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Abstract

Small amounts (~0.1 at.%) of Ag are known to stimulate nucleation of the metastable phase Ω during artificial ageing of the conventionally quenched Al-4Cu-0.3Mg (wt.%) alloy. Because of its close similarities to Ag in atomic size, valency and crystal structure, it might be expected that Au would also modify precipitation in this alloy. Since Au has a very low solubility in Al, rapid solidification technique was used to increase its solid solubility. It has been revealed that Au interacts preferentially with Al to form precipitates of an intermediate Al₂Au phase after rapid solidification, rather than promoting nucleation of the Ω phase.

1. Introduction

Ageing processes in conventional cast and wrought Al-Cu-Mg alloys may be changed by microalloying additions of small amounts (0.1 at.%) of Ag [e.g.,1,2]. Depending upon the Cu:Mg ratio, three new metastable precipitates have been reported, all of which stimulate greater response to age hardening [3]. Special attention has been paid to alloys with high Cu:Mg ratios in which Ag promotes formation of a metastable precipitate Ω , the characteristics of which are now well known [e.g., 4-6]. Atom probe studies of these Al-Cu-Mg-Ag alloys [7-9] have shown that rapid co-clustering of Mg and Ag atoms occurs immediately after quenching and ageing at elevated temperatures. There is also evidence that vacancies are bound to these clusters [7]. Cu atoms then diffuse to the Mg-Ag clusters leading to the nucleation and growth of Ω which precipitates as a fine dispersion of thin plates that form on the $\{111\}_{\alpha}$ planes [8,9]. The density of Ω plates that precipitate in the presence of Ag is much greater than that occurs in ternary Al-Cu-Mg alloys in which Ω only occurs in isolated regions, and at relatively high ageing temperatures [10].

Au has characteristics very similar to Ag; it has the same atomic diameter (0.2884 nm compared with 0.2889 nm for Ag), valency and each has a fcc crystal structure [11]. Furthermore, a comparison of the binary Mg-Au and Mg-Ag phase diagrams shows that the compound MgAu melts at 1150°C, whereas MgAg melts at the lower temperature of 820°C [12]. This indicates that Mg and Au may interact more strongly than Mg and Ag. Thus, there is reason to believe that Au has the potential to act like Ag in modifying ageing processes in Al-Cu-Mg alloys by stimulating nucleation of the Ω phase.

There are, however, three significant differences between Au and Ag that may influence their interactions with the elements present in an Al-Cu-Mg alloy. One is that Au is known to be strongly attracted to Cu [13], whereas Ag and Cu have very little mutual solid solubility below 250°C [14]. The second difference is that the Au-vacancy binding energy in Al is estimated as 0.38eV which is significantly greater than the Ag-vacancy binding energy (0.14eV) [15]. The other difference is that the solid solubility of Au in Al is very low, being a maximum of only 0.35 wt.% (0.048 at.%) at 640°C [16,17]. In this regard, rapid solidification does offer the opportunity to increase solid solubility, and Toda and Maddin [18] have reported that the solubility of Au in Al may be extended to 2.5wt.% (0.35at.%). The present work has involved the use of melt-spinning to prepare rapidly solidified thin foils of the alloy Al-4Cu-0.3Mg (wt.%) with and without additions of Ag or Au, so as to compare the effects of these two microalloying elements.

2. Experimental Procedures

Small ingots of three alloys with nominal compositions of Al-4Cu-0.3Mg, Al-4Cu-0.3Mg-0.4Ag and Al-4Cu-0.3Mg-0.7Au (wt.%) were cast in an induction furnace and used to prepare thin ribbons by melt spinning in an argon atmosphere on a Cu wheel rotating at a speed of 6000 rpm. These rapidly solidified ribbons were examined in the as-quenched and the aged (200°C/30 min.) conditions, using a CM20 analytical transmission electron microscope (TEM) operating at 200kV. Specimens suitable for TEM were prepared by thinning the ribbons electrolytically in a mixture of nitric acid and methanol (1:2 by volume), using a window technique at -30°C.

3. Results and Discussion

3.1 Al-4Cu-0.3Mg :

Figure 1 shows a bright field electron micrograph and selected area electron diffraction (SAED) pattern from a rapidly solidified foil of the ternary alloy Al-4Cu-0.3Mg. The dominant feature of the microstructure is the presence of quenched-in defects, notably, dislocation loops that form through the collapse of discs of vacant lattice sites [19].

No precipitates are evident although a weak streaking in the SAED that passes through the matrix reflections is characteristic of the presence of GP zones. The occurrence of these zones may be attributed to rapid diffusion of solute atoms, which is facilitated by the high supersaturation of vacancies that would also result from rapid solidification. Another possibility is that the foil ribbon may have separated from the copper wheel during melt spinning which would reduce the rate of cooling and lead to premature nucleation of these zones. The large circled particle (arrowed), which is one of several present in all foils observed in the present investigation, may be due to the compound Al_4C , or carbon particles picked up from the graphite crucible used for melt-spinning. For the purposes of the present investigation, these large particles have been ignored.



Figure 1: As rapidly solidified ternary alloy showing dislocation loops and faint evidence for GP zones in the SAED pattern with beam direction along $<100>_{\alpha}$.



Figure 2: Bright field micrograph near $<110>_{\alpha}$ showing precipitation of the Ω phase after ageing the ternary alloy at 200°C for 30 min.

Figure 2 shows a bright field transmission electron micrograph of the ternary alloy aged for 30 min. at 200°C. This reveals the presence of a uniform dispersion of fine precipitates on the {111}_{α} planes which are confirmed by the SAED pattern to be the Ω phase. No evidence was found for the presence of other possible precipitates θ ", θ ' or S (S'). Faint streaking in the SAED pattern is attributed to the fact that the Ω plates are so thin. The presence of relatively high number density of Ω plates is in contrast with that observed in the conventionally processed ternary Al-4Cu-0.3Mg alloy aged at 200°C in which only occasional plates of the Ω phase have been reported [20]. The high supersaturation of vacancies attained by rapid quenching is helpful in enhancing rate of clustering of Mg atoms. In addition, minimisation of elastic strain energy [21] associated with segregation of Mg atoms on the {111}_{α} planes promotes clustering of Mg atoms. It is suggested that Mg atoms easily segregate to {111}_{α} planes following rapid solidification and such a process may favour nucleation of the Ω phase which then grows on {111}_{α} planes.

3.2 Al-4Cu-0.3Mg-0.4Ag

Figure 3 shows a bright field electron micrograph from the Ag containing alloy in the rapidly solidified condition. The micrograph contains several dislocation lines together with some much finer defects. No recognisable dislocation loops were observed which suggests that vacancies have been retained in the supersaturated solid solution. The SAED pattern does not reveal of the presence of any precipitates. Ageing for 30 min. at 200°C again resulted in precipitation of a uniform dispersion of the Ω phase, although comparisons of Figures 2 & 4 shows that the Ω phase is larger in Figure 4 suggesting that growth has been accelerated in the presence of Ag.



Figure 3: As rapidly solidified Ag-containing alloy showing no evidence of dislocation loops or precipitation. $B=<110>_{\alpha}$.



Figure 4: Ag-containing alloy after ageing for 30min. at 200°C showing the presence of the Ω phase. **B**=<110>_{α}.

3.3 Al-4Cu-0.3Mg-0.7Au.



Figure 5: As rapidly solidified Au-containing alloy showing no evidence of dislocation loops. Precipitate reflections in the SAED pattern is indicated by an arrow. $B=<100>_{\alpha}$.

Figure 6: As rapidly solidified Au-containing alloy showing precipitate reflections that are attributed to ordered Al₂Au phase (η '). B=<112>_{α}.

Figure 5 shows a bright field electron micrograph taken from the rapidly quenched Aucontaining alloy. Dislocation lines are visible and dislocation loops are again absent which is similar to the Ag-containing alloy. However, in contrast to the other two alloys, the rapidly quenched Au-containing alloy shows the presence of fine precipitates. The SAED pattern shows {110}_{α} reflections (marked by an arrow). These reflections with mixed indices are absent when the SAED pattern is taken from the α -AI matrix (e.g., inset Figure 1). These extra reflections are indicative of the presence of a precipitate phase. Although these reflections are to be expected in the presence of the well known θ' phase, the observed microstructural features of fine precipitates are different.

In order to characterise the precipitate phase shown in Figure 5 in more detail, the electron beam direction was changed to $<112>_{\alpha}$. Figure 6 shows the corresponding bright field electron micrograph and the diffraction pattern. The SAED pattern consists of many precipitate reflections that can be indexed as arising from an intermediate phase with a composition Al₂Au, known as η' (crystal strycture tetragonal) [16]. Only the $<110>_{\alpha}$ reflections would have been present if the precipitates were to be the equilibrium cubic Al₂Au phase, known as η (crystal structure C1). Thus, unlike Ag, that is known to associate itself with Mg, Au seems to associate preferentially with Al. Moreover since the Auvacancy interaction is stronger than Ag-vacancy interactions, free vacancies may not be readily available to facilitate possible Au-Mg interactions.



Figure 7: Au-containing alloy showing no evidence of η' phase or Ω phase after heat treating at 200°C for 30 min. B=<112>_{α}.

Figure 7 shows a bright field electron micrograph from Au-containg alloy aged for 30 min. at 200°C. The electron beam direction is kept again close to $<112>_{\alpha}$ so that a direct comparison can be made with the as-quenched rapidly solidified microstructure. The micrograph shows few dislocation lines, but the fine precipitates observed after rapid solidification are absent. The SAED pattern does not exhibit precipitate reflections attributed to η' or to η . Thus, the η' particles must have dissolved on ageing at 200°C. Further, there is no evidence of the Ω phase. However, the microstructure does contain precipitate-like features that are yet to be characterised. The absence of precipitate reflections indicates that precipitates, if any, are sparse and that may not have been diffracting strongly.

4. Conclusions

- Rapid solidification results in excess quenched-in vacancies which have promoted nucleation of a uniform dispersion of the Ω phase in the ternary alloy AI-4Cu-0.3Mg aged for 30 min. at 200°C. This phase is only sparsely dispersed following a conventional quenching treatment.
- 2. The formation of Ω phase in Ag-containing alloy, that is conventionally quenched and aged, is not modified by rapid solidification processing and ageing.
- 3. During rapid solidification, Au atoms appear to interact preferentially with AI resulting in intermediate precipitation of the tetragonal Al_2Au (η ') phase.
- 4. Ageing the Au-containing alloy at 200°C leads to dissolution of Al₂Au.
- 5. Unlike Ag, Au does not stimulate nucleation of the Ω phase after ageing at 200°C for 30 min. This is attributed to strong Au-vacancy interaction that would have prevented Mg atoms segregating onto {111}_a planes, leading to nucleation of this phase as has occurred in the other two alloys.

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