# PRECIPITATION OF TRANSITION ELEMENTS DURING HOMOGENIZATION OF Al-Mg-Si–Cu ALLOY BILLETS

**Takayuki TSUCHIDA and Shigeru OKANIWA**

Research and Development Center, Nippon Light Metal Co., Ltd.
Kambara 1-34-1, Kambara-cho, Ihara-gun, Shizuoka-ken, 421-3203 Japan

**ABSTRACT** The precipitation behavior of transition elements in Al-Mg-Si-Cu alloy ingot was investigated by electrical conductivity measurement and chemical analysis of the element composition in solid solution. The increase of the addition of one transition element reduced other transition elements' solid solubility in the homogenized billets. The increase of Si addition also reduced the solid solubility of transition elements in the homogenized state. Dispersoids in the homogenized ingots with a diameter between 0.2 to 0.5 $\mu$ m were estimated to be Al(Fe, M)Si and $Al_5Cu_2Mg_8Si_6$.

**Keywords:** *Solid Solution, Precipitates, Dispersoids, Transition Elements, Intermetallic Compounds, Ingot Homogenization*

## 1. INTRODUCTION

6XXX alloys are commonly used for structural purposes in the form of sheets, plates or extrusions. Cu is one of the most common elements added to Al-Mg-Si alloys to improve their strength. For structural applications, controlling the grain structure of materials is another important factor to achieve the required performance[1]. It is usual to add some amount of transition elements in order to generate fine second phase particles (dispersoids) and to control the grain structure. Mn and Cr are the most common elements added to Al-Mg-Si alloys for the purpose of grain structure control. Furthermore, some amount of Fe also contained in material severely affects the structure of second phase particles[2]. The effect of the transition element bearing dispersoids on the structure control depends on the size and distribution of these particles. Though the state of these elements is changing during the whole production process, homogenization heat treatment takes the most important part of the process to control the size distribution of dispersoids. These transition elements precipitate or remain in solid solution in an as cast ingot and elements remain as supersaturated solid solution precipitate during the homogenization heat treatment. These elements interact with each other during precipitation, and therefore the behavior of elements should be cleared quantitatively for the effective control of the distribution of dispersoids and, in it turn, grain structure and the properties of Al-Mg-Si alloys. So the investigation on the precipitation behavior of Mn, Cr and Fe in Al-Mg-Si-Cu alloys with a different level of Mn and Cr addition was carried out.

## 2.EXPERIMENTAL PROCEDURE

The billets (extrusion ingots) of Al-Mg-Si-Cu alloys, with a diameter of 96mm and a different level of $Mg_2Si$ and excess Si and a different content of Mn, Cr content were DC cast. The chemical composition of samples is shown in Table1 (hereafter mass% represented by %). The composition of $Mg_2Si$ and excess Si calculated from the composition of Mg and Si is also listed in Table1. If the precipitation of AlFeSi intermetallic compound during DC casting is take into consideration, the estimated quantity of excess Si in as cast billet will be reduced by 0.06% from the value in Table1. So the range of excess Si composition is estimated to be 0 (Balance) to 0.6%. The compositions of Cu and Fe were chosen at a constant level of ~0.4mass% and ~0.18mass% respectively. Another element added was 0.01% of Ti for the purpose of grain refinement of the ingot. The casting temperature of the billets was about 963 to 973K. Homogenization heat treatment was carried out at 813K for 4h. Here the heating rate was kept at 100K/h and after the heat treatment the billets were cooled faster than the cooling rate of 200K/h with the cooling fan.

Table 1 Chemical composition of specimens(mass%)

| | Si | Fe | Cu | Mg | Mn | Cr | Ti | Excess Si | $Mg_2Si$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.38 | 0.18 | 0.37 | 0.56 | <0.01 | 0.20 | 0.01 | 0.06 | 0.88 |
| 2 | 0.68 | 0.18 | 0.36 | 0.56 | <0.01 | 0.21 | 0.01 | 0.36 | 0.88 |
| 3 | 1.00 | 0.18 | 0.36 | 0.58 | <0.01 | 0.21 | 0.01 | 0.66 | 0.92 |
| 4 | 0.53 | 0.18 | 0.37 | 0.82 | <0.01 | 0.21 | 0.01 | 0.05 | 1.30 |
| 5 | 0.85 | 0.19 | 0.38 | 0.81 | <0.01 | 0.21 | 0.01 | 0.38 | 1.28 |
| 6 | 1.16 | 0.18 | 0.37 | 0.83 | <0.01 | 0.20 | 0.01 | 0.68 | 1.31 |
| 7 | 0.73 | 0.19 | 0.41 | 1.09 | <0.01 | <0.01 | 0.01 | 0.10 | 1.72 |
| 8 | 0.71 | 0.19 | 0.39 | 1.08 | <0.01 | 0.11 | 0.01 | 0.08 | 1.71 |
| 9 | 0.71 | 0.19 | 0.39 | 1.10 | <0.01 | 0.21 | 0.01 | 0.07 | 1.74 |
| 10 | 0.69 | 0.18 | 0.37 | 1.06 | 0.20 | <0.01 | 0.01 | 0.08 | 1.67 |
| 11 | 0.71 | 0.18 | 0.38 | 1.06 | 0.19 | 0.10 | 0.01 | 0.10 | 1.67 |
| 12 | 0.70 | 0.18 | 0.38 | 1.09 | 0.20 | 0.20 | 0.01 | 0.07 | 1.72 |
| 13 | 0.70 | 0.19 | 0.38 | 1.10 | 0.38 | <0.01 | 0.01 | 0.06 | 1.74 |
| 14 | 0.70 | 0.18 | 0.38 | 1.11 | 0.40 | 0.10 | 0.01 | 0.06 | 1.75 |
| 15 | 0.71 | 0.20 | 0.39 | 1.12 | 0.40 | 0.20 | 0.01 | 0.06 | 1.77 |
| 16 | 0.87 | 0.19 | 0.38 | 1.10 | <0.01 | 0.21 | 0.01 | 0.23 | 1.74 |
| 17 | 1.01 | 0.18 | 0.37 | 1.09 | <0.01 | 0.21 | 0.01 | 0.38 | 1.72 |
| 18 | 1.18 | 0.18 | 0.38 | 1.10 | <0.01 | 0.21 | 0.01 | 0.54 | 1.74 |
| 19 | 1.34 | 0.18 | 0.37 | 1.07 | <0.01 | <0.01 | 0.01 | 0.72 | 1.69 |
| 20 | 1.34 | 0.19 | 0.37 | 1.10 | <0.01 | 0.10 | 0.01 | 0.70 | 1.74 |
| 21 | 1.34 | 0.19 | 0.38 | 1.10 | <0.01 | 0.21 | 0.01 | 0.70 | 1.74 |
| 22 | 1.26 | 0.19 | 0.38 | 1.11 | 0.20 | <0.01 | 0.01 | 0.62 | 1.75 |
| 23 | 1.37 | 0.19 | 0.36 | 1.11 | 0.20 | 0.10 | 0.01 | 0.73 | 1.75 |
| 24 | 1.31 | 0.18 | 0.37 | 1.09 | 0.20 | 0.20 | 0.01 | 0.68 | 1.72 |
| 25 | 1.33 | 0.19 | 0.38 | 1.11 | 0.41 | <0.01 | 0.01 | 0.69 | 1.75 |
| 26 | 1.30 | 0.19 | 0.38 | 1.10 | 0.39 | 0.11 | 0.01 | 0.66 | 1.74 |
| 27 | 1.29 | 0.18 | 0.38 | 1.09 | 0.41 | 0.20 | 0.01 | 0.66 | 1.72 |

The electrical conductivity at 293K, in the unit of %IACS, was measured using a digital conductivity meter, AUTOSIGMA 2000 of Hocking NDT Ltd., to estimate the change of the elements in solid solution. The average of the five different data on the longitudinal cross section of billets was adopted.

The compositions of Mn, Cr and Fe in solid solution were measured directly with ICP analysis of the filtrate of hot phenol dissolution.

EDX analysis was carried out for the residues of hot phenol dissolution extracted from sample 27, which contains Mn, Cr, Cu and Fe at the same time, in transmission electron microscopy to characterize the dispersoids' chemical composition without the influence of aluminum matrix.

## 3. RESULTS AND DISCUSSION

The effects of $Mg_2Si$ and excess Si content on the electrical conductivity are shown in Fig.1. In as cast billets, electrical conductivity $\sigma$ decreases by 3% with increasing $Mg_2Si$ content from 0.9% to 1.7%. It also decrease with the increase of excess Si from 0%(balance) to 0.6%. After the homogenization, on the contrary, electrical conductivity increases with increasing excess Si content and the difference in electrical conductivity between the samples with a different level of $Mg_2Si$ content becomes smaller as compared to that of the as cast billets. So the electrical conductivity changes during homogenization and $\Delta\sigma$ becomes larger with increasing $Mg_2Si$ and excess Si content.

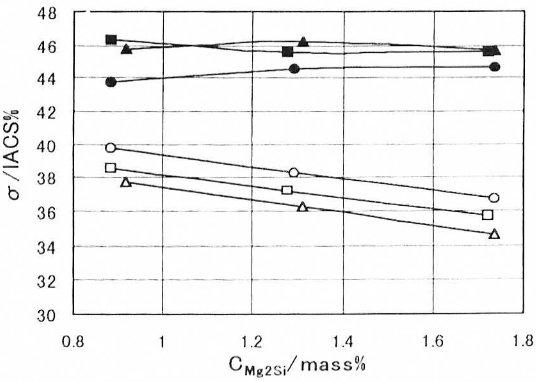


Fig.1 The effect of $Mg_2Si$ and excess Si on the electrical conductivity of Al-Mg-Si-Cu alloy billets.
As cast: ○ Balance □:0.3%excessSi △:0.6%excessSi
Homogenized: ●:Balance ■:0.3%excessSi ▲:0.6%excessSi

Fig.2 shows the effect of transition elements' composition $C_{TM}$, that is, the sum of $C_{Mn}$ and $C_{Cr}$, on the electrical conductivity of the samples 7 to 15 and 19 to 27, which have 1.7% of $Mg_2Si$ and excess Si of ~0% and ~0.6% respectively. Here, $C_X$ represents the total composition of each element X. As shown in Fig.2 a), the electrical conductivity decreased steeply, that is, from 42~44%IACS to 30~32%IACS with increasing $C_{TM}$ from 0 to 0.6%. And the electrical conductivity of samples with 0.6% excess Si was somewhat larger than that of balance composition. After the homogenization, the difference between samples with a different level of transition elements content becomes smaller, so the difference between the maximum and minimum values of electrical conductivity changes from 14%IACS in the as cast billets down to around 5%IACS in the homogenized billets.

These changes in electrical conductivity during the homogenization are attributed to the precipitation of the added elements. To confirm this, the compositions of Mn, Cr and Fe in solid so-

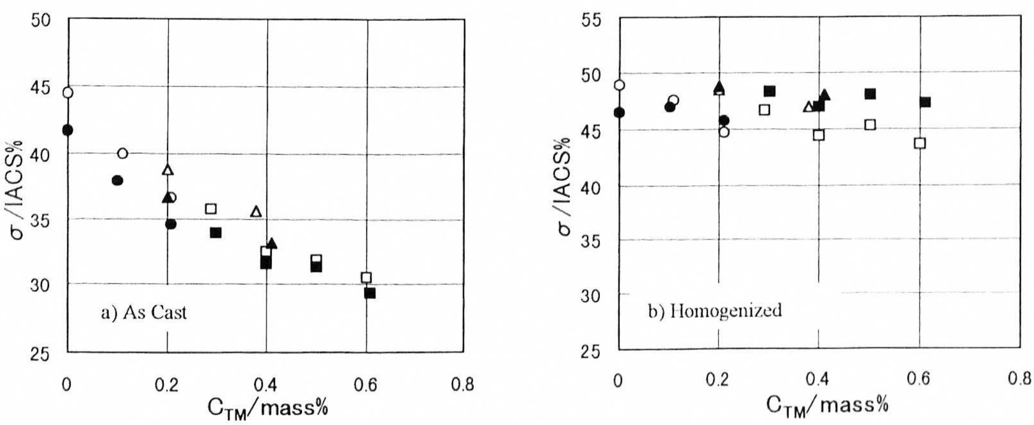


Fig2 The effects of transition elements on the electrical conductivity of Al-Mg-Si-Cu alloy billets.
Balance: ○:Cr □:Cr+Mn △:Mn 0.6% excess Si: ●:Cr ■:Cr+Mn ▲:Mn

lution were measured by chemical analysis. The results are listed in Table 2. The lower limit of the analysis is 0.0005%. The content of Fe in solid solution is smaller about one order as compared to that of Mn and Cr, both in the as cast and homogenized billets. The results for the samples with 0.2% Cr are summarized in Fig.3. $S_{Mn}$, $S_{Cr}$, $S_{Fe}$ represent compositions of each elements in solid solution in the unit of mass%. In the as cast billets, as shown in Fig.3, $S_{Mn}$ increases almost linearly with increasing $C_{Mn}$. $S_{Cr}$ and $S_{Fe}$, and on the contrary, slightly decreases with increasing $C_{Mn}$. As compared to the data of as cast billets, $S_{Mn}$ ,$S_{Cr}$ and $S_{Fe}$ decrease in homogenized billets, but the tendency is very similar to each other and the effect of Mn addition is more clearly shown in the homogenized billets. These results indicate that each element interacts during casting and homogenization. To investigate the interaction between transition elements and other added elements, Mg and Si, quantitatively, multi-regression analysis was carried out on the relation between total added composition $C_X$ and that in solid solution $S_X$. The results of the analysis were summarized in the following equations. In the as cast billets,

Table 2 Composition of transition elements in solid solution (mass%)

| | As cast billet | | | Homogenized billet | | |
|---|---|---|---|---|---|---|
| | Mn | Fe | Cr | Mn | Fe | Cr |
| 1 | 0.0008 | 0.0255 | 0.1520 | 0.0005 | 0.0010 | 0.1230 |
| 2 | 0.0008 | 0.0325 | 0.1540 | <0.0005 | 0.0006 | 0.0974 |
| 3 | 0.0008 | 0.0216 | 0.1450 | <0.0005 | <0.0005 | 0.0943 |
| 4 | 0.0009 | 0.0277 | 0.1570 | <0.0005 | 0.0013 | 0.1040 |
| 5 | 0.0008 | 0.0361 | 0.1280 | <0.0005 | 0.0012 | 0.0982 |
| 6 | 0.0009 | 0.0288 | 0.1460 | <0.0005 | <0.0005 | 0.0604 |
| 7 | 0.0012 | 0.0274 | <0.0005 | 0.0010 | 0.0050 | <0.0005 |
| 8 | 0.0011 | 0.0440 | 0.0825 | 0.0005 | 0.0026 | 0.0572 |
| 9 | 0.0009 | 0.0280 | 0.1540 | <0.0005 | 0.0019 | 0.1030 |
| 10 | 0.1470 | 0.0254 | <0.0005 | 0.0569 | 0.0009 | <0.0005 |
| 11 | 0.1400 | 0.0204 | 0.0717 | 0.0396 | 0.0007 | 0.0402 |
| 12 | 0.1360 | 0.0239 | 0.1360 | 0.0324 | <0.0005 | 0.0690 |
| 13 | 0.2730 | 0.0369 | <0.0005 | 0.0703 | 0.0005 | <0.0005 |
| 14 | 0.2440 | 0.0191 | 0.0650 | 0.0548 | <0.0005 | 0.0310 |
| 15 | 0.2640 | 0.0204 | 0.1290 | 0.0444 | <0.0005 | 0.0512 |
| 16 | 0.0008 | 0.0311 | 0.1430 | <0.0005 | <0.0005 | 0.1020 |
| 17 | 0.0008 | 0.0283 | 0.1480 | <0.0005 | 0.0008 | 0.0971 |
| 18 | 0.0009 | 0.0250 | 0.1550 | <0.0005 | <0.0005 | 0.0861 |
| 19 | 0.0010 | 0.0383 | <0.0005 | 0.0008 | 0.0021 | <0.0005 |
| 20 | 0.0009 | 0.0356 | 0.0776 | <0.0005 | <0.0005 | 0.0465 |
| 21 | 0.0010 | 0.0448 | 0.1490 | <0.0005 | <0.0005 | 0.0628 |
| 22 | 0.1440 | 0.0281 | <0.0005 | 0.0418 | 0.0009 | <0.0005 |
| 23 | 0.1320 | 0.0245 | 0.0741 | 0.0225 | <0.0005 | 0.0265 |
| 24 | 0.1260 | 0.0265 | 0.1360 | 0.0185 | <0.0005 | 0.0494 |
| 25 | 0.2740 | 0.0238 | <0.0005 | 0.0491 | 0.0005 | <0.0005 |
| 26 | 0.2440 | 0.0221 | 0.0648 | 0.0359 | 0.0008 | 0.0171 |
| 27 | 0.2590 | 0.0211 | 0.1340 | 0.0293 | <0.0005 | 0.0372 |

$$S_{Mn} = 0.66C_{Mn} \quad (1)$$

$$S_{Cr} = 0.70C_{Cr} \quad (2)$$

$$S_{Fe} = 0.03\text{-}0.02C_{Mn} \quad (3)$$

In the homogenized billets,

$$S_{Mn} = 0.11C_{Mn}\text{-}0.08C_{Cr}\text{-}0.01C_{Si}+0.03 \quad (4)$$

$$S_{Cr} = \text{-}0.07C_{Mn}+0.34C_{Cr}\text{-}0.03C_{Si}+0.05 \quad (5)$$

$$S_{Fe} = \text{-}0.003C_{Mn}\text{-}0.008C_{Cr}\text{-}0.008C_{Si}+0.003 \quad (6)$$

Eqs. (1) and (2) indicate that about 70% of the Cr and Mn remains as solid solution and the addition of these elements little affect to other precipitation characteristics in the as cast billets. On the other hand, Mn reduces Fe in solid solution, even in as cast billet, as represented by (3). After the homogenization, compositions of Mn, Cr and Si affect the solid solubility of Mn, Cr and Fe. $S_{Mn}$ increases with the increase of Mn addition but is reduced by the existence of Cr and Si. This indicates that these elements precipitate together as the dispersoids during the homogenization.

EDX analysis was carried out on the chemical composition of the dispersoids which were extracted from homogenized billet of sample 27. There were two types of fine dispersoids around .2 to 0.4 $\mu$ m with a different chemical composition together with two types of coarse size , >1 $\mu$ m, constituents. As compare with the results of X-ray diffraction in Table 3, the coarse constituents should be $Mg_2Si$ and $\alpha$ Al(Fe·M)Si, here Cr, Mn, and Cu expected to be in M position. Based on the results of EDX analysis, one type of fine dispersoids contains Al, Fe, Mn, Cr, Cu and Si, the other one contains Al, Cu, Mg and Si. Compositions of Fe, Mn, Cr and Cu in these dispersoids, obtained by the quantitative EDX analysis , were somewhat different to each other, but the total amount of these elements almost the same in one type of dispersoids. So the composition ratio is estimated to be as follows.

$$\text{Al: (Fe+Mn+Cr+Cu) : Si} = 74.1 : 14.9 : 13.6 \fallingdotseq 5:1:1 \quad (7)$$

$$\text{Al : Cu : Mg : Si} = 28.7 : 6.2 : 35.5 : 30.1 \fallingdotseq 5:1:6:5 \quad (8)$$

The dispersoids with the composition indicated by (7) is the same as those of $Al_5FeSi$ ( $\beta$ - AlFeSi). As compared to Mn or Cr, only a little amount of Fe remains in solid solution in as cast billet, but each dispersoid contains Fe from 0.3 to 2.4at%. But these dispersoids generally have more Mn and/or Cr content than that of Fe. There remains the possibility of their being $Al_{15}(Mn,M)_3Si_2$ containing Fe, Cr and Cu at the M position. The TEM photographs of the extracted fine dispersoids is shown in Fig.4. The shape of the dispersoids with the composition described above is plate like as shown Fig.4-a).

The composition of the other fine dispersoids, that is, $Al_5CuMg_6Si_5$ was not reported up to the

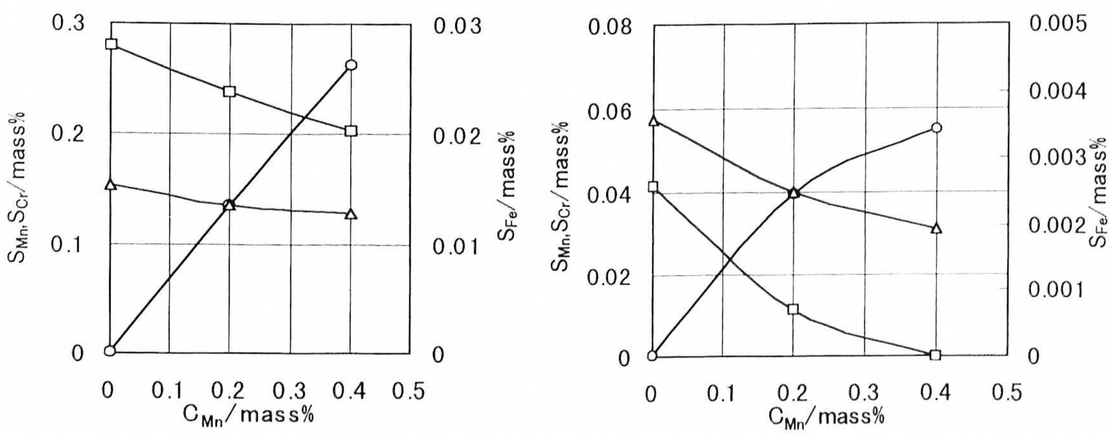


Fig.3 Effect of Mn on the composition of transition elements in solid solution in the billets.
O:Mn □:Cr △:Fe

present [3]. Referring to the results of XRD, this should be the $Al_5Cu_2Mg_8Si_6$, but its composition ratio differs considerably from that of stoichiometric composition. The dispersoids of this composition is mainly have rod shape.

Table 3 XRD measurement results of Al-1.3%Si-1.1%Mg-0.4%Cu-0.4%Mn-0.2%Cr (kcount)

| α -Al(Fe·M)Si | $Al_5Cu_2Mg_8Si_6$ | $Mg_2Si$ |
|---|---|---|
| 8.0 | 7.3 | 9.5 |

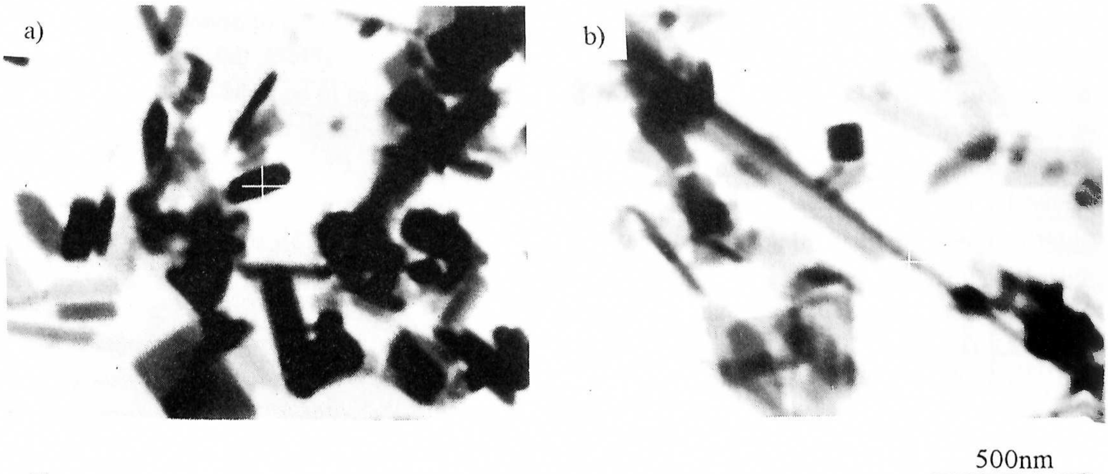


Fig.4 Example of TEM photographs of fine dispersoids extracted from Al-1.3%Si-1.1%Mg -0.4%Cu-0.4%Mn-0.2%Cr. a) Al(Fe·M)Si b) AlCuMgSi

## 4. CONCLUSIONS

The characteristics of precipitation behavior of transition elements, that is, Mn, Cr and Fe in the Al-Mg-Si-Cu alloys were investigated.

1. About 70% of Cr and Mn remains as solid solution and the addition of these elements little affect other precipitation characteristics in the as cast billets. On the other hand, Mn reduces Fe in solid solution, even in as cast billet.
2. The composition of the transition elements bearing dispersoid, which contains Mn, Cr, Cu and Fe at the same time, is estimated to be $Al_5(Fe \cdot M)Si$ in the case of Mn and Cr added alloys. The other type of precipitates with a diameter between 0.2 to 0.5 $\mu$ m is estimated to be $Al_5Cu_2Mg_8Si_6$ with a non-stoichiometric composition.
3. The precipitation characteristics of Mn, Cr and Fe were summarized quantitatively as the effect of an added amount of elements on the composition of the elements in solid solution.

## REFERENCES

[1] G. Burger, P. Wycliffe, C. Gabryel and D.J. Lloyd: Mater. Sci. Forum **242**, part 4, Proc. 5th Int. Conf. on Aluminum Alloys, Grenoble, France (1996), 101.

[2] A. Conte and T.H. Sanders Jr.: Mater. Sci. Forum **242**, part 4, Proc. 5th Int. Conf. on Al Alloys, Grenoble, France (1996), 119.

[3] L.F. Mondolfo: Aluminum Alloys, Butter Worths, London, England(1976), 759