

Supplementary Material (SM)

Effect of Sn and In on the natural ageing kinetics of Al-Mg-Si alloys

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Tests of restricted two-component analysis (“1½ component” analysis)

Restricted two-component analysis involves fixing one of the positron lifetime components, in our case the longer one (τ_v) associated to vacancy-related defects. Thus, reliable knowledge about this component is required because with a wrong change the analysis will go wrong. We base our choice of the value of τ_v on:

- Results of three-component decompositions that yield an almost unchanged value of 0.245 ns for the first 70 min of NA [1].
- Theoretical data on positron lifetimes in various defects (summary in Ref. [2]).

In order to assess the reliability of the analysis presented in Fig. 3, especially the fact that $I_{f+s} = 1 - I_v$ decreases after about 100 min of NA in alloy 4-4, we add the following experiments and analyses:

- An experiment with a high-resolution (0.135 ns) digital spectrometer set up at the University of Halle, data analysis assuming $\tau_v = 0.245$ ns as for Fig. 3, see Fig. S1,
- Assuming not only $\tau_v = 0.245$ ns, but also $\tau_v = 0.240$ ns and $\tau_v = 0.250$ ns, see Fig. S2,
- Assuming a non-constant τ_v that decreases or increases by 0.005 ns, see Fig. S3.

All the measurements and analyses show a decrease of τ_{f+s} and a decrease of I_{f+s} in stage III. There are small quantitative differences in the analyses, which however, do not affect the basic conclusions.

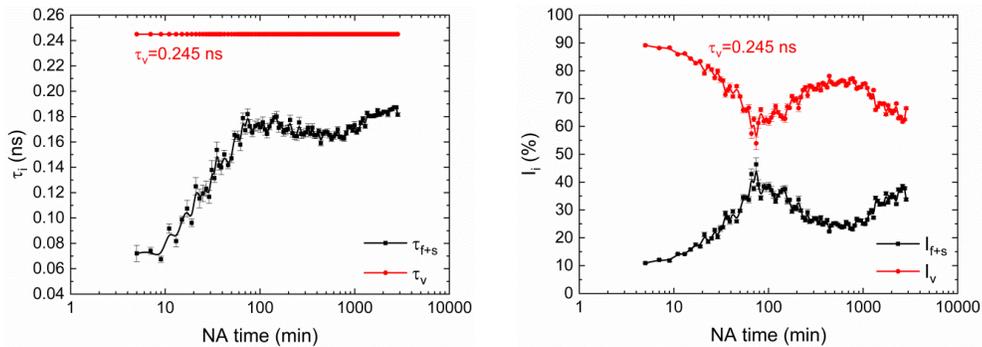


FIG. S1. Positron lifetime measurement on alloy 4-4 and a restricted two-component analysis in analogy to Fig. 3 ($\tau_v = 0.245$ ns).

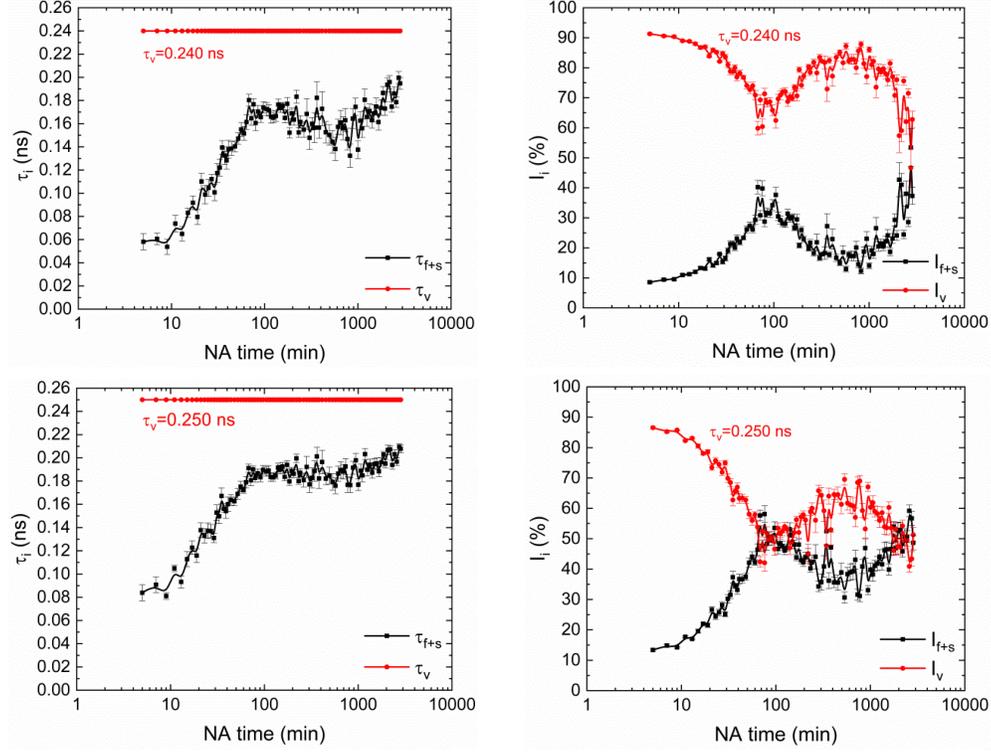


FIG. S2. As Fig. S1, but with a lifetime component τ_v of 0.240 ns (upper line) or 0.250 ns (lower line).

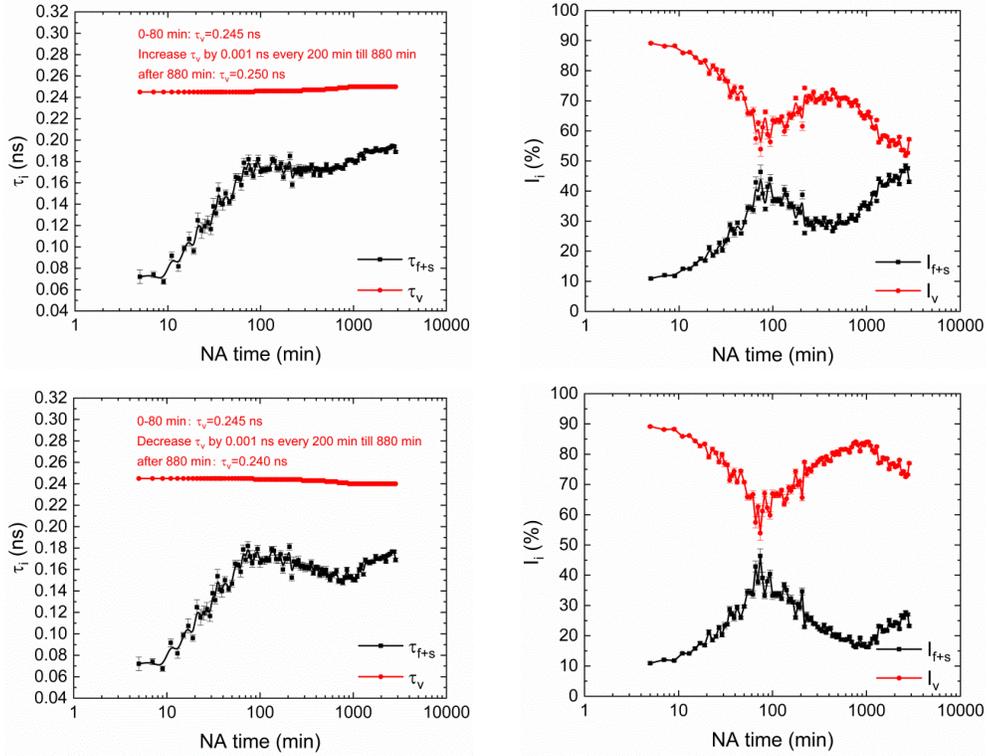


FIG. S3. As Fig. S2, but with the lifetime component τ_v increasing (upper line) or decreasing (lower line) from 0.245 ns to 0.250 ns or 0.240 ns, respectively.

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

The one-component PLT τ_{1C} is not equal to the lifetime $\bar{\tau}$ averaged from individual components although the two terms are often used in a synonymous way. Fig. S4 compares τ_{1C} and $\bar{\tau}$ for alloys 4-4 and 4-4-40Sn. The general course is found to be very similar, with minor deviations for 4-4-40Sn, where $\bar{\tau}$ is slightly lower than τ_{1C} . Especially for short ageing times where the vacancy-related component is strong, characterising a spectrum that contains more than one PLT by just one parameter τ_{1C} leads to this artefact. The discussion of the ageing kinetics, however, is not affected. Thus, the PLT in the quenched alloys can be reasonably described by τ_{1C} .

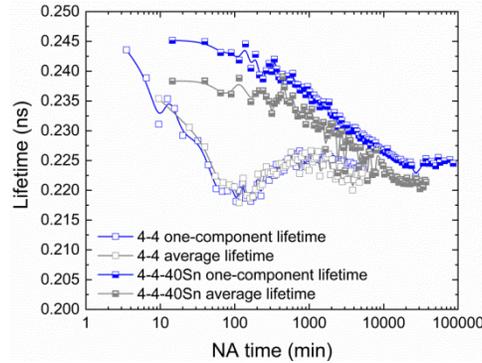


FIG. S4. Comparison between the one-component positron lifetime (from Fig. 1) and the average lifetime (calculated from Fig. 3). No scatter bars are shown to present the data in a clearer manner.

Influence of SHT temperature and Sn content on NA kinetics

The evolution of hardness shown in Fig. S5 also reveals the retardation effect of Sn on NA observed by PALS. In addition to Fig. 5, the influence of SHT temperature and Sn content on suppressing NA as reported in Ref. [3] is studied. For alloy 4-4, hardness remains constant up to 3 d/5 w for 40 ppm/70 ppm Sn addition, respectively, while for 6-8-40/70Sn alloys, stabilisation times are much shorter, i.e. ~ 90 min/200 min, respectively, i.e. higher Sn content leads to longer retardation of NA for both alloys. After this “stabilisation period”, an increase in hardness is observed. The increase of solutionising temperature from 540 °C to 570 °C has very little effect on NA kinetics of 4-4-40/70Sn alloys, other than on the one observed for alloys 6-8-40/70Sn, see Fig. S5, where NA is more delayed for 570 °C solutionising temperature. This has been explained by the higher Sn-solubility for lower Mg or Si content. Accordingly, in the alloys leaner in Mg and Si, a given amount is easier to dissolve and requires lower temperatures [4].

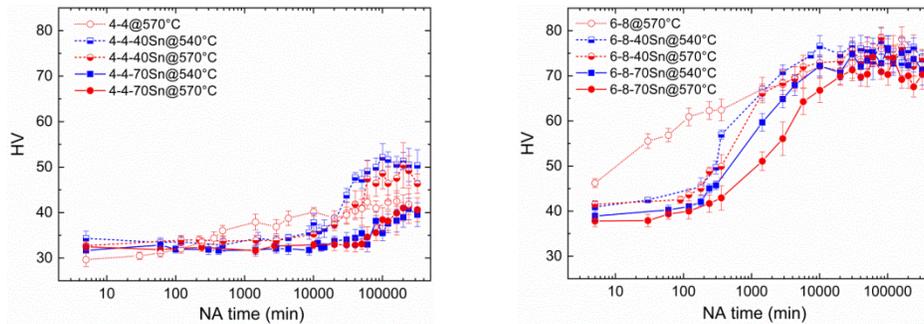


FIG. S5. Influence of SHT temperature (540 °C and 570 °C) and Sn content (40 ppm and 70 ppm) on hardness evolution of 4-4-40/70Sn (l.h.s.) and 6-8-40/70Sn (r.h.s.) alloys during NA.

Influence of Mg/Si ratio, main alloying element content and impurities

In addition to Sn content and SHT temperature as reported by [3,5], there are other factors which may directly or indirectly influence the retardation effect of Sn on solute clustering including, but not limited to, Mg/Si ratio, Mg and Si content as well as impurities such as Fe and Mn. Comparisons are made by using some pure alloys and commercial alloys with and without Sn and measuring the electrical resistivity as a measure for clustering, see Fig. S6.

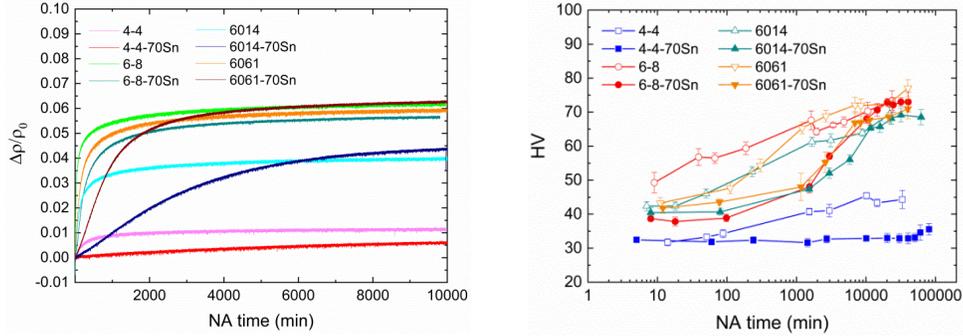


FIG. S6. Comparison between normalized resistivity changes in various alloys during NA on a linear time scale (l.h.s.) and the corresponding hardness evolutions on a logarithmic time scale (r.h.s.).

- Mg/Si ratio, Mg and Si content

The retardation effect of Sn is found to be less pronounced in alloys 6-8-70Sn and 6061-70Sn, moderate in 6014-70Sn, but largest in 4-4-70Sn according to resistivity data shown in Fig. S6. No direct correlation between the Mg/Si ratio and the retardation effect is found, e.g. see alloy 4-4-70Sn with an intermediate Mg/Si ratio (1.25) but the largest effect. However, taking into account the impact of the main alloying elements on Sn solubility [5], the marked differences in solute content between these alloys should be noticed in the first place. It was reported that for a given SHT temperature, Si strongly reduces the solubility of Sn in fcc Al, while for Mg, this effect is smaller [4]. This implies that the effect of Sn on clustering should be weaker in alloys with high Si (Mg) content. Taking alloys 6-8-70Sn and 4-4-70Sn as an example, the former has a considerably higher Si (Mg) content than the latter, which should and does, in turn, give rise to a significant reduction in the number of soluble Sn atoms, i.e. only a smaller fraction of quenched-in vacancies will bind with Sn and more Sn-free solute clusters should be formed in alloy 6-8-70Sn than in 4-4-70Sn. Apart from this, it can be reasonably assumed that the clustering kinetics is comparatively faster in alloy 6-8-70Sn. This is because on the one hand the distances between solutes/clusters (high solute content) are smaller, and on the other, the diffusion of vacancy-solute complexes and bare vacancies would be affected to less extent due to fewer Sn atoms in their surroundings. Thus, the dissolved Sn atoms determine the total effect of retardation and this is small if only a limited amount of Sn is soluble.

- Impurities

6061 and 6061-70Sn alloys with a composition corresponding to alloys 6061(A) and 6061-70Sn(A) used by S. Pogatscher for their studies [3] were intended to reproduce a comparable effect of Sn. In fact, however, Sn exhibits only qualitatively but not quantitatively the effect in prohibiting NA, e.g. the clustering kinetics in 6061-70Sn is even faster than in 6061-40Sn(A) alloy, see Fig. S7.

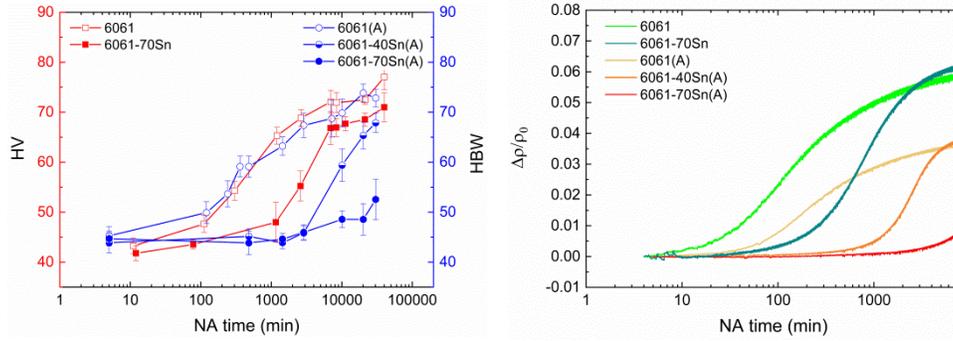


FIG. S7. Hardness evolution (l.h.s.) and normalized resistivity changes (r.h.s.) of the two types of 6061(Sn) alloys investigated during NA. Hardness data of 6061(A) and 6061-40/70Sn(A) alloys (blue spheres) were taken from [3].

It is known that a certain amount of Si will be retained in the Fe-rich intermetallics, which are always present in commercial aluminium alloys and cannot be fully dissolved during and after SHT. Thus, we intentionally reduced the Si content in alloy 6061-70Sn ($\sim 0.1\%$) while keeping Fe as low as possible, aiming at ensuring a similar NA behaviour for 6061-70Sn and 6061-70Sn (A) alloys. But still it seems that the reduction in Si content may not be sufficient, since the Fe/Si ratio of such intermetallics in an Al-0.37Mg-1.02Si-0.26Fe alloy (wt.%) approximately equals 1 as determined by EDX composition analysis [6]. Therefore, the higher retardation potential of Sn in the alloys investigated in Ref. [3] might be due to hitherto differences in alloy processing.

References

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