Thermal Stability and Transition Behavior of Nanoclusters during Two-Step Aging at 250°C in Al-Mg-Si(-Cu) Alloys

JaeHwang Kim^{1,*1}, SeongNyeong Kim^{1,*2}, Equo Kobayashi¹ and Tatsuo Sato²

¹Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan

²Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

Two types of nanoclusters, Cluster (1) and Cluster (2), play an important role in the age-hardening behavior in Al-Mg-Si alloys. Both Cluster (1) formed during natural aging at room temperature and Cluster (2) formed during pre-aging at 100°C cause the higher hardness and higher number density of the β'' phase during the two-step aging at 250°C than those of the single-aged specimen. Both of Cluster (1) and Cluster (2) result in the positive effect of two-step aging even though the mechanism is different. The positive effect of two-step aging for the naturally-aged specimen is caused by the atomic rearrangement from Cluster (1) to the Pre- β'' phase at the early stage of aging at 250°C. On the other hand, Cluster (2) is stable up to 250°C and directly transforms into the β'' phase. The thermal stability of nanoclusters and their transition behavior are discussed based on the age-hardening phenomena. [doi:10.2320/matertrans.M2013411]

(Received November 11, 2013; Accepted February 24, 2014; Published April 11, 2014)

Keywords: aluminum-magnesium-silicon alloy, age hardening, two types of nanoclusters, thermal stability, atomic rearrangement

1. Introduction

Al-Mg-Si alloys have been widely used for body panels of automobiles due to their good hardening response through the formation of precipitates. The precipitation sequence generally accepted in Al-Mg-Si alloys is

where SSSS is the super saturated solid solution and the β phase is the equilibrium phase.^{1,2)} The Cu addition in Al-Mg-Si alloys affects the formation of the precipitates³⁾ as well as the mechanical properties.⁴⁻⁷⁾ Ringer *et al.*⁸⁾ proposed the ‘cluster hardening’ for the rapid hardening at the early stage of aging due to the formation of the Mg-Cu co-clusters in the Al-Cu-Mg alloy. The direct observation of the nanoscale clusters using the atom probe technique⁹⁻¹¹⁾ provides the chemical composition and size distribution of nanoclusters in Al-Mg-Si alloys. Yamada *et al.*¹²⁾ and Serizawa *et al.*^{11,13-15)} found two types of nanoclusters and well explained the characteristics of nanoclusters such as the formation temperature, growth mechanism and interaction with dislocations in Al-Mg-Si alloys. With those phenomena, understanding of the clustering behavior has become extremely attractive since nanoclusters formed during low temperature aging strongly affect the two-step aging or multi-step aging behavior in Al-Mg-Si alloys.⁵⁾

From the current industrial production process for body panels of automobiles, the two-step heat-treatment, natural aging followed by a paint bake process at 170°C for 1.2 ks, i.e., bake-hardening (BH), is generally performed, resulting in the *negative effect of the two-step aging*.¹⁶⁻¹⁸⁾ Understanding of the thermal stability of nanoclusters and their transition behavior at the following aging treatment is quite

important in terms of understanding whether or not nanoclusters serve as the nucleation sites of the strengthening phase. Several studies to understand the thermal stability or reversion behavior have been reported in Al-Ag alloys,¹⁹⁻²²⁾ Al-Cu alloys²³⁻²⁵⁾ and Al-Mg-Si alloys.^{26,27)} Serizawa *et al.*²⁷⁾ found that Cluster (1) formed during natural aging (NA) is stable up to aging at 180°C and does not directly transform into the β'' phase based on the electrical resistivity measurements and three dimensional atom probe (3DAP) analysis. On the other hand, Cluster (1) is thermally unstable during two-step aging at high temperature such as aging at 240°C,²⁷⁾ but the transition behavior has not been clearly revealed yet. The thermal stability of two types of nanoclusters during the two-step aging at high temperature are still unclear and are investigated in the present study.

2. Experimental Procedure

AA6022 (Cu-free Al-Mg-Si alloy) and AA6111 (Cu-added Al-Mg-Si alloy) supplied by Furukawa-Sky Aluminum Corp. (now: UACJ Corp.) were used in this study. The chemical compositions are shown in Table 1. The solid solution heat treatment (ST) is performed at 560°C for 1.8 ks, followed by quenching into the ice-water at 0°C to keep for 60 s. The as-quenched condition is abbreviated as AQ. Single aging performed at 250°C isothermally just after ST is abbreviated as SA. In order to understand the role of two types of nanoclusters in the two-step aging behavior, two different two-step aging treatments were performed. The natural aging (NA) for 604.8 ks followed by artificial aging (AA) at 250°C was performed. Therefore, this process can be described as NA-AA. Another two-step aging is that the pre-aging (PA) at 100°C for 3.6 ks followed by artificial aging (AA) at 250°C is performed. Therefore, this process can be described as PA-AA.

Micro Vickers hardness measurements using Mitsutoyo HM-102 were performed within 0.3 ks after each heat treatment in order to minimize the NA effect. Seven hardness measurements for each aging condition were obtained. The maximum and minimum values were not used and the

*¹Graduate Student, Tokyo Institute of Technology. Present address: Research and Development Division, Hyundai Motor Group, Gyeonggi-do 437-815, Korea

*²Graduate Student, Tokyo Institute of Technology

Table 1 Chemical compositions of the alloys (mass%).

Alloy	Mg	Si	Cu	Mn	Fe	Ti	Zn	Cr	Al
AA6022	0.612	0.979	0.001	0.119	0.117	0.006	0.004	0.044	Bal.
AA6111	0.621	0.994	0.727	0.12	0.129	0.055	0.005	0.044	Bal.

average of the remaining five was used. The electrical resistivity measurements by a four-probe method with 120 mA direct current were performed at -196°C using liquid nitrogen.⁵⁾ The wire prepared for the electrical resistivity measurement had a diameter of 1.0 mm and a gage length of 300 mm. The specimens for the observation of transmission electron microscopy (TEM) were electro-polished using Struers-Tenopol-5 with solution (33 vol% HNO_3 + 67 vol% CH_3OH) at -30°C in order to observe the precipitates using JEM3010 with 300 kV accelerating voltage.

3. Results

Figure 1 shows the hardness changes during aging at 250°C with the different heat-treatment conditions in the both Cu-free and Cu-added alloys. The hardness increases during NA and PA are due to the nanocluster formation. More increase of hardness during NA and PA in the Cu-added alloy than in the Cu-free alloy is found. It is noted that the nanocluster formation is accelerated by the Cu addition. The hardness decrease for the NA samples, but hardness increase for the PA samples at the early stage of aging at 250°C is confirmed in the both Cu-free and Cu-added alloys. Namely, Cluster (1) is partially dissolved and Cluster (2) directly transforms into the strengthening phase. The hardness decrease for the NA samples at the early stage of aging at 250°C is more clearly shown in the case of the Cu-added alloy. In the case of the Cu-free alloy, the peak hardness of the NA-AA and PA-AA is dramatically increased compared with SA during aging at 250°C . Time to approach peak hardness for the two-step aged samples is shifted into the longer time than the SA one. In the case of the Cu-added alloy, the peak hardness of the NA-AA and PA-AA is slightly higher than the SA during aging at 250°C . Time to approach peak hardness is similar between the two-step aged samples and SA one. The higher peak hardness is obtained by the Cu addition regardless of heat-treatment histories.

Figures 2 and 3 show the electrical resistivity changes during aging at 250°C with the different heat-treatment conditions in the Cu-free and Cu-added alloys, respectively. Electrical resistivity is increased during NA and PA due to the nanocluster formation. This is also confirmed based on the hardness measurement. Substantial decrease of the electrical resistivity is due to the formation of precipitates. The PA-AA sample shows a similar behavior with the SA sample during aging at 250°C , whereas the NA sample shows decrease in the electrical resistivity just after aging at 250°C . It is noted that Cluster (2) directly transforms into the strengthening phases, but Cluster (1) is partially dissolved at the early stage of aging at 250°C . Different thermal stability of nanoclusters during two-step aging at 250°C is confirmed. Serizawa *et al.*²⁷⁾ also found that nanoclusters formed during

Fig. 1 Hardness changes during aging at 250°C with different heat-treatment conditions in the (a) Cu-free and (b) Cu-added alloys. SA, NA-AA and PA-AA represent single aging at 250°C , natural aging for 604.8 ks and aging at 250°C , aging at 100°C for 3.6 ks and aging at 250°C , respectively. BI stands for before isothermal aging at 250°C .

NA for 3.6 ks are thermally unstable during aging at 240°C . The decrease of hardness and electrical resistivity for the NA samples at the early stage of aging at 250°C is confirmed. The detail of this phenomenon is discussed at the next section.

Figure 4 shows the TEM micrographs with the different heat-treatment conditions in the Cu-free and Cu-added alloys. The higher number density of the precipitates is confirmed in order of the PA-AA, NA-AA and SA samples with the assumption that the specimen thickness of all specimens are similar (around 50 nm). Figure 5 shows the TEM micrograph aged at 250°C for 0.3 ks after NA for 604.8 ks from the Al matrix in a $\langle 001 \rangle$ zone axis in the Cu-added alloy. Two different needles or cross-sections of precipitates are clearly confirmed. In order to clarify the crystal structure of the precipitates, high resolution TEM images are observed as shown in Fig. 6. Marioara *et al.*²⁾ explained that the β'' phase can be determined through observation of the cross-sections having the monoclinic angle as shown in Fig. 6(a) in the Cu-free alloy. Matsuda and Ikeno²⁸⁾ explained that the precipitates can be determined based on the measurement of two types of the angle and lattice parameter. Two types of the angle means the angle of the interior one of the

Fig. 2 Electrical resistivity changes during aging at 250°C with different heat-treatment conditions in the Cu-free alloy: (a) changes of electrical resistivity from AQ and (b) early stage changes from before isothermal aging at 250°C. SA, NA-AA and PA-AA represent single aging at 250°C, natural aging for 604.8 ks and aging at 250°C, aging at 100°C for 3.6 ks and aging at 250°C, respectively. BI stands for before isothermal aging at 250°C.

Fig. 3 Electrical resistivity changes during aging at 250°C with different heat-treatment conditions in the Cu-added alloy: (a) changes of electrical resistivity from AQ and (b) early stage changes before isothermal (BI) aging at 250°C. SA, NA-AA and PA-AA represent single aging at 250°C, natural aging for 604.8 ks and aging at 250°C, aging at 100°C for 3.6 ks and aging at 250°C, respectively. BI stands for before isothermal aging at 250°C.

parallelogram network inside precipitates and the angle between the one side of the parallelogram network inside precipitates and the $\langle 100 \rangle$ direction of the Al matrix. They defined the β'' phase as follows. The lattice parameter is 0.67 and 0.77 nm. The interior one of the parallelogram network inside precipitates is 75° and the angle between the one side of the parallelogram network inside precipitates and the $\langle 100 \rangle$ direction of the Al matrix is 20° . Namely, the precipitate in Fig. 6(b) represents the β'' phase in the Cu-added alloy. The plate-like L phase with the cross-section elongated along $\langle 100 \rangle$ Al is previously reported based on the TEM observations³⁾ and atom probe results²⁹⁾ in the Cu-added Al-Mg-Si alloys. The L phase is shown in Fig. 6(c). The β'' phase with full line and the plate-like L phase with dotted line are shown in Fig. 5 of the Cu-added alloy. The cross-section of the β'' and L phases are circled. The present authors⁷⁾ found that the main strengthening phase is the β'' phase during aging at 170°C when the small amount of the Cu is added into the Al-Mg-Si alloy. Also, much higher number density of the β'' phase is confirmed than the L phase as shown in Fig. 5.

4. Discussion

4.1 Atomic rearrangement at the early stage of the two-step aging

The *negative effect of the two-step aging* should be overcome in order to utilize the Al sheets to the body panels of automobile. The *negative effect of the two-step aging* is generally caused by the nanocluster formation during NA which does not directly transform into the β'' phase during aging at around 170°C. However, both the NA-AA and PA-AA specimens show the higher hardness compared with the directly aged samples during aging at 250°C as shown in Fig. 1. Namely, the *positive effect of the two-step aging* is clearly confirmed. In order to confirm the main strengthening phases during the two-step aging, the precipitates just before the peak hardness for the NA specimens are confirmed, representing the β'' phase in the both Cu-free and Cu-added alloys as shown in Fig. 6. It draws the discussion whether or not Cluster (1) serves as nucleation sites for the β'' phase during the two-step aging. The hardness is increased during NA due to the formation of Cluster (1) as shown in Fig. 1.

Fig. 4 TEM micrographs aged at 250°C for 0.3 ks of the Cu-free ((a), (c), (e)) and Cu-added ((b), (d), (f)) alloys. (a), (b): SA (250°C for 0.3 ks), (c), (d): NA-AA (natural aging for 604.8 ks and 250°C for 0.3 ks) and (e), (f): PA-AA (pre-aging at 100°C for 0.6 ks and 250°C for 0.3 ks) respectively.

Fig. 5 TEM micrograph of the Cu-added alloy aged at 250°C for 0.3 ks after natural aging for 604.8 ks. Precipitates in the full line and dotted line boxes are the β'' and L phases, respectively. The cross-section of each precipitate is circled.

From the hardness decrease at the early stage of the two-step aging at 250°C as shown in Fig. 1, dissolution of nanoclusters is expected. At the same time more nucleation sites for the β'' phase are expected in the NA specimen than that of the SA specimen based on the TEM results. The present authors define that the Pre- β'' phase is the nucleus of the β''

phase. From this, the *atomic rearrangement* from Cluster (1) to the Pre- β'' phase at the early stage of the two-step aging at 250°C can be deduced for the NA-AA specimen. Perfect reversion of nanoclusters during aging at 250°C is hard to be accepted. If so, the NA specimen shows the lower hardness compared with the SA specimen since the high amount of vacancies are annihilated at the early stage of the two-step aging at 250°C. The effect of the atomic rearrangement on the transition behavior during the two-step aging is described in the next section.

4.2 Thermal stability of nanoclusters and their transition behavior

There is no hardness decrease for the PA-AA specimen, but hardness decrease for the NA-AA specimen at the early stage of the two-step aging at 250°C as shown in Fig. 1. Namely, two types of nanoclusters show the different thermal stability. Serizawa *et al.*¹¹⁾ found that the changes of the Mg/Si ratio inside nanoclusters with the aging time are different between Cluster (1) and Cluster (2). At the same time, they also found that very small size of nanoclusters exists for the both nanoclusters. Serizawa *et al.*¹³⁾ also found that two types of nanoclusters show the different internal structure based on the 3DAP analysis where the frequency of the nearest

Fig. 6 HRTEM micrographs showing the β'' phase aged at 250°C for 0.3 ks after natural aging for 604.8 ks in the both (a) Cu-free and (b) Cu-added alloys and the L phase aged at 250°C for 0.3 ks after natural aging for 604.8 ks in the (c) Cu-added alloy.

Fig. 7 Schematic diagram showing the different transition behavior of nanoclusters, Cluster (1) and Cluster (2), into the β'' phase. Gibbs energies, G , corresponding to the states of SSSS, Cluster (1), Cluster (2) and the β'' phase are represented. (a) Atomic rearrangement occurs from Cluster (1) to the Pre- β'' phase at the early stage of aging at 250°C and the Pre- β'' phase evolves into the β'' phase based on the hardness results (b) Cluster (2) directly transform into the β'' phase during aging at 250°C based on the hardness results.

neighbor distance of Mg–Mg, Si–Si and Mg–Si pairs of solute atoms is counted. It is important to note that the thermal stability of nanoclusters does not fully depend on the size of nanoclusters, but is affected by the atomic arrangement (internal structure) of nanoclusters. Figure 7 shows the schematic diagram showing the different transition behavior of nanoclusters into the β'' phase. The Pre- β'' phase and Cluster (2) are assumed that those internal structures are similar to that of the β'' phase in terms of that both the Pre- β''

phase and Cluster (2) directly transform into the β'' phase based on the hardness results. Even though both the NA-AA and PA-AA specimens show the *positive effect of two-step aging* at 250°C as shown in Fig. 1, two different mechanisms can be accepted. At this moment, the present authors could not reveal the crystal structure or inter-atomic bonding state of the Pre- β'' phase yet. The present authors consider that the Pre- β'' phase is formed through the rearrangement of the solute atoms inside nanoclusters which is probably closed to the β'' phase. The Pre- β'' phase is considered as the different one from Cluster (2) since the formation behavior is different. Figure 8 shows the schematic diagram of the *atomic rearrangement and positive effect* behavior for the NA specimen. Cluster (1) is formed during NA. There is the *atomic rearrangement* from Cluster (1) to the Pre- β'' phase at the early stage of aging at 250°C. The pre- β'' phase serves as the nucleation sites for the β'' phase during aging at 250°C. Finally, higher number density of the β'' phase is formed, resulting in the higher hardness than the SA specimen. On the other hand, Cluster (2) is formed during pre-aging at 100°C and directly transform into the β'' phase during aging at 250°C.

The present authors newly propose the ‘atomic rearrangement during the two-step aging’ in Al–Mg–Si alloys. This proposal does not fully follow the reversion phenomena in Al–Mg–Si alloys by Uchida and Yoshida³⁰⁾ where they explained that GP zones formed during NA (corresponding Cluster (1) in this study) are decomposed by the reversion treatment. It is noted that the higher hardness and number density of nucleation sites for the β'' phase cannot be explained just because of the reversion behavior. Further, Cluster (1) formed during NA does not directly transform into the β'' phase during aging at around 170°C, resulting in the *negative effect of the two-step aging* in Al–Mg–Si alloys. The present authors strongly emphasize the *atomic rearrangement* from Cluster (1) into Pre- β'' phase where the thermal stability of nanoclusters and their transition behavior into the strengthening β'' phase can be explained.

5. Conclusions

Investigating that the thermal stability of nanoclusters and their transition behavior into the strengthening phase is quite important to understand the relationship of the nanocluster

Fig. 8 Schematic illustrations showing structure changes during the single aging (SA) and two-step aging for the natural aging specimen. Cluster (1) is first formed during natural aging. The atomic rearrangement occurs from Cluster (1) to the Pre-β'' phase at the early stage of aging at 250°C. The Pre-β'' phase transforms easily into the β'' phase. On the other hand, Cluster (2) is formed during pre-aging at 100°C and directly transform into the β'' phase during aging at 250°C.

formation during the low temperature aging and the age-hardening behavior in Al–Mg–Si alloys. The thermal stability of nanoclusters and their transition behavior into the β'' phase is investigated using the electrical resistivity and hardness measurements and TEM observation. The obtained results are summarized as follows.

- (1) The positive effect of two-step aging is found in the both NA-AA and PA-AA specimens during the two-step aging at 250°C.
- (2) The atomic rearrangement from Cluster (1) to Pre-β'' phase at the early stage of aging at 250°C causes the high number density of the β'' phase, resulting in the higher hardness than that of the SA specimen.
- (3) Cluster (2) formed during aging at 100°C is stable up to aging at 250°C, and directly transforms into the β'' phase resulting in the higher number density of the β'' phase as well as the higher hardness.
- (4) Thermal stability of nanoclusters does not fully depend on the size of nanoclusters, but is strongly affected by the internal structure of nanoclusters.

REFERENCES

- 1) K. Matsuda, Y. Sakaguchi, Y. Miyata, Y. Uetani, T. Sato, A. Kamio and S. Ikeno: *J. Mater. Sci.* **35** (2000) 179–189.
- 2) C. D. Marioara, S. J. Andersen, H. W. Zandbergen and R. Holmestad: *Metall. Mater. Trans. A* **36** (2005) 691–702.
- 3) C. D. Marioara, S. J. Andersen, T. N. Stene, H. Hasting, J. Walmsley, A. T. J. Van Helvoort and R. Holmestad: *Philos. Mag.* **87** (2007) 3385–3413.
- 4) J. Kim and T. Sato: *J. Nanosci. Nanotechnol.* **11** (2011) 1319–1322.
- 5) J. Kim, E. Kobayashi and T. Sato: *Mater. Trans.* **52** (2011) 906–913.
- 6) J. Kim, H. Tezuka, E. Kobayashi and T. Sato: *Kor. J. Mater. Res.* **22** (2012) 329–334.
- 7) J. Kim, C. D. Marioara, R. Holmestad, E. Kobayashi and T. Sato: *Mater. Sci. Eng. A* **560** (2013) 154–162.
- 8) S. P. Ringer, K. Hono, T. Sakurai and I. J. Polmear: *Scr. Mater.* **36** (1997) 517–521.
- 9) M. Murayama and K. Hono: *Acta Mater.* **47** (1999) 1537–1548.
- 10) M. Torsæter, H. S. Hasting, W. Lefebvre, C. D. Marioara, J. C. Walmsley, S. J. Andersen and R. Holmestad: *J. Appl. Phys.* **108** (2010) 073527.
- 11) A. Serizawa, S. Hirose and T. Sato: *Metall. Mater. Trans. A* **39** (2008) 243–251.
- 12) K. Yamada, T. Sato and A. Kamio: *J. Jpn. Inst. Light Met.* **51** (2001) 215–221.
- 13) A. Serizawa and T. Sato: Proc. 11th International Conference on Aluminium Alloys (ICAA-11), ed. by J. Hirsch, B. Skrotzki and G. Gottstein, (2008) pp. 698–704.
- 14) A. Serizawa, W. J. Poole and T. Sato: Proc. 11th International Conference on Aluminium Alloys (ICAA-11), ed. by J. Hirsch, B. Skrotzki and G. Gottstein, (2008) pp. 915–921.
- 15) A. Serizawa, W. J. Poole and T. Sato: *Philos. Mag. Lett.* **90** (2010) 279–287.
- 16) D. W. Pashley, J. W. Rhodes and A. Sendorek: *J. Inst. Metals* **94** (1966) 41–49.
- 17) K. Yamada, T. Sato and A. Kamio: *Mater. Sci. Forum* **331–337** (2000) 669–674.
- 18) L. Zhen and S. Kang: *Scr. Mater.* **36** (1997) 1089–1094.
- 19) Y. Hirose, K. Asano and K. Hirano: *J. Jpn. Inst. Light Met.* **20** (1970) 589–594.
- 20) Y. Hirose, K. Asano and K. Hirano: *J. Jpn. Inst. Light Met.* **20** (1970) 595–600.
- 21) Y. Hirose, K. Asano and K. Hirano: *J. Jpn. Inst. Light Met.* **21** (1971) 7–11.
- 22) K. N. Murty and K. I. Vasu: *J. Mater. Sci.* **6** (1971) 39–47.
- 23) F. Nakamura, N. Matsumoto, K. Furukawa and J. Takamura: *Philos. Mag.* **36** (1977) 1355–1365.
- 24) M. Kanno, H. Suzuki and T. Kitayama: *J. Jpn. Inst. Light Met.* **26** (1976) 526–530.
- 25) T. Sato, Y. Kojima and T. Takahashi: *J. Jpn. Inst. Light Met.* **27** (1977) 488–492.
- 26) W. F. Smith: *Metall. Trans.* **4** (1973) 2435–2440.
- 27) A. Serizawa, S. Hirose and T. Sato: *Mater. Sci. Forum* **519–521** (2006) 245–250.
- 28) K. Matsuda and S. Ikeno: *J. Jpn. Inst. Light Met.* **50** (2000) 23–36.
- 29) M. Torsæter, W. Lefebvre, C. D. Marioara, S. J. Andersen, J. C. Walmsley and R. Holmestad: *Scr. Mater.* **64** (2011) 817–820.
- 30) H. Uchida and H. Yoshida: *J. Jpn. Inst. Light Met.* **46** (1996) 427–431.