A Quantitative Study of Precipitation of Metastable Phases in an Al-1.94 at% Cu Alloy during Isothermal Aging at 373 K

Sung-Kyu Son^{1,*}, Mahoto Takeda², Kyu-Seop Park², Masanori Mitome³,
Yoshio Bando³, Ki-Woo Nam⁴ and Chang-Yong Kang⁴

¹Research Laboratory for High-Voltage Electron Microscope, Kyushu University, Fukuoka 812-8581, Japan

²Department of Materials Engineering (SEISAN), Yokohama National University, Yokohama, 240-8501, Japan

³Advanced Materials Laboratory, National Institute for Materials Science, Ibaraki 305-0044, Japan

⁴Faculty of Engineering, Pukyong National University, Busan, 608-739, Republic of Korea

Precipitation behavior of metastable phases in an Al-1.94 at% Cu alloy during isothermal aging at 373 K was investigated by means of Vickers microhardness tests, DSC measurements and TEM observations. The size distribution of the precipitates was quantitatively investigated based on the TEM, HRTEM and HAADF-STEM images, and statistical parameters that fit the precipitate size distribution were determined under a log-normal distribution approximation. We have successfully estimated the volume fraction of copper in precipitates, and found that the G.P.(II) formation results in increases of volume fraction of metastable particles, mean size and hardness.
[doi:10.2320/matertrans.47.3001]

(Received June 22, 2006; Accepted October 27, 2006; Published December 15, 2006)

Keywords: aluminum-copper alloy, size distribution, quantitative evaluation, high-angle annular dark-field scanning transmission electron microscopy, differential scanning calorimetry, Vickers microhardness

1. Introduction

Al-Cu is a well-known precipitation-hardening aluminum alloy, and a large number of studies have been devoted to investigating the hardening mechanism and precipitation process of the alloy. According to the previous studies which dealt with the precipitation behavior of Al-Cu alloys, it has been commonly accepted that the sequence of precipitated phases in this system is: supersaturated solid solution (ssss) → Guinier-Preston zone (I) (G.P.(I)) → G.P.(II) (or θ'') → θ' → stable θ .¹⁻³⁾ Recently, more detailed studies revealed that the G.P.(II) and the θ'' phase have slightly different thermal stabilities, and thus the two particles should be considered as two different metastable phases.⁴⁻⁷⁾ Apart from the dispute over the stability of metastable phases, it is also recognized that the size distribution and density of precipitates, as well as the characteristics of the precipitate phases, significantly influence the properties of precipitation-hardening alloys. Therefore, the quantitative study of the precipitation process is regarded as another important direction to conduct from both the experimental and theoretical points of view.

Direct transmission electron microscopy (TEM) observations are essential to investigate the density and size distribution of precipitates, since electron microscopy is a unique technique to provide the information on individual precipitates and their spatial distribution. Despite such the advantages of the technique, quantitative studies have confronted various difficulties due to the nature of electron scattering such as strong dynamical diffraction, and the overlapping of precipitates. Yoshida and co-workers⁸⁾ applied the weak-beam TEM observation technique to investigate the size distribution of G.P. zones, in addition to the

conventional TEM technique. They concluded that the size distribution of the precipitates follows a normal distribution, except at the early stage of G.P.(I) formation. Boyd and Nicholson investigated the coarsening rates and particle-size distribution, and insisted that the coarsening kinetics of the G.P.(II) zones are in good quantitative agreement with the Lifshitz-Wagner theory.⁹⁾ An investigation combining small-angle neutron scattering (SANS) and TEM also revealed the temporal evolution of the precipitate sizes, *i.e.*, the diameter and thickness of the disk-shaped G.P. zones in an Al-4 wt% Cu alloy.¹⁰⁾

Most of the experimental studies, however, examined a small number of aging conditions or alloy compositions, as elaborate work is required to accumulate a series of data on the sizes and number of precipitates. Thus, statistical approaches to the size distribution of precipitates have been scarcely adopted so far, despite the recognition of the importance of quantitative studies. The lack of systematic examination of the precipitation sequence has caused serious insufficiencies in applying quantitative analysis to the precipitation sequence in Al-Cu alloys.

The recent development of the HAADF-STEM technique opened a new chapter in the quantitative study of size distributions of precipitates in alloys. This state-of-the-art technique is extremely useful for the investigation of precipitation phenomena in aluminum alloys, in particular. The present study is intended to investigate the changes of the density and size distribution of metastable phase precipitates during an aging process, using transmission electron microscopy combined with HRTEM and HAADF-STEM. A series of experimental data obtained for size distributions was also statistically examined.

2. Experimental Procedure

The composition of the alloy used in this experimental

*Present address: R&D Division, Hynix Semiconductor Inc., San 136-1 Ami-ri Bubal-eub, Icheon-si Kyounggi-do 467-701, Korea

study is Al-1.94 at%Cu. After solution treatment in an air furnace at 823 K (550°C) for 3600 s, the alloy was quenched in ice water. The specimens were subsequently aged in an oil bath for various periods up to 3.6×10^7 s at 373 K. A Shimadzu HMV-2000 Vickers hardness tester was used with 0.98 N load. DSC measurements were conducted using a Rigaku TAS300-8230D with a heating rate of 1.67×10^{-1} K/s. TEM observations were conducted to determine size distributions of precipitates under different aging conditions using a Hitachi H-800 microscope at 175 kV. High-resolution TEM (HRTEM) observations were carried out using a Topcon EM-002B microscope at 180 kV accelerating voltage. A JEM-3100FEF TEM equipped with a Schottky-type field emission gun was also operated at 300 kV for HRTEM observations, as well as high-angular annular dark-field scanning transmission electron microscopy (HAADF-STEM) and electron energy-loss spectroscopy (EELS).¹¹⁾ The thickness of TEM specimens was determined using plasmon-loss peaks in the EELS measurements.¹²⁾ All TEM experiments were conducted with the specimens oriented along the (001) zone axis under the symmetric illumination condition.

The size distribution of precipitates was estimated directly from the TEM and HRTEM negatives with the assistance of a commercial software package (Photoshop 6). In order to obtain the statistical information on the precipitate distributions, more than three areas in each TEM specimen were observed and more than two hundred particles were counted for each aging condition. Although the overlapping of precipitates may reduce the accuracy of the statistical data analysis, it seems that the overlapping did not cause inaccuracies in the present analysis because the foil thickness was not much thicker than the diameter of precipitates.

Since it was clarified in previous reports by the present authors⁵⁻⁷⁾ that four types of metastable phase precipitates are formed before the intermediate θ' phase formation, we have adopted a new interpretation of the precipitation sequence in an Al-Cu alloy: supersaturated solid solution (ssss) $\rightarrow$ solute clusters $\rightarrow$ G.P.(I) $\rightarrow$ G.P.(II) $\rightarrow$ θ'' $\rightarrow$ θ' $\rightarrow$ stable θ at low temperatures.

3. Results and Discussion

3.1 Precipitation behavior

Figure 1 shows the Vickers hardness (HV) of an Al-1.94 at%Cu specimen in isothermal aging at 373 K. The hardness curve for the Al-Cu specimen has four stages. Although the Vickers hardness (HV) started from the lowest value at the as-quenched state, the hardness increased with aging time in the first stage of aging. The hardness reached a plateau and the hardness was kept at a constant level in the second stage. After passing over the plateau, the curve again increased until it attained a peak hardness in the third stage after aging for 3.0×10^7 s. In the fourth stage, the HV hardness decreased with aging time.

Figure 2 shows the DSC curves with endothermic reactions that are attributed to the dissolution of metastable phases in an Al-1.94 at%Cu specimen aged at 373 K. Systematic DSC measurements at various times up to 3.0×10^7 s revealed the existence of three endothermic

Fig. 1 Vickers hardness of an Al-1.94 at%Cu specimen during isothermal aging at 373 K.

Fig. 2 DSC curves of an Al-1.94 at%Cu specimen aged at 373 K for various times.

peaks in the DSC thermograms under 550 K. From the interpretation in previous papers,⁵⁻⁷⁾ we concluded that the first endothermic peak corresponds to the dissolution of solute clusters, the second to G.P.(I) dissolution, and the third to G.P.(II) dissolution.

To examine the microstructures of the specimens, we conducted HRTEM and HAADF-STEM observations. Figure 3 shows a set of HRTEM micrographs for an Al-1.94 at%Cu specimen aged at 373 K for (a) 6.0×10^2 s, (b) 6.0×10^5 s and (c) 3.0×10^7 s, respectively. Although these HRTEM images provide the details about the precipitates, such as the diameter, thickness, and atomic spacing, the images must be interpreted with the help of contrast simulations, *e.g.*, multi-slice calculation, based on an electron dynamical diffraction theory, since the contrast of the phase-contrast images changes with the defocus and/or specimen thickness.

In the present HRTEM observations, small and large

Fig. 3 HRTEM images obtained from an Al-1.94 at%Cu specimen aged at 373 K for (a) 6.0×10^2 s, (b) 6.0×10^5 s and (c) 3.0×10^7 s.

monolayer platelets were observed as shown in Figs. 3(a) and 3(b), respectively. Referring to the fact that the solute clusters and GP(I) zones show slightly different thermal stability in DSC measurements (Fig. 2), we classified the monolayer platelets into both of the solute clusters and the G.P.(I) zones. As for the difference of the solute clusters and the G.P.(I) zones, the complete understanding has not been obtained yet. However, it may be noted that the precipitation sequence should be considered based on not only the structural but also the compositional evolution of the second phase particles. A possible interpretation may be drawn from the studies suggesting that the copper content inside the monolayer platelets is changed, depending on the size.^{13–15)}

Unlike the HRTEM images, on the other hand, the HAADF-STEM image is formed by incoherent electron waves. HAADF-STEM imaging can distinguish solute clusters, G.P.(I) and G.P.(II) by collecting scattering electrons at sufficiently high angles, as shown in Fig. 4. The contrast of solute aggregates observed in a HAADF-STEM micrograph can be simply interpreted by the atomic number differences, *i.e.*, the so-called “Z-contrast”.¹⁶⁾ Hence, the HAADF images of Fig. 4 directly reflect the distributions of heavier constituent elements; that is, the site atoms with a bright contrast in HAADF-STEM micrographs are directly attributed to Cu atoms.^{5,17)}

The HRTEM and HAADF-STEM images confirmed that monolayer Cu-rich clusters smaller than 5 nm in size are

observed as tiny straight lines in the specimen aged at 373 K for 6.0×10^2 s (a). Single-layered solute platelets, *i.e.*, G.P.(I) zones, were precipitated in the specimen aged for 6.0×10^5 s (b). In the specimen aged for 3.0×10^7 s, two Cu-rich {100} planes separated by three Al-rich {100} planes are formed as the G.P.(II) zones (c).

Comparing the present microstructures with the hardness curve in Fig. 1 and the DSC thermograms in Fig. 2, we confirmed that the first stage, with increasing HV hardness, was due to the formation of small solute clusters. In the second stage, the plateau of the HV curve was attributed to the monolayer G.P.(I). In the third stage, the formation of bi-layer G.P.(II) resulted in the second increase in hardness. Further aging to 3.0×10^7 s achieved the peak hardness during the formation of the G.P.(II). The present result on the microstructures is consistent with the DSC measurements done in this study.

3.2 Size distribution of precipitates

In this study, we investigated the size distribution of precipitates using two mathematical functions in statistics. In principle, we could use various types of mathematical functions for the statistical approach. Most of previous studies, however, have applied either the normal distribution function or log-normal distribution function to the quantitative examination of the size distribution.^{8,18)} In the present study, therefore, we adopted both distribution functions.

Fig. 4 HAADF-STEM images obtained from an Al-1.94 at% Cu specimen aged at 373 K for (a) 6.0×10^2 s, (b) 6.0×10^5 s and (c) 3.0×10^7 s.

Fig. 5 Comparison of precipitate size distribution curves under normal distributions of (a) size X and (b) $\log X$ for an Al-1.94 at% Cu specimen aged at 373 K for 6.0×10^6 s.

Figure 5 shows hypothetical curves fitted to the experimentally obtained size distribution of precipitates formed in an Al-1.94 at% Cu specimen aged at 373 K for 6.0×10^6 s. The fitting curve in Fig. 5 (a) is based on a normal distribution equation:

$$f(X) = \frac{1}{\lambda\sqrt{2\pi}} \exp\left\{-\frac{(X-\xi)^2}{2\lambda^2}\right\} \quad (1)$$

where

ξ is the geometric mean

λ is the variance.

and, the curve in Fig. 5(b) follows a log-normal distribution equation:¹⁹⁾

Fig. 6 Log-normal distribution curves of precipitation sizes in an Al-1.94 at% Cu specimen aged at 373 K for several aging times.

$$f(X) = \frac{1}{\sqrt{2\pi}\sigma X} \exp\left\{-\frac{(\log X - \mu)^2}{2\sigma^2}\right\} \quad (2)$$

where

μ is $\log \xi$

σ is $\log \lambda$.

The normal distribution curve agreed on the left side of the peak, but the log-normal distribution curve agreed at the center of the peak. The deviation between the approximating curves and the experimental data is larger in the former case (Fig. 5(a)) than in the latter case (Fig. 5(b)). Therefore, we concluded that the plots of the experimental size distribution can be more closely fitted with the log-normal distribution curve. A similar tendency of the size distribution was reported in some previous studies.^{9,20)} It should be noted that the normal distribution function seems to have less adaptability in a case such that the driving force promoting to the growth of precipitates is present, in addition that the size of precipitates is only positive value.

Figure 6 shows the size distribution curves of precipitates during aging from 6.0×10^2 s to 3.0×10^7 s at 373 K. After shorter aging, the size of the precipitates is smaller and the distribution is narrower. With a longer aging treatment, the curve moves to the right due to the growth of precipitates and becomes broader; that is, both the size and dispersion are increased.

Figure 7 shows the changes of mean size and standard deviation in the isothermal aging. The mean size remained unchanged at the early stage of aging and increased after 10^6 s. The standard deviation also shows a similar tendency to the mean size. This result suggests that the majority of the metastable phase has significantly changed after 10^6 s. At

Fig. 7 Change of mean size and standard deviation obtained from size distributions of precipitates in an Al-1.94 at%Cu specimen aged at 373 K.

around this aging time, the precipitates with double-layer contrast were observed in the present HRTEM and HAADF-STEM observations, as shown in Figs. 3 and 4. Therefore, the formation of G.P.(II) resulted in the remarkable increases of mean size and standard deviation in the curves. Comparison of Figs. 1 and 7 reveals a close relation between the increase of mean size and the increase of hardness up to the aging time with a peak hardness. Thus, we can conclude that the formation of G.P.(II) leads to a notable increase in both size of precipitates and hardness.

3.3 Quantitative evaluation of volume fraction of precipitates

In the previous section, the sizes of precipitates were measured from two-dimensional TEM images. In order to estimate quantitatively the volume fraction, the foil thickness of TEM specimens was evaluated by EELS using the plasmon-loss spectrum.

The value determined may include a margin of error of few percent since an amorphous surface layers may be also involved, however, the estimation provides a much more accurate value than other procedures, such as the measurement of thickness fringes in a two-beam diffraction condition. In order to obtain a constant thickness of TEM specimens, we kept the electric polishing conditions as same as possible and tried to observe clear HRTEM images, as shown in Fig. 3. All thickness values of fifteen specimens used for the TEM and HRTEM observations fell between 25 and 34 nm with the EELS thickness measurements. Consequently, we assumed in the present study that all the specimens have a thickness of 30 nm for the purpose of the quantitative evaluation.

Figure 8 shows the change in total Cu content of precipitates with aging time. We made two assumptions in this calculation. Firstly, the precipitate of platelets is assumed to comprise 100% Cu content, for simplicity. Secondly, all precipitates are assumed to be embedded inside the thin foil, but no precipitates was cut by the foil surfaces. The breakdown of the latter assumption may give a significant influence if the diameters of the precipitates become large.^{21,22)} However, most of the precipitates were less than 30 nm in diameter, so that serious diversity hardly occurs in

Fig. 8 Change in total volume fraction of Cu precipitated in the second-phase particles with aging time for an Al-1.94 at%Cu specimen aged at 373 K.

Fig. 9 Change in heat measured from the area of endothermic peaks of DSC measurements for an Al-1.94 at%Cu specimen aged at 373 K.

this study. In Fig. 8, the total Cu content of G.P. zone particles can be determined at about 0.8 at% Cu. The total amount of copper that was condensed in the precipitates should be multiplied by 3/2, resulting in approximately 1.2 at% in total, if we take the precipitates lying on the foil plane into account. The curve of Cu content increased from the early stage of aging due to the formation of solute clusters. The plateau stage is attributed to the formation of G.P.(I) and the formation of G.P.(II) results in an increase in Cu content.

Figure 9 shows the change of heat estimated from the endothermic peaks in DSC measurements. A number of previous studies using DSC measurements confirmed that the exothermic/endothermic heats appearing in the DSC curves are quantitatively related to the amount of precipitates formed in the aging treatments.^{23–25)} The heat can be related to the total quantity of dissolution of metastable phases. We notices that the curve shown in Fig. 9 has a very similar tendency to the curve in Fig. 8. That is, both the amount of the precipitated copper and the heat increase with aging time,

a plateau appears in the stage of G.P.(I) formation, and both curves again increase at the stage of G.P.(II) formation. A possible reason of the difference at the early stage of aging may arise from the fact that small precipitates with very weak contrast cannot be counted into the volume fraction from TEM images.

It is confirmed from Figs. 8 and 9 that the quantitative examination of the volume fraction successfully combined TEM observations with the hardness and DSC measurements. Comparing the results of hardness and size distribution to the quantity of the precipitates, the hardness and the mean-size of precipitates are attributed to the change of the quantity of the precipitates. In particular, the appearance of G.P.(II) resulted in the increases of volume fraction of metastable particles, mean size, and hardness.

The present study is intended to examine the quantitative aspects of the precipitation of an Al-Cu alloy. Precipitation hardening has been previously interpreted by some qualitative models, such as the Orowan mechanism. But most of the quantitative discussions have been based on only the average of the experimental data, and the temporal changes of the size distribution and the characteristics of the individual particles have seldom been included. The results shown in Fig. 9 suggest that a further quantitative treatment of the microstructural aspects can be made. If the general formula of size distributions in precipitation-hardening alloys is obtained against the aging-condition parameters, more quantitative discussion may occur in this field. In the present study, we used some working assumptions. The feasibility of the assumptions is still under consideration. Further investigation into these topics is required in future.

4. Conclusions

In the present study, we investigated the precipitation behavior in an Al-1.94 at%Cu alloy aged at 373 K by means of the Vickers microhardness tests, DSC measurements and TEM observations. This study confirmed that the precipitation behavior of the alloy specimens supports the interpretation proposed by the present authors. The microstructure of the precipitates evolves through solute clusters, G.P.(I) and G.P.(II) in Al-1.94 at%Cu specimens isothermally aged up to 3.0×10^7 s at 373 K.

From the quantitative viewpoint, the size distributions of the precipitates can be fitted to a log-normal distribution curve at each condition. The mean size and standard deviation of the curves remained at constant levels at the early stage of aging, and then increased at the stage of G.P.(II) formation. The volume fraction of copper in the

precipitates was successfully estimated from the hardness tests, DSC measurements and TEM observations.

Acknowledgements

This work was partly supported by “Nano-technology Support Project” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. The authors acknowledge this support.

REFERENCES

- 1) A. Guinier: *Acta Crystal.* **5** (1952) 121–130.
- 2) J. M. Silcock, T. J. Heal and H. K. Hardy: *J. Inst. Met.* **82** (1953–1954) 239–248.
- 3) M. J. Starink and P. V. Mourik: *Mater. Sci. Eng. A* **156** (1992) 183–194.
- 4) S. K. Son, M. Takeda and T. Endo: *Z. Metallk.* **96** (2005) 358–361.
- 5) S. K. Son, M. Takeda, M. Mitome, Y. Bando and T. Endo: *Materials letters* **59** (2005) 629–632.
- 6) M. Takeda, S. K. Son, Y. Nagura, U. Schmidt and T. Endo: *Z. Metallk.* **96** (2005) 870–873.
- 7) S. K. Son, M. Takeda and T. Endo: *Mater. Sci. Forum* **475–479** (2005) 353–356.
- 8) H. Yoshida: *J. Japan Inst. Metals* **40** (1976) 1216–1223.
- 9) J. D. Boyd and R. B. Nicholson: *Acta Metal.* **19** (1971) 1379–1391.
- 10) S. Czeccor, L. Lochte, G. Gottstein, P. Staron and R. Kampmann: *phys. Stat. sol.(a)* **182** (2000) 631–639.
- 11) M. Mitome, Y. Bando, D. Golberg, K. Kurashima, Y. Okura, T. Kaneyama, M. Naruse and Y. Honda: *Microsc. Res. Tech.* **63** (2004) 140–148.
- 12) M. Karlik, B. Jouffrey and S. Belliot: *Acta Mater.* **46** (1998) 1817–1825.
- 13) R. Bauer and V. Gerold: *Z. Metallk.* **57** (1966) 181–186.
- 14) A. Fontaine, P. Lagarde, P. Naudon, D. Raoux and D. Spanjaard: *Phil. Mag.* **B40** (1976) 17–30.
- 15) M. Takeda, Y. Nagura, A. Igarashi and T. Endo: *Z. Metallk.* **93** (2002) 204–207.
- 16) N. D. Browning, M. F. Chisholm and S. J. Pennycook: *Nature* **366** (1993) 143–146.
- 17) T. J. Konno, K. Hiraga and M. Kawasaki: *Scripta Mater.* **44** (2001) 2303–2307.
- 18) T. Miyazaki: Master course thesis (Yokohama National University, 2004).
- 19) S. D. Harkness, R. W. Gould and J. J. Hren: *Phil. Mag.* **19** (1969) 115–128.
- 20) P. B. Hirsch, A. Howie, R. Nicholson, D. W. Pashley and M. J. Whelan: *Electron Microscopy of Thin crystals*, (Butterworths, London, 1965) pp. 424–427.
- 21) J. M. G. Crompton, R. M. Waghorne and G. B. Brook: *Brit. J. Appl. Phys.* **17** (1966) 1301–1305.
- 22) D. Shah and C. Altstetter: *Mater. Sci. Eng.* **26** (1976) 175–183.
- 23) A. M. Zahra, M. Laffite, P. Visier and M. Winterberger: *Aluminium* **52** (1976) 357–360.
- 24) M. J. Starink and P. Van Mourik: *Mat. Sci. Eng.* **A156** (1992) 183–194.
- 25) K. Fukui, M. Takeda and T. Endo: *Mater. Trans.* **46** (2005) 880–884.