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Microscopic aspects of artificial ageing in Al-Mg-Si alloys

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Al-Mg-Si alloys with a low solute content (0.4 %Mg, 0.4 %Si) and higher contents (Mg+Si = 1.4%, all in wt.%) were solutionised, quenched and then artificially aged (AA) at 180 °C, after which positron annihilation lifetime spectroscopy was applied to obtain information about precipitation and vacancy evolution during ageing. Hardness measurements were carried out to complement the measurements of positron lifetime. AA was carried out in four different heating media and allowed for varying the heating rate from 2.4 to 170 K/s. The main result of the study is that there is a competition between vacancy losses and precipitation. The more precipitation takes place before and during AA, the more vacancies are retained and act back on clustering. Higher solute content, slower heating to 180 °C, natural pre-ageing before AA and slower quenching after solutionising were found to have a comparable effect explainable by pre-precipitation before AA.

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1. Introduction

The technologically important 6XXX series of age-hardenable alloys is based on the ternary system Al-Mg-Si. After solutionising and quenching, artificial ageing (AA) at typically 180 °C leads to the formation of a series of metastable precipitates that increase strength. 6XXX alloys are well investigated and the precipitation sequence is known, however, not in all details and not under all circumstances (alloy compositions, multi-stage treatments, etc.) [1]. Even the simplest case – direct AA after quenching – bears some unknown problems. The earliest precipitates are assumed to have the fcc structure of the host metal and to transform later to monoclinic GP zones and $\beta''$ precipitates.
[2-4], but how this happens and how the precipitates grow is not known with certainty [5,6]. Moreover, the role of vacancies in the first stages of AA is not clear. After quenching, the high site fraction of vacancies formed at the solutionising temperature is partially preserved. During AA, excess vacancies anneal out and eventually the vacancy site fraction approaches the equilibrium value at, say 180 °C, but how fast this happens is not clear because vacancy annihilation is influenced by interactions with dislocations and growing precipitates [7]. Solute supersaturation is also a crucial factor since it provides the driving force for precipitation. How it varies during AA is not exactly known.

We intend to contribute to the understanding of the role of vacancies and solutes in the early (but also later) stages of AA. We study very short AA treatments down to 0.3 s and also vary the heating rate from ‘room temperature’ to 180 °C. The main tool employed is positron annihilation lifetime spectroscopy (PALS). This method is sensitive to both vacancies and clusters/precipitates and has been applied previously to explain the NA behaviour in identical alloys [8,9]. Another objective is to specify the pronounced differences in ageing behaviour between lean Al-Mg-Si alloys (Mg+Si≤1%) and more concentrated ones.

We study pure ternary model alloys to keep out possible effects of both common solute atoms such as Cu that might influence precipitation and intermetallic-forming elements such as Fe and Mn that might lower the Si content. Most investigations are carried out on one lean alloy (~0.4% of both Mg and Si, similar to the industrial alloy 6060) and one alloy higher in solute (0.6% Mg, 0.8% Si, similar to the industrial alloy 6005).
2. Experimental

Pure ternary aluminium alloys were provided by Hydro Aluminium (Bonn) as described elsewhere [8,10]. Compositions are specified in the format ‘n-m’, where ‘n’ stands for the Mg, ‘m’ for the Si content in 1/10 wt.% throughout this paper. Alloy ‘4-4’ contains 0.39 wt.% Mg (0.43 at.%) and 0.40 wt.% Si (0.38 at.%), alloy ‘6-8’ 0.59 wt.% Mg (0.66 at.%) and 0.79 wt.% Si (0.76 at%) as determined by optical emission spectroscopy.

Samples of (10 × 10 × 1) mm³ size were prepared for both PALS and hardness measurements. Samples were ground and ultrasonically cleaned with alcohol for clean surfaces. Solution heat treatment (SHT) was performed at 540 °C for 1 h followed by ice water quenching. After quenching, one of the following heat treatments was carried out: (i) Natural ageing (NA) at ‘room temperature’ (RT, 20 ± 2 °C). As the activation energy for NA is of the order of 80 kJ/mol [8], variations within this range can lead to changes of the NA kinetics of ~35%. (ii) Artificial ageing (AA) in one of four different media (see below) followed by measurement at RT. (iii) Natural pre-ageing (NPA) for 5, 30 or 80 min followed by AA, after which measurements were conducted at RT again.

Four different AA media were used to study the influence of the heating rate to 180 °C on precipitation behaviour: (i) Highly thermally conductive and low-melting liquid metal (‘LM’) Bi57Sn43. The Al-Mg-Si samples were kept in motion to ensure faster heating to 180 °C. Hereafter, the sample surfaces were controlled by using optical microscopy and positron annihilation lifetime spectroscopy to rule out a possible influence of a coating after AA in LM. The positron lifetime (PLT) for LM is 240 ps. Such a contribution was not found in any spectrum [11]. (ii) Silicon Oil (‘Oil’) as widely used as AA medium. Samples were also kept in motion during AA. (iii) A molten salt (‘MS’) mixture of 53% KNO₃ + 40% NaNO₂ + 7% NaNO₃ with a low melting point of 142 °C and high operation range [12]. During AA,
the samples were kept in a resting position to obtain a slower heating rate. (iv) Controlled heating plates (‘HP’) heated at an initial rate of 3 K/s. Samples were sandwiched between two aluminium buffer plates to damp temperature oscillations caused by the temperature controller. A 0.5-mm thick thermocouple (‘TC’) was inserted into holes drilled into the edge of test specimens to measure the temperature courses given in Figure 1. The time to reach 170 °C is 0.9 s for LM, which we call ‘fast heating’, 6 s for Oil and 10 s for MS, which we call ‘intermediate heating’ and 63 s for the HP, ‘slow heating’. The corresponding average heating rates up to 170 °C are 170 K/s, 25.5 K/s, 15.3 K/s and 2.4 K/s, respectively.

Almost all positron annihilation lifetime experiments were carried out at the laboratory in Berlin (‘B’). Two identical samples were assembled to a sandwich with the positron source in between and an aluminium foil wrapped around it. This was done either after quenching from SHT or after AA and required about 2 min during which the sample remained at RT. Measurement details are given in Sec. S1. PLT was then measured continuously at RT. Either a one-component lifetime $\tau_{1C}$ was obtained, or decompositions into two components labelled by numbers $\tau_i$ in the order of increasing lifetime, the corresponding intensities $I_i$. As we will later argue that the longer lifetime component contains two (unresolved) components we will adopt the notation $\tau_1$ and $\tau_{2+3}$ for the two components. The former then corresponds to annihilation in the bulk, the latter in solute clusters and in vacancy-related defects. Just in one case, it was measured at the Charles University in Prague (‘P’) at −40 °C using a spectrometer with a higher time resolution [13] in order to slow down ageing kinetics and to be able to collect $>4 \times 10^6$ annihilation events in PLT spectra for a reliable multi-component analysis.

Hardness tests were carried out after a given AA time using a Vickers microhardness tester (MHT-10). The load force was 100 gf and the dwell time 10 s. 10 indentations were averaged for each sample.
3. Results

3.1. Natural primary and secondary ageing

Figure 2 shows the evolution of $\tau_{1C}$ as a function of ageing time at RT for the alloys 4-4 and 6-8 directly after quenching (‘AQ’) and after 100 min of AA and after AA for 1 s in LM for alloy 6-8. The curves labelled ‘AQ’ show multi-stage behaviour comprising an initial decrease from a high value, a re-increase after $\sim100$ (4-4) and 45 min (6-8) and an indication for another decrease for long times [8]. The samples that undergo natural secondary ageing (NSA) after AA behave differently. In Figure 2a, alloy 4-4 starts from a low value of 193 ps, remains constant for $\sim1$ h, after which $\tau_{1C}$ increases. In alloy 6-8, however, $\tau_{1C}$ is constant for 1 day. In Figure 2b, $\tau_{1C}$ increases from the beginning at a high rate in alloy 6-8. For other AA times a varying behaviour is observed which will be described elsewhere. In this paper, we either take the average of the PLT before it starts increasing (Figure 2a) and use it as $\tau_{1C}$ that characterises a given AA or extrapolate to zero NSA time (Figure 2b). Note that $\tau_{1C}$ is not identical to the average lifetime $\bar{\tau}$ as discussed in the Sec. S2 but the two values are very close together so that $\tau_{1C}$ can be safely used.

3.2. Artificial ageing of lean alloy 4-4

One-component positron lifetime. The evolution of $\tau_{1C}$ versus AA time in different heating media is shown in Figure 3a. The black point corresponds to the ‘as-quenched’ state (more precisely after $\sim2$ min after quenching). The course of $\tau_{1C}$ depends on the medium used for AA. Fast heating in LM may cause the shortest $\tau_{1C} \sim166$ ps. This is a reduction by 77 ps with respect to the value measured directly after quenching. For 1 s AA the values vary considerably in the 10 experiments carried out by manually dipping a sample into the metal. The $\tau_{1C}$ does not vary much up to 5 min of AA, with a slight minimum for $\sim3$ s AA in LM. Higher $\tau_{1C}$ values were measured after intermediate-rate heating in Oil, namely 218 ps and 197 ps after 2 s and 10 s, respectively, with a slight ensuing decrease up to 1 min.
of AA. The decrease caused by AA in Oil is therefore much lower than for fast heating. AA in MS for up to a few minutes yields similar results as AA in Oil, and the results of AA for slow heating on the heating plate are also comparable. In all heating media, $\tau_{1C}$ starts to increase for longer AA. A stable $\tau_{1C}$ is found after long AA time with $\sim 235$ ps as seen for AA in Oil.

**Two-component positron lifetimes.** It was in some cases possible to decompose spectra into two contributions ($\tau_1$, $\tau_{2+3}$) and the corresponding intensities ($I_1$, $I_{2+3}$), see Figure 4a,b. Each value represents the state after AA and is based on data accumulated during NSA up to 15 to 30 min after quenching as long as $\tau_{1C}$ remained constant or was only slowly changing (data accumulation at RT, $\sim 5 \times 10^5$ counts, see Sec. S1). Heating in LM (highest heating rate) leads to a different course than heating either in Oil, MS or on the HP (intermediate and slower heating rates). 1 s in LM produces a $\tau_{2+3}$ around 220 ps and an intensity $I_{2+3}$ around 50% (215 ± 1 ps, 50 ± 1% at -40 °C, see crossed squares in Figure 4). Up to 5 min of AA these values do not change notably, but after 30 min of AA $I_{2+3}$ increases to 68%. At even longer AA times $\tau_{2+3}$ also increases and reaches 235 ps while $I_{2+3}$ goes up to 75%. Intermediate and slow heating either in Oil, MS or on the HP yield $I_{2+3}$ values about twice as high as for analogous AA in LM (Figure 4b) for AA times up to 5-10 min while the measured $\tau_{2+3}$ values are about the same as for AA in LM. Longer AA times (≥30 min) let $\tau_{2+3}$ increase to 235 ps with $I_{2+3}$ eventually being between 70 and 85%.

**Hardness.** Figure 3b shows the evolution of HV compared to that of $\tau_{1C}$ during AA in Oil. A negligible initial change in HV up to 2 min of AA is followed by an increase to a maximum of 70 HV after ~1000 min of AA, after which over-ageing commences. The main increase in HV takes place after 30 min of AA, which is later than the increase of $\tau_{1C}$ that sets in already after 1 min of AA. Over-ageing reduces HV, but not $\tau_{1C}$. 

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3.3. Artificial ageing of concentrated alloy 6-8

One-component positron lifetime. Figure 3c shows $\tau_{1C}$ of alloy 6-8 measured after AA in two media (LM and Oil). 1 s of AA in LM decreases $\tau_{1C}$ by $\sim$40 ps compared to the AQ state, while for 2 s AA in Oil, $\tau_{1C}$ is reduced only by $\sim$10 ps. Increasing the AA time leads to a continuous increase to 213 ps after 2 min AA in LM followed by a slight decrease to a minimum of 211 ps after 30 min AA, while a continuous decrease to a minimum of 209 ps after 30 min AA in Oil is observed. Longer AA times ($\sim$3.5 days) cause an increase of $\tau_{1C}$ to a maximum of around 235 ps as in alloy 4-4.

An extra experiment was carried out by dipping a sample into LM held at 300 °C for $\sim$0.3 s in order to achieve an even higher heating rate than in LM at 180 °C. The end temperature in this experiment was estimated to be around 200 - 230 °C. $\tau_{1C}$ after this treatment was shown to be even lower than after AA for 1 s at 180 °C in LM (red point in Figure 3c).

Two-component positron lifetimes. Lifetime decompositions in alloy 6-8 are more difficult than in alloy 4-4, most likely because positron trapping is closer to saturation in most cases. Only after AA for 0.3 s in LM at 300 °C, clear indication for two-component behaviour was found with a bulk contribution of 16%.

Hardness. The hardening response in Figure 3d shows a negligible change during the first 2 min of AA in Oil followed by a slight increase up to 5 min AA. The further increase of hardness to 93 HV coincides with a minimum of $\tau_{1C}$ after 30 min of AA. A maximum of hardness was achieved after 100 min AA, followed by a plateau ranging between 100 and 110 HV up to $\sim$15 h AA. Hardness therefore peaks earlier than $\tau_{1C}$, which takes 3.5 d of AA. Over-ageing for long AA times is pronounced. Figure 3d also shows some hardness values of samples AA in LM and show a negligible effect of the AA medium.
3.4. Further experiments

Figure 5 shows results of $\tau_{1C}$ measurements after short AA for 1 s in LM for four more alloys, namely 5-5, 4-10, 8-6, and 10-4 (code as defined in experimental) [14]. The value obtained for alloy 5-5 lies slightly above that for alloy 4-4, while the values for the alloys with a combined Mg and Si content of 1.4 wt.% lie close to the value for alloy 6-8. Figure 5 also presents the evolution of $\tau_{1C}$ in alloy 4-4 after a combination of a NPA step (5, 30, or 80 min, see upper axis) and short AA for 1 s in LM. NPA does have a strong effect on $\tau_{1C}$ after AA as it increases $\tau_{1C}$ by up to 25 ps.

4. Discussion

4.1. Interpretation of PALS signals

Positron spectra in rather complex systems such as Al-Mg-Si alloys that contain vacancies and different types of precipitates are rarely caused by positron annihilation in just one kind of trap. Instead, competitive annihilation in different ways is likely: (i) Positrons can annihilate in the free bulk without being trapped. If all positrons annihilate in this way their corresponding measured lifetime will be around 160 ps [15,16]. If some positrons annihilate in traps, an apparent reduced bulk lifetime ($\tau_1 \leq 160$ ps) is measured according to the trapping model [17]. (ii) Positrons trapped in mono-vacancies have a lifetime around 245 ps to 250 ps [15]. If a vacancy form a complex with either a Mg or Si atom it has been estimated that the lifetime is modified only marginally (1-3 ps increase for Mg, 1-2 ps decrease for Si) [18,19]. If vacancies are surrounded by more Mg and Si atoms (vacancy-cluster complex), there are no reliable data for the corresponding lifetime. Buha assumes a typical lifetime of 221 ps in such complexes [20]. However, this value might vary with the chemical composition of a cluster and since it was derived from one-component spectra it is not clear whether this value is correct. (iii) Vacancy-free clusters of Mg and Si atoms, with possibly some Al in between, can also trap positrons. Lifetimes of 200 ps [8], 214 ps [20] or 215 ps [9] have been postulated. Coherent GP zones
and β” precipitates are expected to give rise to positron lifetimes slightly lower than the clusters formed during NA, e.g. 210 ps [20-22]. As precipitates become semi- or incoherent during prolonged ageing, the associated positron lifetime increases [22,23].

In this paper, we assume that positrons have only three ways to annihilate: either in the bulk, giving rise to a lifetime of ≤ 160 ps [15], in vacancy-free solute clusters, GP zones or β” precipitates where the lifetime is typically around 210 - 215 ps [20], or in defects containing a vacancy (245 ps) [15]. We neglect that clusters and zones (both with or without an attached vacancy) might have a range of different sizes and compositions which in turn would lead to a range of positron lifetimes and that annihilation in vacancies is modified by the site occupation around the vacancy. Currently, there is no way to measure or calculate such lifetime distributions. In many cases we measure a one-component positron lifetime \( \tau_{1C} \) only and have to deduce indirectly what might have changed its value during ageing. As positrons can annihilate in three different ways, changes of the average of the three partial lifetimes can be explained by an increase or decrease of one of the three contributions as outlined in Table 1. In some cases, a change can have different reasons and additional information is required.

The evolution of \( \tau_{1C} \) during NA has been studied previously [8] and is also given in Figure 2, where the first \( \tau_{1C} \) value measured after quenching is 243 ps in alloy 4-4 and 233 ps in alloy 6-8. Previous work has shown that in alloy 4-4, at least 85% of the positrons annihilate in vacancy-related traps in this as-quenched state [9]. The initial value in alloy 6-8 is 10 ps lower in accordance with Ref. [8]. This is not due to NA after quenching since experiments in which the sample was quenched to 77 K directly from SHT and PALS was carried out at low temperature have yielded the same results [9]. It is rather suspected that during quenching clustering sets in and the corresponding positron trapping component with a typical lifetime around 215 ps reduces \( \tau_{1C} \). This represents the initial state after
quenching and determines what happens during ensuing AA. The processes during further NA have been discussed in the literature [8,9,24].

4.2. Microscopic model for phenomena during short AA

The different effect of short AA in Oil/MS/HP on the one hand and LM on the other must be related to the different heating rates applied. In Oil and even more in MS and on the HP, the sample spends a few seconds more at temperatures lower than 180 °C while the temperature is ramping up. It takes the centre of the sample ~6 s to reach 170 °C in Oil, 10 s in resting salt, 63 s on the HP, but less than 1 s in LM, see Figure 1. We propose the following microscopic model and provide evidence in the following sections:

Excess vacancy migration is thermally activated and its rate is given by an Arrhenius law involving a migration activation energy of $H_v^{\text{mig}}$. Vacancy-solute binding energies are in the range of some tens of meV [25], i.e. in the range of thermal energies at RT. Thus binding weakens as the temperature increases and vacancy-solute complexes dissolve faster. The same holds for solute clusters, just that cluster-vacancy complexes live longer as the binding energy approximately scales with the number of atoms in the cluster [26]. Clusters are therefore stronger pinning points for vacancies than individual solute atoms. According to the vacancy-pump idea [27], vacancies transport solute atoms, deliver them to other solute atoms or already formed clusters and detach after. The residence time in a cluster increases rapidly with cluster size [26]. Therefore, of all available excess vacancies, only a part is “free” at a time, given by the size of the clusters and temperature as shown in Figure 6.

At RT, vacancies move slowly through a solid solution, assist in forming clusters before eventually getting irreversibly trapped by a vacancy sink (dislocation or grain boundary). Therefore, the longer the samples remain at RT or moderately above, the more clusters can be formed. At a higher
temperature, vacancies move faster and spend less time at solutes and clusters. One could say that the solid solution becomes more permeable for a vacancy as temperature increases.

When heating rapidly from 20 °C to 180 °C as given by the upper arrow in Figure 6, the fraction of free vacancies increases from an already high value (here 71%) to 89%. Few vacancies interact with other solutes, while the rest diffuse to sinks and get lost there before assisting clustering. The vacancy site fraction will approach the much lower value of the thermal equilibrium.

If however heating is slower (middle and lower arrow) to an end temperature, the time around 20 °C is already sufficient to allow the free vacancies to form some clusters. This implies jumping to the next curve labelled N = 2. Here, the fraction of free vacancies is much smaller, i.e. more vacancies deliver solute atoms and go to clusters and spend time within – excess vacancies will be lost later to sinks than when heating fast. Thus a chain of successively larger clusters is formed that sustains further clustering. In this case, once a temperature has been reached at which solute atoms no longer bind vacancies, clusters will already have formed that can retain vacancies at this temperature and above due to the higher binding energy between vacancies and clusters. Eventually the vacancies will be liberated and migrate to sinks but the clusters will remain.

As a consequence, an alloy contains more clusters after slow heating and more positrons annihilate there with a lifetime of 200 - 215 ps. This brings $\tau_{1c}$ closer to such values. After heating fast, fewer clusters have formed and many more positrons annihilate in the bulk, which is why $\tau_{1c}$ is closer to the lifetime in the bulk (160 ps).
4.3. Interpretation of positron lifetimes after AA and verification of model

4.3.1. Lean alloy 4-4, fast heating

After fast heating and short AA (1 s to 5 s) in LM, $\tau_{2+3}$ is between 205 and 220 ps (Figure 4a) – a mean value of 215 ps points at predominant trapping in clusters, indicating that most traps are cluster-related and only few vacancies contribute. A good part of the positrons, however, annihilates in the bulk as $I_{2+3}$ is just around 50% (Figure 4b). These values are confirmed by the experiments conducted at -40 °C (crossed squares in Figure 4). According to the two-state trapping model [17], we can calculate how high the fraction of vacancies or clusters would be if either clusters or vacancies were the only trap. Figure 7 shows that the lowest value for $\tau_C \approx \bar{\tau}$ of around 163 ps corresponds to site fractions of vacancy-related defects of $1.3 \times 10^{-6}$. That of clusters is only slightly higher when assuming that clusters have the same specific trapping coefficient $\mu$ as mono-vacancies. In the case that clusters trap positrons at a larger specific rate as suspected in the literature [28] the cluster site fraction could be much below. The scatter of experimental values of $\tau_C$ or $\bar{\tau}$ and especially values of $\bar{\tau}$ much higher than 164 ps are thought to be the consequence of premature cooling between solutionising and AA and non-ideal heating conditions during the manually conducted procedure.

At the solutionising temperature, the site fraction of vacancies should have been $1.4 \times 10^{-4}$. Calculations of the initial vacancy site fraction after very fast quenching predict $6 \times 10^{-5}$ (for an Al-0.4Mg-1Si alloy) [29]. This implies that AA for 1 s has reduced the vacancy site fraction by at least a factor of 46 and probably even more as the positron signal is also caused by clusters. Therefore, the above postulated scenario of quick vacancy losses to sinks (however, possibly not of all excess vacancies) and limited cluster formation upon fast heating is supported by the positron data.
According to calculations, it takes 50 s to reduce the excess vacancy density to 10% the original value after quenching at 1000 K/s and further 50 s to reach the equilibrium vacancy site fraction at 180 °C, \( x_{\text{vac}}^{180^\circ \text{C}} = 7 \times 10^{-8} \) (however, in an alloy with a higher Si content and after 2 min of NPA) [29], a value too low to influence the positron lifetime spectra. The assumption is that vacancies are trapped by dislocation jogs (grains are too large – 0.5 mm [8] – to have an effect). The rate at which a diffusing vacancy jumping \( \Gamma \) times per second meets a dislocation jog (site fraction \( x_{\text{jog}} \)) is
\[
 p = \Gamma \frac{x_{\text{jog}}}{1.3} = v_D \frac{s_v}{e} e^{-\frac{H_v^{\text{mig}}}{kT}} \frac{n_d}{n_p a},
\]
where \( v_D = 5 \times 10^{13} \, \text{s}^{-1} \), \( s_v = 2 \), \( H_v^{\text{mig}} = 0.62 \, \text{eV} \) (59.8 kJ/mol) [30]. A dislocation density of \( n_d = 3 \times 10^{11} \, \text{m}^{-2} \) with a jog spacing of probably \( n_p = 5 \) (not given, but customary in Ref. [7]) is used. For \( T = 453 \, \text{K} \), we obtain \( p = 2.3 \times 10^{-2} \, \text{s}^{-1} \), i.e. it takes 43 s to annihilate a vacancy on average. Our experiments indicate that this annihilation rate should be at least 50 times higher than this. Therefore, there must be a much higher vacancy sink density than assumed in [29]. If dislocation jogs are the main vacancy sink then the associated dislocation density should be higher than \( 1.5 \times 10^{13} \, \text{m}^{-2} \). Similar values were found in quenched Al-10Mg alloys (\( 5 \times 10^{13} \, \text{m}^{-2} \)) [31], Al-1.2Si alloys and in pure Al following quenching (\( 2.2 \times 10^{13} - 10^{14} \, \text{m}^{-2} \)) [32-34]. Therefore it remains unclear what the reason for fast vacancy loss is.

Ageing up to 5 min should therefore eliminate all possibly still present excess vacancies and the equilibrium vacancy site fraction is then reached [29]. The roughly constant \( \tau_{1\text{C}} \) indicates slow clustering/precipitation in this stage. For 30 min of AA \( \tau_{2+3} \) remains unchanged but for 100 min and 200 min AA it has increased (to 223 ps and 235 ps, resp., Figure 4a). Obviously, the character of the positron traps changes upon AA. For 30 min of AA, coherent phases dominate but for longer AA a different trap must be involved. A vacancy-related trap cannot be the reason for the increased lifetime since prolonged AA does not increase the density of such traps any more as all vacancies are
in thermal equilibrium. In accordance with Refs. [22] and [35] we assume that additional open volume associated with the partial incoherency of the precipitates formed at this stage causes the increase of \( \tau_{2+3} \). The precipitation sequence involves a transition from early GP zones to \( \beta'' \) and/or \( \beta' \) and eventually \( \beta \) precipitates – the degree of lattice mismatch and eventually incoherency increases in this order. \( \beta' \) formation is associated with global shrinkage of a sample [36,37], for which the tensile stresses around individual \( \beta' \) precipitates are accountable (other than for \( \beta'' \) where the stresses are compressive). This facilitates the formation of open volume. As \( I_{2+3} \) remains at around 80% but \( \tau_{2+3} \) increases, \( \tau_{1c} \) is notably increased to almost 235 ps (Figure 3a).

4.3.2. Lean alloy 4-4, intermediate and slow heating

After slower heating (in Oil, MS, HP), the positron traps are much more densely distributed and fewer positrons annihilate in the bulk and more in traps. For example, traps contribute around ~80\% to annihilation after just 5 s AA in MS, whereas it is below 50\% after fast heating, see Figure 4b. \( \tau_{2+3} \) is similar to that in LM. This indicates that most positrons annihilate in clusters and not in vacancy-related defects but more such clusters have formed after slower heating.

For 2 s AA in Oil, the highest temperature reached is 130 °C. We do not have two-component decompositions for this measurement but assume that here some excess vacancies still contribute to the lifetime spectrum, which is why \( \tau_{1c} \) is still close to 220 ps.

A problem encountered when displaying results for short AA after intermediate or slow heating is that of an ambiguous definition of ageing time. In Figure 3a, for example, the two-sided arrow compares AA in LM for 5 s and that in Oil for 10 s as heating in LM/Oil takes about 0.9 s/6 s to reach 170 °C. The positron lifetime difference is 27 ps in these comparable cases. Fig. S3 helps to compare the four different heating media by showing the true time above 170 °C.
During prolonged AA up to 5 min in MS, $I_{2+3}$ remains mostly constant and so does $\tau_{2+3}$ (Figure 4a,b). As excess vacancies are lost quite fast, their loss cannot be the reason for the further decrease of $\tau_{1C}$, which eventually leads to such low values as 190 ps for 5 min in Oil. Therefore, a small increase of bulk annihilation seems likely (see Table 1, the increase, however, does not show in Figure 4b). A possible scenario is: residual vacancies are quickly reduced to below the detection limit after a few tens of seconds of AA. Of the clusters formed during heating to 180 °C that helped to retain vacancies, the smaller ones dissolve within 5 min. This gives rise to some bulk annihilation and the minimum of $\tau_{1C}$. Formation of GP zones takes place with a delay, first slowly as reflected by an only small increase of hardness from 27 to 33 HV perhaps due to small GP zone size (Figure 3b), but eventually precipitation leads to a re-increase of $\tau_{1C}$ within 30 min of AA as bulk annihilation vanishes. The even slower heating on the HP leads to higher values of $\tau_{1C}$ than by heating in Oil and MS due to further increased clustering during heating.

For even longer AA (200 min), $\tau_{2+3}$ increases (Figure 4a). As for fast heating, this points at the generation of incoherency between precipitates and matrix as discussed above. For such long AA times the positron results are the same for all heating rates. Therefore, clusters are seen to transform into a state, where they create stronger lattice strains and eventually more incoherency without much coarsening. This also leads to a notable hardness increase from 33 to 70 HV after 16 h of AA.

4.3.3. Concentrated alloy 6-8, fast heating

To further verify the interpretations presented we now compare alloys 4-4 and 6-8, both for fast heating. As mentioned in Sec. 4.1, the lower $\tau_{1C}$ value after solutionising and quenching given in Figure 3c for alloy 6-8 as compared to alloy 4-4 (Figure 3a) reflects the fact that pre-existing clusters have formed during quenching. These clusters interact with the migrating vacancies during heating
and delay their migration to sinks. These diffusing vacancies give rise to further precipitation. This happens even when the alloy is heated fast and extrapolated $\tau_{1C}$ values no lower than 190 ps are observed after heating for 1 s at 180 °C and 0.3 s at 300 °C in LM. This shows that pre-existing clusters limit the lifetime decrease observed in alloy 6-8.

Even for short AA ($\leq 30$ s), positron trapping is close to saturation and reliable two-component decompositions cannot be obtained. Flash ageing at 300 °C produces a bulk contribution of 16%. Compared to alloy 4-4 (1 s in LM), this is a much lower bulk contribution (there: > 50%). Measurements on a similar alloy have yielded a bulk component of ~10% [35], however after slow heating.

Due to this small bulk annihilation, $\tau_{1C}$ is below 200 ps for 1 s and 5 s of AA. The increase of $\tau_{1C}$ for 1 s, 5 s and 30 s of AA from 193 ps to 210 ps must be related to the disappearance of the bulk component and the concomitant formation of clusters or precipitates that are formed faster during AA than in alloy 4-4 (where they occur mainly after 5 min of AA, see Figure 3a). The reason for this could be that solute supersaturation is still high after short AA as only few clusters have formed. This provides a fast driving force for further nucleation and precipitation during AA. Moreover, the loss of vacancies takes place at a lower rate in alloy 6-8 compared to alloy 4-4 and therefore precipitation is faster.

Between 2 min and 30 min of AA, $\tau_{1C}$ shows a slight decrease or constant value, the reason for which is not entirely clear. Perhaps some GP zones (~210 ps) are formed. A re-increase in $\tau_{1C}$ to 226 ps till the end point of ageing (2460 min) suggests a distribution of semi-coherent particles dense enough to trap most positrons.
4.3.4. Concentrated alloy 6-8, intermediate heating rate

Slower heating in Oil modifies the course of $\tau_{1C}$ during short AA compared to fast heating. $\tau_{1C}$ equals 223 ps after 2 s of AA and the end temperature of 180 °C is not reached in the sample. As heating is rather slow clustering can proceed and limit vacancy annihilation. The total trap density is close to saturation, which is why we cannot decompose into 2 components. $\tau_{1C}$ (223 ps) is therefore between the values of clusters and vacancy-type defects.

Accepting the above mentioned idea that in alloy 6-8 the equilibrium vacancy concentration is reached later than in alloy 4-4, the further decrease to 215 ps is explainable. The ensuing decrease to 210 ps (30 min AA) is similar to the situation in alloy 4-4 just that the decrease does not go so far. This points at positron trapping into a much denser distribution of clusters or precipitates. Staab et al. report a similar decrease for alloys 6013 and 6061 (206 ps to 203 ps and 213 ps to 208 ps, resp.) [22]. They do not specify the type of AA treatment but moderate heating, e.g. in Oil, is likely. The same applies to Buha et al., who measure a decrease from 214 ps to 207 ps for a 6061 alloy [20]. The amplitude of change in $\tau_{1C}$ is smaller in both studies than in the current work. Banhart et al. measure a decrease from 209 ps to 204 ps for alloy 6-8 aged at 180 °C in Oil [38]. Thus, both the amplitude and the absolute values are lower than given here. The latter might be due to different adjustments of the spectrometers used. No interpretation for the decrease is given in Refs. [38] and [22]. In Ref. [20], the formation of GP zones is held responsible for the decrease. Nevertheless, Resch et al. find a constant one-component lifetime between 3 min and 160 min of AA [35]. The minimum of $\tau_{1C}$ roughly coincides with the maximum of hardness as already noted by Staab et al. [22].
For AA $\geq 300$ min, $\tau_{1C}$ increases again to values above 215 ps (Figure 3d). Saturated trapping into increasingly semicoherent precipitates can be held responsible for this as in alloy 4-4. However, the increase actually takes place at a later time than in alloy 4-4 ($\sim 150$ min, Figure 3b). This appears unexpected at first sight since hardness increases more in alloy 6-8 than in alloy 4-4 at $\sim 5$ min of AA (Figure 3b,d) and thus the faster appearance of $\beta''$ and $\beta'$ precipitates might be expected for alloy 6-8. However, it has been found that in alloys with a high Mg+Si content (comparable to alloy 6-8) the peak aged state contains mainly $\beta''$ precipitates, whereas in low Mg+Si alloys (comparable to alloy 4-4) predominantly [39] (or partially [40]) $\beta'$ precipitates are formed without first forming $\beta''$ precursors. As $\beta'$ is less coherent with the matrix than $\beta''$, positrons trapped there could have a longer lifetime.

The asymptotic values for long ageing are the same in both alloys aged in Oil ($\sim 235$ ps). The increase is also much more pronounced in this study than in other work [20,22]. Only Resch et al. [35] find a comparable increase to 231 ps after 2 weeks of AA at 180 °C. Over-ageing for 1 week at 180 °C lets precipitates coarsen and hardness correspondingly decrease but the value for $\tau_{1C}$ remains high. Apparently even the coarsened particles trap all positrons efficiently and prevent the appearance of a bulk component that would reduce $\tau_{1C}$ again.

4.3.5. Lean alloy 4-4, additional NA before AA

The experiments in alloy 4-4 in which natural pre-ageing (‘NPA’) was performed before AA to form clusters, see Sec. 3.4, verify the idea that clusters formed in alloy 6-8 during quenching before AA limit the loss of vacancies and the associated decrease of $\tau_{1C}$ during AA. As discussed in Ref. [9], during NA (called ‘NPA’ here) clusters grow continuously and vacancies are slowly lost. 5 min of NPA already has a small influence on the extent of $\tau_{1C}$ decrease after 1 s AA in LM. After 30 min or 80 min of NPA, the post-AA value is comparable to the one measured in alloy 6-8 after short ageing in LM. Thus, even
though the clusters are formed during NPA here, their effect is similar to the clusters formed in alloy 6-8 during quenching. This is shown in Figure 5 where increasing NPA is seen to increase the value of $\tau_{1C}$ after quenching continuously from that for alloy 4-4 to that for alloy 6-8.

4.3.6. Additional alloys

Figure 5 also demonstrates how an increasing total level of solute increases the value of $\tau_{1C}$ after quenching. The four alloys with a constant sum of solutes Mg+Si but different Mg:Si ratio perform in a very similar way.

4.3.7. Lean alloy 4-4, different quenching rates

In a previous study, the positron lifetime in alloy 4-4 directly after quenching was studied for different quenching rates (no AA involved) [9,14]. Slow quenching was found to lead to a lower initial $\tau_{1C}$ than fast quenching. One can argue that slow quenching allows the alloy to age more during cooling and is equivalent to a short NA or AA treatment during which some initial clusters or precipitates are formed. The longer this extra ageing, the lower the value of $\tau_{1C}$. This is in line with the argument in the previous paragraphs.
5. Conclusions

Artificial ageing (AA) of solutionised and quenched Al-Mg-Si alloys of different compositions leads to a big decrease of one-component positron lifetime $\tau_{1C}$ measured before AA.

In the lean alloy heated to 180 °C within 1 s, vacancies diffuse to sinks quickly and do hardly assist precipitation. The state produced is that of a sparse population of clusters and some residual excess vacancies. Therefore, positrons annihilate with a short lifetime in the bulk lattice since most of them are not trapped. The fast observed annihilation points at a high site fraction of vacancy sinks.

This positron lifetime is always longer and hence the trap density higher when clusters or precipitates are formed before or during AA, thereby limit further vacancy losses, which in turn enables further clustering - a self-amplifying effect. This happens when:

- The alloy contains more solute: in this case, clusters are formed already during quenching after solutionising.
- The alloy is heated slowly to 180 °C: in this case, clustering sets in at lower temperatures, which then delays losses of vacancies at higher temperatures.
- The alloy is naturally pre-aged before AA: the clusters formed act in the way described above.
- The alloy is quenched slowly from the solutionising temperature: again, more clusters are formed during quenching before AA.

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**Figure captions**

**Figure 1.** Heating profiles in the four different media used for AA at 180 °C. The starting time was arbitrarily set to 1 s to be able to use a logarithmic time scale. Note that the linear heating ramp of HP appears as an exponential on this scale. Kinks in the heating curve in salt point at the melting of a crust of solid salt forming upon immersion of a cold sample. In Oil some changes of slope are also observed.

**Figure 2.** One-component positron lifetime $\tau_{1C}$ in alloys 4-4 and 6-8 after solutionising and quenching (‘AQ’) during NA and after AA a) for 100 min in LM (4-4) and Oil (6-8), the period of constant positron lifetime and the corresponding average values and standard deviations are also given, b) for 1 s in LM (6-8), linear extrapolation of the fast changing lifetime to zero NSA time is demonstrated.

**Figure 3.** (a,c) Evolution of the one-component positron lifetime $\tau_{1C}$ in alloys 4-4 (a) and 6-8 (c) as a function of AA time in different heating media. The red symbols in c) correspond to 0.3 s annealing at 300 °C. (b,d) $\tau_{1C}$ compared to hardness as a function of AA time in the Oil bath for alloy 4-4 (b) and for the Oil bath and LM for alloy 6-8 (d).

**Figure 4.** Trap component ‘2+3’ as derived from positron lifetime decompositions for alloy 4-4. Different symbols specify the AA medium used. (a) Positron lifetime $\tau_{2+3}$. (b) Corresponding intensity $I_{2+3}$. Solid and open symbols represent two independent experiments carried out in Berlin at RT (‘B’), while crossed squares are measured in Prague at -40 °C (‘P’). The broken lines indicate the trend of the (‘B’) measurements discussed in the text.
**Figure 5.** $\tau_{1C}$ for various alloys with different Mg and Si contents after 1 s AA in LM. Data for alloys 4-4 and 6-8 is the same as in Figure 3a,c (one value chosen for 4-4). For alloy 4-4 an additional NPA step (5, 30 or 80 min) has been included before AA.

**Figure 6.** Explanation of influence of heating rate based on thermodynamic model of Pogatscher et al. [41]. After solutionising at 540 °C and subsequent fast quenching the excess vacancies repartition in a short time compared to the time needed to reach vacancy sinks of free vacancies and vacancies bound to a solute atom (N = 1) or clusters containing N atoms. The fraction of free vacancies is given by
\[
\frac{x_{\text{free}}(T)}{x_{\text{tot}}(T)} = \frac{1 + z_N c_N \exp(E_N / RT)}{1 + z_N c_N \exp(E_N / RT_{\text{shift}})},
\]
where N takes 5 different values, the vacancy-solute/cluster interaction energy is taken as $E_N = N \times 50$ meV using an approximation discussed in Ref. [26], $z_N$ the coordination number of a solute/cluster and $c_N$ the site fraction of solutes $c_1 = 0.8\%$ and clusters chosen as $c_N = 2^{-N+1}c_1$, the latter to express lower cluster than solute fractions.

**Figure 7.** Intensities of cluster or vacancy components that lead to an average positron lifetime $\bar{\tau}$ assuming that either only clusters ($\tau_2 = 215$ ps) or vacancies ($\tau_3 = 245$ ps) are present and using Eq. 3.33 of Ref. [42] to calculate $\kappa_i = \mu \chi_i$. $\mu = 250$ ps$^{-1}$ [43,44] was used to obtain $\chi_i$. For clusters the same value of $\mu$ was used despite the suspicion that it might be higher [28]. The points are the experimental values obtained for 1 s of AA of alloy 4-4 taken from Figure 3a.
Table 1. Underlying mechanism governing the change of the averaged ($\bar{\tau}$) or one-component positron lifetime ($\tau_{1C}$) during ageing. ‘+’ and ‘−’ denote an increase or decrease of a specific contribution.
Figure 2b

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The graph shows the relationship between NA/NSA time (s) and $\tau_{1c}$ (ps) for alloy 6-8. The data points indicate a decrease in $\tau_{1c}$ with increasing NA/NSA time, reaching a value of 192.5 ps (extrapolated) at a specific time. Two curves are plotted: one for AQ and another for AA 1s.
Figure 3a

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Figure 5

The graph shows the influence of solute content and NPA time on $\tau_{1C}^{1s-LM}$ at 20°C. The x-axis represents $x_{Mg} + x_{Si}$ (at.%) ranging from 0.8 to 1.6. The y-axis represents $\tau_{1C}^{1s-LM}$ (ps) ranging from 160 to 200. The green line indicates the influence of solute content, while the red line represents the influence of NPA time. The data points are labeled with corresponding values.
| Time Interval | Decrease of $\bar{\tau}$ or $\tau_{1C}$ | Increase of $\bar{\tau}$ or $\tau_{1C}$ |
|--------------|---------------------------------|---------------------------------|
| > 245 ps     | – V: vacancy loss                | – C: reduction of clusters      |
|              | + C/Z/P: cluster/zone/precipitate | + O: generation of open volume  |
|              | formation                        | (incoherency)                   |
|              | + B: increasing bulk             | + Mg: Mg addition to clusters   |
|              |                                 | – B: reduction of bulk          |
| 210-215 ps   | – V: vacancy loss                | – C: reduction of clusters      |
|              | – C: reduction of clusters       | + C/Z/P: cluster/zone/precipitate |
|              | + B: increasing bulk             | formation                       |
| < 160 ps     |                                 | – B: reduction of bulk          |
Graphical Abstract

The diagram illustrates the transformation process of different phases in a material:

1. **β'' + β''\(\rightarrow\)**\(\rightarrow\)\(\rightarrow\) GP \(\rightarrow\) β' + β"
2. **β' + β''\(\rightarrow\)**\(\rightarrow\)\(\rightarrow\) GP \(\rightarrow\) β' + β''

The process is influenced by fast and slow heating conditions.

- Al
- Mg
- Si
- Vac
- Vac
- Cluster

**Processes:**
- Fast heating
- Slow heating