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MICROSTRUCTURE AND PROPERTIES OF SPRAY DEPOSITED HIGH Li Al-Li-Mg-Ge-Zr ALLOYS

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Introduction

Al-Li alloys have been the subject of intense study for many years due to the pronounced effect of Li in reducing density and increasing elastic modulus of aluminum alloys (1). The addition of Li beyond that currently used in commercial Al-Li alloys, such as 8090 (Al-2.7Li-1.6Cu-1.3Mg), would result in an even lower density and higher modulus (2). Unfortunately, as the Li content is increased, the mechanical properties are degraded by the formation of a continuous network of the equilibrium δ (AlLi) phase at grain boundaries (3). Although the continuous network of the equilibrium phase may be eliminated by rapid solidification (RS) powder metallurgy (PM) processing, the presence of oxide stringers along prior powder particle boundaries significantly reduces the ductility and toughness of RS/PM Al-Li alloys (4). As a result, recent efforts are being devoted to using spray deposition to synthesize high Li aluminum alloys (5). Since the effective cooling rate during spray deposition typically falls in the range of $10^3 \sim 10^4$ K/s. Moreover, this approach avoids the drawbacks associated with prior droplet boundaries (6).

In the present investigation, spray deposition processing is utilized for the synthesis of high Li Al-Li alloys. An alloy system, Al-Li-Mg-Ge-Zr, is introduced in an effort to enhance our understanding of the behavior of high Li Al-Li alloys. The addition of Cu to Al-Li alloys promotes the formation of S' (Al₂CuMg) precipitates which are quite promising for the alleviation of deformation localization (7). Unfortunately, the formation of coarse intermetallics and the increase in density brought about by large additions of Cu to high Li Al-Li alloys present limitations (4). Hence the effect of small additions of Cu to the alloy was also investigated in the present work.

Experimental

A composition, Al-3.8Li-1.0Mg-0.4Ge-0.2Zr (in wt. %, designated herein as ALI-3) and a modified composition Al-3.8Li-1.0Mg-0.5Cu-0.4Ge-0.2Zr (in wt. %, designated as ALI-4) with 0.5% addition of Cu were selected for the present investigation. The alloys were each prepared using spray atomization and deposition. The starting alloy was superheated to 800°C in under Ar gas at atmospheric

pressure. The molten alloy was then transported through a ceramic delivery tube and subsequently atomized using Ar gas at dynamic atomization pressure of 1.24 MPa. Following atomization, the spray of droplets was collected using a water cooled, rotating Cu substrate, positioned at a distance of 460 mm from the atomizer. The selection of processing parameters was made based on results from numerical simulations described elsewhere (8).

The spray deposited alloys were then extruded and heat treated. For the extrusion experiments, the spray deposited alloys were machined into 25.4 mm diameter billets and the billets were extruded at 400°C to an extrusion ratio of 16:1. The extruded alloys were solution heat treated at 540°C for one hour, followed by water quenching. Aging experiments were conducted at 150°C and 170°C.

The microstructures of as-spray deposited and extruded alloys were characterized using optical microscopy, X-ray diffraction analysis and transmission electron microscopy (TEM). TEM studies were carried out on a PHILIPS CM20 TEM equipped with an energy dispersive spectrometer (EDS). The tensile properties of extruded and aged alloys were determined at ambient temperature according to ASTM standard E8-81 in an Instron tensile testing machine. Room temperature hardness tests were carried out using a Rockwell B scale with a load of 100 kg.

Results and Discussion

Microstructure

The optical micrographs presented in Fig. 1 exhibit the typical microstructures of as-spray deposited alloys ALI-3 and ALI-4, which were characterized by equiaxed grains with a grain size in the range of $10 \sim 30 \,\mu\text{m}$. Secondary phases, clearly visible in both alloys, are distributed both at grain interiors and within the grains boundaries. Compared with the microstructures of ingot cast high Li Al-Li alloys, the grain boundary phases were fine and generally discontinuous (9). X-ray diffraction revealed that the phases present were the equilibrium Al₄Li₉ and δ (AlLi) phases. The coarse and continuous networks of equilibrium phases formed in ingot cast Al-Li alloys with high Li contents have been shown previously to be particularly deleterious when present at grain boundaries (10).

Figure 2 (a) show the typical TEM microstructure of the extruded and aged alloy ALI-3. The major microstructural feature is the formation of a high volume fraction of δ' (Al₃Li), with a large proportion of composite precipitates in which the δ' phase surrounds the LI₂ β' (Al₃Zr) core. Although a small amount of the equilibrium δ phase is located within the grains, this type of homogeneous distribution



Figure 1. Optical micrographs of spray deposited alloys: (a) Al-3.8Li-1.0Mg-0.4Ge-0.2Zr(ALI-3); and (b) Al-3.8Li-1.0Mg-0.5Cu-0.4Ge-0.2Zr(ALI-4).



Figure 2. TEM micrographs of spray deposited and aged alloys: (a) ALI-3, aged at 170°C for 24 h,; (b) ALI-4, aged at 170°C for 90 h.

of δ phases benefits the toughness of the alloy through slip homogenization instead of degrading it (2). EDS analysis showed that the small additions of Ge formed insoluble particles with a size of approximately 10 µm in the microstructure. As a result of their size, these particles will not disperse the heavy strain localization associated with shearable δ' precipitates. In alloy ALI-4, which contains 0.5 wt. % Cu, there is precipitation of other phases in addition to the δ' , β' and δ phases. Figure 2 (b) shows the S' precipitates inside of a grain in the alloy which has been aged at 170°C for 90 hrs.

Aging Behavior

Figure 3 shows a summary of the hardness values for alloys ALI-3 and ALI-4 for an aging time of up to 300 hrs. The general responses to aging of both alloys were similar, i. e., a rapid increase in hardness at short aging times followed by marginal changes in hardness at long hours. As shown in Fig. 3, the peak aging condition for both alloys determined at 170°C was reached at 90 hrs. The 150°C aging response obtained for alloy ALI-3 revealed that peak aging conditions were not yet reached after 300 hours of aging. It is evident from the results that the hardness of the 0.5 wt. % Cu containing alloy (ALI-4) is greater than that of the non-copper containing alloy (ALI-3) when aging time is less than 20 hours, especially during early stages of aging.



Figure 3. Hardness versus aging time for alloy ALI-3 at 170°C and 150°C, and for alloy ALI-4 at 170°C.



Figure 4. TEM dark-field micrographs of δ' precipitates for underaged samples of alloys ALI-3 and ALI-4 at 170°C for various times: (a) ALI-3, 0.1 h, (b) ALI-4, 0.1 h; (c) ALI-3, 1.4 h, (d) ALI-4, 1.4 h; (e) ALI-3, 14 h, (f) ALI-4, 14 h.

TEM studies were conducted on samples of both alloys aged at 170°C for 0.1, 1.4, 14, 24, 90 and 300 hrs. The results showed that during the aging time from 0.1 to 14 hrs a high volume fraction of δ' phases formed and coarsened rapidly in alloy ALI-3, resulting in a rapid increase in hardness of the alloy (see Fig. 3 and 4). During further aging, the δ' particles gradually coarsened, while the hardness of the alloy increased slowly (see Fig. 2 and 3). There is also the development of precipitation free zones (PFZ's) along the grain boundaries as aging proceeds to the overaged condition. The alloy containing 0.5 wt. % Cu (ALI-4) exhibits similar precipitation of δ' phases, but the formation and coarsening of δ' phase occurs faster than in the non-copper containing alloy (ALI-3) during the aging time from 0.1 to 14 hrs (see Fig. 4). This observation is consistent with the aging response in which the hardness of alloy ALI-4 is greater than that of alloy ALI-3, when the aging time is less than 20 hrs (see Fig. 3). Detailed TEM analysis revealed that the formation and coarsening of the S' phase in alloy ALI-4 is sluggish and its volume fraction is quite small even in the overaged condition. In the underaged condition there is virtually no precipitation of the S' phase. These results suggest that the small additions of copper to alloy ALI-3 increased hardness during the early stages of aging through solid solution strengthening and by decreasing the solid solubility of Li in the matrix, which enhances δ' precipitation.

Alloy	Condition	σ _{ys} (MPa)	ours (MPa)	El. (%)
ALI-3	170°C, 2 hrs	378	510	4.7
	170°C, 24 hrs	477	578	3.4
	170°C, 90 hrs	513	573	3,7
ALI-4	170°C. 2 hrs	426	548	4.2
	170°C, 24 hrs	485	601	4.0
	170°C, 90 hrs	523	617	3.7
ALI-3	150°C, 2 hrs	325	482	5.9
	150°C, 24 hrs	385	515	4.5
ALI-4	150°C, 2 hrs	354	492	6.0
	150°C, 24 hrs	422	539	3.4

 TABLE 1

 Room Temperature Tensile Properties of Extruded and Aged Al-Li Alloys

Mechanical Properties

The room temperature tensile properties of the extruded and aged alloys ALI-3 and ALI-4 are listed in Table 1. According to the aging curves shown in Fig. 3, 2 hrs and 24 hrs aging at 150°C represent under aged conditions, whereas 2 hrs, 24 hrs and 90 hrs at 170°C represent the under-, near-peak and peak-aging conditions, respectively. One of the interesting observations is that the yield strengths and ductilities of alloys ALI-3 and ALI-4 are comparable in the near-peak aged and peak aged conditions. This observation suggests that the effect of 0.5% addition of copper on the yield strength is minimal in the near-peak aged and peak aged conditions, which agrees with the microstructural observation that there was virtually no precipitation of the S' phases in the underaged specimens.

Another interesting observation is that 0.5 wt. % addition of Cu to alloy ALI-3 led to a $30 \sim 48$ MPa improvement in yield strength in the early stages of aging, but this improvement is not accompanied by an improvement in ductility. This behavior is consistent with the aging response, in which the small additions of Cu to alloy ALI-3 increased the hardness of the alloy and promoted δ' precipitation through solid solution strengthening and by decreasing the solid solubility of Li in the matrix.

Although the yield strengths of alloys ALI-3 and ALI-4 are comparable in the near-peak aged and peak aged conditions, there were differences of 23 and 44 MPa in their ultimate tensile strengths, respectively. These results suggest that the extent of work hardening of the alloy containing 0.5 wt. % Cu (ALI-4) is higher than that of the non-copper containing alloy (ALI-3). The high work hardening characteristics of alloy ALI-4 are primarily attributed to the solid-solution-strengthening effect of copper in the alloy.

Conclusions

- (1) Spray deposited high Li Al-3.8Li-1.0Mg-0.4Ge-0.2Zr alloy exhibited a fine equiaxed microstructure with fine secondary phases Al₄Li₉ and δ (AlLi) distributed both within grains and at grain boundaries. After extrusion and aging, the alloy exhibited a small amount of δ phase within the grains and a high volume fraction of δ' precipitates, some of which were noted to contain β' cores.
- (2) The aging response of the alloy exhibited a rapid increase in hardness at short aging times, followed by marginal changes in hardness at long hours. The addition of 0.5 wt. % Cu to the alloy enhanced the precipitation of δ' , therefore increasing the hardness and leading to a 30 ~ 48 MPa improvement in yield strength during the early stages of aging. By the small addition of Cu, an improvement of 44 MPa in ultimate tensile strength was achieved in the peak aged condition.

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