’, i.e. having a relatively short second step, which increases hardness only slightly, at another temperature does not alter the NSA hardening behaviour. However, further increasing the weight of the second step then modifies the NSA kinetics and make it closer to the NSA of single-step PA at that temperature.
5. Two-step pre-ageing and its effect on multi-stage ageing

Fig. 5.2. (a) Hardness during NSA after various PA treatments. (b) Hardness increase during NSA normalised by a factor $\Theta^{-1}$ similar to Fig. 4.9b but with the curve of ‘H’ as reference. Dashed curve is for guidance.

Hardness after NSA and further PB is shown in Fig. 5.3. PB hardness keeps constant for some NSA time before it decreases, similar to Fig. 4.3e–g. Curves of ‘L’ series (‘L’, ‘L1’, ‘L2’) are generally lower than ‘H’ series and the decrease is also smaller.

Fig. 5.3. Hardness after NSA and further PB for various PA conditions shown as a function of NSA time.

5.1.2. Electrical resistivity measurements

Ex-situ electrical resistivity measurement were carried out at liquid nitrogen temperature (−196 °C). For the AQ condition, a resistivity of $1339 \pm 11 \ \text{n}\Omega\cdot\text{cm}$ was obtained. Fig. 5.4 gives the resistivity change during various ageing experiments. For single step isothermal ageing at
160 °C, electrical resistivity first increases up to 10 min, after which the resistivity drops down. The resistivity increase is higher for ageing at 80 °C for the same ageing time, and no maximum is observed during ageing for ~3500 min. If ageing at 160 °C is interrupted and followed by ageing at 80 °C (‘H1’ and ‘H2’), resistivity further increases and eventually beyond the level of maximum for isothermal ageing at 160 °C. Transition from 80 °C to 160 °C (‘L1’ and ‘L2’) firstly accelerates the resistivity increase. Similar to isothermal ageing at 160 °C, resistivity will finally decrease after the appearance of the maximum.

![Resistivity change during ageing at 160 °C and 80 °C as well as various two-step ageing treatments. Ageing at different temperatures are shown in connecting curves in different colours. Transitions between two steps are marked by dashed lines. Inserts show enlarged areas. States after various PA treatments are denoted by labels.](image)

**Fig. 5.4.** Resistivity change during ageing at 160 °C and 80 °C as well as various two-step ageing treatments. Ageing at different temperatures are shown in connecting curves in different colours. Transitions between two steps are marked by dashed lines. Inserts show enlarged areas. States after various PA treatments are denoted by labels.

5.1.3. **DSC**

**Fig. 5.5** displays the DSC traces of differently pre-aged samples. Several exothermic peaks can be observed, analogous to the curves presented in **Fig. 4.5**. Just that the peak a in the AQ curve (Fig. 4.5) is not seen. With an increasing weight of ageing at 80 °C after 160 °C (‘H’ → ‘H1’ → ‘H2’), peak b1 shrinks and peak d grows. A higher fraction of ageing at 160 °C after 80 °C (‘L’ → ‘L1’ → ‘L2’) decreases the amplitude of peak d and enhances peaks b1 and b2.
5. Two-step pre-ageing and its effect on multi-stage ageing

![DSC traces](image)

**Fig. 5.5.** DSC traces after various single- and two-step PA treatments at a heating rate of 10 K/min. Labels of the peaks are adopted from Fig. 4.5.

5.2. Discussion

5.2.1. Microstructure evolution during two-step PA

5.2.1.1. Cluster formation

Cluster formation during single-step isothermal PA at 160 °C and 80 °C was discussed already in the previous chapter, Sec. 4.2. Clusters formed at 160 °C are larger and sparser than those formed at 80 °C. This is also reflected in the plot of hardness change as a function of resistivity change (Fig. 5.6) by a much smaller resistivity increase for 160 °C (‘H’) than 80 °C (‘L’) after reaching same hardness (change). If ageing at 160 °C is followed by ageing at 80 °C (‘H1’ and ‘H2’), the courses deviate from the original trend and show a higher resistivity change, suggesting independent formation of denser clusters at 80 °C. Meanwhile, pre-formed clusters might also further grow because the slope of the second stage is generally higher than the same stage in the curve for ‘L’. The same applies to ‘L1’ and ‘L2’ that some pre-formed clusters are reverted or new clusters at 160 °C are formed. The influence of the second stage is larger when it is longer (‘H2’ and ‘L2’).
5.2.1.2. Vacancy site fraction evolution

Vacancy site fraction evolution during PA is experimentally difficult to measure, because the specific positron lifetimes for clusters and mono-vacancies are too close together to enable a reliable decomposition of the lifetime spectra. Therefore, we chose alternatively the simulation approach to show the trend of vacancy evolution during PA treatments.

The simulation was performed employing software MatCalc with the FSAK vacancy generation and annihilation kinetics [78]. Simulated results are shown in Fig. 5.7. Vacancy site fraction starts after SHT from a level of $\sim 2 \times 10^{-4}$ and is partially reduced during quenching. During ageing, vacancy site fraction tends to move to its thermal equilibrium level, i.e. annihilation of excess vacancies occurs if higher than equilibrium or otherwise generation of new vacancies happens. Simulation shows that the thermal equilibrium site fraction is reached after almost all PA treatments, except for ‘L1’ (Fig. 5.7d), which is only slightly below equilibrium. Note that certain assumptions were adopted for the simulations, e.g. only dislocation jogs and grain boundaries are considered as sources and sinks for vacancy annihilation and generation whereas Frank loops are ignored, and a dislocation density of $10^{11}$ m$^{-2}$, jog line fraction of 0.02, grain size of 100 µm were inputted in the simulation. Most importantly, simulation was performed assuming a pure Al system without any alloying elements, which in fact can interact with vacancies [95] and influence their annihilation/generation kinetics [83] or form solute clusters which act in a similar way [72,
These factors, especially the latter one, will have important implications on vacancy evolution and will be discussed in the next section.

**Fig. 5.7.** Simulation of vacancy evolution during single- (a, b) and two-step ageing treatments (c–f). States after PA are denoted by labels and dashed lines.

### 5.2.2. Influence of two-step PA on NSA and PB hardening

It has been shown in the previous chapter and again presented here that PA at various temperatures result in different NSA stability and PB hardening. Single-step PA at higher
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temperature (160 °C) results in higher PB hardening, while a higher NSA stability is favoured by PA at lower temperature (80 °C) (Fig. 5.1 – 5.3). NSA hardening kinetics and PB hardening after the combined two-step PA treatments fall between that of the two reference single-step PA treatments. This compromised effect is analogous to PA at an intermediate temperature, e.g. 120 °C. In fact, ‘H2’ and ‘L2’ treatments do result in a comparable NSA hardening to single-step PA 120/120, just the PB hardening of the two-step PA conditions are slightly inferior (Fig. 5.8).

![Diagram](image)

Fig. 5.8. Hardness after NSA and further PB of the samples in ‘H2’ and ‘L2’ conditions compared with the corresponding hardness of PA 120/120 condition. Data for PA 120/120 is presented also in Fig. S1A, Appendix A1.

As discussed in Sec. 4.2.2.2, the NSA clustering rate in a simple model is dependent on 1) the number of mobile vacancies, 2) solute supersaturation, and 3) the number of PA clusters. The rate increases with more mobile vacancies, higher solute supersaturation, or higher PA cluster density as solutes can attach to these clusters. Solute consumptions by PA clustering are assumed approximately the same as similar hardnesses are reached after various PA treatments. Therefore, mobile vacancy site fraction and PA cluster density are more relevant in this case. The number densities of PA clusters in ‘H1’ and ‘H2’ states should be higher than in ‘H’ but lower than in ‘L’. The mobile vacancy site fraction during the second ageing step is supposed to move towards the thermal equilibrium at 80 °C. However, NSA kinetics for ‘H1’ and ‘H2’
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are still faster than ‘L’ (Fig. 5.2), suggesting that the mobile vacancy site fraction is still higher than that in ‘L’. This is not in accordance with the simulated results in Fig. 5.7 as the simulation shows a much faster excess vacancy annihilation. Therefore, either the FSAK model overestimates the excess vacancy annihilation kinetics or the vacancy annihilation is delayed by other mechanisms. As stated in Sec. 5.2.1.2, the influence of solute clusters on vacancy evolution is neglected in the simulation. Previously, in Sec. 4.2.2.2., we proposed that the trapping of vacancies by PA clusters can be involved in the process of modulating the number of total vacancies as well as mobile vacancies at NSA temperature, thus narrowing the difference between the mobile vacancy site fractions after PA at different temperatures. Here, we use the same model (Eq. 4.4 and Fig. 4.11) to schematically show how vacancy annihilation process can also be delayed by such mechanism (Fig. 5.9). From the graph, the red and the blue lines mark the level of total vacancies when the mobile vacancy site fraction reaches thermal equilibrium level under the trapping effect (Fig. 4.11). When temperature changes from 160 °C to 80 °C, a repartitioning of vacancies in the matrix and trapped in clusters is assumed to occur rapidly, which follows the change in $\eta$ in Fig. 4.11. This reduces the mobile vacancy site fraction to a level lower than equilibrium at 160 °C but higher than equilibrium at 80 °C, which markedly decreases the driving force for excess vacancy annihilation (route 3 compared with route 1). Meanwhile, the total amount of vacancies to annihilate defined by route 2 is much higher than that without considering trapping effect (route 1). Altogether, the annihilation of excess vacancy will be delayed by the vacancy trapping effect. Similarly one could also expect that under such model the kinetics of vacancy generation will be delayed when temperature increases from 80 °C to 160 °C. Thus, the PA clusters act like buffers, retarding both vacancy annihilation and generation.

The hardness of the two-step PA treated samples after PB lies between the hardnesses of two single-step PA treated samples. From the viewpoint of clusters, two-step PA might produce a mixture of clusters independently formed at 160 °C and 80 °C, which differ in the ability to transform into strengthening phases during PB. This is also shown by DSC traces in that the size of the $b1$ peak, which was interpreted as the ability of direct transformation of PA clusters into strengthening precipitates [12], lies in the middle of the two reference samples for two-step PA samples. Thus, a compromised PB response might be obtained. If we extend the vacancy trapping model mentioned in the previous paragraph to 180 °C, one would also expect that vacancy generation at 180 °C will be slower than without trapping. The question is just how long it will be delayed and whether it causes a notable hardening difference. From the
current experiments, we may conclude that ageing for 13 min is not enough for equilibrium to be reached at 160 °C. However, at a higher temperature the trapping effect will be weaker, the vacancy generation rate will be enhanced and vacancy migration will be faster. Altogether, the time needed can be much shorter than at 160 °C. Therefore, the vacancy trapping mechanism can potentially contribute to the different PB responses after PA at different temperatures but requires more investigations, especially on the vacancy generation dynamics.

![Diagram](image)

**Fig. 5.9.** Schematic representation of how vacancy trapping mechanism delays the excess vacancy annihilation. Route 1 represents the mobile (and total) vacancy fraction difference without vacancy trapping effect. Route 2 and 3 represents the total and mobile vacancy fraction differences considering trapping effect.

### 5.3. Conclusions

In this study, we performed various PA programmes consisting of two steps at two different temperatures, namely 160 °C and 80 °C. The microstructural evolution during two-step PA was probed by electrical resistivity and hardness measurements. The effect of such two-step PA treatments on NSA and PB hardening was compared with the independent single-step PA
treatments at the two temperatures. Although no higher NSA stability and PB hardening than single-step PA were obtained, these experiments still provided valuable information on microstructural evolution during two-step PA. The following conclusions can be drawn.

- Based on the resistivity evolution during two-step PA, we found clustering in the second step is a mixture of independent formation of new clusters and further evolution or reversion of previous clusters.
- By performing two-step PA, we obtained a PB hardenability and a NSA stability in the intermediate range of the two reference states.
- The sequence of two-step PA matters. ‘H1’ and ‘L2’ have similar hardness increase at both 80 °C and 160 °C, but they do not behave similarly during NSA and PB. The same applies to ‘H2’ and ‘L1’ conditions. Moreover, having a short time at another temperature in the second step does not cause a big effect, i.e. ‘H1’ and ‘H’ are similar, and ‘L1’ is analogous to ‘L’. All these point to the importance of the starting temperature of PA.
- We found vacancy annihilation and generation during the second step PA are much slower than simulated by the FSAK model in pure Al. A possible explanation is that PA clusters formed during the firsts step have a trapping effect to vacancies, thus buffereing the evolution of vacancy site fraction towards equilibrium. Whether this contributes to the differences in PB hardening requires more investigation.
6. Influence of quench rate on multi-stage age hardening

Motivation:

- To understand the quenching processes
- To investigate the influence of quench rate on subsequent ageing behaviour

6.1. Experimental results

6.1.1. Hardness measurements

6.1.1.1. Single-stage hardening (AA, PA, and NA)

Hardening during AA of the alloy after SHT and various quench conditions is given in Fig. 6.1. For samples after T1-type quenches (complete quench to room temperature), initial hardnesses are the same within ±1 HBW. The times needed to reach peak age are also similar for all conditions (240 min), while the peak hardnesses are lower for slower cooling, with 112 HBW, 108 HBW and 99 HBW for IWQ, VC, and AC, respectively. In contrast to the later stages, early stage hardening (up to 5 min) appears to be slightly stronger for the VC and AC samples than for IWQ. Two T2-type quenched conditions are exposed to AA, namely VC_200 and AC_200. VC_200 samples show the same hardnesses as VC samples in the as-quenched condition, after PB, and at peak age condition, while AC_200 samples exhibit a slightly lower hardness in the as-quenched condition only.

For two T1-type quenched samples, namely IWQ and VC, hardening during ageing at a typical PA temperature (100 °C) is shown in Fig. 6.2. The small hardness difference after quenching is seen to be diminished after 30 min of ageing and the hardening is almost identical during the next ~1400 min of ageing. Hardening curves start to differ after ageing for 2880 min. At a similar hardness level, the difference between the two hardening curves is slightly smaller for ageing at 100 °C than 180 °C.
6. Influence of quench rate on multi-stage age hardening

Fig. 6.1. Hardness during AA after various T1 quenches and two T2 quenches. Inserted graph shows early stage AA of T1-quenched samples on a linear time scale. Arrows denotes the T2-type quenched samples.

Fig. 6.2. Hardness during ageing at 100 °C after two T1 quenches: IWQ and VC.
NA hardening curves after all three T1-type quenches are given in Fig. 6.3. For all quenching conditions, hardness increases markedly during approximately the first 60 min of NA, after which hardening continuously slows down. This is best seen by fitting the NA hardness evolution by the Starink-Zahra equation [117] and taking derivatives. The fits yield an R-square value higher than 0.998 for all three curves, better than for the JMAK type equation, which is often used for representing precipitation kinetics.

![Graph showing NA hardness vs time for different quench conditions](image)

Fig. 6.3. Hardness of samples during NA after various T1 quenches. Solid curves represent the data fitted by the Starink-Zahra equation: 

\[ H = H_0 + H_1 \left(1 - \left[ \frac{(kt)^n}{\eta} + 1 \right]^{-\eta} \right), \]

with \( H_0 \) the hardness at the as-quenched state, \( H_1 \) the maximum hardness increase during NA, \( t \) the NA time, and \( k, n, \eta \) the kinetic parameters [117], respectively. Initial hardness points represent NA for 5 min, which is the typical time needed for the measurement. Derivatives (hardening rate) of the fitted hardnesses are shown as dashed curves.

6.1.1.2. Two-stage hardening (NA + PB)

When almost no NA is applied, PB leads to hardnesses of ~98 HBW, ~93 HBW, and ~83 HBW for IWQ, VC, and AC, respectively, see Fig. 6.1 and initial values in Fig. 6.4a. As NA time increases, PB hardness initially declines rapidly and then levels off to a similar level. The PB response is higher for faster quenched samples when NA is shorter than 90 min but lower when
6. Influence of quench rate on multi-stage age hardening

NA is longer (Fig. 6.4b). The absolute decrease of PB hardness after NA relative to the initial value is smaller for the slower cooled samples. After plotting the relative PB decrease as a function of hardness increase during NA (Fig. 6.4c), the influence of NA on PB hardening can be divided into two stages. During the first, the PB hardness decrease is significant and proportional to the NA hardness increase. During the second, PB hardness decreases much slower and eventually stagnates although NA still hardens the material. The transition between the stages occurs at different NA hardesses, whereas the corresponding NA times are quite similar for all quenched conditions, namely 90 min or 120 min. The PB response plotted against the NA hardness increase (Fig. 6.4d) shows initial differences but the same final value.

Fig. 6.4. (a) PB hardness after various NA times. The first points are after NA for ~0.5 min, the interval for transferring samples from the cooling device to the oil bath for ageing. (b) PB response as a function of NA time. (c) Decrease of PB hardness plotted as a function of the hardness increase after NA. (d) PB hardening response plotted as a function of the hardness increase. NA time is an implicit parameter in both (c) and (d). The blue dashed curve in (c) is the corresponding curve of an ice-water quenched sample pre-aged at 100 °C for 10 min and then NSA before final PB, taken from Fig. 4.3.
6.1.1.3. Multi-stage hardening (PA + NSA and PA + NSA + PB)

Applying PA effectively suppresses hardening during subsequent NSA, the extent of which depends on PA temperature and time (Fig. 6.5a) but hardly on whether IWQ or VC have been employed (the small offset ±1 HBW reflects effects of different alloy batches). Longer PA at 100 °C (from 10 min to 4 h) causes a stronger suppression of NSA. When similar PA hardness is achieved by PA at 100 °C for 4 h and 140 °C for 30 min, NSA hardening kinetics for PA conducted at 100 °C is slower by a factor of 2.

IWQ and VC samples behave differently when a final PB treatment is performed after PA (Fig. 6.5b, 1st, 3rd and 5th column). For the same ageing condition, VC samples age to a lower PB hardness than IWQ samples. These hardness differences are reduced when 4 weeks of NSA are introduced after PA (2nd and 4th column). When comparing PA treatments at different temperatures that lead to similar hardnesses, PA at 140 °C appears to be superior for achieving a higher PB hardness for both IWQ and VC samples (3rd vs. 5th column). Therefore, the result previously found for IWQ samples [118] is still applicable to slower cooled samples, i.e. at lower PA temperature the alloy shows less NSA while at higher PA temperature a higher PB potential is encountered. This implies that the suggestions derived in Sec. 4.2.3 for improved PA treatments based on close-to-ideal quenching conditions are also valid for industrial quenching conditions based on slower quenches.
Fig. 6.5. Comparison of the hardness of IWQ and VC samples (a) during NSA after various PA treatments, and (b) after PB of various aged states. Data for IWQ were presented in Fig. 4.3.

6.1.2. TEM

TEM was performed on samples after all three T1-type quenches as well as after subsequent AA for 4 h. Special attention was paid to secondary particles in the microstructure. Only one type of particle, named P1, can be observed in the microstructure of the IWQ sample, while at least two types of particles, P1 and P2, can be seen for VC and AC. EDX analysis reveals that P1 contains primarily Fe, Si and Mn beside Al, while P2 consists of mainly Mg and Si (Appendix B1, Fig. SB1). P1 particles are observed in many shapes, mostly spherical or ellipsoidal, whereas P2 particles are mostly rod-shaped and are aligned along ⟨100⟩ directions of the Al matrix. Moreover, P2 particles are mostly attached to P1 (Fig. 6.6) or are observed at grain boundaries. After AA for 4 h, a high number density of fine needle precipitates aligned along the ⟨100⟩ directions of the matrix are found in the grains.
6.1.3. DSC

The variance in quench rate does not have much influence on the principal structure of the DSC signal of the as-quenched samples (Fig. 6.7) as all traces exhibit the same exothermal peaks during heating, namely peaks $a - c, f$, and the positions of the peaks are very similar, just the amplitudes of some peaks vary. The labelling of the peaks is in accordance with Fig. 4.6, and no exotherm $d$ or endotherm $e$ can be observed. As quench rate decreases from IWQ to AC, peaks $a$ and $b$ are reduced, the former much more. The heat effect of peak $f$ is small for all three curves. Peak $c$ is found not to change systematically with the quench rate, possibly due to a small residual baseline drift.
6. Influence of quench rate on multi-stage age hardening

6.1.4. PALS

Fig. 6.8a shows one-component positron lifetimes ($\tau_{1c}$) of differently quenched (T1) samples during NA. After the fastest quench (IWQ), $\tau_{1c}$ starts from $\sim232$ ps, then slightly increases during the first minutes of NA. A pronounced decrease to $\sim222$ ps characterises the next stage (up to $\sim120$ min), which is then followed by a slow re-increase to $\sim225$ ps. A decreasing lifetime is found at the end of measurement. If samples have undergone a slower quench, $\tau_{1c}$ starts from a much lower value ($\sim217$ ps for both VC and AC) than for IWQ. For VC, $\tau_{1c}$ increases markedly within the first 20–30 min to $\sim230$ ps and subsequently almost joins the curve for IWQ. The positron lifetime for AC also increases to a similar level as the VC curve but takes longer (50–60 min). The course of the curve during subsequent NA is similar to the one for IWQ except that it is delayed.

Similar curves are also obtained for samples that have undergone a T2-type of quenches (Appendix B2, Fig. SB2). The difference lies only in the first value of $\tau_{1c}$ and how fast $\tau_{1c}$ increases to a maximum. Fig. 6.8b shows the first values after quenching in Fig. SB2 and values extrapolated to zero NA time. For both AC and VC, $\tau_{1c}$ during quenching first decreases and then increases, with a transition between the stages at 200 °C. The lowest lifetime achieved for the AC samples is lower than that for VC samples. The curves for ‘NA 0’ are in general lower than the curves for ‘First measured LT’.
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Fig. 6.8. Single-component positron lifetimes (a) during NA after various quenches (T1), (b) after VC and AC quenches interrupted at various temperatures (T2). The ‘First measured LT’ typically took 4 – 8 min to measure at ‘room temperature’ due to sample preparation and data acquisition. ‘NA 0’ means that the data in (a) and Appendix B2, Fig. SB2 were extrapolated to zero NA time. The states (1) and (2) are analysed in Appendix B3, Fig. SB3.

6.2. Discussion

During SHT high amounts of solutes and vacancies are dissolved in the matrix. The solubilities of both decrease as temperature drops during quenching and supersaturated solutes and vacancies precipitate out of the matrix or annihilate at sinks, respectively. The remaining quenched-in solutes and excess vacancies are then available for subsequent age hardening. Varying the quench rate after SHT has a considerable impact on the microstructure as well as on the various subsequent ageing treatments, which we will discuss in terms of the behaviour of solutes and vacancies as well as their interplay.

6.2.1. Influence of quench rate on the as-quenched state

The microstructure after quenching is significantly influenced by the quench rate as primarily reflected by TEM and PALS results. Fe-containing particles (P1 in Fig. 6.6a) found in all samples are dispersoids typically formed during homogenization [119, 120], whereas the Mg-
Si containing particles (P2) are only found in VC and AC samples but not for IWQ, indicating that they are precipitates formed during quenching. Fast quenching in ice-water suppresses the formation of such precipitates. By measuring the in-situ heat evolution during cooling, Milkereit et al. characterised two precipitation reactions [121, 122]: A high-temperature reaction occurring typically from 500 °C down to ~380 °C represents the precipitation of equilibrium β phase, while a low-temperature reaction happens from 380 °C down to ~250 °C and stands for precipitation of β' and B' phases. The high-temperature reaction is negligible for quench rates higher than 0.17 K/s [121]. Similar results were obtained by Strobel et al. [123]. This and the observation that the shape of the precipitates we find is closer to β' and B' as described in Ref. [121] instead of to the typical plate shape for β imply that for our quenching conditions, the low-temperature reaction is dominant. As precipitates are mostly attached to dispersoids these seem to be their nucleation sites in accordance with the literature [124-127].

We now consider positron lifetimes during various quenches. The measured \( \tau_{1c} \) represents a weighted average of positron lifetimes in various microstructural features and the value of \( \tau_{1c} \) reflects their relative contributions. Positron annihilation in mono-vacancies, solute clusters, and bulk Al is most relevant, yielding characteristic lifetimes of ~245 ps, ~210 to 220 ps, and \( \leq 160 \) ps respectively [64].

After direct quenching in ice-water, a lifetime of 232 ps is obtained in agreement with previous observations [63, 71, 128, 129]. Such a high \( \tau_{1c} \) indicates that it is dominated by the contribution of a vacancy-related component but the temperature dependence of \( \tau_{1c} \) as measured by [64] has shown that a small fraction of clusters is also present. During slower cooling down to 200 °C, \( \tau_{1c} \) is seen to decrease (Fig. 6.8b), which is clear evidence of a vacancy site fraction reduction due to annihilation at sinks (dislocation jogs, grain boundaries, possibly also incoherent surfaces of dispersoids etc.). Although formation of vacancy clusters or dislocation loops could also decrease \( \tau_{1c} \) due to an overall smaller density of positron traps, it is not considered the reason here since such loops tend to dissolve at temperatures above 200 °C [130]. Precipitate formation on dispersoids will also contribute little to the change of positron lifetime, because the number density of precipitates, even if growing on every dispersoid (\( \sim 10^{18} \) m\(^{-3} \) [126, 131] = site fraction \( 1.6 \times 10^{-11} \)), is too low to trap positrons. The lower measured lifetime for AC_200 than for VC_200 therefore indicates higher vacancy losses during slower quenching.
According to Fischer et al. [78] and Falahati et al. [103], quenching at 1000 K/s (realistic value for IWQ) results in a vacancy site fraction after quenching ~25 times higher than at 27 K/s and ~125 times higher than at 5 K/s. The state reached at 200 °C after VC or AC (and mostly preserved by the subsequent interrupting IWQ) should consist of a low vacancy-related contribution, a minor contribution from pre-precipitated atoms and a high bulk contribution to explain the low measured $\tau_{1c}$. A calculation of the vacancy site fractions associated to the positron lifetimes marked by arrows in Fig. 6.8b yields the values indicated in Appendix B3 Fig. SB3, under the assumption of the absence of any clusters (see right axis of Fig. 6.8b). Accordingly, the ratio of vacancy site fraction drops to 1/33 th or 1/66 th of its original value during VC or AC to 200 °C, respectively, which is in the range predicted in Refs. [78, 103]. The presence of clusters formed above such temperature would imply even lower vacancy fractions at 200 °C because such clusters will result a lifetime component higher than 160 ps.

During cooling to below 200 °C $\tau_{1c}$ increases for both VC and AC, which must be due to the replacement of the bulk component ($\leq$160 ps) by another component with a higher lifetime. As the vacancy site fraction cannot re-increase, the formation of clusters or nuclei of precipitates should be the reason. This argument is supported by the final lifetime (~217 ps) that falls into the typical cluster positron lifetime range for clusters (~210 to 220 ps). Fig. 6.1 shows that the clustering contribution to hardness increase is at the most 2 HBW (AC_200 compared with AC) or even unnoticeable (VC_200 compared with VC). Assuming that positron lifetime is much more sensitive to the formation of very small clusters than hardness, the precipitated solute is seen to form small clusters in this case. The reduction of peak $a$ in the DSC traces (Fig. 6.7) that is associated to clustering [15, 39] can be caused by both the reduction of solute concentration and by a lower excess vacancy fraction after quenching. During heating an equilibrium vacancy fraction is reached only at temperatures well above peak $a$ so that the differences in excess vacancies can actually modify the DSC trace in this way.

In summary, slower quenching reduces the vacancy site fraction by at least 1-2 orders of magnitude (possibly even more), lowers the solute supersaturation (SS) owing to pre-precipitation, and prompts solute clustering primarily below 200 °C.

6.2.2. Influence of quenching conditions on subsequent ageing

The hardness data demonstrates that the influence of the quenching condition on subsequent age-hardening is strongly dependent on the ageing condition, particularly the temperature
applied. AA hardening behaves very differently for different quenches, whereas this difference is smaller for NA. For PA and also PA+NSA hardening is quite similar although quenches are different. Such a difference is likely to be associated with the different mechanisms for ageing at different temperatures. Thus, the influence of quench rate on ageing behaviour will be discussed based mainly on ageing temperature.

6.2.2.1. **High-temperature ageing (AA or PB)**

Slower quenching leads to a higher loss of (i) vacancies and (ii) dissolved solutes, both losses negatively affecting hardening. (iii) The properties of the clusters formed during quenching could also differ and affect AA, depending on the type of clusters. It is generally assumed [52] that in solute-rich Al-Mg-Si alloys clusters formed at PA temperature will act as nuclei of strengthening precipitates (mainly $\beta''$) during AA, whereas the clusters formed at NA temperature will cause a detrimental effect on AA (Fig. SB5). From the PALS measurements (Fig. 6.8b), clustering phenomena during cooling are observed mainly below 200 °C. Thus, AA after VC_200 (and AC_200) is an interesting reference state as only little prior precipitation has taken place. The PB hardnesses as well as the peak age hardnesses of VC_200 (and AC_200) treated samples are similar to those of the VC (and AC) sample in which clustering has taken place (Fig. 6.1). This indicates that cluster formation during quenching has no negative impact on subsequent AA, suggesting that most clusters formed during cooling are PA clusters that can develop into $\beta''$, most likely because most of them are formed notably above ‘room temperature’.

Next, the influence of these three factors on AA kinetics is discussed. The AA process is divided into various stages as schematically given in Fig. 6.9 according to the evolution of hardness after two quenches, namely IWQ and VC. A possible scenario of the evolution of solute supersaturation (SS) and vacancy site fraction (VF) is deduced qualitatively. In the early stage AA (stage I in Fig. 6.9), a slightly higher hardening is observed for VC samples than for IWQ samples. As discussed above, SS and VF are both lower for the VC sample than for the IWQ sample after quenching, and both factors should negatively influence the hardening rate. Therefore, it must be the clusters formed during VC that enhanced the precipitate formation during AA by acting as nuclei or precursors.
As ageing proceeds, the importance of these quenched-in clusters vanishes because more nuclei are gradually formed during AA. After that, the hardening rate is dominated by the available solutes and vacancies. Thus, the hardness of IWQ samples increases faster and eventually overtakes the hardness of VC samples, until the largest difference is reached after ~30 min of AA (stage II in Fig. 6.9). Subsequent ageing further hardens the material to the peak age state, during which the difference between the two hardening curves is approximately constant (stage III in Fig. 6.9). It indicates that the SS and VF in two samples are the same in this stage. In
other words, the extra solute supersaturation in IWQ sample has been fully transformed to the higher hardness at the latest by the end of previous stage II. However, the question remains for the role of a higher vacancy site fraction in IWQ than in VC during stage I and II. During AA, the vacancy site fraction after quenching will move from highly excess towards the much lower thermal equilibrium (Appendix B3, Fig. SB3). The positive influence on hardening kinetics of having a higher number of quenched-in excess vacancies after IWQ exists only until thermal equilibrium has been reached. Thus, if the equilibrium is reached rapidly in the early stage of AA (denoted as route ‘1’ in Fig. 6.9), as calculated by simulations [82, 103], then a higher hardening in stage II for IWQ should be purely due to the higher SS. However, if the vacancy annihilation is not that fast (route ‘2’ in Fig. 6.9), e.g. delayed by trapping in clusters, and a considerably higher vacancy site fraction still continues to exist in IWQ sample than in VC sample for a few tens of minutes, then the higher hardening in stage II for IWQ should be a co-contribution of both higher SS and VF resulting from faster quench. Which mechanism is more likely, however, cannot be decided from the current measurements and requires further investigations.

6.2.2.2. Intermediate temperature ageing (PA)

Hardening during PA at 100 °C (Fig. 6.2) for IWQ and VC quenched samples exhibits a difference at high hardness levels, which should be a result of different SS. However, this difference can be almost ignored before hardness reaches ~80 HBW. As there is a substantial amount of clusters formed during PA, as shown by the hardness increase, quenched-in clusters should not have a beneficial effect here (unlike for AA). Therefore, the very similar PA hardening between IWQ and VC samples should be a result of almost the same VF. This can also be verified by the analogous NSA kinetics after PA for IWQ and VC samples (Fig. 6.5a). Thus, it is believed that the initial VF difference after quenching in IWQ and VC samples is eliminated even after just 10 min of PA. Using this argument, we can further conclude that the hardness difference after further PB (Fig. 6.5b, 1st, 3rd, 5th column) in IWQ and VC samples should be due to the SS difference. It means that a higher vacancy site fraction is not necessary for achieving a higher PB hardness in IWQ sample, but it does not prove that the higher vacancy site fraction in IWQ sample was not involved in stage II (Fig. 6.9), because more vacancies might just speed up the establishment of the difference.
6.2.2.3. Low-temperature ageing (NA)

The influence of different quenches on NA kinetics is notably smaller than on AA (about 1/3 in terms of the difference in final hardness). Hardening rates differ in the initial stage of NA but become similar at the latest 100 min (Fig. 6.3). This fits very well with the PALS results that the courses of positron lifetimes are similar after an initial period of divergence (Fig. 6.8a). The details of the increase of positron lifetime in the initial period are still not fully understood, but are supposed to be linked to clustering, because such increase is not observed in binary Al-Mg alloys (Fig. SB5).

That the initial hardening rate is lower for slower quenched samples is understandable as supersaturations of both solutes and vacancies are lower. It is less obvious why hardening rates are so similar during prolonged NA. The equalisation of the SS in various samples might be explained as the hardness increase is higher for faster quenched sample. However, it has to be further explained how the different vacancy fractions after various quenches (at least 1-2 orders of magnitude apart, Fig. 6.8b) equalise so quickly during NA. Vacancy annihilation down to the equilibrium eliminates any difference but if the equilibrium was reached after 100 min of NA we would not observe the fast hardening at this time in Fig. 6.3 as excess vacancies are generally accepted a condition for such rapid NA [53, 80, 81]. Simulations also show that the time to equilibrium is 3 orders of magnitude longer than 100 min [78, 103]. Therefore, there must be a mechanism that removes vacancies faster from a high-vacancy than from a low-vacancy configuration. We propose two mechanisms which enable the elimination of the vacancy difference immediately after different quenches.

(i) The first is based on the formation of vacancy clusters. Vacancy clusters or their condensed structure, dislocation loops, are widely observed in quenched aluminium and its alloys [89-91]. Higher excess vacancy site fractions due to higher solutionising temperatures or higher quench rates were found to increase the number density and the total amount of vacancies in dislocation loops [90, 132-134]. Such loops might not only form during quenching but also during ageing at low temperature [92, 135] and vacancy clusters can be as small as di-vacancies, tri-vacancies etc. [136] so that they might not occur in TEM images. As for our case, if a higher amount of vacancies present after faster quench leads to a stronger vacancy clustering during the initial period of NA, a much faster mobile vacancy reduction would be expected in the fast quenched alloy and the vacancy difference after different quenches could be substantially reduced. The fraction of non-clustered vacancies in the matrix should be still enough to assist NA, which can
be interpreted by the solute-vacancy interaction that retains vacancies and inhibits formation of large loops [90, 132].

(ii) The second possible mechanism is related to the consumption of vacancies by Si-rich clusters. It has been claimed that clusters formed during NA are first Si-rich and then enrich in Mg [62, 63]. Recently, it was found by atom probe tomography that Si-rich clusters have a lower atomic density than clusters of other compositions [57], suggesting a higher vacancy site fraction in those clusters. Based on these arguments, we can imagine that excess vacancies are quickly reduced in the initial stage of NA as they are incorporated in Si-rich clusters. If more Si-rich clusters in the faster quenched sample are formed possibly because of a higher Si supersaturation, more vacancies will be consumed and the difference compared to the slower quenched sample will be reduced.

6.2.2.4. Negative effect of NA

The term ‘negative effect’ refers to the delayed AA hardening kinetics after prior NA and, more importantly in practice, the compromised PB hardness. The origin of the effect is widely attributed to the formation of NA clusters, although the exact mechanism is still in controversy. Serizawa et al. [52] and Aruga et al. [55] argue that NA clusters are difficult to either grow into $\beta''$ or dissolve during AA, thus decreasing the supersaturation of freely available solutes and consequently the hardening during AA. Zandbergen et al. [53, 54] argue that the increase of the nucleation barrier for the $\beta''$ phase due to the formation of NA the decrease of solute concentration (even if only a few %), which markedly suppresses the nucleation rate of the $\beta''$ phase. Pogatscher et al. [72] attribute the retardation of AA hardening to the depletion of mobile excess vacancies which are “imprisoned” by the NA clusters. To discuss which mechanism is more likely is out of the scope of the current study, but these discussions allow us to discuss the distinct negative effects (Fig. 6.4 & Fig. 6.5b) introduced by different quench rates, i.e. why PB hardnnesses are more similar after longer NA.

The reference state in Fig. 6.4a,c is that of zero NA. We have argued in Sec. 6.2.2.1. that the difference in PB hardening comes from the difference in SS after different quenches but we are not sure whether a higher initial VF is also involved in it because the equilibration time is unknown as shown in Fig. 6.9. However, the fact that the hardness difference after PA+PB is also removed by additional NSA (Fig. 6.5b, 1st vs. 2nd column, 3rd vs. 4th column) rules out the possibility that it is the reduction in VF difference during NSA that leads to a similar PB
hardness after NA, because there should be no vacancy difference after PA as discussed in Sec. 6.2.2.2.

**Fig. 6.4c** shows that the loss of PB hardness with progressing NA is not uniform but can be roughly divided into two stages where the decrease mainly comes from the first stage. A similar slope for all the curves in this stage implies that the negative effect in differently quenched samples share some similarities. Each NA hardening by 1 HBW reduced PB hardness by ~2.3 HBW. The times for the first stage are all within the initial 120 min, pointing at initial NA cluster formation having the biggest effect on PB. Such clusters are formed more in fast quenched samples than in slow quenched ones during NA as the hardness at the end of the first stage has increased more with higher quench rate (**Fig. 6.3**) and consequently the decrease of PB hardness is larger too. As initial NA clustering is often attributed to preferential formation of Si-rich clusters we can suspect that such clusters inhibit PB most. The effects of these clusters can be two-fold. First, they lock solutes which will be temporarily not available for further precipitation. Second, they influence the mobile vacancy site fractions by trapping as described in Sec. 6.2.2.3. When there are few mobile vacancies available, the precipitation rate will be limited by the number of these vacancies which transport the solutes to precipitates.

Now we consider another feature observed during slow cooling, the formation of PA clusters. PA is well known to suppress NA clustering and the associated negative effect on AA. The corresponding decrease of PB hardness shown as a function of NSA hardening taken place after a typical PA treatment (10 min at 100 °C) after IWQ from our previous study [118] is shown in **Fig. 6.4c**. Similar to slow quenching, PA also leads to a reduced negative effect despite the same hardness increase due to NA/NSA clustering. A possible explanation is that PA clusters act as nuclei for the β” phase during PB, which are hard to be provided after NA without prior PA. It is supposed that the PA clusters formed during slower quenching would have a similar effect, although their sizes must be very small due to missing hardening (**Fig. 6.1**). Their sizes can possibly increase provided time during NSA is enough to allow solutes to reach them, which probably explains why they are more effective in later stage of NA but less in early stage (**Fig. 6.4b**).

### 6.3. Conclusions
We have investigated the influence of quenching conditions (fast=IWQ→VC→AC=slow) after SHT on the microstructure and subsequent multi-stage age-hardening kinetics of an AA6014 alloy by means of DSC, TEM, hardness, and PALS measurements. We find:

- During slow quenching (VC or AC), precipitates are formed heterogeneously on dispersoids and at grain boundaries unlike in the fast quenched IWQ sample. More vacancies annihilate during quenching before reaching 200 °C for slower quenching, as observed by positron lifetime measurements. Clusters are primarily formed during quenching below 200 °C.

- The AA hardness for slower quenched samples is initially slightly higher compared to faster quenched samples due to formation of PA clusters or nuclei for precipitates during quenching, but in technologically more important later stages of AA falls back due to a lower solute supersaturation.

- NA hardening rates after various quenches are different only within the initial ~100 min, after which the hardening rates are almost identical. The rapid equalised mobile vacancy site fraction could be caused by vacancy clustering and vacancy consumption by Si-rich clusters.

- PA hardening in IWQ and VC samples are almost identical, when PA hardness is not larger than 80 HBW. NSA hardening after PA are also similar for IWQ and VC samples. The trade-off effect previously found for samples after IWQ still applies to the VC condition, i.e., PA at lower temperature enhances the stability during NSA but decreases the maximum PB hardening potential and vice versa.

- PB hardening is higher for faster quenches samples when no NA or NSA is applied. However, this difference gradually diminishes as NA or NSA is longer. Less formation of Si-rich clusters in the initial NA stage and the formation of PA clusters during quenching might have contributed to this effect.

As for the worthy future experiments, a reliable decomposition analysis of PALS spectra should be performed to reveal the vacancy site fractions after various quenches and to verify the existence of a vacancy cluster component. Atom probe tomography might be useful in identifying the clusters after quenches and monitoring the composition of the clusters formed during NA.
7. Characterisation of clustering and precipitation during linear heating

**Motivation:**

- DSC is widely used, but ageing during linear heating is less understood.

- To characterise linear heating also by other methods.

### 7.1. Results

#### 7.1.1. Hardness measurements

**7.1.1.1. Linear heating of as-quenched samples**

The hardnesses of the ice-water quenched (IWQ) samples during linear heating (LH) from room temperature (~20 °C) to a given end temperature at various heating rates are given in Fig. 7.1. The courses of the hardness curves for all heating rates are similar, just the exact values might vary. During LH, hardness first increases as temperature increases, after which a plateau is reached. The temperature for reaching the plateau is increasing with a higher heating rate, while the hardness level of the plateau is decreasing, with ~60 HBW for 3 K/min (Fig. 7.1a), ~55 HBW for 10/min (Fig. 7.1b), and ~50 HBW for 50 K/min (Fig. 7.1c). Hardness after the temporary plateau meets a rapid increase which happens for higher heating rates at higher temperatures, which peaks at 240 °C for 3 K/min, 260 °C for 10/min, and 280 °C for 50 K/min. Peak hardness decreases with a higher heating rate. Further heating to higher temperature (max. 320 °C) decreases the hardness.

**7.1.1.2. Linear heating vs. isothermal ageing**

Isothermal ageing was also performed on as-quenched (AQ) samples at various temperatures for same times needed to reach such temperatures by linear heating, which can be described as 

\[ t_{iso} = \frac{t_{LH}^{target} - 20 \degree C}{\phi} \]

with \( \phi \) the heating rate. The hardness curves of such ageing treatments are also presented in Fig. 7.1 in comparison with ageing by LH. According to the hardness after
ageing, the plots can be divided into four regimes. In regimes I and III, hardness obtained by isothermal ageing is higher than by LH, while the opposite is observed in regimes II and IV. The transitions between the regimes are delayed to higher temperature with increasing heating rate.

![Graphs showing hardness for different heating rates](image)

**Fig. 7.1.** Hardness of the AQ samples after LH (solid) to a target temperature or after isothermal ageing (open) for the same time at the terminal temperature of the linear heating. Time taken for LH or isothermal ageing is indicated in the upper axis. Heating rates are 3 K/min in (a), 10 K/min in (b), and 50 K/min in (c).
7.1.1.3. Linear heating of NA and PA samples.

Samples are pre-aged into four different states, namely natural pre-ageing for 60 min (NA 60), PA at 100 °C for 60 min (PA 100/60), PA at 120 °C for 60 min (PA 120/60), and PA at 160 °C for 10 min (PA 160/10). The hardness of these pre-aged samples during LH are given in Fig. 7.2. For the NA 60 samples, hardness starts from ~50 HBW and increases during ensuing LH until a plateau is reached, similar to the behavior of the non-pre-aged samples (Fig. 7.1b). The differences lie in the later stage that hardness for NA 60 slightly decreases after heating to 180 – 220 °C while there is pronounced hardening for non-pre-aged sample during LH in the same temperature regime. The peak hardness is also lower for NA 60 sample than non-pre-aged sample.

PA at higher temperature (100 °C to 160 °C) diminishes the initial hardening during LH, which is seen as only marginal hardness enhancement by LH up to 160 °C. Subsequent ageing hardens the samples significantly until the peak is reached at 240 °C. For these three PA conditions, peak hardness is seen higher as the PA temperature increases.

Fig. 7.2. Hardness of the various pre-aged samples during linear heating at 10 K/min. AQ curve is the same as Fig. 7.1b and shown for comparison.
7. Characterisation of clustering and precipitation during linear heating

7.1.2. DSC

7.1.2.1. Directly after quenching

DSC traces of the AQ samples under various heating rates are presented in Fig. 7.3a. Measurements were performed from 0 °C for 3 K/min and 10 K/min, and -70 °C for 50 K/min, but the curves are displayed from 20 °C, where a pronounced signal is seen to start. Notation of the exothermic peaks and endothermic troughs are kept consistent with Fig. 4.5. It is seen that exothermic peaks a – c are all delayed to higher temperature as heating rate increases. In particular, the size of peak a decreases with a higher heating rate. Moreover, an endothermic trough e can be identified in the curve of 50 K/min but not for other heating rates.

![DSC traces](image)

Fig. 7.3. DSC traces of samples (a) in the AQ states heated at various rates, (b) in various pre-aged states heated at 10 K/min. Curves for PA states at intermediate temperatures are taken from Fig. 4.5. All curves are normalised by heating rate.
7.1.2.2. After NA and PA

Fig. 7.3b shows DSC curves after the same NA and PA treatments as introduced previously in Fig. 7.2 for hardness measurements after LH. The DSC traces show an exothermic peak \( a \) for sample NA 60 but not for other pre-aged samples. The same applies for the endothermic trough \( e \). Peak \( b \) is positioned at much lower temperature (~220 °C) for samples PA 100/60, PA 120/60, and PA 160/10 than for sample NA 60 (~254 °C). Peak \( c \), which appears to be similar for PA samples, is lower for NA 60.

7.1.3. Electrical resistivity

The electrical resistivity of a sample during linear heating was measured \textit{in situ} and the temperature contribution to resistivity was corrected following the method described in Sec. 3.3.4. Besides, in order to minimise the measurement errors between different samples, especially the error caused by cross section and length measurement, we normalised the resistivity by assuming the resistivity at 20 °C always being 3911 nΩ cm as given in Sec. 4.1.2. The details of such normalisation are archived in Appendix C1. Fig. 7.4 displays the resistivity change during LH before and after the linear correction of the phonon resistivity \( \Delta \rho \) (i.e. the residual change due to microstructural evolution). \( \Delta \rho = 0 \) applies for all curves before LH starts. Under a heating rate of 3 K/min, \( \Delta \rho \) first increases and peaks at 80 °C, after which it drops slightly and reaches period where \( \Delta \rho \) is almost stable. From 160 °C, resistivity starts to decrease slowly and then rapidly when temperature reaches 200 °C. An almost linear decrease is observed up to ~240 °C, which is then followed by a kink and another rapid decrease. The curve for 10 K/min shows a similar trend but a lower initial peak and delayed decreasing stages. The initial peak is not pronounced under a heating rate of 50 K/min. \( \Delta \rho \) increases for all curves at the end stage in the shaded area, where the linear ‘baseline’ differs from the resistivity change during the second heating (see Sec. 3.3.4).

7.1.4. PALS

Positron lifetimes during NA after quenching or during NSA after various LH pre-treatments are given in Fig. 7.5. Note that the lifetimes measured during NA in the AQ sample are systematically lower (~3 ps) than previously presented in Chap. 4 and Chap. 6, which should be attributed to different source corrections or spectrometer offset (Appendix, C2), which plays only a minor role here because the same applies to all curves. Compared with the AQ sample,
the positron lifetimes after LH are different and their evolution during NSA varies. Generally, lifetimes evolution during NSA is small for almost all the samples, but the evolution is slightly larger and the lifetimes are more converged for samples heated with higher rates. For samples heated only to 60 °C, an increase (max. 5 ps) can be observed in the initial stage which later vanishes. Such increase is most pronounced in sample heated at 50 K/min.

Fig. 7.4. Resistivity change during LH after linear correction of resistivity contribution due to temperature. Shaded area is where the temperature-dependent resistivity change is off the linearity.
Fig. 7.5. Single-component positron lifetimes in the AQ sample during NA and in samples during NSA after LH at various heating rates to certain temperatures. Label ‘x_y’ refers the sample heated to x °C at y K/min.
The lifetime evolution during LH can be approximated by collecting the first lifetimes measured after LH as presented in Fig. 7.6. For all three heating rates, the lifetime during LH first decreases when temperature is below 220 °C, after which lifetime recovers back and eventually after heating to 300 °C above the initial lifetime. The first decrease before 220 °C seems to contain three stages, namely a rapid drop during heating to 60 °C, a more stable period with only slight lifetime decrease between 60 °C and 180 °C, and another obviously decrease from 180 °C to 220 °C. The amplitude of the decrease and re-increase seems to be smaller for 50 K/min than the other two heating rates.

![Fig. 7.6. Positron lifetimes during LH (obtained after NSA for 5 min). The first point corresponds to the lifetime after NA for 5 min without any LH pre-treatment. Different colours represent various heating rates.](image)

### 7.2. Discussion

#### 7.2.1. Overview of the processes during LH

It has been demonstrated that microstructural changes can be detected by various methods. An overview of all relevant properties is demonstrated in Fig. 7.7. Apart from the DSC heat flow, hardness, resistivity change, and single-component positron lifetimes shown already in Fig. 7.1 – Fig. 7.6, integrated heat flow from 20 °C provides another measure for the progress of the phase transformation. One issue worth addressing is that DSC measurements all start from below 20 °C, so that the influence of the initial instability of the device on DSC signals can be
well separated. However, all other techniques were performed on samples which were linearly heated from ~20 °C. Although the DSC traces start to show observable peaks only from ~20 °C or above, it is still not clear whether the period below 20 °C will bring an influence on the course of the traces. Therefore, another independent measurement starting from 20 °C was conducted to compare with the one currently shown in Fig. 7.7a (Appendix C3, Fig. SC3). It is demonstrated that heating from 0 °C produces almost the same curve as from 20 °C but not with the initial peak influenced by the unstable device. Thus, DSC results and the corresponding integrals can be used for correlation and comparison with other measurements.
7. Characterisation of clustering and precipitation during linear heating

Fig. 7.7. Overview of the evolution of all properties during LH at (a) 3 K/min, (b) 10 K/min, (c) 50 K/min. Different stages are separated by vertical lines. Horizontal dashed lines mark the zero levels of the corresponding measures.

The course of the DSC curve separates the graph into 5 stages. In order to distinguish these from the ones introduced in Fig. 7.1, arabic numbers 1 – 5 are used here. In the following, we will discuss the microstructural features in each of stages 1 – 4 separately based on the evolution of the properties. Stage 5 is not discussed since the DSC baseline correction in this stage is not reliable.

**Stage 1:**

A pronounced DSC heat flow peak characterises stage 1. It is generally accepted that this peak is correlated to clustering phenomena [15, 39], and some have reported that it could consist of more than 1 peak [16, 20, 52]. Since DSC measures the total heat of all reactions in the material, it cannot be ruled out that two or more clustering peaks coexist and are so close together that they virtually have merged into one peak, but for simplicity we do not distinguish these details. The clustering peak at low heating rate is much larger than that at high heating rate, analogous to hardness change, which increases in this stage synchronously with DSC heat integral. The relationship between these two properties will be further discussed in Sec. 7.2.3. During cluster formation, the electrical resistivity first increases and then slightly decreases before the peak ends, which is clearly seen for both 3 K/min and 10 K/min. The initial increase of resistivity is
found to increase approximately linearly with the heat produced by clustering (Fig. 7.8). The offset marked by the arrows between the two curves might be caused by a very small baseline drift in the DSC curve. This ‘anomalous’ resistivity increase was interpreted as caused by the formation of solute clusters which scatter the conduction electrons most at a critical size [137], with solute depletion in matrix also taken into consideration. This critical size in Al-Zn alloy was found to be ~10Å by X-ray small-angle scattering [138] at the resistivity maximum and independent of the ageing temperature [139], but no such data is available for the Al-Mg-Si system. Nevertheless, since this resistivity anomaly appears in the initial stage of ageing at a wide range of temperatures (Fig. 4.4, Fig. 5.4 and in Ref. [59, 65]), it can be assumed that as long as new clusters are formed, their sizes always start from below the critical size and then increase to above the critical size during further ageing, thus causing the ‘anomalous’ resistivity increase. Therefore, the decrease after the maximum of resistivity change during LH (Fig. 7.7) in stage 1 indicates a process of growth or coalescence of the clusters formed at lower temperatures. Some new clusters might still be formed or some previously formed low temperature clusters might dissolve at higher temperature, but these alone are not able to cause the DSC exotherm and resistivity decrease at the same time.

In stage 1, the positron lifetime decreases significantly to a level of 220 ps – 222 ps. Interestingly, this has been almost accomplished already after heating to 60 °C (or even lower, but undetected) regardless of the heating rate and thus also time. In particular, the cluster formation, if approximated to be proportional to the DSC heat emitted, during heating at 50 K/min to 60 °C is rather small (Fig. 7.7c), as also supported by the small hardness and resistivity increase. The reasons for positron lifetime to decrease in such a early stage and at low temperature, if we simply compare it to NA, can be formation of clusters or loss of excess vacancies, both of which are time-dependent, i.e. longer time promotes both processes. In the samples heated by 3 K/min and 10 K/min, there is a strong clustering peak. The positron lifetime decrease can be largely attributed to positrons trapped in clusters, but it seems hard to explain the similar positron lifetime in the sample heated to 60 °C at 50 K/min because the clustering there is not very pronounced. Therefore, either (i) positrons are so sensitive to the clusters that just a small fraction of the clusters (50 K/min) will saturate the positron trapping, or (ii) this lifetime drop is more dominated by the vacancy loss. The lifetime reincrease in the early stage of NSA for sample ‘60_50’ is similar to that found for the slow quenched condition (Fig. 6.7) which, as discussed in Sec. 6.2.3.1, is not fully understood, but should be related to clustering, because such increase is not observed in Al-Mg alloy (Fig. SB5). This similarity
suggests that for 50 K/min the assumption (ii) is more likely, i.e. the initial lifetime drop is mainly caused by vacancy loss. Further clustering during heating changes lifetime only marginally, because the specific positron lifetime in clusters are quite similar to the current value.

**Stage 2:**

Properties in stage 2 behaves quite similarly for 3 K/min and 10 K/min but different than for 50 K/min. The main difference is that an endothermic trough is observed in the curve for 50 K/min, while in the same stage only a small bump but no endotherm is observed for 3 K/min and 10 K/min. It is not so likely that this is a baseline correction error because other properties also seem to show a difference between the heating rates. For instance, hardness continuously increases in stage 2 for 3 K/min and 10 K/min but has halted during 200 °C – 240 °C for 50 K/min. From the resistivity-DSC integral plot (Fig. 7.8), it is seen that the resistivity decreases moderately for both 3 K/min and 10 K/min but much stronger for 50 K/min. Some DSC curves in the literature also show in the same stage a clear endothermic trough [16, 20, 102, 107, 140], whereas some do not [15, 19, 100]. Alloys used in different literatures are always different, which probably explains the discrepancies. However, in the current study, this should not be the case as we are investigating the same alloy. As mentioned above, DSC might be a complex of multiple simultaneous reactions. For example, if exothermic precipitation and endothermic dissolution occur at the same time and precipitation is stronger, the dissolution trough can be hidden. However, if significant precipitation and dissolution of clusters occurred in parallel, a higher resistivity decrease would be expected similar to that in stage 3 instead of just a marginal reduction as observed. Therefore it is more likely that the clusters formed at low temperature under slow heating rates are mostly stable so that few of them dissolve in this stage. The slow evolution of them causes the small exotherm in that regime. This also points to a conclusion that clusters formed at different heating rates behave differently during heating. Positron lifetime decreases slightly in this regime, but little difference is shown between different heating rates, just the evolution corresponding to faster heating (50 K/min) is delayed to higher temperature.

**Stage 3:**

In stage 3, a strong precipitation peak can be seen. This peak is generally considered as formation of β" precipitates [15, 39]. Resistivity decrease and hardness increase are both
significant in this stage. The obvious asymmetric structure at 3 K/min indicates that there are superposed peaks. This has been also pointed out by Ref. [15] by fitting it with two symmetric peaks. This feature is also observed when PA at intermediate temperature is carried out (Fig. 7.3), and the double-peak structure is more obvious with decreasing heating rate. Therefore, it is very likely that slow heating and PA have a similar effect on this double-peak structure. It was claimed that the double-peak structure correspond to two paths of β" phase formation [12]. Our DSC measurements (Fig. 4.5 and Fig. SA4) show that PA promotes the first subpeak while NSA promotes the second. Therefore, it can be also postulated that heating at low rate (3 K/min) there is a stronger pre-precipitation, sometimes named differently, such as GP zone formation [128]. This is reflected by the positron lifetimes that are ~210 ps – 212 ps at the position of the first subpeak, similar to values given in the literature [128, 141]. However, this low value is not observed for 50 K/min, indicating that such process is missing or very weak. If we associate this phenomenon with the cluster behaviour in stage 2, it is postulated that some stable clusters after stage 2 might further evolve and eventually cause this subpeak. Positron lifetime after the full peak shows a very high value (~225 ps for 3 K/min and 10 K/min, ~230 ps for 50 K/min). Such a high value indicates that the precipitates contain a high fraction of open volume [71, 141], possibly due to semi-coherent or incoherent interfaces. Different to what is considered to have caused their high lifetimes (β' phase), we believe that in our case the majority are still β" precipitates, but probably they are sparse and large so that open volume such as dislocations set in to compensate the strain energy.

**Stage 4:**

In this stage, formation of β' or B' phases is expected according to Ref. [15, 39]. These precipitates show even higher positron lifetimes due to a higher extent of semi- or in-coherency. Resistivity continues to decrease due to further matrix depletion and coarsening of the precipitates. Hardness also shows a continuous decrease, indicating that they are fewer and coarser strengthening phases.

In summary, the course of the property evolution during the LH reflects a complex of various processes. Slow heating and fast heating behave very differently already from the beginning, and the influence lasts even to the high-temperature regime.
7. Characterisation of clustering and precipitation during linear heating

Fig. 7.8. Resistivity change as a function of DSC integral in various stages. Resistivity curve for 50 K/min was firstly smoothed (Appendix C4, Fig. SC4) before plotting. Dashed lines in each plot shows the linearity during the evolutions. LH proceeds towards a higher integrated DSC value, except for 50 K/min in stage 2, as pointed out by the arrow 2. Data for 50 K/min in stage 4 was not plotted due to the DSC baseline issue.

7.2.2. Comparison between LH and isothermal ageing

Fig. 7.1 compares the hardness after ageing by LH and same time isothermal ageing at the end temperature of LH. Four regimes are shown separated by crossovers of hardness curves. In each regime, there are maybe more than one possible process, and it is probably more complicated from one regime to another. Therefore we will be discussing primarily based on conditions where the largest differences are shown in each regime. On the crossover points should be the transition of the different dominated mechanisms in adjacent regimes. We firstly analyse regimes III and IV, where the relationships are easier to understand, then regimes I and II will be analysed.
In regime III, hardness is higher for isothermal ageing than for LH. In this temperature regime for isothermal ageing, $\beta''$ formation would be expected. During LH, as indicated by DSC, $\beta''$ formation is not yet initiated. As the most strengthening precipitates, more formation of the $\beta''$ precipitates should result in a higher hardness. A longer time at high temperature and less formation of clusters at low temperature which normally cause ‘negative effect’ should be the reason for more formation of $\beta''$ precipitates during isothermal ageing.

In regime IV, LH produces a higher hardness than isothermal ageing, which can be caused by three reasons. First, the highest difference occurs at $\sim 250 ^\circ C$ or higher, at which it has been reported that $\beta'$ precipitates directly form $[48, 142]$. Such precipitates are sparse and large, thus contributing less to strengthening than $\beta''$. During LH, the DSC curve shows that regime IV is generally during the peak $\beta''$ or after the peak. Thus, the phases in the regime IV could differ. Second, ageing at high temperature in regime IV might be ‘positively’ influenced by the clusters formed during lower temperature. Such phenomenon has been reported in several works $[48, 72]$. The reason, however has been discussed differently. Pogatscher et al. $[72]$ argue that it is due to the release of trapped vacancies in clusters, while Liu et al. $[48]$ explained it as the reversal of precipitation pathway. The third reason is the time of ageing at higher temperature. In regime III, a longer time at higher temperature contributes to higher strengthening because generally it is still in the underaged state due to low temperature and short time. However, kinetics are much faster at high temperatures and the ageing time in regime IV might result in an overaged state. For example, it takes 30 min in the same alloy to peak-age at $250 ^\circ C$ $[141]$, which is much shorter than the time used for LH to reach $250 ^\circ C$ at $3 \text{ K/min}$. In this case, shorter time at higher temperature favours a higher hardness. Altogether, a higher hardness by LH can be explained.

In regime I, isothermal ageing results in a slightly higher hardness. It is known that clustering prevails in this temperature regime. If we assume an activation energy $E_a$ for this process, then the rate of clustering $\dot{\alpha} \propto \varphi(\alpha) \exp \left( - \frac{E_a}{kT} \right) c_{\text{vac}}(t)$, with $c_{\text{vac}}$ the vacancy site fraction, which is very high after quenching and early stage ageing. $\varphi(\alpha)$ is related to solute supersaturation which should be similar for LH and isothermal ageing as they start from the same state and solute consumption during ageing is small. During LH, $\exp \left( - \frac{E_a}{kT} \right)$ should be smaller than the isothermal counterpart as the temperature is always lower before the final temperature is reached. The vacancy site fraction during LH should be higher than during isothermal ageing as the annihilation is expected to be faster at higher temperature. The final result depends on
Clustering in regime II is rather complicated as clustering in this regime might involve two types of objects having two different kinetics. Haase et al. pointed them out by showing two peaks in the iso-time hardening curves (Fig. 2 in [143]). APT by Serizawa et al. [52] showed that not only the chemistry but also the growth kinetics are different between the two clusters, called cluster(1) and cluster(2). Therefore, a simple analytical model as discussed for regime I above would be not suitable to solve the complex case, especially for LH. Alternatively we choose an indirect approach to compare the differences between low-temperature and high-temperature ageing and their consequences on LH. For this, DSC curves in four different conditions are compared, as given in Fig. 7.9. These curves have already been introduced in Fig. 7.2, Fig. 7.3, and Fig. 4.5, but here we just show the clustering peak. It is found that: 1) PA 100/10 eliminates the clustering peak; 2) NA 60 causes larger clustering peak than in the AQ condition; 3) the clustering peak arises again after applying some NSA after PA. It is worth noting that NA 60 and PA 100/10 reach a similar hardness of ~50 HBW. Therefore, that the clustering peak for NA 60 is pronounced but not for PA 100/10 points to the conclusion that vacancies are eliminated faster at PA temperature. More interesting are findings 2) and 3), where the amplitude of the clustering peak increases after NA/NSA. As both the available solutes and vacancies should be less after NA/NSA clustering, it must be that the clusters formed at low temperature (NA) have enhanced the clustering during ensuing LH. Such a mechanism could be attributed to the growth of theses clusters formed at low temperature. Therefore, we found at least two mechanisms which could explain why LH results in higher hardness than isothermal ageing, namely less annihilation of vacancies and the growth of clusters formed at low temperature.
Fig. 7.9. DSC curves of the AQ sample and various pre-aged samples.

7.2.3. Linear property changes

During linear heating, many properties were found to change linearly with the DSC heat integral. If we assume that the DSC heat integral is approximately proportional to the volume fraction of the phase formed, the proportionality factor of which might vary with different phases, then we can correlate the volume fraction of formed phase and the corresponding property change during LH. For instance, Fig. 7.10a plots the hardness increase during clustering peak in stage 1 and also in stage 2 before reaching the endothermic trough (only for 50 K/min) in a function of the integrated DSC heat flow. The linearity fits for all heating rates and also for samples naturally aged. This observation agrees with the short range order strengthening model proposed by Starink at al [109] that cluster strengthening is proportional to the volume fraction of the clusters.

The formation of $\beta''$ can also be shown in an approximately linear relationship, but only before the maximum is reached (Fig. 7.10b). PA samples in this case were used to avoid the formation of clustering. Since $\beta''$ should be energetically more stable than clusters, the higher fitted slope for $\beta''$ than clusters (Fig. 7.10a) points to a higher strengthening effect of $\beta''$ precipitates.

Apart from hardness, linearity was also observed for the resistivity change during linear heating in various stages (Fig. 7.8). Although not the whole curve fits to a linear relationship, it is still an interesting feature as it primarily occurs when the rate is the highest in that stage. The
correlation between the microstructure and the corresponding property change behind these linearities are currently not fully understood and probably can be further investigated in the future. Nevertheless, these findings are still useful as an empirical description of the property relationships.

Fig. 7.10. Hardness increase as a function of DSC integral (a) during the clustering peak, (b) during the β” formation peak in PA samples. Integration of the DSC heat flow is always performed from 20 °C to a end value.

7.3. Conclusions

We developed a device to perform linear heating (LH) on samples with various geometries, which was previously only achievable by DSC. Multiple indirect methods were used to follow the microstructural evolution during LH at various heating rates as well as after pre-treatments. Following conclusions can be drawn.

- Phase evolution at different heating rates is very different, especially for the highest heating rate applied (50 K/min). The differences are already found in the initial clustering stage and also at higher temperatures. It is very likely that the variations in the high-temperature regime are correlated to the clustering at lower temperature.
- It is suggested that clusters formed during slow heating (3 K/min and 10 K/min) in our alloy are mostly stable so that they can further evolve during ensuing heating, but the clusters formed during fast heating (50 K/min) are less stable and will partially dissolve.
- LH can result in a higher or lower hardness compared with isothermal ageing for the same time, depending on the temperature, at which LH ends and isothermal ageing is conducted.
In particular, regime II shows that LH results in higher hardness, which is considered to be due to lower vacancy loss and/or growth of clusters formed at lower temperature regime. Such growth of clusters mechanism are also observed in LH of other ageing conditions.

- Linearities are found during LH between the hardness change and the DSC integral as well as between resistivity change and DSC integral.
8. Summary

Solute clustering and precipitation during multi-stage ageing in a commercial AA6014 alloy are systematically investigated in this study, covering 1) the role of pre-ageing (PA) in multi-stage ageing treatments, 2) the influence of quench rate on multi-stage ageing treatments, 3) the clustering and precipitation behaviour during linear heating, all by means of various characterisation methods including hardness testing, transmission electron microscopy, electrical resistivity measurements, thermoanalysis, and positron lifetime measurements. Conclusions corresponding to each specific study are stated at the end of chapters 4 – 7. Here, the most general findings pointed out in various chapters are summarised:

1) Direct vacancy annihilation alone cannot explain the excess vacancy evolution during natural ageing (NA or NSA). This has been demonstrated by the NA kinetics after various quenches or by the NSA kinetics after various PA treatments. Other mechanisms such as vacancy clustering and vacancy trapping by clusters must play a role in the reduction of vacancies.

2) During multi-stage ageing, clusters formed in early stages play a very important role in later stages, not only in a direct manner by transforming to precipitates, causing e.g. different PB hardening effects after PA at different temperatures but also indirectly by influencing the vacancy evolution by vacancy trapping, which regulates the mobile vacancy site fraction by repartitioning the total vacancies (quick process) and buffering vacancy annihilation and generation (slow process).

Besides, the current study shows a way to improve industrial PA strategies and demonstrates that the behaviour of samples during multi-stage ageing under simulated industrial conditions is similar to that of samples processed by water quenches with just slightly inferior PB hardening. Industry might benefit from the current study to design better processes and improve the alloy properties.
Appendix A

Supplemental material to the effect of PA to NSA and PB hardening

A1. Additional hardness data

Fig. SA1 – SA3 show the hardening of the alloy during NSA and after subsequent PB for alloys that have been pre-aged under different conditions.

The curves in Fig. SA1a–h are analogous to those in Fig. 4.3a,e, just that PA conditions differ. Fig. SA1i-n correspond to Fig. 3c,g.

![Graphs showing hardness changes over NSA and PB time]
Multi-stage ageing in an Al-Mg-Si alloy

Fig. S1. (a, c, e, g) Hardening curves during NSA after PA at various temperatures for various times. (b, d, f, h) Hardnesses after additional PB. (i, k, m) Comparison of NSA after PA to other hardnesses than those given in Fig. 4.3(c) of Chap. 4 (60 HBW). (j, l, n) Displays hardnesses after additional PB.

Fig. SA2 displays hardness after PA and NSA as a function of PA hardness. A continuous evolution from short NSA time to long NSA time is seen. NSA hardness increases first in the low PA hardness regime and at high PA temperature regime.

Fig. SA3 corresponds to Fig. SA2, just that a final PB was carried out. The final PB hardness changes most after the first week of NSA in the low PA hardness regime.
Fig. S4.2. Hardness after NSA as a function of PA hardness and temperature. Different graphs correspond to different NSA times. f) is identical to Fig. 4.3d in Chap. 4.
Fig. SA3. Similar to Fig. SA2 but with additional PB. f) is identical to Fig. 4.3h in Chap. 4.

A2. Additional DSC measurements

Fig. SA4a – c shows DSC traces of alloys pre-aged at 100 °C for 60 min, 240 min, and pre-aged at 120 °C for 60 min and then NSA for various times. The trends of the DSC curve evolution for increasing NSA time are similar, just that the influence of the same NSA time on the DSC curve is dependent on PA condition. The heat content for clustering during ageing (PA and/or NSA) can be estimated by $\Delta H_{\text{ageing}} = H_{AQ} - H_{\text{after ageing}}$, where $H$ is the
integrated DSC heat flow from $T_a$ to $T_e$, $H = \int_{T_a}^{T_e} \frac{dQ}{dt} dT$. $T_a$ is the temperature before the first reaction begins, and $T_e$ the temperature at which equilibrium is reached, e.g. above the solution heat treatment temperature. However, as pointed out by Esmaeili et al. [19, 144], due to a high baseline drift in the higher temperature regime, a lower $T_e$ can also be chosen as long as all relevant precipitation/dissolution peaks are covered within the temperature range. We choose $T_a = 50 ^\circ C$ and $T_e = 315 ^\circ C$ because DSC curves before $T_a$ and after $T_e$ are converged. $H_{AQ}$ is constant, thus $H_{after\ ageing} = \Delta H_{ageing} + H_{AQ}$. Fig. 4.8 shows hardness plotted as a function of the DSC integral for samples pre-aged and subsequently naturally aged (in cases where DSC and hardness were both measured). A linear relationship is seen although with some fluctuations possibly due to different samples and possibly some baseline drift. If the heat signal is assumed to be proportional to the precipitated volume the latter is also proportional to hardness after NSA.
Multi-stage ageing in an Al-Mg-Si alloy

Fig. SA4. DSC traces of samples PA a) at 100 °C for 60 min, (b) 240 min, (c) PA at 120 °C for 60 min with and without ensuing NSA.
A3. Retardation factor from resistivity measurements

Retardation factors were determined using hardness curves and collapsing them into one master curve by normalising the NSA time with $\theta^{-1}$. As electrical resistivity is more sensitive to clustering than hardness, it might detect earlier changes during NSA. Fig. SA5 shows the data of Fig. 4.4d on a linear time scale. A linear increase is found at the beginning of NSA with almost no incubation time. Thus the retardation factor can be calculated from the slope of the initial resistivity increase [71]. Here relative retardation of PA 80/480 to PA 160/10 is 12, which is larger than the value obtained from hardness ($R_\theta \approx 3$) but still smaller than the ratio between PA equilibrium vacancy site fractions ($R_c \approx 58$). This underlines the importance of PA clusters in determining the mobile vacancy site fraction and strengthen the arguments in Sec. 4.2.2.2. The main conclusions remain the same.

![Fig. SA5](a) (a) Same as Fig. 4.4d but plotted with linear NSA time. (b) the initial linear increase stage of PA 80/480 and PA 160/10. Curves in (b) have been smoothed by filtering artefact data points (sudden drops [145]) and averaging every 5 points.

A4. Possible other cluster strengthening mechanism

PA clusters formed at different temperatures but yielding the same hardness were assumed in Sec. 4.2.2 to consume the same fraction of solute supersaturation. Now we discuss if clusters formed at different temperatures have a different strengthening effect. The ‘Weak obstacle’ model [34, 146, 147] assumes a relationship between hardness increase and fraction of solute clusters, $\Delta \mathcal{H} \propto \sqrt{\alpha} \cdot \sqrt{r}$ with $r$ the radius of solute clusters. Since clusters formed at higher temperature have on average a larger radius [53], a smaller fraction of solutes is consumed when the same hardness is reached by PA at higher temperature. As a consequence, the
retardation factor ratio will be smaller than the one following from Fig. 4.10 if the same solute fraction has to be consumed at different PA temperatures. This does not affect the main conclusions of the work.

A5. Fitting hardness data by various kinetic models

We attempted to obtain kinetic parameters by fitting the hardness data during NSA, $\mathcal{H}(t)$, by two known functions. We present them here although none of these attempts yielded consistent kinetic parameters to illustrate the difficulties involved. The problems encountered are:

- The function does not represent the data well
- Representation is good but the use of too many parameters makes usage of function questionable.

<table>
<thead>
<tr>
<th>Function</th>
<th>parameters</th>
<th>function $\mathcal{H}(t) =$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Single Avrami [148]</td>
<td>$\mathcal{H}_0, \mathcal{H}_1, k, n$</td>
<td>$\mathcal{H}_0 + (\mathcal{H}_1 - \mathcal{H}_0)\left[1 - e^{-kt^n}\right]$</td>
</tr>
<tr>
<td>2 Starink-Zahra [117]</td>
<td>$\mathcal{H}_0, \mathcal{H}_1, k, n, \eta$</td>
<td>$\mathcal{H}_0 + (\mathcal{H}_1 - \mathcal{H}_0)\left{1 - \left[\left(\frac{kt}{\eta}\right)^n + 1\right]^{-\eta}\right}$</td>
</tr>
</tbody>
</table>

Function #1 does not yield satisfactory fit results and the values for the Avrami-coefficient $n$ are unrealistically low in some cases ($n = 0.5$ for 10 min NA), see Fig. SA6a. For longer PA times $n \approx 1$ is found. The conditions for JMAK are not fulfilled in our case because the vacancy fraction is continuously decreasing, which is why use of the JMAK model is questionable.

By enforcing $n = 1$ for all the fits we obtain a rate constant $k$ that can be compared to the retardation factor $\Theta^{-1}$ (Figs. 7 and 8 in [118]). We see that the general course is the same but $k$ tends to be larger than $\Theta^{-1}$ by a factor up to 5.
Fig. SA6. (a) Fit with Function #1. (b) comparison of rate constant \( k \) obtained by fitting with constant Avrami index \( n = 1 \) and retardation factor obtained in [118].

Fig. SA7 shows that function #2 fits the NSA curves quite well. However, the parameters obtained do not vary in a continuous way, indicating over-determination of the function (too many parameters).
The same applies to a double-stage JMAK function, i.e. a generalisation of Function #1 with two \( k \) and \( n \) parameters and a weight factor for the two contributions, leading to 7 free parameters. This allows for a good fit but not to derive meaningful parameters (fit not shown).

### A6. Modelling of NSA clustering consider excess vacancy annihilation and vacancy trapping by NSA clusters

In the main text of the current work (Sec. 4.2.2.2), we showed that NSA hardening is delayed after applying PA, and especially, to different extents when PA temperature varies while keeping PA hardness constant (as long as >55 HBW). NSA kinetics is faster after PA at higher temperature (for a shorter time) than at lower temperature (for a longer time), with a factor of \(~3\) for PA at 160 °C and 80 °C, whereas the equilibrium mobile vacancy site fraction at 160 °C is \(~58\) times higher than at 80 °C.

Here we discuss whether such discrepancy can be explained by vacancy losses due to annihilation at sinks or vacancy trapping in NSA clusters (Zurob’s model [93]). The kinetic master equation (Eq. (4.1) in the main text) is simplified here to Eq. (SA1) using \( \alpha_{NSA} \) to

---

Fig. SA7. Fitting using Function #2.
represent the relative fraction of total clustered solutes during NSA, and \((1 - \alpha_{NSA})\) as the simple function related to supersaturation, i.e. \(\varphi \equiv 1\). Since we have a non-equilibrium excess vacancy site fraction, which is influenced concurrently by annihilation kinetics and trapping, we solve the master equation numerically instead of analytically.

\[
\frac{d\alpha_{NSA}}{dt} = a \times (1 - \alpha_{NSA}) \times c_{vac}(t).
\]  

(SA1)

**Vacancy annihilation during NSA**

Two excess vacancy annihilation models were found in the literature, proposed by Schulze et al. [87, 88] and Fischer et al. [78] respectively. Schulze’s model assumes that the annihilation rate of vacancies is proportional to the excess vacancy site fraction to a power of \(q\) (Eq. (SA2), where \(q = 1\) is the most simple case [87]), while Fischer’s model gives an annihilation rate in Eq. (SA3) if we consider only annihilation at dislocation jogs and no hydrostatic stress. \(b_1, b_2\) are both constants governing kinetics. For both models, the difference between the vacancy site fractions after PA at 160 °C and 80 °C starts with ~58 at the beginning of NSA and gradually goes to 1 during NSA, as illustrated in Fig. SA8. The difference between the two models is Fischer’s model eliminates the vacancy discrepancy faster than Schulze’s model \((q = 1)\). Thus, Fischer’s model will be used in the following discussion.

\[
\frac{dc_{vac}(t)}{dt} = b_1 \times (c_{vac}(t) - c_{vac}^{eq})^q
\]  

(SA2)

\[
\frac{dc_{vac}(t)}{dt} = b_2 \times c_{vac}(t) \times \ln\left(\frac{c_{vac}(t)}{c_{vac}^{eq}}\right)
\]  

(SA3)

**Fig. SA8.** (a) Schematic evolution of vacancy fraction during NSA after PA at different temperatures. \(b_1\) and \(b_2\) are adjusted to produce similar annihilation kinetics after PA at 80 °C by both models. Fischer’s model gives much faster annihilation after PA at 160 °C. (b) Ratio of the vacancy site fractions during NSA after PA at different temperatures.
Vacancy trapping by NSA clusters

Here we take into account that vacancies are trapped by emerging NSA clusters. One model describing such phenomenon was established by Zurob et al. [93] by assuming that the probability of a trapped vacancy to escape from a cluster is proportional to the Boltzmann weight of the interaction energy between the cluster and the vacancy, which is proportional to the number of solute atoms in the cluster due to the number of successful jumps required to escape from the cluster. If the number of clusters remains constant and just their size increases during NSA, then we can express the mobile vacancy site fraction by Eq. (SA4), where $m$ and $n$ are adjustable constants, and $n$ is negative. Note that this model is based on kinetic arguments, which is different from the thermodynamic approach proposed by Pogatscher et al. [83], although they result in similar equations. Since only mobile vacancies can annihilate, $c_{\text{vac}}(t)$ in Eq. (SA3) has to be replaced by $c_{\text{vac,mob}}(t)$ when vacancy trapping is considered.

\[
\frac{c_{\text{vac,mob}}(t)}{c_{\text{vac}}(t)} = m \times \exp(n \times \alpha_{NA}). \tag{SA4}
\]

Using the above mentioned models, i.e. Eq. (SA3) and (SA4) with $c_{\text{vac}}(t)$ in Eq. (SA3) replaced by $c_{\text{vac,mob}}(t)$, Fig. SA9 demonstrates the simulated kinetics during NSA after PA at two representative temperatures (160 °C and 80 °C) under various vacancy annihilation and trapping effects by changing the adjustable constant parameters. The initial kinetic difference stems from different equilibrium vacancy site fractions at 160 °C and 80 °C (factor 58). This difference remains (weak annihilation or strong trapping) or gets larger, but is not reduced to 3 as obtained from the experiments.
Fig. S49. Schematic representation of $\alpha_{\text{NSA}}$ as a function of $t_{\text{NSA}}$ after PA at 160 °C and 80 °C under various vacancy annihilation and trapping conditions. Stronger trapping: $n$ decreases (more negative). Faster annihilation: $b_2$ increases.
Appendix B

Supplemental material regarding effect of quench rate on multi-stage ageing

B1. Additional TEM images and EDX analysis

(a)  

(b)  

(c)  

(d)
Fig. SB1. (a – d) Bright-field TEM images of samples after (a) AC, (b) AC and AA for 4 h, (c) IWQ, (d) IWQ and AA for 4 h. (e – f) EDX spectrum of the particles shown in (a).

Two types of particles (P1 and P2) can be observed in the as-quenched state AC sample but only one type (P1) can be seen in IWQ sample (Fig. SB1a and c). EDX analysis (Fig. SB1e and f) show that P1 contains Si, Mn, and Fe, which is typical intermetallic particles (dispersoids) in 6xxx alloys. P2 contains mainly Mg and Si, which should be quenched-in precipitates heterogeneously grown on dispersoids. After AA for 4 h (Fig. SB1b and d), needle precipitates can be seen in the matrix. Around dispersoids there are precipitate free zones. The width of these zones is seen larger if quench is slower.

B2. PALS measurements of T2-type quenched samples during NA

Fig. SB2 shows how positron lifetimes evolve at ‘room temperature’ after slow quenches (VC and AC) from 540 °C that were interrupted at a given temperatures (100 °C to 400 °C) by a fast IWQ quench to preserve the configuration. Most curves feature an initially low value of $\tau_{1c}$, a subsequent increase and a merger into a curve that is almost the same for all the experiments including those in Fig. 6.7a. The insets show the data used for the extrapolation to zero NA time on a linear time scale. Fig. 6.8b shows the initial and these extrapolated values. The mechanism of NSA is not discussed in this work because of the lack of a consistent theory.
Fig. SB2. Positron lifetimes $\tau_{1c}$ measured during NA of samples quenched in a T2 fashion as shown in Fig. 3.3 for (a) VC, and (b) AC.
B3. Vacancy site fraction calculation

Calculating vacancy fractions from positron lifetime data usually requires decompositions of lifetime spectra into 2 or more components. In this work, we measure $\tau_{1c}$ only, which, however, is very close to the average positron lifetime that one would calculate from individual components:

$$\tau_{1c} \approx \bar{\tau} = l_0 \tau_0 + l_{vac} \tau_{vac}, \quad l_0 + l_{vac} = 1,$$

where the index 0 refers to the reduced bulk lifetime and '$vac' refers to annihilation in vacancy-related defects. $\tau_{vac} = 245$ ps assumed [149].

By applying an equation of the two-state trapping model [150] we obtain:

$$\tau_0 = \frac{1}{\frac{1}{\tau_B} + \kappa_{vac}},$$

$$l_{vac} = \frac{\kappa_{vac}}{\frac{1}{\tau_B} - \frac{1}{l_{vac}} + \kappa_{vac}},$$

where $\tau_B \approx 160$ ps is the lifetime in defect-free aluminium, and $\kappa_{vac}$ is the positron trapping rate of the vacancy-related defect. A relationship applies between $\kappa_{vac}$ and the site fraction of the vacancies $x_{vac}$:

$$x_{vac} = \frac{\kappa_{vac}}{\mu},$$

where $\mu$ is the positron trapping coefficient of a vacancy in aluminium. Combining Eq.(SB1) – (SB4) eventually leads us to the site fraction of vacancies:

$$x_{vac} = \frac{\frac{\tau_B}{\mu \tau_B} - \bar{\tau}}{\tau_B (\bar{\tau} - \tau_{vac})}.$$  

Using a commonly accepted value for the specific trapping rate in aluminium, $\mu = 250$ ps$^{-1}$ [151], we can calculate the vacancy site fraction from the one-component positron lifetime. Fig. SB3 shows the results, which, however, should not been taken too literally due to the approximations used (mainly the absence of clusters and usage of $\tau_{1c} \approx \bar{\tau}$). The presence of clusters would contribute with a lifetime component around 215 ps and would require fewer vacancies to explain a given $\bar{\tau}$. 


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Fig. SB3. Vacancy site fraction calculated using Eqs. (SB1-SB4) as a function of positron lifetime assuming validity of the positron trapping model for one trap related to vacancies characterised by a lifetime of 245 ps. The upper three arrows correspond to $\tau_{1c}$ (extrapolated to zero NSA) as measured after three quenches, the lower one marks the equilibrium vacancy fraction at 180 °C as calculated from the formation enthalpy and vibrational entropy of mono-vacancies in Al [114].

B4. Positron lifetimes of Al-Mg alloy after T1-type quenches

Fig. SB4 displays the positron lifetime evolution in a binary Al-Mg alloy after quenching. It is the analogue to the measurements in Fig. 6.7. Obviously, very little evolution of $\tau_{1c}$ is observed.
Fig. SB4. Positron lifetimes $\tau_{1c}$ during NA of binary Al-0.5Mg (wt.%) alloy after various T1-type quenches.

B5. AA hardening after NA

Alloy 6014 shows the well-known ‘negative effect’ of NA on AA as AA directly after solutionising and quenching leads to a much faster and eventually higher degree of hardening as AA after 1 week of intermediary NA, see Fig. SB5.

Fig. SB5. Hardening curves during AA directly after IWQ and after NA for 1 week.
Appendix C

Supplemental material to linear heating experiments

C1. Normalisation of electrical resistivity

Electrical resistivity calculated using Eq. (3.1) assumes the thickness of the sample \( h = 0.3 \) mm, the width of the meander \( b = 1 \) mm, the length of the measured part \( L = 349 \) mm, and the cross section \( A = h \times b \). All these quantities are nominal values as manufactured by cold rolling and laser cutting, and do not account for manufacturing errors and differences in individual samples. This error can be minimised by more precise measurements of the geometries for each sample, or alternatively without measuring the geometry but assuming that the resistivity measured in Sec.4.1.2 (3911 nΩ·cm at 20 °C) applies to all samples. The resistivity at any temperature can be represented as Eq. (SC1)

\[
\rho = \frac{u}{u_{20^\circ C}} \times 3911 \text{ n}\Omega \cdot \text{cm} ,
\]

where \( u_{20^\circ C} \) is the voltage of the sample at 20 °C. If room temperature before start is higher than 20 °C, Eq. (SC2) was used to extrapolate the curve to 20 °C.

\[
u_{20^\circ C} = u_0 + u'(20 - T_0) ,
\]

with \( u_0 \) being the voltage before heating up and \( T_0 \) the corresponding temperature. \( u' \) is the temperature coefficient of the voltage which can be obtained by linear fitting of the voltage during the second heating up to 300 °C.

Fig. SC1 shows resistivity during the second ramp obtained without (Fig. SC1a) and with (Fig. SC1b) such normalisation. It is clearly shown that by employing this method differences between various samples are minimised.
Appendix C

Fig. SC1. Resistivity change during the second ramp LH at various heating rates calculated (a) by Eq. (3.1) and nominal geometries of the sample, or (b) by fixing the resistivity at 20 °C and apply Eqs. (SC1, SC2).

C2. PALS lifetime offsets caused by different source corrections

Positron lifetimes during NA in AQ samples were measured many times in this work during 3 years. The lifetimes measured in Fig. 7.5 is observed to be lower than those presented before in Fig. 4.6 and Fig. 6.7. All these curves are now replotted together in Fig. SC2 for a better visualisation. It is seen that the difference between the curves is a systematic offset. It is speculated that this offset is caused by different source corrections as exemplified in Ref. [63] or spectrometer offsets caused by variations of calibrations that are renewed regularly. Although all source corrections were aimed to yield ~160 ps for pure Al, small differences might still occur. As all lifetime analyses in Sec. 7.1.4 were conducted using the same source correction, this does not change the relative positions of the curves on the figures, and thus also the discussions based on the lifetime evolution, just the absolute lifetime values might be slightly different to other experiments batches. Thus, comparison of lifetimes between different experiments with different source corrections should be done with care.
Fig. SC2. Single-component lifetimes during NA in three AQ samples appeared in this thesis. SC1 corresponds to the curve in Fig. 7.5. SC2 corresponds to the curve in Fig. 6.7a, and SC3 corresponds to the curve in Fig. 4.6.

C3. DSC measurements starting from different temperatures

In the main text, DSC curves and the integrals of samples heated from 0 °C and even lower were used to compare the properties obtained by other measurements such as resistivity and hardness.

Here we show in Fig. SC3 the DSC traces of two AQ samples started from 0 °C and 20 °C respectively. Heating rate was chosen to be 3 K/min because the time spent between 0 °C and 20 °C is the longest. It shows that the starting temperature has very limited influence on the DSC curve, especially below 300 °C where the features are of most interest. The small differences can be caused by different samples or baseline correction, which can be ignored. Moreover, the instability of DSC device apparently has influenced the first peak in the measurement with starting temperature 20 °C.
Appendix C

Fig. SC3. DSC measurements of the AQ samples with different starting temperatures.

C4. Smoothing of resistivity curve for 50 K/min

The resistivity change as a function of temperature during linear heating at 50 K/min is much noisier than other two heating rates. The reason for that is the temperature control of our heating device at high heating rate is less precise than other two. In order to minimise the noise, Savitzky-Golay smoothing using 2 order polynomial function with 10 points in each bin was applied, as demonstrated in Fig. SC4. Smoothed curve has a much smaller variation and has kept the main features of the curve.

Fig. SC4. Smoothing of the resistivity change curve using Savitzky-Golay method with 2 order polynomial function and 10 points per fitting bin.
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