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ATOM-PROBE ANALYSIS OF G.P. ZONES IN AN Al-1.7 at% Cu ALLOY

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Abstract

G.P. zones in an Al-1.7 at% Cu alloy aged at 383 K for 8000 min were analyzed by atom probe FIM. The layer-by-layer concentration profiles in the <100> direction were obtained from several G.P. zones. Generally, the G.P. zones were found to consist of several copper enriched layers, the maximum composition of which was 50 at% in this aging condition. Although some uncertainty exists as to the copper content, it can be concluded that none of the copper enriched layers approach the pure copper concentration. Some G.P. zones showed two well separated copper enriched regions, others showed a broad single peak in copper concentration. Therefore, it was concluded that this aging stage is a transition from a G.P. 1 to a G.P. 2 stage. The present result together with the previous atom-probe data indicates that there is a distinct stage for G.P. 2 zones which have two separated copper enriched layers in the (200) planes.

I. Introduction

According to the X-ray diffraction study by Gerold (1), G.P. 1 zones in Al-Cu alloys are single pure Cu plates on (200) planes. This simple model has been widely accepted so far. After Gerold's study, several models have been proposed on the basis of the X-ray diffraction data (2-5). However, the structure and the composition of the G.P. 1 zones have not been determined unambiguously.

As to the structure of the G.P. 2 zones or theta" (hereafter denoted as G.P. 2 zone), Gerold's model is also widely accepted. According to the model, a G.P. 2 zone consists of two pure Cu (200) layers separated by three Al layers. In other words, a G.P. 2 zone is tetragonal with a=0.404 nm and c=0.768 nm. This model is qualitatively supported by both TEM and FIM observations (6,7).

Auvrey et al. (8) suggested that single- and multi-layer zones with essentially 100 at%Cu coexist in the G.P. 1 stage of Al-1.7at%Cu alloy aged at room temperature for an extended period of time. In the last decade, the structure of G.P. zones in Al-Cu alloys has become a topic of intense study by many workers with various experimental techniques such as TEM (6,9-14), EXAFS (15,16), FIM (7,17,18), SAXS (19) and SANS (20).

In their most recent work, Matsubara and Cohen (21) concluded that G.P. 2 zones did not have a different structure from G.P. 1 zones, and suggested that the G.P. 2 zone is just a growth stage of the G.P. 1 zone. Thus, their conclusion is that there is no G.P. 2 zone which is typically described with the structural model of Gerold having three Cu (200) layers separated by three Al layers. Although they gave an explanation for the electrical resistivity change which had been interpreted as an evidence of the existence of a G.P. 2 stage, it does not seem that their explanation is successful for interpreting the specific heat curve indicating individual stages for the G.P. 1 and G.P. 2 zones (22,23).

There have been many examinations of the structure of G.P. zones using electron microscopy (6,9-14). Although TEM is a very powerful technique for observing and determining the structure of small precipitates such as G.P. zones, the interpretation of the image is not necessarily simple. Thus, the
structure of G.P. zones cannot be determined simply from imaging contrast (12,14).

Therefore, the main controversies at this point are as follows;

1) Whether or not G.P. 1 zones are single layer.
2) Whether or not G.P. 1 zones are 100 at% Cu.
3) Whether G.P. 2 zones are just thick G.P. 1 zones or instead have a unique structure consisting of two copper rich layers separated by aluminum layers.
4) What is the composition of G.P. 2 zones.

The present atom-probe study attempts to clarify the structure of G.P. zones in Al-Cu alloy. The aging condition was chosen to be the same as that of Matsubara and Cohen's work for G.P. 2 zones (21). The structures of G.P. 1 and G.P. 2 zones will be discussed using the present results together with the previous atom-probe results (25,26).

**II. Experimental**

An Al-1.7at%Cu alloy ingot was prepared from high purity materials by inert-gas induction melting in a carbon crucible. After annealing at 823 K for 3 days, the ingot was drawn into wire 0.3 mm in diameter. The samples were annealed for 1 h in a vacuum at 823 K in a vertical tube furnace and free fall quenched in ice water. Samples were then immediately aged at 383 K for 8000 min. According to Matsubara and Cohen (21), this aging condition is classified as G.P. 2 state. Specimens for FIM were prepared by electropolishing at 3 V a.c. in a solution of HNO3 with a small addition of water.

An energy compensated time-of-flight atom probe FIM was used in the present study. The details of the instrument have been described elsewhere (24). The atom-probe analysis was performed with random area analysis in the <100> direction. From the long data chain (more than 60000 signals), only the regions whose copper content is much higher than any other regions were selected for data analysis. More than 7 G.P. zones were detected in this random analysis. The diameter of the zones were much larger than that of the (200) planes in the field ion tip; therefore, it is certain that all the data came from within the diameter of the zone. The fact that the highest composition level obtained in the present study is almost the same as that obtained in the previous study with selective area analysis (26) is also an indication that the probe hole covered only G.P. zones. The conditions for the atom-probe analysis were as follows; specimen temperature, about 30 K; vacuum, $8 \times 10^{-10}$ Torr; pulse ratio $V_{\text{pulse}}/V_{\text{dc}}$, 0.15.

**III. Results**

The concentration depth profiles in the <100> direction of G.P. zones in Al-1.7at%Cu alloy aged at 383 K for 8000 min which was determined in the same way as described in reference (25) are shown in Fig. 1-a,b,c,d. Common features are

1) The copper enriched layers extend about 10 layers.
2) The maximum concentration is 40 to 50 at% Cu.
3) There is a large concentration fluctuation in the <100> direction.
4) The copper concentration profile is diffuse rather than discrete.

There is a high copper concentration peak in Fig. 1-a and -b, and the concentration fluctuates between 5 to 20 at% at the tails. This feature of the zone is similar to that described by Matsubara and Cohen (21) except for the concentration of the copper enriched layers. The G.P. zones seem to be just thick copper clusters consisting of several copper enriched (200) planes. In Fig. 1-c and -d, the concentration fluctuation seem to be more significant, and two high level copper enriched regions separated by less copper enriched layers are discernible in each (200) depth profiles.

In order to compare the present result with the previous ones as to the G.P. 1 zones in the aging stage at 403 K for 1000 min and the G.P. 2 zones in the aging stage at 423 K for 2880 min, the concentration depth profiles for each stage are reproduced from references (25) and (26), as shown in Fig. 2 and Fig. 3.

**IV. Discussion**

**IV-1. G.P. 1 zone (25)**

As shown in Fig.2, the composition of the G.P. 1 zone is about 30 at%, which is close to the composition of Al2Cu. This suggests that the miscibility gap for the G.P. 1 zones lies within the two phase region of
aluminum solid solution and Al₃Cu. The zone consists of four Cu enriched layers, each of which has approximately the same composition within the statistical error. Considering this a broad G.P. 1 zone, the question was whether or not single layer G.P. zones also exist. In the field ion microscopic observation, it was clearly shown that a fair number of G.P. zones displayed single line bright contrast (7,18). However, when the G.P. zones were observed parallel on (200) planes, they always displayed multi-layer contrast. The atom-probe analysis always showed there were more than three copper enriched layers in the <100> direction. There is a possibility that the field evaporation did not proceed exactly layer-by-layer. Then, the spatial resolution in the <100> direction would be broadened. The total number of the data chain from the four copper enriched layers was approximately 100. It was made certain that the average number of detected ions per layer was approximately 20 to 25 in this analysis. Then, even if two layers evaporated simultaneously, it does not seem to be probable that a single layer G.P. zone could be broadened to more than four layers in the atom-probe data. It is also clear that if the G.P. zone indeed consists of multi-layers of pure copper suggested by Matsubara and Cohen (21), 100 at% Cu should have been recorded with the atom-probe regardless of the details of the evaporation process. Therefore, it is most probable that the G.P. zone is actually as shown in Fig. 2. As to this stage, since the accumulated data were not so many, the question must be kept open.

IV-2. G.P. 2 zones (26)

As to G.P. 2 zones, at least one thing seems to be clear: there are two Cu peaks in the concentration profile separated by two or three less concentrated layers as shown in Fig. 3. This concentration depth profile was reproducible, and it is hard to believe that the two peaks in copper concentration profile were accidentally obtained. The concentration change is not discrete as expected from the tetragonal model of Gerold (1); rather it is pretty diffuse. The extended number of copper enriched layers is more than 10. If the field evaporation does not proceed exactly layer-by-layer, the concentration depth profile will be broadened. Therefore, there is a possibility that the actual concentration depth profile is a little more discrete and the maximum composition is a little higher. After all, although the details are different, the general nature of this concentration profile is favorable to the tetragonal model of Gerold in the sense that there are two copper peaks separated by less concentrated layers in the <100> direction. Actually, G.P. 2 zones display two separated bright lines in the field ion micrographs (7,17). Therefore, it seems to be more realistic to distinguish this stage for G.P. 2 zones as has been generally believed in the past. However, the atom-probe analysis indicates that the composition of the copper rich layers does not reach 100 at% Cu as expected from the tetragonal model. Note that this analysis was done with selected area analysis, i.e., it was certain that the probe hole entirely covered the G.P. zones; therefore, the only possibility of matrix contribution is from subsurface layers if the evaporation did not proceed exactly layer-by-layer. The number of copper enriched layers is also more than that expected from the Gerold's model, the concentration change is diffuse in the <100> direction. The maximum composition of the copper enriched layers was about 50 at% Cu.

IV-3. G.P. zones aged at 383 K for 8000 min

The maximum copper concentration of the G.P. zones at 383 K for 8000 min was 40 to 50 at%, as is the case of the G.P. 2 zones in the alloy aged at 423 K for 2880 min. The number of copper enriched layers extended for more than 10 (200) layers, and a large concentration fluctuation was found. The nature of the concentration fluctuation could be categorized in two ways. One type has only one strong Cu peak in the concentration depth profile, as shown in Fig. 1-a and -b. The number of copper enriched layers extended to about 10 (200) planes, the maximum composition of which was 40 at%. Although the composition of the zone does not agree with that suggested by Matsubara and Cohen (21), the general nature of the zone is similar to that suggested by them. This zone could be a coarsened G.P. 1 zone, in the sense that only a single copper peak exists in the concentration profile in the <100> direction. Both the concentration of copper and the number of copper enriched layers were increased in this stage compared with the G.P. 1 state described in the previous section.

Another type of concentration depth profile found in this aging condition exhibited two strong peaks in copper concentration as shown in Fig. 1-c and -d. Although each copper enriched layer is not distinctly discernible in this aging stage, the general feature of the concentration depth profile is similar to that of G.P. 2 zones shown in Fig. 3 in the sense that there are two copper enriched regions separated by less concentrated layers. The maximum concentration is 40 to 50 at% Cu, which is the same as that of the other type. The concentration depth profile Fig. 1-d showed three less concentrated layers between two more concentrated copper enriched layers, which is similar to a feature of G.P. 2 zones as described.
Therefore, it seems to be a little bit difficult to describe the feature of the G.P. zones in this aging stage distinctly. G.P. zones having both features of G.P. 1 and G.P.2 coexist in this aging stage. Therefore, it seems to be more reasonable to believe that this aging stage is a transition from G.P. 1 to G.P. 2 stage. Zones having features of both G.P. 1 and G.P. 2 coexist in the Al-1.7at%Cu alloy aged at 383 K for 8000 min.

To sum up, G.P. 1 zones are generally three to four layers thick and the average copper content is about 30 at%. G.P. 2 zones have two copper enriched regions separated by a few less concentrated (200) layers. The transition stage contains the zones having features of both G.P. 1 and G.P. 2 zones. The composition of the zones at this stage is higher than that of the initial stage of G.P. 1. Therefore, the possible precipitation sequence is as follows: G.P. 1 zones which are either single or multi-layer with about 30 at% Cu coarsen as aging proceeds; at the same time, the copper concentration of G.P. 1 zones also increase. In the transition stage, both G.P. 1 zones which are more enriched with copper and G.P. 2 zones which have two copper enriched regions coexist.

G.P. 2 zones would increase the number of copper enriched layers periodically in the <100> direction; therefore, an atom-probe study of later stages of precipitation would be helpful to understand the precipitation sequence more clearly.

V. Conclusion

G.P. zones in Al-1.7at%Cu alloy aged at 383 K for 8000 min have been analyzed by the atom-probe FIM. The present result together with the previous results as to the G.P. 1 zones and G.P. 2 zones, lead to the following conclusions:

1) G.P. 1 zones are either multi- or single-layer with approximately 30 at% Cu.
2) G.P. 2 zones have two copper enriched regions, the maximum composition of which is approximately 50 at%, separated by two to three less concentrated (200) layers.
3) G.P. 1 zones increase their copper content to approximately 50 at% in the coarsening stage, and the number of copper enriched layers reaches about 10.
4) It seems to be more reasonable to conclude that G.P. 1 and G.P. 2 zones each have a distinct stage.

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References

16) B. Lengeler and P. M. Eisenverger, Decomposition of Alloys - the early stages, edited by P. Haasen et
al., Pergamon, 1984, p. 121.
Physical and Mechanical Properties, vol. 1, edited by E. A. Starke, Jr., and T. H. Sandars, Jr.,
EMAS, 1986, p.635.

Fig. 1 Concentration depth profiles in the <100> direction of G.P. zones in Al-1.7at%Cu 
alloy aged at 383 K for 8000 min.
Fig. 2 Concentration depth profile in the $<100>$ direction of a G.P. zone in Al-1.7at%Cu alloy aged at 403 K for 1000 min. Reproduced from reference (25).

Fig. 3 Concentration depth profile in the $<100>$ direction of a G.P. zone in Al-1.7at%Cu alloy aged at 423 K for 2880 min. Reproduced from reference (26).