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#### Abstract

The role of quenched-in vacancies on the tin-assisted nucleation of the  $\theta'$  phase in the Al-1.7at.%Cu-0.01at.%Sn alloy was investigated by naturally ageing the alloy for different times before artificial ageing at 200°C. The introduction of the natural ageing stage was found to cause a small negative effect on the magnitude of the peak hardness for 200°C artificial ageing. The presence of a narrow (60-100 nm) precipitate-free zone (PFZ) around grain boundaries, compared with the large (>800 nm) PFZ typical of the binary Al-1.7at.%Cu alloy, confirms the long-held belief that tin atoms trap quenched-in vacancies. A similarly narrow, but slightly smaller PFZ (40-80 nm) is characteristic of the binary Al-0.01at.%Sn alloy. It is suggested that Sn controls the diffusion of Cu atoms through a relatively strong interaction between solute atoms of Sn and Cu.

#### 1. Introduction

The  $\theta'$  phase in Al-Cu-based alloys is known to nucleate with difficulty in the absence of lattice defects such as dislocations or clusters of microalloving elements [1]. Tin is one of the microalloying elements that are most effective at facilitating the nucleation of  $\theta'$  [2]. At 200°C in Al-1.7at.%Cu, one hundredth of an atomic percent of tin is sufficient to cause a 30% increase in peak hardness and reduce by one order of magnitude the ageing time necessary to reach that point [2]. To date there are still a number of different, conflicting explanations for the effectiveness of tin in nucleating  $\theta'$ , such as a decrease in interfacial energy [3-6], the accommodation of the volumetric component [7], or the shear component [8] of the misfit strain energy, and tin's vacancy-controlled, fast diffusivity in aluminium, causing tin to precipitate first and serve as heterogeneous nucleation sites for  $\theta'$  [5]. In one model [8] the presence of vacancy clusters is also crucial to the nucleation mechanism. A more recent study [9] strongly suggested that tin and copper atoms interact at the very early stages of the solid solution decomposition, in fact before tin can precipitate into its preferred crystallographic form. However, the key role of vacancies before and during nucleation of  $\theta$ ' remains unclear. Are vacancies simply there to accelerate the clustering of diffusing tin and copper solute atoms, or/and do they also participate to the nucleation mechanism, as has been shown to be the case in the AI-Si alloy system [10] and as suggested by one model [8].

These questions have motivated the present investigation, which attempted to modify the concentration of quenched-in vacancies through the use of appropriate heat treatments, and observe the resulting hardening response and microstructure. The ternary Al-1.7Cu-0.01Sn (all compositions are in atomic percents unless stated otherwise) and the binary Al-0.01Sn and Al-1.7Cu alloys were examined. The alloys were subjected to natural ageing prior to the usual artificial ageing process. The micro-hardness was measured, and transmission electron microscopy performed for some of the ageing conditions.

# 2. Experimental Procedures

The three alloys, Al-4wt%Cu-0.05wt%Sn (Al-1.7Cu-0.01Sn), Al-4wt%Cu (Al-1.7Cu) and Al-0.05wt%Sn (Al-0.01Sn) were melted from high purity elements and cast into chilled iron moulds. The ingots were cut into disks 3 mm in diameter and 0.2-0.5 mm thick. The disks were solution treated for 30 minutes at 525°C in a salt bath, cold-water quenched, aged at room temperature (natural ageing, NA) for 0, 24 and 72 h, then aged at 200°C (artificial ageing, AA) in an oil bath for times ranging between 1 min and 24 h.

TEM samples were electro-polished in a nitric acid-methanol solution. The different ageing regimes subjected to the three alloys are summarised in Table 1. The hardness tests were conducted on a micro-hardness tester, using applied loads of 100 or 300 g. TEM was carried out on a Philips CM20 instrument and a JEOL 2011 instrument, both operated at 200 kV.

Alloy	NA time	AA time at 200°C
Al-1.7Cu	0	0 - 82 h
	72 h	0 - 24 h
Al-1.7Cu-0.01Sn	0	0 - 300 min
	24 h	0 - 300 min
	72 h	0 - 120 min
AI-0.01Sn	0	3 min, 3 h
	72 h	3 min, 3 h

Table 1: Ageing regimes applied to the Al-1.7Cu-0.01Sn, Al-1.7Cu and Al-0.01Sn alloys.

#### 3. Results

Figure 1 shows the evolution of alloy hardness as a function of ageing time at 200°C for a binary alloy Al-1.7Cu (Figure 1(a)) and a ternary alloy Al-1.7Cu-0.01Sn (Figure 1(b)) having undergone an intermediate step of natural ageing (22±2°C). The hardness curves show that the natural age hardening response (i.e. hardness before the start of artificial ageing) increases with natural ageing time for both the ternary and the binary alloys. However, the tin-containing alloy responds much less to natural ageing than Al-1.7Cu. Additionally, the peak hardness of Al-1.7Cu-0.01Sn exhibits a small decrease as a result of natural ageing. In contrast, the introduction of a natural ageing step in the ageing treatment of Al-1.7Cu results in a small increase in the peak hardness. No change in the kinetics of ageing is apparent for either the binary or the ternary alloy.



Figure 1: Hardness curves for (a) Al-1.7Cu and (b) Al-1.7Cu-0.01Sn with or without natural ageing (NA) preceding artificial ageing at 200°C.

When examining naturally-aged Al-1.7Cu-0.01Sn alloys by TEM, narrow precipitate-free zones (PFZ) were found surrounding virtually all grain boundaries. One such example, approximately 80 nm in width, is presented in Figure 2(a). Variations were observed in the PFZ width in samples of identical ageing condition; an increase in natural ageing time also produced a slight increase in the average PFZ width. The average PFZ width was measured to be 80±20 nm for 72 h NA. It is likely that the variation in measured PFZ width arises from different grain boundary structures. A comparison with PFZ in the binary alloy Al-0.01Sn (see for example Figure 2(b)) indicates an average PFZ width that is only slightly, but measurably smaller (60±20 nm). Since only about ten grain boundaries were examined, better statistics is required for confirmation of this difference. These values are much smaller than that typically observed in Al-1.7Cu (see Figure 2(c)), which is of the order of 1  $\mu$ m in the alloy subjected to 72 h NA, and 500 nm in the absence of NA [12]. It should also be noted that natural ageing causes a significant refinement in the distribution of  $\theta'$  in Al-1.7Cu, whereas little change is apparent in the naturally aged tin-containing alloys.

Figure 3 shows grain boundary precipitates in tin-free and tin-containing Al-1.7Cu alloys subjected to identical ageing conditions (72 h NA + 1 h AA). In both cases the larger particles were determined to be Cu-rich by EDX, and are hence likely to be the equilibrium phase  $\theta$  (Al<sub>2</sub>Cu), but could also be the intermediate phase  $\theta'$  [12]. Some tin precipitates were also commonly found in Al-1.7Cu-0.01Sn (see black arrow in Figure 3(b)). Although the grain boundary particle distribution is much coarser in the ternary alloy (Figure 3(b)) than in AI-1.7Cu (Figure 3(a)), there is no clear evidence to suggest that a lower amount of solute atoms are involved in the former case. Little observable difference was also found in the degree of grain boundary precipitation with or without natural ageing in the ternary alloy, as shown in Figure 4. The same observation was made concerning the precipitates nucleating within the grain. Ternary alloys subjected to natural ageing before 3 min AA at 200°C exhibited the same combination of  $\theta'$  and tin particle as reported in [11]. Figure 4(c) shows one such group, with the tin precipitate clearly in the new orientation relationship with respect to the aluminium matrix [9,11]. Finally, it is worth noting that in all cases, tin particles were frequently observed in association with the Cu-rich precipitates found at grain boundaries.



Figure 2: TEM micrographs of typical precipitate-free zones (PFZ) around grain boundaries in (a) Al-1.7Cu-0.01Sn, (b) Al-0.01Sn and (c) Al-1.7Cu alloys, in the 72 h NA + 1 h, 3 h and 7 h AA conditions, respectively.



Figure 3: TEM micrographs showing grain boundary precipitates in (a) Al-1.7Cu and (b) Al-1.7Cu-0.01Sn following 72 h NA + 1h AA. The particle distribution is much coarser in the ternary alloy. The precipitates are the Cu-rich  $\theta$  or  $\theta'$  phase in both cases; in the tin-containing alloy small tin particles are also present (black arrow in (b)).



Figure 4: TEM micrographs showing grain boundary precipitates in Al-1.7Cu-0.01Sn (a) without or (b) with a natural ageing step of 72h preceding artificial ageing at 200°C for 3 min. No clear increase in grain boundary precipitation is visible. In both cases tin particles (white arrow) are present at the grain boundary; they are frequently associated with the Cu-rich precipitates. (c) shows a lattice image of one of the typical  $\theta'$ -Sn groups observed in the naturally aged alloy.

#### 4. Discussion

From the typical width of the precipitate-free zones observed around grain boundaries in the three alloys investigated, it is clear that the precipitation of the  $\theta'$  phase is controlled, kinetically at least, by that of the tin phase (which may or may not be the  $\beta$ -Sn phase [11]). This is also apparent from the fact that, for identical heat treatment, with or without natural ageing [11] the precipitate number density is the same in the ternary and binary alloy Al-0.01Sn. The narrowness of the PFZ in the tin-containing alloys [13] is strongly indicative of the trapping effect that tin atoms have on vacancies, in contrast to the case of the binary Al-1.7Cu alloy, in which the wide PFZ reflects a significant loss of guenched-in vacancies to the grain boundaries. It is still not clear what effect this has on the diffusion of Cu. The most common view [2,14] is that the strong interaction between tin and vacancies causes a lowering of the diffusion rate of Cu atoms, which would explain the large reduction in the natural ageing response observed in the ternary alloy compared with Al-1.7Cu. However, some of the observations presented here and elsewhere [11] suggest an alternative interpretation. Specifically, the slightly wider PFZ measured in Al-1.7Cu-0.01Sn compared with AI-0.01Sn, the little impeded diffusion of Cu atoms to grain boundaries, and the absence of individual precipitates of  $\theta$ ' and  $\beta$ -Sn, with or without natural ageing, are

suggestive of a strong interaction between Sn and Cu atoms, which may or may not be mediated by vacancies. The existence of a strong Sn-Cu interaction is not implausible on the basis that many Sn-Cu intermetallic phases exist, and that the smaller atomic size of Cu relative to aluminium may accommodate, partly at least, the compressive strain in the aluminium matrix around the large Sn atom.

## 5. Summary and Conclusion

- Precipitate-free zones observed around grain boundaries in the ternary Al-1.7Cu-0.01Sn alloy, naturally aged and then aged at 200°C, are much narrower than those typical of Al-1.7Cu, but are slightly larger than in Al-0.01Sn. The natural ageing step causes a significant increase in the PFZ size of Al-1.7Cu, but not in the tin-containing alloys.
- The introduction of a natural ageing stage up to 72 h long before artificial ageing at 200°C has little effect on the peak hardness of an Al-1.7Cu alloy, with or without 0.01 at.% Sn.
- The above observations, and the fact that all alloys exhibit approximately the same degree of solute diffusion to the grain boundaries, imply that tin strongly reduces the diffusion rate of vacancies to grain boundaries and other potential vacancy sinks. They also suggest the presence of diffusing Cu-Sn groups.

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