EFFECTS OF SMALL ADDITIONS OF Mg AND Ag

ON PRECIPITATION PROCESS OF

Al-Cu-Li-(Mg)-(Ag)-Zr ALLOYS[①]

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ABSTRACT   The effects of small Mg and Ag additions on precipitation process of Al-Cu-Li-(Mg)-(Ag)-Zr alloys were studied. The results show that the independent roles of Mg additions are to promote the precipitation of GP zones, θ' and T_1 phases; the independent roles of Ag additions are to retard the formation of GP zones, stimulate the T_1 precipitation; the combined additions of Mg and Ag increase and accelerate the precipitation of T_1 phases. It is suggested that the strong interaction of Mg with Ag may be favorable to the formation of stacking faults and acting as catalyst for linking Li and Cu atoms required for the T_1 precipitation. The potent role of independent Mg additions in promoting the precipitation of θ' is also effective in presence of Ag, but it is weakened due to the strong interaction of Mg with Ag.

Key words   Al-Li alloys   microstructure   precipitation   silver   magnesium

1   INTRODUCTION

In ternary Al-Cu-Mg alloys with high Cu: Mg mass ratios, small additions of Mg promote the precipitation of strengthening phases which consist of the tetragonal θ' phase (Al_2Cu) and the orthorhombic S' as well as S phases (Al_2CuMg)[1,2]. Small additions of Ag to Al-Cu-Mg alloys with high Cu: Mg ratios are well known to stimulate the formation of a new phase designated as Ω phase[3-6]. The existence of Ω phase was previously considered as a result of a combined effect of Mg and Ag[7]. However, recent studies have shown that Ω phases were also present in ternary Al-Cu-Mg alloys free of Ag[8,9], indicating that only small additions of Mg are essential for the precipitation of Ω phase and Ag serves rather to enhance the precipitation of Ω phase kineticly at the expense of θ' phases. The nucleation mechanism of Ω phase as well as the roles of Mg and Ag on the nucleation process of Ω phase are still unknown.

Similarly, it has been found that the additions of Ag and Mg can significantly improve aging hardening behavior of Al-Cu-Li alloys. Recently, a family of weldalite[R] Al-Cu-Li alloys with minor amounts of Mg and Ag additions have been successfully developed to exhibit excellent properties with or without prior cold work upon natural and artificial aging[10]. Their ultra-high strength in the peak-aged condition is primarily attributed to the uniform dispersion of T_1 phases(Al_2CuLi).

The T_1 phase is similar to Ω phase in several aspects. T_1 phase appears as the semicoherent plates on the $\{111\}_\alpha$ planes with the same orientation relationship to the matrix as Ω phase and has a similar structure to Ω phase with an approximate 2: 1 ratio (c: a)[11]. Because of the commonness between T_1 and Ω phases, the roles of Mg and Ag on the precipitation process of T_1 may be reasonably similar to the way of Mg and Ag influencing the precipitation of Ω phase. The recently registered Weldalite[R] 049-

type Al-Cu-Li-Mg-Ag alloy 2195, which has served as an essential tank material in NASA's Lightweight Shuttle Tank Program[12], exhibits great developing potential. But the independent and combined effects of Mg and Ag on the precipitation process in Al-Cu-Li-Mg-Ag alloys are still uncertain. This paper studies the independent and combined roles of Mg and Ag in precipitation process in 2195 alloy.

2 EXPERIMENTAL PROCEDURE

The experimental alloys were cast as 5 kg ingots in argon atmosphere and their compositions are listed in Table 1. The ingots were homogenized, scalped and rolled to 2 mm-thick sheets. The specimens cut from the sheets were solution heat treated at 504 ℃ for 1 h in a salt bath, then quenched into cold water and subsequently aged at 180 ℃ without prior cold work. Thin foil specimens for transmission electron microscopy (TEM) analysis were prepared by mechanical grinding and twin-jet electropolishing in a solution of 1/3 nitric-acid and 2/3 methanol

cooled to - 30 ℃ at 12~ 15 V. After being polished, the Ag-containing specimens were dipped in a solution of 50% nitric-acid in H2O to remove any redeposited Ag from the electrolytes. Microstructural studies were carried out in an H-800 microscope operating at 175 kV.

Table 1 Chemical compositions of experimental alloys(%)

Alloy	Cu	Li	Mg	Ag	Zr	Ti	Al
2195	3.97	1.07	0.43	0.42	0.15	0.11	bal
M(Ag-free 2195)	4.01	1.06	0.39	0	0.19	0.11	bal
A(Mg-free 2195)	4.03	1.06	0	0.36	0.18	0.10	bal

3 RESULTS

Fig. 1 shows bright-field (BF) TEM images of the alloys at the early aging stage (4 h) at 180 ℃. Only aged for very short time (4 h), alloy 2195 has precipitated a certain amount of plate-like phases, some of which have grown to some
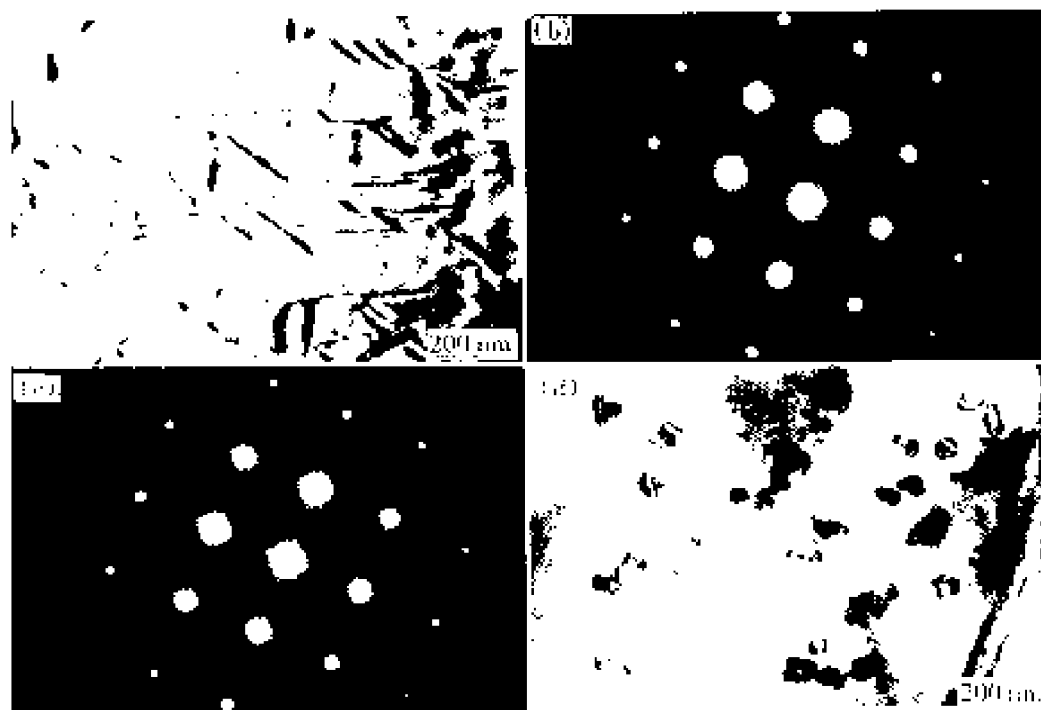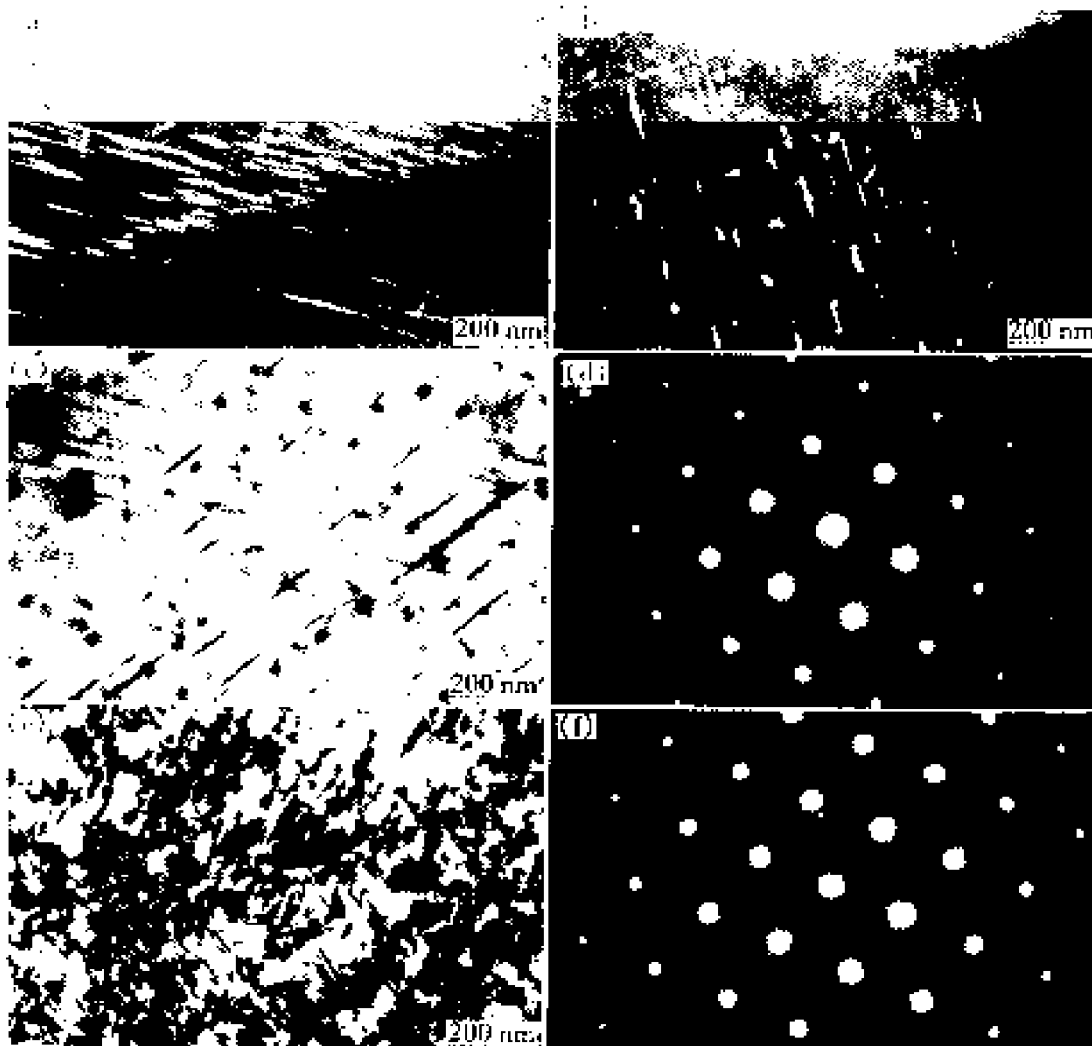

Fig. 1 Microstructures of specimens aged for 4 h at 180 ℃
(a) —Precipitates in alloy 2195; (b) —SAED pattern for alloy 2195 with [100] α zone axis;
(c) —SAED pattern for alloy M with [100] α zone axis; (d) —Dislocation loops in alloy A

extent (Fig. 1(a)). The selected area electron diffraction (SAED) pattern (Fig. 1(b)) corresponding to a [100]$_\alpha$ zone axis reveals the streaks along the $\langle 100 \rangle_\alpha$ positions due to θ' phases and four symmetrically distributed spots at the 1/ 3 and 2/ 3 g { 220} $_\alpha$ positions due to T_1 phases. The SAED pattern (Fig. 1(c)) of alloy M exhibits diffusing streaks without intensity maxima along the $\langle 100 \rangle_\alpha$ directions, indicating the presence of GP zones containing monolayers of Cu lying on disks on the { 100} $_\alpha$ planes[13]. On the contrary, in alloy A no GP zones and precipitates but many dislocation loops occur (Fig. 1(d)) in the same aging condition.

Fig. 2(a), (b) show dark-field(DF) TEM

micrographs for alloy 2195 peak-aged at 180 ℃ for 10 h. A large number of T_1 plate phases are primarily precipitated on the subgrain boundaries. A certain amount of T_1 plates are observed in the matrix together with a less density of two edge-on variants of the θ' phase, which are parallel and perpendicular to each other as shown in Fig. 2(b). For alloy M aged at 180 ℃ for 10 h, a non-uniform dispersion of T_1 plates occurs while θ' precipitates display more uniform distribution (Fig. 2(c)). The associated SAED pattern taken with a [110]$_\alpha$ zone axis (Fig. 2(d)) reveals the T_1 and θ' reflection spots. The microstructure of alloy A in the same condition is provided in Fig. 2(e). It is noted that numerous

Fig. 2 Microstructures of specimens aged for 10 h at 180 ℃
(a), (b) —T_1 and θ' dark-field micrographs of alloy 2195, respectively;
(c) —T_1 and θ' bright-field micrographs of alloy M; (d) —SAED pattern for alloy M with [110]$_\alpha$ zone axis;
(e) —Very fine plate-like precipitates in alloy A; (f) —SAED pattern for alloy A with [110]$_\alpha$ zone axis

plate-like phases with very small sizes are uniformly precipitated. The SAED pattern with a [110]$_\alpha$ zone axis reveals the two sets of streaks along the $\langle 111 \rangle_\alpha$ directions and two sets of spots at the 1/3 and 2/3 g {220}$_\alpha$ positions which are characteristics of the four variants of the T_1 phase (Fig. 2(f)). No extra reflections are visible in the SAED pattern, indicating that the fine plates almost exclusively consist of T_1.

Overaging alloy 2195 at 180 ℃ for 40 h causes only a slight change of the distribution and size of T_1 which is shown in Fig. 3 (a), a negligible decrease in density of θ' plates is also observed (Fig. 3(b)). Alloy M overaged for 40 h

presents the existence of a uniform distribution of T_1 plates which are similar in size (Fig. 3 (c)), together with decreased density of θ' plates (Fig. 3(d)). It is likely that overaging alloy M appears to result in dissolution of θ'. Figs. 3(e), (f) show the microstructures in alloy A further aged for 40 h to obtain peak-aging, large platelets of T_1 and θ' are pricipitated in separated regions.

4 DISCUSSION

It is clear that Mg addition in alloy M favors the formation of GP zones at the early aging
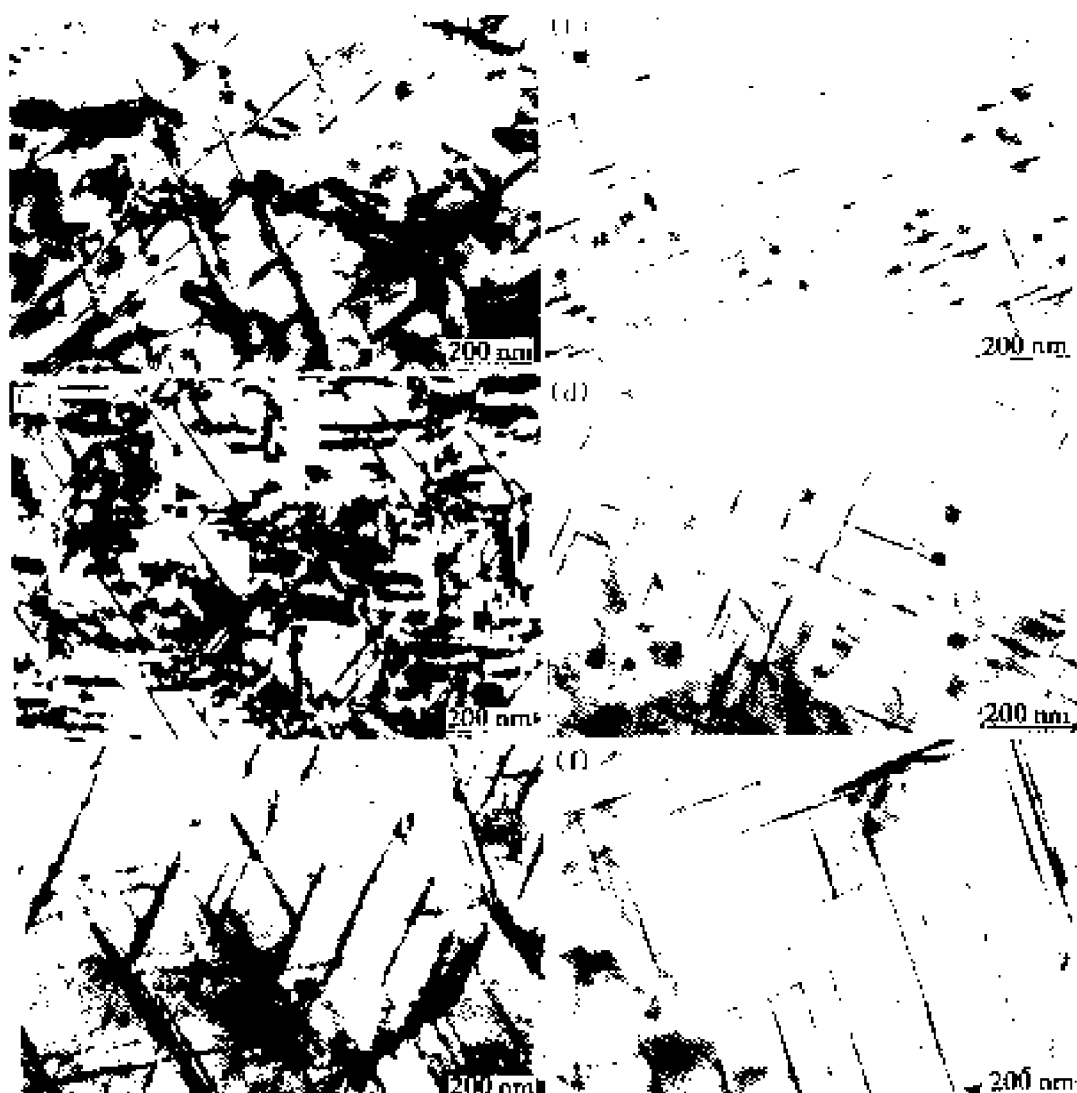
Fig. 3 Microstructures of specimens aged for 40 h at 180 ℃
(a), (b) —T_1 and θ' bright-field micrographs in alloy 2195, respectively;
(c), (d) —T_1 and θ' bright-field micrographs of alloy M, respectively;
(e), (f) —T_1 and θ' plates bright-field micrographs of alloy A, respectively

stage and then promotes the precipitation of θ' phases during subsequent aging. In addition, the fact that the T_1 phases, which were minor in an Al-4Cu-1.1Li-0.2Zr alloy[14] and were even absent in an Al-4.0Cu-1.24Li-0.16Zr alloy[15], precipitated in alloy M indicates that Mg addition also stimulates the precipitation of plate-like T_1 phases.

It is known that the Mg-vacancy binding energy in Al alloys with a significant amount of Cu (4% ~ 6%) has been proposed to be high by Armitage[16] and Garg et al[17]. Thus it is assumed that Mg has a high binding energy with vacancies in the present alloys. As proposed by Wyss et al[2] and Ringer et al[18], the high Mg-vacancy binding energy contributes to the formation of Mg-vacancy pairs which would be arranged in clusters with vacancies and multiple solute atoms. On the other hand, because of the strong Cu-Mg interaction[19], some Mg-vacancy clusters may seize Cu atoms to form Cu-Mg-vacancy clusters. Entwistle et al[20] put forward that the formation of GP zones was promoted by Cu-Mg-vacancy groups diffusing together. At the elevated aging temperatures, these GP zones would act as nuclei for θ'' phases and subsequently evolve into θ' phases[21]. Meanwhile, the vacancies associated with GP zones would be liberated at elevated aging temperatures with increasing aging time, so as to assist the growth of θ' phases through enhancing the Cu diffusion. θ' phases which are uniformly nucleated on GP zones would compete to grow independently till Cu solutes are depleted, resulting in an uniform dispersion of θ' plates as observed in alloy M.

T_1 phase, as hexagonal shaped plates with a {111}$_\alpha$ habit plane, is generally postulated to nucleate on stacking faults on the {111}$_\alpha$ planes in terms of stacking faults mechanism by dissociation of $b = 1/2\langle 110 \rangle$ perfect dislocations into $b = 1/6\langle 112 \rangle$ partial dislocations[22]. It is well known that the stacking fault energy of aluminum can be lowered by addition of the most soluble elements such as Mg, Ag and Li. When these elements are added individually or together, stacking faults on the close packed {111}$_\alpha$ planes are more easily to form. Since Mg pos-

sesses a larger atomic size than Al, some Mg atoms maybe form as disk shape on the {111}$_\alpha$ planes since the $\langle 111 \rangle$ orientation of disk shape exhibits the minimum elastic strain energy among all possible shapes and orientations[23]. So it is likely that some Mg additions in the present alloy may segregate to the {111}$_\alpha$ planes as Mg clusters which would lower the stacking fault energy and therefore favor the formation of {111}$_\alpha$ stacking faults. The {111}$_\alpha$ Mg clusters together with {111}$_\alpha$ stacking faults provide favorable nucleation sites for T_1 phases.

As predicted by data in Ref. [19], it can be assumed that Ag isn't ready as Mg to interact preferentially with Cu. Polmear[24] has reported that the effects of Cu and Ag in Al-Zn-Mg-Cu-Ag alloys were independent and thus there is no possibility of presence of Cu-Ag co-clusters. These evidences confirm that Ag has little interaction with Cu and therefore fails to favor the formation of Ag-Cu-vacancy clusters as Mg-Cu-vacancy clusters formed in alloy M, thus no GP zones observed in alloy A at early aging stage. In addition, Ag has no strong binding energy with vacancies[19]. As a result, in the early aging stage alloy A contains a large number of dislocation loops which form due to the collapse of vacancies retained in the quench.

Since GP zones which act as nucleation sites of θ' in alloy M are retarded by Ag additions in alloy A, the θ' phase would only nucleate heterogeneously on dislocations[25] or vacancy clusters[26], thus θ' phases with less density are heterogeneously precipitated in alloy A.

Ag is also the element to reduce the stacking fault energy as Mg. It was suggested that Ag would segregate to the {111}$_\alpha$ stacking faults on the basis of Suzuki interaction in Al-Ag alloys[27]. So it is expected that the presence of Ag would provide favorable nucleation sites for T_1 phases. However, it appears that the nucleation of T_1 phases requires sufficient aging time, because Li and Cu atoms must diffuse to the {111}$_\alpha$ stacking faults as nucleation sites. This diffusion process requires longer time. So at the early aging stage no T_1 phases were observed.

The strong Mg-Ag interaction would make

the preferred attraction of Mg with Ag be favored over that of Mg with Cu[19]. Ringer et al[18] have actually detected Mg-Ag co-clusters co-existing with Cu clusters in an Al-1. 9Cu-0. 3Mg-0. 2 Ag (mole fraction, %) alloy and they proposed that Ag effectively captured Mg atoms to form Mg-Ag co-clusters instead of Mg-Cu co-clusters which formed numerously in the ternary Al-1. 7Cu-0. 3Mg(mole fraction, %) alloy. Likewise, it is suggested in the present study that Mg atoms would trap Ag in preference to Cu to form Mg-Ag co-clusters. Since Mg has larger atomic size than Al while Ag has almost equal atomic size to Al, Mg-Ag co-clusters tend to form on the $\{111\}_\alpha$ planes so as to minimize elastic strain energy. Moreover, both Mg and Ag may reduce the stacking fault energy via Suzuki interaction and therefore favor the formation of stacking faults on the $\{111\}_\alpha$ planes.

On the other hand, because of the strong affinity of Li with Ag and Mg with Cu, in subsequent aging Li and Cu atoms may migrate to the Mg-Ag clusters to form Li-Ag-Mg-Cu co-clusters. The Mg-Ag co-clusters may be acting as a " catalyst" and " bridge" for the link of Li and Cu atoms required for the formation of T_1 phase, which would accelerate the precipitation process to form T_1 phases due to supply of Li and Cu atoms together. Thus the T_1 precipitation is not only enhanced but also accelerated by combined additions of Mg and Ag.

The potent role of independent Mg additions in promoting the formation of θ' phases is still effective in alloy 2195, but the effect is weakened due to the favored attraction of Mg with Ag over that of Mg with Cu, resulting in less number of Mg atoms available to form Cu-Mg-vacancy groups. In addition, as T_1 and θ' compete for Cu atoms, the enhanced precipitation of T_1 in alloy 2195 maybe responsible for decrease in the precipitation of θ' plates as well.

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