

## Supplementary Material

### **Clustering phenomena in quenched Al, Al-Mg, Al-Si and Al-Mg-Si alloys**

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In this supplement we present a brief literature overview describing ageing in alloys related to the ones discussed in this paper and some electrical resistivity and hardness data that support the conclusions of the paper.

#### **SM1. Literature review: Clustering in Al, Al-0.05Mg, Al-0.5Si and in Al-0.4Mg-0.4Si alloys**

As described in [1,2], for Al, up to  $2 \times 10^{-5}$  mono-vacancies are preserved after quenching in ice water, some of them form small but stable vacancy clusters, the rest diffuse to the nearest sinks during NA. The growth of vacancy clusters leads to a reduction in the concentration of vacancy-type defects, as indicated by the decrease in  $I_3$  (80% to 15%) since the distance between clusters decreases, while the corresponding PLT  $\tau_3$  increases from 0.250 to 0.290 ns, see Fig. 2. Thus, the increasing positron annihilation in the bulk causes the decrease of  $\tau_{1C}$  shown in Fig. 1a.

Al-0.05Mg and Al-0.5Si alloys exhibit qualitatively similar behaviors – the only difference is that instead of mono-vacancies, di-vacancies (~0.270 ns) or even tri-vacancies (~0.300 ns), which are small in size but high in number density (intensity in positron spectrum >60%), are formed already during quenching. Their subsequent growth, however, is much less pronounced than for pure Al, as reflected by the almost constant  $\tau_3$  and slightly decreasing  $I_3$  shown in Figs. 2a,b. Solute clustering can be theoretically [3] (repulsive interactions) and experimentally [2,4,5] excluded.

On the contrary, for Al-0.4Mg-0.4Si alloy, the binding between Mg-Si appears favorable based on atomistic calculations (+0.042 eV [3]), and the solute/vacancy ratio is much higher. The combined effect of both leads to the formation of Si-Mg clusters. In this case, vacancies can hardly aggregate but are temporarily trapped by Si and Mg atoms and assist in their diffusion during NA. The complex pattern of the  $\tau_{2+3}$  and  $I_{2+3}$  evolutions in Al-0.4Mg-0.4Si (Fig. 2) can be correlated with the formation (stage II) [1,6], growth and coarsening (stage III) [7-9], and eventually ordering of solute clusters (stage IV), which compete with vacancy-solute complexes and the bulk in trapping positrons during NA.

## SM2. Electrical resistivity and hardness

During natural ageing of an Al-Mg-Si alloy its electrical resistivity and hardness vary. In both cases, solute clusters, which accordingly act as scattering centers for electrons or hinder the movement of dislocations, respectively, can provide further information on clustering kinetics.

In this study, the evolution of electrical resistivity was recorded in-situ using a standard 4-point method. The results are presented as the normalized increase of resistivity  $\Delta\rho/\rho_0$  as a function of NA time. Brinell hardness was measured using a Qness 60M tester. A load of 10 kg with 10 s loading time was applied. Each data point represents the average of 10 hardness measurements. Similar features were found in these experiments which coincide with PALS observations (formation of small vacancy clusters during quenching and Si-rich solute clusters during NA), see Fig. S1, as further discussed below.

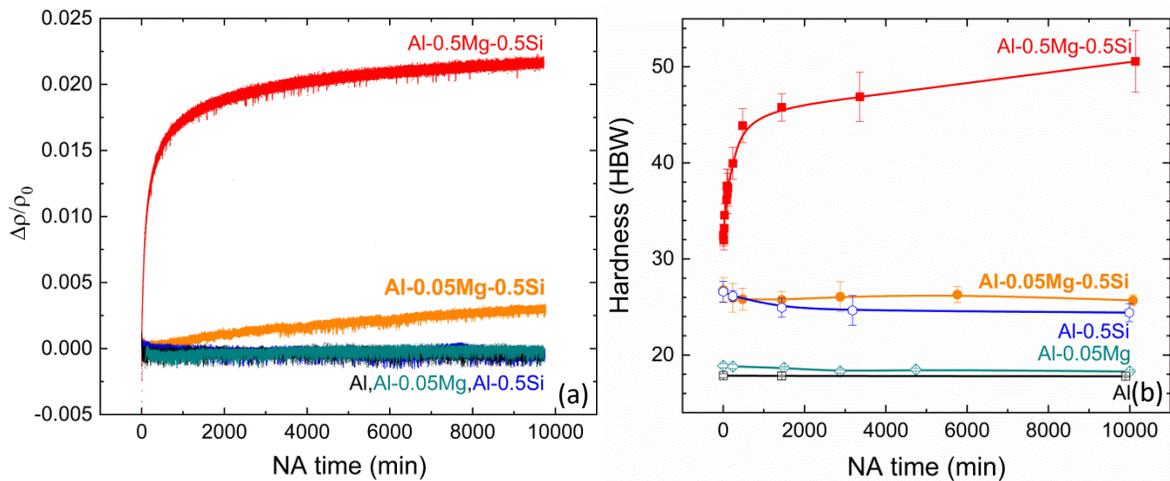


Figure S1. a) Normalized increase of electrical resistivity and b) hardness evolution in pure Al, Al-0.05Mg, Al-0.5Si and Al-0.05Mg-0.5Si alloys during NA.

Various scattering contributions such as at vacancies [10,11], impurities [12], solute clusters [13,14] and even GP zones [15] are known to affect the electrical resistivity of Al alloys. However, it appears that in this study, vacancy clustering alone might be insufficient to cause a measurable change in resistivity evolution of the quenched pure Al, Al-0.05Mg and Al-0.5Si alloys. In contrast, a moderate increment of resistivity during NA of alloy Al-0.05Mg-0.5Si clearly indicates the formation of solute clusters. For Al-0.5Mg-0.5Si, the even faster and much more pronounced increase can be ascribed to larger sizes and/or higher number densities of solute clusters, see Fig. S1a.

Despite the analogous pattern of hardness evolution during NA as resistivity for the same set of alloys there is no sign of hardening in alloy Al-0.05Mg-0.5Si at first sight, see Fig. S1b. This different behaviour of resistivity (and PLT) and hardness actually points at the sensitivity issue: The solute clusters formed in alloy Al-0.05Mg-0.5Si are too small to have a measurable effect on hardness, which is mainly increased by cluster size, but they are able to increase resistivity and decrease PLT  $\tau_{1C}$  [16,17] due to their sensitivity to cluster number density. However, irrespective of the methodologies applied, all results can be explained by the formation of small Si-rich Si-Mg co-clusters in alloy Al-0.05Mg-0.5Si due to the same microscopic reasons. Furthermore, it can be reasonably suspected that the fast increase of  $\Delta\rho/\rho_0$  and hardness in Al-0.5Mg-0.5Si alloy at the beginning of NA is associated with PALS stage II (Si-dominated) and the subsequent slow increase can be correlated to stage III (Mg-dominated).

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