

# In Situ Heating Positron Annihilation Lifetime Spectroscopy Experiments on an Al–Mg Alloy

John Banhart,\* Zi Yang, Qianning Guo, Meng Liu, Maik Butterling, Maciej Oskar Liedke, Eric Hirschmann, and Andreas Wagner

The binding between vacancies and Mg atoms in an aluminum solid solution is not fully understood but essential for understanding its role in age hardening of many Al alloys. After annealing and quenching, Mg prevents the loss of excess vacancies during natural ageing and forms complexes containing one, possibly two, vacancies, and various Mg atoms. By heating the alloy after natural ageing, these complexes are dissolved, i.e., natural ageing is reverted. This reversion process is studied by in situ positron annihilation lifetime spectroscopy utilizing the very high count rate at the accelerator driven facility ELBE. Positron spectra are continuously acquired during heating at rates between 3 and 50 K min<sup>-1</sup>. After correcting for the contributions of the oxidized surface and decomposing spectra into components, the process can be followed in detail and is found to take place in distinct stages: first, the number of vacancy–Mg complexes is reduced and then the liberated vacancies agglomerate into clusters that eventually dissolve at even higher temperatures.

generation and loss of vacancies, solute clustering, or precipitation. It has been applied to many alloys including aluminum alloys.<sup>[1–4]</sup> The lifetime of a positron depends on the local electron density and when a positron annihilates with an electron its lifetime depends on where it annihilates, for example, in a vacancy, in a dislocation, in a solute cluster, or in a more complex object. The basic output of PALS is the mean positron lifetime, which provides averaged information about many microscopic features, but the interpretation of such data can be challenging. In some cases, more than one individual lifetime can be extracted from measured spectra. In such a case, properties of individual features, for example, vacancies, can be derived. Usually, such analysis requires the acquisition of a number of annihilation

## 1. Introduction

Positron annihilation lifetime spectroscopy (PALS) is sensitive to many defects in solids, which makes the method a valuable tool for studying subtle changes of microstructure such as the

events sufficient to yield good statistics, which makes PALS a rather slow method in comparison with, for example, the measurement of electrical resistivity which is also sensitive to atomic defects. For the measurement of a single sample typically several million counted positron annihilation events are recommended when aiming at separating two lifetime components.<sup>[5]</sup> When operated with standard radioactive <sup>22</sup>Na positron sources at a typical count rate between 500 and 1000 s<sup>-1</sup>, this takes ≈1 h. If a sample changes over time, e.g., upon an applied temperature, and such changes are to be captured, a series of measurements have to be made and an interruption of the thermal treatment might be necessary. If only a single lifetime component is involved or an average of lifetimes is sufficient, data acquisition can be a lot faster. Al–Mg–Si alloys of different compositions have been studied in this way with a time resolution of just 2 min, which was sufficient to follow the process of natural ageing (NA) directly after solutionizing and quenching.<sup>[6]</sup> This comes much closer to in situ studies but is still too slow and the data quality not good enough to be applicable to faster changes such as in heating cycles as known from differential scanning calorimetry (DSC) measurements.

The mono-energetic positron spectroscopy “MePS” system operated at the electron linear accelerator for beams with high Brilliance and low emittance (ELBE) facility of Helmholtz-Zentrum Dresden–Rossendorf allows one to measure PALS spectra in a much shorter time due to a 100 times higher count rate compared to conventional <sup>22</sup>Na-isotope-based spectrometers. At such rates, positron spectra meeting the conditions for a

J. Banhart, Q. Guo  
Institut für Werkstoffwissenschaften und –technologien  
Technische Universität Berlin  
Hardenbergstr. 36, 10623 Berlin, Germany  
E-mail: banhart@helmholtz-berlin.de

J. Banhart, Z. Yang, M. Liu<sup>[†]</sup>  
Institut für Angewandte Materialforschung  
Helmholtz-Zentrum Berlin für Materialien und Energie GmbH  
Hahn-Meitner-Platz 1, 14109 Berlin, Germany

M. Butterling, M. O. Liedke, E. Hirschmann, A. Wagner  
Institut für Strahlenphysik  
Helmholtz-Zentrum Dresden-Rossendorf  
Bautzner Landstraße 400, 01328 Dresden, Germany

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adem.202300490>.

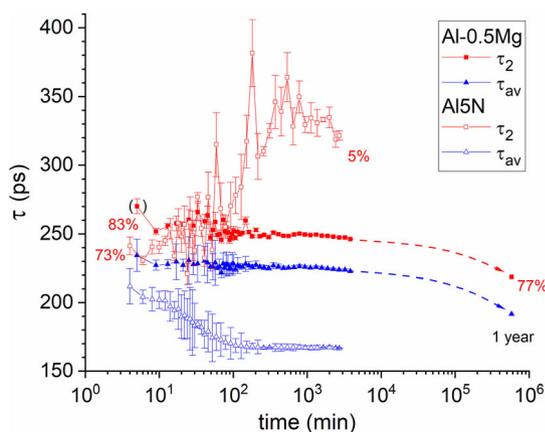
<sup>[†]</sup>Present address: Department of Aluminum Alloys, Chongqing Guochuang Light Alloy Research Institute Co., Ltd., Kecheng Road 108, Chongqing 400039, China

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lifetime decomposition of positron spectra can be acquired in just tens of seconds. Given that the beamline is equipped with an in situ heating device, experiments mimicking DSC analyses seem feasible. One potential difficulty is the low positron energy available there. Whereas in  $^{22}\text{Na}$  spectrometers high-energy positrons penetrate some 100  $\mu\text{m}$  into aluminum samples and annihilate there, the currently highest available positron energy of 10 keV at MePS implants positrons only a few 100 nm deep into aluminum alloys, implying that not only the bulk alloy but also the surfaces, featuring roughness, adsorbed molecules, and oxides contribute to positron trapping and annihilation.

Mg is an important element that is contained in almost any technologically important age-hardenable aluminum alloy. Therefore, understanding its interaction with vacancies helps comprehend the formation of strengthening precipitates in aluminum. It has been found that the presence of Mg atoms modifies the evolution of vacancies notably.<sup>[7,8]</sup> Figure 1 shows such difference by comparing the positron lifetime evolution during natural ageing after annealing at 540 °C and quenching an Al-0.5 at%Mg and a pure Al (purity 5 N) sample using a  $^{22}\text{Na}$ -based spectrometer. The defect lifetime ( $\tau_2$ ) of pure Al increases from initially 241 ps and an intensity of 73% to values above 300 ps, indicating that vacancies agglomerate to clusters of vacancies. As their number is lower and vacancies are also lost to vacancy sinks, the intensity decreases to just 5%. The scenario is very different in Al-Mg alloy. There,  $\tau_2$  is initially higher than 250 ps and dominates the spectrum with 83% intensity. The high initial value points at some di-vacancies apart from single vacancies that are attached to Mg atoms. During natural ageing,  $\tau_2$  decreases slowly, reaching 246 ps after 3 days but continuing to decrease and reaching 219 ps and 77% intensity after 13 months. This change points at an evolution of defects.



**Figure 1.** Evolution of average and defect positron lifetimes of Al-0.5 at%Mg alloy and pure Al (5 N purity) during natural ageing at 20 °C after solutionizing at 540 °C and quenching. Measurement was done with a  $^{22}\text{Na}$ -based spectrometer. Individual spectra were collected every 4 min ( $1.8 \times 10^5$  annihilation events) for the first 3000 min. For long ageing times, various spectra were summed up to make them equidistant on the logarithmic time scale, to improve statistics and to reduce the number of points. Another measurement representing the state after about 13 months of ageing was carried out on Al-0.5 at.%Mg samples prepared for the experiments at MePS.

Some of the decrease is explainable by the disappearance of di-vacancies but 219 ps is also too low for the single vacancy or vacancy-Mg complexes, which should be around 245 ps. Possibly, various Mg atoms have decorated the vacancy and brought it down to the 219 ps measured. The average lifetimes ( $\tau_{\text{av}}$ ) in Figure 1 (blue data) show the influence of Mg even clearer: Mg gives rise to an always higher positron lifetime and to a much slower decrease due to its interactions with vacancies.

Another way to study such interactions is to conduct isochronal annealing experiments, such as the ones that have been applied to Al-Cu,<sup>[9]</sup> Al-Sn, and Al-In alloys.<sup>[10]</sup> A preliminary study on Al-Mg alloys was carried out in our group using conventional  $^{22}\text{Na}$ -based spectroscopy.<sup>[7,8]</sup> In stage-annealing experiments, the interruption of heating is necessary because positron spectra cannot be measured in situ at high temperature when using Kapton-encapsulated positron sources, but these interruptions could influence the course of the entire experiment as the samples might evolve during temperature ramping or measurement at 20 °C. Moreover, the number of temperature steps that can be realized quickly reaches a practical limit. For this reason, we now perform this experiment with a 100 times higher count rate and apply in situ measurement and continuous heating.

## 2. Experimental Section

The Al-0.5 at% Mg binary alloy was cast by Hydro Aluminium Bonn from Al(5 N) and Mg(4 N) elements. Chemical analyses showed that the samples contained 75 ppm Si and less than 10 ppm Zn and Fe. The alloy was rolled to a sheet of 1 mm thickness. Samples were annealed at 540 °C in an air circulation furnace and quenched in ice water. Natural ageing was conducted in a Peltier-cooled incubator at 20 °C. Some of the samples were exposed to 540 °C for 3 h and cooled down slowly over 24 h to obtain soft-annealed materials and to allow the vacancies to anneal out. Some Al-Mg-Si and Al-Cu alloys with one side mechanically polished (MP) and the other side not treated were also measured for matters of comparison. They were naturally aged after solutionizing in a nitrogen atmosphere in a drop furnace and quenching in ice water, or they were annealed at 400 °C for 3 h and cooled down slowly to obtain a soft annealed state. The samples then underwent a surface treatment to reduce the thick oxide layers as much as possible. This will be discussed in the next section.

PALS was carried out on the superconducting linear-accelerator-based pulsed variable-energy slow positron beam MePS operating at the ELBE facility at Helmholtz-Zentrum Dresden-Rossendorf.<sup>[11]</sup> At this facility, mono-energetic positrons were generated by means of pair production from pulsed 30 MeV electrons impinging on a tungsten moderator. The unique time structure of each electron pulse (temporal width of less than 5 ps) was transferred to the positron pulse and therefore the prerequisite for a well-defined start signal for PALS. After a magnetic guiding system of around 11 m, the positron bunch broadened in time and needed to be improved by the help of a chopping and bunching system. The final time resolution of the spectrometer (full width at half maximum (FWHM) of the resolution function) was around 230 ps with two overlapping resolution functions. As the positrons emitted gamma rays upon

annihilation in the sample material, stop signals were created that were detected by a CeBr<sub>3</sub> scintillation detector coupled to a Hamamatsu R13089-100 photomultiplier. The energy of slow positrons was varied between 1 and 10 keV for the purpose of checking sample quality and a constant 10 keV for the actual in situ experiments. Positron spectra were digitally recorded and processed using an in-house developed software employing a ADQ14DC-2X digitizer from Teledyne SP Devices with 14 bit vertical resolution and 2 Giga samples per second horizontal resolution<sup>[12]</sup> and mainly analyzed with software LT9.<sup>[13]</sup>

Positron spectra were decomposed into various components that were related to the surface contributions (one or two lifetimes  $\tau_i$  and intensities  $I_i$ ) and the alloy (one or two lifetimes  $\tau_j$  and intensities  $I_j$ ), where

$$\sum_i I_i + \sum_j I_j = 1 \quad (1)$$

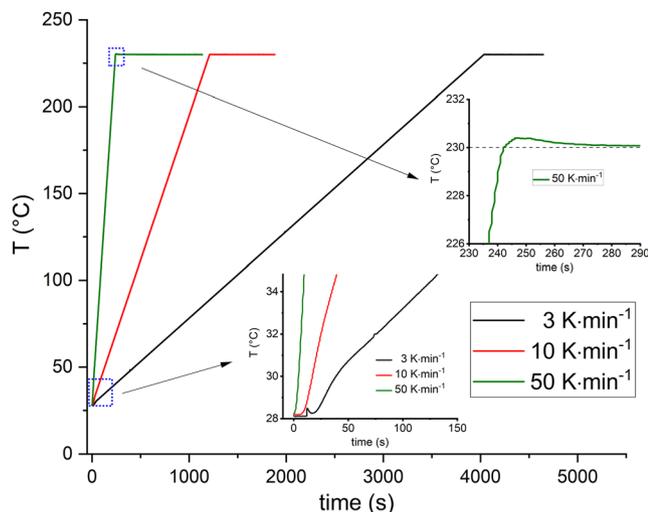
The overall average lifetime  $\tau_{av}$  can be calculated as

$$\tau_{av}^{tot} = \sum_i I_i \tau_i + \sum_j I_j \tau_j \quad (2)$$

and the average lifetime related to the bulk alloy  $\tau_{av}^{bulk}$  (excluding surface contributions)

$$\tau_{av}^{bulk} = \frac{\sum_j I_j \tau_j}{\sum_j I_j} \quad (3)$$

Samples were heated with a resistive heating plate positioned at the location of the beam focus on the backside of the sample holder. The temperature was measured with a thermocouple in direct contact with the sample. After adjustment of the controller, heating rates up to 50 K min<sup>-1</sup> could be implemented with little deviation from the ideal course and minimal overshoot (<0.3 K) after reaching the maximum temperature, see **Figure 2**.



**Figure 2.** Heating curves of the three samples at three heating rates. The insets show magnifications at the onset of heating and after reaching the maximum temperature of 230 °C.

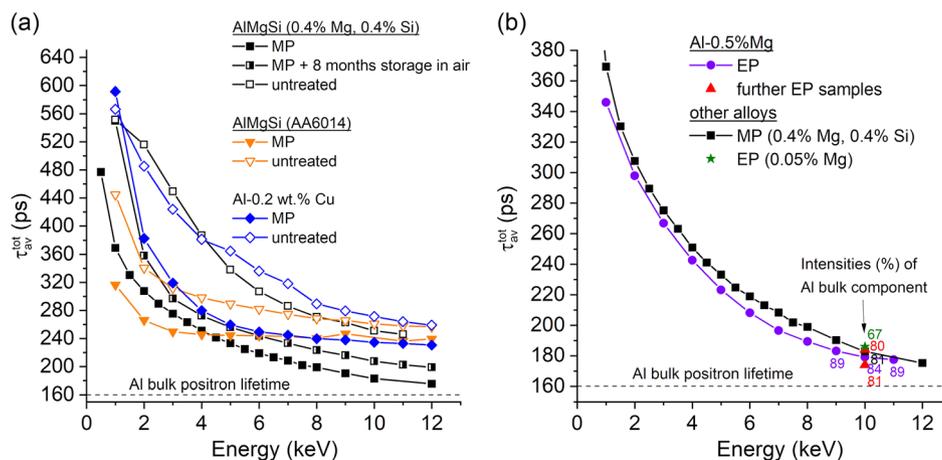
The experiments and the corresponding analysis progressed in three steps: 1) Investigation of soft-annealed alloys with an expected single-component lifetime of the defect-free aluminum bulk ( $\approx 160$  ps<sup>[14]</sup>) to determine the contributions of the surface. 2) Measurement on naturally aged samples and corresponding analysis using the knowledge on the contribution of the surfaces obtained in 1. The positron lifetimes of these contributions were left unchanged just their total intensity was different order of words allowed to vary to account for variations in surface properties such as thickness of the oxide layers between different samples. 3) Finally, in-situ measurement during linear heating on the samples already characterized in 2 and analysis using fixed parameters characterizing the surface contributions before heating obtained in 2. The underlying assumption was that the surface remained unchanged during heating in high vacuum.

### 3. Determination of Surface Contributions

The surface contributions include positron annihilation in the surface image potential and in the oxide layers (Lynn et al. reported  $\approx 400$  ps for an oxidized clean Al(100) surface<sup>[15]</sup>), the latter formed during solutionizing at high temperature and subsequent exposure to water during quenching in our case. Such layers can grow to a considerable thickness (hundreds of nm) and exhibit a complex structure (various polymorphs) and also contain pores. At 10 keV energy, a large fraction of positrons will be implanted in this layer and not deeper in the metal, which will influence the positron lifetime spectrum. The larger those contributions, the more difficult a proper correction and separation of the bulk contributions of the alloy. Thus, we investigated ways to reduce the thickness of the oxide layer and characterized the following samples: 1) alloys without surface treatments (untreated); 2) alloys with modified surfaces obtained by mechanical polishing (MP) while applying only little pressure and using very fine diamond pastes to minimize creation of defects in the material; and 3) electropolishing (EP) at  $-20$  °C and 20 to 30 V for 2–10 min using either commercial “Struers A2” electrolyte containing perchloric acid and ethanol or a nitric acid/methanol mixture.

The untreated surface of solutionized and quenched alloys had a slightly matt surface and a yellowish hue. As expected, PALS measurements showed a strong signal from the surfaces that obscured the signal of the sample (**Figure 3a**). As the positron energy increases, the average positron lifetime decreases, implying that the contributions from the surface become smaller, but still the average positron lifetimes at 10 keV positron energy were found to be much higher than those measured by <sup>22</sup>Na-PALS, for example, 271 ps instead of 170 ps for a naturally aged Al-0.2wt%Cu alloy,<sup>[16]</sup> 261 ps instead of 222 ps for a naturally aged AA6014 (Al-Mg-Si) alloy,<sup>[17]</sup> and 251 ps instead of 160–165 ps for a soft-annealed Al-0.4%Mg-0.4%Si alloy, in which most solutes have gone to grain boundaries or remain in solid solution where they do not trap positrons as also found previously.<sup>[18]</sup> These measurements indicate that untreated samples are not suitable for measurements at the available positron energies due to too strong surface influences.

The aforementioned samples were MP on one side to a mirror surface to reduce the thickness of the oxide layer. Spontaneous reoxidation in air occurs after polishing, but the thickness of such



**Figure 3.** Energy-dependent average positron lifetimes of various aluminum alloy samples with different surface statuses. a) Mechanically polished (MP) surfaces compared with untreated (oxidized) surfaces. Samples are either solutionized and naturally aged AA6014 and Al-0.2wt%Cu alloys or a soft-annealed Al-0.4 at%Mg-0.4 at%Si alloy. b) Electropolished (EP) surface compared with MP surface of various soft-annealed alloys. The labels on some data points denote the intensity of the bulk aluminum component after doing a three-component fit to separate the contributions of the surface (two components) from the contribution of the defect-free bulk aluminum (one component) with a known and fixed lifetime.

oxides will be just 4–10 nm.<sup>[19]</sup> Test measurement on these samples at MePS at a range of positron energies leads to varying results (Figure 3a). Similar to the untreated samples, the average positron lifetimes of the polished samples decrease as a function of the increasing positron energy, but the overall curves appear much lower than those of the untreated samples. This indicates that removing the oxide layer formed at high-temperature annealing indeed lowers the contributions of the surfaces and more information related to the alloy can be obtained. Furthermore, for the Al-0.4at%Mg-0.4at%Si sample, we remeasured the MP surface after having stored it unprotected in air for 8 months. We observe a higher overall curve after such a long time, indicating that oxidation re-increases the surface contributions. Although mechanical polishing improves the measurements, various problems, however, are identified with such samples. First, it can be seen that the average positron lifetimes at 10 keV for some samples are still much higher than expected as mentioned earlier. This might point at mechanically deformed surfaces and corresponding induced defects despite of the extreme care taken during polishing (polishing with minimal pressure). Moreover, the surface quality of mechanical polishing is not always consistent. On the best MP sample (soft-annealed Al-0.4 at%Mg-0.4 at%Si), we obtain a surface contribution of about 20% at 10 keV (Figure 3b), which is acceptable since it is in the same range as the source corrections applied in conventional <sup>22</sup>Na-PALS. Other measurements on a number of alloys (not shown here) however revealed much higher surface contributions of up to 50% of the total signal, rendering the measurements not usable and showing that mechanical polishing is not reproducible enough.

Electropolishing was then applied to soft-annealed samples. The resulting samples had a shiny surface but slightly more mattness than the MP specimens. In analogy to the previous measurements, we also applied the energy scan at MePS on one such sample (soft-annealed Al-0.5 at%Mg alloy), as shown in Figure 3b (purple symbols). The average lifetime decreases as the energy is increased and gets closer to the value for

defect-free and surface-contribution-free aluminum (horizontal line) as positrons are implanted into increasingly deeper layers of the sample. This is similar to the course of the previous measured samples, but the entire curve is slightly lower than the best MP alloy (5 ps at 10 keV and more at lower positron energies). Data for two more samples (red triangles) are added, where only measurements at 10 keV were carried out and confirm that less than 20% of the signal is due to surfaces and the average lifetime is around 180 ps in all three cases, i.e., the results are reproducible. It follows that electropolishing gives rise to a generally better surface treatment in terms of slightly lower surface contributions and more consistent results than mechanical polishing. Still, care has to be taken when analyzing the data as we found an outlier on an Al-0.05 at%Mg alloy, also electropolished (EP, green star in Figure 3b), where the influence of the surface layer is above 30%. This might be due to the fact that positrons with 10 keV energy are very sensitive to variations of the surface.

The planned upgrade of the beamline to 20 keV should be very helpful for avoiding such problems, but for the current measurements, we need an additional criterion to help us determine whether the surface contributions were corrected properly: We use the lifetimes measured in several characteristic states using a conventional <sup>22</sup>Na-spectrometer as the reference and only select samples that correspond well to these expected values after correcting for surface contributions, see later in Section 4.1.

When determining the lifetimes of the surface contributions, we tried both using two-component (one for bulk and one for surface) and three-component (one for bulk and two for surface) free fittings on the soft-annealed samples, considering the complexity of the surface contributions. The criterion is that the bulk lifetime should be around 160 ps. This is obtained in the three-component fitting but not in the two-component fitting, with a better fit quality also in the former. Thus, the two-component fitting was adopted, and the two components with 412 and 32 ps with a fixed intensity ratio of 2:1 were used for representing the surface contributions.

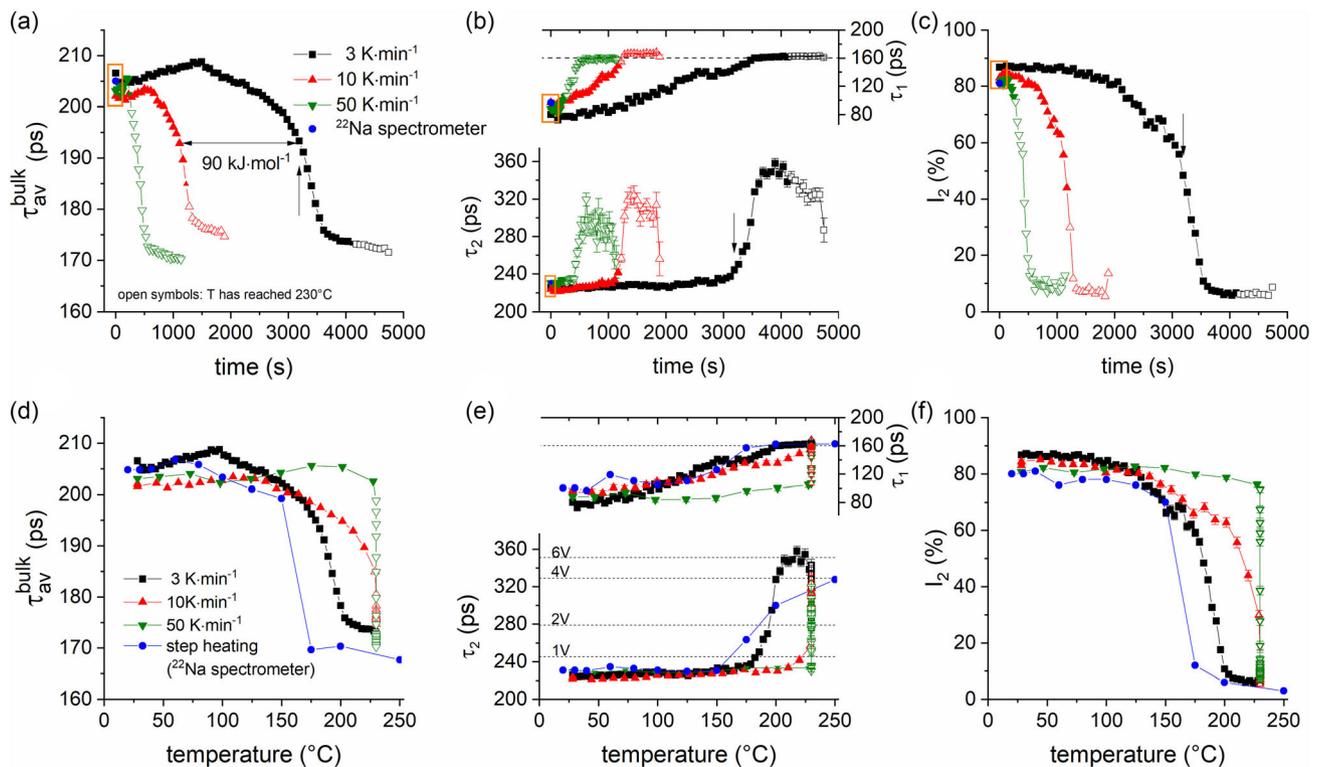
## 4. Heating Experiments

### 4.1. Naturally Aged Samples before Heating

In total, 7 EP Al-0.5 at%Mg samples naturally aged for 12 or 18 days were characterized. From their positron spectra, the contributions of the surfaces determined for a soft-annealed sample were subtracted. We allowed the total intensity of the surface corrections to be a free parameter while fixing the individual two lifetimes (412 and 32 ps) and the relative fraction of the two (2:1). This decision is based on the assumption that only the thickness of an oxide film and not its properties vary between the samples and therefore the lifetime components remain the same. To determine whether the surface correction is done properly, we compare the lifetimes of the remaining components that are related to the alloy as well as the average lifetime obtained according to Equation (3), with the values which we know from previous measurements.<sup>[7]</sup> We selected three samples which meet our criteria (3, 10 and 50 K min<sup>-1</sup> in Figure 4), which contain surface contributions of 8.6%, 13.9%, 10.3%, respectively. These samples including the soft-annealed samples had all been EP with “Struers A2 electrolyte,” which might point at a better polishing quality than for the other electrolyte. For each of the three samples, this state is shown in Figure 4a,b in the orange boxes, serving as the starting point of the heating experiments.

We first note that both the defect lifetime  $\tau_2$  (between 224 and 231 ps) and average lifetime  $\tau_{av}^{bulk}$  (around 205 ps) values here are slightly lower than the values measured by the <sup>22</sup>Na spectrometer after natural ageing for 3 days presented in Figure 1 but close to the values measured after 2 months in an earlier study<sup>[7]</sup> (blue circles in Figure 4). Therefore, the differences could be due to different natural ageing times and possibly also some small differences between the PALS spectrometers used. The values measured here are slightly larger than reported for commercial 5000 series alloys, where the average positron lifetime after long natural ageing was between 191 and 194 ps, however after quenching from 500 °C.<sup>[20]</sup> Another source reports, a value of 206 ± 2 ps for Al-0.5 at%Mg after quenching from 600 °C and an unspecified natural ageing time,<sup>[18]</sup> which is also compatible with our result.

The positron lifetimes obtained in the naturally aged state have been discussed to be caused by positron trapping and annihilation in vacancies trapped and stabilized by Mg atoms.<sup>[7,8]</sup> During natural ageing, the vacancies initially quenched-in from 540 °C diffuse through the lattice and are pinned by Mg atoms instead of being absorbed by vacancy sinks such as dislocation jogs and grain boundaries. This is why at 20 °C the positron lifetime does not quickly decrease to values typical for the pure Al lattice as it is the case in the absence of Mg as shown in Figure 1.



**Figure 4.** a) Average positron lifetime ( $\tau_{av}^{bulk}$ ), b) decomposed positron lifetimes ( $\tau_1$  and  $\tau_2$ ) and, c) defect-related component intensity  $I_2$  displayed as a function of time after the beginning of heating for three different heating rates. Data after reaching 230 °C are shown as open symbols. Orange boxes mark values measured before the onset of heating. d–f) Data in (a–c) as a function of temperature. Each data point in the curves of 3, 10, and 50 K min<sup>-1</sup> represents analysis of 6.3, 4.7, and 2.1 million annihilation events, respectively. Defect lifetime values  $\tau_2$  calculated for single vacancies (1 V) or vacancy clusters (nV) are given in (e). Data from preliminary study<sup>[7]</sup> using <sup>22</sup>Na spectrometer and stage heating are given in blue color.

## 4.2. Heating (Reversion) Experiments

Samples characterized in the previous paragraph were heated at different heating rates. For the analysis, the surface contributions described in the previous paragraph were subtracted. Figure 4a shows the average of the two resolved components of positron lifetime during heating at three different rates. After heating sets in,  $\tau_{av}^{bulk}$  first increases slightly, after which a very pronounced decrease sets in, which then levels off and still continues after the measurements have ended. Only for the lowest heating rate most of the measurements take place at increasing temperature, whereas for the higher heating rates, the maximum temperature of 230 °C is reached before and a part of the measurement takes place isothermally (open symbols).

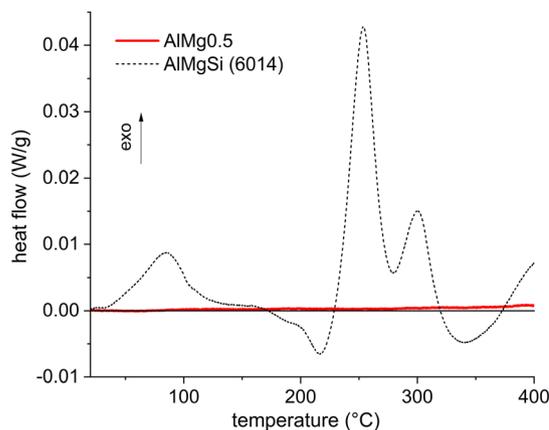
As discussed earlier, long natural ageing produces rather stable vacancy–Mg complexes. During heating, vacancies detach from the previously formed complexes and gradually disappear though vacancy sinks, hence the rapid decrease of  $\tau_{av}^{bulk}$ . The two-component decomposed lifetimes ( $\tau_1$  and  $\tau_2$ ) given in Figure 4b tells us more about the nature of this reversion process. Upon heating, the lifetime of the defect-related component ( $\tau_2$ ) initially remains unchanged before a rapid increase sets in (vertical arrow in Figure 4b for the lowest heating rate), followed by a maximum around 290–370 ps and an ensuing re-decrease. The onset of this increase roughly coincides with an average lifetime of 190 ps in Figure 4a, i.e., not with the onset of decrease of  $\tau_{av}^{bulk}$  but with an approximate half-reduction (corresponding vertical arrow in Figure 4a for the lowest heating rate). The reasons are the lifetime of the positrons annihilating in the bulk  $\tau_1$  (upper graph of Figure 4b) and the intensity  $I_2$  corresponding to  $\tau_2$  that is shown in Figure 4c.  $I_2$  starts from above 80% in the NA state ( $84\% \pm 22\%$  in ref. [18]) and is reduced to very small values during linear heating. In fact, it starts to decrease earlier than  $\tau_2$  starts to increase.  $\tau_1$  is initially much lower than the positron lifetime in pure Al bulk ( $\approx 160$  ps) due to the presence of the defects, thus also called “reduced bulk lifetime.” As the number of defects is declining during heating, this lifetime component approaches 160 ps. In analogy to  $I_2$ , the increase of  $\tau_1$  is also earlier than that of  $\tau_2$ . The interpretation is that the evolution of the positron traps takes place in distinct stages: first, they are reduced in number as reflected by the decrease of  $I_2$  while the characteristic lifetime  $\tau_2$  is largely unchanged. Then, the characteristic lifetime increases sharply, reflecting a change in structure. This is a transient state as upon further rising temperature  $\tau_2$  decreases again while its intensity  $I_2$  fades out.

It is useful to depict this data as a function of temperature for the different heating rates, which is done for the average (in Figure 4d) and decomposed (in Figure 4e) lifetimes and in Figure 4f for the corresponding intensity. All points measured at the maximum temperature now occur on a line, but below 230 °C, we see that the curves for different heating rates are similar, but there is a shift to higher temperature for higher heating rate. Such a shift is analogous to shifts measured in DSC experiments. The magnitude of the shift could be used to apply a Kissinger-type analysis assuming that the same value of positron lifetime represented the same state for any heating rate, but as we only have two measurements, in which the maximum temperature is not reached before the positron lifetime decreases, this

does not have a sound basis. However, by evaluating the time at which  $\tau_{av}^{bulk}$  has reached 192 ps, for example, and using the temperature, at this time as an input into the Kissinger equation yields an “activation energy” of 0.93 eV, which is the right order of magnitude for what one would expect from a process dominated by the migration of vacancies (0.58–0.60 eV<sup>[21]</sup>) and some binding energy terms of the order a few 100 meV. For a reliable analysis, one would need to apply some more heating rates.

Figure 4e relates the increase of  $\tau_2$  to the calculated lifetimes of positrons in vacancy clusters in aluminum.<sup>[22]</sup> Accordingly, the values reached correspond to clusters of six vacancies. The results obtained by conventional <sup>22</sup>Na-based spectroscopy<sup>[7]</sup> is also shown. Although the effective heating rate was not constant and increased from 2.4 to 4.8 K min<sup>−1</sup> in those experiments, the results confirm the basic course of positron lifetime measured here. The same applies to the intensity of the defect component  $I_2$  shown in Figure 4f. The decrease is increasingly shifted to higher temperatures as the heating rate increases.

These in situ positron lifetime experiments allow us to sketch a picture of the reversion of the naturally aged microstructure in this Al–Mg alloy. The initial state consists of mainly single vacancies pinned to Mg atoms. As the site fraction of Mg ( $5 \times 10^{-3}$ ) is 35 times higher than that of vacancies during solutionizing at 540 °C ( $1.4 \times 10^{-4}$ ), it is likely that more than one Mg atom attach to vacancy–Mg complexes. The binding energy between Mg atoms and vacancies is discussed controversially in the literature. Most calculations suggest values between slightly negative (repulsive)<sup>[23]</sup> and slightly attractive by some 10 meV<sup>[24,25]</sup> while some, mostly older experiments, suggest stronger attraction.<sup>[26]</sup> Possibly, the stability of the NA state of this alloy that is still slightly off the equilibrium is given by the binding of small groups of Mg atoms around a vacancy. Larger clusters or precipitates should not form in our Al–Mg alloy since the solubility of Mg in equilibrium at 20 °C is around 1%, thus we are in the single-phase region. This is confirmed by DSC experiments



**Figure 5.** Differential scanning calorimetry (DSC) traces of Al–0.5 at% Mg alloy after long natural ageing measured at 10 K min<sup>−1</sup> featuring an essentially flat line that is undistinguishable from the usual non-compensated baseline drift. For matters of comparison, the trace for an AA6014 alloy after solutionizing at 540 °C, quenching, and natural ageing for 1 day is shown, where strong signals including clustering (first exotherm), dissolution (first endotherm), and precipitation (two following exotherms) are observed.

on both of the as-quenched state<sup>[7]</sup> and the naturally aged state, see **Figure 5**, that do not show any prominent formation or dissolution peaks within the confidence given by baseline stability.

During heating vacancies are initially liberated from the least stable vacancy–solute complexes and diffuse to vacancy sinks and disappear but some vacancies condense into larger clusters and lead to the emergence of a long lifetime component (>300 ps) with a low intensity (below 20%, eventually just 10%). Vacancies could nucleate around the more stable fraction of vacancy–Mg complexes, impurity atoms, or themselves like in pure Al, and let them further grow for a while until the rising temperatures finally dissolve these clusters and the defect lifetimes go down again toward the single vacancy values and eventually the defect component disappears.

## 5. Outlook and Conclusions

The experiments conducted at the positron facility MePS at the accelerator of Helmholtz–Zentrum Dresden–Rossendorf showed that time-resolved in situ studies of ageing processes in aluminum alloys can be carried out with sub-minute time resolution during which the nature of specific defects can be measured.

The current study revealed that dissolution of the vacancy–solute(s) complexes in the naturally aged state takes place in various stages: first, the least stable complexes dissolve, then for a transitional stage vacancies attach to the last remaining complexes for a while, until finally all the complexes are dissolved. Such unique insights into the dynamics of subtle microstructural features are not resolvable by any other method as seen by DSC performed on the same samples that did not yield any information.

A drawback of the current configuration clearly was the limitation to 10 keV positron energy that gave rise to quite high contributions of the sample surfaces (about 20%) and associated complicated data correction procedures and many samples that could not be analyzed properly. Future upgrades of the beamline promise energies up to at least 20 keV, which should largely remove the problem.

A higher maximum temperature, say up to 400 °C, of the heating system would make studies of age hardening in aluminum alloys even more rewarding since this is the usual temperature range in which DSC experiments are performed. Such an upgrade of the MePS beamline is planned, too.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

Al–Mg, alloy, aluminium, natural ageing, positron annihilation lifetime spectroscopy, vacancies

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