# Coincidence Doppler Broadening and 3DAP Study of the Preprecipitation Stage of Al(-Li)-Cu-Mg(-Ag) Alloys

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### Abstract

Positron annihilation and three-dimensional atom probe (3DAP) techniques are employed to investigate the pre-precipitation of solute clustering in Al-Cu-Mg, Al-Cu-Mg-Ag and Al-Li-Cu-Mg-Ag alloys. Not only by observing the solute clusters using 3DAP but also by detecting quenched-in vacancies and their vacancy-solute complexes using positron lifetime and coincidence Doppler broadening (CDB) of positron annihilation, we reveal the effect of vacancy-solute interactions in the solute clustering in the early stage of the precipitation in the Al alloys. The present success shows that the combination of positron annihilation and 3DAP is very useful to study the mechanism of the solute clustering.

### 1. Introduction

In spite of extensive studies, the atomic scale mechanism of the solute clustering and the hardening in the initial stage of aging remains unsolved for various AI alloys. Recently, the pre-precipitation of solute clusters, which are too small to be observed even by high-resolution transmission electron microscopy (TEM), has been directly observed by three-dimensional atom probe (3DAP) technique which can map the elemental distribution in nearly atomic scale, and their morphology has been revealed [1]. However, the 3DAP can not detect vacancies, which play essential roles through their interactions with solute atoms. Thus, in order to understand the mechanism of the clustering, detailed atomic scale process of the association of solute atoms with the vacancies should be clarified.

Positron is the only probe that is able to detect vacancy-type defects in metals sensitively [2-5]. Since positively charged nuclei are absent at vacancy-type defects, positrons are sensitively trapped and annihilate there with the surrounding electrons, conveying the information on the local electronic environment around the vacancy-type defects. Positron lifetime spectroscopy provides information on the size of the vacancy clusters and their number density. Coincidence Doppler broadening (CDB) is a recently developed technique, which enables us to identify the solute atoms bound to vacancies [6,7].

Thus, it is expected that useful information on the clustering mechanism will be obtained by combining positron annihilation with 3DAP. In this paper, we report several successful examples of this kind of study for Al-Cu-Mg, Al-Cu-Mg-Ag and Al-Li-Cu-Mg-Ag. By comparing the results for the three alloys as-quenched and aged at 180°C for 15s, the interactions between the vacancies and Ag and Li atoms are discussed.

## 2. Experimental

The three alloy samples of AI-1.9Cu-0.3Mg, AI-1.9Cu-0.3Mg-0.2Ag and AI-5.1Li-1.9Cu-0.3Mg-0.2Ag (at.%) were prepared by melting high-purity materials in an induction furnace in vacuum and casting them into an iron mould.

After homogenization heat treatment, the samples were cut to  $8 \times 8 \times 1 \text{ mm}^3$  plates for CDB measurement,  $\Phi 3 \times 1 \text{ mm}$  disks for TEM observation, and  $0.3 \times 0.3 \times 10 \text{ mm}^3$  square rods for 3DAP analysis. They were solution heat treated at 530°C for 30 min in a Pyrex tube under an argon atmosphere and then water quenched. They were aged immediately at 180°C for 15s.

The positron annihilation (CDB and positron lifetime) measurements, 3DAP and TEM observations were performed for all samples although only a part of the results are shown in this paper. All the positron annihilation experiments were performed at 150K to reduce the effect of room temperature aging during the measurements. The details of the methods and the results are described in ref. [8-10].

In analysing the CDB spectra, we calculate 'CDB ratio curves' which are given by the ratio of the CDB spectra to that for the well-annealed pure AI. As shown in Figure 1, the shape of the ratio curve in the high-momentum region is characteristic of each element, so we can identify with which elements of solute atoms annihilate positrons by comparing the obtained ratio curve with the elemental reference curves in Figure 1. Ag is characterized by a peak around  $12 \times 10^{-3}$ mc (c is the speed of light and m is the electron rest mass) (contribution by 4*d*-electrons), and Cu is characterized by a broad peak around  $15 \times 10^{-3}$ mc with a long tail extending to the higher momentum (contribution by 3*d*-electrons). The Mg ratio curve is characterized with a minimum near  $8 \times 10^{-3}$ mc and small peak around  $12 \times 10^{-3}$  mc, but its intensity is much lower than those for Ag and Cu, so obtaining a characteristic curve from the samples with 0.3at.%Mg is considered to be difficult. The ratio curve for Li does not show any characteristic feature, so there is almost no sensitivity of vacancy-Li complex by the CDB method. These low sensitivities to Mg and Li are due to the absence of *d*-electrons in Mg and Li, which are in contrast to the case of Cu and Ag.

# 3. Results and Discussion

**AI-Cu-Mg:** Before describing the effect of Ag and Li doping, we mention the AI-Cu-Mg ternary alloy. This system is well known for its rapid hardening in the initial stage of aging [11-13]. Several mechanisms have been reported for the origin of the rapid hardening: the homogeneous formation of GPB zone [14], co-clustering of Mg and Cu atoms [15], and heterogeneous nucleation of S' phase on dislocations [16]. However, using 3DAP and TEM, Reich et al. [17] claimed that they are not the origin of the initial rapid hardening, but suggested that a solute-dislocation interaction causes the hardening based on thermomechanical treatment results,

Figure 2 shows the CDB ratio curves and positron lifetimes for the Al-Cu-Mg as-quenched and aged at 180°C for 15s where the initial hardening takes place. In the as-quenched state, the positron lifetime (218 ps) is much longer than that of the bulk Al (166 ps), indicating the survival of a large number of quenched-in vacancies due to the solute-vacancy interactions. The estimated vacancy concentration is in the order of 10<sup>-5</sup> in atomic fraction [18,19]. In the shape of the CDB ratio curve of the as-quenched sample, the characteristic shape of Cu (Figure 1) is slightly observed.



Figure 1: CDB ratio curves for pure Cu, pure Mg, pure Ag and as-quenched Al-3.3Li alloy with respect to well annealed pure Al. Ratio curves for pure Cu and pure Ag are reduced to 20% in amplitude.

The fraction of positrons which annihilate with the electrons of Cu atoms is roughly estimated to be about 4% (see ref. [8] for estimation of the fraction). This value is not so high compared with the Cu content (1.9at.%) in the alloy considering that Cu has a higher positron affinity than AI [20,21]. Thus, we conclude that most of the quenched-in vacancies are not bound to the Cu atoms.

The characteristic shape of Mg (Figure 1) is hardly observed in the CDB ratio curve because of the low sensitivity to Mg as mentioned in section 1. However, it is reasonable to consider that the vacancies are stabilized by associating with Mg atoms (Vacancy-Mg complexes) because the vacancies are mobile at room temperature without forming their vacancy-solute complexes.

After aging at 180°C for 15s, the positron lifetime shows a marked decrease from 218 ps to 201 ps.



Figure 2: CDB ratio curves and positron lifetimes for Al-Cu-Mg as-quenched and aged at 180°C for 15s. Ratio curve for pure Cu reduced to 10% in amplitude is also shown for a reference.

This indicates that the number density of the vacancies decreases rapidly during the short time aging. The CDB ratio curve also changes drastically; the Cu signal (Figure 1) clearly increases as shown in Figure 2. The fraction of positrons which annihilate with the electrons of Cu atoms is roughly estimated to be about 10%, suggesting that the vacancies are bound to Cu atoms after aging for 15s. These results indicates that vacancy-Mg complexes rapidly migrate to vacancy sinks along dislocations and form

vacancy-Mg-Cu complexes during the 15s aging at 180°C. This supports the interpretation that the pinning of the dislocations by Mg and Cu atoms is the origin of the initial rapid hardening [8].

Al-Cu-Mg-Ag: A minor addition of Ag to Al-Cu-Mg alloys strongly affects the clustering behaviour and the subsequent precipitation process. In an AI-Cu-Mg alloy without Ag, a large number density of dislocation loops form after aging at 180°C for 15 s followed by water guenching [9]. This is consistent with the results that the vacancy-Mg complexes formed by guenching can easily migrate to vacancy sinks, *i.e.* dislocations, incorporating Cu atoms during the short time aging as stated above. On the other hand, in the case of Ag containing alloy, a high number density of Ag-Mg co-clusters form after the short time aging as shown in Figure 3(a), instead of the formation of dislocation loops. Such a difference can be understood by considering the interaction between the quenched-in vacancies and the Ag and Mg atoms as follows. The CDB ratio curves and positron lifetimes for the AI-Cu-0.3Mg-0.2Ag as-guenched and aged at 180°C for 15s are shown in Figure 3(b). In the as-guenched state, the positron lifetime (219 ps) is very close to that of the Al-Cu-Mg, indicating the surviving of quenched-in vacancies with nearly the same concentration as that of the Ag-undoped sample. However, the CDB ratio curve of the Agdoped alloy is guite different from that of the as-guenched Ag-undoped sample; not only the Cu peak component with the long tail in the high momentum region (>15×10<sup>-3</sup>mc) but also the Ag peak component around 12×10<sup>-3</sup>mc are observed even though the Ag content (0.2at.%) is one order of magnitude lower than the Cu content (1.9at.%).



Figure 3: (a) 3DAP elemental map of Al-Cu-Mg-Ag aged at 180°C for 15s. Integrated concentration depth profile calculated from small selected volume of the map is also shown. (b) CDB ratio curves and positron lifetimes for Al-Cu-Mg-Ag as-quenched and aged at 180°C for 15s. Ratio curve for pure Cu reduced to 9% in amplitude and synthesized ratio curve of pure bulk Cu (4% in amplitude) and Ag (9% in amplitude) are also shown for references (broken and solid curves, respectively).

These results mean that some of the vacancies are bound to Ag atoms as well as Mg atoms, i.e. vacancy-Ag-Mg complexes, in the as-quenched state of the quaternary alloy. Here it should be noted that the Cu peak component does not suggest incorporation of Cu to the vacancy-Ag-Mg complexes since this component intensity reflect the Cu content (1.9at.%) and the positron affinity of Cu, as seen for the Al-Cu-Mg alloy.

After aging at 180°C for 15 sec, the positron lifetime decreases from 219 ps to 209 ps, which indicates the decrease of the number density of the vacancies. However, the lifetime is longer than that for the Al-Cu-Mg after the same aging (201 ps), suggesting that the slight Ag addition delays the recovery of the vacancies.

The Ag peak around  $12 \times 10^{-3}$  mc in the CDB ratio curve becomes higher after the aging, indicating the increase of positron annihilation with the electrons of Ag atoms. These results suggest that the vacancy-Mg complexes are stabilized by further accompanying Ag atoms, which promotes the co-clustering of Ag and Mg atoms by aging rather than by the formation of dislocation loops.

**AI-Li-Cu-Mg-Ag:** In AI-Cu-Mg-Ag and AI-Li-Cu-Mg-Ag alloys, it is well known that the uniformly dispersed plate-like precipitates on the {111} planes designed as  $\Omega$  and T<sub>1</sub>, respectively, are formed after prolonged aging, resulting in the drastic improvement of the mechanical properties. The structures of  $\Omega$  and T<sub>1</sub> are very similar; Ag and Mg atoms strongly segregate to the {111}  $\Omega/\alpha$  and T<sub>1</sub>/ $\alpha$  interfaces [22,23]. However, the preprecipitation clustering behavior is different; while a high number density of Ag-Mg co-clusters form after short time aging in the AI-Cu-Mg-Ag alloy, Ag-Mg co-clusters are not formed in the Li containing AI-Li-Cu-Mg-Ag alloy as shown in Figure 4(a) [10,24].

Figure 4(b) shows the CDB ratio curves and positron lifetimes for the Al-Li-Cu-Mg-Ag asquenched and aged at 180°C for 15s. In the as-quenched state, the positron lifetime (184 ps) is much shorter than that for the Al-Cu-Mg-Ag (219 ps), indicating the lower vacancy concentration (estimated to be in the order of 10<sup>-6</sup> in atomic fraction [18,19]).



Figure 4: (a) 3DAP elemental map of Al-Li-Cu-Mg-Ag aged at 180°C for 15s. Integrated concentration depth profile calculated from small selected volume of the map is also shown. (b) CDB ratio curves and positron lifetimes for Al-Li-Cu-Mg-Ag as-quenched and aged at 180°C for 15s.

This means that vacancies with a concentration of an order of  $10^{-5}$  annihilate during quenching by the presence of 5.1 at.% Li. The diffusion of Li atoms is known to be fast in AI from the fact that  $\delta'$  (Al<sub>3</sub>Li) precipitate rapidly during quenching. In Al-Li binary alloys, quenching can not suppress precipitation of  $\delta'$ , indicating that Li migrate fast with vacancies during quenching. Since Li concentration is 5.1 at.%, one out of twenty atoms are Li.

Since the coordination number in the fcc lattice is 12, more than half of vacancies must be associated with Li atoms. While vacancies migrate with Li, they will annihilate at vacancy sinks. This may be the reason why the concentration of quenched-in vacancies in the Li containing alloy is one order magnitude smaller than that in the quaternary alloy. This would suppress the kinetics of the subsequent precipitation process as reported in [10]. The positron lifetime is unchanged after aging at 180°C for 15s.

In the CDB ratio curve, a hump around  $12 \times 10^{-3}$ mc due to the Ag electrons are slightly observed in the as-quenched state, similar to the case of Al-Cu-Mg-Ag. This suggests that some vacancies are bound to Ag atoms in this alloy as well. However, the change of the CDB ratio curve by aging is quite different from that in the alloys without Li. While the Ag peak enhances markedly for the Al-Cu-Mg-Ag after the short time aging (Figure 3(b)), it does not appear in the Li-containing alloy, indicating that the Li alloying suppresses the formation of vacancy-Ag-Mg complexes. Since Li appears to be associated with vacancies as stated above, the formation of vacancy-Mg complex will be suppressed. As a result, vacancy-Mg-Ag complexes do not form in the Li-containing alloy.

#### 4. Conclusion

We revealed that the difference interaction between vacancies and Mg, Ag and Li atoms causes the different behaviour of the solute clustering in Al-Cu-Mg, Al-Cu-Mg-Ag and Al-Li-Cu-Mg-Ag as shown above. The present success demonstrates that by combining positron annihilation with 3DAP useful information on the clustering mechanism can be obtained.

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