MICROSCOPIC STRUCTURES OF METASTABLE PHASES IN Al-Ag BINARY ALLOYS
T. Sakurai, A. Jimbo, T. Hashizume, A. Sakai, K. Osamura, T. Nakamura

To cite this version:

HAL Id: jpa-00225659
https://hal.archives-ouvertes.fr/jpa-00225659
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MICROSCOPIC STRUCTURES OF METASTABLE PHASES IN Al-Ag BINARY ALLOYS

T. SAKURAI, A. JIMBO, T. HASHIZUME, A. SAKAI, K. OSAMURA' and T. NAKAMURA'

The Institute for Solid State Physics, The University of Tokyo, Tokyo, Japan
Department of Metallurgy, Kyoto University, Kyoto, Japan

Abstract - Morphology and chemical composition of metastable phases in an Al-5.72at% Ag alloy have been investigated by means of atom-probe field ion microscopy. The $\eta$-G.P. zone appears to have an ordered structure and its average solute concentration is 45.8at% Ag at 413 K. The $\epsilon$-G.P. zone is spherical in shape and its composition is 35.7at% Ag. The $\gamma'$ metastable phase is plate-like precipitates lying on the (111) lattice planes, whose composition has been determined for the first time to be 33.3at% Ag.

I - INTRODUCTION

Since the discovery of metastable coherent clusters by Guinier /1/, the structures and growth processes of G.P. zones have been extensively investigated in Al-Ag alloys /2/. The metastable phase diagram with respect to G.P. zones was given by Baur and Gerold /3/. The precipitation sequence is described as follows. Depending on aging temperature, three types of G.P. zones precipitate. Below approximately 443 K, disordered $\eta$'-G.P. zones are formed and they are transformed to ordered $\eta$-G.P. zones. Above 443K, disordered $\epsilon$ - G. P. zones precipitate. At a later stage of aging, the metastable $\gamma'$ phase appears. The equilibrium phase in this composition is $\gamma$ phase.

Although the precipitation behaviors mentioned above have been generally accepted for long time, there exist still some uncertainties concerning the structures of these metastable phases. In order to shed a light on these problems, direct observations on an atomic scale are most helpful. In the present study, the structures of both $\eta$ and $\epsilon$ zones as well as $\gamma'$ metastable phase have been investigated by means of an AP-FIM and compared with the results obtained by other techniques, such as small-angle X-ray scattering.
II - EXPERIMENTAL PROCEDURE

An Al-5.72at% Ag binary alloy was solution-treated at 823 K for 6ks and then quenched into ice water. After the specimen was aged at 413 K or 463 K, it was electrochemically polished into a fine needle tip.

The details of the AP-FIM used in the present work were reported elsewhere/4/. The specimen tip is mounted on the manipulator and cooled down to approximately 30 K. After a good quality of hydrogen FI image is observed, the atom-probe analysis is performed using pulse ratio of 0.2 to 0.4 and repetition rate of 60 Hz.

III - RESULTS AND DISCUSSION

Fig. 1 shows the hydrogen FI images for the specimens aged at 413 K for 6 ks (a) and for 60 ks (b) and aged at 463 K for 60 ks (c).

![Hydrogen field ion micrographs of an Al-5.72 at% Ag alloy aged at 413 K for 6 ks (a) and 60 ks (b) and aged at 463 K for 60 ks (c).](image)

Bright spots are Ag rich precipitates. Their size became larger and coarsened with increasing aging time as seen in the figure (a to b). Their shape appears to be spherical in those figures and we could not observe any facets or features characteristic to the octahedron. The present observation contradicts with the results by Alexander et al./4/ who proposed the octahedral zones on a basis of the high resolution electron microscopy. This discrepancy may be attributed to the difference in particular particle sizes examined.

A typical result of the atom-probe analysis of these zones is shown in Fig. 2. The probe-hole was adjusted onto the (111) crystal plane. The layer-by-layer evaporation was realized and the number of atoms covered by a probe-hole was 51.4 per layer in average. The Ag concentration rises gradually at the edge of the zone from the matrix value (0.6 at% Ag) since the probe-hole covers both the matrix and the zone of our interest at the interface. We note that the Ag concentration oscillates at the central part of the zone in the range of 25 to 50 at% Ag with an average of 37 at%. This may be due to the

![Ag concentration profile of the η zone obtained upon aging at 413 K for 6 ks.](image)
fact, a zone has an ordered structure along the <111> crystal orientation. Using a series of atom-probe data, the autocorrelation analysis was performed and the result is shown in Fig. 3. The correlation, \( G( r_j ) \), decreases rapidly as the distance between adjacent layers increases. After reaching a minimum at \( r_j = 3.6 \text{nm} \), \( G( r_j ) \) increases again and shows a peak at \( r_j = 6.3 \text{nm} \). The first minimum of \( r_j \) gives the average cross-sectional dimension of the zone, \( \bar{L} \), while the position of the maximum yields the average distance between the neighbouring zones, along the probing column. The latter quantity is called the one-dimensional interparticle distance, \( L_u \).

![Autocorrelation on the fluctuation of the Ag concentration for an Al-5.72 at\% Ag aged at 413 K for 6 ks.](image)

When the specimen was aged at 413 K for 60 ks, the size of the zone increased as shown in Fig. 1 (b). The solute concentration inside the zone is uniform and approximately 45.8 at\% Ag, slightly higher than that obtained by a shorter aging (Fig. 1 (a)). The results on the structure of \( \eta \) zones are summarized in Table 1, along with the data of small-angle X-ray scattering measurements/5/.

### Table 1. Summary of the size and interparticle distance of \( \eta \) zones

<table>
<thead>
<tr>
<th>Annealing</th>
<th>AP-FIM</th>
<th>SAXS /17/</th>
</tr>
</thead>
<tbody>
<tr>
<td>413 K</td>
<td>3.6 nm</td>
<td>2.1 nm</td>
</tr>
<tr>
<td>413 60</td>
<td>5.3 nm</td>
<td>3.0 nm</td>
</tr>
</tbody>
</table>

The average cross-sectional length, \( \bar{L} \), is equal to \( 4/3R \) for the identical spherical particles with radius R. In practice, however, the zones have a size distribution as its mean radius, \( \mu \), and the standard deviation, \( \sigma \), and they are given in the table. Taking into account the size distribution, the present data of the length, \( \bar{L} \), is qualitatively consistent with the SAXS result. The one-dimensional interparticle distance, \( L_u \), may be different from the three dimensional distance, \( L_t \), as determined by SAXS measurements. When the fine zones distribute homogeneously (the specimen aged for 6 ks), \( L_u \) obtained by AP-FIM is smaller than \( L_t \). On the other hand, when the large zones are widely separated (the specimen aged for 60 ks), \( L_u \) becomes larger than \( L_t \).

For the specimen aged at 463 K for 60 ks, both spherical clusters and plate-like precipitates are observed as shown in Fig. 1 (c) and Fig. 4. The clusters are identified as \( \varepsilon \) zone and the platelets as the metastable \( \gamma' \) phase. The solute concentration of the spherical zone is found to be 35.7 at\% Ag. The concentration averaged over
five γ' precipitates was determined to be 33.3 at% Ag and the concentration profile inside the precipitate was found homogeneous. This is the first time the composition of γ' phase was determined. From a series of FI images obtained sequentially during field evaporation, the relative positions and sizes of individual precipitates (ε and γ') can be reconstructed (Fig. 5). The thickness of platelet γ' phase is in the range of 2.3 to 7.9 nm and the size of ε zone is approximately 30 nm. Recently Howe et al. /8/ examined the thick γ' layers and observed that there exist interfacial ledges whose height is more than two atomic layer high.

Fig. 4. A series of H FI images of an Al-5.72 at% Ag aged at 463 K for 60 ks, showing the evolution of the disk-shaped γ' precipitate (appeared as a ring).

Fig. 5. A schematic of the arrangement of disk-shape γ' precipitates appeared in Fig. 4.

However our atom-probe work did not revealed any ledges in thin γ' layers examined so far.

An interesting observation as to the γ' precipitate is that the solute concentration becomes higher near the interface of the precipitate with thickness of one or two layers as is shown in Fig. 5. It is suggested that this solute segregation may well be the initial stage of nucleation of the stable γ phase.

Fig. 6. Concentration profile of Ag within the γ' zone for an Al-5.72 at% Ag aged at 463 K for 60 ks. The enrichment of Ag is evident at the boundary.
IV - CONCLUSION

We have demonstrated that our focusing-type ToF atom-probe is capable of studying aging effects by analyzing the compositional profile of metastable phases in a small scale, using an Al-5.72at% Ag alloy aged at both 413 K and 463K.

REFERENCES