

# Ageing characteristics and microstructure of Al-4Mg-1.5Cu alloys containing silver and lithium<sup>①</sup>

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**Abstract:** The ageing behavior and microstructures of the Al-4Mg-1.5Cu alloys containing silver and lithium have been studied. The results show that the effect of Li is to increase the rate of hardening, however, lithium additions in the range of 0 to 2.0% does not progressively change age hardening and precipitation process in the alloy of Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr aged at 200 °C, and significant age hardening and strengthening response only occur with the addition of 2.0% Li. TEM investigation results show that the remarkable increase of age hardness and strength is attributed to the fine dispersion of  $\delta'$ , Z phase and spherical  $\text{Al}_3\text{Zr}/\text{Al}_3\text{Li}$  compound particles in the 2.0% Li containing alloy.

**Key words:** Al alloy; ageing; microstructure; lithium; silver

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## 1 INTRODUCTION

The role of trace elements on ageing of Al alloys has been extensively studied and has been recently reviewed by Polmear, Ringer and Prabhu et al.<sup>[1-4]</sup>. It was found that the small addition of silver can stimulate enhanced age hardening in certain Al-Cu-Mg alloys, and this effect is evident for a wide range of compositions selected in the ( $\alpha + \theta$ ), ( $\alpha + S$ ) and ( $\alpha + S + T$ ) phase fields of the ternary phase diagram<sup>[5-7]</sup>. The addition of Ag to Al-Cu-Mg alloys with high Cu to Mg ratios stimulates the formation of an hexagonal-shaped precipitate phase, designated  $\Omega$ , which occurs on matrix {111} planes. The effect of Ag is to increase the rate of hardening, raise the plateau and peak hardnesses whilst also decrease the duration of the hardness plateau and time taken to peak hardness in the alloy in the  $\alpha + S$  phase field<sup>[8]</sup>. And a MBED study by Chopra et al.<sup>[9]</sup>, has shown that a {111} phase, now designated  $X'$ , forms in the Al-2.5% Cu-1.5% Mg-0.5% Ag alloy, possessing an hexagonal structure and oriented such that  $(0001)_{X'} \parallel (111)_\alpha$ . As with Al-Cu-Mg alloys in the  $\alpha + S + T$  phase field, the addition of 0.5% Ag to the alloy Al-1.5% Cu-4.0% Mg promotes the formation of a new phase, designated Z. A CBED investigation indicated that it has a FCC structure, with lattice parameter  $a = 1.999 \text{ nm}$ <sup>[10]</sup>, and an atom probe analyses show the composition in the range of Mg 0.2-0.25, Cu 0.20, Al 0.5-0.6, and Ag enriched in the precipitate to levels as high as 5% (mole fraction)<sup>[11]</sup>. Since an

abnormal age hardening was observed in Al-4Cu-0.3Mg alloys containing silver and lithium by Polmear and Chester<sup>[12]</sup>, which is attributed to the fine dispersion of the three intermediate precipitates  $\Omega$ ,  $\theta'$  and  $S'$ , a new family of Al-Li alloys—Wedalite 049 were developed by Pickens and his co-workers<sup>[13]</sup>, and they reported that the ultra high strength of this family of alloys derives from the addition of minor Ag and Mg to the Al-Cu-Li alloys. But up to now most of the investigations were concentrated on the Al-Cu-Mg alloys containing silver and lithium in the  $\alpha + \theta$ ,  $\alpha + \theta + S$  and  $\alpha + S$  phase field. In this paper the ageing characteristics and microstructures of Al-4Mg-1.5Cu alloys (in the  $\alpha + S + T$  phase field) containing silver and lithium are studied.

## 2 EXPERIMENTAL

The alloys were prepared by melting and casting under argon atmosphere, and their compositions are listed in Table 1. The ingots were homogenized, scalped, then hot rolled and finally fabricated to 2 mm-thick sheets by cold rolling. The specimens were solution treated and quenched into cold water, then aged at 200 °C. The age hardening response of the experimental alloys were monitored by microhardness tester (SHIMADZU) using a 1.96 N load. Tensile specimens were machined from the sheets along the longitudinal directions, and the tensile tests were carried out at room temperature on Instron 8019. Foils for TEM were electropolished using a 33% nitric acid + 67% methanol solution at around -40 °C. Exami-

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**Table 1** Nominal(actual) composition of studied alloys(mass fraction, %)

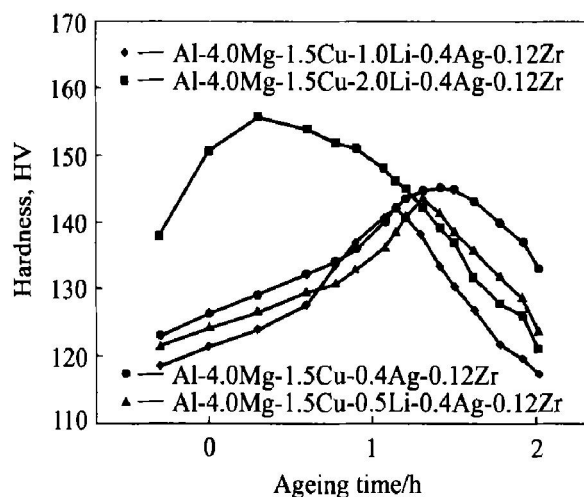
Alloy	Mg	Cu	Li	Ag	Zr	Al
A	4.0(3.98)	1.5(1.51)	0	0.4(0.39)	0.12(0.12)	Bal.
B	4.0(3.96)	1.5(1.48)	0.5(0.51)	0.4(0.39)	0.12(0.12)	Bal.
C	4.0(3.97)	1.5(1.47)	1.0(1.10)	0.4(0.41)	0.12(0.12)	Bal.
D	4.0(3.95)	1.5(1.48)	2.0(2.10)	0.4(0.39)	0.12(0.12)	Bal.

nation for TEM was carried out in a Philips CM12 electron microscope with an accelerating voltage of 120 kV.

### 3 RESULTS

#### 3.1 Age hardening response

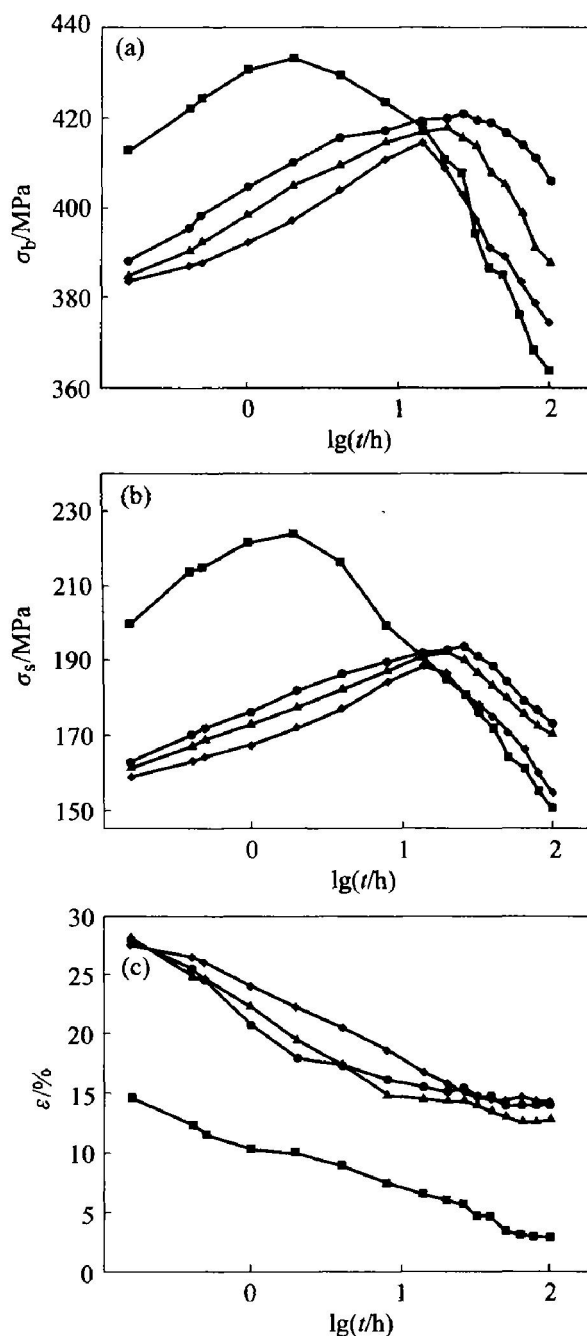
The age hardening curves at 200 °C for *A*, *B*, *C* and *D* alloys are plotted in Fig. 1. It can be seen that the form of the ageing curves of the four alloys is very similar, and only one ageing peak was observed during the whole ageing process at 200 °C. However, compared with the Li-free alloy *A*, the time taken to peak hardness is decreased by the addition of Li. The more the Li content, the shorter the time taken to peak hardness. It's interesting to note that there is little difference in the peak hardness value among alloy *A*, *B* and *C* although the alloy *B* and *C* contain 0.5% Li and 1.0% Li, respectively. And the significant increase of the peak hardness occurs only by the addition of 2.0% Li.



**Fig. 1** Hardness—time curves for alloy *A*, *B*, *C* and *D* aged at 200 °C

#### 3.2 Tensile properties

The tensile properties—ageing time curves at 200 °C for alloy *A*, *B*, *C* and *D* are shown in Fig. 2. It is found that the form of the tensile strength—ageing time curves is similar to the hardnesses—ageing time curves. There is no progressive age strengthening observed in alloy *A*, *B* and *C*. However, there is a remarkable increase of



**Fig. 2** Tensile properties vs ageing time curves for alloy *A*, *B*, *C* and *D* aged at 200 °C

- —Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr;
- ▲ —Al-4.0Mg-1.5Cu-0.5Li-0.4Ag-0.12Zr;
- ◆ —Al-4.0Mg-1.5Cu-1.0Li-0.4Ag-0.12Zr;
- —Al-4.0Mg-1.5Cu-2.0Li-0.4Ag-0.12Zr

tensile strength in the 2.0% Li-containing alloy *D*, especially the yield stress (Fig. 2(b)). As with the

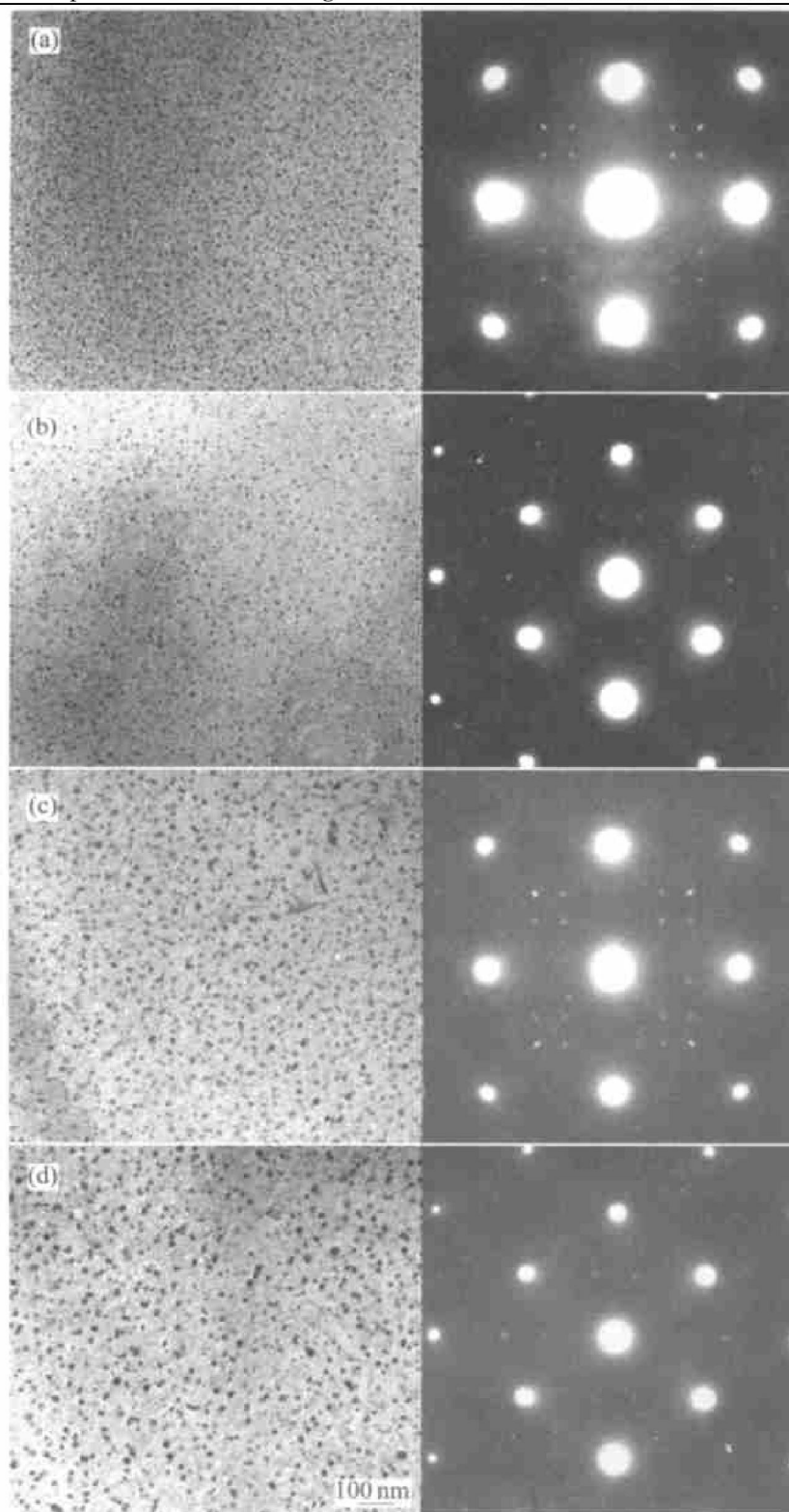
percentage elongation, it keeps almost the same level for alloy *A*, *B* and *C*, and a remarkable decrease was observed in alloy *D*.

### 3.3 Microstructure

Bright field(BF) TEM images of the peak aged and overaged microstructure for alloy *A* during ageing at 200 °C were recorded close to the  $\langle 100 \rangle_{\alpha}$  and  $\langle 110 \rangle_{\alpha}$  zone axis and examples are shown in Fig. 3.

Ageing alloy *A* to peak hardness at 200 °C leads to precipitation of a finely dispersed *Z* phase, since characteristic reflections near  $1/3$  and  $2/3$   $g\{220\}$  are visible in the SAED pattern<sup>[10]</sup>. And the *Z* phase is particularly resistant to coarsening, for the microstructure is still dominated by the fine dispersion of *Z* phase in this alloy aged at 200 °C for 83 h.

The transmission electron micrographs of the



**Fig. 3** Bright field transmission electron micrographs and corresponding selected area electron diffraction patterns from Al-4Mg-1.5Cu-0.4Ag-0.12Zr alloys aged at 200 °C for different durations (Electron beam is parallel to  $\langle 001 \rangle_{\alpha}$  in (a) and (c); electron beam is parallel to  $\langle 011 \rangle_{\alpha}$  in (b) and (d))  
(a), (b) —26 h; (c), (d) —83 h

peak aged alloy *C* are shown in Fig. 4. From the  $\langle 100 \rangle_a$ ,  $\langle 110 \rangle_a$  BF, DF images and corresponding SAED patterns, there are sparsely distribution of  $\delta'$  precipitates and *S* phase present in this alloy together with *Z* phase. But it's apparent that the *Z* phase is quite coarse compared with the Li-free alloy *A*.

TEM investigations indicated the homogeneous distribution of  $\delta'$  and *Z* phase together with spherical compound particles in alloy *D* aged for 2 h (Fig. 5). EDXS results (Fig. 5(f)) show the compound particles consist of Zr. MBED study (Fig. 5(e)) shows that the compound particles possess the same structure of  $\delta'$  phase.

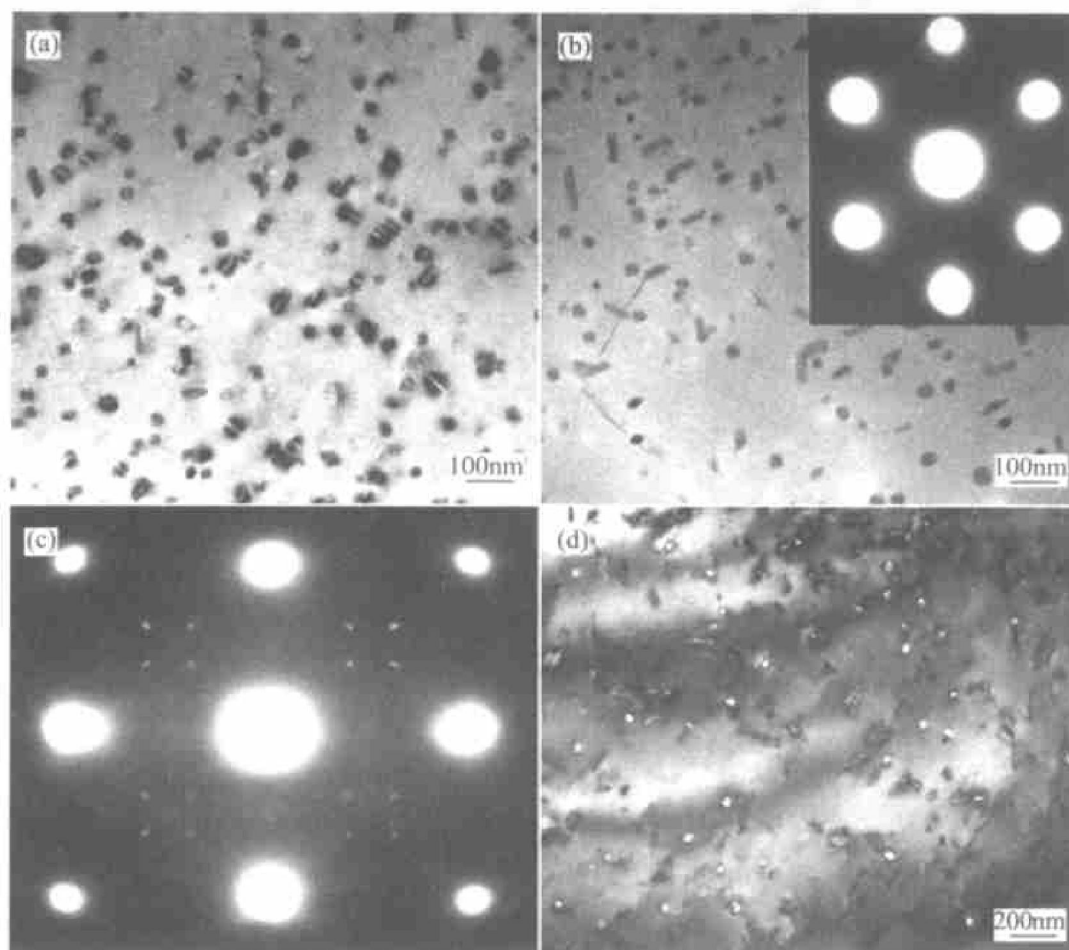
#### 4 DISCUSSION

Investigations carried out earlier<sup>[12]</sup> showed that the peak hardness increase progressively with increasing amounts of lithium from 0 to 1% into Al-4Cu-0.3Mg-0.4Ag alloys, and less response to hardening is observed with the alloy containing 2.5% Li. The present work did not observe the similar trend, it seems that only when 2.0% Li addition can give rise to the

significant age hardening response in Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr alloys, and the peak hardness and strength keep almost the same level with addition of Li from 0 to 1%. Judging from the fact that the more the lithium content, the shorter the time it will take to reach the peak hardness, the effect of Li is to increase the rate of hardening, and this is attributed to the present of  $\delta'$  precipitates.

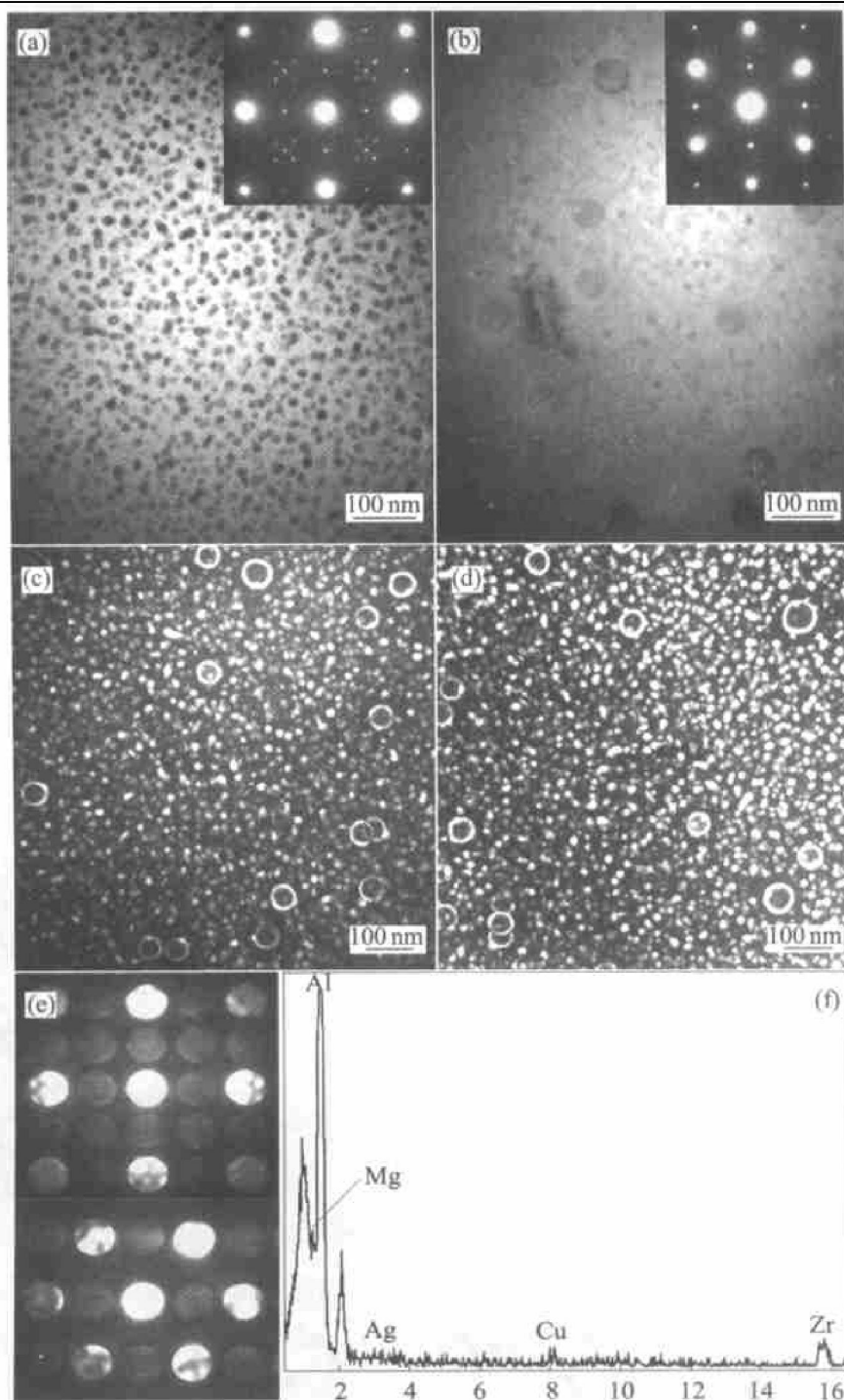
The microstructure is dominated by the fine *Z* phase in the Li-free Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr alloy, whereas there are  $\delta'$  precipitates present in the Li-containing alloy *C* and *D*, thus its effect on the microstructure is to precipitate  $\delta'$  phase. The present of  $\delta'$  phase should increase the ageing hardness and strength, however, there is no increase of ageing hardness and strength observed in the addition of 0.5% Li and 1.0% Li alloys. Judging from the fact that the coarse *Z* phase and sparsely distribution of  $\delta'$  in alloy *C*, the addition of 0.5% Li and 1.0% Li has the effect of reducing the density and increasing dimension of the *Z* phase which are finer in the Li-free alloy *A*.

As studied before<sup>[14]</sup>, trace additions of parti-



**Fig. 4** Transmission electron micrographs and SAED patterns of Al-4Mg-1.5Cu-0.4Ag-1.0Li-0.12Zr alloys aged at 200 °C for 14 h

(a) — $\langle 001 \rangle_a$  BF image; (b) — $\langle 011 \rangle_a$  BF image and corresponding SAED pattern;  
(c) —Corresponding SAED pattern recorded from (a); (d) — $\langle 011 \rangle_a$  DF image



**Fig. 5** Transmission electron micrographs of Al-4Mg-1.5Cu-0.4Ag-2.0Li-0.12Zr alloys aged at 200 °C for 2 h

(a)  $\langle 001 \rangle_a$  BF image and corresponding SAED pattern; (b)  $\langle 011 \rangle_a$  BF image and corresponding SAED pattern; (c)  $\langle 001 \rangle_a$  DF image; (d)  $\langle 011 \rangle_a$  DF image; (e)  $\langle 001 \rangle_a$  and  $\langle 011 \rangle_a$  MBED pattern recorded from compound particles; (f) EDXS spectrum from compound particles

cular elements in Al-Cu alloys such as Cd, In, Sn, Ag, Mg and Li can influence the age-hardening performance at room or elevated temperatures through different effects on the nucleation and precipitation process. The difference can be interpreted in terms of two major factors, i.e., solute-solute interaction and solute-vacancy interaction. From the enthalpy of solution at infinite dilution, the negative enthalpy values of Mg-Cu, Ag-Mg and Ag-Li show that Mg-Cu, Ag-Mg and Ag-Li pairs are ready to form thermo-dy-

namically. On the contrary, the positive enthalpy values indicate that Cd-Cu, In-Cu, Sn-Cu and Ag-Cu pairs would be unstable thermodynamically. The interaction of solute-vacancy is determined by the solute-vacancy binding energy ( $E_b$ ), and  $E_b$  for Mg, Li, Cd, In, Sn is high whereas  $E_b$  for Cu and Ag is low. The negative enthalpy values of Ag/Li and Ag/Mg indicate that the interaction of Ag/Li is stronger than that of Ag/Mg, thus Ag/Li co-cluster is easier to form than Ag/Mg co-cluster is. Meanwhile, the



more the Ag/Li co-cluster formed, the less the Ag/Mg co-cluster can be formed because most Ag atoms are trapped by Li and less Ag atoms are available for Mg, thereby the volume fraction of  $Z$  phase decreases. On the other hand, the vacancies released during the formation of Ag/Li cluster can promote the diffusion of solute atoms, which leads to the coarseness of  $Z$  phase.

Judging from the present EDXS and MBED results, the spherical compound particles precipitated in alloy  $D$  is  $Al_3Zr/Al_3Li$  compound particles. These results agree with TEM analyses of Joh et al.<sup>[15]</sup>, who found  $Al_3Li$  phase surrounds the  $Al_3Zr$  core which precipitates at the initial stage of ageing. In contrast with alloy  $B$  and  $C$ , the  $Z$  phase and  $\delta'$  are extremely finely dispersed in the 2.0% Li-containing alloy  $D$ . When the above data are considered together, the significant increase of age hardness and strength is attributed to the fine dispersion of  $\delta'$ ,  $Z$  phase and spherical  $Al_3Zr/Al_3Li$  compound particles in alloy  $D$ .

## 5 CONCLUSIONS

1) The effect of Li is to increase the rate of hardening. However, lithium additions in the range of 0 to 2.0% does not progressively change age hardening and precipitation process in the alloy Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr aged at 200 °C, and significant age hardening and strengthening response only occur with the addition of 2.0% Li.

2) The microstructure is dominated by  $Z$  phase in Al-4.0Mg-1.5Cu-0.4Ag-0.12Zr alloy, and this precipitate is particularly resistant to coarsening, which can give rise to the slow over ageing process.

3) The significant increase of age hardness and strength is attributed to the fine dispersion of  $\delta'$ ,  $Z$  phase and spherical  $Al_3Zr/Al_3Li$  compound particles in the 2.0% Li-containing alloy  $D$ .

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