Compositional Characterization of Cu-Rich Phase Particles Present in As-Cast Al-Cu-Mg(-Li) Alloys Containing Ag

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The effects of small additions of Ag on the aging of wrought Al-Cu-Mg(-Li) alloys, involving widespread nucleation of Cu-rich Ω (and T_1) phase precipitates, are known. This article examines the influence of small additions of Ag on the nature of Cu-rich θ-Al_2Cu, S-Al_2CuMg, and T_1-Al_2CuLi phases present in appropriate as-cast Al-Cu, Al-Cu-Mg, and Al-Cu-Li-Mg alloys. Using a combination of light microscopy, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA), it is shown that neither independent nor combined additions of Ag and Mg to the binary Al-Cu alloy alter the composition of the θ phase; however, there are differences in the ways the θ phase is evolved in Al-Cu-Mg alloys with and without Ag. Ag additions to the Al-Cu-Mg alloy result in the formation of an Al-Cu-Mg–based ternary phase, having a Cu content similar to that of the θ phase and containing small amounts of Mg; rapid rates of cooling cause the retention of this phase in the as-cast alloy. Relatively large amounts of both Ag and Mg are always located in the peripheral regions of such a phase. This phase is readily replaced by θ phase upon annealing at 450 °C. The S phase of the ternary Al-Cu-Mg system is identified in this alloy and is found to dissolve small amounts of Ag. In the case of the Al-Cu-Li-Mg-Ag alloy, two major changes are observed: both Ag and Mg are always present in relatively large amounts in the peripheral regions of the T_1 phase, and the S-phase particles are once again found to dissolve small amounts of Ag. These results are discussed in light of the known compositional features of the precipitates formed in the artificially aged Al-Cu-Mg(-Li)-Ag alloys, to reveal that examination of phases present in the as-cast microstructure is a contributory step toward determining the locations of trace alloy additions in the phase precipitates of interest.

I. INTRODUCTION

THE as-cast microstructure of most age-hardenable Al alloys consists of cored dendrites of Al solid solution with a variety of constituents (/phases) being present at the grain boundaries or interdendritic spaces.[1,2,3] Depending on the alloy compositions and aging conditions, many of such phases reprecipitate during artificial aging following solution treatment and quenching.[2,3,4] The chemistry (in terms of the amounts of alloying elements) and the lattice parameters of the phases present in the as-cast alloy may not always be similar to those of the same type of phases (*i.e.*, phases having the same compound formulae) when present in the heat-treated alloy.[2,3,4] The phase particles present in the as-cast alloy could be, on the other hand, utilized effectively (due to their coarse nature) to obtain firsthand information regarding their possible association with a specific alloying element. Of further interest, the as-cast alloy may often contain metastable phases, and studies involving such phases may provide a basis for further understanding of the phase transformations that occur in the alloy. The present article is concerned with the influence of small additions of Ag on the nature of the Cu-rich phases of commercial interest, *i.e.*, θ, S, and T_1, present in appropriate as-cast alloys based on Al-Cu, Al-Cu-Mg, and Al-Cu-Li-Mg.

It is well known that trace additions of Ag to Al-Cu-Mg alloys, having compositions lying within the *θ-containing* phase fields (*i.e.*, $\alpha + \theta$ and $\alpha + \theta + S$) of the ternary Al-Cu-Mg phase diagram,[5] greatly increase the nucleation

frequency of the Ω phase during artificial aging.[6–17] The Ω phase, precipitated in the form of thin plates on $\{111\}_{Al}$ matrix planes, is regarded as the chemically modified coherent form of the equilibrium *θ-Al_2Cu phase*.[13–16] Using quaternary Al-Cu-Mg-Ag alloys, it has been demonstrated through several carefully designed experiments that Ω can nucleate readily upon aging at temperatures as high as 470 °C,[16] while prolonged aging even at 200 °C causes this phase to be replaced by the θ phase.[14,17] These results apparently demonstrate that, between θ and Ω, the formation of the latter phase is definitely easier, that Ω is replaced by θ and not *vice-versa*, and that a possibility of Ω or similar structures being stabilized by Ag in the as-cast microstructure of these alloys exists. No work has, so far, been carried out to examine the influence of Ag on the nature of the phases present in the as-cast Al-Cu-Mg alloy.

Small additions of Ag and Mg to Al-Cu-Li alloys are also known to enhance the nucleation of the plate-shaped T_1 (Al_2CuLi) phase during artificial aging.[18,19] Once again, there is no record in the literature of the influence of Ag on the nature of the phases present in the as-cast microstructure of these alloys. One of the major advantages associated with the detection of T_1, and, possibly, Ω or similar structures, in the as-cast alloys is that the locations of Ag and Mg within these coarse particles could be determined with greater accuracy.

Ag and/or Li additions to Al-Cu-Mg alloys, having compositions lying within the $\alpha + \theta + S$ phase field,[5] do not inhibit the formation of the S(Al_2CuMg) phase during artificial aging.[8,20] It has recently been suggested that Ag is associated with the S phase formed in Al-Cu-Mg-Ag alloys.[17] However, because of the small size of the S rods, the authors[17] could not conclude whether Ag is present

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within the S phase (or located at the S/Al matrix interfaces). It is also not known whether the composition of the S phase present in the Li-containing alloys gets modified by Ag. Detection and examination of coarse S particles present in the as-cast alloys may provide suitable answers to such queries.

In this article, using light microscopy, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA), results on the compositional analysis of major Cu-rich phases present in as-cast Al-Cu-Ag, Al-Cu-Mg, Al-Cu-Mg-Ag, and Al-Cu-Li-Mg-Ag alloys are presented. Emphasis is placed on the determination of the locations of Ag and Mg within the Cu-rich phases of interest.

II. EXPERIMENTAL PROCEDURE

A. *Alloy Compositions and Selection of Alloys*

The mass compositions of the as-cast alloys examined in the present investigation are Al-4Cu-0.5Ag, Al-4Cu-0.5Mg, Al-4Cu-0.5Mg-0.5Ag, Al-5Cu-1.2Li-0.5Mg-0.5Ag, and Al-2.5Cu-1.5Mg. The reason for the examination of the Al-Cu-Ag alloy is to find out whether Ag additions bring about any change in the composition of the binary θ phase. The reason for the examination of the Al-4Cu-0.5Mg alloy is twofold: first, to find out whether Mg additions modify the composition of the θ phase, and, second, to find out the chemistry of the phases present in this alloy, because it serves as reference for all other Mg-bearing alloys (particularly in relation to the S-phase analysis, as detailed later in this article in sections III B-D) examined in this work. The composition of the Al-4Cu-0.5Mg alloy lies within the $\alpha + \theta + S$ phase field of the ternary Al-Cu-Mg phase diagram.[5] As a result, both θ and S would be present as solidification products in the as-cast alloy.[1,2,3] The reason for the examination of the Al-Cu-Mg-Ag and Al-Cu-Mg-Li-Ag alloys is to evaluate the influence of Ag additions on the nature of the major Cu-rich phases present in such alloys, *i.e.*, θ and S in the Al-Cu-Mg alloy and T_1 and S in the Al-Cu-Li-Mg alloy. The reason for the selection of the particular alloy compositions for these alloys is that such alloys are currently being developed for commercial applications,[18,21] and that sufficient data already exist in the literature regarding the nature of the phases that form in such alloys during artificial aging.[8,17–20]

The presence of T_1 phase in the as-cast Al-Cu-Li-Mg-Ag alloys of Weldalite compositions has been evidenced.[22,23] The presence of S phase in such as-cast alloys could be verified readily from the thermal analysis results of these alloys. Thermal analysis was undertaken in DUPONT* dif-

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ferential scanning calorimetry (DSC) 9900 instrument using standard procedure.[24] Figures 1(a) and (b) present DSC traces showing major transformations during heating of the as-cast Al-4Cu-0.5Mg and Al-5Cu-1.2Li-0.5Mg-0.5Ag alloys, respectively. The endotherms in Figures 1(a) and (b) represent melting of various microstructural constituents. It should be noted that the onset of a major endothermic reaction at about 507 °C (the corresponding positions in the curves marked with arrows in Figures 1(a) and (b)) is common for both the alloys. The beginning of this endothermic
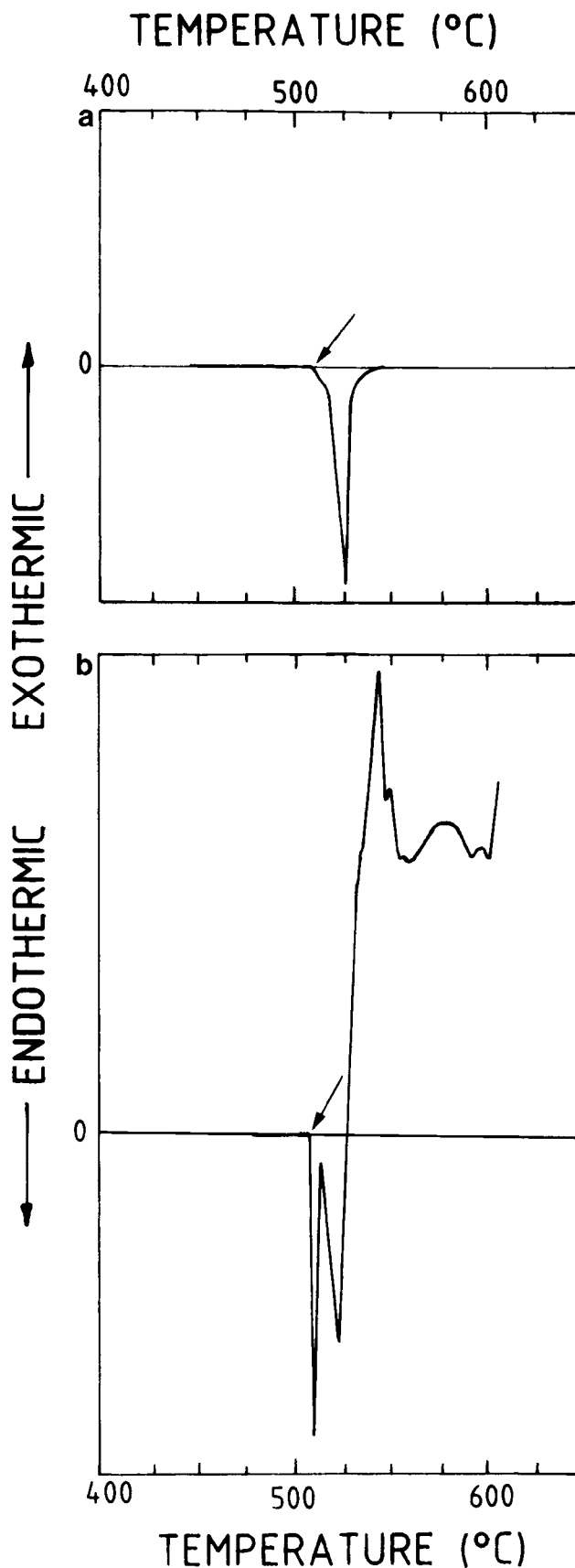

Fig. 1—DSC traces showing major transformations during heating of as-cast (*a*) Al-4Cu-0.5Mg and (*b*) Al-5Cu-1.2Li-0.5Mg-0.5Ag alloys. The arrows in (a) and (b) point out the onset of the endothermic reactions at about 507 °C.

reaction is well known to be associated with the melting of phase mixtures involving the S phase of the ternary Al-Cu-Mg system.[2,3] This implies that S phase is present in the as-cast microstructure of both the alloys. This clarifies further why Mg additions to Al-Cu-Li alloys reduce the upper limit on temperatures for ingot homogenization.[23] In Figure 1(b), several other overlapping reactions occurring over a wide range of temperatures may be noted. These reactions are not observed in Figure 1(a) and are associated with phases like T_1 and T_B (Al_7Cu_4Li) of the constituent Al-Cu-Li system.[22,23] In this article, results of the compositional analysis of only the relevant T_1 phase are presented.

The reason for the selection of the Al-2.5Cu-1.5Mg alloy is, on the other hand, to evaluate the effects of variation in Mg content on the composition of the ternary S-phase particles present in the as-cast and the corresponding annealed alloys. The resultant data are, in turn, used to substantiate the compositions of the S-phase particles present in the as-cast Al-4Cu-0.5Mg alloy. The reason why the annealed Al-4Cu-0.5Mg–based alloys were not examined for this purpose is that the S particles present in the as-cast alloys were fewer in number and that such particles appear not to survive the particular annealing conditions used in this work.

B. *Alloy Processing*

The alloys were prepared in an induction furnace under an argon atmosphere. The alloying elements (with the exception of Li, which was added in the elemental form) were added in the form of Al-based master alloys. The master alloys were, in turn, prepared from high-purity Al, Mg, Cu, and Ag. The alloys were cast in a mild steel mold. The thickness of these as-cast ingots was 30 mm. In the case of the Al-4Cu-0.5Mg and Al-4Cu-0.5Mg-0.5Ag alloys, however, thinner ingots cast in a copper mold and having a thickness of 12 mm were also made. This was to examine the influence of the increased rate of cooling (during and post solidification) on the compositions of the phases present in the resultant as-cast microstructures. It was observed that the microstructure of only the Ag-bearing alloy was influenced by the changes in the rate of cooling. Unless otherwise stated, the results described in this article correspond to the materials taken from the 30-mm-thick as-cast ingots.

The atomic absorption spectrophotometric method was used for the bulk chemical analysis of Li in the Li-bearing alloy. The as-cast materials were then characterized to examine the morphology and the compositions of the relevant Cu-rich phases present. In order to verify changes in the compositions of these phases due to thermal exposure, Al-2.5Cu-1.5Mg and Al-4Cu-0.5Mg-0.5Ag alloys were annealed at 450 °C for times ranging from 0.5 to 15 hours. This particular annealing temperature was selected on the basis that it is well below the minimum solidus temperature of these alloys.

C. *Alloy Characterization*

Light microscopy, together with SEM, were used to reveal typical features associated with the as-cast alloys. The scanning electron micrographs presented in this article were taken in the back-scattered electron imaging mode to facilitate identification of the Cu (atomic number 29)–rich particles. The SEM was carried out on the scanning electron microscope attached to an EPMA instrument, operating at 20 kV. The EPMA was performed on a CAMECA CAMBAX microanalyzer operating at 20 kV. A quantitative X-ray wavelength-dispersive spectroscopy (WDS) system, attached to the EPMA instrument, was used to analyze the chemistry of the phase particles present in the as-cast and in the heat-treated alloys. The instrument was equipped with the MAGIC-IV analytical program for ZAF corrections.[25] Elemental X-ray mapping and elemental line-scan tracing were carried out using EPMA in order to facilitate determination of the location of alloying elements (especially Ag and Mg) within the phase particles. All the analyses using EPMA were carried out on polished but unetched samples.

III. RESULTS

A. *Characterization of Al-4Cu-0.5Ag alloy*

Figure 2(a) presents a scanning electron micrograph which shows a typical as-cast microstructure of the alloy. The micrograph reveals that elemental partitioning has occurred during solidification, leading to the formation of second-phase particles at the grain boundaries. The continuous network of coarse particles at the grain boundaries appears bright. This implies that these particles are rich in elements having a high atomic number. Quantitative X-ray WDS analysis of these particles on EPMA revealed the following composition range: 49.2 to 50.8 wt pct Cu, 0.00 to 0.06 wt pct Ag, and the balance Al. It may be noted that the Cu content of these particles is close to that of the equilibrium θ-Al_2Cu phase, *i.e.*, 52.5 to 53.9 wt pct.[26] Also, the analysis shows that Ag could not always be detected in these particles, and when detected (as reflected in the upper limit of the composition range for these particles, *i.e.*, 0.06 wt pct), the values are well below the average Ag content of the matrix, *i.e.*, 0.46 wt pct, as determined by X-ray WDS analysis of the matrix. The occasional presence of small amounts of Ag in these particles is, therefore, attributed to the matrix contribution to the analysis. This implies that these particles represent the θ phase of the constituent Al-Cu system.

Figure 2(b) presents a scanning electron micrograph which shows a magnified image of the θ particle that is marked by an arrow in Figure 2(a). Figure 2(c) presents elemental line-scan traces which demonstrate that the particle in Figure 2(b) is, indeed, rich in Cu; that there is no evidence of segregation of excess amounts (*i.e.*, amounts in excess of what is present in the matrix) of Ag in the peripheral regions (shown by small arrows in Figure 2(b)) of the particle; and that the Ag content of the matrix is, of course, well above that which could be present within the particle. These results definitely suggest that Ag additions to the binary Al-Cu alloy do not bring about any change in the composition of the binary θ phase.

B. *Characterization of the Al-4Cu-0.5Mg and Al-2.5Cu-1.5Mg Alloys*

Figure 3(a) presents a scanning electron micrograph which shows the distribution of coarse Cu-rich particles present in the as-cast Al-4Cu-0.5Mg alloy. Quantitative X-ray WDS analysis of these particles on EPMA revealed that these particles are of two different types. The major one of the two phases, mostly having irregular shapes (marked by arrows in
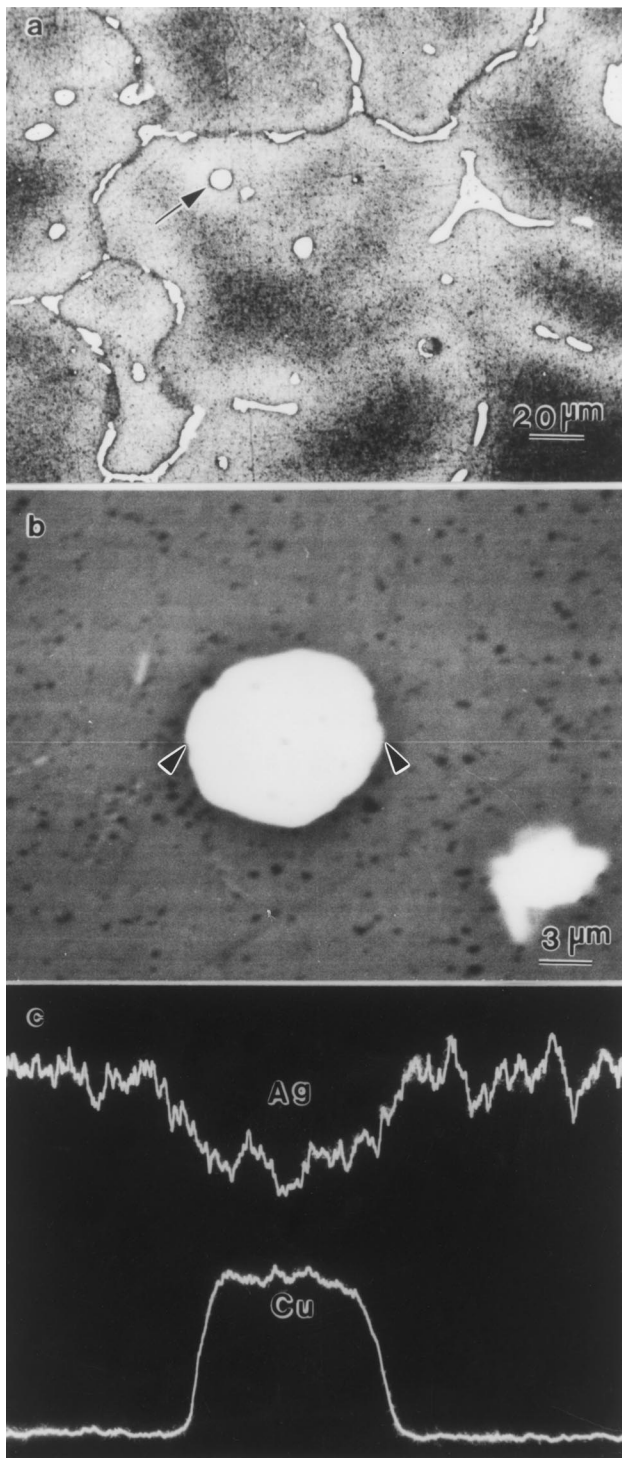
Fig. 2—Scanning electron micrographs obtained from the as-cast Al-4Cu-0.5Ag alloy showing (*a*) as-cast microstructure and (*b*) a magnified image of the θ particle arrowed in (a). (*c*) Ag and Cu line-scan traces, respectively (labeled), of the θ particle shown in (b).

Fig. 3—Scanning electron micrographs obtained from the as-cast Al-4Cu-0.5Mg alloy showing (*a*) distribution of coarse Cu-rich particles and (*b*) a magnified image of a θ particle. (*c*) Mg line-scan traces of the θ particle shown in (b).

Figure 3(a)), is found to have the following composition range: 49.77 to 50.93 wt pct Cu, 0.32 to 0.35 wt pct Mg, and the balance Al. However, the minor phase, mostly having the circular shape (marked by arrows and labeled S), is found to contain 42.57 to 44.97 wt pct Cu, 3.04 to 3.73 wt pct Mg, and the balance Al. It may be noted that the Cu content of the major phase is close to that of the binary θ
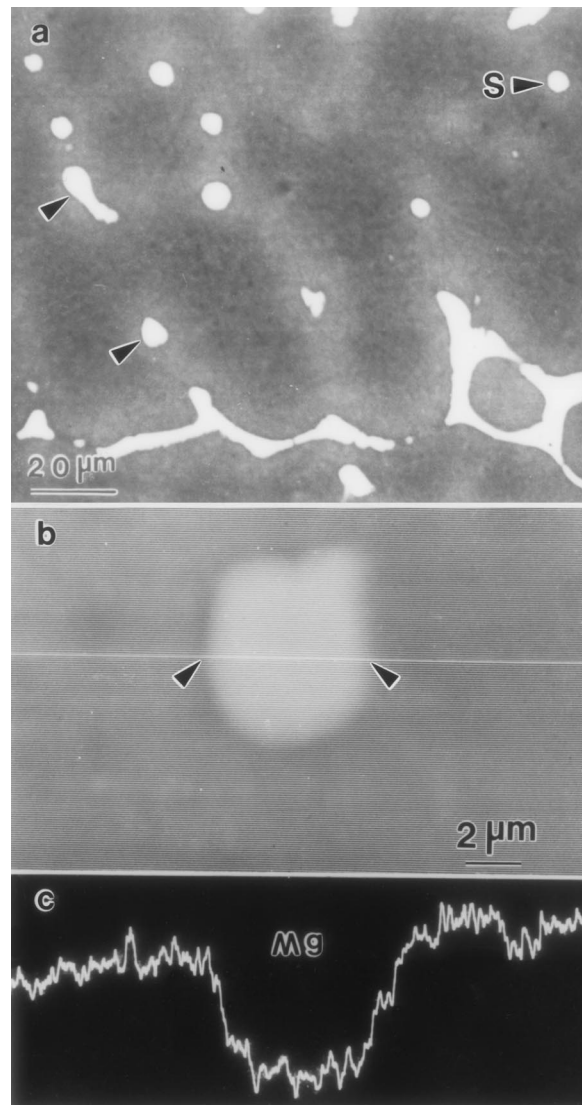
phase.[26] However, the Mg content of these particles is below the average Mg content of the matrix, *i.e.*, 0.47 wt pct, as determined by X-ray WDS analysis of the matrix. This tends to suggest that the apparent presence of Mg in association with the θ phase is likely to be due to the matrix contribution to the analysis. Such an interpretation is consistent with the previous reports that the θ phase does not dissolve Mg.[1,2,16] The major Cu-rich phase is, therefore, identified to be the binary θ phase.

Figure 3(b) presents a scanning electron micrograph which shows a magnified image of a θ particle present in the alloy. Figure 3(c) presents line-scan traces for Mg which demonstrate that there is no evidence of segregation of excess amounts (*i.e.*, amounts in excess of what is present in the matrix) of Mg in the peripheral regions (indicated by small arrows in Figure 3(b)) of the particle.

The Cu content of the minor phase present in the alloy is close to that of the equilibrium S phase (having the composition of 46 wt pct Cu, 17 wt pct Mg, and the balance Al).[2]
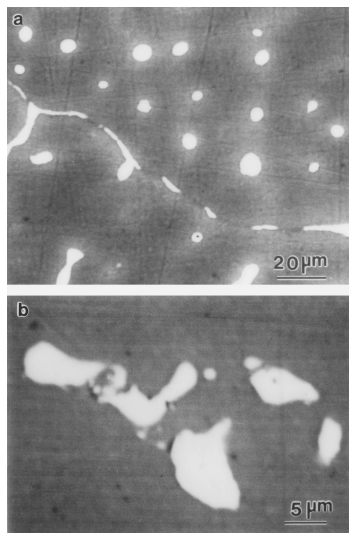
Fig. 4—Scanning electron micrographs obtained from the Al-2.5Cu-1.5Mg alloy showing distribution of S particles in (*a*) as-cast and (*b*) annealed (*i.e.*, 15 h at 450 °C) microstructure.

However, the Mg content of these particles is well below that of the equilibrium S phase. In order to verify whether this is due to the lower Mg content of the alloy itself, the Al-2.5Cu-1.5Mg alloy (having a composition lying within the α + S phase field of the ternary Al-Cu-Mg phase diagram[5]) was examined in the as-cast as well as in the heat-treated conditions.

Figure 4(a) presents a scanning electron micrograph which shows the distribution of phase particles in the as-cast Al-2.5Cu-1.5Mg alloy. Many of these particles have a circular shape. According to the ternary Al-Cu-Mg phase diagram,[5] the particles shown in Figure 4(a) must represent the S phase.[1,2,3] Quantitative X-ray WDS analysis of these particles revealed the following composition range: 38.81 to 46.16 wt pct Cu, 3.73 to 10.11 wt pct Mg, and the balance Al. Figure 4(b) presents a scanning electron micrograph which shows the presence of coarse particles in the cast Al-2.5Cu-1.5Mg alloy when annealed at 450 °C for 15 hours. Quantitative X-ray WDS analysis of these particles revealed the following composition range: 38 to 44 wt pct Cu, 16.5 to 19.08 wt pct Mg, and the balance Al. It should be noted that the Mg content of the equilibrium S phase (*i.e.*, 17 wt pct[2]) is now well within the composition range of Mg obtained for the particles present in the annealed material. These results point out that the ternary Al-Cu-Mg–based phase particles present in as-cast Al-4Cu-0.5Mg and Al-2.5Cu-1.5Mg alloys do represent the initial stages of formation of the S phase. Also, comparisons of the Mg contents of the ternary Al-Cu-Mg–based particles (hereafter termed S particles) present in the as-cast Al-Cu-Mg alloys reveal that the respective Mg content (or, possibly, the Mg:Cu ratio) of these alloys does indeed determine the Mg content of the S particles formed in the corresponding as-cast microstructure of these alloys.

C. *Characterization of the Al-4Cu-0.5Mg-0.5Ag Alloy*

Figure 5(a) presents a scanning electron micrograph which shows a typical as-cast microstructure of the Al-4Cu-0.5Mg-0.5Ag alloy. The presence of coarse second-phase particles
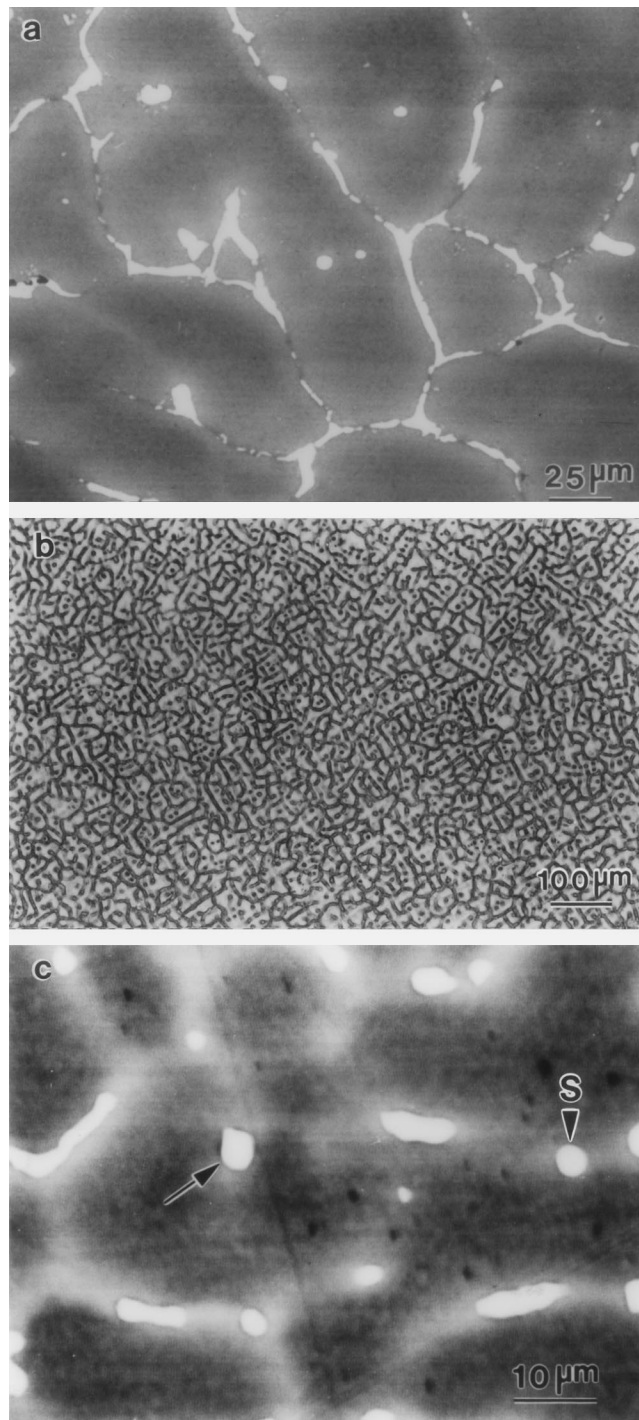

Fig. 5—(*a*) Scanning electron micrograph showing a typical as-cast microstructure of the Al-4Cu-0.5Mg-0.5Ag alloy. (*b*) Light micrograph showing a typical as-cast microstructure of an Al-Cu-Mg-Ag alloy sample obtained from the thinner as-cast ingot of the alloy. (*c*) Scanning electron micrograph obtained from the alloy sample in (*b*) showing the presence of coarse particles at the grain boundaries.

at the grain boundaries is evident in the micrograph. Quantitative X-ray WDS analysis of these particles revealed that these particles are of two different types. The major one of the two phases, having mostly irregular shapes, is found to have the following composition range: 49.67 to 50.51 wt pct Cu, 0.20 to 0.32 wt pct Mg, 0.00 to 0.06 wt pct Ag, and the balance Al. The minor phase, mostly having a circular

shape, is, on the other hand, found to have the following composition range: 42.65 to 45.51 wt pct Cu, 6.36 to 9.16 wt pct Mg, 2.41 to 2.68 wt pct Ag, and the balance Al. It should be noted that the Cu content of the major phase is similar to that of the binary θ phase observed in the constituent Al-Cu-Mg and Al-Cu-Ag systems. The observed levels of Ag and Mg in these particles, compared to the average Ag and Mg contents of the matrix, *i.e.*, 0.39 and 0.43 wt pct (as determined by the X-ray WDS analysis of the matrix), implies that the apparent association of Ag and Mg with the particles is due to the matrix contribution to the analysis. The major Cu-rich phase must, therefore, represent the binary θ phase. Elemental line-scan tracing revealed that there is no conclusive evidence of segregation of excess amounts of either Ag or Mg in the peripheral regions of these θ particles.

Figure 5(b) presents a light micrograph which shows a typical as-cast microstructure of an Al-Cu-Mg-Ag alloy sample obtained from the thinner as-cast ingot of the alloy. The same alloy sample, when viewed on SEM at higher magnification, reveals the presence of coarse second-phase particles at the grain boundaries (Figure 5(c)). Quantitative X-ray WDS analysis of these particles, once again, revealed that these particles are of two different types. The minor one of the two phases, mostly having a circular shape (marked by an arrow and labeled S) is found to have the composition range similar to that of the circular particles observed in the previous sample of this alloy (Figure 5(a)). However, the major phase, having mostly irregular shapes, is found to have the following composition range: 48.97 to 51.54 wt pct Cu, 0.69 to 1.98 wt pct Mg, 0.02 to 0.08 wt pct Ag, and the balance Al. The observed low levels of Ag in these particles are, once again, attributed to the matrix contribution to the analysis. However, the detection of up to 1.98 wt pct Mg in these particles (compared to the average Mg content of the matrix being 0.38 wt pct) points out that these particles must contain small amounts of Mg and that these particles must represent an Al-Cu-Mg–based ternary phase.

Figure 6(a) presents a scanning electron micrograph which shows a magnified image of one major Cu-rich ternary-phase particle, marked by an arrow in Figure 5(c). Figures 6(b) through (d) present elemental line-scan traces which demonstrate that the particle is, indeed, rich in Cu and that both Ag and Mg are concentrated in large amounts (*i.e.*, in amounts well above the average Ag and Mg contents of the matrix) in the peripheral regions of the particle.

Figure 7(a) presents a scanning electron micrograph which shows a magnified image of another major Cu-rich ternary-phase particle, and Figure 7(b) presents an Ag X-ray map of such a particle. Figure 7(b) reveals that Ag is, indeed, located in the peripheral regions of the particle. Given this relatively large-scale solute segregation, the term peripheral (actually implying particle/matrix boundary) rather than interface is used, because interfaces involve a few atomic layers of regions only. Quantitative X-ray WDS analysis of the peripheral regions of these particles revealed the following composition range: 24.5 to 29.7 wt pct Cu, 4.78 to 8.52 wt pct Mg, 2.76 to 6.43 wt pct Ag, and the balance Al. Considering the dilution effect of the Al matrix, together with that of the particle itself, to this analysis, it could only be inferred, however, that both Ag and Mg are, indeed, present in large amounts in the peripheral regions of the major Cu-rich ternary-phase particles.

Figure 8(a) presents a scanning electron micrograph which shows a magnified image of a typical particle present in the alloy (*i.e.*, the thinner as-cast ingot sample) annealed at 450 °C for 15 hours. Figures 8(b) and (c) present elemental line-scan traces which demonstrate that neither Ag nor Mg are segregated in the peripheral regions of this particle. Quantitative X-ray WDS analysis of this, as well as other such particles, showed that they have the following composition range: 49.89 to 50.49 wt pct Cu, 0.26 to 0.34 wt pct Mg, 0.00 to 0.09 wt pct Ag, and the balance Al. This analysis is similar to that obtained for the θ particles present in the as-cast Al-Cu-Mg alloy as well as in the previous Al-Cu-Mg-Ag alloy sample (Figure 5(a)). This implies that the major Cu-rich ternary phase in the as-cast alloy has now been replaced by the binary θ phase. Further experiments revealed that the major Cu-rich ternary phase is, in fact, replaced by θ phase within 0.5 hours at 450 °C.

The Cu and Mg contents, as well as the morphology of the minor Cu-rich phase particles present in the as-cast alloy samples, are comparable to those of the S particles observed in the as-cast Al-Cu-Mg alloy. The presence of as high as 2.68 wt pct Ag (*i.e.*, when compared to the average Ag content of the matrix, which is 0.39 wt pct) in these particles reveals, on the other hand, that the S phase definitely dissolves Ag. Figure 9(a) presents a scanning electron micrograph which shows a magnified image of one S-phase particle present in the alloy. Figures 9(b) and (c) present elemental line-scan traces which demonstrate that both Ag and Mg are present within the particle and that there is no evidence of segregation of excess amounts of either Ag or Mg in the peripheral regions of this particle.

D. *Characterization of the Al-5Cu-1.2Li-0.5Mg-0.5Ag Alloy*

Figure 10(a) presents a scanning electron micrograph which shows the distribution of the phase particles present in the as-cast Al-Cu-Li-Mg-Ag alloy. Quantitative X-ray WDS analysis of these particles showed that they (*i.e.*, the phases of present interest) are of two different types. The major one of the two, having mostly irregular shapes, has the following composition range: 49.91 to 51.03 wt pct Cu, 0.07 to 0.13 wt pct Mg, 0.03 to 0.09 wt pct Ag, and the balance Al. The other phase is found to contain 41.52 to 43.82 wt pct Cu, 2.01 to 3.28 wt pct Mg, 2.02 to 2.39 wt pct Ag, and the balance Al. It should be pointed out that Li (atomic number 3) could not be analyzed using the X-ray WDS analysis, although it is possible that both the phases are associated with Li.[22,23,27]

The Cu content of the major phase is comparable to that of the θ phase observed in the constituent ternary and quaternary alloy systems. The apparent Ag and Mg contents of the major phase are, on the other hand, below the average Ag and Mg contents of the matrix, *i.e.*, 0.28 and 0.26 wt pct, respectively, and the apparent association of these elements with the major phase is, therefore, attributed to the matrix contribution to the analysis. Figure 10(b) presents a scanning electron micrograph which shows a magnified image of one major Cu-rich phase particle (marked by an arrow in Figure 10(a)). Figures 10(c) and (d) represent elemental line-scan traces which reveal that both Ag and Mg are segregated in excess amounts in the peripheral regions of the particle.
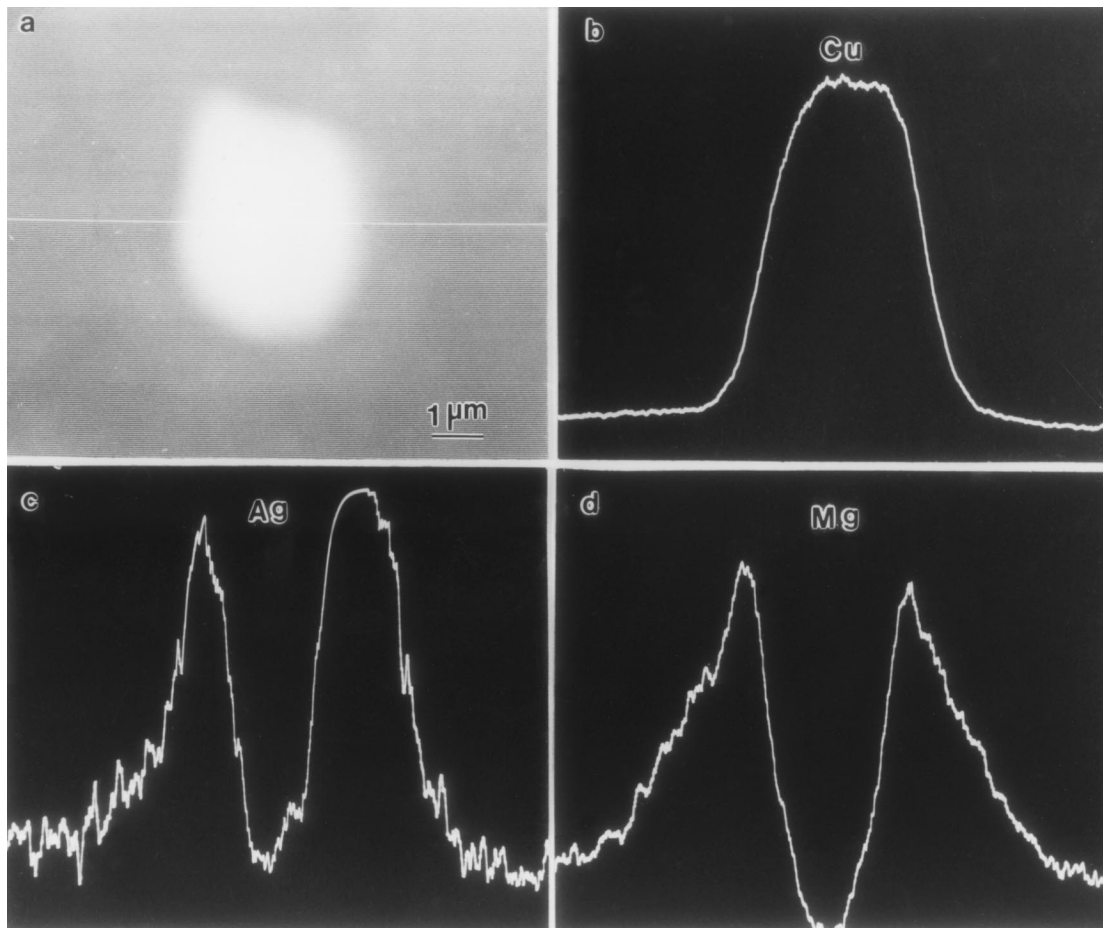
Fig. 6—(a) Scanning electron micrograph obtained from the as-cast Al-4Cu-0.5Mg-0.5Ag alloy showing a magnified image of a major Cu-rich ternary phase particle arrowed in Fig 5(c). (b) through (d) Cu, Ag, and Mg line-scan traces, respectively, of the particle shown in (a): note the presence of excess amounts of Ag and Mg in the peripheral regions of the particle.

Figure 11(a) presents a scanning electron micrograph which shows a magnified image of one major Cu-rich phase particle. Figures 11(b) and (c) present X-ray maps of Ag and Mg, respectively, which demonstrate that both these elements are, indeed, segregated in the peripheral regions of the particle.

The Cu and Mg contents of the minor Cu-rich phase are comparable to those of the S phase observed in the constituent Al-Cu-Mg system. The Ag content of the minor phase is also comparable to that observed in the S particles formed in the constituent Al-Cu-Mg-Ag system. This implies that the minor phase does represent the S phase. Figure 12(a) presents a scanning electron micrograph which shows a magnified image of one S particle present in the alloy. Figures 12(b) and (c) represent elemental line-scan traces which reveal that both Ag and Mg are, indeed, present within the particle and that there is no indication of segregation of these elements in the peripheral regions of the particle. These characteristics are comparable to those of the S-phase particles present in the Li-free Al-Cu-Mg-Ag alloy.

IV. DISCUSSION

Examination of phases present in the as-cast microstructure of age-hardenable Al alloys has always provided important information regarding the nature of the precipitates that may form in such alloys during artificial aging.[2,3] The general observation has been that the phases present in the as-cast microstructure dissolve back to the solution during the homogenization treatment (and the solution treatment) and reprecipitate in the alloy under suitable aging conditions. The reprecipitated phases represent either the compounds of the same phases, *i.e.*, those present in the as-cast microstructure, such as T_1 in the Al-Cu-Li system,[23] or their metastable versions, for example, θ' (metastable θ-Al_2Cu) in the Al-Cu system.[2]

Recently, observations have been made of one Cu-rich phase, Ω, which appears as a minor phase in the ternary Al-Cu-Mg system.[8] The nucleation frequency of the Ω phase is, however, greatly accelerated by the presence of small additions of Ag in the alloy, to the extent that Ω becomes the major strengthening phase in the age-hardened microstructure.[6–17] High-angle grain boundaries in such alloys also nucleate Ω precipitates predominantly.[28] Most investigators agree that the Ω phase (like the T_1 phase in the Al-Cu-Li system[2] and unlike the θ phase in the Al-Cu system[2]) has no precursory structure, can nucleate up to very high temperatures,[16] and has a chemistry and crystal structure close to those of the equilibrium θ phase.[13,14,15] It is these results that inspired the initiation of the present work.
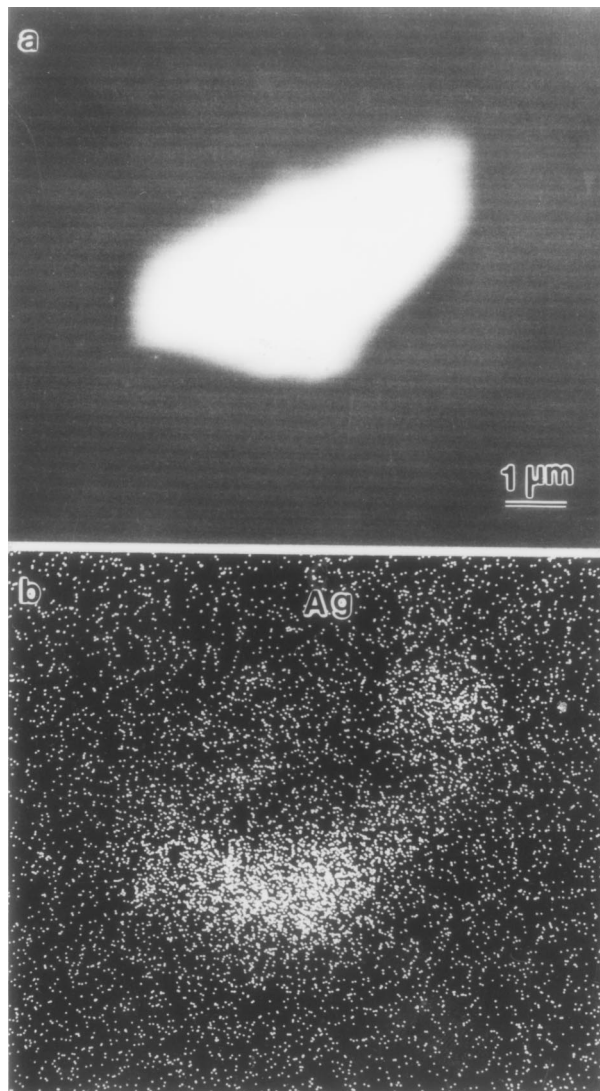
Fig. 7—(a) Scanning electron micrograph showing a magnified image of a major Cu-rich ternary phase particle present in the as-cast Al-4Cu-0.5Mg-0.5Ag alloy and (b) Ag X-ray map of the particle shown in (a).
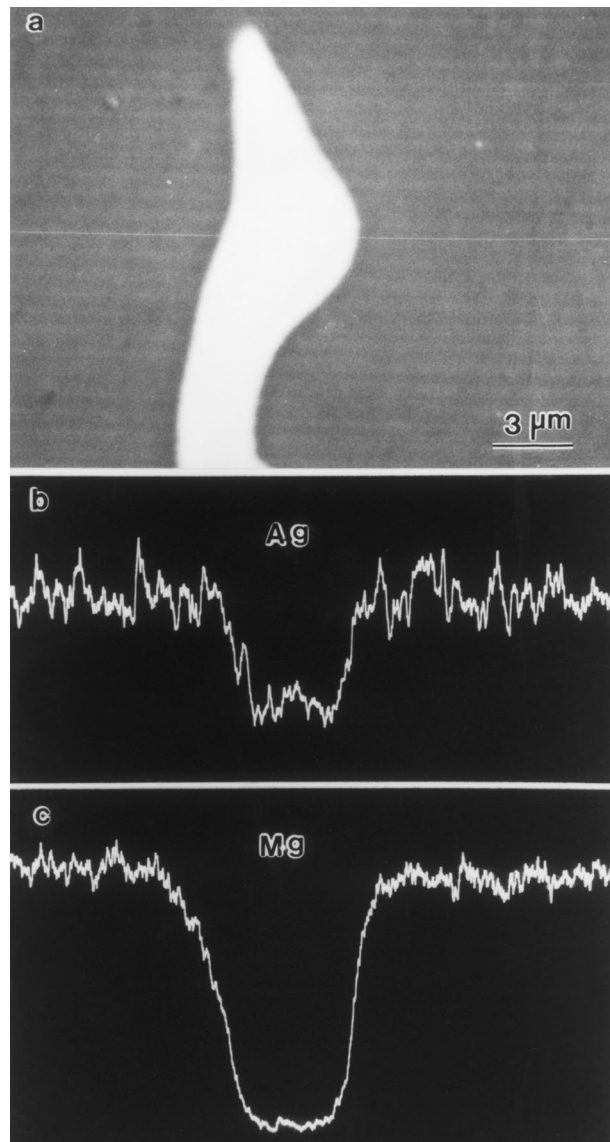

Fig. 8—(a) Scanning electron micrograph showing a magnified image of a particle present in the cast Al-4Cu-0.5Mg-0.5Ag alloy annealed at 450 °C for 15 h. (b) and (c) Ag and Mg line-scan traces, respectively, of the particle shown in (a).

There exist similarities, and, yet, striking differences, in the compositional details of the θ and Ω phases formed in the heat-treated Al-Cu-Mg-Ag alloys. The Cu content of the Ω phase is close to that of the θ phase.[16] On the other hand, unlike in the case of the θ phase, Ω is always associated with both Ag and Mg, being segregated at the Ω/Al interfaces.[10] It has also been pointed out that the Ω phase may contain small amounts of Mg,[10] an element which has, on the other hand, no solubility in the θ phase.[2,16] A further major feature of the Ω phase is its metastable nature, i.e., it becomes unstable and gets replaced by θ phase upon prolonged annealing, even at temperatures which are well below the temperatures at which the precipitate can nucleate readily.[14,17] This, together with the reported different compositional features of the Ω phase formed under different aging conditions, i.e., the presence of both Ag and Mg within the phase,[29] the presence of Mg alone within the phase,[10] and the segregation of Ag and Mg at the Ω/Al matrix interfaces,[10,30] point out that Ω is, indeed, a metastable phase. Studies have further pointed out that Li additions to the Al-Cu-Mg-Ag alloys replace the Ω phase by T_1[18,19,31] and that

both Ag and Mg segregate at the T_1/Al interfaces.[30,32] It is these characteristic features of the major Cu-rich phases formed in the artificially aged Al-Cu-Mg(-Li)-Ag alloys that explain and support the observations made in the present work.

A. Al-4Cu-0.5Ag and Al-4Cu-0.5Mg Alloys

The presence of θ-Al$_2$Cu in the as-cast Al-Cu-Ag alloy is in agreement with previous reports that it is the only Cu-rich phase at the Al end of the ternary Al-Cu-Ag system.[2] The absence of Ag in θ is also in agreement with the previous reports that Ag has no solubility in the θ phase.[2,16] Both θ and S phase particles could be identified in the as-cast Al-4Cu-0.5Mg alloy. This is in accordance with the ternary Al-Cu-Mg phase diagram,[5] which shows that binary θ and ternary S phases would be present as solidification products in as-cast Al-Cu-Mg alloys having compositions lying within
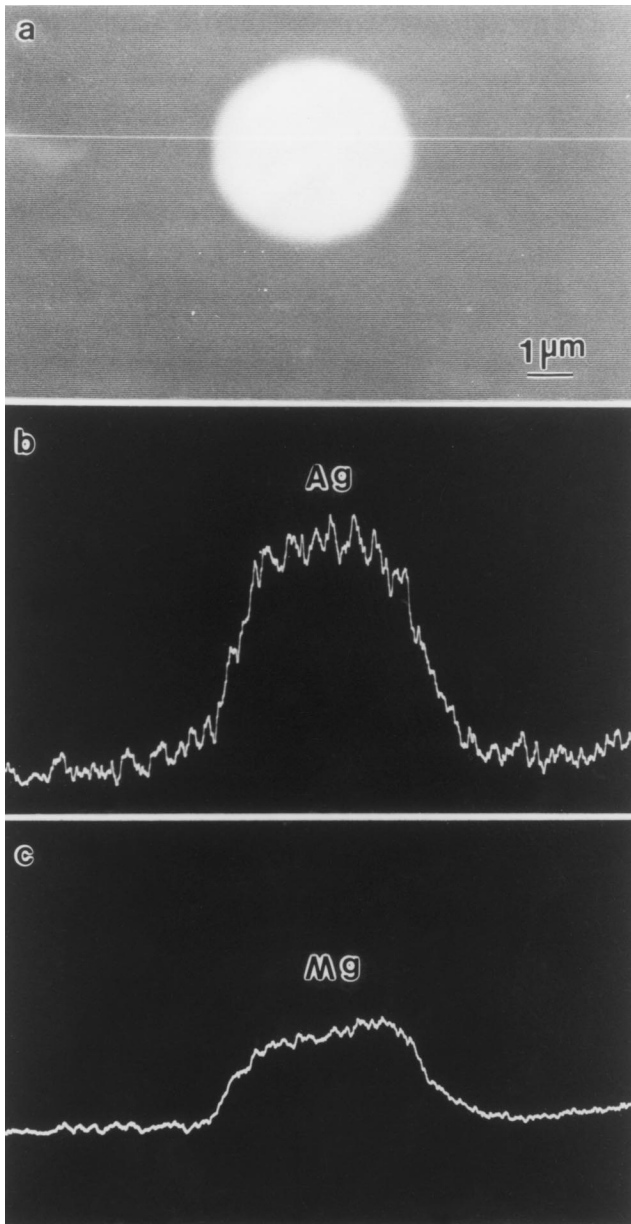
Fig. 9—(*a*) Scanning electron micrograph showing a magnified image of one S-phase particle present in the as-cast Al-4Cu-0.5Mg-0.5Ag alloy. (*b*) and (*c*) Ag and Mg line-scan traces, respectively, of the S-phase particle shown in (a).

the $\alpha + \theta + S$ phase field.[1,2,3] This, together with the present results and interpretations that the θ phase does not dissolve Mg, are also consistent with those reported earlier.[2,16,17]

B. *Al-4Cu-0.5Mg-0.5Ag Alloy*

The most striking feature associated with the phases detected in this alloy system is the presence of a previously undocumented ternary Al-Cu-Mg–based phase in the thinner as-cast ingot of the alloy. The rate of cooling clearly plays, therefore, a critical role in the retention of this phase in the as-cast microstructure. This implies, in turn, that it is a metastable phase. The Cu content of this phase is comparable to that of the θ phase; however, the presence of small
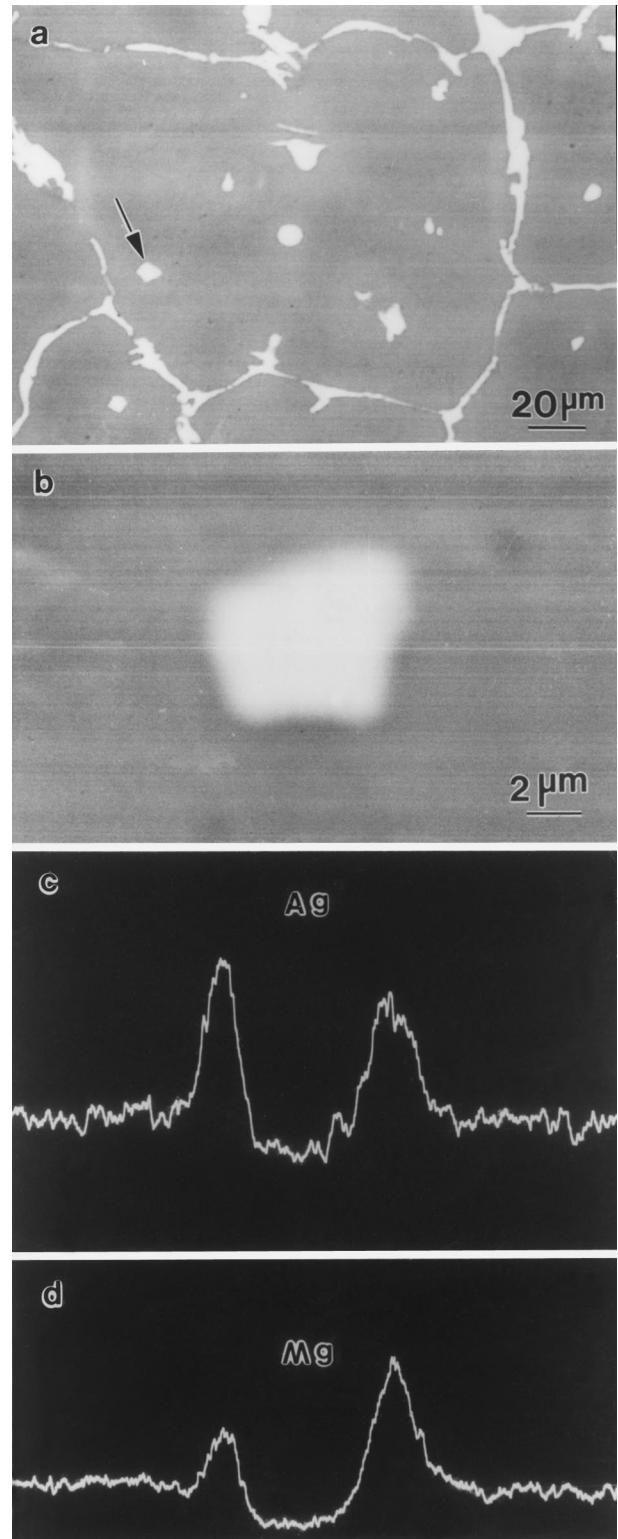

Fig. 10—Scanning electron micrographs obtained from the as-cast Al-5Cu-1.2Li-0.5Mg-0.5Ag alloy showing (*a*) typical distribution of the phase particles and (*b*) a magnified image of a major Cu-rich phase particle. (*c*) and (*d*) Ag and Mg line-scan traces, respectively, of the particle shown in (b): note the presence of excess amounts of both Ag and Mg in the peripheral regions of the particle.

amounts of Mg within the phase, together with the presence of relatively large amounts of both Mg and Ag in the peripheral regions of this phase, make it chemically different from
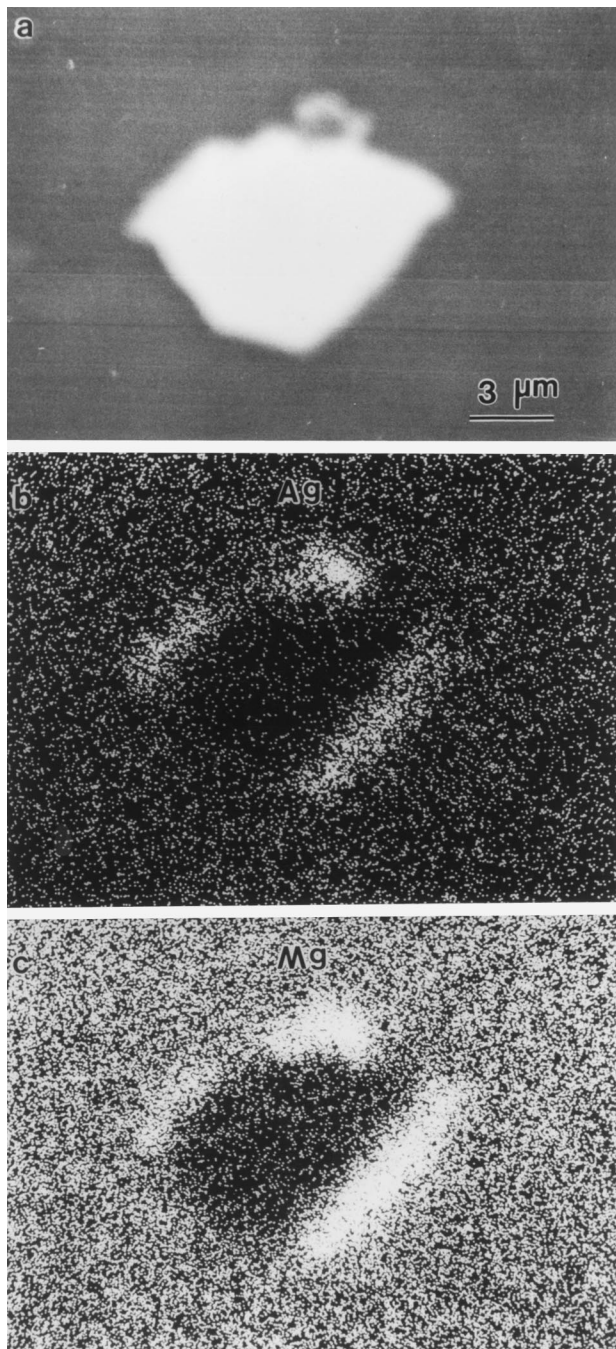
Fig. 11—(*a*) Scanning electron micrograph showing a magnified image of one major Cu-rich phase particle present in the as-cast alloy containing Li. (*b*) and (*c*) Ag and Mg X-ray maps, respectively, of the particle shown in (a): note the presence of excess amounts of both Ag and Mg in the peripheral regions of the particle.

Fig. 12—(*a*) Scanning electron micrograph showing a magnified image of one S particle present in the as-cast alloy containing Li. (*b*) and (*c*) Ag and Mg line-scan traces, respectively, of the S-phase particle shown in (a).

the binary θ phase. It may further be noted that the apparent peripheral segregation of alloying elements of this magnitude must be selective in nature, and that this cannot merely be a result of elemental segregations commonly encountered during solidification. This is because such events are not associated with the S phase present in the same as-cast alloy. The present metastable ternary phase has no parallel to the phases previously identified in the as-cast microstructure of Al-Cu-Mg–based alloys.

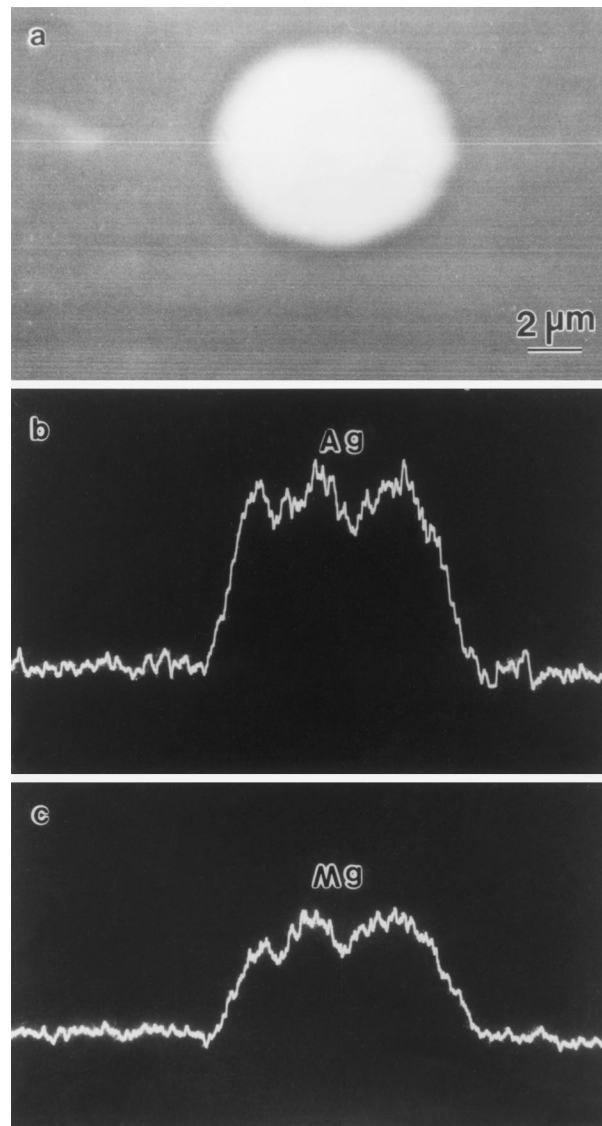On the other hand, the characteristic features of the present ternary phase strongly resemble those of the Ω phase, which precipitates as the major phase in the age-hardened micro-structure of the present alloy.[6–17] Such an interpretation receives support from the recent work of Howe,[10] that the Ω phase may contain small amounts of Mg. The appearance of the present phase, in association with excess amounts of both Ag and Mg located in the peripheral (implying particle/ Al matrix boundary) regions, is also another major feature of the Ω phase.[10]. Yet another major feature of Ω is its metastable nature. It should be noted that a similar nature is, indeed, exhibited by the present ternary phase in that it is readily replaced by θ upon annealing at 450 °C . In fact, this appears to be the reason why this phase is not observed in the relatively thicker as-cast ingots, *i.e.*, the slowly cooled as-cast ingots of such alloys. The implication is that the rapid rates of cooling cause the retention of this phase, while the slower rates of cooling lead to the replacement of this phase by the θ phase.

The origin of the present metastable phase, resembling

Ω,[10,29,30] is explained as follows. At the beginning, Ag and Mg atoms are integral parts of the solute atoms (/atom clusters) which form the Cu-rich θ phase. The strong attraction between Ag and Mg, owing to the large difference in electronegativity between them (i.e., 0.7[33]), together with the consideration that Mg is a larger atom than both Cu and Al,[2] make such a proposition feasible. However, the insolubility of Ag and Mg in the θ phase,[2,16] requires that these two elements be rejected during the growth of the θ phase. The consequence is the expulsion of Ag and Mg atoms during the growth of the θ phase and the observation of an apparent segregation of Ag and Mg in the peripheral regions of these particles. Annealing at 450 °C expedited the expulsion of Mg, still remaining in small amounts within the major phase, and the removal of the peripheral segregation of the Ag and Mg atoms. The result is the replacement of the major phase by the binary θ phase.

The minor Cu-rich phase, identified to be the S phase, is always found to dissolve small amounts of Ag. This provides the necessary support to an earlier work,[17] clarifying that Ag is present within the S phase formed in the heat-treated microstructure of an Al-4Cu-0.3Mg-0.4Ag alloy. The present results point out that, at the beginning, the Ag atoms are an integral part of the solute atoms which form the Al_2CuMg-based S phase and that the Ag atoms once incorporated into the S-phase structure remain essentially so until the phase dissolves. Such a proposition is consistent with the present observation that Ag does not segregate in the peripheral regions of the S-phase particles, thereby implying that Ag is not rejected during the growth of the S phase. Referring to the compositions of the S particles formed in the ternary Al-Cu-Mg system, it may further be noted that Ag additions have the effect of increasing the Mg content of the S particles. This is attributed to and consistent with the known attraction between Ag and Mg,[33] together with the fact that Ag reduces the solubility of Mg in Al.[2]

C. Al-5Cu-1.2Li-0.5Mg-0.5Ag Alloy

The principal features associated with the major Cu-rich phase present in this alloy are that the Cu content of this phase is similar to that of the θ phase, that this phase does not dissolve either Ag or Mg, and that both Ag and Mg are present in excess amounts in the peripheral regions of this phase. It is pointed out that although Li could not be analyzed using the X-ray WDS facilities, the present phase is recognized to be T_1, i.e., the major phase of the constituent Al-Cu-Li system. Such an interpretation receives support from the facts that the Cu content of the T_1 phase (i.e., 52.8 wt pct)[2] is similar to that of the θ phase (i.e., 52.5 to 53.9 wt pct),[26] that Li additions to the Al-Cu-Mg-Ag alloy stabilize the T_1 phase,[31] and that both Ag and Mg are observed to segregate at the T_1/Al matrix boundaries.[30,32] It is proposed that, at the early stages of formation, both Ag and Mg must be integral parts of the solute atoms (/atom clusters) which form the Cu-rich T_1 and S phases. However, once again, the insolubility of Ag and Mg in the T_1 phase[2] requires that these two elements be rejected during the growth of the T_1 phase. The result is the expulsion of Ag and Mg during the growth of the T_1 phase and the observation of an apparent segregation of Ag and Mg in the peripheral regions of the T_1 particles (Figure 11).

The circular S-phase particles present in this alloy are also found to dissolve small amounts of Ag. This implies that Li additions to the Al-Cu-Mg-Ag alloy do not interfere with either the morphology of the S particles or the extent of the solubility of Ag in the S phase. The latter is consistent with the observation that Ag is not rejected during the growth of the S phase. Furthermore, given the presence of Ag within the S phase formed in both the artificially aged[17] as well as the present as-cast Al-Cu-Mg-Ag alloys, it is reasonable to propose likewise that the S-phase precipitates formed in the age-hardened microstructure of the Li-bearing Al-Cu-Mg-Ag alloys[20] will also have contained Ag.

The essence of the present results and interpretations is that the principal compositional features of the phase particles present in the as-cast alloy are preserved in the fine precipitates of the same phases when formed in the corresponding age-hardened microstructure. The present results, accordingly, demonstrate that a contributory step toward determining the locations of trace alloy additions within the phase precipitates of interest lies in the examination of the same phases when present in the as-cast microstructure of such alloys.

V. SUMMARY AND CONCLUSIONS

The influence of 0.5 wt pct of Ag on the nature of the Cu-rich phases of interest, i.e., $\theta(Al_2Cu)$, $S(Al_2CuMg)$, and $T_1(Al_2CuLi)$, present in appropriate as-cast Al-4 wt pct Cu, Al-4 wt pct Cu-0.5 wt pct Mg, and Al-5 wt pct Cu-1.2 wt pct Li-0.5 wt pct Mg alloys has been examined. The results demonstrate the following.

1. Independent or combined additions of Ag and Mg (0.5 wt pct each) to the binary Al-4 wt pct Cu alloy do not bring about any change in the composition of the binary θ-Al_2Cu phase. There exist, however, differences in the ways the θ phase is evolved in the constituent ternary alloys (i.e., Al-Cu-Mg and Al-Cu-Ag) and in the quaternary (i.e., Al-Cu-Mg-Ag) alloy.
2. A previously undocumented ternary Al-Cu-Mg–based phase is detected in the Al-4 wt pct Cu-0.5 wt pct Mg-0.5 wt pct Ag alloy. This phase is metastable in nature, in that only rapid rates of cooling cause the retention of this phase in the as-cast microstructure. The Cu content of this phase is similar to that of the θ phase, while the Mg content of this phase varies in the range of ~0.7 to about 2 wt pct. Both Ag and Mg are always located in relatively large amounts in the peripheral (implying particle/Al matrix boundary) regions of this phase. This phase is readily replaced by θ phase upon annealing at 450 °C.

It is proposed that, at the beginning, Ag and Mg atoms are integral parts of the solute atoms (/atom clusters) which form the Cu-rich θ and S phases. However, the insolubility of Ag and Mg in the θ phase causes these elements to be rejected during the growth of the θ phase, and this gives rise to the observation of an apparent segregation of Ag and Mg in the peripheral regions of such particles. Annealing at 450 °C quickened the process of the expulsion of Mg, still remaining in small amounts within the metastable phase, as well as the removal of the peripheral segregation of Ag and Mg atoms. The

result is the replacement of the metastable ternary phase by the binary θ phase.

3. Ag additions to the Al-4 wt pct Cu-0.5 wt pct Mg alloy modify the composition of the S (Al_2CuMg) phase by incorporating small amounts of Ag ($<$3 wt pct) into the phase. Segregation of excess amounts of Ag in the peripheral regions of the S-phase particles is not observed, implying that Ag is not rejected during the growth of the S phase and that Ag has solubility in the S phase.

4. The T_1 phase present in the as-cast Al-5 wt pct Cu-1.2 wt pct Li-0.5 wt pct Mg-0.5 wt pct Ag alloy does not contain either Ag or Mg. Both Ag and Mg are, however, always located in relatively large amounts in the peripheral regions of the T_1-phase particles. It is proposed that, at the beginning, Ag and Mg atoms are integral parts of the solute atoms (/atom clusters) which form the Cu-rich T_1 and S phases. However, the insolubility of Ag and Mg in the T_1 phase causes these elements to be rejected during the growth of the T_1 phase. The result is the observation of an apparent segregation of Ag and Mg in the peripheral regions of the T_1-phase particles.

5. Ag additions to the Li-bearing alloy modify the composition of the S phase in the same manner as in the Li-free alloy, $i.e.$, by incorporating small amounts of Ag ($<$3 wt pct) into the S phase. Ag is not found to segregate in excess amounts in the peripheral regions of the S-phase particles, implying that Ag is not rejected during the growth of the S phase and that Ag has solubility in the S phase.

The present results, when compared to the known compositional features of the Cu-rich phase precipitates formed in the age-hardened microstructure of Al-Cu-Mg(-Li)-Ag alloys, reveal that, in both cases ($i.e.$, as-cast and age hardened), the locations of Ag (and Mg) in the major Cu-rich phases of interest are similar. This implies that a prior examination of phases present in the as-cast microstructure is a contributory step toward determining the locations of trace alloy additions within the phase precipitates of interest.

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