Reversion of solute/vacancy complexes and clusters in Al-Mg/Si/Cu binary and Al-Mg-Si ternary alloys

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Scientific background

Al-Mg-Si alloys are brought to maximum hardness by solutionising at 540°C, quenching and subsequent artificial ageing at 180°C. Natural ageing at 'room temperature' between quenching and artificial ageing is known to have a negative effect on hardening which is why it is being studied. Atom clusters formed at room temperature are held responsible for the effect [1]. A study carried out with different methods has shown that clustering is not a continuous process but goes through a series of distinct stages. Electrical resistivity, hardness evolution, thermal effect of clustering and positron lifetime reflects these stages very clearly [2], but the nature of microscopic processes is not yet clear. The exact interactions governing the formation of clusters is not known. In the most simple case, it is the interaction energy between vacancies and solute atoms, in the more complex case that between solutes and between vacancies and clusters.

Al-Mg-Si alloys have extensively studied by ^{22}Na-based PALS. For example, samples were solutionised and quenched, after which the positron lifetime was continuously measured during 'room temperature' ageing. One observes a complex behaviour of positron lifetime as a function of time, characterised by an initial decrease for about 1 hour, a re-increase for typically 8 h and a final decrease. Fig. 1 shows a typical example [3]. The study of binary alloys, e.g. Al-Mg, is also valuable since the interactions between vacancies and solutes can be studied directly. Fig. 1b shows that the effect of initial ageing at 20°C (left panel) is partially reversed by ensuing heating to 250 °C. The main effect is the strong decrease of the defect signals and the corresponding increase of free positron annihilation. Various stages are observed, but the measurements are not reliable enough to conclude on the various stages and mechanisms. Reversion experiments in ternary alloy are even more challenging due to difficulties in decomposing lifetime spectra [4].

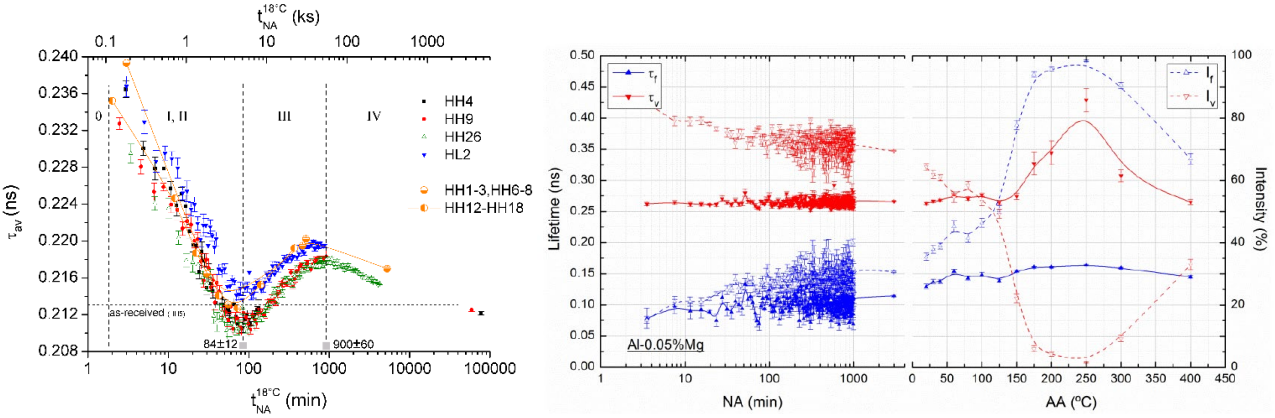

Fig. 1. a) Evolution of average positron lifetime in alloy Al-0.4Mg-0.4Si after solutionising at 540°C, quenching into ice water and measurement at 18°C. Various samples were measured, thus demonstrating good reproducibility [2]. b) Data for a dilute Al(Mg) alloy, left: Evolution of two positron lifetime components during natural ageing (after solutionising and quenching) and, right: reversal of clustering during isochronal annealing at increasing temperatures (10 min for each step) [5]. All measurements using our conventional ^{22}Na-based spectrometer.

Motivation for the proposal

As clustering is rather fast, in-situ experiments are time-limited, especially because after solutionising and quenching ageing initially proceeds fast. Therefore, the reverse way has been suggested. Instead of observing clusters during formation, pre-formed clusters are dissolved by heating to high temperature. The previously clustered solute atoms are released back into the matrix ('reversion') [4]. This process starts from a thermally stable state and is more easily controllable in a positron lifetime

spectrometer because handling of fast evolving samples is not necessary. Moreover, if low-energy positrons are involved, proper surface preparation is important to minimize positron annihilation in residual oxide layers and in defects created during polishing, which takes time.

In a first test experiment in September 2020 it was found that samples that show a single bulk lifetime of 160 ps in our ^{22}Na-based spectrometer exhibited just a 10%-20% intensity contribution of a higher lifetime (~300 ps) for ≥10 keV positron energy and otherwise the correct bulk lifetime. The samples had been polished very gently with various suspensions to obtain a mirror-like surface with only thin oxide layers and a low defect level. Thus, it was concluded that experiments at ELBE are possible and reversion experiments are especially suited since there is no need for quick sample preparation.

Based on this result we investigated binary Al-Mg and Al-Si, Al-Cu and ternary Al-Mg-Si alloys that had been solutionised, quenched and naturally aged for 1 week, after which their surface was prepared in the same way as for the test samples. Such alloys contain solute and/or vacancy clusters. These clusters are dissolved by linear heating to 230°C while measuring the PALS spectrum in-situ. The experiments were successful, but we noted a much higher influence of the surface than in previous experiments (intensities exceeding 50%). The reason must be the manual polishing process that is difficult to repeat in exactly the same way.

Only in one case could the influence of the surface be subtracted. The resulting average lifetime during reversion of naturally aged Al-Mg0.05 alloy reflects a mixture of annihilation in clusters and in the bulk and drops from initially 220 ps to 175 ps, reflecting the dissolution of clusters, see Fig. 2. A previous result obtained with a ^{22}Na-based spectrometer shows a comparable decrease, but at lower temperatures.

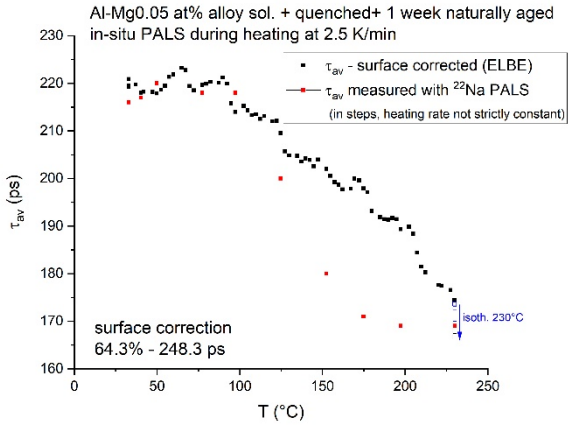

Fig. 2: Average positron lifetime measured in-situ during slow heating of previously naturally aged Al-Mg0.05 sample. The contribution from the surface has been determined by using data obtained for the initial stage by ^{22}Na-based PALS [8]. With this correction, the course of lifetime during dissolution of clusters is similar to the one measured previously [5] but shifted to higher temperatures.

Dissolution takes place largely at temperatures above 100°C, which seems to contradict the reported very low interaction energies between vacancies and Mg atoms (typ. 20 meV [7]). Two stages can be discerned, one up to 100°C with little change, the other from 100°C to 230°C. Due to the uncertainty with the influence of the oxide layer, no reliable two-component decomposition is available.

In a next step we wish to repeat and improve the measurements by applying two measures:

- Instead of mechanical polishing we will apply electropolishing. Such electropolishing can remove a few 100 µm of the surface without inducing mechanical stresses and defects. First trials with our alloys showed that good surfaces can be prepared. The remaining oxide films are very thin.
- Electropolishing allows us to provide reference samples which can be used for measuring the residual surface effects. For this, we will soft anneal samples and then remove the surface by

electropolishing. Provision of such references was not possible using mechanical polishing because soft annealing changes the surface oxide layer and polishing of such surfaces is not equivalent to polishing of not annealed samples. In contrast, electropolishing with its deep removal of surface regions does allow for preparing exactly equivalent reference samples. Data from such will be used to correct the data for the samples obtained during in-situ heating.

Experimental plan

We plan to characterise binary Al-0.05%Mg, Al-0.05%Si, Al-0.2%Cu alloys and one ternary Al-0.4Mg-0.4Si alloys (again). These alloys are all available as 1-mm thick sheets and 10x10 mm size and have been electropolished. In addition, soft-annealed and electropolished samples are available for single-temperature reference measurements.

We will measure previously naturally aged (containing clusters and solute vacancy complexes) samples in an electropolished state under conditions of constant heating from 20 °C to 230 °C with 3 different heating rates up to the maximum of 100 K/min. The positron energy is set to the highest possible value (10 keV or even). Spectra are continuously acquired with a timestamp which allows to relate it to a given temperature. The single-temperature reference samples are measured at 10 different energies.

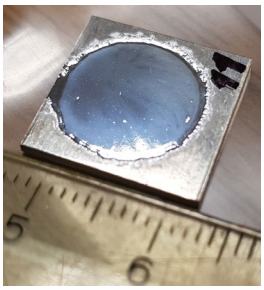

Fig. 3. Appearance of electropolished Al-Mg sample with material in the central sphere removed.

Calculation of beamtime requested

- One single heating experiment takes 2.5 hours (mounting, evacuating chamber, setting parameters), if everything runs smoothly perhaps slightly less. This time is longer than estimated in the previous proposal. The reference samples, however, can be processed in 90 minutes based on previous experience.
- With 4 alloys and 3 heating rates 30 hours are needed. Measuring the reference samples takes 6 hours, i.e. in total **36 hours**.

Results exected and impact

The measurements will allow us to assess binding energies in atomic clusters and to elucidate why Mg-vacancy complexes are more stable than predicted by all current calculations. Reversion measurement of the long naturally aged dilute Al(Cu) alloy may support the formation of solute clusters in very lean Al(Cu) alloys which is suggested in our recent study. Moreover, we hope to obtain explanations for the observed multi-stage decomposition behavious of clusters of vacancies and solute atoms and seek to promote the appliaction of the reversion method to other heat treatable alloys.

References

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