

Supplemental Material:

Co-evolution of vacancies and solute clusters during artificial ageing of Al-Mg-Si alloys

Mazen Madanat ^{a,b}, Meng Liu ^{a,b,*}, Xingpu Zhang ^a, Qianning Guo ^a, Jakub Čížek ^c and John Banhart ^{a,b}

^a Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany

^b Helmholtz Zentrum Berlin, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

^c Charles University, V Holešovičkách 2, 18000 Praha 8, Czech Republic

*corresponding author: meng.liu@helmholtz-berlin.de,

now at Chinalco Materials Application Research Institute Co., Ltd., Beijing, China

S1. Details of positron lifetime spectroscopy

Spectrometer in Berlin (B): Analog fast-fast coincidence spectrometers arranged in a co-linear geometry and equipped with Hamamatsu (H3378-50) photomultiplier tubes coupled with either BaF₂ or plastic scintillators (EJ-232) were used. The spectrometer equipped with BaF₂ scintillators was mainly used to obtain the course of the one-component lifetime (τ_{1C}) since for this its resolution of 245 ps was sufficient. A ²²Na source of ~15 μ Ci activity in a Kapton envelope was used and a count rate of 350-400 s⁻¹ achieved. To suppress backscattering, a 7-mm thick lead shield was applied between the sample and the start detector. A second spectrometer was coupled with plastic scintillators and had a resolution of 193 ps to 203 ps and a count rate of ~800 s⁻¹ using a source with an activity of ~45 μ Ci. The sample-to-detector distance was smaller here as no lead shield is needed. The spectra obtained were used for decompositions into 2 lifetime components.

Data sets were stored once every minute and later summed up to spectra representing longer times to provide the better statistics needed for lifetime decompositions. Usually, data representing 3-4 min (~10⁵ counts) were summed up for one-component analyses, and 15-30 min for positron lifetime decompositions (~5x10⁵ counts or more).

Data analysis was done using programme LT9 [1]. Pure annealed Al, measured positron lifetime 160 ps, was used to obtain the positron source contributions to the spectra, which amount to ~11% with a ~400 ps component from the Kapton foil and the sodium salt and <1% with ~3 ns from positronium formation. These source contributions were subtracted from the spectra. Data analysis usually started by fitting only one component, yielding lifetime τ_{1C} . A further component can be added in two-component fits. To ensure the reliability of such an approach, the fitting residual and fit variance were

required to improve after the addition of a further component. Moreover, the fitting procedure was required to be stable and not depend on the starting conditions in a sensitive way and the average lifetime calculated from the decomposed component was required not to deviate from the one-component lifetime τ_{1C} by more than 10 ps. The good resolution of the spectrometer used allowed for two-component analyses with three free parameters (two lifetimes and one intensity) in some cases, more easily for alloy 4-4 than for alloy 6-8.

Spectrometer in Prague (P). The high-resolution digital spectrometer is described in Ref. [2]. In the associated experiments a sample was kept at -40 °C throughout measurement and $\sim 5 \times 10^6$ counts were accumulated (count rate 50 s^{-1}).

S2. Positron lifetime extrapolation procedure

Figure S1(a) shows the evolution of τ_{1C} as a function of ageing time at ‘room temperature’ for alloys 4-4 and 6-8 directly after quenching (‘AQ’). The curves show multi-stage behaviour during NA comprising an initial decrease from a high value, a re-increase after ~ 100 min (4-4) or 45 min (6-8) and an indication for another decrease for long times. This behaviour has been discussed in Ref. [3] and elsewhere and is not the subject of this paper.

The samples that undergo natural secondary ageing (NSA) after artificial ageing (AA) behave differently. In Fig. S1(a), alloy 4-4 starts from a low value of 193 ps, remains constant for ~ 1 h, after which τ_{1C} increases. In alloy 6-8, however, τ_{1C} is constant for 1 day. In Fig. S1(b), τ_{1C} in alloy 6-8 increases from the beginning at a high rate. For other AA times a varying behaviour is observed. In this paper, we either take the average of the PLT before it starts increasing, Fig. S1(a), and use this value as the τ_{1C} that characterises a given AA or extrapolate to zero NSA time, Fig. S1(b), in cases where τ_{1C} does not show a regime of constant values. The background of the τ_{1C} variation during NSA is very complex and not the subject of the present paper.

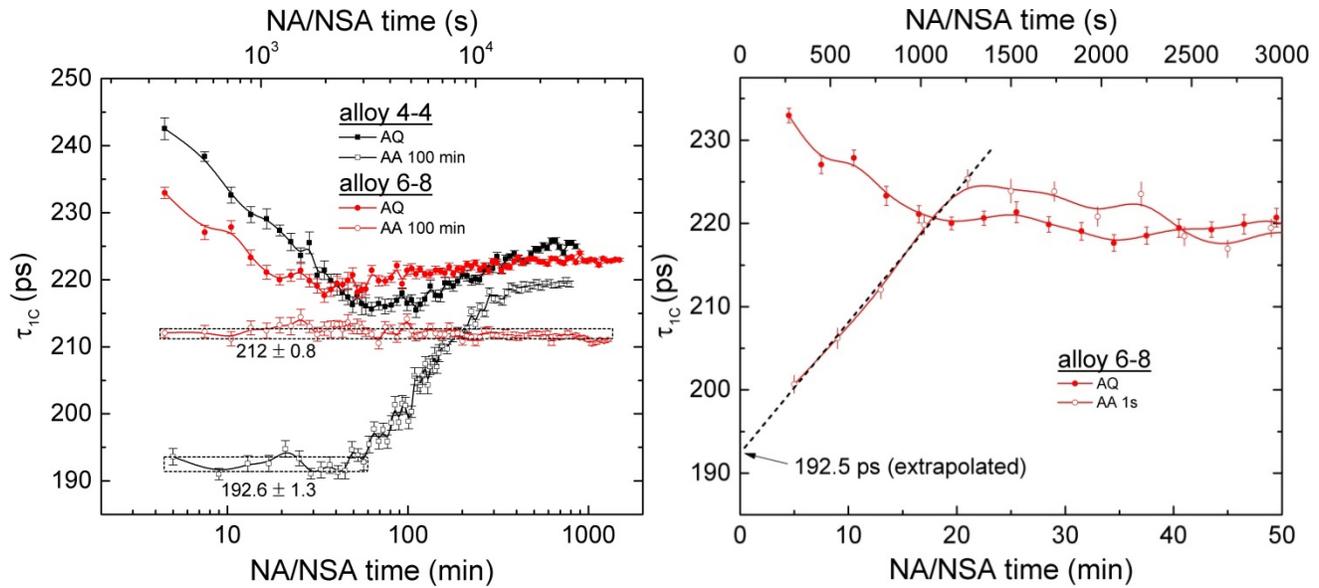


FIG. S1. One-component positron lifetime τ_{1C} in alloys 4-4 and 6-8 after solutionising and quenching ('AQ') during NA and after AA during NSA. a) AA for 100 min in LM (4-4) and oil (6-8), the periods of constant positron lifetime and the corresponding average values and standard deviations (boxes) are also given, b) AA for 1 s in LM (6-8), linear extrapolation of the fast changing lifetime to zero NSA time is demonstrated.

S3. Comparison between τ_{1C} and $\bar{\tau}$

The advantage of fitting positron spectra by just one lifetime component is that this procedure is very robust and allows one to evaluate spectra that contain 10^5 counts only [2]. The disadvantage is that in some cases τ_{1C} might deviate from the average obtained by decomposing spectra into components ($\tau_1, \tau_2 \dots$ with corresponding intensities I_1, I_2, \dots) (leading to a smaller fitting residual) and averaging the components after $\bar{\tau} = \sum I_j \tau_j$. Figure S2 shows the comparison of the two quantities for two measurements. The data show natural secondary ageing after AA as in Fig. S1, which we do not discuss in detail in this paper but which provides a good example that τ_{1C} is mostly slightly larger than $\bar{\tau}$ but the difference is small, typically 3 ps. Therefore, for giving interpretations of the course of positron lifetime during natural or artificial ageing, τ_{1C} is often sufficient. Note that although the $\bar{\tau}$ values derived from two-component decompositions shown in Fig. S2 appear meaningful, the individual components τ_1, τ_2 are often not reliable if the number of available counts in a spectrum is too low (here just $1 \times 10^5 - 2 \times 10^5$ counts).

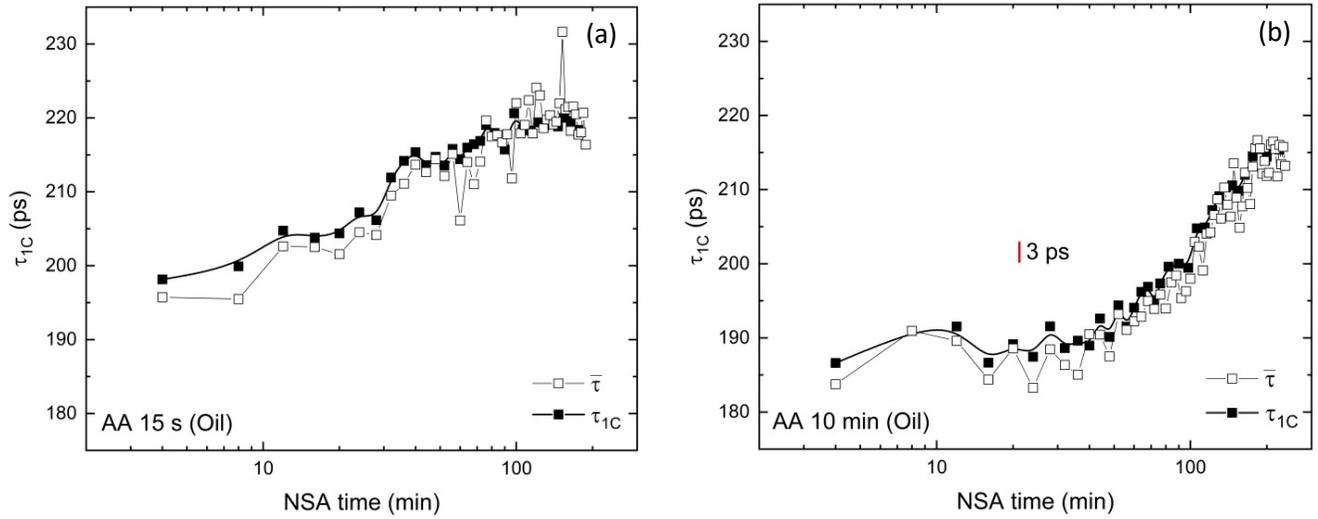


FIG. S2. Comparison between the one-component lifetime τ_{1C} and the average lifetime $\bar{\tau}$ obtained by two-component decomposition of spectra and subsequent averaging. Alloy 4-4 after AA during NSA.

However, there are cases where the differences between τ_{1C} and $\bar{\tau}$ are bigger. Simulations of artificially generated spectra (where the contributions are known) show that whenever a large vacancy component comes with a small bulk component, τ_{1C} can be up to 15 ps higher than $\bar{\tau}$ and the one-component fit is associated with a large variance. The reason is that the lifetime spectrum contains two very different components in this case, 90% of the vacancy-related component 245 ps and 10% of the reduced bulk contribution of 30 ps. Such a special situation does not occur often, but accidentally just for alloy 4-4 after quenching, where the measured $\tau_{1C} = 243$ ps corresponds to a $\bar{\tau}$ just around 230 ps [4].

References

- [1] J. Kansy, LT Programs, URL= <http://prac.us.edu.pl/~kansy/index.php?id=lt92>, accessed 16.05.2020
- [2] F. Bečvář, J. Čížek, I. Procházka, J. Janotová, The asset of ultra-fast digitizers for positron lifetime spectroscopy, Nucl. Instru. Meth. Phys. Res. A 539 (2005) 372-385.
- [3] J. Banhart, M.D.H. Lay, C.S.T. Chang, A.J. Hill, Kinetics of natural aging in Al-Mg-Si alloys studied by positron annihilation lifetime spectroscopy, Phys. Rev. B 83 (2011) 014101.
- [4] M. Liu, J. Čížek, C.S.T. Chang, J. Banhart, Early stages of solute clustering in an Al-Mg-Si alloy, Acta Mater. 91 (2015) 355-364.