

## The Relationship between Precipitation Behavior and Alloy Composition in an Al-Mg-Si Alloy

MahotoTakeda<sup>1</sup>, Masahiro Oguri<sup>1</sup>, Takero Kikuchi<sup>1</sup>,  
Kota Uesugi<sup>1</sup>, Koichiro Fukui<sup>1</sup> and Masanori Mitome<sup>2</sup>

<sup>1</sup> Department of Materials Engineering, Yokohama National Univ., 79-5

Tokiwadai Hodogaya, Yokohama 240-8501, JAPAN

<sup>2</sup> Materials Laboratory, National Institute for Materials Science,

Namiki 2-choume, Tukuba, Ibaraki 305-0044, JAPAN

Precipitation behavior in Al-Mg-Si, Al-Mg and Al-Si alloys have been investigated, by means of Vickers microhardness tests, DSC measurements and TEM observations. The DSC scans revealed that those three classes of alloys essentially behave as precipitation alloys. The initial stage of precipitation in a ternary Al-Mg-Si alloy comprises those occurring in binary Al-Mg and Al-Si alloys. The present EDX examination revealed that the solute composition gradually changes inside the precipitates. Namely, Mg content is higher at the center and Si contents higher at the edge of the  $\beta''$  precipitates, respectively. The EDX examination suggests that Mg clustering initially occurred, and subsequently Si atoms were segregated into Mg clusters. The results of EDX analyses are consistent with the DSC measurements showing that Mg and Si atoms have slightly different stabilities and mobilities in Al matrix. These results also reinforce the interpretation previously presented by the present authors.

**Keywords:** Al-Mg-Si, precipitation, isothermal aging, TEM, DSC

### 1. Introduction

Precipitation behavior in an Al-Mg-Si alloy has been investigated for a long period as one of the most important subjects remained in research field of aluminum alloys. Previous studies revealed that the behavior depends on both alloy compositions and external parameters such as aging temperature and time. In the early stage of research on Al-Mg-Si, presented an interpretation that the phase decomposition of the ternary alloy occurs on a quasi-binary Al-Mg<sub>2</sub>Si section of the phase diagram [1-3]. Most of successive studies have taken over this interpretation until 1980s. However, a number of works have appeared since late 1980s, which reported that quasi-stable precipitates have an atomic composition different from the relation, Mg/Si=2/1 [4-10]. But the reported compositions of precipitates have shown a relatively large variety even in cases that the precipitates appearing in similar treatments were targeted. In addition, this ternary alloy show complicated behavior in two-step aging, which behavior makes researchers puzzled for a long time. These two features of precipitation behavior have not yet been interpreted, fully consistent with the rest of phenomena. A decade before, the present authors have presented an interpretation that two types solute atoms have thermal stability different from each other, and the diffusion occurs at different times in isothermal aging, according to a systematic DSC measurements [11]. That is to say, the interpretation developed by the present authors is based on independent reactions of two solute atoms, instead of the serial and chemically restricted reaction which the conventional interpretation has stood for. Although apparently the idea of independent reactions has not been widely accepted up to now, a number of significant results favorable to the new interpretation have been accumulated so far. Thus, the present work was intended to verify the feasibility of the interpretation to the precipitation behavior in an Al-Mg-Si alloy.

## 2. Experimental

In this study, we examined the precipitation processes of Al-Mg-Si, Al-Si and Al-Mg alloys. The alloy compositions of the specimens are shown in Table 1. All specimens used in this work were solution treated at eutectic temperatures of individual alloy systems for 3.6ks, and subsequently quenched in ice-water. Al-Mg-Si specimens were annealed at 433K and 483K, Al-Mg at 373K and 473K, and Al-Si at 483K, respectively, for various times as isothermal aging treatments. The Vickers microhardness tests were carried out for examining the precipitation processes. TEM observations were conducted using Hitachi H-800 and JEOL 3010FEF microscopes. DSC measurements were also carried out at a heating rate of 10 K/min, using a RIGAKU DSC TAS300-8230D.

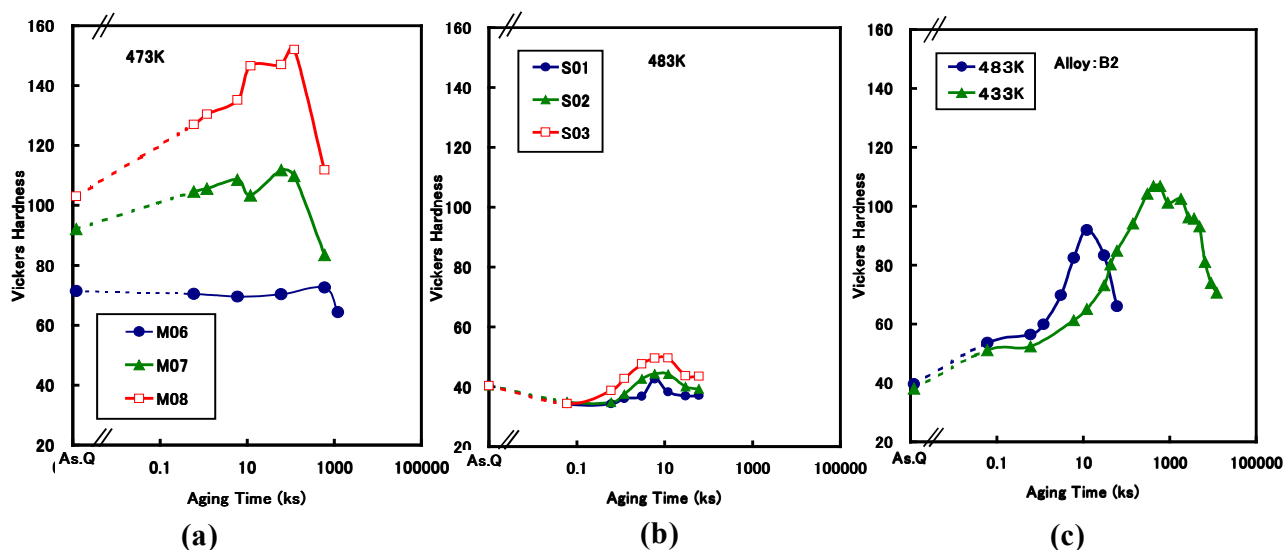
**Table 1 Compositions (mol%) of Al-Mg-Si, Al-Si and Al-Mg alloys**

Alloy	Mg	Si	Al	Mg <sub>2</sub> Si	Excess Si
B2	0.83	0.40	bal.	1.19	0.04
S01	-	0.40	bal.	1.24	0.17
S02	-	0.80	bal.	1.25	0.29
S03	-	1.20	bal.	1.25	0.54
M06	3.6	-	bal.	1.23	0.62
M07	7.2	-	bal.		
M08	10.0	-	bal.		

## 3. Results and discussion

### 3.1 Vickers microhardness tests

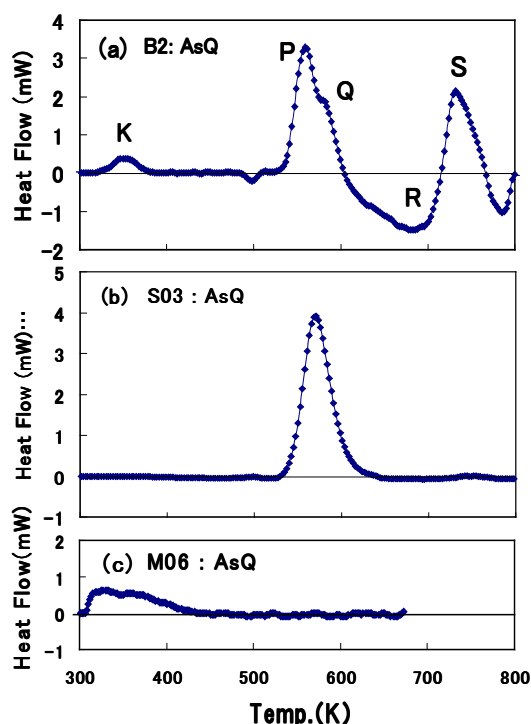
To investigate the Vickers hardness (HV) changes of an Al-Mg, Al-Si and Al-Mg-Si alloys with aging time, we measured the hardness of the specimens isothermally aged at 433K, 473K and 483K. Figure 1 shows the HV curves obtained for Al-Mg, Al-Si and Al-Mg-Si alloys, respectively. The hardness of each alloy gradually increases and attains the peak, and then decreases due to overaging.



**Fig.1 Vickers microhardness of (a)Al-Mg, (b)Al-Si and (c)Al-Mg-Si alloys aged**

### 3.2 DSC measurements

DSC measurements provide us a lot of useful information about the thermal stability of the quasi-stable/stable phases. We applied the DSC calorimetry to examine the precipitation behavior in the specimens receiving several aging treatments together with an as-quenched specimen in previous works [7, 11]. In the series of investigations, we confirmed that the exothermic peak P decreased with the aging time, but independent of other peaks. As was also pointed out in the previous work, the temperature of exothermic peak P in a ternary Al-Mg-Si alloy almost coincides with that of exothermic peak in a binary Al-Si alloy [11]. In the present work, we re-examined DSC curves of an Al-Mg alloy. Figure 2 shows the DSC curves obtained for Al-Mg-Si, Al-Si and Al-Mg specimens. Close examinations revealed that a binary Al-Mg alloy shows an exothermic peak between RT and 373K [12], although the peak was previously overlooked due to small magnitude of the peak. The position of the exothermic peak agrees to that of peak K appearing in the ternary Al-Mg-Si alloy. Thus, the present DSC measurements confirm that the exothermic peaks K and P are corresponding to the exothermic peaks appearing in an Al-Mg and Al-Si alloys. This fact is a crucial point to understand the precipitation behavior in a ternary Al-Mg-Si alloy, not only under a single aging but also under a two-step aging.



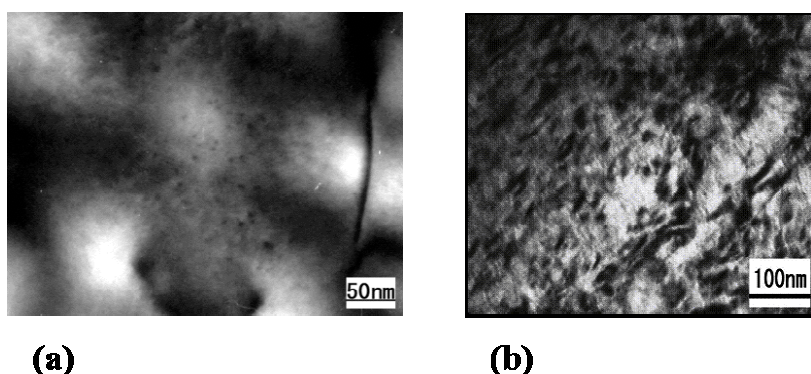
**Fig.2 DSC curves of (a) Al-Mg-Si B2 alloy, (b) Al-Si S03 alloy and (c) Al-Mg M06 alloy, as quenched**

Close examinations revealed that a binary Al-Mg alloy shows an exothermic peak between RT and 373K [12], although the peak was previously overlooked due to small magnitude of the peak. The position of the exothermic peak agrees to that of peak K appearing in the ternary Al-Mg-Si alloy. Thus, the present DSC measurements confirm that the exothermic peaks K and P are corresponding to the exothermic peaks appearing in an Al-Mg and Al-Si alloys. This fact is a crucial point to understand the precipitation behavior in a ternary Al-Mg-Si alloy, not only under a single aging but also under a two-step aging.

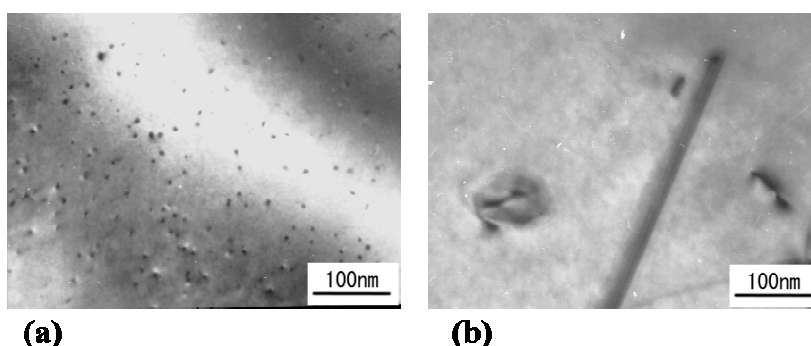
### 3.3 TEM observations

#### A. Microstructures of Al-Mg and Al-Si alloys

In this section, we first discuss the microstructure of an Al-Mg alloy. We obtained a series of TEM images of the microstructures of this alloy on isothermal aging at 373K and 473K, respectively. Figure 3 shows bright field TEM images of Al-3.6%Mg (M06) specimens aged 373K for 0.6ks and Al-7.2%Mg (M07) specimens aged 473K for 60ks. Tweed patterns of tiny Mg precipitates appeared after the isothermal annealing at 373K for 0.6ks even for a short period. On the other hand, a number of large Mg rich precipitates are formed in an Al-7.2at%Mg specimen with the aging at 473K for 60 ks. One can notice that the images of Mg precipitates are not clearly observed but blurred at the particle-matrix interfaces. Mg atoms tend to make a cluster, due to the ionic character of Mg in Al matrices as shown in Fig.3. But the benefit of total energy is not large due to Mg clustering, so that the stability of a cluster is small, compared with precipitates formed in a normal precipitation hardening alloy.



**Fig.3 Bright-field TEM image of Al-Mg specimens (a) M06 aged at 373K for 0.6ks and (b) M07 aged at 473K for 60ks**

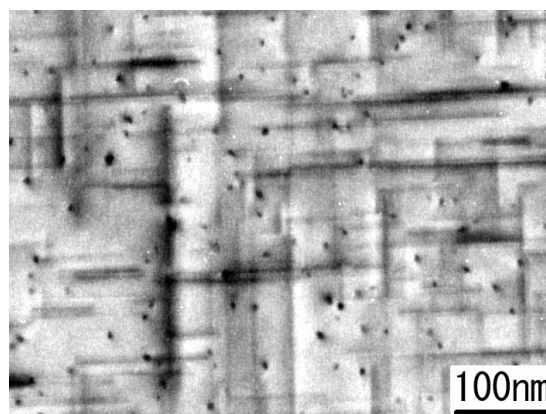


**Fig.4 Bright-field TEM images of Al-1.2%Si S03 specimens aged at 483K for (a) 0.6ks and (b) 6ks**

Figure 4 shows the microstructures of an Al-1.2%Si (S03) alloy aged at 483K for 0.6ks and 6ks. In this alloy, granular and rod-shape precipitates are typically formed. Although rod-shape precipitates in an Al-Si alloy possess an aspect-ratio slightly larger than in Al-Mg-Si alloy, the axis of the precipitates is oriented along the  $\langle 0,0,1 \rangle$  of Al matrices, and this tendency is common to the rods formed in Al-Mg-Si alloys.

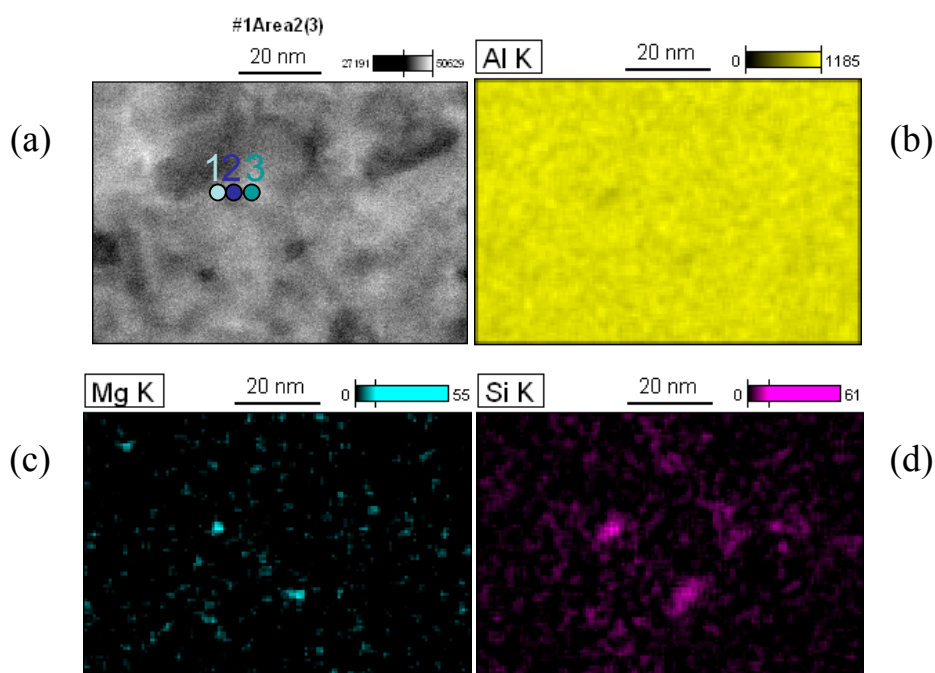
#### **B. Microstructural evolution in an Al-Mg-Si alloy**

The conventional interpretation to the precipitation in an Al-Mg-Si alloy is based on the following sequence;  $sss \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta$ . However, the detail of precipitates has not been clarified yet in structure and composition. Figure 5 shows a bright-field TEM image of the Al-Mg-Si (B2) alloy aged at 433K for 60ks. In the ternary Al-Mg-Si alloy specimen, the precipitates are outstandingly observed. Although a lot of rod-shape precipitates are formed at peak condition, granular precipitates are also seen in the specimen after a short annealing as already pointed out in many investigations. Comparing the results obtained by TEM observations and DSC measurements, a question about homogeneity of precipitates emerges up. We tried to examine the compositional analysis inside precipitates using an



**Fig.5 Bright-field TEM image of Al-Mg-Si B2 specimen aged at 433K for 60ks**

FE-TEM equipped with an EDX spectrometer. We could expect that the diameter of electron beam is small enough to examine atomic composition inside a particle. Figure 6 shows a set of element map of Al-Mg-Si (B2) aged at 383K for 600ks. The element map indicates that both Mg and Si atoms tend to be segregated into same positions. But the map (d) also shows that the distribution of Si atoms is slightly broad.



**Fig.6 (a) dark field STEM image,(b) Al K  $\alpha$  map, (c) Mg K  $\alpha$  map and (d) Si K  $\alpha$  map in Al-Mg-Si B2 alloy aged 383K for 600ks**

We also examined local positions inside a  $\beta''$  phase precipitate by EDX point analysis. The obtained result of the compositions are shown in Table 2. Position 1 is at the center of the precipitate and positions 2 and 3 deviated from the center. Table 2 revealed that the local composition is not homogeneous, but Mg content is decreasing from the center to the edge of the precipitate. This result of point analysis also confirms that the Mg is localized at the center and Si atoms are surrounding to the Mg rich core. The analytical result and DSC curves suggest a possible interpretation that the Mg atoms first make solute aggregates and subsequently Si atoms are precipitated at Mg clusters. This interpretation seems compatible with not only TEM observations but also DSC measurements. The present results also confirm that Mg and Si atoms have a slightly different stabilities and mobilities in Al matrix. It might be denoted that a theoretical study based on the EHMO calculation also supports the interpretation of inhomogeneous solute distribution inside the precipitates [13, 14], although the present paper only described the compatibility of the experimental results and the interpretation of two elementary reactions.

**Table 2 Atomic compositions of three postions.The position 1 is central area, 2 is adjacent to 1 and 3 is near the edge of nrecipitate.**

position	Mg(at%)	Si(at%)
1	3.74	3.69
2	1.53	3.19
3	0.14	0.7



#### 4. Conclusions

Precipitation behavior in Al-Mg-Si, Al-Mg and Al-Si alloys have been investigated, by means of the Vickers microhardness tests, DSC measurements and TEM observations. The present study confirmed that those three alloys are precipitation alloys. The solute composition gradually changes inside the precipitates. Mg content was higher at the center and Si contents higher at the edge of the precipitates, respectively. The initial stage of precipitation in a ternary Al-Mg-Si alloy consists of the reactions occurring in Al-Mg and Al-Si alloys. That is, Mg clustering initially occurs, and subsequently Si atoms are segregated into Mg clusters. These results also reinforce the interpretation that Mg and Si atoms have slightly different stabilities and mobilities in Al matrix.

#### References

- [1] G.Thomas: J. Inst. Metals, 90 (1961-62) 57.
- [2] M.H.Jacobs: Phil.Mag.26(1972)1.
- [3] R.P.Wahi and M. Von Heimendahl: phys.stat.sol.(a), 24(1974)607.
- [4] J.P.Lynch, L.M.Brown and M.H.Jacobs: Acta Metall., 30(1982)1389.
- [5] G.A. Edwards, K. Stiller, G.L. Dunlop and M.J. Couper: Acta Mater., 46( 1998) 3893.
- [6] M. Murayama and K. Hono: Acta Mater. 47(1999) 1537.
- [7] M.Takeda, F.Ohkubo, T.Shirai and K.Fuki: J.Mater.Sci., 33(1998)2385.
- [8] H.W.Zandbergen, S.J.Andersen and J.Jansen: Science, 277(1997)1221.
- [9] S.J. Andersen, H.W. Zandbergen, J. Jansen, C. TrAholt, U. Tundal and O. Reiso: Acta Mater. 46 (1998) 3283.
- [10] K. Matsuda, T. Naoi, K. Fujii, Y. Uetani, T. Sato, A.Kamio and S. Ikeno: Mater. Sci. Eng. A262 (1999) 232.
- [11] M.Takeda, T.Kurumizawa, S.Sumen, K.Fukui and T.Endo: Z. Metallkd, 93(2002) 523.
- [12] M.J.Starink and A.M.Zahra: Acta Mater. 46(1998)3381.
- [13] T.Uda: Master thesis, (1997, Kyoto University)
- [14] S.Yamamoto: *Democritus' Atomism and Materials Science* (in Japanese), Showado (2005).