Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 1033-1038

GP Zone Facets in Al-4, 15 & 30 wt% Ag Alloys

K. Matsuda[1], H. Daicho[1], G.J. Shiflet[2] and S. Ikeno[1]
[1]Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama, 930-8555, Japan
[2]Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904 USA

The morphology and faceting of Guinier-Preston (GP) zones in three Al-Ag alloys (Al-3.8, 15, 30 wt % Ag) were investigated by high resolution transmission electron microscopy. Al-Ag GP zones are considered to be a truncated octahedron and have facets of {111} and {100} planes with the matrix. The percentage of faceting along the interphase boundary was found to decrease with increasing aging temperature similar to previous studies. Contrary to other reports, current results show that facet percent does not remain constant with increasing GP zone size when isothermally heat treated. Facets were observed to be dominant at lower aging temperatures and smaller diameter GP zones. Silver content of the alloy was also important and found to alter facet percentage.

Keywords: *Al-Ag alloy, Guinier-Preston zone, faceting.*

1. Introduction

Interfacial structure studies in Al alloys are replete, primarily of plate-shaped precipitates, such as, θ' in Al-Cu. In Al-Ag alloys there are many reports directed at interfacial structure of the γ'-phase during growth or the dissolution process. GP zones, however, present a particular inherent difficulty in obtaining any quantitative interfacial analysis because of their small size and similar structure with the matrix. Only a few descriptions concerning the interphase boundary structure of GP zones in Al-Ag alloys [1-4] are reported. There are two identified types of GP zones, namely η and ε [5]. η occurs at temperatures under ca. 200 ^{o}C, whilst ε forms at higher temperatures. Results concerning composition differences between the two GP zones varies, as does their reported shapes. The η'-GP zone is formed during quenching, and grows or transforms to η-GP zone if the specimen is aged below 200 ^{o}C.

Alexander *et al.* [2] confirmed with TEM that GP zones in an Al-17.6 wt% alloy have facets on their interphase boundary at lower temperatures (they did not specify which GP zone, η or ε, they observed) and they correlated the facet findings with an equilibrium structure determined from discrete lattice modelling to assist in the construction of a Wulff plot. An important conclusion was, at a given temperature, the amount of faceting does not change with zone size. They worked from 160 to 350 ^{o}C and showed qualitative agreement between their predictions and {111} and {100} type faceting measured from conventional TEM. Agreement was improved when a sub-regular thermodynamic solution model was used to calculate the required phase field, instead of employing a regular solution model, which was necessitated by the asymmetrical miscibility gap in Al-Ag. Their modelling also required that GP zones faceting be assisted by high silver concentration gradients with the matrix. In the present paper, along with different heat treatment temperatures and times, three alloys are investigated to examine the role of silver supersaturation on facet occurrence. The morphology and structure of GP zones in Al-Ag alloys are also investigated by high resolution transmission electron microscopy (HRTEM) to test the constant faceting conclusion of ref. 2 at an isothermal temperature as the GP zone grows.

2. Experimental procedures

Al-3.9, 15 and 30 wt% Ag alloys were made from 99.99% Al and 99.999% Ag shot. The ingots obtained were rolled, encapsulated and homogenized at 550 °C for 4 days. These ingots were rolled again, solution heat treated at 550 °C for 20 min. and then aged at temperatures between 50-200 °C for systematically longer times. Usually water quenching was performed after solution heat treatment. Some samples were quenched to aging temperatures directly to avoid formation of the η′-GP zone [5]. TEM samples were prepared by electrolytic polishing using a solution of methanol:nitric acid = 4:1. HRTEM (Topcon EM 002B) was operated at 120kV to avoid damaging the foil during observation. GP zones were observed up to 1.6 million X magnification and images are shown with no image processing.

3. Results and Discussion

Fig.1 shows TEM images of the three Al-Ag alloys aged at 50, 100, 150 and 200 °C, all for 1 hour. The visible transformation phase in this figure is the GP zone, whose contrast results from silver partitioning as there is little strain. Going down each column in Fig. 1 highlights zone diameters are significantly larger as alloy silver content increases at a constant temperature and time. GP zones for constant Ag contents aged at lower temperatures, for example at 50 °C, are smaller than those aged at 200 °C for this fixed 1 hr. time. The mean size of GP zones in the 4% Ag sample aged at 200 °C is 6.13 nm, and 2.95 nm in the same alloy aged at 50 °C. The size of η-GP zones are about 2-3 nm as reported by Baur and Gerold [5], so GP zones less than 3 nm in the sample aged at 50 °C are referred to as η-GP zones with no further evidence.

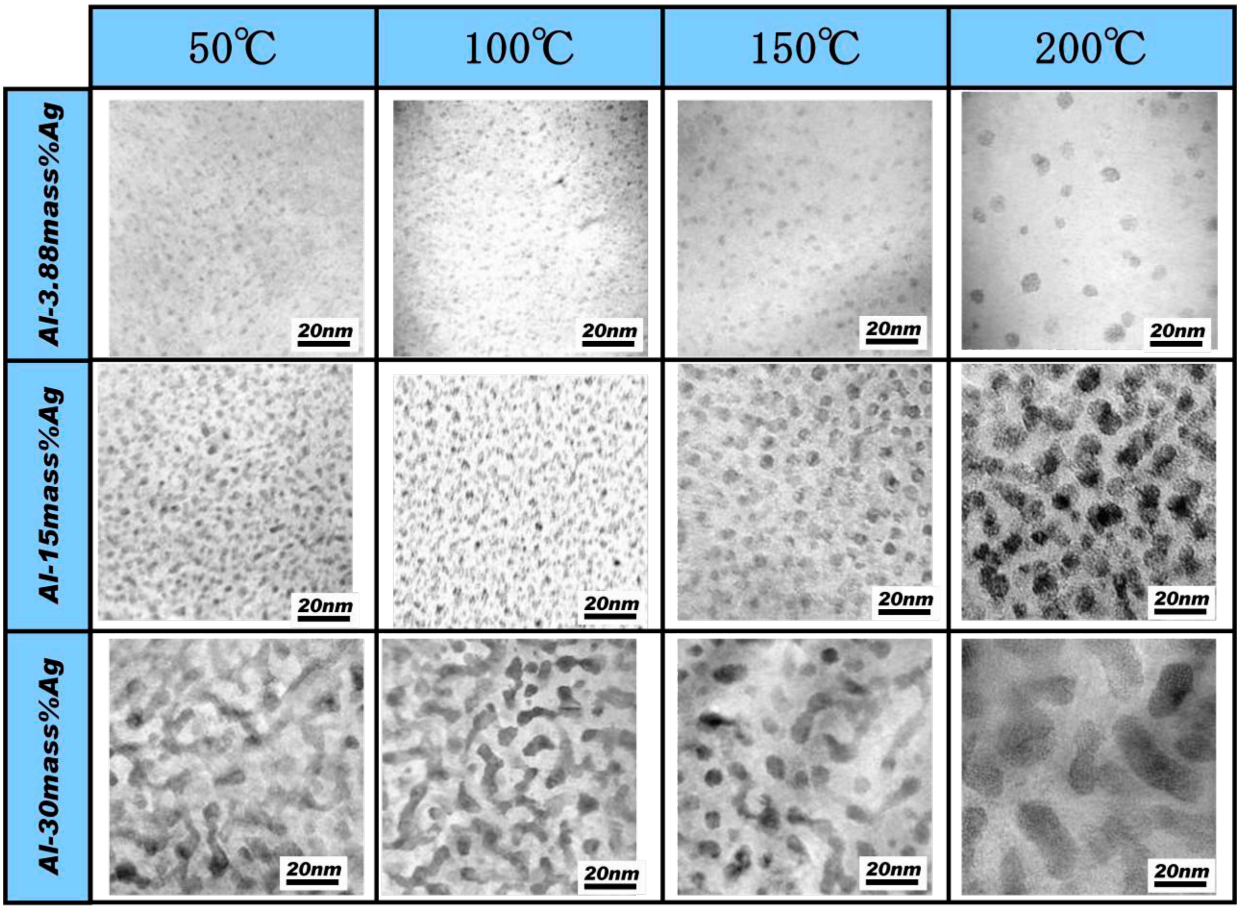


Fig. 1. Series of TEM images of GP zones in Al-4% Ag (top row), Al-15% Ag (middle row) and Al-30%Ag bottom row. Aged for 1 hour at 50, 100, 150 and 200 °C (columns left to right).

For the 30% Ag in Fig. 1, discrete particles that are apparent in lower Ag contents, now yield to zone interconnectivity resembling a spinodal transformation. This morphology occurs at all temperatures. Examining the zones formed in a 15% Ag alloy at a constant temperature (200 ^{o}C) with increasing times (Fig. 2) demonstrates that the zone size increases with time, as expected, but with a decrease in density, which is consistent with a combination of growth and coarsening

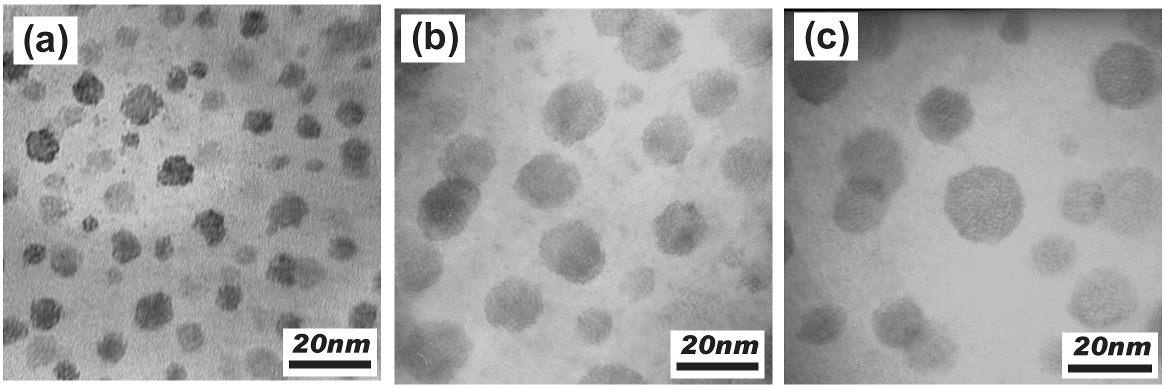


Fig. 2. Growth and coarsening in Al-15% Ag aged at 200 ^{o}C for (a) 1 hr, (b) 10 hr and (c) 16.7 hr. Notice the zone size increasing and density decreasing with time.

A higher resolution examination for the same 15% Ag GP zones shown in Fig. 2, reveals not only the increasing size at the fixed 200 ^{o}C temperature (Fig. 3), but also the HRTEM images highlight prevalent facets which are particularly clear at earlier times (small zone size). The zones are formed by isothermal heat treatments for times of 1, 5 and 16.7 hr.

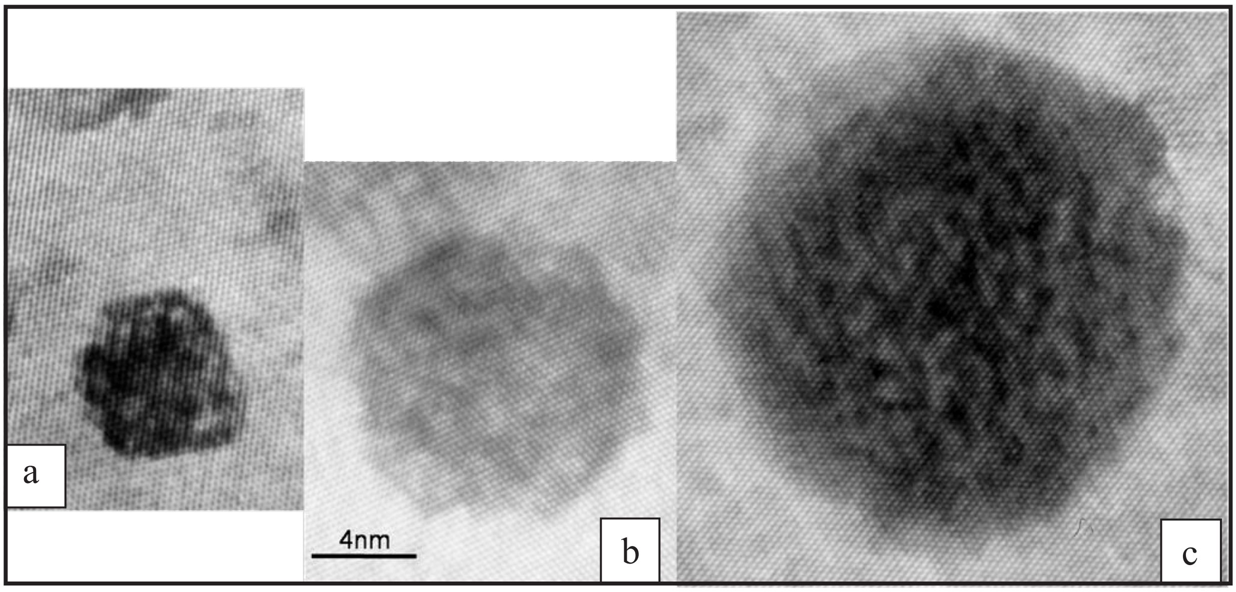


Fig. 3. Two TEM images of GP zones in Al-15% Ag isothermally heat treated at 200 ^{o}C for (a) 60 min. (b) 300 min. and (c) 1000 min. The 4 nm scale bar applies to all images.

Fig. 4 graphically illustrates much of the preceding, where the GP zone size increase is rapid at early times and after about 2.5 hr (ca. 10 ks) growth/coarsening is steady. Along with growth, Fig. 4 also shows the {111} facet percent. As particles grow at a constant temperature the {111}-facet percentage is not constant and decreases from approximately 50 to 30% where it holds steady over this time scale. This is in conflict with the conclusion of Alexander *et al.*, who note in their Al-17.6 wt.% Ag alloy that "there was no variation in the amount of faceting as a function of either reaction time or precipitate size." This result was necessary for their study which modelled the equilibrium shape based on Wulff plots; this theoretical approach requires that as the zone grows, strain energy must be a minimum and Ag diffusivity fast enough for the required energy balances to occur which will produce, and ensure that, the equilibrium facet morphology will be maintained.

Coupled with faceting percentage changing with zone size and reaction time at a fixed temperature, the effect of overall alloy silver concentration also has an effect. This is illustrated in Fig. 5 where the three Al-Ag alloy's facet percent is plotted against zone size for all the temperatures and times investigated. Results follow a similar pattern demonstrated in Fig. 4 where as the zone diameter increase, the facet percent decreases, at least for 111-facets. In addition, the trends in Fig. 5 for each alloy further indicate that as the Ag content increases the facet percent increases relative to the lower Ag containing alloy(s).

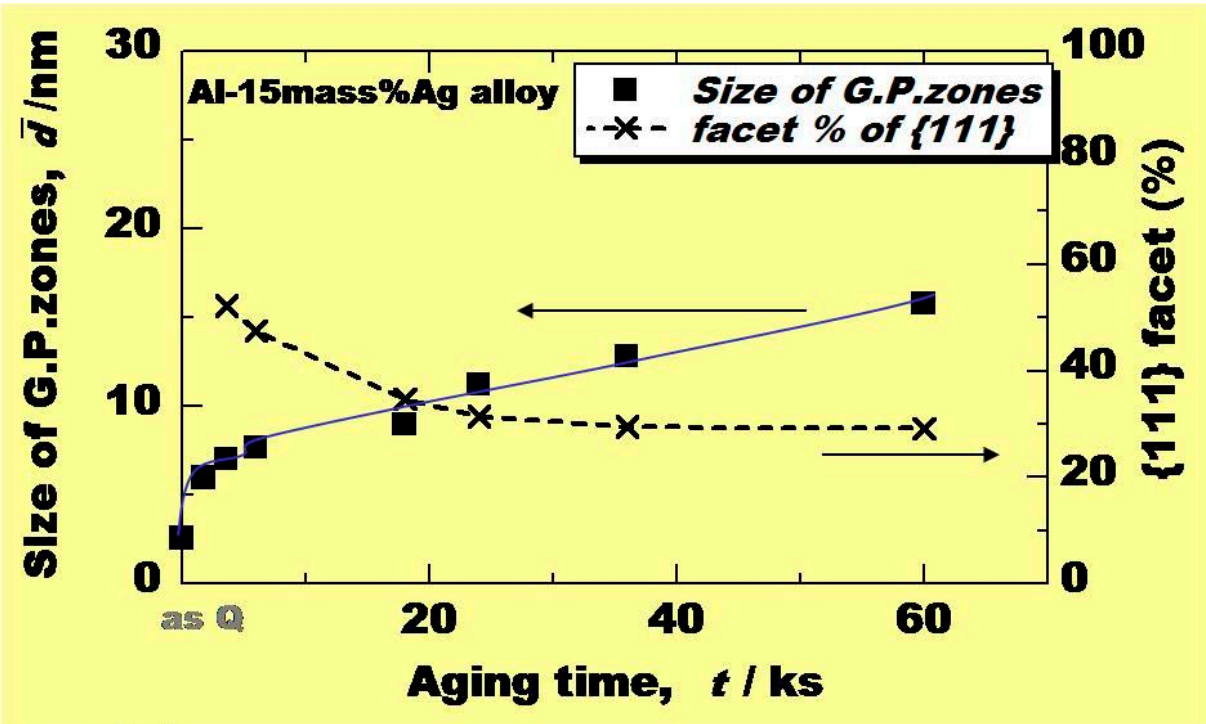


Fig. 4. Plot showing GP zone diameter as a function of aging time (left-hand axis) and {111} facet percentage plotted against the same aging time. "as Q" is "as quenched". Al-15%Ag at 200 ^oC.

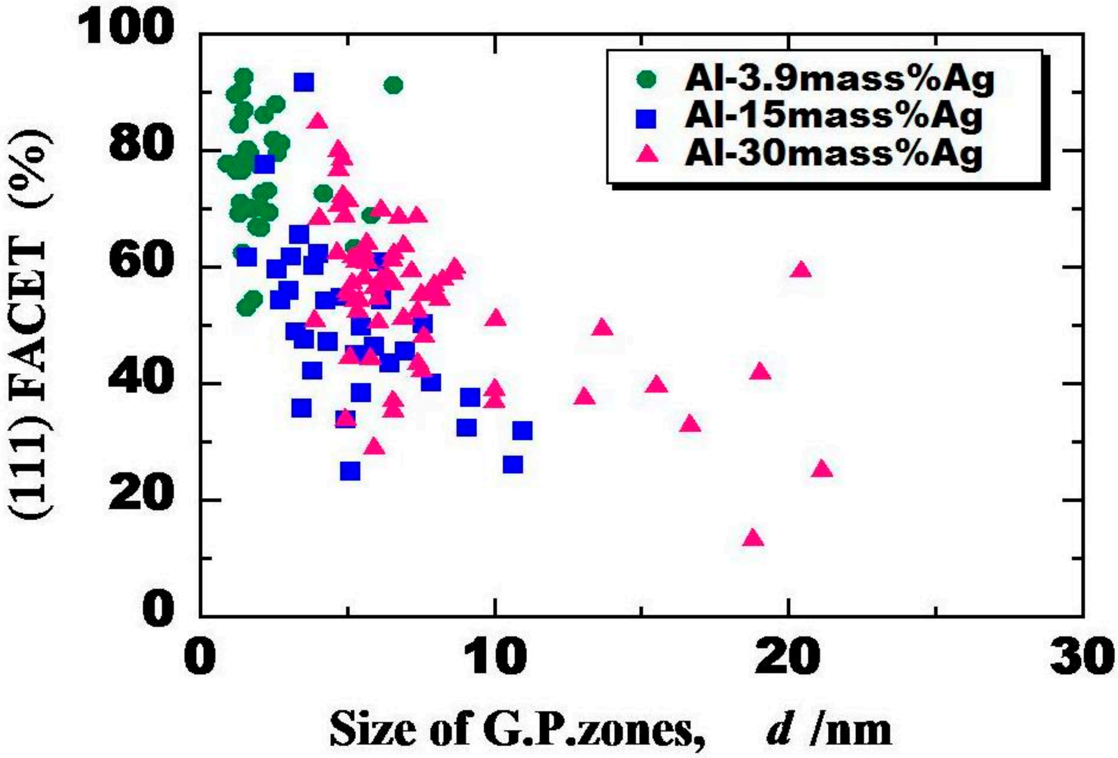
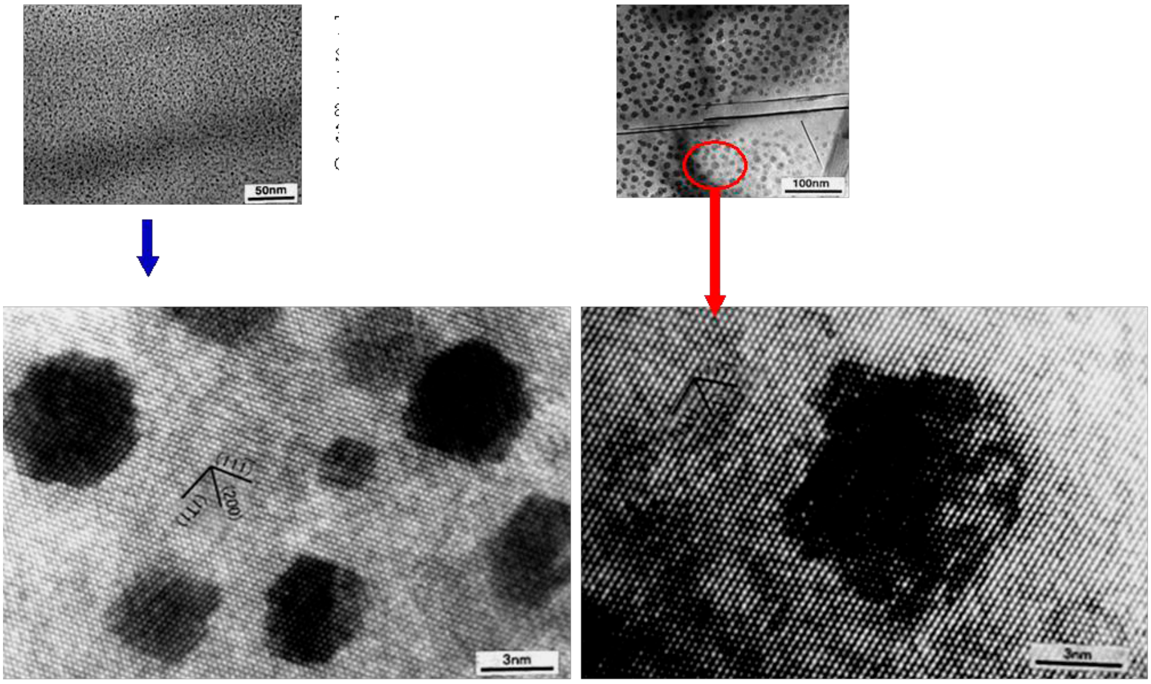


Fig. 5. Plot of 111- facet % as a function of GP zone size for Al-3.9% Ag (circles), Al-15% Ag (squares) and Al-30% Ag (triangles). This result is for all aging conditions from 50 to 200 ^{o}C.

Fig. 6a is a good representation of the facetting sharpness that occurs at lower temperatures (150 ^{o}C). Several zones are visible and facets are apparent and crisp, particularly the {111} facets are sharp. Fig. 6b is the same Al-15Ag alloy heat treated 50 ^{o}C higher in temperature than Fig. 6a. At 200 ^{o}C the facets are less strong, but some of this is the apperance of growth ledges along the broad faces.

Results herein show that GP zone growth and coarsening is dependent on alloy Ag content, which is not unreasonable, for certainly alloys varying from 3.9% Ag to 30% Ag have different nucleation and growth driving forces simply based on the phase diagram and the asymmetrical miscibility gap. The Ag concentration differences between the matrix and GP zones can further enhance faceting and results indicate that GP zones which have higher Ag concentration show sharper facets, at least at early reaction times. Previous research by Matsuda *et al.* [6] demonstrated with Energy Dispersive Spectroscopy (EDS) that small GP zones have shaper Ag gradients at the GP/Al interface than larger zones.

We could not find convincing evidence for a difference between the ε- and η-GP zone, especially concerning ordering in the η-GP zone [3], even with HRTEM. However, if we were to classify the two kinds of zones, *viz*., ε- and η-GP zones, the larger size zone is the ε-GP zone and that which has fewer facets and is smaller is the η-GP zone, which is also strongly faceted, but this is speculative [7].



(a) (b)

Fig. 6. HRTEM images of Al-15% Ag aged at (a) 150 ^{o}C for 1 hour and (b) 200 ^{o}C for 1 hour. Both images are taken from alloys experiencing a direct quench from the heat treatment temperature. Upper images show the uniform distribution of the zones. The plates in (b) are γ'. [011] zone.

4. Conclusions

GP zones in Al-4, 15 and 30 wt% Ag alloys were aged at several temperatures and observed by HRTEM to clarify their morphology and faceting. GP zones exhibit facets along the zone:matrix interphase boundary on {111} and {100} planes of the matrix, similar to the general observations by Alexander *et al.* Facets of {111} planes develop predominately rather than {100} planes. Facets are much more apparent at lower aging temperature and for smaller zones. Facets are shown to depend strongly on the size of G.P. zone and on the alloy Ag content. The dependence between zone size during growth and the amount of faceting, at a constant temperature, is not consistent with the previous conclusions/assumptions in ref. 2.

References

[1] J. E. Gragg, Jr. and J. B. Cohen: Acta Met. 19 (1971) 507-519.
[2] K. B. Alexander, F. K. Legoues, H. I. Aaronson and D. E. Laughlin: Acta Met. 32 (1984) 2241-2249.
[3] K. Osamura, T. Nakamura, A. Kobayashi, T. Hashizume and T. Sakurai: Acta Met. 34 (1986) 1563-1570.
[4] P. A. Dubey, B. Schonfeld and G. Kostorz: Acta Met. 39 (1991) 1161-1170.
[5] R.Baur and V.Gerold, Acta Met. 10 (1962) 637-647.
[6] K. Matsuda, H. Daicho, G. J. Shiflet and S. Ikeno: *Aluminum Alloys, their Physical and Mechanical Properties*, ICAA8, Ed. by P. J. Gregson and S. J. Harris (Materials Sci. Forum, Trans Tech Publ., Switzerland, 2002) Vol. 396-402, pp. 887-892.
[7] K. Matsuda, H. Daicho, G. J. Shiflet and S. Ikeno: *Aluminum Alloys, their Physical and Mechanical Properties*, ICAA7, Ed. by E. A. Starke, T. H. Sanders and W. A. Cassada (Materials Sci. Forum, Trans Tech Publ., Switzerland, 2000) Vol. 331-337, pp. 1019-1025.