Effects of Microalloying Tin and Combined Addition of Silver and Tin on the Formation of Precipitate Free Zones and Mechanical Properties in Al-Zn-Mg Alloys*

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The additions of microalloying tin and (silver and tin)-combination were performed to modify the precipitate microstructure in the vicinity of grain boundaries with precipitate free zones (PFZs) and mechanical properties in Al-Zn-Mg alloys. In the Sn-containing alloy, TEM observation showed that some precipitates were sparsely formed within the region of PFZs of the Al-Zn-Mg ternary alloy. The quantitative analysis of the chemical compositions in precipitates showed that tin mainly contributes to nucleation in the vicinity of grain boundaries through the suppression of the vacancy depletion. This is well explained by the favorable interaction of tin with vacancies. The (Ag+Sn)-containing alloy formed a very narrow PFZ width and corresponding tensile properties were remarkably improved, which shows that tin enables to reduce the amount of microalloyed silver in Al-Zn-Mg alloys. [doi:10.2320/matertrans.L-MZ201123]

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1. Introduction

In aluminum alloys, precipitation strengthening is one of the most important techniques to increase mechanical strength. However, the precipitation morphology in the vicinity of grain boundaries is greatly different from that in grain interiors; i.e. precipitate free zones (PFZs) and grain boundary precipitates are formed around grain boundaries. Especially, it is characteristic of the Al-Zn-Mg alloy that the width of PFZs is larger than that of other age-hardenable alloys. Research into the characterization of PFZs is essential because they are believed to affect greatly the mechanical properties of these alloys.1–6 Our work has also revealed that presence of PFZ adversely affects the fracture properties of the alloys by correlating mechanical properties to microstructural parameters.7–9

It is known that small additions of various alloying elements (microalloying element) often change the morphology, spatial distribution and size of precipitates.10–17 As for the change of precipitation morphology in the vicinity of grain boundaries, silver dramatically reduces the width of PFZs compared with that in Al-Zn-Mg ternary alloys under the same aging conditions,18–23 because silver increases the density of nucleation sites in the vicinity of grain boundaries, which is quite effective to improve mechanical properties.7–9 However, the Ag-containing alloy is not suitable for industrialization from the viewpoint of costs. For industrialization, it is necessary to find the low-priced microalloying elements, having the same effects as silver. Our recent work has clearly shown that nanoscale clusters (i.e. nanoclusters) are formed within PFZs in the Al-Zn-Mg ternary alloy using three-dimensional atom probe (3DAP).24 The presence of nanoclusters implies the possibility of precipitation in the vicinity of grain boundaries through accelerating nucleation and growth in the alloy by microalloying elements.

In general, tin has been considered to have attractive interaction with vacancies in the aluminum matrix,25 and is expected to change the precipitate morphology, especially in the vacancy depletion region such as PFZs.26,27 However, no results have been reported on the investigation of precipitate morphology with PFZs in the Al-Zn-Mg alloy containing tin. Moreover, the evaluation of the precipitation phenomenon under the combination of silver and tin has not been reported, and the microstructural changes with PFZs are expected to improve mechanical properties. In the present work, therefore, the effects of microalloying tin and (silver and tin)-combined addition on PFZ formation of the Al-Zn-Mg alloy have been investigated using micro-Vickers hardness, transmission electron microscopy (TEM), 3DAP and tensile test.

2. Experimental Procedure

The chemical compositions of the alloys are listed in Table 1. For simplicity, an Al-2%Zn-2%Mg alloy (in mol%) containing 0.01% tin and (0.04% silver and 0.01% tin)-combined are designated as the Sn-containing alloy and the (Ag+Sn)-containing alloy, respectively. The ingots were homogenized at 743 K for 172.8 ks, then hot- and cold-rolled to sheets. The specimens were solid solution-treated at 743 K for 3.6 ks in a salt bath, and then quenched into iced-water and kept for 60 s. Aging treatments were carried out in silicon oil baths at 433 K. Micro-Vickers hardness was measured with a load of 500 g for 15 s. Precipitate microstructures were observed using a JEM3010 microscope with an EDX system at an accelerating voltage of 300 kV. 3DAP analysis was performed using an Imago Scientific Instruments (Madison,
WI) 3DAP with a delay-line detector at a specimen temperature of 25 K in ultra-high vacuum (background pressure of <10^{-8} Pa), using voltage pulses at a pulse fraction of 15\%. Tensile testing was carried out using an Instron-type tensile testing machine with a cross-head speed of 0.017 mm/s at RT.

3. Results

3.1 Micro-Vickers hardness change and 3DAP analysis

The isothermal aging curves of hardness for the Sn-containing and (Ag+Sn)-containing alloys aged at 433 K are shown in Fig. 1. For comparison, aging curves for the Al-Zn-Mg ternary and Ag-containing alloys are also plotted.23) In the as-quenched condition, hardness values of all alloys are almost identical. The maximum hardness of the Sn-containing and (Ag+Sn)-containing alloys are little bit lower and higher than that of the Al-Zn-Mg ternary alloy, respectively, however, the aging curves of these alloys are not dramatically changed compared with that of the Ag-containing alloy.

To characterize quantitatively the clustering formed in the initial stage of aging, 3DAP analysis was applied to the Sn-containing and (Ag+Sn)-containing alloys. Figures 2 and 3 show 3DAP maps of the Sn-containing and the (Ag+Sn)-containing alloys aged at 0.6 ks. Aluminum atoms are not shown in order to illustrate the distributions of solute atoms more clearly. Some clusters were observed and the chemical concentrations of each cluster were quantified in Table 2. The ratio of Zn/Mg ratio is below 2 (which is the value of the stable phase \(\gamma_1 (MgZn_2)\)), as has been observed in previous reports.7,22) In the Sn-containing alloy, tin was little incorporated within a cluster, whereas a certain amount of tin and silver is recognized in the (Ag+Sn)-containing alloy.

Fig. 1 Isothermal aging curves of Al-Zn-Mg alloys containing various additional elements during aging at 433 K.

3.2 TEM microstructure and EDX analysis in the vicinity of grain boundaries with PFZs

The microstructural changes around grain boundaries are shown in Fig. 4 for the Sn-containing alloy (Fig. 4(a)–(c)) and the Al-Zn-Mg ternary alloy (Fig. 4(d))23) aged at 433 K. The precipitates in grain interiors were identified to be \(\gamma_1\) in the under aging, \(\eta^\prime\) and/or \(\eta\) in the peak aging and \(\eta\) in the...
over aging conditions from the diffraction patterns regardless of the addition of tin. Large width of PFZs was observed when aged for 10.8 ks (Fig. 4(a)), similar to the Al-Zn-Mg ternary alloy. However, while no precipitates were observed within PFZs during aging in the Al-Zn-Mg alloy (Fig. 4(d)), it should be noted that some precipitates were sparsely observed within PFZs during aging in the Sn-containing alloy (Fig. 4(b)). These precipitates were gradually coarsened with aging time (Fig. 4(c)).

The chemical compositions of the precipitates formed within PFZs were quantified by the EDX analysis, since it is quite difficult to measure accurately solute distributions within the very small scale of the vicinity of grain boundaries using the conventional 3DAP analysis. Figure 5 shows Cliff-Lorimer plots showing relative ratios of solute concentrations within precipitates in the vicinity of a grain boundary in the Sn-containing alloy aged for 43.2 ks and 259.2 ks. The slope of the line of the tin concentration is confirmed as negative, showing the indication that there is a certain amount of tin in the precipitate. The relative ratio of the precipitates is (a) Zn: 49.7, Mg: 49.2, Sn: 0.4 (η') and (b) Zn: 63.2, Mg: 36.6, Sn: 0.1 (η), indicating that tin is certainly incorporated in the precipitate in the vicinity of grain boundaries, on the contrary to the precipitation in grain interiors (Table 2).

Figure 6 shows microstructural changes around grain boundaries for the (Ag+Sn)-containing, low Ag-containing alloy and Ag-containing alloy aged at 433 K for 10.8 ks. Al-2Zn-2Mg-0.04Ag alloy (in mol%), which is containing the same amount of silver as the (Ag+Sn)-containing alloy, was prepared in the comparison with the (Ag+Sn)-containing alloy. For simplicity, this alloy is designated as the low Ag-containing alloy. The narrower PFZ (<50 nm) was observed at an under-aging condition in the (Ag+Sn)-containing alloy (Fig. 6(a)), whereas it is clear that precipitates were sparsely observed in the vicinity of a grain boundary in the low Ag-containing alloy (Fig. 6(b)). It should be noted that, although the total amount of microalloying element in the (Ag+Sn)-containing alloy (0.05 mol%) is smaller than that in the Ag-

![Fig. 4 TEM images around grain boundaries in the (a)-(c) Sn-containing and (d) Al-Zn-Mg ternary alloys aged at 433 K for (a) 10.8 ks, (b) 86.4 ks and (c) and (d) 259.2 ks.](image1)

![Fig. 5 Cliff-Lorimer plots showing relative ratios of solute concentrations within precipitates in the vicinity of grain boundaries in the Sn-containing alloy aged at 443 K for (a) 43.2 ks and (b) 259.2 ks.](image2)
containing alloy (0.07 mol%), the precipitate morphology is similar to that of the Ag-containing alloy (Fig. 6(c)).

3.3 Tensile properties

The relationship between 0.2% proof stress and elongation to fracture is shown in Fig. 7 for the investigated alloys aged at 433 K. Tensile properties of the Al-Zn-Mg ternary and Ag-containing alloys are also plotted. Each line starting from A.Q. (as-quenched) corresponds to the sequence of the aging time. In the investigated alloys aged at 433 K, the plots of the Sn-containing alloy lie near that of the Al-Zn-Mg ternary alloy, that is, the proof stress is increased and the elongation is decreased with aging time, followed by the simultaneous decreases in the proof stress and elongation in the over-aging condition. On the other hand, the plots of the (Ag+Sn)-containing alloy are located in the upper right direction compared with those of these two alloys, and near those of the Ag-containing alloy. If compared under the same level of proof stress, therefore, the elongation of the (Ag+Sn)-added alloy is about one and a half times as large as that of the Al-Zn-Mg ternary and Sn-containing alloys. This strongly supports that the (Ag+Sn) addition is quite effective to improve both the proof stress and elongation of Al-Zn-Mg alloys.

4. Discussion

4.1 Effects of tin addition

From the results of hardness measurement and 3DAP analysis, tin is considered to be less effective to accelerate the precipitation in grain interiors of Al-Zn-Mg alloys. However, TEM observation and EDX analysis results clearly showed that some precipitates containing tin were sparsely observed within PFZs and gradually coarsened with aging time, whereas no precipitates were observed within PFZs during aging in the Al-Zn-Mg alloy (Fig. 4). This greatly suggests that tin assists the nucleation in the vicinity of grain boundaries, regardless of less effectiveness of age-hardenability in grain interiors. In the Al-Zn-Mg ternary alloy, nanoscale clusters exist within PFZs and their growth stops because vacancies are released to grain boundaries. In the Ag-containing alloy, on the other hand, Ag atoms preferentially trap vacancies and solute atoms migrating to grain boundaries and form finely precipitates. In the present work, therefore, the remarkable change observed in the vicinity of grain boundaries resulting from tin addition indicates that tin traps vacancies migrating to grain boundaries and then forms precipitates. This is well interrupted by the interaction energy of atom and vacancies by a first-principles calculation based on a full-potential KKR-Green’s function method, i.e. tin possesses greatly attractive
interaction with vacancies (−0.305 eV). Therefore, the role of tin in the vicinity of grain boundaries is considered as follows. Although tin has less acceleration of precipitation in grain interiors, tin traps the vacancies migrating to grain boundaries and suppresses the vacancy depletion in the vicinity of grain boundaries. Therefore nucleation gradually occurs in the vicinity of grain boundaries and then clusters can grow. As increasing aging time, precipitates (η') containing tin begin to be observed by TEM, and then grow to stable phase (η). However, the limitation of nucleation site due to the small amount of addition of tin (0.01%) causes sparse distributions of precipitates.

The microstructural change with PFZs by tin addition was less attributed to tensile properties (Fig. 7). It is well known that grain boundary precipitates also affect greatly the fracture of alloys. The average size of a grain boundary precipitate was therefore evaluated, and the result is shown in Fig. 8. The average size means the average radius which is calculated from measuring the area of a grain boundary precipitate using image analysis. The error bars are estimated from the standard deviations on the respective data. In the Al-Zn-Mg ternary alloy, the size of a grain boundary precipitate monotonously increases through the diffusion of solute atoms within PFZs to grain boundaries. In the Sn-containing alloy, on the other hand, the growth rate of the grain boundary precipitate become lower compared with that of the Al-Zn-Mg ternary alloy. This clearly shows that solute atoms migrate not only to grain boundaries but also to precipitates within PFZs. However, the tensile properties of the Sn-containing alloy are almost the same as that of the Al-Zn-Mg ternary alloy. This supports fine and highly dense distribution of precipitates, i.e. the narrower width of PFZ is mainly attributed to tensile properties. Actually, the width of PFZ in the (Ag+Sn)-containing alloy is very similar to that of the Al-Zn-Mg ternary alloy. These suggest that the combined addition of silver and tin enables to reduce the amount of microalloyed silver in Al-Zn-Mg alloys, which is quite useful for industrialization in the viewpoint of cost.

The effects of microalloying tin and (silver and tin)-combined addition on the precipitate microstructure near grain boundaries of the Al-Zn-Mg alloy have been investigated using micro-Vickers hardness, TEM, 3DAP and tensile test. It was found that precipitates were sparsely observed within PFZs and gradually coarsened with aging time in the Sn-containing alloy, whereas no precipitates were observed within PFZs during aging in the Al-Zn-Mg alloy. This is well explained by the favorable interaction with vacancies, i.e. tin traps vacancies migrating to grain boundaries and suppresses the vacancy depletion in the vicinity of grain boundaries.

5. Conclusions

The effects of microalloying tin and (silver and tin)-combined addition on the precipitate microstructure near grain boundaries of the Al-Zn-Mg alloy have been investigated using micro-Vickers hardness, TEM, 3DAP and tensile test. It was found that precipitates were sparsely observed within PFZs and gradually coarsened with aging time in the Sn-containing alloy, whereas no precipitates were observed within PFZs during aging in the Al-Zn-Mg alloy. This is well explained by the favorable interaction with vacancies, i.e. tin traps vacancies migrating to grain boundaries and suppresses the vacancy depletion in the vicinity of grain boundaries. The combined addition of tin and silver clearly showed that tensile properties of the (Ag+Sn)-containing alloy are remarkably improved due to fine and highly dense distribution of precipitates and the very narrower width of PFZ in the vicinity of grain boundaries. Based on the present work, it can be concluded that tin enables to reduce the amount of microalloyed silver in Al-Zn-Mg alloys.
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