# EFFECT OF Sc-ADDITION ON THE PRECIPITATION BEHAVIOR OF AN Al-Li-Mg-Cu ALLOY

**Chung-Hyung JOH*, Toshiharu KATSUBE*, Kazuhiro YAMADA** and Yasuhiro MIURA****

* Graduate Student, Kyushu University
** Department of Materials Science and Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581 Japan

**ABSTRACT** The influence of Sc addition on the precipitation characteristics of an Al-Li-Mg-Cu alloy was investigated by electrical reisitivity measurement, DSC and TEM observation. The Sc-added alloy showed slightly higher hardness , compared to the Sc-free alloy. This is probably due to the combined effects of solution hardening and grain refinement caused by the Sc addition. Growth of the $\delta$ ' -$Al_3Li$ particles in the Sc containing alloy was somewhat retarded, but the corsening process is still obeyed by the Lifshitz-Slyzov-Wagner theory(LSW). The results of electrical resisitivity measurement were successfully analysed and explained by the use of the modifidied-Avrami's equation. The estimated activation energy for the precipitation of $\delta$ '- $Al_3Li$ is 80kJ/mole, which is somewhat larger than the corresponding value, 62.5kJ/mol[2] or 74kJ/mol[3], previously reported for the 8090 alloy. The width of PFZ in overaged condition slightly decreased by the Sc addition, which suggests a larger interaction of Sc with vacancies than Li.

**Keywords:** *Sc, $\delta$ ' -$Al_3Li$ precipitate, L1$_2$-$Al_3Sc$ compound, PFZ*

## 1. INTRODUCTION

The Li containing Al alloys have low density and high elastic moduli compared to other conventional structural Al alloys such as Al-Cu and Al-Zn-Mg base alloys. Weight-saving up to 10% can be attained by replacing conventioal structural Al alloys with Al-Li alloys[4]. On account of these favorable effects, Al-Li base alloys have been paid much attention to as a new structural material. More exploitation for these alloys, however, is limited becase of their low ductility and fracture toughness. Main cause of the low ductility and/or toughness is the slip localization during deformation due to the low resistance of the $\delta$ '-precipitates for shearing by glide dislocations[1]. Research has been made in an attempt to improve the ductility and toughness, by the addition of transition elements such as Zr, Mo,Ti and etc. Transition metals, generally, have low solubility to Al and form intermetallic compounds with high melting points. Scandium is the lightest among transition elements and, when added to Al, forms L1$_2$-$Al_3Sc$ compound which is stable up to 1600K. A remarkable hardening due to a uniform distribution of fine L1$_2$-$Al_3Li$ particles has been reported of heat treated Al alloys with a small addition of Sc[1]. Improvements in corrosion resistance , superplasticity and weldability, as well as strength, have been made of Al alloys by the addition of Sc.

In the present investigation, the effect of the addition of Sc on the precipitation characteristics in a Al-Li-Mg-Cu alloy is studied by using hardness test, electrical reisitivity measurement, DSC and TEM observation. .

## 2. EXPERIMENTAL PROCEDURE

Ingots of two kinds of Al-Li-Mg-Cu alloys, one with 0.1mass%Sc and the other free of Sc, were prepared. The results of the chemical analysis for the alloys are shown in Table 1. After normalized, the alloy ingots were hot-extruded to 4mm thick plates. Out of the plates, rectangular specimens were prepared. They were solutionized at 793K in a salt bath, and quenched into the iced water. Isothermal aging at 433K was carried out in a silicone oil bath. Vickers hardness was measured, using a Shimadzu HMV-2000 hardness tester, on the specimen plane perpendicular to the extrusion direction. Specimens for measuring electrical resistivity were 2mm×100mm× 0.3mm in size, and they were prepared from the 4mm thick plate by hot rolling. Electrical resistivity was measured by the four-terminal potentiometric method with the constant direct current of 400mA during aging at 433K, 473K and 523K. DSC measurements with a constant heating rate(10K/min) were made in an Ar gas atmosphere up to 823K, in order to study the precipitation reactions. Thin films for TEM observation were prepared using a twin-jet electro-polishing apparatus with a solution 30% nitric acid and 70% methyl alcohol. An electron microscope, JEOL-200CX, of the HVEM Laboratory of Kyushu University was used.

Table 1 chemical compositions of A and B alloys used in this experiment

(wt.%)

| ALLOY | Li | Mg | Cu | Zr | Sc | Al |
|---|---|---|---|---|---|---|
| A | 2.71 | 2.02 | 0.50 | 0.13 | - | bal. |
| B | 2.5 | 2.0 | 0.5 | 0.1 | **0.1** | bal. |

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

**3.1. PRECIPITATION HARDENING:** Hardness variations as a function of aging time in the alloys are shown in Fig. 1. Black circles denote the Sc-added alloy and white circles the Sc-free alloy. The hardness differnce appeared in the as-quenched condition is considered to come from the solution hardening effect by Sc and also from the grain refinement effects caused by dispersed Sc compounds. Hardness difference becomes decreased as aging time passed. At the overaging stage hardness increases again at $10^6$sec. This is due to the precipitation of S' $Al_2CuMg$ phase, as is reported for 8090 alloy by the previous authors[5].

**3.2. DSC ANALYSIS:** The DSC curves for both Sc-added and Sc-free alloys are shown in Fig. 2. The four exothermic peaks appeared in are thought to be caused by, in the increasing order of temperature, GPB formation, $\delta$'-$Al_3Li$, S'-$Al_2CuMg$ and $\delta$-AlLi precipitations. It is seen that the temperatures corresponding to each peak for the Sc-added alloy are slightly shifted to the higher temperature sides, suggesting that Sc in solution could limit the precipitation reactions.

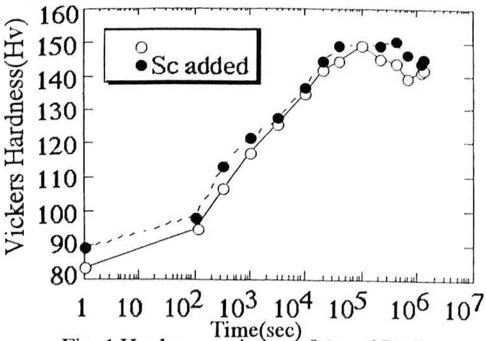


Fig. 1 Hardness variation of A and B alloys as a function of aging time at 433K

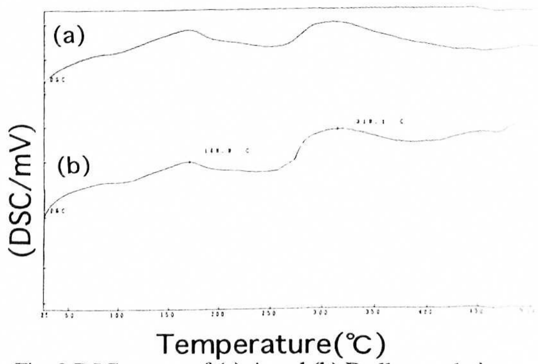


Fig. 2 DSC curves of (a) A and (b) B alloys solution treated at 793K for 0.5hr and water quenched

**3.3. ELECTRICAL RESISTIVITY:** Electrical resistivity measurement has been widely used together with other methods for the investigation of precipitation reaction during aging. The fraction, $Y$, precipitated at the time $t$ is expressed by the equation (1), well known as the modifided-Avrami-Johnson-Mehl equation[2].

$$Y=1-exp(-Kt)^n \qquad (1)$$

Here, $n$ and $K$ are constants. $K$ depends upon the rate of precipitation reaction and changes sensitively with temperature as in the following equation.

$$K=K'exp(-Q/RT) \qquad (2)$$

Here, $Q$ is the activation energy and $R$ is gas constant.
From equations (1) and (2), equation (3) is derived.

$$log ln(1/(1-Y))=nlogt+nlogK \qquad (3)$$

There is a linear relation between $log\ ln(1/(1-Y))$ and $logt$. The constants $n$ and $K$ can be experimentally determined from the slope and the intercept. Consequently, the activation energy for the precipitation reaction can be determined by plotting $lnK$ against $1/T$. In the following paragraphs, the present data of resistivity measurements will be analysed using the modifided-Avrami-Johnson-Mehl equation. Variation of specific resitivity( $\rho$ ), fraction precipitated (Y) and $logln(1/(1-Y))$ with $logt$ at 433K and 473K are shown in Fig. 3 and in Fig. 4, respectively. Specific resistivity of the Sc-added alloy is considerably larger than that of the Sc-free alloy. In both Fig. 3 and Fig. 4, a linear relationship is observed in region I and II of the $logln(1/(1-Y))$ vs $logt$ curves. This implies that two different precipitation reactions are taking palce independently in each region. The region I corresponds to the precipitation of $\delta$'-$Al_3Li$ phase, and the region II to that of S'-$Al_2CuMg$ phase. In addition to regions I and II, region III exists in the case of 473K aging, corresponding to the precipitation of the stable $\delta$-AlLi phase. From the results shown above and the result for 523K, a linear relation between $ln(dY/dt)$ and each reciprocal temperature(1/T) at $Y$= 0.05 is obtained as shown in Fig. 5. The activation energy for the precipitation of the $\delta$'-$Al_3Li$ phase can be estimated, from the slope of the straight line, to be about 80kJ/mol for both specimens Sc-added and Sc-free. This value is somewhat higher than those values, 62.5kJ/mol and 74kJ/mol, previously reported for 8090 alloy[2,3].

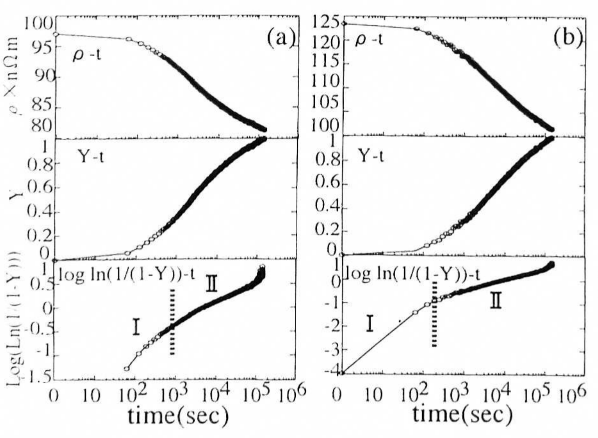


Fig. 3 Specific resisitivity $\rho$, fraction Y and logln(1/(1-Y)) for A and B alloys aged at 433K as a function of aging time

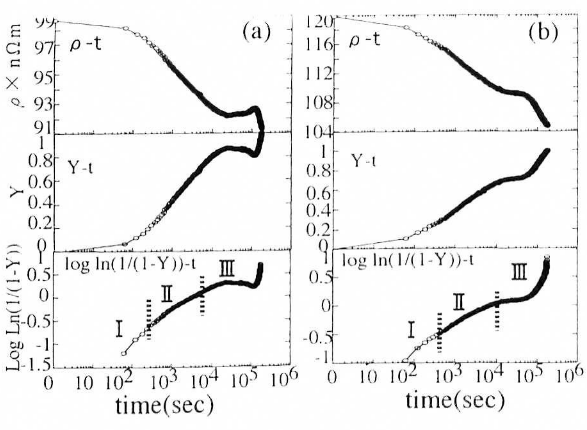


Fig.4 Specific resisitivity $\rho$, fraction Y and logln(1/(1-Y)) for A and B alloys aged at 473K as a function of aging time

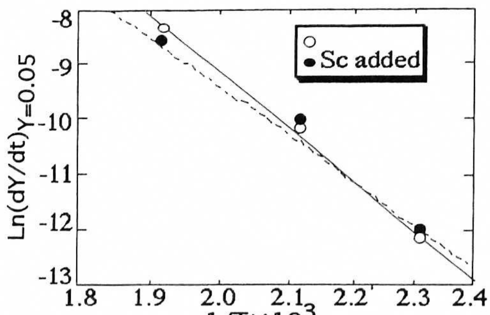


Fig. 5 Activation energy for δ 'phase of Aand B alloys derived from the relation 1/T and ln(dY/dt) at Y=0.05

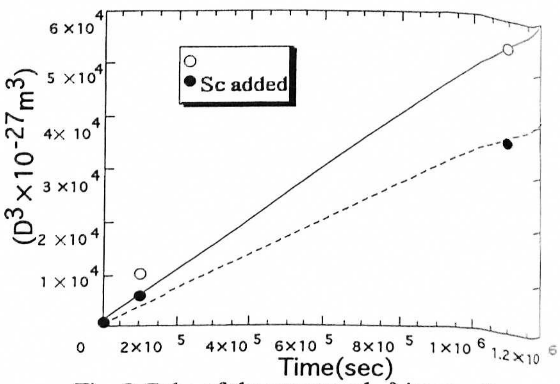


Fig. 8 Cube of the measured δ 'mean diameters for Aand B alloys as a function of aging time aged at 433K

### 3.4.TEM OBSERVATION

**Growth of δ ' -Al$_3$Li :** TEM observation of the precipitation microstructures in the Sc-containing and the Sc-free alloys aged at 433K was carried out. Emphasis was placed on the precipitation and growth of the δ ' -Al$_3$Li phase. In Fig. 6, electron micrographs of as quenched alloys are shown. For each specimen, a fine dispersion of the δ ' -Al$_3$Li phase is seen, which is consistent with the well known fact that the δ ' -Al$_3$Li phase is extraordinary fast to precipitate and a fine distribution of the precipitates is observed even in the as-quenched condition of the Al-Li alloys containing ~2mass%Li. Among the phases, other than δ ' -Al$_3$Li, that will precipitate at the initial stage of aging are Al$_3$Sc and Al$_3$Zr.

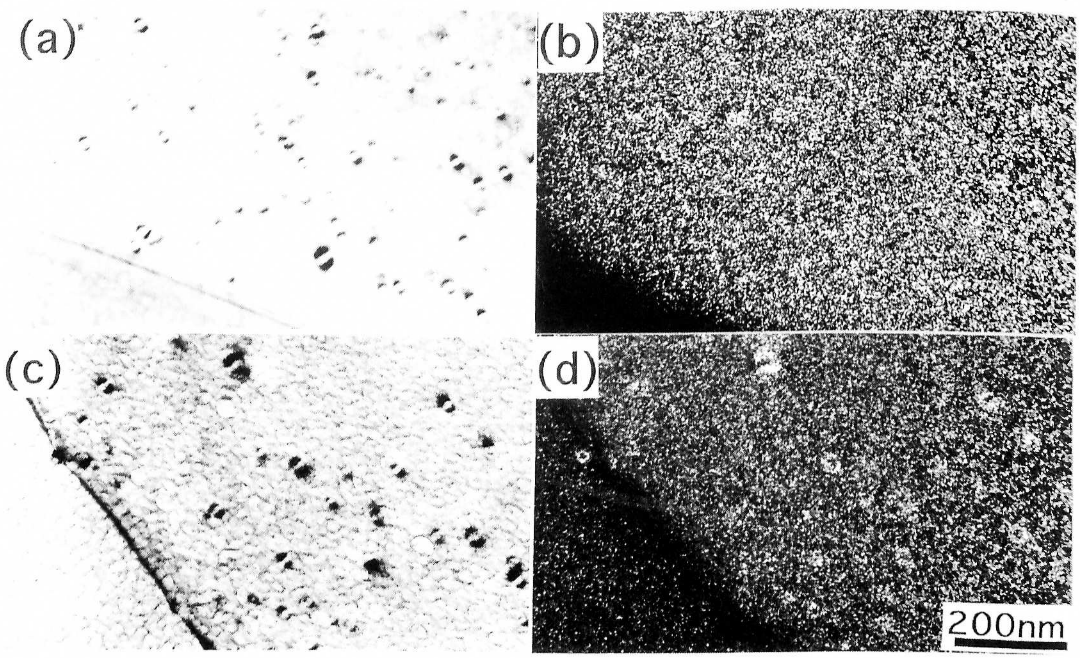


Fig. 6 BF and DF images of (a)(b); A and(c)(d);B alloys as quenched from 993K

The large coherency strain contrasts of spherical symmetry are due probably to the formation of composite compounds, $Al_3Li/Al_3Sc$ or$Al_3Li$ /$Al_3Zr$. where $Al_3Li$ phase surrounds the $Al_3Sc$ or $Al_3Zr$ core. $Al_3Sc$ and $Al_3Zr$ compounds can beformed easily during manufacturing or normalizing stage. The large energy for $Al_3Sc$ and $Al_3Zr$ due to the coherency strain with the matrix can be alleviated by the formation of the composite compounds. Fig. 7 shows dark field images of $\delta$ ' -$Al_3Li$ precipitates at different aging conditions. The $\delta$ ' phases for each specimens are homogeneously precipitated. It is seen from Fig. 8 that mean diameter(D) for both Sc-added and Sc-free alloys increases in proportion to $t^{1/3}$, where t is aging time. But, the slope for the Sc-added alloy is apparently decreased, suggesting that the growth rate of the $\delta$ ' -$Al_3Li$ precipitates is limited by the presence of Sc.

**Grain boundary PFZ:** In the overaging condition, PFZ( $\delta$ '-free-zone) appeared at grain boundaries as shown in Fig 9. Width of the PFZ tends to be narrower in the Sc-containing alloy than in the Sc-free alloy. It is thought that affinity of Sc with lattice vacancies is larger than that of Li and the rate of diffusion of Li atoms to grain boundaries is somewhat limited.

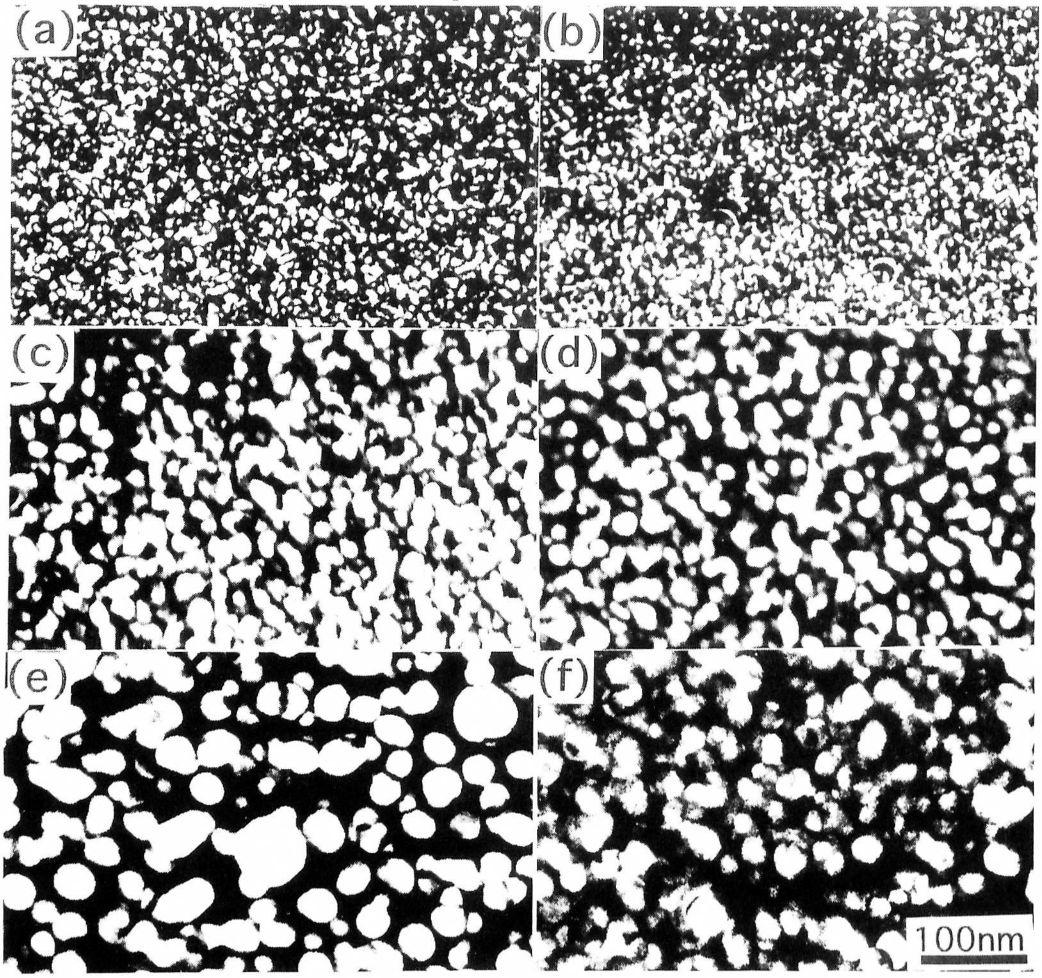


Fig. 7 DF images of $\delta$ ' particles for A and B alloy coarsened as afunction of aging time (a)(b);$10^{3.5}$sec,(c)(d);$10^{5}$sec and (e)(f);$10^{6.04}$sec

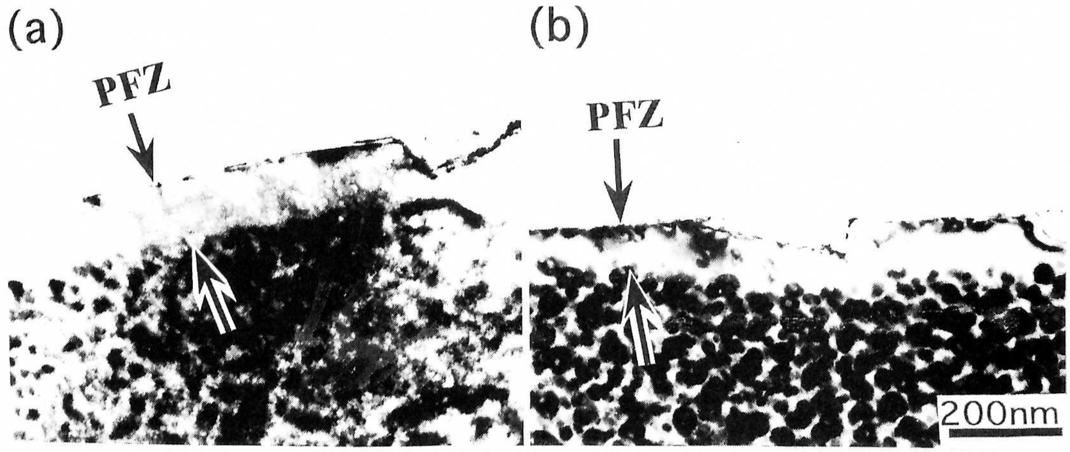


Fig. 9 Comparision PFZ's width for (a)A and (b) B alloys created near grain boundary at over aging(at 433K for $10^{6.04}$sec)

## 4. SUMMARY

The results of the present experimental study on the precipitation behaviors of Al-Li-Mg-Cu(Zr) alloys, Sc-added and Sc-free, are summarized as follows.

(1) In both alloys, Sc-added and Sc-free, the $\delta$ ' -$Al_3Li$ particles coarsen in proportion to $t^{1/3}$. A decreased coarsening rate is observed for the Sc-added alloy.

(2) The temperatures corresponding to the peaks in the DSC curves tend to shift slightly to the higher temperature side for the Sc-added alloy, suggesting the rates of precipitation and dissolution are influenced by Sc in solution.

(3) Specific electrical resistivity of the Sc-added alloy is higher than that of the Sc-free alloy. The relation between the specific resistivity change corresponding to the precipitation of the $\delta$ ' -$Al_3Li$ phase and aging time obeys the modified Avrami-Johnson-Mehl equation. There is a negligible difference in the estimated activation energies($\sim$80kJ/mol) for the precipitation of the $\delta$ ' -$Al_3Li$ phase between the alloys.

(4) In the over aged condition, decreased widths of PFZ at grain boundaries are observed in the Sc-added alloy.

**Acknowledgments:** The present investigation was supported by The Light Metals Educational Foundation Inc., Osaka, Japan.

## REFERENCE

[1] X.J.Jiang, Y.Y.Li, W. Deng, L.Y.Xiong, W.M.Wu, X,J,Gao, and C.X.Shi: Advances in Cryogenic Engineering,1994,vol.40,pp1669-1375
[2] A.LUO, D.J.LLOYD, A.GUPTA and W.V.YOUDELIS:Acta metall. meter. Vol.41, No.3, pp.769-776,1993
[3] M.J.Starink and P.J.Gregson : Materials Science forum vols.217-222(1996),pp.673-678
[4] B.C.PARK: Ph.D. Thesis of Korea advanced institute of Science and Technology, May 1997
[5] T. OHNISHI and T. ITO: J. Japan Inst. The Light Metals,1988,vol.38,no.5,pp.276-280